International Conference

«CURRENT PROBLEMS IN CATALYSIS»

Catalysis
CPC-2023
Ukraine

PROCEEDINGS

National Academy
of Sciences of Ukraine

L.V. Pysarzhevskii Institute
of Physical Chemistry

National Academy of Sciences of Ukraine
L.V. Pysarzhevskii Institute of Physical Chemistry of NAS of Ukraine

International Conference

«Current Problems in Catalysis»

CPC-2023

Kyiv, Ukraine

September 25-29, 2023

PROCEEDINGS

Kyiv-2023

UDC 544.47
P93

Proceedings of the International conference «Current problems in catalysis» CPC-2023 (Kyiv, September 25—29, 2023). — Kyiv: Akademperiodyka, 2023. — 180 p.

Proceedings Book contains the scientific presentations of participants of the International Conference «Current Problems in Catalysis», CPC-2023 organized by the National Academy of Sciences of Ukraine and L.V. Pysarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine (Kyiv, September 25—29, 2023).

The presented materials highlight the latest achievements in catalysis obtained in leading scientific centres in 15 countries, including Ukraine, Azerbaijan, Hungary, Japan, Kazakhstan, Poland, USA, Belgium, Finland, Germany, Slovakia, Spain, Norway, China and Serbia. The topics of the abstracts cover modern fundamental and applied problems of catalysis: modern substances and materials for heterogeneous and homogeneous catalytic processes in the gas phase and solutions; production and design of new nanoscale and nanophase substances and materials for catalysis; catalysts for the synthesis of functional substances and materials for the chemical industry; heterogeneous catalytic processes of renewable raw materials processing; heterogeneous catalytic processes for hydrogen energy; catalysis for environmental protection, elimination of harmful emissions; photo-, electro- and photo- electrocatalysis.

The publication is prepared for publication
by the Organizing Committee of the Conference.

The materials are printed in the author's version without editing.

Compilers:
Dr. N.V. VLASENKO, Dr. O.Z. DIDENKO

Reviewers:
Corresponding Member of the NAS of Ukraine C.M. ORLYK,
Corresponding Member of the NAS of Ukraine S.O. SOLOVIEV

Approved for printing:
The Scientific Council of the L.V. Pysarzhevskii Institute of Physical Chemistry
of the National Academy of Sciences of Ukraine

ISBN 978-966-360-486-2

Матеріали Міжнародної конференції “Сучасні проблеми каталізу” CPC-2023: (м. Київ, 25—29 вересня 2023 р.). — Київ: Академперіодика, 2023 — 180 с.

У збірці опубліковано тези наукових доповідей учасників Міжнародної конференції “Сучасні проблеми каталізу” CPC-2023, організованої відділенням хімії Національної академії наук України та Інститутом фізичної хімії ім. Л.В. Писаржевського НАН України (м. Київ, 25—29 вересня 2023 р).

Представлені матеріали висвічують останні досягнення в галузі каталізу, що отримані у провідних наукових центрах 15 країн, серед яких Україна, Азербайджан, Угорщина, Японія, Казахстан, Польща, США, Бельгія, Фінляндія, Німеччина, Словаччина, Іспанія, Норвегія, Китай та Сербія. Тематика доповідей охоплює сучасні фундаментальні та прикладні проблеми каталізу: сучасні речовини та матеріали для гетерогенних і гомогенних каталітичних процесів в газовій фазі та розчинах; виробництво і проектування нових наномасштабних та нанофазних речовин і матеріалів для каталізу; каталізатори для синтезу функціональних речовин і матеріалів для хімічної промисловості; гетерогенні каталітичні процеси переробки відновлюваних сировинних матеріалів; гетерогенні каталітичні процеси для водневої енергетики; каталіз для охорони навколишнього середовища, ліквідації шкідливих викидів; фото-, електро- та фотоелектрокаталіз.

Видання підготовано до друку Організаційним комітетом Конференції.

Матеріали друкуються в авторському варіанті без редагування.

Укладачі:
канд. хім. наук Н.В. ВЛАСЕНКО, О.З. ДІДЕНКО

Рецензенти:
член-кореспондент НАН України С.М. ОРЛИК,
член-кореспондент НАН України С.О. СОЛОВЙОВ

Затверджено до друку Вченою радою
Інституту фізичної хімії ім. Л.В. Писаржевського НАН України

Scientific Committee:

L. Borkó, Prof. (Hungary)
V. Brei, Corr. Member of NAS of Ukraine (Ukraine)
N. Golub, Prof. (Ukraine)
V. Goncharuk, Full Member of NAS of Ukraine (Ukraine)
B. Dzinyak, Prof. (Ukraine)
S. Dzwigaj, Prof. (France)
K. Dossumov, Full Member of KazNANS (Kazakhstan)
M. Zabochnitska, Prof. (Poland)
V. Zazhigalov, Corr. Member of NAS of Ukraine (Ukraine)
E. Ismailov, Prof. (Azerbaijan)
G. Kamalov, Full Member of NAS of Ukraine (Ukraine)
S. Kolotilov, Prof. (Ukraine)
V. Koshechko, Full Member of NAS of Ukraine (Ukraine)
S. Kurta, Prof. (Ukraine)
S. Kuchmiy, Corr. Member of NAS of Ukraine (Ukraine)
J. Mrowiec-Białoń, Prof. (Poland)
L. Oleksenko, Prof. (Ukraine)
I. Opeida, Prof. (Ukraine)
S. Orlyk, Corr. Member of NAS of Ukraine (Ukraine)
L. Patrylak, Prof. (Ukraine)
Yu. Pyatnitsky, Prof. (Ukraine)
S. Soloviev, Corr. Member of NAS of Ukraine (Ukraine)
P. Strizhak, Corr. Member of NAS of Ukraine (Ukraine)
O. Strojuk, Prof. (Germany)
L. Tovazhnyansky, Corr. Member of NAS of Ukraine (Ukraine)
N. Turaeva, Prof. (USA)

Organising Committee:

Chairman:
Vyacheslav Koshechko, Full Member of NAS of Ukraine

Co-Chairmen:
Peter Strizhak, Corr. Member of NAS of Ukraine
Sergii Soloviev, Corr. Member of NAS of Ukraine
Sergii Kolotilov, Prof.

Conference Secretary:
Nina Vlasenko, Dr.

Working Group:
Andrii Trypolskyi, Dr. Hab.
Gulnara Kosmambetova, Dr. Hab.
Igor Bychko, Dr.
Olga Larina, Dr.
Olga Didenko, Dr.
Iryna Stolyarchuk, Dr.
Valerii Chedryk
Oksana Zikrata

PREFACE

Catalysis impacts a wide range of industries and aspects of our lives. It enables the efficient production of essential products, contributes to environmental protection, supports energy sustainability, and drives advances in fields like pharmaceuticals and materials science. Its role in improving the efficiency and sustainability of chemical processes is crucial for addressing the challenges of the 21st century. Studies in catalysis are rapidly advancing, driven by the need to create new catalytic processes and enhance existing ones through the application of new functional materials, including nanomaterials, for practical use in various fields.

The international conference "Modern Challenges in Catalysis" was organized by the L.V. Pysarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine and held in Kyiv. The conference was dedicated to the research findings on current issues in catalysis, encompassing a wide range of chemical, photochemical, electrochemical, and other processes.

The Proceedings book presents thesis of presentations at the International Conference «Current Problems in Catalysis». Heterogeneous catalysis plays a crucial role for fuel production that has been considered in the Conference. Through meticulous analysis and practical examples, it elucidates the intricate processes by which catalysts enable the conversion of raw materials into a diverse array of fuels, ranging from traditional fossil fuels to cutting-edge renewable energy sources like hydrogen and biofuels. Particular interest has been paid to the synthesis of modern substances and the fabrication of novel materials, offering invaluable insights into their applications across a wide spectrum of heterogeneous and homogeneous catalytic processes in both gas and liquid phases. The latest advancements in materials science and catalysis allows effective designing, characterizing, and optimizing catalysts to enhance their efficiency and selectivity, making it an indispensable resource for researchers, chemists, and engineers seeking to push the boundaries of innovation in the field of catalysis. Most of the reported studies are exploring production and design of the novel nanoscale and nanophase substances and materials for catalysis that opens new avenues for and application of nanomaterials in catalysis, e.g., for the synthesis of functional substances and materials for chemical industry with broad spectrum of applications.

Various studies were reporting an exploration of heterogeneous catalytic processes applied to the processing of renewable raw materials, highlighting the role played by catalysts in the sustainable utilization of natural resources. It does not only elucidate the fundamental principles underlying catalytic technologies but also shows practical applications and case studies, showcasing how catalysts can transform a wide range of renewable feedstocks, such as biomass, agricultural residues, and waste materials, into valuable and eco-friendly products. Part of reports were dedicated to heterogeneous catalysis for environmental protection that plays the critical role in eliminating harmful emissions, making it an indispensable resource for anyone concerned about the pressing issues of pollution and sustainability. Catalysis allows to reduce, transform, and even entirely eliminate various hazardous emissions and pollutants from industries such as automotive, petrochemical, and manufacturing. With a keen focus on the design, development, and optimization of catalysts, it provides practical insights into creating cleaner, greener technologies that have a positive impact on environment. The issues and current studies in the novel domains of photo-, electro-, and photoelectrocatalysis have been also considered, encompassing both fundamental aspects and their applications.

The International Conference "Current Problems in Catalysis" was attended by over 200 scientists from 15 countries around the world. The topics of more than 80 oral presentations covered the following areas of modern catalysis:

- Modern substances and materials for heterogeneous and homogeneous catalytic processes in the gas phase and solutions
- Production and design of the novel nanoscale and nanophase substances and materials for catalysis
- Catalysts for the synthesis of functional substances and materials for chemical industry
- Heterogeneous catalytic processes of processing renewable raw materials
- Heterogeneous catalytic processes for hydrogen energy
- Catalysis for environmental protection, elimination of harmful emissions
- Photo-, electro- and photoelectrocatalysis

The conference is aimed at fostering closer cooperation among specialists in the field of catalysis, exchanging expertise, and formulating prospective directions in catalysis to create a new generation of catalysts, coordinate scientific research, and increase the interest of students, graduate students, and young scientists in this promising field.

The research results presented at the conference advance and deepen modern understanding of the catalytic properties of advanced materials, the mechanisms of chemical transformations, and highlight recent achievements in the development of new high-efficiency catalytic technologies for their application in industry, transportation, agriculture, medicine, and other sectors of the economy.

The presentations discuss pressing issues in catalysis and outline paths for further development of scientific research aimed at addressing both fundamental and applied current challenges in modern catalysis.

ORANIZING COMMITTEE

SCIENTIFIC PROGRAM

25 September 2023 (Monday)

Opening of the Conference

10.00-10.10 Opening speech:

Professor Vyacheslav.G. Koshechko
L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine

Morning

(offline session)

Chairperson:
Professor Svitlana M. Orlyk

10.10-10.35 **P-1** **Heterogeneous Catalysis for Fuel Production**

P.E. Strizhak

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

10.35-10.55 **O-1** **Nanostructured SiC and TiC supports for cobalt and Co/Mn Fischer-Tropsch catalysts**

S.O. Alekseev[1,2]*, N. Kruse*[2]

[1]Taras Shevchenko National University of Kyiv (*Ukraine*)
[2]Voiland School of Chemical Engineering and Bioengineering, Washington State University (*USA*)

10.55-11.15 **O-2** **Transition metals oxides / *N*-hydroxyphthalimide systems in catalysis of the aerobic oxidation of benzylic C-H bonds**

I.A. Opeida[1]*, R.B. Sheparovych*[2]*, W.Ya. Suprun*[3]

[1]L. M. Lytvynenko Institute of Physical-Organic Chemistry and Coal Chemistry, NAS of Ukraine (*Ukraine*)
[2]Department of Physical Chemistry of Fossil Fuels InPOCC (*Ukraine*)
[3]Institute of Chemical Technology, Martin-Luther-Universität Halle-Wittenberg, (*Germany*)

11.15-11.30 **S-1** **Composite coating with photocatalytic properties**

I.S. Makyeyeva, N.B. Gruschak, M.I. Gook

Kyiv National University of Technology and Design *(Ukraine)*

11.30-12.00 ***Coffee Break***

12.00-12.25 **P-2** **Examples on the development of new catalytic processes**

V.V. Brei

Institute for Sorption and Endoecology Problems, NAS of Ukraine (*Ukraine*)

12.25-12.45 **O-3** **Experience in the use of a catalytic fuel additive when burning bituminous coal**

I. Volchyn[1,2]*, V. Mokretskyy*[2]

[1]Thermal Energy Technology Institute, NAS of Ukraine (*Ukraine)*
[2]National University of Food Technologies (*Ukraine*)

12.45-13.00 **S-2** **Vapor phase dealloying method for fabricating porous metallic materials**

O.S. Roik[1], O.M. Yakovenko[1], V.E. Sokolskii[1], M.D. Akulcheva[2], N.V. Kotova[1], N.V. Golovataya[1], P. Švec[3], V.P. Kazimirov[1]

[1]Taras Shevchenko National University of Kyiv (*Ukraine*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[3]Institute of Physics, Slovak Academy of Sciences (*Slovakia*)

13.00-14.00 ***Lunch***

Evening

(offline session)

Chairperson:

Professor Valerii O. Zazhigalov

14.00-14.25 **P-3** **Prospects for the creation of new nanocomposite catalysts for the oxidative conversion of C_{1-4}-alkanes and carbon dioxide for the production of hydrogen/syngas and valuable organic compounds**

S.O. Soloviev

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

14.25-14.45 **O-4** **Switchable multicomponent heterocyclizations with controlled chemoselectivity: application of catalysis**

V.A. Chebanov

State Scientific Institution “Institute for Single Crystals”, NAS of Ukraine (*Ukraine*)

14.45-15.05 **O-5** **Photoactive materials based on modified titanium dioxide: properties and perspectives for application in processes of ecological catalysis**

T.A. Khalyavka[1], N.D. Shcherban[2], S.V. Camyshan[1], G.V. Korzhak[2]

[1]Institute for Sorption and Endoecology Problems, NAS of Ukraine (*Ukraine*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

15.05-15.25 **O-6** **Catalysis of hydrodehalogenation, C-C- and C-N-coupling reactions of haloarenes by carbene complexes of palladium chloride**

V.Sh. Saberov[1], O.S. Avksentiev[1], V.I. Yenya[1], G.F. Rayenko[2], N.I. Korotkikh[1]

[1]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
[2]L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, NAS of Ukraine (*Ukraine*)

15.25-15.40 **S-3** **Catalytic activity of an optimized aluminium-nickel-molybdenum catalyst**

D.S. Kamenskyh[1,2], T.V. Tkachenko[1], O.V. Markitan[3], V.O. Yevdokymenko[1]

[1]V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine (*Ukraine*)
[2]V. Bakul Institute for Superhard Materials, NAS of Ukraine (*Ukraine*)
[3]Chuiko Institute of Surface Chemistry, NAS of Ukraine (*Ukraine*)

15.40-16.05 ***Coffee Break***

16.05-16.30 **P-4** **Synthesis and study properties of nanocomposites as electrodes material for chemical power sources**

M.O. Danilov, I.A. Rusetskyi, S.S. Fomanyuk, G.Ya. Kolbasov

Institute of General and Inorganic Chemistry, NAS of Ukraine (*Ukraine*)

16.30-16.50 **O-7** **Fumed silica as an efficient support for acrylic acid production catalysts**

R.V. Nebesnyi[1], O.M. Orobchuk[1], S.V. Khalameida[2], V.V. Sydorchuk[2], V.V. Ivasiv[1]

[1]Lviv Polytechnic National University (*Ukraine*)
[2]Institute for Sorption and Endoecology Problems, NAS of Ukraine (*Ukraine*)

16.50-17.05 **S-4** **Regeneration of poisoned Pd/C catalysts in the sodium formate dehydrogenation reaction as part of the "formate/bicarbonate" cycle**

V.M. Melnychuk, I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

17.05-17.20 ***Discussion***

26 September 2023 (Tuesday)

Morning

(offline session)

Chairperson:

Professor Sergii O. Soloviev

10.00-10.25 **P-5** **Mechanochemistry and sonochemistry in nanosized materials and catalysts preparation**

V.O. Zazhigalov[1], O.V. Sachuk[2], O.V. Kiziun[1], O.A. Diyuk[1]

[1]Institute for Sorption and Problems of Endoecology, NAS of Ukraine (*Ukraine*)
[2]State Scientific Research Forensic of Centre of the MIA of Ukraine (*Ukraine*)

10.25-10.45 **O-8** **Core-shell nanoparticles as hybrid electrocatalysts for water splitting**

I.V. Zatovsky[1], D.S. Butenko[2]

[1]F.D. Ovcharenko Institute of Biocolloidal Chemistry, NAS of Ukraine (*Ukraine*)
[2]Southern University of Science and Technology (*China*)

10.45-11.05 **O-9** **Production of ethyl esters of fatty acids from domestic plant oils: present and prospects**

L.K. Patrylak[1,2]*, S.V. Konovalov*[1]*, S.O. Zubenko*[1]*, V.O. Yevdokymenko*[1]*, A.V. Yakovenko*[1]*, D.Z. Davitadze*[1]

[1]V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine (*Ukraine*)
[2]National Technical University of Ukraine “Igor Sikorskyi Kyiv Polytechnic Institute” (*Ukraine*)

11.05-11.25 **O-10** **Mechanism of methanol conversion into dimethyl ether or formaldehyde on graphene-like materials with defects: quantum chemical study**

O.S. Karpenko[1]*, I.B. Bychko*[2]*, P.E. Strizhak*[2]

[1]Chuiko Institute of Surface Chemistry, NAS of Ukraine (*Ukraine*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

11.25-11.55 ***Coffee Break***

11.55-12.20 **P-6** **Hierarchical zeolites and their nanocomposites as cycloaddition reaction catalysts**

O.V. Shvets, M.M. Kurmach, D.V. Kyryliuk

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

12.20-12.40 **O-11** **Hydrothermal approaches for synthesis of catalysts and their supports**

S. Khalameida, V. Sydorchuk

Institute for Sorption and Problems of Endoecology, NAS of Ukraine (*Ukraine*)

12.40-13.00 **O-12** **Catalytic processes of renewable feedstocks and wastes conversion for hydrogen-rich synthesys gas and hydrogen production**

O.M. Dudnyk

Thermal Energy Technology Institute, NAS of Ukraine (*Ukraine*)

13.00-14.00 ***Lunch***

Evening

Chairperson:

Professor Volodymyr V. Brei

14.00-14.25 **P-7** **Basic trends in catalysis of the hydrodehalogenation reaction of haloarenes**

N.I. Korotkikh[1]*, V.Sh. Saberov*[1]*, O.S. Avksentiev*[1]*, G.F. Rayenko*[2]*, L.M. Vakhitova*[2]

[1]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
[2]L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, NAS of Ukraine (*Ukraine*)

14.25-14.45	**O-13**	**Bioethanol steam reforming over ferrites: interplay of redox and acid-base properties** *L.Yu. Dolgikh* L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
14.45-15.05	**O-14**	**Optimization of the methanol production process on the CHM-Y industrial catalyst** *M.M. Baran[1], T.V. Tkachenko[1], D.S. Kamenskyh[1,2], V.H. Burdeyny[1], V.O. Yevdokymenko[1]* [1]V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine (*Ukraine*) [2]V. Bakul Institute for Superhard Materials, NAS of Ukraine (*Ukraine*)
15.05-15.25	**O-15**	**Mechanochemical, microwave and sonochemical modification of tin dioxide and its photocatalytic properties** *M. Samsonenko[1], S. Khalameida[1], V. Sydorchuk[1], J. Skubiszewska-Zięba[2], V. Starchevskyy[3], L. Kotynska[1]* [1]Institute for Sorption and Problems of Endoecology, NAS of Ukraine (*Ukraine*) [2]Maria Curie-Skłodowska University (*Poland*) [3]Lviv Polytechnic National University (*Ukraine*)
15.25-15.40	**S-5**	**Chemoselective photoredox catalyzed fluoroalkylcyclization of *N*-allyl-4,5-dihydro-3*H*-benzo[*b*]azepin-2-amines** *I.Yu. Danyliuk, M.V. Vovk* [1]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
15.40-16.00		***Coffee Break***
16.00-16.20	**O-16**	**Catalytic properties and resource characteristics of modified nickel composites in the processes of oxidative reforming of C_1-C_4 alkanes** *V.I. Chedryk[1], S.M. Orlyk[1], O.D. Vasylyev[2]* [1]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*) [2]I.M. Frantsevych Institute for Problems of Materials Sciences, NAS of Ukraine (*Ukraine*)
16.20-16.35	**S-6**	**Electrochromic and gasochromic processes of oxide films of transition metals** *S.S. Fomanyuk, V.O. Smilyk, I.A. Rusetskyi, M.O. Danilov, G.Ya. Kolbasov* Institute of General and Inorganic Chemistry, NAS of Ukraine (*Ukraine*)
16.55-16.50	**S-7**	**Oxygen recovery catalysts in models of lithium-air batteries** *D.V. Patlun[1], I.S. Makyeyeva[1], V.G. Khomenko[1], V.Z. Barsukov[2]* [1]Kyiv National University of Technology and Design (*Ukraine*) [2]Institute for Sorption and Problems of Endoecology, NAS of Ukraine (*Ukraine*)
16.50-17.15		***Discussion***

27 September 2023 (Wednesday)

Morning

(offline session)

Chairperson:

Professor Stepan Y. Kuchmiy

10.00-10.25 **P-8** **Progress in the catalytic properties of carbon nanomaterials in hydrogenation of organic substances**

I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

10.25-10.40 **S-8** **Catalytic conversion of ethanol to ethylene on Ce-impregnated mesoporous silica with functional sulfonic and phosphonic groups**

N.G. Kobylinska[1], V.V. Tomina[2], O.A. Dudarko[2], D. Duraczyńska[3], K. Pamin[3], E. Serwicka[3]

[1]A.V. Dumansky Institute of Colloid and Water Chemistry, NAS of Ukraine (*Ukraine*)
[2]Chuiko Institute of Surface Chemistry of the NAS of Ukraine (*Ukraine*)
[3]Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences (*Poland*)

10.40-10.55 **S-9** **Dehydration of bio-isobutanol into liner butene isomers over zeolites of different framework types (FER, MFI, FAU and BEA)**

O.V. Zikrata, O.V. Larina

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

10.55-11.10 **S-10** **Gas phase synthesis of carbon nanospheres, structure and properties**

S.M. Pleskun, E.V. Polunkin, V.S. Pyliavskiy

V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine (*Ukraine*)

11.10-11.25 **S-11** **Binary and ternary electrolytic rhenium alloys as electrocatalysts of hydrogen evolution reaction**

Yu.S. Yapontseva, T.V. Maltseva, V.S. Kublanovsky

V.I. Vernadsky Institute of General and Inorganic Chemistry, NAS of Ukraine (*Ukraine*)

11.25-11.50 ***Coffee Break***

11.50-12.10 **O-17** **Carbon nanospheres: Synthesis in liquid phase, structure and properties**

E.V. Polunkin[1], S.M. Pleskun[1], V.S. Pyliavskiy[1], A.D. Rud[2], D.P. Vinnichenko[3]

[1]V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, NAS of Ukraine (*Ukraine*)
[2]G.V. Kurdyumov Institute for Metal Physics, NAS of Ukraine (*Ukraine*)
[3]Institute of Pulse Research and Engineering, NAS of Ukraine (*Ukraine*)

12.10-12.25 **S-12** **Size dependence of the Fermi level position in ZnO nanoparticles and its effect on the catalytic activity in the CO oxidation**

O.Z. Didenko, G.R. Kosmambetova, P.E. Strizhak

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

12.25-12.40 **S-13** **Selective hydrogenation of polyfunctional organic compounds using catalysts based on rhenium sulphide**

A.S. Poturai[1], *V.V. Subotin*[2,3], *S.V. Ryabukhin*[1,3,4], *D.M. Volochnyuk*[1,3,4], *S.V. Kolotilov*[2]

[1]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[3]Enamine Ltd. (*Ukraine*)
[4]Taras Shevchenko National University of Kyiv (*Ukraine*)

12.40-12.55 **S-14** **Modelling the CPE phenomenon for methane reforming**

M.O. Vilboi[1], *V.R. Trishch*[1], *G.S. Yablonsky*[2], *D. Constales*[3]

[1]National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute»(*Ukraine*)
[2]Washington University in St. Louis (*USA*)
[3]Ghent University (*Belgium*)

12.55-13.10 **S-15** **Comparative characteristics of the catalysis of the transesterification reaction by carbenes and the hydroxide form of anionite AB-17-8**

V.*Sh. Saberov*[1], *O.S. Avksentiev*[1], *V.I. Yenya*[1], *G.F. Rayenko*[2], *N.I. Korotkikh*[1]

[1]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
[2]L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, NAS of Ukraine (*Ukraine*)

13.10-14.00 ***Lunch***

Evening

(online session)

Chairperson:

Dr. Igor B. Bychko

14.00-14.25 **P-9** **The role of the catalysts' bifunctionality in the multistage processes**

S.M. Orlyk

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

14.25-14.45 **O-18** **Synthesis of new complex oxide acid catalysts and study of their properties**

N.P. Golub[1], *Ye.O. Golub*[2], *A.A. Kozma*[1], *A.O. Kuznietsova*[1], *V.I. Gomonaj*[1]

[1]Educational and Scientific Institute of Chemistry and Ecology, Uzhhorod National University (*Ukraine*)
[2]Faculty of Medicine, Uzhhorod National University (*Ukraine*)

14.45-15.00 **S-16** **Kinetics and mechanism of methanol dehydration on acid sites of composite catalysts H-ZSM-5–Al_2O_3**

A.I. Trypolskyi, N.V. Vlasenko, O.O. Zhokh

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

15.00-15.15 **S-17** **Mesoporous phosphate-stabilized tungsten-zirconium oxide composition as a catalysts for glycerol dehydration**

E.V. Senchylo, N.V. Vlasenko, G.R. Kosmambetova

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

15.15-15.30 **S-18** **Heterogeneous photoelectrocatalysis of porous ZnO plate with micro- and nano elements**

L. Hrytsak, V. Vasil'ev, B. Turko

Ivan Franko National University of Lviv (*Ukraine*)

15.30-15.45 **S-19** **Removal of harmful emissions from electrode production in a catalytic reactor with a ferrite loading**

O.I. Ivanenko[1], *S.D. Dovholap*[1], *A.I. Trypolskyi*[2], *P.E. Strizhak*[2], *T.A. Overchenko*[1]

[1]National Technical University of Ukraine "Igor Sikorskyi Kyiv Polytechnic Institute" (*Ukraine*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

15.45-16.00 ***Coffee Break***

16.00-16.20 **O-19** **Development of acid and bifunctional mixed oxides as effective catalysts for the transformations of renewable raw materials**

S.V. Prudius, N.L. Hes, O.I. Inshina, V.V. Brei

Institute for Sorption and Endoecology Problems, NAS of Ukraine (*Ukraine*)

16.20-16.35 **S-20** **Determination of thermochemical properties of divalent metal orthophosphates by semi-empirical methods**

A.A. Kozma[1], *N.P. Golub*[1], *Ye.O. Golub*[2], *D.V. Davyda*[1], *V.I. Gomonaj*[1]

[1]Educational and Scientific Institute of Chemistry and Ecology, Uzhhorod National University (*Ukraine*)
[2]Faculty of Medicine, Uzhhorod National University (*Ukraine*)

16.35-16.50 **S-21** **Catalytic oxidation of sulfides at presence of Co^{II}, Fe^{III} and Mn^{II} complexes**

Yu.L. Lishchenko[1,2], *S.O. Sotnik*[1,2], *A.S. Poturai*[2,3], *S.V. Ryabukhin*[2,3,4], *D.M. Volochnyuk*[2,3,4], *S.V. Kolotilov*[1]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[2]Enamine Ltd. (*Ukraine*)
[3]Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)
[4]Taras Shevchenko National University of Kyiv (*Ukraine*)

16.35-16.50 **S-22** **Fabrication of electrocatalysts for green hydrogen production using deep eutectic solvents**

V.S. Protsenko, D.O. Makhota, O.D. Sukhatskyi, L.S. Bobrova,
T.E. Butyrina, F.I. Danilov

Ukrainian State University of Chemical Technology (*Ukraine*)

16.50-17.15 ***Discussion***

28 September 2023 (Thursday)

Morning

(online session)

Chairperson:

Professor Peter E. Strizhak

9.30-9.55 **P-10** **Nanocomposite catalysts with reduced or zero content of platinum group metals for hydrogenation of organic compounds**

S.V. Kolotilov

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

9.55-10.15 **O-20** **Phase composition of MnOx-Na_2WO_4/SiO_2 catalyst and thermodynamics of the size dependent stability of manganese oxides nanoparticles in the oxidative condensation of methane to C_2 hydrocarbons**

E.H. Ismailov[1]*, S.N. Osmanova*[1,2]*, G.R. Azimova*[1]*, A.N. Mammadov*[1,3]*,*
D.B. Taghiyev[1]*, J.W. Thybaut*[4]

[1]Institute of Catalysis and Inorganic Chemistry *(Azerbaijan)*
[2]Khazar University *(Azerbaijan)*
[3]Azerbaijan Technical University *(Azerbaijan)*
[4]Ghent University *(Belgium)*

10.15-10.35 **O-21** **Polyfunctional catalysts for tandem processes of $C_{2,4}$ bio-alcohol conversion into industrially important organic compounds**

O.V. Larina

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

10.35-10.50 **S-23** **Insight into structural and physicochemical properties of ZrO_2-SiO_2 monoliths with hierarchical pore structure. Effect of zirconium precursor**

A. Ciemięga[1]*, K. Maresz*[1]*, M. Sitarz*[2]*, M. Krzywiecki*[3]*, J. Mrowiec-Białoń*[1]

[1]Institute of Chemical Engineering Polish Academy of Sciences (*Poland*)
[2]AGH University of Science and Technology (*Poland*)
[3]Institute of Physics, CSE, Silesian University of Technology (*Poland*)

10.50-11.05 **S-24** **Use of spent alumina in the production of an adsorbent for drying nitrogen at a catalytic reformer**

Kh.A. Nasullaev[1], I.S. Abdurakhmanova [2], Sh.T. Gulomov[1], R.G. Khadjiev[3], D.P. Turdieva[1]

[1]Uzbek Research Chemical-Pharmaceutical Institute (*Uzbekistan)*
[2]National University of Uzbekistan (*Uzbekistan)*
[3]Bukhara Oil Refinery Ltd. (*Uzbekistan)*

11.05-11.20 **S-25** **Effects of cerium oxide on the activity of Fe-Ni/Al_2O_3 catalyst in the decomposition of methane**

N. Makayeva[1,2], G. Yergaziyeva[1,2], S. Soloviev[3], N. Khudaibergenov[4], M. Annisova[1], M. Mambetova[1,2], K. Dossumov[1]

[1]Institute of Combustion Problems *(Kazakhstan)*
[2]Al-Farabi Kazakh National University *(Kazakhstan)*
[3]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[4]Satbayev University *(Kazakhstan)*

11.20-11.50 ***Coffee Break***

11.50-12.10 **O-22** **Structural background of the synergetic bimetallic effect of NiMo/MgO catalysts in methane pyrolysis**

A. Beck[1], M. Németh[1], T.I. Korányi[1], Gy. Sáfrán[1], L. Borkó[1], Zs.E. Horváth[1], I. Rigó[2], A. Horváth[1]

[1]Centre for Energy Research (*Hungary*)
[2]Wigner Research Centre for Physics (*Hungary*)

12.10-12.30 **O-23** **Methyl acetate production from methanol in vapor-phase tandem process on Ni-Cu based catalysts**

A.Yu. Kapran, L.M. Alekseenko, V.I. Chedryk

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

12.30-12.45 **S-26** **Catalysis for CO_2 utilization using bio-resources**

M. Zabochnicka[1], P.E. Strizhak[2], G.R. Kosmambetova[2], S. Szufa[3], R. Bhosale [4], G. Piechota[5], G. Kumar[6]

[1]Czestochowa University of Technology *(Poland*)
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[3]Lodz University of Technology *(Poland*)
[4]University of Tennessee *(USA)*
[5]GP CHEM. Laboratory of Biogas Research and Analysis *(Poland*)
[6]Institute of Chemistry Bioscience and Environmental Engineering, University of Stavanger (*Norway*)

12.45-13.00 **S-27** **Ethanol conversion on copper catalysts**

M. Mambetova[1,2], G.Yergaziyeva[2,3], K. Dossumov[1,2]

[1]The Center of Physico-Chemical Methods of Research and Analysis *(Kazakhstan)*
[2]Institute of Combustion Problems *(Kazakhstan)*
[3]Al-Farabi Kazakh National University *(Kazakhstan)*

13.00-14.00 ***Lunch***

Evening

(online session)

Chairperson:

Professor Sergii V. Kolotilov

14.00-14.20 **O-24** **Effect of temperature cycling on Ni-M (La-, Mg-) catalysts in CO_2 conversion of methane**

A.M. Manabayeva[1,2], *S.A. Tungatarova*[2,3], *D.Yu. Murzin*[4]

[1]Kazakh-British Technical University *(Kazakhstan)*
[2]D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry *(Kazakhstan)*
[3]Al-Farabi Kazakh National University *(Kazakhstan)*
[4]Abo Akademi University (*Finland*)

14.20-14.40 **O-25** **Influence of nickel and copper additives on catalytic properties of Mg-Al-Y oxide catalyst in the guerbet condensation of ethanol and 1-butanol**

K.V. Valihura[1,2], *O.V. Larina*[1], *S.O. Soloviev*[1], *B. Alonso Fariñas*[2], *A.L. Villanueva Perales*[2], *J.F. Vidal Barrero*[2]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[2]Universidad de Sevilla (*Spain*)

14.40-15.00 **O-26** **Efficient sugar hydrogenation over Ru nanoparticles deposited onto mesoporous molecular sieves**

N. Shcherban[1], *G. Araujo-Barahona*[2], *I. Kopa*[1], *T. Salmi*[2], *D. Murzin*[2]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine
[2]Abo Akademi University (*Finland*)

15.00-15.15 **S-28** **Intermediates in catalytic systems for metathesis of olefins based on WCl_6 and organoaluminium compounds according to dynamic light scattering and electron paramagnetic rezonance data**

S.N. Osmanova[1,2], *S.A. Suleymanova*[1], *T.G. Zeynalova*[3], *E.H. Ismailov*[1]

[1]Institute of Catalysis and Inorganic Chemistry (*Azerbaijan*)
[2]Khazar University *(Azerbaijan)*
[3]Azerbaijan University of Architecture and Construction *(Azerbaijan)*

15.15-15.30 **S-29** **Nickel phosphides based composite multifunctional electrocatalysts for oxygen reduction, oxygen and hydrogen evolution reactions**

O.O. Pariiska, D.O. Mazur, Ya.I. Kurys, V.G. Koshechko, V.D. Pokhodenko

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

15.30-15.50 ***Coffee Break***

15.50-16.10 **O-27** **Air-stable nickel catalysts for hydrogenation of organic compounds**

M.O. Ivanytsya[1,2]*, V.V. Subotin*[1,2]*, A.V. Terebilenko*[1,3]*, P.S. Yaremov*[1]*,*
O.O. Pariiska[1]*, Y.M. Akimov*[3]*, I.E. Kotenko*[1]*, T.M. Sabov*[4]*,*
M.M. Kurmach[1]*, S.V. Ryabukhin*[2,5,6]*, D.M. Volochnyuk*[2,5,6]*, S.V. Kolotilov*[1]

[1] L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[2] Enamine Ltd. (*Ukraine*)
[3] M.G. Kholodny Institute of Botany, NAS of Ukraine (*Ukraine*)
[4] V.E. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine (*Ukraine*)
[5] Taras Shevchenko National University of Kyiv (*Ukraine*)
[6] Institute of Organic Chemistry, NAS of Ukraine (*Ukraine*)

16.10-16.25 **S-30** **Titanosilicate zeolites as catalysts for epoxidation of cyclic olefines with H_2O_2**

M.M. Kurmach[1]*, A.O. Samotoi*[1]*, S.O. Sotnik*[1,2,3]*, P.S. Yaremov*[1]*,*
O.V. Shvets [1]*, N.D. Shcherban* [1]

[1] L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
[2] Taras Shevchenko National University of Kyiv (*Ukraine*)
[3] Enamine Ltd. (*Ukraine*)

16.25-16.50 **P-11** **Electronic models of catalytic processes**

N. Turaeva

Webster University, Saint Louis (*USA*)

16.50-17.10 **O-28** **Catalytic cycle and deactivation: kinetico-thermodynamic interplay**

G.S. Yablonsky[1]*, Z.J.G. Gromotka*[2]*, N.M. Ostrovskii*[3]*, D. Constales*[2]

[1] Washington University, St. Louis (*USA*)
[2] Ghent University (*Belgium*)
[3] Euro Gas (*Serbia*)

17.10-17.30 ***Discussion***

29 September 2023 (Friday)

Morning

(online session)

Chairperson:

Dr. Olga V. Larina

10.00-10.25 **P-12** **Happy photocatalysts and unhappy photocatalysts: to go beyond the identification problem**

B. Ohtani[1]*, M. Takashima*[2]

[1] Hokkaido University and Nonprofitable Organization touche NPO (*Japan*)
[2] Department of Energy Science and Engineering, Nagoya University (*Japan*)

10.25-10.45	**O-29**	**Novel materials – efficient catalysts for methane decomposition and its oxidative conversion to hydrogen and/or synthesis gas** *K. Dossumov*[1,2]*, M. Mambetova*[1,2]*, G. Yergaziyeva*[2]*, M. Anissova*[2]*, N. Makayeva*[2]*, N. Khudaibergenov*[2] [1]The Center of Physico-Chemical Methods of Research and Analysis *(Kazakhstan)* [2]Institute of Combustion Problems *(Kazakhstan)*
10.45-11.00	**S-31**	**On the possibility of use of waste zeolite adsorbents of type A** *Sh.T. Gulomov, A.R. Sultanov* Uzbek Research Chemical-Pharmaceutical Institute *(Uzbekistan)*
11.00-11.15	**S-32**	**Plasma-catalytic dry reforming of propane with chromium (III) oxide based catalysts in dielectric barrier discharge reactor** *D.E. Samoylenko*[1]*, V.I. Kornaha*[2]*, P. I. Kyriienko*[1] [1]L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*) [2]V.E. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine (*Ukraine*)
11.15-11.30	**S-33**	**Hydrogenation of carbon dioxide to methanol at atmospheric pressure by bentonite-based catalysts with supported mono-, bi-, and tri-nuclear ferrocene derivatives** *A. I. Rustamova*[1]*, S.N. Osmanova*[1,2]*, Z.M. Mammadova*[1]*, E.H. Ismailov*[1] [1]Institute of Catalysis and Inorganic Chemistry *(Azerbaijan)* [2]Khazar University *(Azerbaijan)*
11.30-11.50		***Coffee Break***
11.50-12.10	**O-30**	**Influence of oxygen evolution overvoltage on selectivity of oxygen transfer reactions** *O. Shmychkova, T. Luk'yanenko, A. Velichenko* Ukrainian State University of Chemical Technology (*Ukraine*)
12.10-12.30	**O-31**	**Influence of the platinum surface state on the electrocatalytic selectivity of the electrochemical synthesis of sodium hypochlorite** *D.V. Girenko, A.B. Velichenko* Ukrainian State University of Chemical Technology (*Ukraine*)
12.30-12.45	**S-34**	**On the thermodynamics of ethanol conversion into hydrogen and propylene** *Y.I. Pyatnitsky, L.Yu. Dolgikh, I.L. Stolyarchuk, L.M. Senchylo* L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)
12.45-13.00	**S-35**	**Catalytic methods of decontamination and protection of the surface of different materials from contamination with radioactive dust** *S.A. Kurta, I.F. Myroniuk* Vasyl Stefanyk Precarpathian National University (*Ukraine*)
13.00-14.00		***Lunch***

Evening

(online session)

Chairperson:

Professor Peter E. Strizhak

14.00-14.20	**O-32**	**Methanol production from biogas** *L. Rodin*[1], *V. Kharitonov*[1], *A. Jakovičs*[2] [1]Chemical Technological Company LLC (*Ukraine*) [2]University of Latvia (*Latvia*)
14.20-14.40	**O-33**	**The conversion of fructose to alkyl lactates and levulinic acid on Sn-containing catalysts** *N.L. Hes, S.V. Prudius, A.M. Mylin, V.V. Brei* Institute for Sorption and Endoecology Problems, NAS of Ukraine (*Ukraine*)
14.40-14.55	**S-36**	**Ternary nanostructures Ni(Co)/Pd as catalysts for the reduction of *p*–nitrophenol** *L.I. Bazylyak*[1], *A.R. Kytsya*[1,2] [1]L.M. Lytvynenko Institute of Physical-Organic Chemistry and Coal Chemistry, NAS of Ukraine (*Ukraine*) [2]G.V. Karpenko Physico-Mechanical Institute, NAS of Ukraine (*Ukraine*)
14.55-15.10	**S-37**	**Electrocatalytic conversion of carbon dioxide to formaldehyde and methanol** *V. Viazovyk, A. Kamensky* Cherkasy state technological university *(Ukraine)*
15.10-15.20		***Coffee Break***
15.20-15.35	**S-38**	**Synthesis of the F-TiO_2/CuO particles via coprecipitation method** *D.S. Sofronov*[1], *O.M. Lebedynskiy*[2], *M. Rucki*[3], *S.S. Minenko*[4] [1]Institute for Single Crystals, NAS of Ukraine (*Ukraine*) [2]State Scientific Institution «Institute for Single Crystals», NAS of Ukraine (*Ukraine*) [3]Kazimierz Pulaski University of Technology and Humanities in Radom (*Poland*) [4]Institute for Scintillation Materials, NAS of Ukraine (*Ukraine*)
15.35-15.50	**S-39**	**Highly sensitive chemiluminescence determination of citrate ions based on the enhancement of the luminol reaction catalyzed by cobalt (II)** *Yu.I. Mazna, N.G. Kobylinska, O.V. Zuy* A.V. Dumansky Institute of Colloid and Water Chemistry, NAS of Ukraine (*Ukraine*)

15.50-16.10 **O-34** **Catalytic properties of N-doped reduced graphene oxide in hydrogenation of ethylene and acetylene and direct ethane dehydrogenation processes**

O.O. Abakumov, I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, NAS of Ukraine (*Ukraine*)

16.10-16.30 ***General Discussion***

16.30 **Closing of the Conference**

PLENARY LECTURES

P-1

HETEROGENEOUS CATALYSIS FOR FUEL PRODUCTION

P.E. Strizhak

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine,
Prosp. Nauky, 31, Kyiv, 03028 Ukraine, pstrizhak@hotmail.com

Heterogeneous catalysis plays a crucial role in fuel production exploring various chemical reactions that convert raw materials into usable fuels. Large-scale production of modern motor fuels is possible of different heterogeneous catalytic processes, e.g., hydrocracking, reforming, catalytic cracking, hydroprocessing, hydrogenation, etc. That was a driving force to develop new catalysts during last decades, particularly, zeolites or metal oxides hydrocracking, platinum or palladium containing catalysts for reforming, tungsten sulfide containing catalysts for hydrodesulfurization, etc. Progress in a production of modern motor fuels shows that heterogeneous catalytic processes provide a large scale production contrary to other technologies which are limited either by technological peculiarities, like technologies based on a conversion of sun light, or limitations in a production, like technologies based on electricity. Today we are facing a demand to explore new types of fuels or new pathways for hydrocarbons production. Both these ideas cannot be realized without development of new heterogeneous catalytic processes and new catalysts to realize these processes.

Today, hydrogen is considered as one of the possible candidates as a fuel for the future. Hydrogen can be produced from renewables. Therefore, hydrogen is the renewable energy carrier. Hydrogen has the highest gravimetric heating value among all fuels, 142 MJ kg^{-1}. There is no pollution during hydrogen combustion. Various approaches are used for the development of new technologies for hydrogen production. The thermal treatment of biomass is found to have some advantages. A variety of biological process is also considered to be very promising. However, both these approaches require considerable efforts for the by-products and waste elimination. Only the heterogeneous catalytic production of hydrogen is capable not only to overcome possible disadvantages of new technology but also to satisfy the large scale production of hydrogen minimizing investments for the technical realization. The ethanol steam reforming (ESR) gives a promising way for hydrogen production from renewable feedstock. We show that ferrites exhibit a good performance for ESR. Moreover, based on a developed catalyst, we develop an energetically effective process for hydrogen production.

Hydrocarbon production may be based on well-established Fischer-Tropsch Synthesis. Solid catalysts, often based on metals like iron, cobalt, or nickel supported on various substrates, are used to facilitate this process. We have developed effective catalysts for preferential production of synthetic naphtha, synthetic fuels like diesel and jet fuel, or light fraction of hydrocarbons. Moreover, based on these developments we introduce a cheap promoted iron-containing catalysts for direct conversion of gas obtained by a gasification of wastes, bio-wastes, coal or their mixtures. Technological problems related to a use of the catalyst and various feedstocks are discussed. We are also reported progress achieved in a development of catalysts for carbon dioxide hydrogenation.

Water-gas shift reaction (WGSR) is an important catalytic process in the industrial production of hydrogen and hydrogen-based synthesis. WGSR is also used to optimize the H_2/CO ratio, particularly, after gasification of raw materials. WGSR produces additional hydrogen using gases remaining after steam reforming for the production of liquid hydrocarbons in the Fisher-Tropsch reaction. Significant interest in WGSR is relevant to fuel cell applications for the production of CO-free hydrogen-rich mixtures. We investigated the catalytic performance of a nanocomposite catalyst, 3%FeOx/CNT, consisting of carbon nanotubes (CNT) supporting iron oxide nanoparticles, in WGSR. The catalyst's performance was evaluated by analyzing the temperature dependence of CO conversion, the effect of the steam/CO ratio, the catalyst's stability, and the impact of Fe loading. Furthermore, we compare the performance of 3%FeOx/CNT with other CNT-supported catalysts previously reported in the literature.

Biodiesel production may play an important role for transformation of renewables to motor fuel. We have performed a study of various heterogeneous catalysts to improve the process. Moreover, we are developing catalysts for utilization of bioglycerol, byproduct of the biodiesel production. Glycerol oligomerization in a liquid phase was studied over the acid-base bifunctional catalysts for the following oxides: TiO_2, ZrO_2, CeO_2, binary CeO_2–ZrO_2 systems, and purely basic oxide MgO. The phase composition and surface area have been estimated by XRD and BET. The acid and basic properties of catalysts have been characterized using the quasi-equilibrium thermal desorption (QE-TD) of NH_3 (acidity) and CO_2 (basicity). Attenuated total reflectance FTIR (ATR-FTIR) spectroscopy provided qualitative insights into the interactions in the oxide-glycerol systems. A comparison of catalytic and acid-base properties of the oxide systems showed that the reaction requires the presence of both acid and base sites in the catalyst. Moreover, the strength of base sites should exceed the strength of acid sites.

Glycerol dehydration is another pathway for its transformation. The catalytic performance of the phosphate-stabilized WO_x-ZrO_2 compositions in gas-phase glycerol dehydration has been studied. It was found that, depending on the concentration of WO_3, catalysts direct the process either toward the formation of acrolein or allyl alcohol. Catalysts with a low content of WO_x are characterized by the presence of strong Lewis sites Zr^{4+} and W^{6+}. In these catalysts, metal ions probably act as a of redox sites, which determines their activity in glycerol hydrogenolysis with the formation of allyl alcohol. Increased (more than 20 wt.%) concentrations of tungsten oxide contribute to the shielding of a part of W^{6+} and Zr^{4+} sites by polytungstate surface complexes, which are strong Brønsted acid sites. This contributes to the dehydration of glycerol with the detachment of two water molecules and thus determines the process selectivity due to a change in the direction of the process towards the formation of acrolein.

All these studies allow us to speculate that heterogeneous catalysis opens new roots for using alternative feedstocks for fuel production, e.g. conventional fuels based on hydrocarbons and fuel of the future based on hydrogen. Development of new chemical processes and novel catalysts show unrestricted possibility to transform renewable resources to fuel. Important part of these developments is related to a possibility to apply current technological solutions and available resources for fuel production, both, hydrocarbons and hydrogen. Therefore, heterogeneous catalysis is unavoidable in achieving efficient and cost-effective fuel production, which is crucial for a wide range of applications, including transportation, clean energy generation, industrial processes, and fuel cell technologies. It plays a vital role in the sustainable production of conventional and alternative fuels, contributing to energy security and environmental sustainability.

All these studies were performed despite the unprovoked invasion of Ukraine by Russia, supported by Belarus. The author is thankful to the Armed Forces of Ukraine for serving our country and protecting our freedoms.

P-2

EXAMPLES ON THE DEVELOPMENT OF NEW CATALYTIC PROCESSES

V.V. Brei

Institute for Sorption and Endoecology Problems, National Academy of Sciences of Ukraine, General Naumov Str., 13, Kyiv, 03164 Ukraine, brei@ukr.net

The main features of some catalytic technologies developed by Institute for Sorption and Endoecology Problems in cooperation with Techinservice Manufacturing Group are discussed: namely, HPPOa process producing propylene oxide from propylene and hydrogen peroxide with use of acetonitrile as solvent instead of methanol; vapour-phase hydrogenation of pyrolysis olefin C_4-$_5$ fraction on the Cu-containing catalyst instead of liquid-phase Axens process on the Pd/Al_2O_3 catalyst; direct high-temperature chlorination of ethylene into vinyl chloride instead of traditional Vinolit process. The HPPOa installation (2000 PO t/y) has been started at Kalush Karpatnaftochim plant in 2020.

The new technology producing racemic lactide from available glycerol and the one stage process obtaining n-butanol from bioethanol are presented also.

P-3

PROSPECTS FOR THE CREATION OF NEW NANOCOMPOSITE CATALYSTS FOR THE OXIDATIVE CONVERSION OF $C_{1\text{-}4}$-ALKANES AND CARBON DIOXIDE FOR THE PRODUCTION OF HYDROGEN / SYNGAS AND VALUABLE ORGANIC COMPOUNDS

S.O. Soloviev

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine,
Prosp. Nauky, 31, Kyiv, 03028 Ukraine, soloviev@ukr.net

The most realistic scenario for the future economy advancement is a development of new technologies based on the involvement of carbon dioxide and $C_{1\text{-}4}$-alkanes in the synthesis of valuable organic compounds. It allows both reducing the anthropogenic pressure on the environment and obtaining value-added chemicals from renewable sources (biogas) and raw materials that are now almost not used (mine, associated gases, etc.). Creating technologies aimed at the rational consumption of natural resources is the relevant task. First of all, it concerns such components of natural gas as $C_{3,4}$-alkanes used as automobile fuel. Therefore, the processes of conversion of lower (C_1-C_4) alkanes involving CO_2 into hydrogen / syngas are the subject of intensive research by scientists in leading scientific centres of numerous countries. The possibility of using CO_2 as a mild oxidizer to transform natural gas components (propane, butane) into valuable products, namely olefins and dienes, is an interesting prospect.

All known catalysts for the dry (or) CO_2 reforming of methane (DRM) quickly lose their initial activity due to their carbonization. The imbalance between the rates of activation of CH_4 and CO_2 molecules is the reason. We have recently found that Ni-BEA zeolite catalysts prepared by incorporating nickel cations into a partially dealuminated zeolite matrix are high active in DRM, with methane conversion occurring without carbon accumulation, which may be due to changes in the process mechanism. C-H bond activation of methane molecule is more easily over atomically dispersed nickel in Ni-BEA than over the surface of deposited nickel nanoparticles, but subsequent dissociation of the surface intermediates $CH^*_3 \rightarrow CH^*_2 + H^*$ is complicated. Therefore, it likely to be the interaction of CH^*_3 fragment with surface oxygen with CO formation. Activation of CO_2 can be carried out on surface basic sites by the formation and subsequent destruction of surface carbonates or formates. It should be expected that modifying catalysts based on oxide (Ni-Al_2O_3/cordierite) and zeolite (Ni-BEA) systems with metal oxide additives that combine basic properties of the surface with high oxygen mobility of the crystal lattice (Ce, La, Y oxides etc.) will be an effective method of increasing the activity. Regulation of acid-base properties of the surface will be carried out by introducing of MgO into the catalysts, which will control a dissociation rate of CH_4 molecule. A combination of cold plasma, which will activate CO_2 at a relatively low temperature, and a catalyst, on which surface the interaction of activated reagents with the formation of target products, CO/H_2, will occur, can be a promising way to intensify DRM processes. The main focus will be to establish a relationship between nature, physicochemical properties of the catalyst, the parameters of plasma generation on DRM (activity/selectivity) to achieve high product yields. Biogas (40-70% CH_4, 30-45% CO_2, 1-1000 ppm H_2S) is an important raw material for syngas production. The potential production of biogas in Ukraine is estimated at 30–40 billion m^3/year. Increasing sulfur resistance of reforming catalysts can be done by modifying them with rare earth metal compounds (CeO_2, La_2O_3), which are able to act as a "trap" for sulfur compounds.

A new trend in the study of DRM process is the focus on the development of catalytic systems and technological solutions that will allow to conduct DRM at $CO_2/CH_4>1$ to obtain syngas enriched with CO. Such mixtures are more valuable raw materials than H_2, necessary for a number of industrial processes. The difficulty of implementing the concept of "super-dry reforming of methane" is the need for simultaneous use of the DRM catalyst and the system sorbent+catalyst for the reduction of CO_2 with hydrogen.

Propylene and butadiene (BD) are among the main intermediates of the petrochemical industry, which are obtained as by-products of steam cracking of oil to ethylene. However, since 2010, due to the reorientation of raw materials for the production of ethylene from oil to shale gas, the production of propylene and BD from oil has decreased. This has updated the study of alternative "non-petroleum" methods for producing propylene and BD, in particular by oxidative dehydrogenation of propane-butane mixture.

It is expected that purposeful construction (design) of zeolite catalysts, formation of active sites: acid-base ones by incorporation of heteroelements Ga(Zn,Cr) into the BEA crystal lattice and dopants addition will allow one to develop effective catalysts for oxidative dehydrogenation of alkanes with CO_2 to obtain olefins. The mesoporous matrix of BEA zeolite will act as a nanoreactor for synthesis and stabilization of nanosized particles of transition metal oxides, which will increase the number of redox sites for the reagent activation.

The process of oxidative dehydrogenation of n-butane (ODB) is now considered as one of the promising directions for the production of BD on the necessary scales. In this process the use of CO_2 as a mild oxidizer will allow significantly increasing its productivity towards the target product due to suppression of hydrocarbon excessive oxidation. First of all, the oxidative dehydrogenation of butane to BD is of practical interest with the involvement of CO_2, since carbon dioxide is a milder oxidant compared to oxygen and others. Therefore, the vast majority of researches related to the use of oxidants, other than oxygen, focus mainly on CO_2, which will reduce the proportion of complete combustion of reaction products.

The flexibility of the process of integration/release of structure oxygen atoms is important for ODB catalysts. Transition metal application as an active phase for such catalysts is appropriate, since such elements can adopt several different stable oxidation states due to partially filled d-orbitals. Ni and Mo can be effective in the activation and dehydrogenation of butane/butenes, while Bi will provide dissociation and lattice integration of oxygen atoms for catalyst regeneration. Under the condition of certain active site localization for the various stages of the n-butane→n-butene→1,3-butadiene tandem process over complex polyfunctional catalysts, increasing the BD selectivity and yield can be achieved by combining the properties of 3d transition metal compounds for the activation of alkanes with R-H bond breaking (Ni, Cr) and oxides included in the catalysts for the n-butene dehydrogenation into BD (in particular, Fe, Mo, Bi).

Metal oxides (Cr, Fe, Co, Ga, V, Bi, Mo) and Pt-Sn deposited on alumina or zeolite of MFI type are the most active and studied catalysts for oxidative dehydrogenation of alkanes. A common disadvantage of known dehydrogenation catalysts is a decrease in their activity in time due to side effects of cracking and oligomerization over acid sites, which necessitates the further search for ways to increase the activity, selectivity and stability of alkane dehydrogenation catalysts, in particular with CO_2.

Thus, the activity and selectivity of known catalysts in these processes is determined by the redox and acid-base properties, structural and dimensional characteristics, which depend not only on the nature of the active components and other components of the catalytic composition (dopants, promoters), but also on their interaction nature with the carrier.

P-4

SYNTHESIS AND STUDY PROPERTIES OF NANOCOMPOSITES AS ELECTRODES MATERIAL FOR CHEMICAL POWER SOURCES

M.O. Danilov*, I.A. Rusetskyi, S.S. Fomanyuk, G.Ya. Kolbasov

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Academic Palladin Avenue,32/34, Kyiv, 03142 Ukraine, danilovmickle@rambler.ru

Fuel cells or chemical power sources in which electrocatalytic processes occur are classified as alternative or small-scale energy. At present, in terms of total energy capacity, the energy generated by all current sources in the world is equal to the energy generated by nuclear, thermal and hydroelectric power plants combined. Therefore, research related to the generation of electric current is very relevant at the present time. Our work considers the synthesis and study of the electrocatalytic properties of hybrid composites and the development of a mechanism for their preliminary evaluation for use in chemical power sources as electrode materials.

To date, there is no unified theory that allows describing electrocatalytic processes. We have proposed an approach of electrochemical reactions localization, which explains the catalytic properties of the studied materials, and on its basis, we have developed the basic principles for designing electrocatalytic materials [1]. By changing the route of electrochemical reactions from a catalyst to a support or vice versa, one can influence the electrocatalytic properties. If we assume that the adsorption of the reagent and the attachment of electrons are localized and proceed in parallel either on the catalyst or on the carrier, and the particles of the reactant diffuse through the interface between the catalyst and carrier phases, then by selecting the appropriate catalyst–carrier pair, it is possible to influence the electrocatalytic properties of such electrodes. In the literature, such processes are called spillover. The difference in the value of the electrochemical overvoltage of the release of the studied reagent in a given medium between the catalyst and the support can be used to judge its catalytic activity. This approach was considered in relation to the following electrochemical reactions occurring in chemical power sources such as:

1. Oxygen reduction reaction occurring in oxygen (air) electrodes of fuel cells;
2. Hydrogen oxidation reaction occurring in hydrogen electrodes of fuel cells;
3. The reaction of electrochemical accumulation of hydrogen occurring in the hydride electrode of a nickel-metal hydride battery.

The following materials were chosen and synthesized as catalyst carriers: graphene oxide (GO), graphene, partially unzipped multi-walled carbon nanotubes (PUMWCNTs), graphite-like carbon nitride (g-C_3N_4). These materials have a developed specific surface, a porous structure, and the presence of similar defects in the structure, which make it possible to act as an effective catalyst carrier. An electrochemical synthesis of GO and reduced graphene oxide from multi-walled carbon nanotubes has been developed and proposed. An approach to the selection of oxidizing agents for the production of graphene oxide and reducing agents for the synthesis of reduced graphene oxide based on electrochemical reactions of carbon oxidation and reduction in acidic and alkaline media has been proposed [2].

Graphene quantum dots were synthesized and their ability for application as electrode materials was shown [3].

Method for the electrochemical production of PUMWCNTs with the possibility of controlling the degree of their opening, which makes it possible to obtain catalytic materials with predetermined properties, was developed. This was achieved by controlling the process by time and the potential of anodic oxidation.

A thermochemical method for the synthesis of nanocomposites based on g-C_3N_4 and PUMWCNTs was proposed. Composites with various ratios of initial materials (melamine, urea, and PUMWCNTs) were synthesized and studied. It is shown that at a ratio of urea to melamine of 2:1 and PUMWCNTs in quantity of 0.5 g, were obtained electrode material with characteristics approaching those of electrodes containing platinum. According to our approach, the best catalysts for oxygen reduction will be materials with a large value of the coefficient a in the Tafel equation, and therefore they will have a larger overvoltage of molecular oxygen release on them. Catalysts with a lower coefficient a will have a lower catalytic activity in the oxygen reduction reaction.

As a catalyst for the oxygen reduction reaction, mixed oxides of molybdenum and tungsten with a high oxygen evolution overvoltage were chosen, which were deposited on multiwalled carbon nanotubes. On these oxygen electrodes was obtained current density 600 mA/cm^2 at an electrode polarization of 350 mV, which approaches to the characteristics of electrodes containing platinum [4]. According to the approach of localization of reactions developed by us, for a fuel cell consisting of a hydrogen electrode with an alkaline electrolyte, catalysts with a low overvoltage of hydrogen evolution in an alkaline medium should be used.

While for the reaction of electrochemical accumulation of hydrogen occurring on the metal hydride (MG) electrode of a nickel-metal hydride battery, metals with a high overvoltage of molecular hydrogen evolution in an alkaline medium must be used to coat hydride-forming alloys. Thus, the approach of localization electrochemical reactions for electrochemical reactions developed by us makes it possible to evaluate the electrocatalytic properties of composite materials and makes it possible to synthesize new hybrid materials with desired properties for electrodes of chemical power sources. The prospects of using the developed materials for the creation of oxygen electrodes for fuel cells, for lithium ions electrodes, photoanodes, and for the synthesis of luminescent quantum dots of graphene are shown.

References:

1. M.O. Danilov, G.Ya. Kolbasov, I.A. Rusetskii, I.A. Slobodyanyuk, ECS Transaction. **40** (2012) 133.
2. M.O. Danilov, I.A. Slobodyanyuk, I.A. Rusetskii, G.Ya. Kolbasov, in: M. Aliofkhazraei, N. Ali, W.I. Milne, C.S. Ozkan, S. Mitura, J.L. Gervasoni (Eds), Graphene Science Handbook. Fabrication Methods, CRC Press/Taylor & Francis Group, 2016, p. 205.
3. M.O. Danilov, S.S. Fomanyuk, G.I. Dovbeshko, O.P. Gnatyuk, I.A. Rusetskyi, G.Ya. Kolbasov, Journal of the Electrochemical Society. **168** (2021) 044514.
4. M.O. Danilov, G.A. Kolbasov, SOP Transactions on Catalysis. (2015) 1.

P-5

MECHANOCHEMISTRY AND SONOCHEMISTRY IN NANOSIZED MATERIALS AND CATALYSTS PREPARATION

V.O. Zazhigalov[1]*, O.V. Sachuk[2], O.V. Kiziun[1], O.A. Diyuk[1]

[1]Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Naumov str., 13, Kyiv, 03164 Ukraine
[2]The State Scientific Research Forensic of Centre of the MIA of Ukraine, Bogomoletz st., 10, Kyiv, 01601 Ukraine, vazazh@ukr.net; zazhigal@ispe.kiev.ua

The results of mechanochemistry and sonochemistry use for preparation of nanosized materials and their use in different catalytic reactions will be presented. The mixtures of two oxides or one oxide-one metal salt were used in the synthesis what permits to decrease the harmful pollutants in environment. Mechanochemical synthesis was realized in air and sonochemical treatment was effected in water solution at room temperature.

The synthesis of perovskites. The samples of $BaTiO_3$, $CaTiO_3$, $SrTiO_3$, $PbTiO_3$, $BiFeO_3$, $LiNbO_3$ with high specific surface area (2-10 times more than obtained traditional methods) were prepared by these two methods and their physical-chemical properties were determined.

The synthesis of core-shell structure composites. The treatment of oxides mixtures MoO_3-CeO_2, TiO_2-SnO_2, TiO_2-ZrO_2 permits to prepare the nanodimension composites with the core-shell structure, their properties were determined.

The synthesis of new compounds in different nanogabitus. The nanocompounds of zinc molybdate and bismuth molybdate in form of rods, needles, spheres were prepared. Their properties were determined.

Treatment of the compounds on the base of vanadium oxide. The samples of V-Ti-O, V-Si-O, V-Ce-O, V-P-O were prepared on the base of this two technique and their properties were studied.

Catalytic properties. The catalytic properties of the synthesized samples were studied in processes of gas phase oxidation of methane to formaldehyde, ethane to ethylene, propane to propylene, butane (in different hydrocarbon concentration) to maleic anhydride, furane, butene and butadiene, pentane to maleic and phthalic anhydrides, benzene to phenol by oxygen, ethanol to acetaldehyde. The photocatalytic activity of the sample was studied in the processes of oxidative degradation of herbicides and drugs. The obtained results show that the most part of the prepared catalysts demonstrates better activity, selectivity and productivity than well known catalysts of these processes.

P-6

HIERARCHICAL ZEOLITES AND THEIR NANOCOMPOSITES AS CYCLOADDITION REACTION CATALYSTS

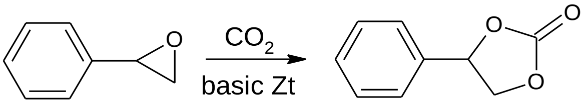
O.V. Shvets*, M.M. Kurmach, D.V. Kyryliuk

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, alexshvets@ukr.net

Zeolites are most used heterogeneous catalysts for the industrial and fine organic synthesis acid-base and redox processes. Hierarchical zeolites are materials with combine two or more levels of pores. The role of the hierarchy in zeolites is manifested both in increasing the accessibility of zeolite active centres on the surface of inter- or intracrystalline mesopores compared to traditional zeolites and in changing the strength of acid and basic centres located on the external surface. Such variation changes the activity and selectivity of catalysts based on hierarchical zeolites. This work presents the results of the catalytic properties study for hierarchical zeolites in cycloaddition reactions of alkene or epoxides under CO_2 pressure.

Hierarchical zeolites (BEA, MFI, MOR and FER zeolites nanosheets, MTW and MOR nanorods and BEA nanoparticles with different chemical composition) were obtained by soft template methods using Gemini-type surfactants as structure-directing agents (SDA) [1]. Prepared hierarchical zeolites possess high specific external surface, mesopore volume and high availability of active centres for bulk molecules. The basic properties of zeolites were developed by changing the composition of zeolites, ion exchange or supporting of basic oxides on the zeolite surface. An important feature of the basic catalysts for this reaction was the neutralization of Brønsted acid centres. Basic properties of zeolite materials by benzene and $CDCl_3$ spectral probes, CO_2 volumetric adsorption and TPD of CO_2 were studied.

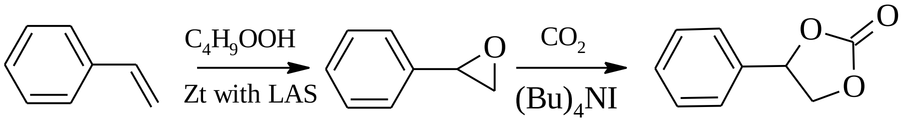
On the example of conversion of styrene epoxide into 4-phenyl-1,3-dioxolan-2-one it is shown that Cs-form of hierarchical zeolites, titanosilicates, template-containing hierarchical zeolites, basic zeolite nanocomposites as well as mesoporous molecular sieves with anchored basic groups show high catalytic activity in this reaction (conversion of styrene epoxide up to 98.7%) and a fairly high selectivity for target product (43.0 - 100%). The main by-product of the reaction is 1-phenylethane-1,2-diol - the product of hydrolysis of the original epoxide.



The basicity, adsorption and catalytic properties of complex magnesium/cerium oxides and their nanocomposites using hierarchical zeolites of structural types BEA, MTW or mesoporous materials of type MSM-41 with basic properties as well as titanosilicate hierarchical zeolites with BEA, MTW and MFI topology in the reaction of the synthesis of cyclic carbonates from styrene under CO_2 pressure were studied.

It is shown that the doping of CeO_2 by magnesium oxide leads to an increase in the basicity of materials, including those deposited on hierarchical zeolites or mesoporous materials It is shown that CeO_2 exhibits moderate catalytic activity (styrene conversion up to 74%) in the first stage (epoxidation of styrene with tert-butyl alcohol hydroperoxide) of the tandem reaction of styrene conversion into cyclic carbonate (the catalyst of the second stage is tetrabutylammonium iodide). The selectivity for the target product is up to 83%, among the side products are compounds of deep oxidation of styrene (ketoalcohols, diketones, etc.). Doping CeO_2 with magnesium oxide leads to a slight decrease in selectivity for the target product (up to 61%), but an increase in conversion (up to 93%). The application of mixed magnesium/cerium oxides on hierarchical zeolites of different chemical composition of structural types BEA, MTW or on mesoporous materials of the type MSM-41 leads to a significant increase in the conversion of styrene (up to 95 – 100%) while maintaining sufficiently high selectivity (up to 78 – 80.5 %) by target product – 4-phenyl-1,3-dioxolan-2-one. The maximum achieved yield of the target product is 80.5%.

It is shown that titanosilicate zeolites are characterized by the presence of Lewis acid centers (50 – 200 μmol/g according to pyridine ad/desorption data at 150 °C) and exhibit weak basic properties (concentration of retained CO_2 from TPD CO_2 curves – no more than 25 μmol/g). All investigated samples (BEA, MTW, and MFI series of titanosilicate zeolites) show sufficiently high catalytic activity (styrene conversion 75 – 100%) in the first stage (epoxidation of styrene with hydroperoxide of tert-butyl alcohol) of the tandem reaction of the transformation of styrene into cyclic carbonate (the catalyst of the second stage is tetrabutylammonium iodide).



The selectivity for the target product varies in the range (60-100%), among the by-products are compounds of deep oxidation of styrene (ketoalcohols, diketones, etc.). The conversion of styrene in the studied reaction increases with the concentration of Lewis acid centers, the selectivity is the highest for MFI titanosilicate zeolites. The simultaneous introduction of Ti and Al atoms into the BEA-type zeolite structure leads to a significant decrease in selectivity for the target product, apparently due to the appearance of Brønsted acid centers in the structure. Additional ion exchange for cesium cations in aluminotitanosilicate zeolites leads to an increase in selectivity for cyclic carbonate, which opens up the prospects of using such materials as catalysts for both stages of the studied tandem process of synthesis of cyclic carbonates from styrene under CO_2 pressure.

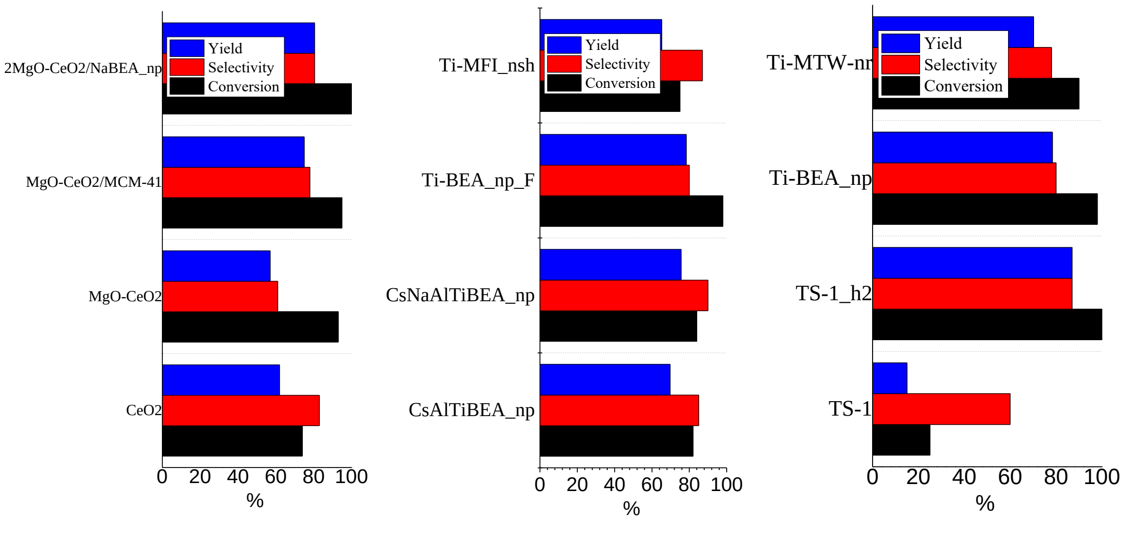


Fig. 1. Catalytic properties of zeolites in cyclic carbonate synthesis from styrene under CO_2 pressure.

Thus, hierarchical zeolite materials with basic centers show high catalytic activity in conversion of styrene epoxide into 4-phenyl-1,3-dioxolan-2-one. Hierarchical zeolite materials with Lewis acid centers show high catalytic activity in cyclic carbonate synthesis from styrene under CO2 pressure. The role of the hierarchy of zeolite materials is manifested both in increasing the accessibility of zeolite active centers on the surface of mesopores compared to traditional zeolites and in changing the strength of acid centers located on the external surface, which changes the activity and selectivity of catalysts based on hierarchical zeolites in acid-base reactions.

P-7

BASIC TRENDS IN CATALYSIS OF THE HYDRODEHALOGENATION REACTION OF HALOARENES

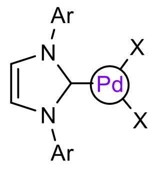
N.I. Korotkikh[1]*, V.Sh. Saberov[1], O.S. Avksentiev[1],
G.F. Rayenko[2], L.M. Vakhitova[2]

[1]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Acad. Kukharia St., 5, Kyiv, 02660 Ukraine, nkorotkikh@ua.fm*
[2]*L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Kharkiv road, 50, Kyiv, 02160 Ukraine*

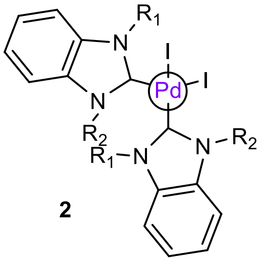
The review report is devoted to the catalytic reactions of hydrodehalogenation (HDH) of haloarenes, which has recently gained importance in fine organic synthesis and as a promising method of disposal of haloarene production waste, in particular, persistent organic pollutants (POPs). The urgent need for their utilization promoted the development of reaction methods using hydrogen-containing reagents (molecular hydrogen, organic hydrides, alcohols and formates in an alkaline medium - the so-called hydrogen transfer reactions), electron transfer reactions (photoinitiated reduction, reduction under the influence of electron donors, electrocatalytic processes), reduction reactions with metals, catalytic processes under the influence of inorganic compounds and organic complexes of metals. Some reactions take place at high temperatures (catalysis by metal oxides), some - under relatively soft conditions, even at room temperature (hydrogen transfer reactions). Among the methods of hydrodehalogenation, deuterodehalogenation of haloarenes should be singled out separately, which allow obtaining aromatic deutero compounds. These directions of works are the main trends in the development of the HDH methods.

Considerable material has been accumulated on the use of HDH for the neutralization of various haloarenes - toxins, pesticides, fire-resistant additives, in particular, dioxins, hexachlorobenzene, DDT, pentachlorophenol, tetrabromobisphenol A, pharmaceutical preparations - triclosan, diclofenac, chlorophen, etc.

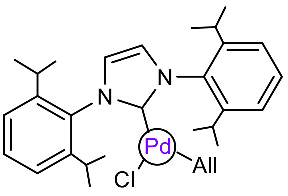
An important place among reaction catalysts is occupied by nanoparticles of metals (palladium, nickel, gold, etc.), in particular, heterobimetallic composites, which exhibit increased catalytic efficiency in relation to monometallic nanocatalysts. Very high efficiency in hydrogen transfer reactions is shown by carbene (imidazole-2-ylidene) complexes with steric protection by 2,6-dibenzhydrylaryl (dbmp, dbep) substituents **1** (TON up to 300,000 when carrying out the reaction of hexachlorobenzene with metal alkoxides at a temperature of 80 °C) [1,2], to a lesser extent - triazolylidene analogs [3]. High catalytic effects in the *p*-dibromobenzene reaction were obtained for *cis*-biscarbene complexes of palladium iodide **2** (TON up to 98000, t-BuOK, isopropanol, 70 °C), and under microwave irradiation with a complex catalyst of imidazol-2-ylidene **3** and palladium-allyl chloride (TON 4000, TOF up to 120000 h^{-1}, t-BuOK, isopropanol, 120 °C). A new direction of HDH is the use of heterobimetallic carbene complexes **4**, which are more effective than catalysts with two identical metal atoms (homobimetallic).



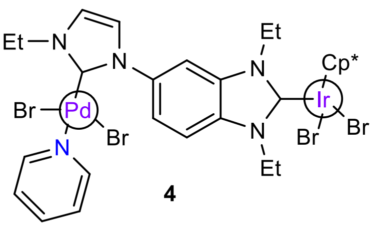
1
Ar = dbmp, dbep;
X = Cl, I



2

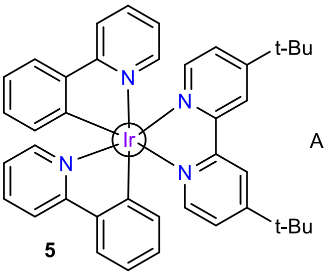


3

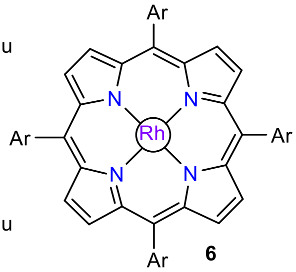


4

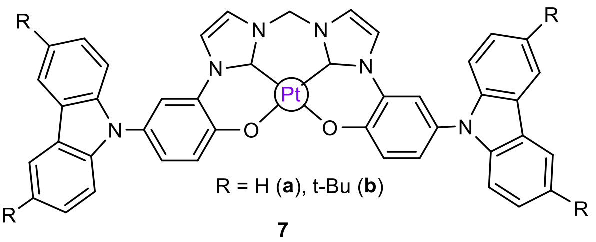
Complexes of iridium and pyridines **5** [4], bipyridines, phenanthroline, diimines, rhodium porphyrin complexes **6**, chelated biscarbene complexes of platinum **7**, etc., occupy a significant place in the search for highly effective photoinitiators of the HDH reaction. The advantage of the method is soft process conditions (even at room temperature) and the use of visible diode light (λ 360-440 nm).



5



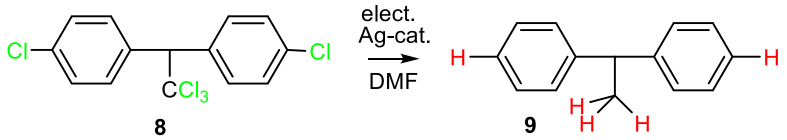
6

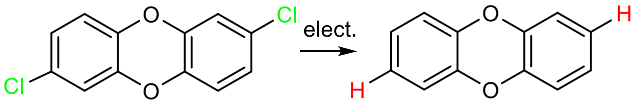


R = H (**a**), t-Bu (**b**)

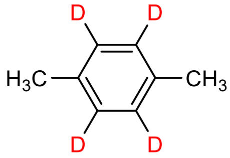
7

A considerable number of works are devoted to the use of electrocatalytic methods in the disposal of POPs. In this way, it is possible to completely dehalogenate DDT **8** (up to **9**), chloro-substituted dibenzofurans, dibenzodioxins **10** (up to **11**), but the degradation of the most toxic representatives of the latter has not been studied.

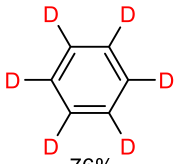




10 **11**



12 96%



13 76%

Using nanolayered cadmium selenide photocatalysis, it was possible to obtain tetradeutero-*p*-xylene **12** and hexadeuterobenzene **13** from the corresponding halogenated benzenes in high yields.

HDH of haloarenes promises to become the main industrial method of POPs disposal in the future.

References:

1. N.I. Korotkikh, O.P. Shvaika. Organic reactions catalysis by carbenes and metal carbene complexes. LAP Lambert Academic Publishing, 2015, 385 p.
2. V. Sh. Saberov, D. A. Evans, N. I. Korotkikh, A. H. Cowley, T. M. Pekhtereva, A. F. Popov, O. P. Shvaika, Dalton Trans. **43** **(**2014) 18117 – 18122.
3. N. V. Glinyanaya, V. Sh. Saberov, N. I. Korotkikh, A. H. Cowley, R. R. Butorac., D. A. Evans, T. M. Pekhtereva, A. F. Popov, O. P. Shvaika, Dalton Trans. **43** **(**2014) 16227 – 16237.
4. M. K. Cybulski, D. McKay, S. A. Macgregor, M. F. Mahon, M. K. Whittlesey, Angew. Chem. Int. Ed. **56** (2017) 1515 –1519.

P-8

PROGRESS IN THE CATALYTIC PROPERTIES OF CARBON NANOMATERIALS IN HYDROGENATION OF ORGANIC SUBSTANCES

I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, igorbyhko@ukr.net

During last decade, a wave of studies dedicated to the carbon nanomaterials such as multi-walled carbon nanotubes (CNT) and reduced graphene oxide (rGO) catalytic activity in the hydrogenation reactions have been reported. Particularly, for the first time, in our group it was reported that rGO and CNT are materials that provides a catalytic activity in the gas-phase hydrogenation reactions with molecular hydrogen at ambient pressure [1,2]. It was proposed a few different mechanisms of this reaction. However, the structure of catalytic active sites on the surface of the carbon nanomaterials in the hydrogenation reaction is still an open problem. It was shown that H_2 activation can take place at the carbon atom vacancies. A possibility of H_2 activation by frustrated Lewis pairs on the carbons surface has been also discussed.

The main objective of presented research is the determination of the influence of the structure and functionality of CNT and rGO on the catalytic activity in the hydrogenation of organic substrates by molecular hydrogen on the example of ethylene hydrogenation. The ethylene hydrogenation is a simple model gas-phase reaction that convenient to establish a dependence between the structural, functional parameters of carbon nanomaterials and their catalytic properties. Additionally catalytic activity of CNT and rGO was shown in the acetylene hydrogenation and selective hydrogenation of nitrocompounds to corresponding aminocompounds in the liquid phase. It was shown, that the catalytic activity of rGO strongly depends on its structural characteristics. An increase in the surface area and a decrease in the oxygen content enhance the catalytic activity of rGO. The defectiveness and oxygen content are crucial for the catalytic performance of rGO obtained either by thermal reduction of graphene oxide in hydrogen or by reduction of graphene oxide with hydrazine. This conclusion has significant implications for the potential applications of rGO as a hydrogenation catalyst.

The comparison of catalytic activity of different carbon materials, as well as conventional metal-based catalysts are presented in Fig1.

Obtained results show that non-activated carbon nanomaterials do not exhibit catalytic activity. Increasing the temperature of activation from 100°C to 400°C increases the catalytic activity by three orders of magnitude. Further temperature increase leads to a decrease in catalytic activity. An increase in the CNT diameter significantly decreases the catalytic activity. The obtained ethylene conversion rate at 150 ^{o}C for CNT is 0.02 $mmol\cdot g^{-1}\cdot s^{-1}$ which is higher compared to rGO, and, however, significantly lower compared to 0.25%Pt/SiO_2 with 0.84 $mmol\cdot g^{-1}\cdot s^{-1}$.

Our results shows the high stability of CNT and rGO compared to the typical hydrogenation catalysts in hydrogen-rich and ethylene-rich atmospheres. This result offers new opportunities for the application of nanocarbon-based catalysts in the hydrogenation reaction at high temperatures, which is extremely important to replace catalysts operating under conditions where the metal-containing catalysts deactivate due to the formation of the carbonaceous deposits.

The catalytic activity of CNT and rGO in the ethane direct dehydrogenation reaction at temperatures up to 700 ^{o}C was studied. The selectivity for ethylene of 80–90 % was achieved. The high stability of catalysts at 700 °C was demonstrated. It was shown that ethane and hydrogen are adsorbed on the same adsorption sites and hydrogen suppresses ethane dehydrogenation

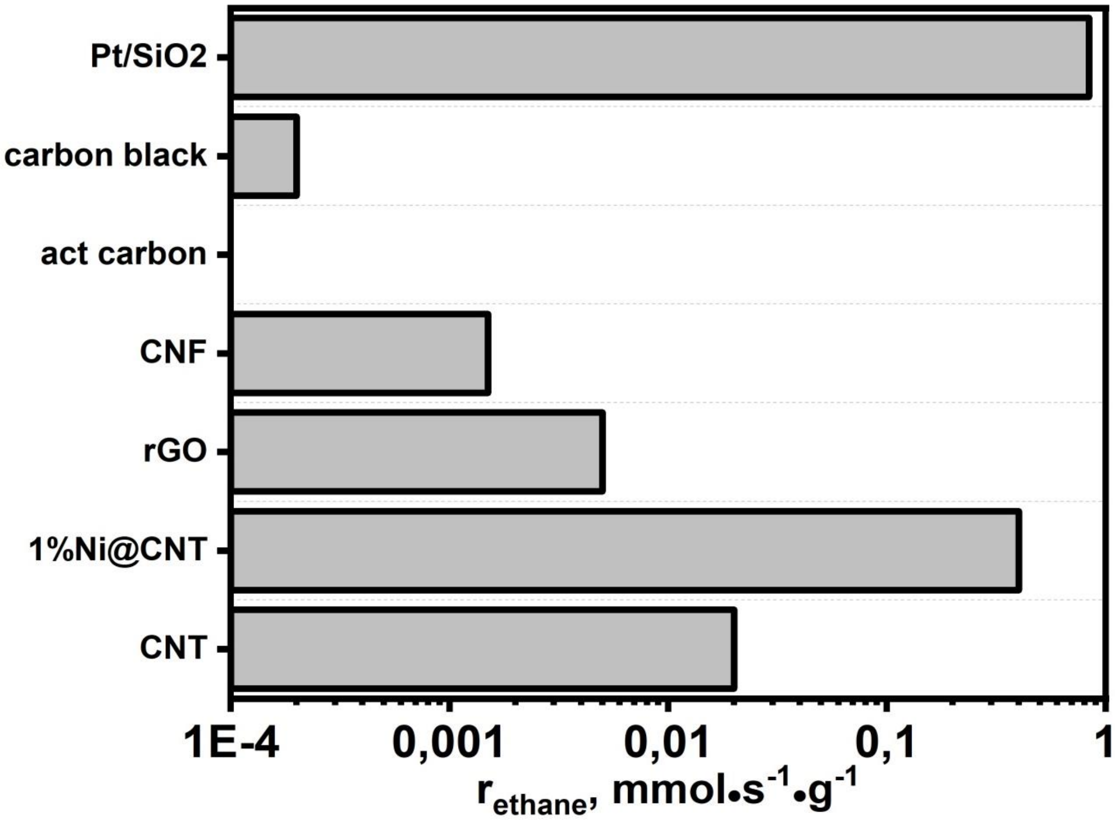


Fig. 1. Comparison of catalytic activity of carbon nanomaterials in the ethylene hydrogenation at 150 ^{o}C. CNF – carbon nanofibers; Pt/SiO$_2$ – 0.25% Pt supported on SiO$_2$.

The applying carbon-encapsulated Ni nanoparticles supported by CNT (Ni@CNT) was used as an approach to increase of the catalytic activity of carbon nanomaterials in the hydrogenation reactions. Surface of obtained nanocomposites does not contain Ni and corresponds to CNT. The content of Ni was found to strongly influence the catalytic properties of Ni@CNT. Samples containing 1% of Ni demonstrated the highest activity for both the hydrogenation of the C=C bond and the dehydrogenation of ethane. Investigation of the catalytic properties of Ni@CNT nanocomposites shows that an increase in the Ni content increases their catalytic activity in both gas and liquid-phase hydrogenation reactions involving molecular hydrogen as well as in dehydrogenation of ethane. Encapsulated Ni nanoparticles do not engender the creation of novel active sites and that the hydrogenation reaction mechanism for Ni@CNT composites is identical to that of CNT. The main effect influences the catalytic activity of Ni@CNT is the Schwab effect, which represented by a charge transfer. Although this effect may be offset by the high oxygen content and defectiveness of CNT.

References:

1. I. Bychko, P. Strizhak, Full. Nanot. Carb. Nanostr. **26** (2018) 804.
2. T. Perhun, I.Bychko, A. Trypolsky, P. Strizhak., Theoret. Exp. Chem. **48** (2013) 367.

P-9

THE ROLE OF THE CATALYSTS' BIFUNCTIONALITY IN THE MULTISTAGE PROCESSES

S.M. Orlyk

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine,
Prosp. Nauky, 31, Kyiv, 03028 Ukraine, orlyk@inphyschem-nas.kiev.ua

The actual heterogeneous-catalytic processes (also tandem processes) are multistage, and effective catalysts are designed by forming *functional centers of various nature* on their surface. Therefore, understanding the bi(poly)functionality of catalysts is critically important.

The results of the design bifunctional metal-oxide and zeolite catalysts based on the dependences: composition – physical-chemical characteristics – catalytic properties are presented for the processes of "small molecules" (nitrogen oxides, methane, ethylene) conversion, and tandem processes of (bio)ethanol conversion with obtaining valuable products (1,3-butadiene, 1-butanol). The role of catalysts' bifunctionality (in particular, the number and strength of redox and acid-base centers) is considered in ensuring the efficiency of the oxidation-reduction processes [1, 2] (Table).

Table. Current processes over solid-phase bifunctional catalysts

Process	Bifunctional catalysts /redox, acid-base sites	Effect of catalyst bifunctionality on	
		process stages	process indices
Selective catalytic reduction of nitrogen oxides by hydrocarbons	Rh–Me_xO_y / ZrO_2 (M = Co, Cr, Ce); CoO(Mn,Fe)/SO_4^{2}/ZrO_2	Activation of NO and C-H bond	Increase in NO conversion
SCR of N_2O by hydrocarbons	FeZSM-5 (Y, M)	Activation of N_2O and C_nH_m	Increase in N_2O conversion
Partial oxidation of C_3, C_4 alkanes by NO, N_2O	P–Mo-HPA/ZrO_2, (Fe, Al)–MCM-41	Activation of NO, N_2O and C_nH_m	Increase in selectivity (i-propanol)
Ethylene epoxidation by nitrous oxide	Ag+M_2O/cordierite (M=Cs, K, Na)	Prevents C_2H_4O oxidation	Increase 2 times in ethylene oxide yield
Deep methane oxidation	M_xO_y/ZrO_2(Al_2O_3) (M = Mn, Co, Cr)	Activation of C-H bond	Lower temperature of reaction beginning
CO_2(dry)-reforming and tri-reforming of methane, steam conversion of C_2-C_4 alkanes	NiO-Al_2O_3 (Li, Na, K) (CeO_2,La_2O_3)/ cordierite	Inhibition of the catalyst' surface carbonization	Increase the operation stability
Ethanol conversion into 1,3-butadiene (ETB process)	ZnO/ZrO_2-SiO_2; Cu(Ag)/MgO–SiO_2; Zn-La-Zr-Si-oxides	EtOH dehydrogenation, AA condensation	Increase in activity/ stability catalysts (ETB, aq. ethanol)
Guerbet condensation: EtOH → 1-butanol (BuOH) → 2-ethylhexanol (2EH)	Mg-Al(La,Ce) oxides Mg(Sr)-Ca-phosphate hydroxyapatites	Increase of acetaldehyde formation stage	Increase in activity, selectivity to BuOH, 2EH
SCR NO by C_2H_5OH	Ag/BEA	Reagent activation	H_{2-} promoting effect
EtOH-to-BD (ETB-process)	M-TaSiBEA(M-Ag, Cu, Zn), NbSiBEA	EtOH dehydrogenation to AA	Increase in activity to BD formation
Propane dehydrogenation with CO_2	Zn,Ga (Ta,Nb)BEA	Activation of C_3H_8 and CO_2	Increasing activity/ selectivity to C_3H_6

Issues related to the impact/role of bi(poly)functionality of the surface of complex oxide catalytic systems considered to ensure the efficient progress (an increase of indices) of the tandem process of ethanol conversion with doubling of the carbon chain for the selective obtaining of 1,3-butadiene. In particular, regulation of the acid-base properties of the surface by introducing a dehydrogenating component (ZnO, Cu, Ag), modification with rare earth elements [3] to increase the activity and stability of the catalysts in the process of converting ethanol-water mixtures into 1,3-butadiene. Effect of bifunctionality of the complex catalytic systems – Mg-Al (La, Ce)-hydrotalcite derived oxides and Mg(Sr)-modified Ca-phosphate hydroxyapatites (HAP) systems – in Guerbet condensation of ethanol and 1-butanol with carbon chain elongation is considered [4].

The results regarding metal-zeolite catalysts of the BEA structure is presented (role of the silicate module of the zeolite and the nature of the heteroelement in the manifestation of the bifunctionality of the catalysts) for the effective course of the processes: SCR of NO_x, the production of 1,3-butadiene from ethanol, and propylene obtaining by dehydrogenation of propane with CO_2. With the optimal combination of oxidation-reduction and acid-base sites, an increase in the activity, selectivity, and productivity of the catalysts is achieved [5-7].

The activity of Ag/BEA catalysts in the selective reduction of nitrogen oxides (NO_x) with ethanol is due to the presence of acidic and surface redox sites. The Ag’s role involves forming the redox and Lewis acid sites (LAS) over which the reagents are activated. The promoting effect of H_2 is produced by the presence of LAS and Ag-nanoclusters.

On the BEA zeolites with the incorporated heteroelements, it is possible to achieve high selectivity in the production of BD from ethanol on account of the formation of a large number of active sites of the one key steps of the process – aldol condensation of the acetaldehyde (AA). The role of metals (Ag, Cu, Zn) in the M-TaSiBEA catalysts consists in the formation of redox sites for proceeding EtOH dehydrogenation to AA, and in the modification of acid-base sites increasing their activity in the subsequent steps of the process. The highest ethanol conversion rates and selective BD formation with a high (>60%) yield are achieved in the presence of the CuTaSiBEA catalyst.

The adjustment of acid-base characteristics of BEA zeolite catalysts by dealumination of the zeolite (Si/Al=17) followed by the incorporation of heteroelement cations ensures the formation of Ga(Zn)SiBEA compositions (Si/Al=1000) with significantly reduced acidity and basicity, thus increasing their activity/selectivity for propylene production in the CO_2-assisted propane dehydrogenation process. Weak and medium-strength LAS formed by isolated Ga (III) play a key role in the target process over Ga (Ta, Nb)SiBEA catalysts. Propylene yield reaches 37% (873 K) in the presence of the $Ga_{4.0}SiBEA$ catalyst, a higher propylene formation selectivity of 70-77% was achieved over $Ga_{2.0}Ta_{2.0}SiBEA$. Propylene selectivity of 74% and yield of 22% was achieved over the $Zn_{1.0}SiBEA$ catalyst, characterized by mainly medium-strength acid (LAS) and basic sites on the surface.

The presented results demonstrated the effectiveness of bifunctional catalysts in current multistage processes. Understanding bi(poly)functional catalysts will enable the creation of new catalysts with improved characteristics.

References:

1. S.N. Orlik, Kinetics and Catalysis. **49** (2008) 537.
2. S.N. Orlyk, Catalysis Today. **191** (2012) 79.
3. O.V. Larina, P.I. Kyriienko, D.Yu. Balakin, et al., Catalysis Science&Technology. **9** (2019) 3964.
4. O.V. Zikrata, O.V. Larina, K.V. Valihura, et al., ACS Sustainable Chem. Eng. **9** (2021) 17289.
5. N.O. Popovych, O.V. Larina, S.M. Orlyk, et al., Theor. Exp. Chem. **54** (2018) 255.
6. S.M. Orlyk, M.R. Kantserova, V.I. Chedryk, et al., Journal of Porous Materials. **28** (2021) 1511.
7. A.Yu. Kapran, S.M. Orlyk, Theor. Exp. Chem. **58** (2022) 118.

P-10

NANOCOMPOSITE CATALYSTS WITH REDUCED OR ZERO CONTENT OF PLATINUM GROUP METALS FOR HYDROGENATION OF ORGANIC COMPOUNDS

S.V. Kolotilov

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine,
Prosp. Nauky, 31, Kyiv, 03028 Ukraine, s.v.kolotilov@gmail.com

Hydrogenation processes are widely used in large-scale chemical production for obtaining components of motor fuels and oils, solvents, substances for the paint and food industry, as well as in the fine organic chemistry for preparation of active substances for pharmaceuticals and agrochemistry. Currently, the most active commercial hydrogenation catalysts contain metals of platinum group, primarily Pd. Such catalysts have high productivity, but are expensive and toxic (the latter causes the need for thorough purification of hydrogenation products, which is critically important in the case of compounds for medicinal chemistry). Raney nickel is used as an alternative to Pd, but its catalytic activity and selectivity are not high for many tasks.

In this presentation, results of the authors in the field of development of hydrogenation catalysts in the are summarized. Several strategies were applied in order to reduce content of platinum group metals in hydrogenation catalysts: (1) reduction of the content of Pd in the catalyst due to significant increase of its performance; (2) creation of catalysts based on Ni or Co, which possess high performance due to formation of active nanoparticles; (3) development of new catalytic systems based on rhenium or molybdenum sulfides.

The series of Pd- and Ni-containing composites were created by decomposition of the complexes of Pd^0 and Ni^0 at presence of porous carrier. Simple and efficient approaches to the creation of composites of Ni and Co nanoparticles by pyrolysis of the respective M^{II} complexes deposited on porous carriers were proposed. Besides, Ni-containing composites were prepared by reduction of Ni^{II} in pores of porous coordination polymer. The obtained composites had high catalytic performance in the processes of hydrogenation of a wide range of unsaturated organic compounds (alkenes, dienes, alkynes, nitro compounds, carbonyl compounds, heterocyclic compounds of various structures), amination of carbonyl compounds with amines and acetonitrile. The catalytic performance of the nanosized palladium composites, developed in the study, in the processes of hydrogenation of organic compounds was an order of magnitude higher compared to commercially available analogues, making possible to reduce palladium consumption significantly. It was found that the hydrogenation of halogen-containing N- and S-heterocyclic compounds in the presence of rhenium or molybdenum sulfides proceeded with unprecedented selectivity and resulted in formation of products, containing C-Br and even C-I bonds, which opens up a unique possibility for obtaining halogen-containing saturated organic compounds.

The methods for scale-up preparation of some of the catalysts were developed (up to 0.5 kg in one batch). The created catalysts were tested at Ukrainian enterprises of UkrOrgSintez and Enamine LLC. Such catalysts can be considered as an alternative to systems based on platinum metals for the hydrogenation of organic compounds on a laboratory and semi-industrial scale.

This study was partially supported by the project “The development of heterogeneous catalytic processes for the production of liquid synthetic motor fuels from domestic raw for the energy independence of the state” of the National Academy of sciences of Ukraine.

P-11

ELECTRONIC MODELS OF CATALYTIC PROCESSES

N. Turaeva

Webster University, Saint Louis, MO 63119, USA, nigoraturaeva82@webster.edu

Sabatier's principle, well recognized in catalysis, expresses the importance of optimal adsorption where the interaction between the catalysts and adsorbed species should be neither too strong nor too weak. It is manifest in the so-called 'volcano-plots', introduced by Balandin [1], which are now widely used to describe an optimal reaction rate as a function of adsorbate/catalyst properties such as the heat of adsorption. The justification for the volcano relationship arises from the linear Brønsted- or Bell-Evans-Polanyi (BEP) equation describing the dependence of the apparent activation energy on the global reaction enthalpy. The classical volcano curves consider a single reactant, either adsorbent or product. In general, the volcano-shaped reaction rate can be obtained via the interplay of both reactant adsorption and product desorption.

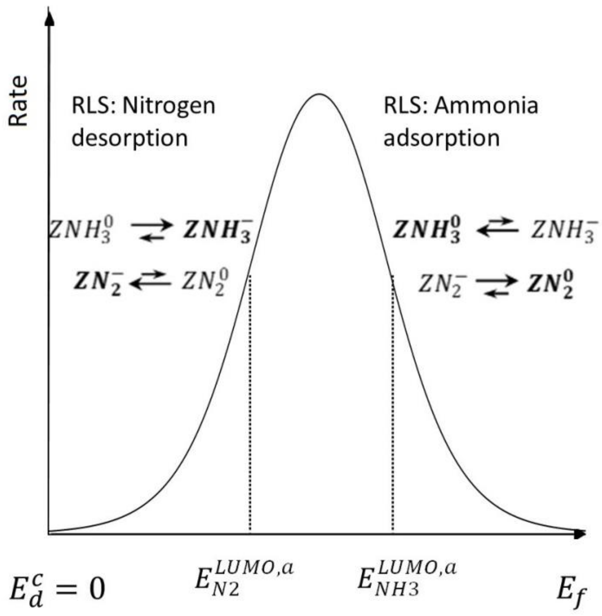


Fig. 1. Scheme for the ammonia decomposition reaction rate with respect to the Fermi level of an arbitrary metal catalyst (E_d^c is set as a reference point). The antibonding LUMOs of adsorbed nitrogen and ammonia species are expected on either side of the rate maximum. RLS = rate limiting step

This can be achieved by considering the role of the Fermi level of the catalysts based on Wolkenstein's electronic theory for semiconductors [2] and d-band theory for transition metals [3]. According to the electronic theory, the Fermi level determines the relative populations of charged and neutral surface intermediates exhibiting different reactivities and involving into the adsorption, reaction, and desorption processes. As a result, the reaction rate of chemical reactions can be represented as a function of the Fermi level, and all factors of the Fermi level of the catalysts, including size, alloying, support materials, addition of promoters or inhibitors, impact on the relative concentrations of surface intermediates and hence on the reaction rate. We applied the electronic theory of catalysis to different chemical reactions such as CO oxidation by gold NPs [4], ammonia decomposition (fig.1) [5], and simple enzymatic reactions. Considering the charge transfer between the catalysts and surface intermediates in the framework of well-established mechanism of chemical reactions allows us to explain the dependence of the reaction rate on the chemical nature of the catalysts, the size of nanoparticles, alloying effect, etc. It has been also demonstrated that the electronic theory of catalysis can be applied to chirality selective growth of single-walled carbon nanotubes [6]. The role of the catalyst in chirality selection was emphasized via optimization of chemisorption strength between the carbon species and the catalysts surface needed to achieve stable nucleation and fast growth rates of the carbon nanotubes.

References:

1. Balandin, A. Advances in catalysis; Elsevier, 1969; pp 1−210.
2. Wolkenstein, T. Advances in Catalysis; Elsevier, 1960; pp 189−264.
3. Hammer, B.; Nørskov, J. K. Advances in catalysis; Elsevier, 2000; pp 71−129.
4. Turaeva, N.; Krueger, H. Catalysts 2020, 10, 288.
5. N. Turaeva, R. Fushimi, G. Yablonsky, The journal of Physical Chemistry C 124(48) (2020) 26310-26319.
6. N. Turaeva, Y. Kim, I. Kuljanishvili, Nanoscale Adv., 2023, 5, 3684-3690.

P-12

HAPPY PHOTOCATALYSTS AND UNHAPPY PHOTOCATALYSTS: TO GO BEYOND THE IDENTIFICATION PROBLEM

B. Ohtani[1]*, M. Takashima[2]

[1]Hokkaido University and Nonprofitable Organization touche NPO, North 4, West 14, Sapporo 060-0004, Japan, bunshoohtani@gmail.com
[2]Department of Energy Science and Engineering, Nagoya University, Furo-cho, Nagoya 464-8603, Japan

How can we design functional solid materials, such as catalysts and photocatalysts? What is the decisive structural parameters controlling their activities, performance or properties? What is obtained as structural properties by popular conventional analytical methods, such as X-ray diffraction (XRD) or nitrogen-adsorption measurement, is limited to bulk crystalline structure and specific surface area, i.e., no structural characterization on amorphous phases, if present, and surface structure has been made so far. This is because there have been no macroscopic analytical methods to give surface structural information including possibly-present amorphous phases. Thus, in the field of material science, not that of organic chemistry, discussion on the properties, activities or performances of solid functional materials has been made without identification. Considering the reason for necessity of strict identification to avoid confusion in the discussion in the field of organic chemistry, now we material scientists may be in the confusion and misunderstandings.

Recently, we have developed reversed double-beam photoacoustic spectroscopy (RDBPAS) which enables measure energy-resolved distribution of electron traps (ERDT) for semiconducting materials such as metal oxides [1-3]. Those detected electron traps (ETs) seem to be predominantly located on the surface for almost all the metal oxide particles, and therefore they reflect macroscopic surface structure, including amorphous phases, in ERDT patterns. Using an ERDT pattern with the data of CB bottom position (CBB), i.e., an ERDT/CBB pattern, it has been shown that metal oxide powders, and the other semiconducting materials such as carbon nitride, can be identified without using the other analytical data such as XRD patterns or specific surface area, and similarity/differentness of a pair of metal-oxide samples can be quantitatively evaluated as degree of coincidence of ERDT/CBB patterns. In this talk, an approach of material design based on the ERDT/CBB-pattern analyses is introduced [4].

Analysis of photocatalytic activity of commercial titania powders using their ERDT/CBB patterns, i.e., arrangement of ERDT/CBB patterns in the order of photocatalytic activity in three kinds of photocatalytic reactions revealed that high-activity (happy) photocatalysts are all alike (similar ERDT/CBB patterns) and a middle or low-activity (unhappy) photocatalysts was inactive in its own way, i.e., inactive due to different reasons. This might be true as activities depend on many factors, known or unknown, and only one factor may reduce the activity even though the other factors are good. Thus, identification of sold functional materials may open up the novel way of design and characterization of solid inorganic materials [4].

References:

1. Nitta, A.; Takase, M.; Takashima, M.; Murakami, N.; Ohtani, B. *Chem. Commun.* **2016**, *52*, 12096-12099. [10.1039/C6CC04999K]
2. Nitta, A.; Takashima, M.; Murakami, N.; Takase, M.; Ohtani, B. *Electrochim. Acta* **2018**, *264*, 83-90. [10.1016/j.electacta.2017.12.160]
3. Nitta, A.; Takashima, M.; Takase, M.; Ohtani, B. *Catal. Today* **2019**, *321-322,* 2-8. [10.1016/j.cattod.2017.12.020]
4. Ohtani, B.; Takashima, M. *Catal. Sci. Technol.* **2022**, *12*, 354-359. [10.1039/D1CY01955D]

ORAL PRESENTATIONS

O-1

NANOSTRUCTURED SiC AND TiC SUPPORTS FOR COBALT AND Co/Mn FISCHER-TROPSCH CATALYSTS

S.A. Alekseev[1,2]*, N. Kruse[2]

[1]*Faculty of Chemistry, Taras Shevchenko National University of Kyiv, 64 Volodymyrska St., Kyiv, 01601 Ukraine, alekseev@knu.ua*
[2]*Voiland School of Chemical Engineering and Bioengineering, Washington State University, Wegner Hall 155, PO Box 646515, Pullman, Washington 99164-6515, USA*

The Fischer-Tropsch (FT) process, known for approximately a century, is a catalytic conversion of a gas blend named syngas (CO + H_2) occurring at elevated temperatures and pressures in the presence of nanodispersed transition metals (usually Co or Fe). Commonly it is used for production Diesel-type fuel, consisted of liquid alkanes. However, nowadays the studies on the FT are mainly directed to the possibility of production of olefins, alcohols and other chemically valuable products. The selectivity of FT catalysts could be tuned by different promoters and additives, particularly, addition of RedOx active oxides such as MnO to cobalt catalyst strongly increases the selectivity of alcohols formation [1]. The catalysts of this type are usually prepared by rapid co-precipitation of metal oxalates mixture followed by its reduction, to give intimate nanocomposite of Co nanoparticles (NPs) with corresponding metal oxide. The diffusion characteristics and mass transfer of the catalyst are governed by porous structure of the catalytic support, while the heat sink from the catalyst, which is important due to high exothermicity of the FT process, depends on its thermal conductivity.

Herein we report an application of porous SiC (por-SiC), SiC nanowires (NWs) and the nanoparticles of SiC and TiC, as the supports for FT catalysts. Monodispersed 9 nm Co NPs were synthesized by so-called hot injection procedure [2] and deposited on por-SiC and SiC NWs; the Co NPs are uniformly distributed within on the supports. As the oxalate co-precipitation is hardly compatible with traditional porous supports, the oxalate-based Co and Co/Mn catalysts were prepared as the composites with SiC and TiC NPs. These catalysts consisted of 1-20 microns size irregularly-shaped porous particles formed by support NPs, active catalyst phase consisted of 10-30 nm faceted cobalt NPs, uniformly distributed within the support; only small quantity of the few-micron size active phase clusters are present.

The catalyst Co/por-SiC demonstrated outstanding specific catalytic activity (117 $\mu mol_{CO} \cdot g_{Co}^{-1} \cdot s^{-1}$) in comparison with identical Co NPs, supported on SiO_2 carriers, high stability and increased selectivity to C_5+ alkanes. The activity of Co/SiC NWs, Co/SiC NPs and Co/Mn/SiC NPs is in the range of 15 – 18 $\mu mol_{CO}\ g_{Co}^{-1}\ s^{-1}$, which is typical for supported Co catalysts, the activity of Co/TiC and Co/Mn/TiC is significantly higher (27 – 30 $\mu mol_{CO}\ g_{Co}^{-1}\ s^{-1}$). Differently from Co/por-SiC, the catalysts Co/SiC NWs, Co/SiC NPs and Co/TiC and TiC NPs have promising selectivity to olefins (20 – 40%), also high chain lengthening probabilities for paraffins on Co/SiC and Co/TiC should be noticed. Both Co/Mn/SiC NPs and Co/Mn/TiC have expectedly good selectivity to alcohols, however the yield of high (C_5+) alcohols on is much higher for Co/Mn/TiC. Strong influence of the support nature on the catalyst selectivity can be explained either by the electronic effects of semiconducting SiC and TiC, or by surface and diffusion phenomena, such as the rate of water byproduct removal.

References:

1. Xiang, Y.Z.; Kruse, N. *Nature Commun.* **2016**, 7(1), 13058.
2. Iablokov, V.; Beaumont, S.K.; Alayoglu, S.; Pushkarev, V.V.; Specht, C.; Gao, J.H.; Alivisatos, A.P.; Kruse, N.; Somorjai, G.A. *Nano Lett.* **2012**, *12(6)*, 3091–3096.

O-2

TRANSITION METALS OXIDES / *N*-HYDROXYPHTHALIMIDE SYSTEMS IN CATALYSIS OF THE AEROBIC OXIDATION OF BENZYLIC C-H BONDS

I.A. Opeida[1]*, R.B. Sheparovych[2], W.Ya. Suprun[3]

[1]L.M. Litvinenko Institute of Physical-Organic Chemistry and Coal Chemistry, National Academy of Sciences of Ukraine, Kharkivs'ke shose St., 50, PC 02155, Kyiv, Ukraine, opeida_i@yahoo.co.uk
[2]Department of Physical Chemistry of Fossil Fuels InPOCC, National Academy of Sciences of Ukraine, Lviv, Ukraine
[3]Institute of Chemical Technology, Martin-Luther-Universität Halle-Wittenberg, Germany

The aerobic liquid-phase oxidation of alkylarene (RH). in the presence of a binary catalytic system containing N-hydroxyphthalimide (NHPI) and supported V, Mn, and Cu oxides have been studied. The heterogeneous catalysts based on single active components such as V_2O_5, MnO_x, and CuO_x and bi-components V_2O_5-MoO_3 V_2O_5-WO_3, and V_2O_5-SbO_x supported onto TiO_2, TiO_2-SiO_2, and Al_2O_3-SiO_2 were prepared and characterized.[1]

Table 1. Composition, textural and physicochemical properties of heterogeneous catalysts based on transition metal oxide supported on TiO_2, TiO_2-SiO_2 or γ-Al_2O_3-SiO_2.

	Abbr.	Catalyst composition [a)]	A_{BET}/ m^2g^{-1} [b)]	PD/ nm [c)]	TA/ mmol g^{-1} [d)]	H_2 ^{cons}/ µmol g^{-1} [e)]
1	TiO_2		105	10,0	0.12	225
2	Mn/Ti-Si	MnO_x/TiO_2-SiO_2	141	10,5	5.6	2178
3	Cu/Al-Si	CuO_x /Al_2O_3-SiO_2	246	6,5	3.1	1670
4	V/Ti	V_2O_5/TiO_2	92	9.3	4.45	2180
5	V-Mo/Ti	V_2O_5-MoO_3/TiO_2	86	9.8	0.53	3750
6	V-Sb/Ti	VO_x-SbO/TiO_2	83	10.5	0.49	3920
7	0.2VWTi	V_2O_5-WO_3/TiO_2	69	20.1	0.16	285
8	2.2VWTi	V_2O_5-WO_3/TiO_2	68	19.1	0.29	970

[a)] determined by RFA analysis; [b)] the specific surface area (A_{BET}); [c)] the overage pore diameter (PD) determined by N_2 adsorption/desorption method; [d)] the total number of acidic sites (TA) determined by TPD of ammonia; [e)] total H_2 consumption determined by TPR at the range 100 –700 °C.

The kinetics of the aerobic liquid-phase oxidation of alkylarene in the presence of a binary catalytic system containing N-hydroxyphthalimide and supported V, Mn, and Cu oxides have been studied. The oxidation experiments were conducted using pure oxygen (760 mm Hg) in a glass microreactor equipped with magnetic stirring. The solvent in all experiments was acetonitrile, the volume ratio of oxidized mixture : solvent 1:1, reactions temperature of 70°C. The major product in cumene oxidation was cumene hydroperoxide, whereas dimethyl phenyl carbinol and acetophenone were found as minor ones. It was observed that catalytic activities of the mono-metallic systems decrease in order $VO_x \cong$ MnOx > CuOx and bi-metallic catalysts showed no catalytic activities.

The comparison of the total acid density (TA) of the TMO-containing catalyst presented in Table 1 and the reaction rate catalyzed with these catalysts oxidation indicates that the surface acidity is essential for the activity of the catalyst.

The effect of catalytic system composition containing MnOx or VOx, NHPI, and AIBN on the oxidation rate was studied (Table 2).

Table 2. Initial rates of cumene oxidation in the presence of different content of AIBN, NHPI, and Mn/Ti-Si or V/Ti. 70 °C, oxygen pressure 0.101 Mpa; Volume ration RH:ACN = 1 : 1. (v/v).

Run	[AIBN], M	[NHPI], M	$MnO_x/TiO_2•SiO_2$, g mL^{-1}	VO_x/TiO_2, g mL^{-1}	$W_{O2}\cdot10^5$, M s^{-1}
1			0.04		< 0.2
2				0.04	< 0.1
3	0.02				1.9
4		0.02			3.7
5	0.02	0.02			8.0
6		0.02	0.04		18.6
7		0.02		0.04	8.1
8	0.02	0.02	0.01		11.5
9	0.02	0.02		0.01	11.1

Based on the experimental data the following important conclusions for understanding the mechanism in the initial period of the process were made:

- the major product, cumene hydroperoxide is formed in a radical chain reaction in the liquid-phase cumene oxidation;

- adding TMO to the reaction mixture, where proceeds radical chain oxidation initiated by azobisisobutyronitrile (AIBN), has little to change the reaction rate – the TMO has little effect on the stages of chain propagation and termination with peroxyl radicals (ROO•);

- the addition of NHPI significantly increases the rate of the AIBN-initiated reaction - NHPI can participate in the initiation of chains and catalyze the stage of their propagation;

- autocatalysis was not observed in any of the kinetic experiments, which is a sign of radical formation in the initiation stage by the reaction of hydroperoxide with TMO is small.

Therefore, two main stages can be distinctly distinguished in the radical chain process of a substrate (RH) oxidation catalyzed with the TMO + NHPI system:

- homogeneous, wherein the liquid phase NHPI catalyzes the formation of the major product hydroperoxide (ROOH) in the chain propagation stage, and

- heterogeneous, where both cocatalysts TMO and NHPI participate in the PINO$^\bullet$ radical formation reaction on the surface of TMO in the chain initiation stage:

$$\text{TMO} + \text{NHPI} \rightarrow \text{TMOH} + \text{PINO}^\bullet$$

A kinetic scheme that takes into account the main features of this process, the participation of TMO in the initiation reactions and NHPI in the initiation and chain propagation reactions is proposed [2].

Mn and V oxide-based catalysts combined with NHPI are promising catalytic systems where a significant synergistic effect is observed in the catalysis of aerobic alkylarene oxidation for the preparation of hydroperoxide. The characteristics of supported TMO can be tuned both by the nature of the TM and by the support properties, which help to find the factors for the development of a new catalytic system with NHPI for the effective low-temperature aerobic oxidation reaction of organic substrates C-H bonds.

References:

1. Suprun W.Y at all.. Molecular Catalysis. (2021). 510, 111683.
2. Opeida, I. at all, . Journal of Catalysis, (2023), 424, 197-210.

O-3

EXPERIENCE IN THE USE OF A CATALYTIC FUEL ADDITIVE WHEN BURNING BITUMINOUS COAL

I. Volchyn[1,2]*, V. Mokretskyy[2]

[1]Thermal Energy Technology Institute, National Academy of Sciences of Ukraine, Andriivska St., 19, Kyiv, 04070 Ukraine, volchyn@gmail.com
[2]National University of Food Technologies, Volodymyrska St., 68, Kyiv, 01601 Ukraine

The issues of combating climate change are global in all areas of human activity. The thermal power industry, which uses hundreds of millions of tons of coal and billions of cubic meters of natural gas to generate electricity and heat, is traditionally one of the largest emitters of carbon dioxide. The decreasing a CO_2 emission can be achieved by increasing the efficiency of using the traditional carbon fuels or burning the carbon-free fuels in boilers. The decreasing the carbon dioxide emissions can be achieved by increasing the efficiency of using traditional carbon fuels or burning carbon-free fuels in boilers. One of the ways to increase boiler efficiency is the use of special fuel additives. These additives can improve the efficiency and intensity of fuel combustion [1-3]. Most often, the fuel additives were developed for solid fuel boilers, as it contributes to the reduction of significant heat losses due to the presence of unburned carbon in the fly ash and bottom ash.

The industrial tests of the use of the REDUXCO catalytic fuel additive were carried out when burning Polish bituminous coal on PAUKER boiler with 100 t/h steam capacity at nitrogen plant in Kędzierzyn-Koźle, Poland. The REDUXCO fuel additive is an aqueous solution of the reaction product of acetic acid and acetylferrocene and butan-1-ol and 2-methylpropan-1-ol and propan-1-ol and propan-2-ol. It is registered in the European Chemicals Agency REACH ECHA [4]. The chemical formula is $C_5H_5FeC_5H_4COC_xH_n$. This additive is a source of formation of free radicals (mainly OH*) in a gaseous environment when it evaporates in a high-temperature environment. The use of REDUXCO catalytic additive contributes to lower activation energy of chemical reactions. As a result, chain radical reactions of gas-phase oxidation of CO and hydrocarbons occur at a higher rate. The fuel torch becomes shorter. In Fig. 1 shows a scheme of chain high-temperature oxidation (combustion) of carbon monoxide. The positive effect of this additive due to chain radical reactions in a gas medium on increasing the efficiency of the water boiler is described in [5].

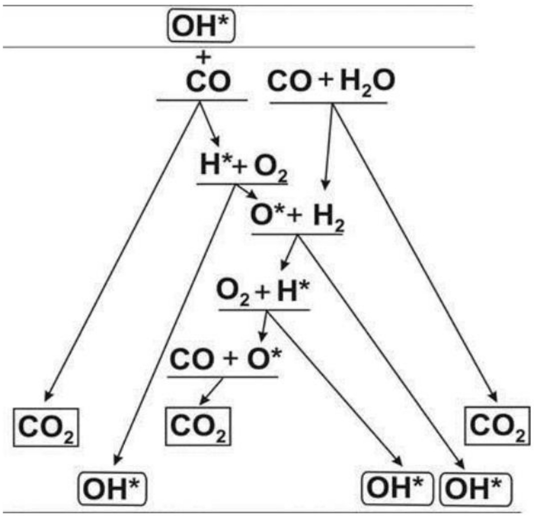


Fig. 1. The chain mechanism of carbon oxide combustion

The REDUXCO catalytic additive as water solution was fed through sprayers into the primary air ducts of the boiler and into the convective pass to reduce nitrogen oxide emission. The efficiency gross of the boiler was determined by direct and indirect methods in two modes – before and after using the additive. During the tests the content of pollutants in flue gas was determined.

In the mode before the use of the REDUSCO additive, the coal ash content A^r was in the range of 26.1–26.9%, moisture content W^r was 9.8-9.9%, the coal lower heat value Q_i^r was 19,810–20,062 kJ/kg. The average daily efficiency gross of the boiler according to the data of the direct balance for this mode was 84.52%, and according to the results of the calculation of the reverse balance (indirect method) was 82.14%. The temperature of the cold air mode before using the additive during this period ranged from 28.5 to 30.5 °C, and the temperature of the flue gas after air-heater was in the range of 171–175 °C for the left side of the boiler and 211–216 °C for the right side. In the future, it was possible to estimate the degree of cleaning of the heating surfaces of the boiler based on the changes in these temperature differences and the temperature of the flue gas.

In the mode of using the additive, the ash content of coal A^r during this period was in the range 24.2–26.4%, moisture content W^r was 8.7–10.1%, and the coal lower heat value Q_i^r was 20,112–20,808 kJ/kg. The average boiler efficiency according to the direct balance in additive mode was 90.72% and using the indirect method was 87.59%. This corresponds to an increase in boiler efficiency by 6.20% and 5.45%, respectively.

The REDUXCO catalytic fuel additive, when inject into a boiler with primary air, intensifies the combustion process. During the tests with additive using, the carbon content of the fly ash and bottom ash was reduced by an average of 10.7-15.1%. During the REDUXCO additive injecting, the heating boiler surfaces are gradually cleaned, as evidenced by the reduction of the temperature difference between the exhaust gas temperatures and the temperature of the hot air by 8-10 °C. The use of the REDUXCO catalytic additive led to a reduction in the amount of fuel consumed calculated using the indirect method by 5.81% and using the direct method by 6.67%. The relative decrease in carbon dioxide emission was 6.54% (indirect method) and 6.83% (direct method). The use of the REDUXCO additive reduces the NOx content in flue gas. The operation of one measurement system for two operating boilers did not make it possible to determine the absolute value of NOx emission reduction, but a decrease in the amplitude of NOx emission values was noted.

References:

1. Chavda, R., Mahanwar, P. (2018) Effect of Inorganic and Organic Additives on Coal Combustion: A Review. International Journal of Coal Preparation and Utilization, Vol. 41, 10, https://doi.org/10.1080/19392699.2018.1536046
2. Messerle, V.E., Paskalov, G., Umbetkaliyeva, K.A., Ustimenko, A.B. (2020) Application of Organic Fuel Additives to Enhance Coal Combustion Efficiency. Thermal Engineering, Vol. 67, No. 2, P. 115–121. https://doi.org/10.1134/S0040601520020044
3. Junga, R., Pospolita, J., Niemiec, P., Dudek, M., Szleper, R. (2020) Improvement of Coal Boiler's Efficiency after Application of Liquid Fuel Additive. Applied Thermal Engineering, Vol. 179. Article 115663. https://doi.org/10.1016/j.applthermaleng.2020.115663
4. REDUXCO. Reaction products of acetic acid and acetylferrocene and butan-1-ol and 2-methylpropan-1-ol and propan-1-ol and propan-2-ol. URL: https://echa.europa.eu/substance-information/-/substanceinfo/100.112.877
5. Przybylski, W., Majcher, M., Borkowski, L., Jaroszek A. (2010) Impact of REDUXCO Catalyst Addition to Incineration Chamber on Effectiveness and Reliability of WR 15-N Boiler Work in Heating Plant in Strzelce Opolskie. Rocznik Ochrona Środowiska, Vol. 12, 947-954.

O-4

SWITCHABLE MULTICOMPONENT HETEROCYCLIZATIONS WITH CONTROLLED CHEMOSELECTIVITY: APPLICATION OF CATALYSIS

V.A. Chebanov

Department of Organic and Bioorganic Chemistry, Division of Functional Materials Chemistry,
State Scientific Institution "Institute for Single Crystals", National Academy of Sciences of Ukraine,
Nauky ave., 60, Kharkiv, 61072 Ukraine, chebanov@isc.kh.ua

Diversity-oriented synthesis (DOS) is a promising and rapidly developing field of modern organic chemistry that focuses on the medicinal-orientated tasks and on obtaining libraries of small organic molecules for high-throughput screening. Among the numerous synthetic tools, multicomponent reactions are perfectly suited for DOS, as they enable the generation of decoration, skeletal, or stereochemical diversity through the simultaneous use of each component of the treatment. Switchable multicomponent heterocyclizations, which can yield multiple final products, are of interest to DOS from the viewpoint of developing methods to control their selectivity [1, 2].

To control the selectivity of multicomponent reactions, the Condition-Based Divergent Strategy had been developed and applied to a wide range of heterocyclizations, e.g., to switch treatment directions between carbonyl-containing CH acids, aromatic aldehydes, and aminoazoles (Fig. 1) [1-6].

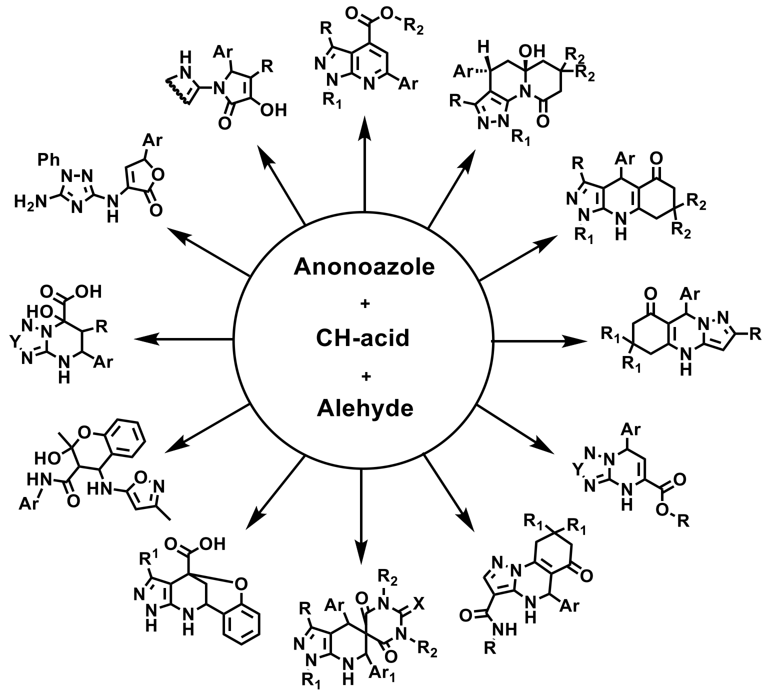


Fig. 1. Condition-Based Divergent Strategy for tuning selectivity of multicomponent reactions.

In the report, the general principles of controlling the directions for such treatments, as well as the synthetic methodology that allows highly selective obtaining certain types of heterocycles are discussed. Special attention is given to the use of various catalysts and non-classical methods.

References:

1. Chebanov V.A., Desenko S.M. Switchable multicomponent heterocyclization for diversity oriented synthesis // Diversity Oriented Synthesis, 2014, 1, 43-63.
2. Murlykina M.V., Morozova A.D., Zviagin I.M., Sakhno Ya.I., Desenko S.M., Chebanov V.A. Aminoazole-based Diversity-Oriented Synthesis of Heterocycles // Frontiers in Chemistry, 2018, 6, article 527
3. Chebanov V.A., Desenko S.M., Lipson V.V., Gorobets N.Yu. Multicomponent-switched reactions in synthesis of heterocycles // Multicomponent Reactions towards Heterocycles: Concepts and Applications (Eds.: E.V. Van der Eycken, U.K. Sharma), Wiley-VCH, Weinheim, Germany 2022, 287-338.
4. Tkachenko V.V., Chebanov V.A. Reactions of 3(5)-Aminoizoxazoles Using Classical Methods of Activation, Microwave Irradiation, and Ultrasonocation // Chemistry of Heterocyclic Compounds, 2016, 52, 11, 866-886.
5. Chebanov V.A., Desenko S.M. Multicomponent Heterocyclization Reactions with Controlled Selectivity // Chemistry of Heterocyclic Compounds, 2012, 48, 566 – 583.
6. Chebanov V.A., Gura K.A., Desenko S.M. Aminoazoles as Key Reagents in Multicomponent Heterocyclizations // in book Topics in Heterocyclic Chemistry, Springer, 2010, Vol. 23, 41–84.

O-5

PHOTOACTIVE MATERIALS BASED ON MODIFIED TITANIUM DIOXIDE: PROPERTIES AND PERSPECTIVES FOR APPLICATION IN PROCESSES OF ECOLOGICAL CATALYSIS

T.A. Khalyavka[1]*, N.D. Shcherban[2], S.V. Camyshan[1], G.V. Korzhak[2]

[1]*Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, General Naumov St., 13, Kyiv, 03164 Ukraine, takhalyavka@ukr.net*
[2]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine*

Nowadays, the creation of new high-performance photocatalysts active in various reactions, for instance, photocatalytic destruction of water pollutants and expired medicines, photocatalytic hydrogen production, etc. is an urgent research problem. The most studied photocatalyst is titanium dioxide. The modification of TiO_2 with non-metals and metals can be an effective way to improve its photocatalytic activity [1, 2].

The aim of our work was to obtain, characterize, investigation of photocatalytic activity of photocatalysts based on titanium dioxide, doped with different amount of carbon, sulphur, tin and lantanium by modified sol gel method and study the effect of titanium dioxide modification on structural, textural, and photocatalytic properties.

X-ray powder diffraction (XRD), scanning electron microscopy with an integrated system for electron microprobe analysis (SEM, EDX), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET) surface area analysis, X-ray photoelectron spectroscopy (XPS), Infrared (IR) and Ultraviolet–visible (UV-Vis) spectroscopies were applied for the powders characterization.

Photocatalytic experiment showed that modified samples exhibit higher photocatalytic activity in the reaction of hydrogen evolution from water-ethanol solutions compare to pristine TiO_2 under UV irradiation due to increasing of specific surface area, developed porous structure and reduce of bandgap.

Modified samples also showed higher photocatalytic activity in the destruction of organic dyes and expired medicines compared to pure titanium dioxide. The destruction of these compounds was confirmed by high separation mass spectrometry.

Photocatalytical activity of different samples did not vary substantially during 5 cycles of exploitation. Accordingly, those nanocomposites are perspective materials for environment-friendly catalysis, providing possibility of purifying wastewater from the compounds resistant to environment and may use for green ecology.

References:

1. T.A. Khalyavka, M.V. Shapovalova, G.V. Korzhak, N.D. Shcherban, O.Y. Khyzhun, S.V. Camyshan, V.V. Permyakov, S.N. Scherbakov, Research on Chemical Intermediates, **48** (2022) 13–28.
2. U. Caudillo-Flores, S. Fuentes-Moyado, G. Alonso-Núnez, I. Barba-Nieto, M. Fernandez-García, A. Kubacka, Chemical Engineering Journal, **457** (2023) 141134.

O-6

COMPARATIVE CHARACTERISTICS OF THE CATALYSIS OF THE TRANSESTERIFICATION REACTION BY CARBENES AND THE HYDROXIDE FORM OF ANIONITE AB-17-8

V.Sh. Saberov[1], O.S. Avksentiev[1]*, V.I. Yenya[1], G.F. Rayenko[2],
N.I. Korotkikh[1]

[1]Institute of Organic Chemistry, National Academy of Sciences of Ukraine, vul. Acad. Kukharia, 5, Kyiv, 02660 Ukraine, nkorotkikh@ua.fm
[2]L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Kharkiv road, 50, Kyiv, 02160 Ukraine

It is known that carbenes effectively catalyze the transesterification reaction of ethyl benzoate with methanol, providing almost quantitative yields of methyl benzoate [1]. The reaction is carried out at room temperature for 4 h (TON up to 6150). The approach was extended to the reaction of vegetable oils, which gives high-quality diesel fuel, and the process is not accompanied by foaming, which is characteristic of industrial technology in the presence of sodium hydroxide. In the same work, it was shown that the reaction is also effectively catalyzed by tetraalkylammonium and ethyltriphenylphosphonium alkoxides (TON up to 1575).

It was interesting to compare the catalytic efficiency of heterogeneous tetraalkylammonium salts using the example of AB-17-8 anionite in the hydroxide form, which is commercially available and cheap, with technologically convenient variants of carbene catalysts. For the generation of carbene (1), 1,3-di(2,6-diisopropylphenyl)-imidazolium perchlorate 2 was used, which was treated with an excess of potassium carbonate.

It was found that the OH form of anionite (10 mol%) catalyzes the reaction of ethyl benzoate with methanol at room temperature, allowing to achieve 89% yield of methyl benzoate for 18 h, and with 5 mol% catalyst 80% yield for 24 h. With the addition of a carbene catalyst (0.04 mol%), the reaction proceeds by 92% for 4 h and by 96% for 8 h. The interaction of sunflower oil with methanol and 0.1 mol% carbene catalyst at room temperature for 12 h gives a quantitative yield of diesel fuel (a mixture of mainly methyl esters of oleic and linoleic acids).

The reaction with benzyl alcohol and OH-anionite (20 mol%) takes place at 100 °C with the removal of ethanol in a nitrogen stream and gives a 96% yield of benzyl benzoate for 24 h. An experiment in such conditions without a catalyst gives 3% of the product for the same time. The reaction in the presence of carbene (0.04 mol%) gives a 97% yield of the product for 3 h. At room temperature, in the presence of molecular sieves 4A (to absorb ethanol), 51% of benzyl benzoate was obtained for 3 h.

The reaction with the secondary alcohol - cyclohexanol - proceeds more slowly even with 10 mol% of carbene 1 at 100 °C for 6 h (product yield 38%).

Therefore, carbene catalysis of the transesterification reaction with primary alcohols is much more efficient than catalysis by OH anionite (by more than two orders of magnitude in the reaction of ethyl benzoate with methanol). Nevertheless, both variants of the process can be considered promising for industrial use. The anionite is easily regenerated, and the consumption of the carbene catalyst is very small.

References:

1. Marichev K. A., Korotkikh N. I., Cowley A. H., Knishevitsky A. V., Saberov V. Sh., Glinyanaya N. V., Rayenko G. F., Shvaika O. P. *Arkivoc*, 4 (2017) 365–376.

O-7

FUMED SILICA AS AN EFFICIENT SUPPORT FOR ACRYLIC ACID PRODUCTION CATALYSTS

R.V. Nebesnyi[1]*, O.M. Orobchuk[1], S.V. Khalameida[2],
V.V. Sydorchuk[2], V.V. Ivasiv[1]

[1]*Department of Technology of Organic Products, Lviv Polytechnic National University, S. Bandery St., 12, Lviv, 79013 Ukraine, roman.v.nebesnyi@lpnu.ua*
[2]*Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Naumov St., 13, Kyiv, 03164 Ukraine*

Previously we developed an efficient silica-supported B-P-V-W oxide catalyst for the production of acrylic acid by aldol condensation of acetic acid with formaldehyde [1]. The porous structure of the catalyst plays a big role in defining its catalytic properties and is highly dependent on the support used [2]. Fumed silica is an interesting choice of catalyst support – it's cheap to produce, highly pure and uniform by properties, and, while non-porous itself, it can be transformed into porous material using variety of methods, including hydrothermal treatment (HTT), which is cheap and efficient method of creating and tuning of the porous structure [3].

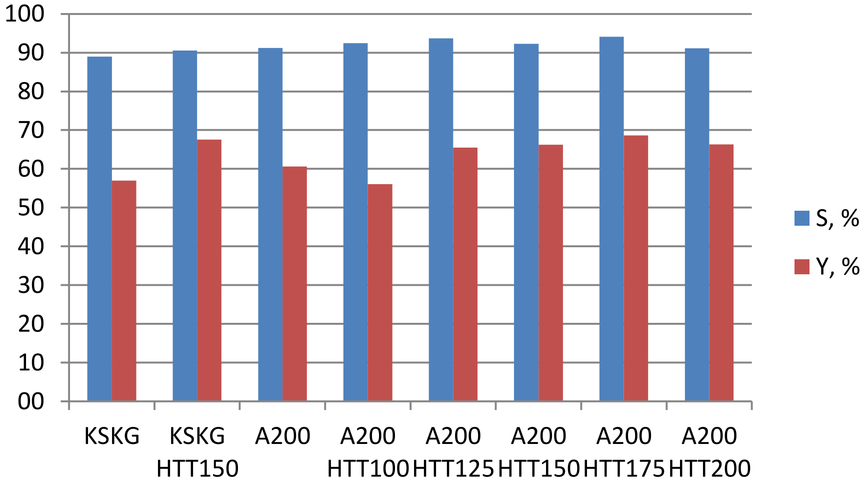


Fig. 1. Selectivity (S) and yield (Y) of acrylic acid using silica gel (KSKG) and fumed silica (A200) supports with and without hydrothermal treatment (HTT) at different temperatures.

We prepared a series of B-P-V-W oxide catalysts using fumed silica A200 as support without and with HTT in the temperature range of 100-200 °C. As shown in the Fig. 1, with the increase of support HTT temperature from 125 °C and above, an increase in both yield and selectivity of acrylic acid is observed, which confirms the positive effect of the HTT on catalyst activity. Moreover, fumed silica supported catalysts demonstrate higher acrylic acid selectivity (up to 94.1%) compared to the previously developed silica gel supported catalyst (90.5%) [1]. The best results were obtained at the HTT temperature of 175 °C, achieving 68.6% acrylic acid yield at 94.1% selectivity. Thus, we can conclude that hydrothermally treated fumed silica is an efficient support for the B-P-V-W oxide catalyst.

References:

1. R. Nebesnyi, Applied Catalysis A, General 594 (2020) 117472.
2. X. Feng, J. Catal. 314 (2014) 132−141.
3. A. Christy, Ind. Eng. Chem. Res. 50 (2011) 5543–5549.

O-8

CORE-SHELL NANOPARTICLES AS HYBRID ELECTROCATALYSTS FOR WATER SPLITTING

I.V. Zatovsky[1]*, D.S. Butenko[2]

[1]F.D. Ovcharenko Institute of Biocolloidal Chemistry, National Academy of Sciences of Ukraine, Kyiv, 03142 Ukraine, zvigo@ukr.net
[2]Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen 518055, China

Pure hydrogen generated via water electrolysis is used in various industrial sectors and is also considered as a potential method of hydrogen production, which can be used as fuel [1]. Moreover, potentially the electrolysis of water combined with renewable energy sources (solar, wind, hydropower) can provide a clear and economically viable source of hydrogen. One of the reasons that keep this technology from being of extensive practical use to date is the sluggish kinetics (high overpotential) of the oxygen evolution reaction (OER) [2]. Thereby, the design of cost-effective, highly efficient, and stable electrocatalysts for overall water splitting is necessary for renewable energy systems. Over the past decades, various compounds of transition metals (oxides/hydroxides, nitrides, borides, chalcogenides, phosphides, complex oxides, phosphates, etc.) have been proposed as economically competitive and efficient electrocatalysts for OER and HER (hydrogen evolution reaction) processes [2]. Here we present an original electrode design strategy that can be used for OER and HER. This strategy is based on the idea of the direct formation of an active catalytic coating on the electrode surface during electrolysis. Within the framework of this report, the prospects for the creation of such electrocatalysts are considered using the example of phosphates and complex oxides (materials-based perovskite oxides).

In most cases, in the electrolysis process in an alkaline medium catalysts based on d-metal phosphates are completely converted to highly active metal oxide-hydroxide forms, which provides an excellent productivity of OER during water oxidation [3]. As an example, hybrid nanocomposites CoOx(OH)y@C were obtained for $Na_4Co_3P_4O_{15}$ (after *in situ* transformation) in our research. The CoOx(OH)y@C composites demonstrate excellent time stability and bifunctional activity (overpotentials for OER and HER are 345–365 and 325–370 mV, respectively, overall water splitting potential close of 0,6 V in the cell at a current density of 10 mA·cm^{-2}) [4]. However, in the result of the interaction of $Na_4Ni_3P_4O_{15}$ and alkaline solution, the initial material was gradually decomposed and *in situ* converted to hybrid $Na_4Ni_3P_4O_{15}/Ni(OH)_2$@C electrocatalysts, with core/shell principle [5]. This type of nanostructure ensures a higher catalytic activity for OER (overpotentials in the range of 280-310 mV at 10-20 mA cm^{-2}). In both cases, the formation of nanoparticles in a carbon matrix has two main advantages: composites have good conductive properties and nanosystem topology is formed during electrolysis. This principle ensures the stability of catalysts for a long time, which is important for industrial applications.

For the case of complex oxides, the transformation of catalysts *in situ* in an alkaline medium was considered for compounds with a perovskite structure. In particular, compounds in the La-Sr-Mn-O and La-Sr-Co-O systems were investigated as electrocatalysts for OER. Electrochemical tests of $La_{0.6}Sr_{0.4}MnO_3$ samples have shown that a decrease in the size of nanoparticles makes it possible to increase the efficiency of their electrocatalytic properties in the oxygen evolution reaction. However, studied processes of the electrochemical destruction of this nanomaterial have shown the voltage limits of their possible practical application, that is 1.7 V in an alkaline medium [6]. Similar Co-containing compounds differ significantly. The obtained series of the $La_{0.6}Sr_{0.4}CoO_3$ nanomaterials showed excellent characteristics as electrocatalysts for overall water splitting. The values of the initial overpotential of oxygen generation were within 265–285 mV (a current density of 10 mA cm^{-2}). These materials retain high catalytic activity during long-term electrolysis, which should be attributed to the formation of a stable amorphization layer on the surface of nanoparticles. In addition, a significant area of the catalytically active surface, resulting from the emergence of stable core-shell nanosystems, can ensure high efficiency of practical use of the material.

References:

1. X.X. Zou, Y. Zhang, Chem. Soc. Rev. **44** (2015) 5148.
2. N.-T. Suen, S.-F. Hung, Q. Quan, N. Zhang, Y.-J. Xu, H.M. Chen, Chem. Soc. Rev. **46** (2017) 337.
3. R. Guo, X. Lai, J. Huang, X. Du, Y. Yan, Y. Sun, G. Zou, J. Xiong, ChemElectroChem, **5** (2018) 3822.
4. I.V. Odynets, N.Yu. Strutynska, J. Li, W. Han, I.V. Zatovsky, N.I. Klyui, Dalton Trans. **47** (2018) 15703.
5. C. Mu, D.S. Butenko, I.V. Odynets, I.V. Zatovsky, J. Li, W. Han, N.I. Klyui, Dalton Trans. **49** (2020) 8226.
6. Z. Gong, W. Xu, N.A. Liedienov, D.S. Butenko, I.V. Zatovsky, I.A. Gural'skiy, Z. Wei, Q. Li, B. Liu, Yu.A. Batman, A.V. Pashchenko, G.G. Levchenko, Phys. Chem. Chem. Phys. **24** (2022) 21872.

O-9

PRODUCTION OF ETHYL ESTERS OF FATTY ACIDS FROM DOMESTIC PLANT OILS: PRESENT AND PROSPECTS

L.K. Patrylak[1,2]*, S.V. Konovalov[1], S.O. Zubenko[1], V.O. Yevdokymenko[1],
A.V. Yakovenko[1], D.Z. Davitadze[1]

[1]*V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Kukharya vul., 1, Kyiv, 02660 Ukraine, lkpg@ukr.net*
[2]*National Technical University of Ukraine "Igor Sikorskyi Kyiv Polytechnic Institute", Beresteiskyi prospect, 37, Kyiv, 03056 Ukraine*

The current full-scale stage of Russian aggression is radically changing the prospects of the fuel and energy complex of Ukraine, in particular oil refining, which has suffered a number of devastating blows. Fuel imports were critical and accounted for up to 80%. The state's needs for diesel fuel in 2020 were met by only 16% of its own production [1]. The war also demonstrated the huge dependence on the energy resources of the aggressor country, not only of Ukraine but also of the other countries, especially countries of the European Union. On the other hand, by 2022, Ukraine was the largest exporter of vegetable oils, which are raw materials for obtaining biodiesel – methyl esters of fatty acids in traditional meaning. In addition, Ukraine has a big network of distilleries producing bioethanol. Despite the unprofitability of obtaining biodiesel, during 2021 the global scale of its production still resumed its growth (up to 37.5 million tons of oil equivalent), after some decline in 2020 during the COVID-19 pandemic [2]. In our country, despite the critical shortage of fuel in the spring of 2022, practically nothing has changed regarding the situation with biodiesel production.

Worldwide, methanol is still the most widely used alcohol for biodiesel production due to its low cost, mild process conditions, and easy separation of products [3–7]. V.P.Kukhar IBOCP of NAS of Ukraine has considerable experience in obtaining ethyl esters of fatty acids, which can also be used as a component of mixed biodiesel fuel. Ethyl esters of fatty acids possess some technical advantages such as better low-temperature and anti-wear properties, slightly higher energy capacity as biodiesel compared with traditional methyl esters of fatty acids. Usually, the superiority of ethanol-based biodiesel is grounded in the prospects of sustainability, full biorenewability, and lower danger of its production due to lower ethanol danger compared to methanol. But in practice, ethanol-based biodiesel, as well as traditional methyl esters of fatty acids, cannot compete with mineral diesel in economic terms. Actually, the world's biodiesel industry owes its formation and development to state policy within individual countries or their associations. Such a policy includes, on the one hand, providing certain financial preferences to producers and consumers of biodiesel and, on the other hand, establishing minimum requirements for the content of biofuels in commercial diesel fuel [7]. However, along with the economic problems of high cost, the main technological problems of obtaining ethyl biodiesel fuel are, firstly, poor separation of target and by-products due to the formation of stable emulsions, and, secondly, the need for deep purification of "raw" biodiesel, which by its own characteristics does not meet the requirements of modern fuel standards [8–10].

The aim of the study was to obtain a reaction system in which the products of transesterification of acylglycerols with ethyl alcohol on an alkaline catalyst are formed with almost complete conversion of raw materials and separate spontaneously without the use of additional components, and the main part of the catalyst is removed from the composition of the ester phase enriched with the target product.

The indicated purpose is achieved by using as an alkaline catalyst the convenient-to-use ethanolic solution of potassium ethylate, as well as optimal conditions for the process, which allow obtaining products with high yields and ensure spontaneous separation into glycerol and ester phases with the removal of the main part of the catalyst in the glycerol phase. Acylglycerols of any origin – natural oils, animal fats, synthetic ones, or their combinations – can act as raw materials for obtaining ethyl esters according to the proposed method. Ethyl alcohol is both a reagent and a solvent for the alkaline catalyst. Partial purification of "raw" biodiesel is possible using various solid sorbents; however, purified ethanol-based biodiesel may not meet the high fuel requirements of the standards in terms of some of the regulated properties. It is interesting that Ukraine is probably the only country in the world to have a separate standard DSTU 7178 [8] for fatty acid ethyl esters alongside DSTU 6081 [9] for fatty acid methyl esters. Purification of "raw" biodiesel by washing creates a large amount of wastewater. Therefore, the best technical option is distillation for the purpose of purification.

As for the engine performance of biodiesel (both ethyl and methyl esters of fatty acids), it is slightly inferior to traditional diesel fuel due to the 10% oxygen content in biodiesel. Usually, the best engine performance and the lowest harmful engine emissions are mutually excluded things. Some negative effects of biodiesel on engine performance may be noticeable with a large fraction of biodiesel in the fuel mixture. When utilizing 7–30% vol. biodiesel blends according to DSTU 8695 [10], such effects are quite limited.

Thus, available own scientific developments confirm the possibility of obtaining high-quality mixed ethyl biodiesel from domestic raw materials, however, only a combination of state policy regarding preferences for producers and consumers of biodiesel together with the introduction of mandatory minimum contents of biodiesel in all commercial diesel fuels can contribute to improving the situation with the production of biodiesel fuel in Ukraine.

References:

1. A. Prokip. State oil refining in the context of guaranteeing energy security. https://uifuture.org/publications/yak-znyaty-palyvnu-petlyu/#more-8866
2. BP Statistical Review of World Energy 2022, 71th edition. June 2022. https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2022-full-report.pdf
3. World biodiesel policies and production / Eds. H. Joo, A. Kumar. New York: CRC Press. 2020.
4. M. Firdaus, M.Yusoff, X. Xu, Z. Guo, J. Am. Oil Chem. Soc. **91** (2014) 525.
5. T. Mizik, G. Gyarmati, Clean Technol. **3** (2021) 19.
6. T. Mizik, Sustainability. **12** (2020) 2626.
7. P.A. Cremonez, M. Feroldi, W.C. Nadaleti, E. de Rossi, A. Feiden, M.P. de Camargo, F.E. Cremonez, F.F. Klajn, Renew. Sust. Energy Rev. **42** (2015) 415.
8. DSTU 7178:2010. Alternative fuel. Ethyl esters of fatty acids of oils and fats for diesel engines. Technical requirements and control methods
9. DSTU 6081:2009. Motor fuel. Methyl esters of fatty acids of oils and fats for diesel engines. Technical requirements.
10. DSTU 8695:2016. Alternative fuel for diesel engines. Technical requirements.

O-10

MECHANISM OF METHANOL CONVERSION INTO DIMETHYL ETHER OR FORMALDEHYDE ON GRAPHENE-LIKE MATERIALS WITH DEFECTS: QUANTUM CHEMICAL STUDY

O.S. Karpenko[1], I.B. Bychko[2], P.E. Strizhak[2]

[1]Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov St., 17, Kyiv, 03164 Ukraine, karpenkooksana@ukr.net
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine

Methanol conversion to dimethyl ether or formaldehyde are large-scale industrial processes. According to this, huge attention is focused on finding ways to reduce the cost of relevant processes. Developing the carbon catalysts for the presented processes is one of the main route to reduce the cost of the methanol conversion. There are presented experimental works where carbon materials, particularly, carbon nanotubes [1], activated carbon, and graphene materials are used as catalysts. However, the reaction mechanisms of methanol conversion interaction in carbon materials are still under discussion.

This report presents the results of quantum chemical calculations by the method of density functional theory (DFT, B3LYP/6-31G (d, p) with the involvement of Grimme dispersion correction) of the main elementary stages of methanol dehydration to dimethyl ether and dehydrogenation to formaldehyde on graphene-like materials (GLM) with defects. As models of GLM were used the polycyclic aromatic hydrocarbon (PAH) $C_{96}H_{24}$ (hydrogenated graphene) and its derivatives. Considered two cases of methanol interaction: with point defects on $C_{96}H_{24}$ (single vacancy) and with $C_{96}H_{24}$ functionalized by oxygen functional groups like hydroxyl (–OH) and carboxyl (–COOH) (see Fig. 1). The systems were tested under different conditions of multiplicity. Computed reaction profiles of the reactions were investigated. The role of the water molecule in the reaction of methanol dehydration to dimethyl ether was studied. Obtained results show that active sites in the dehydration reaction are hydroxyl and carboxyl groups and in the dehydrogenation reaction – single vacancy.

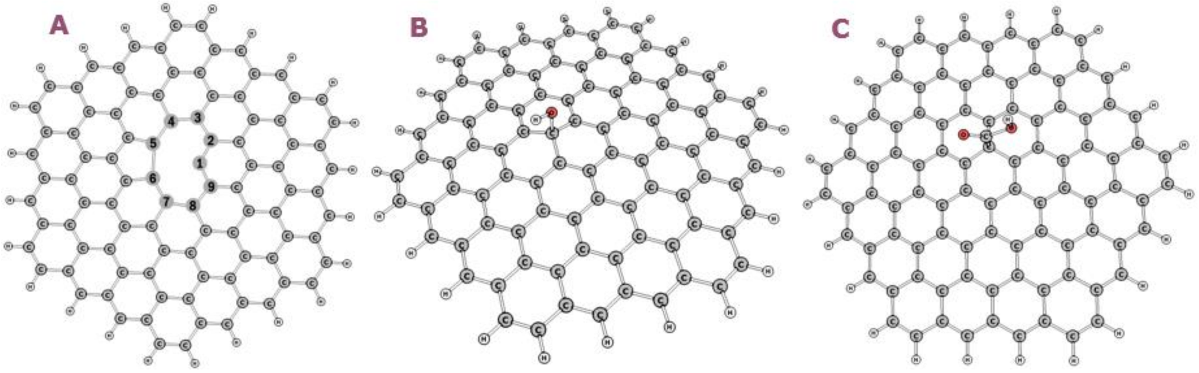


Fig. 1. The derivatives of polycyclic aromatic hydrocarbon $C_{96}H_{24}$:
a – PAH $C_{95}H_{24}$ with single vacancy; *b* – PAH $C_{96}H_{24}OH$; *c* – PAH $C_{96}H_{24}COOH$.

Acknowledgements. This work was supported by the National Research Foundation of Ukraine (grant 2020.02/0050).

References:

1. P. Yan, X. Zhang, F. Herold, F. Li, X. Dai, T. Cao, B.J.M. Etzold, W. Qi, Catalysis Science & Technology. **10** (2020) 4952.

O-11

HYDROTHERMAL APPROACHES FOR SYNTHESIS OF CATALYSTS AND THEIR SUPPORTS

S. Khalameida*, V. Sydorchuk

Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Naumova St., 13, Kyiv, 03164 Ukraine, svkhal@ukr.net

The creation of the desired supramolecular structure is necessary for obtaining effective heterogeneous catalysts and their supports. It is known that the supramolecular structure includes a set of physicochemical characteristics that determine catalytically active materials. These are the parameters of the porous and crystalline structure, structure and morphology of the surface, acid-base and electronic properties. Hydrothermal processes are one of the most effective for the synthesis and regulation of the indicated physicochemical characteristics of potential catalysts. Hydrothermal conditions can be implemented in several procedures: treatment in autoclaves with conventional and microwave heating (HTT and MWT), as well as during ultrasonic and mechanochemical treatments in water (UST and MChT).

Re-condensation (Ostwald repining) processes are the basis of physicochemical transformations during HTT and MWT. Therefore, both the direct synthesis of nano-dispersed materials and their post-synthetic modification can be carried out. As a result, the changes in porous structure parameters in wide limits. Thus, HTT of commercial silica and laboratory zirconium phosphate makes it possible to optimize porous structure of catalysts for processes of aldol condensation and dehydration of isopropanol, respectively. Also, the hydrothermal synthesis of many complex oxides with different structure takes place at a much lower temperature compared to the traditional solid state procedure. Moreover, MWT significantly reduces the duration of such syntheses (sometimes by an order of magnitude). For example, HTT and MWT of wet gel allow to prepare CeO_2-ZrO_2 solid solution with necessary porous, crystal and electronic structure which is active photocatalyst of pollutants degradation under visible irradiation.

At the same time, dispersion-aggregation processes as well as re-packaging of particles in framework of porous solids due to mechanical action of working bodies or cavitation on the solid phase are the main causes of physicochemical transformations during MChT and UST, respectively. In addition, hot spots occur during MChT and UST, which leads to heating of the reaction mixture. In other words, low-temperature or pseudo-hydrothermal conditions will be simulated, which in turn are accompanied by mass transfer processes. The latter contributes to additional changes in physicochemical characteristics. As a result, MChT in water allows to form porous materials from low-dispersed non-porous powders as well as create multi-modal meso-macroporous structure with maximal resistance to sintering at higher temperature. Thus, milling of quartz glass production waste in water results in formation of meso-macroporous silica supports.

The use of the above-mentioned techniques at the stage of wet gel before its drying opens up additional possibilities for regulating the physicochemical properties. In particular, this allows to prepare materials that simultaneously have high value of specific surface area, volume and pore size. This is clearly confirmed on the example of silica as well as oxides and phosphates of titanium, zirconium, tin and cerium. An example of effective application of this approach is doping tin oxide with transition metals through UST of wet gel. As a result, formation of mesoporous structure and narrowing the band gap occur of resulted SnO_2 which makes it photocatalytically active under visible irradiation.

O-12

CATALYTIC PROCESSES OF RENEWABLE FEEDSTOCKS AND WASTES CONVERSION FOR HYDROGEN-RICH SYNTHESYS GAS AND HYDROGEN PRODUCTION

O.M. Dudnyk

Thermal Energy Technology Institute, National Academy of Sciences of Ukraine, Andriivska Str., 19, Kyiv 04070, Ukraine, aldudnyk2018@gmail.com

Hydrogen-rich synthesis gas and pure hydrogen are obtained as a result of the following main conversion processes: steam conversion of high-molecular gaseous compounds, methane, and CO; cracking of high-molecular compounds; pyrolysis and steam gasification of liquid and solid organic raw materials. The cost of hydrogen obtained in the processes of natural gas steam reforming and solid organic material gasification is 1.5-3.0 times less compared to the processes of obtaining hydrogen and oxygen by electrolysis. The reduced cost of obtaining hydrogen is ensured by exothermic reactions of the interaction of carbon with oxygen [1]. The sources for hydrogen production are the initial organic raw material and steam. In modern processes of obtaining hydrogen from organic raw materials, carbon is removed both directly in the conversion processes of the initial raw organic materials (for example, using lime and calcined dolomite), and after conversion using carbon dioxide sorption processes at the output.

The following main experimental installations were created and tested in the Institute of Thermal Energy Technology Institute of the National Academy of Sciences (TETI of the NASU) for: catalytic reforming of methane using industrial Ni- (for steam reforming), Fe-Cr- and Cu-catalysts (for steam conversion of CO) with low-temperature sorption of CO_2 by an aqueous solution of monoethanolamine (MEA) to obtain hydrogen [2]; steam gasification of bituminous coal with carbon capture by lime directly in the zone of gasification, brown coal and solid biomass with carbon sorption by calcined dolomite for the capture up to 60% of carbon both with and without the use of catalysts, with catalytic steam conversion of CO to obtain a mixture of hydrogen and CO_2 and low-temperature capture of CO_2 by aqueous solution of MEA for production of hydrogen [3]; pyrolysis of solid organic waste and coal and steam catalytic reforming of the obtained high-molecular compounds using modern nanostructured Ni- and Fe-catalysts manufactured at the L.V. Pisarzhevsky Institute of Physical Chemistry (IPC) of the NASU and the Indian Institute of Petroleum (IIP) for the production of hydrogen-rich synthesis gas [4, 5].

For the conversion of bio-methane into hydrogen, it was used the following experimental equipment: steam catalytic reformer with Ni-catalyst, steam generator, reactor for catalytic conversion of CO with Fe-Cr and Cu catalysts, and CO_2 sorption reactor with 25% aqueous solution of MEA. The consumption of methane in the reformer was 50 l/h, superheated steam was 0.73 kg/h. The temperature of superheated steam after the steam generator was 530 ^{o}C, the temperature in the lower part of the steam reformer was 783 ^{o}C, the temperature in the Cu-catalyst bad was 235 ^{o}C. Hydrogen yield was 191 l/h. The purity of hydrogen was 96.2%. It is possible to test fuel cells with an electrical capacity up to 200 W using this installation.

For the conversion of solid organic raw materials into hydrogen, it was used the following experimental equipment: steam gasifier, steam generator, catalytic CO conversion reactor, and CO_2 sorption reactor. Solid fuel and calcined dolomite (or quicklime) were loaded into the gasifier. Biomass and coal waste were used for the research. The consumption of superheated steam was 100 to 180 g/min. 92.6 to 94.1% of carbon was removed in the systems for obtaining hydrogen from solid raw materials: 36.8 to 48.5% - in the gasifier (calcined dolomite or lime) and 44.1 to 56.3% in the low-temperature CO_2 capture reactor (with aqueous solution of MEA). The yield of hydrogen was up to 120 l/h. The degree of hydrogen purity was 94.7 to 96.0%. Two products at the same time (hydrogen and activated char coal) were obtained at the installation using birch waste. Fuel cells with an electrical power of up to 125 W can be tested at the installation using solid renewable raw materials.

Currently in the world, significant attention is paid to two-stage processes with pyrolysis of biomass and plastic and steam catalytic reforming of the obtained gaseous compounds. Steam reforming reactions are divided into two groups: heterogeneous catalytic reactions and secondary reactions in the gaseous phase. The most common catalysts for steam reforming are nickel-based catalysts due to their suitable activity and low cost. The following two-stage conversion schemes are tested on experimental and pilot scales: moving bed pyrolyzer and moving bed reformer; fluidized bed pyrolyzer and moving bed reformer; screw pyrolyzer and moving bed reformer; fluidized bed pyrolyzer, entrained flow gasifier and moving bed reformer; spouted bed pyrolyzer and fluidized bed reformer; spouted bed pyrolyzer and moving bed reformer [6].

At the plant for solid organic waste and coal pyrolysis, there was studied carbonization (slow pyrolysis) both with pre-impregnation of samples (CaO, NaOH, H_3PO_4) to increase the yield of carbon with the obtained char coal and to increase hydrogen content in the gaseous conversion products, and without impregnation. Impregnation of the samples with 5% aqueous H_3PO_4 solution was the most effective (for example, due to the impregnation of sunflower husks, the yield of char coal increased from 28.1% to 51.1%). The research was conducted using waste wood, sunflower husks, cotton, paper, plastic (polyethylene, polypropylene, polyester, and polystyrene), cotton and polyester fabric, lignin, sewage sludge of an aeration station, sunflower and onion husks, bagasse, walnut shells, fast-growing algae, bituminous and brown types of power coal [6]. To increase the yield of hydrogen, it was applied a catalytic process of reforming of the obtained gaseous pyrolysis products using Ni-catalysts of IIP and IPC of the NASU and Fe-catalysts of the IPC of NASU. As a result of carbonization of sunflower husks with the use of a nickel catalyst, the hydrogen content in dry gas increased to 52 vol. %. In the case of carbonization of mixture of wood waste (10.5 wt. %) and polypropylene (10.5 wt. %) using slaked lime (76.7 wt. %) and Ni-catalyst (2.3 wt. %), dry gaseous mixture containing hydrogen of 82.1 vol. %, methane of 14.3 vol. %, carbon monoxide of 1.6 vol. %, carbon dioxide of 0.7 vol. %, and high-molecular compounds of 1.3 vol. % was obtained.

References:

1. O.M. Dudnyk, I.S. Sokolovska, in: V.D. Pokhodenko, V.V. Skorokhod, Yu.M. Solonin (Ed), Fundamental problems of hydrogen energetics, NASU: Kyiv, 2010, p. 56-76.
2. O.M. Dudnyk, I.S. Sokolovska, in: S.O. Kudria, V.F. Reztsov (Ed), Renewable Energy and Energy Efficiency in the XXI Century, Interservis: Kyiv, 2021, p. 364-367.
3. O.M. Dudnyk, I.S. Sokolovska, Proceedings of 27th Annual International Pittsburgh Coal Conference, 2010, 1012–1033.
4. A.N. Dudnik, P.E. Strizhak, A.K. Sinha, B. Singh, A.I. Tripol’skii, I.S. Sokolovskaya, S.A. Farooqui, in: V.E. Agabekov, K.N Gusak, Zh.V. Ignatovich (Ed), Alternative sources of raw materials and fuel, BN: Minsk, 2014, vol. 1, p. 211-224.
5. H. Singh, R. Yadav, S.A. Farooqui, O. Dudnyk, A.K. Sinha, International Journal of Hydrogen Energy. **44** (2019) 19573–19584.
6. L. Santamaria, G. Lopez, E. Fernandez, M. Cortazar, A. Arregi, M.J. Bilbao, Energy Fuels. **35** (2021) 17051–17084.

O-13

BIOETHANOL STEAM REFORMING OVER FERRITES: INTERPLAY OF REDOX AND ACID-BASE PROPERTIES

L.Yu. Dolgikh

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, Dolgih.L.Ju@nas.gov.ua

Ethanol steam reforming (ESR) is an attractive, sustainable, and environmentally friendly approach to hydrogen production. The ESR reaction may be represented as follows:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2.$$

Theoretically, it allows to obtain 50% of hydrogen from ethanol and 50% of hydrogen from water. Bioethanol (aqueous solution of 4-12 vol % of ethanol) can be directly employed for steam reforming, thus avoiding the expensive water separation costs, and increasing the process's overall energy efficiency [1]. A wide range of catalysts was explored to obtain the optimum conditions for the ESR reaction, the overwhelming majority were supported metals, including Co, Ni, Cu, Ru, Rh, Pd, Ir, Pt, and oxide supports (MgO, Al_2O_3, ZnO, ZrO_2, La_2O_3, CeO_2, and their combinations) [2, 3]. Only a limited number of other types of catalysts have been employed for this action, among them spinels, and perovskites [4, 5].

The noble metal-free ferrites MFe_2O_4 (M(II) = Mg, Mn, Fe, Co, Ni, Cu, Zn) with a spinel structure showed high activity in the ESR process [6]. The steam reforming processes of either diluted C_2–C_4 alcohols or ethanol/higher alcohols mixtures that reflect the composition of the raw bioethanol were explored. The catalytic properties of ferrites prepared by methods of coprecipitation (the catalyst was denoted as MFe_2O_4-CP) and solvothermal decomposition of heteronuclear complexes (the catalyst was denoted as MFe_2O_4-HC) were studied. The ferrite redox properties and surface acidity and basicity were characterized by the temperature-programmed reduction method (H_2-TPR) and by temperature-programmed desorption of NH_3 (TPD-NH_3) and CO_2 (TPD-CO_2).

Using $MgFe_2O_4$, $MnFe_2O_4$, and $FeFe_2O_4$ 98 – 100% ethanol conversion is achieved in the temperature range between 550 and 650 ºC, whereas hydrogen yield (Y_{H2}) reaches 82-94 % (WHSV = 4000 h^{-1}, 2,7 mol % C_2H_5OH, 50 mol % H_2O, N_2 - balance). The maximum Y_{H2} decreases in order: $MnFe_2O_4 > MgFe_2O_4 > FeFe_2O_4 > CuFe_2O_4 > CoFe_2O_4 > ZnFe_2O_4 > NiFe_2O_4$. $MnFe_2O_4$-CP catalyst exhibits higher hydrogen yield in the temperature range between 450 ºC and 550 ºC compared to $MnFe_2O_4$-HC catalyst. In contrast, a higher hydrogen yield is observed for the $MnFe_2O_4$-HC catalyst at $T > 600$ °C. $CuFe_2O_4$ and $FeFe_2O_4$ showed high (close to equilibrium values) selectivities for acetaldehyde and acetone, respectively. For the ethanol/higher alcohols mixture (propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol, pentan-1-ol (1 mol % of each alcohol), and 4,75 mol % of ethanol) conversion of ethanol, and higher alcohols at 500 ºC are 97% and 83 – 90%, respectively. Selectivity toward hydrogen is ~80%. At 500 ºC productivity toward hydrogen of the steam reforming process is higher for the alcohol mixture in contrast to the water-ethanol mixture without higher alcohols. This difference in productivity is governed by an effective steam reforming of higher alcohols with the utilization of water vapor on the developed catalyst [7].

The ESR process over ferrites predominantly proceeds via a consecutive-parallel reaction pathway, which combines both redox and acid-base stages. The main reactions include dehydrogenation of ethanol to acetaldehyde, aldol condensation of acetaldehyde to acetone, steam reforming of ethanol, acetaldehyde, and acetone to hydrogen and CO_2; no CO was detected in the reaction products up to 550 °C for all explored ferrites [6].

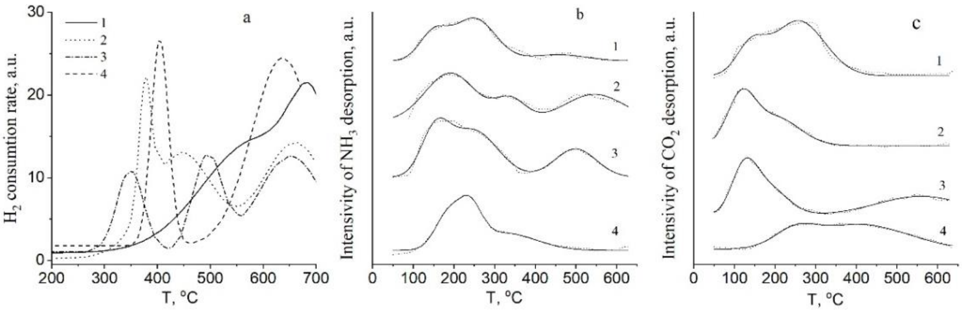


Fig. 1. H_2-TPR (a), TPD-NH_3 (b) and TPD-CO_2 profiles (c) from the surface of spinels: $FeFe_2O_4$ (1), $MgFe_2O_4$ (2), $MnFe_2O_4$ (3), $ZnFe_2O_4$ (4) (for b and c doted line is an experimental curve, solid line is a calculated curve).

The H_2-TPR data highlight that the nature of metal M in the MFe_2O_4 ferrospinels influence significantly on the reductive ability of spinel Fe^{3+} ions (Fig.1a). The values of T_{max} of reduction (which characterize the strength of the oxygen–catalyst bond) increased in order: $MnFe_2O_4 < MgFe_2O_4 < ZnFe_2O_4$. The hydrogen yields in the ESR process on ferrites change antibatically. Consequently, $MnFe_2O_4$ can easier supply oxygen for surface oxidation processes than $MgFe_2O_4$ and $ZnFe_2O_4$. The presence of octahedral Mn^{2+}, Fe^{2+} and Fe^{3+} ions in the spinel structure facilitates redox transformations in the steps of organic intermediates oxidation and water decomposition with the formation of final products (CO_2 and H_2).

Acid-base interactions are involved in the formation of acetaldehyde and acetone during the ethanol transformations on oxides [8]. The surface metal cations $M^{\sigma+}$ in ferrospinels can be attributed to Lewis acid centers and oxygen anions $O^{\sigma-}$ to Brensted base centers. TPD-NH_3 and TPD-CO_2 profiles of stable ferrites have a complex shape, which indicates the presence of low, medium, and high-temperature acid and base sites with different relative amounts of such sites (Fig.1b,c). The ratio of the total number of basic and acid sites has the largest value for $FeFe_2O_4$ and decreases in the following order: $FeFe_2O_4 > MnFe_2O_4 \sim MgFe_2O_4 > ZnFe_2O_4$.

Acetaldehyde is the primary product of the ethanol conversion on the ferrite catalysts. High initial selectivity for acetaldehyde was observed for Zn and Mg ferrites, which, along with basic sites, have a large relative amount of weak acid sites. High acetone selectivity is achieved over $FeFe_2O_4$; ferrites containing other metals (Mn, Mg, and Zn) show lower selectivity. In general, the obtained results indicate that the selectivity of ethanol conversion to acetone over ferrites is determined by the combined effect of the following factors: the presence of medium-strength basic and acid sites on the surface of a catalyst; the ability of surface oxygen of a catalyst to participate in the intermediate redox stages of formation and steam reforming of acetone. An appropriate balance of redox and acid-base properties of the oxide catalyst is required for the high selectivity of the ESR process.

References:

1. M.D. Lazar, L. Senila, M. Dan, M. Mihet, in: A. Basile, A. Iulianelli, F. Dalena, T.N. Veziroglu (Eds), Ethanol Science and Engineering, Elsevier, 2019, chapter 10, p. 257.
2. T. Hou, S. Zhang, Y. Chen, D. Wang, W. Cai, Renew. Sust. Energ. Rev. **44** (2015) 132.
3. S. Ogo, Y. Sekine, Fuel Proc. Techn. **199** (2020) 106238.
4. H. Muroyama, R. Nakase, T. Matsui, K. Eguchi K, Int. J. Hydrogen Energy **35** (2010) 1575.
5. Z. Li, W. Yi, H. Qun, Trans. Nonferrous Met. Soc. China **19** *(*2009) 1444.
6. L.Y. Dolgikh, I.L. Stolyarchuk, L.A. Staraya, Y.I. Pyatnitsky, Theor. Exp. Chem. **54** (2018) 349.
7. L.Y. Dolgikh, A.A. Zhokh, A.I. Trypolskyi, I.L. Stolyarchuk, Y.I. Pyatnitsky, P.E. Strizhak, Sustainable Chemistry for Climate Action, **1** (2022) 100010.
8. J.E. Rorrer, F.D. Toste, and A.T. Bell, ACS Catal., **9** (2019) 10588.

O-14

OPTIMIZATION OF THE METHANOL PRODUCTION PROCESS ON THE CHM-Y INDUSTRIAL CATALYST

M.M. Baran[1]*, T.V. Tkachenko[1], D.S. Kamenskyh[1,2], V.H. Burdeyny[1],
V.O. Yevdokymenko[1]

[1]*V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Academician Kukhar St., 1, Kyiv, 02094 Ukraine, baranmaria48@gmail.com*
[2]*V. Bakul Institute for Superhard Materials, National Academy of Sciences of Ukraine, Avtozavodska St., 2, Kyiv, 04074 Ukraine*

From the beginning of the 20th century until now, industry has the most often used Cu-containing (in particular, $Cu/ZnO/Al_2O_3$) catalysts for methanol synthesis by hydrogenation of carbon oxides [1]. But until now, the search for optimization of the physicochemical characteristics of this catalyst continues. The main focus is on improvement of $Cu/ZnO/Al_2O_3$, selection of conditions for its synthesis [2]. However, the theory of the influence of vibration-acoustic oscillations (VAO) on this process has not yet been sufficiently studied, because it is just starting to gain momentum. Therefore, the goal of our work was to increase the productivity of the methanol process due to the influence of physical phenomena on the hydrogenation reaction of carbon oxides using the copper-zinc-aluminum oxide catalyst CHM-Y (Severodonetsk Low-temperature Methanol) (TU-U-6-04687873.047-2000).

Catalytic studies were carried out on a flow-circulation type laboratory set up in our department, equipped with a vibration-acoustic device. Granular industrial copper-zinc-aluminum oxide catalyst CHM-Y (62.7 % CuO; 32.7 % ZnO; 4.2 % Al_2O_3) (diameter 5.0 mm, height 5.0 mm) was loaded into the reactor. CHM-Y was first reduced in a stream of H_2 at a temperature of 200 °C for 5 h, and then its catalytic tests were carried out. The pressure in the system was created using a mixture of gases with the composition: CO – 63.01 % (mass.), H_2 – 13.15 % (mass.), CO_2 – 23.84 % (mass.), which in the molar ratio is: 1.0:2.92:0.24 respectively. The studies were carried out at different temperatures (180-280 °C) and pressures (0.5-2.0 MPa) in circulation conditions at a volume flow rate of the gas mixture of 600 h^{-1}. Catalytic tests were carried out both under classical conditions and with the use of vibration-acoustic oscillations with a frequency of 30 Hz and a meander shape. The reaction products were identified on «Chrom-5» chromatographs (Czech Republic) with a thermal conductivity detector (catharometer) and «Agilent Technologies 7890A» (USA) with a flame ionization detector.

It was found that the maximum rate of methanol formation is observed at a pressure of 2.0 MPa and a temperature of 220 °C. At these rates, the VAO allowance is $4.8 \cdot 10^{-3}$ $g_{methanol}/(g_{kat} \cdot h)$, which is 20 % more, compare with the classic one. Selectivity to methanol under these conditions is 59 %. However, the maximum value (64.03 % at VAO) is observed at the same temperature, but at a pressure of 1.0 MPa. This is almost 30 % more than under the classical conditions of the process.

References:

1. J.E. Ubong et al., Frontiers in Energy Research, 2020, 8:545431.
2. Dasireddy, V.D.B.C., B. Likozar, Renewable Energy, 2019, vol. 140, pp. 452-460.

O-15

MECHANOCHEMICAL, MICROWAVE AND SONOCHEMICAL MODIFICATION OF TIN DIOXIDE AND ITS PHOTOCATALYTIC PROPERTIES

M. Samsonenko[1]*, S. Khalameida[1], V. Sydorchuk[1], J. Skubiszewska-Zięba[2], V. Starchevskyy[3], L. Kotynska[1]

[1]*Institute for Sorption and Problems of Endoecology, National Academy of Sciences of Ukraine, Naumova St., 13, Kyiv, Ukraine, mashuna.08@gmail.com*

[2]*Faculty of Chemistry, Maria Curie-Skłodowska University, pl. Maria Curie-Skłodowskiej 3, 20 031 Lublin, Poland*

[3]*Institute of Chemistry and Chemical Technologies, L'viv National Polytechnic University, S.Bandera St., 12, L'viv, Ukraine*

Tin dioxide is a wide-gap semiconductor that is widely used as adsorbent, sensor manufacturing, and other [1-3]. The use of SnO_2 as a photocatalyst is limited by its activity only in the UV region. In order to improve the catalytic and adsorption properties of tin (IV) oxide, to obtain materials with the required properties, using the introduction of intrinsic or extrinsic defects in their structure [4]. This can be carried out using alternative methods such as mechanochemical and microwave modification or by doping of metal ions. In particular, doping promotes the increase of photocatalytic activity both under the action of UV-irradiation and in visible light. Due to intense mechanical action using mechanochemical (MChT), microwave (MWT) and sonochemical (UST) treatments, the activation of tin dioxide surface is observed.

Initial precipitated $SnO(OH)_2$ and powder SnO_2 were subjected to mechanochemical treatment and microwave treatment. Also this initial samples $SnO(OH)_2$ and SnO_2 were subjected to UST and MChT with dopants containing cations Ag^+, Zn^{2+}, Cu^{2+}, Co^{2+}, Cr^{3+}, Ce^{4+}, Ti^{4+}, Nb^{5+} and Mo^{6+} with next thermal treatments of doped samples at 300°C and 550°C. The content of dopants in the obtained composition was 5 wt.% based on oxides, as is most often practiced, based on literature data. In the case of doping with silver, its content was 0.5-5 wt. %. Physical-chemical properties of all samples were studied using DTA-TGA, XRD, TEM, SEM and EDS, XPS, adsorption–desorption of nitrogen, UV–Vis- and PL-spectroscopy. All samples were tested as photocatalysts in degradation rhodamine B (RhB), safranin T (ST), methyl orange (MO) and 4-chlorophenol (4-CP) process in aqueous medium under visible irradiation.

Mechanochemical and microwave modification of SnO_2. According to DTA-TG data, the precipitated and high-dispersed commercial samples correspond to composition $SnO(OH)_2$, the low-dispersed – SnO_2. The mechanochemical and microwave treatment of samples leads to partial removal of OH-groups. It is accompanied by transformation of initial $SnO(OH)_2$ into SnO_2. Chemical composition of SnO_2 does not change under modification. According to XRD data, all samples correspond to the tetragonal modification of cassiterite (JCPDS No 41-1445). The initial precipitated sample has a low-crystalline structure, and MChT changes it little. In its turn, MWT contributes to the formation of a more perfect crystal structure. At the same time, the size of the crystallites increases from 2.1 to 4.2 nm. After MChT of tin dioxide powders, a decrease in the intensity and an increase in the width of the reflexes is observed, as a result there is decrease in the size of the crystallites for the modified samples in 2 times. The initial samples are characterized by high specific surface values due to the high content of micropores. As a result of MChT and MWT of deposited samples due to the decrease in the volume of micropores, the specific surface area decreases, the total volume of pores, the volume and size of mesopores increase. A feature of MChT dry xerogel in water is the formation of secondary porosity represented by meso- and macropores.

A homogeneous mesoporous structure is formed as a result of the MWT of wet gels and dry xerogels. UV-Vis spectra show bathochromic shift of absorption edge and corresponding narrowing of band gap for modified SnO_2 samples from 4.2 to 3.5-3.9 eV.

Mechano- and sonochemical doping of SnO_2. It was found that all doped samples can be divided into several groups based on changes in the phase composition. The first group includes samples SnO_2 doped with silver, zinc, copper and cobalt in the form of metal salts with followed by their thermal decomposition. Their phase composition does not change. Also, the presence of separate crystalline phases of dopant additives was not recorded. The second group includes samples of tin dioxide doped with zinc, copper, cerium, chromium and niobium in the form of highly crystalline oxides. In addition to the cassiterite phase, these samples are characterized by the presence of a dopant oxide phase. Along with this, the use of $TiO(OH)_2$ as a dopant leads to the formation to the formation of a solid solution. This is evidenced by: the absence of reflexes of the TiO_2 phase after calcination at 300-550°C; changes in lattice parameters *a* and *c* for doped samples, compared to the initial SnO_2; decrease in the size of crystallites of the doped samples, compared to the initial SnO_2. For SnO_2 samples doped with additives in the form of highly crystalline oxides, an increase in the specific surface area is characteristic. At the same time, lower values of the specific surface are observed for SnO_2 samples doped with metal salts after thermal treatment. When doping wet SnO_2 gels, the total pore volume increases due to the formation of additional meso- and macropores. Also, the introduction of dopants into the structure of tin dioxide contributes to the narrowing of the band gap, but to a different extent. Thus, all doped samples can be conditionally divided into three groups: band gap >3.25eV - SnO_2 doped with zinc, copper, niobium (Nb_2O_5 355m^2/g) and tantalum; within 3.0-3.25eV - SnO_2 doped with cerium, niobium (Nb_2O_5 2 m^2/g), molybdenum, praseodymium and samarium; and <3.0 eV - SnO_2 doped with chromium, cobalt, ferrum, titanium, silver. Silver doping maximally narrows the band gap to 2.59 eV. It is important that the intensity of the photoluminescence bands for doped samples corresponding to the presence of various recombination centers in the structure (for example, oxygen vacancies and other defects) is 1.5-2 times lower, compared to the initial SnO_2.

Photocatalytic properties of modified SnO_2. The initial samples of tin dioxide are inactive in the degradation processes of ST and MO in aqueous solutions under the influence of visible light, but shows minimal activity in the degradation process of RhB due to the process of initiating a photocatalytic reaction by exciting the dye molecules. All types of modification lead to improved functional characteristics of the obtained SnO_2 samples. Mechanochemical and microwave treatment leads to the increased of photocatalytic activity of SnO_2 samples in the range of visible light in the processes of photodegradation of dyes and 4-CP. Doping with all studied metals also contributes to an even greater increase in the photocatalytic activity of tin dioxide. Among the doped samples, SnO_2 samples doped with silver have the highest photocatalytic activity. Moreover, samples doped by UST are more photocatalytically active. The maximum activity in the degradation of dyes and 4-CP was demonstrated by the SnO_2 doped with 1% silver. It is important that in the process of photodegradation, not only the discoloration of solutions occurs, but also mineralization. It can be seen that the degree of mineralization in the best cases reaches 65-70%.

References:

1. V.V. Pham, H.-H. Tran, T.K. Truong, T.M. Cao, J. Nanotechnol. **13** (2022) 96.
2. A.M. Al-Hamdi, U. Rinner, M. Sillanpää, Process Saf. Environ. Prot. **107** (2017) 190.
3. M. Najjar, H. Hosseini, A. Masoudi, A. Hashemzadeh, M. Darroudi, Res. Chem. Intermed. **46** (2020) 2155.
4. A.I. Kryukov, A.L. Stroyuk, S.Ya. Kuchmii, et al., Nanophotocatalysis [in Russian], Akademperiodika: Kyiv, 2013.

O-16

CATALYTIC PROPERTIES AND RESOURCE CHARACTERISTICS OF MODIFIED NICKEL COMPOSITES IN THE PROCESSES OF OXIDATIVE REFORMING OF C_1-C_4 ALKANES

V.I. Chedryk[1]*, S.M. Orlyk[1], O.D. Vasylyev[2]

[1]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, val_c@ukr.net*
[2]*I.M. Frantsevych Institute for Problems of Materials Sciences, National Academy of Sciences of Ukraine, Kyiv, Ukraine*

The anodic direct oxidation of hydrocarbon fuel is an actual trend in the use of oxidative heterogeneous catalysis conceptions in SOFC. Anodes based on nickel and zirconia stabilized with yttrium, scandium, and cerium together with scandium (ScCeSZ) are used in modern SOFC of hydrocarbon fuel (natural gas, propane-butane) [1]. In the case of SOFC running on hydrocarbon fuels, the catalytic properties of the anode materials are extremely important [2], in particular, the resistance to the action of sulfur compounds present in the fuel (mercaptans, hydrogen sulfide) [3]; carbonization of nickel-containing anode’s surface is also a problem [4].

In this work, research results are presented on the effect of the composition of nickel composites based on Sc(Ce)-stabilized zirconia (10Sc1CeSZ) on their activity and resource characteristics (performance stability, carbonization and sulfur resistance) in the processes of oxidative reforming of C_1, C_4 alkanes (methane tri-reforming, TRM and steam-(oxygen) reforming of butane).

Modified nickel catalysts based on stabilized zirconia showed high activity and stability in the tri-reforming of methane and steam (-oxygen) reforming of butane into the operating range SOFC temperatures (600-800^{o}C).

The higher activity of Pt(Pd)-Ni composites in methane tri-reforming is due to the platinum (palladium) catalyzing the exothermic reaction of methane oxidation, nickel – the endothermic steam, and dry reforming of methane (Table 1). Doping of the nickel composite with platinum and palladium also increases the resistance to the deactivating effect of H_2S during the methane tri-reforming process. In the butane steam reforming the positive effect of nickel composite doping with platinum (0.1 wt.% Pt) is manifested by a decrease in temperature on 60-100^{o}C of both reaction beginning and 90% butane conversion [5].

Modification of the nickel composite with copper and cerium dioxide increases its resistance to carbonization in the processes of TRM and steam reforming of butane. The increase in the efficiency of the Ni-Cu-CeO_2 catalyst in the steam reforming of butane is achieved due to the greater dispersion of the deposited nickel and copper, and hence the centers’ number for activation butane (Ni, Cu) and H_2O (CeO_2).

The greatest resistance to H_2S action showed Pt-Ni catalyst: within 2 h of CH_4 and CO_2 conversion decreased by 10-15%, which may be caused by blocking the active centers with surface sulfur-containing compounds. It should be noted that the resistance of catalysts to the action of H_2S coincides with the corrosion resistance of their metallic active components (in the air saturated with H_2O + traces of H_2S) [6]: Cu, Ni < Pt < Pd.

The bench tests (Scribner Teledyne Medusa RD 890CL USA) of the developed fuel cell with optimized anode composition demonstrated the possibility of operation on different types of fuel – H_2, CO, methane, syngas, and showed that using syngas as a fuel, the achieved electrical characteristics are close to those for hydrogen (Fig.1). This indicates the promising use of an external fuel processor for the oxidative reforming of hydrocarbon fuels into syngas over the structured catalysts, in particular Ni/M_xO_y/Al_2O_3/cordierite (M: La, Ce) [7], with subsequent use of syngas as SOFC fuel.

Table. The activity of modified Ni-10Sc1CeSZ composites in the TRM process

Catalyst	T,°C	Conversion, %		
		X(CH_4)	X(CO_2)	X(O_2)
Ni-Cu-CeO_2	600	36	8	83
	700	70	33	84
	800	95	62	87
Pt-Ni	600	85	45	81
	700	99	57	81
	800	100	60	83
Pd-Ni	600	81	36	88
	700	98	63	84
	800	100	65	82

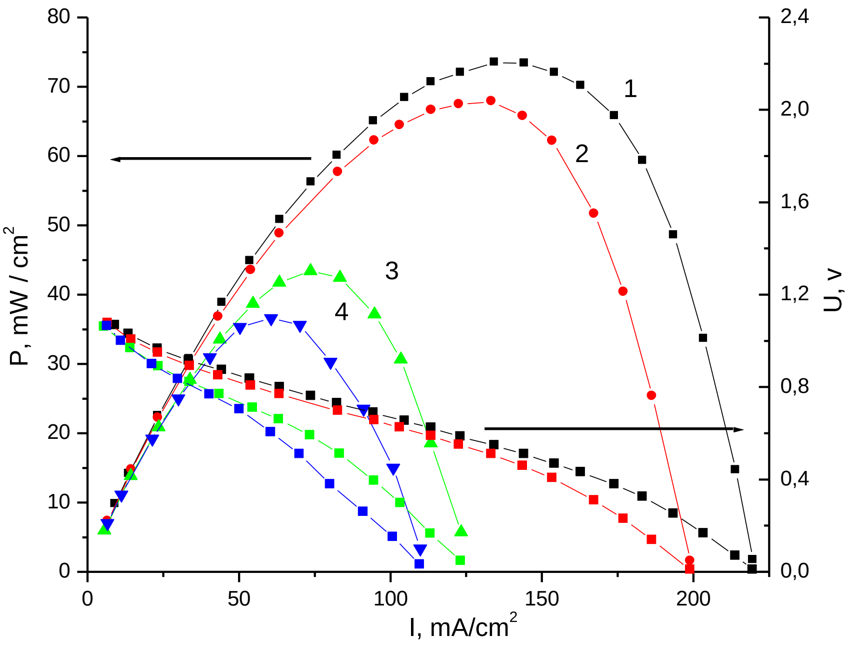


Fig. 1. Test results of electrical characteristics of the developed fuel cell on different types of fuel (5% vol. fuel in Ar): H_2 (1), synthesis gas (2), CO (3), CH_4 (4) (T = 800°C, feed rate fuel – 350·ml·min^{-1}, air – 1000 ml·min^{-1}).

References:

1. Z. Cheng, J. H. Wang, Y. Choi, et al., Energy Environment Science. **4** (2011) 4380.
2. R. J. Gorte, S. Park, J. M. Vohs, et al., Advanced Materials. **12** (2000) 1465.
3. Z. Cheng, M. Liu, Solid State Ionics. **178** (2007) 925.
4. M. Powell, K. Meinhardt, V. Sprenkle, et al., J. Power Sources. **205** (2012) 377.
5. S.M. Orlyk, V.I. Chedryk, S.O. Soloviev, et al., Theor. Exp. Chem. 5**8** (2022) 350.
6. O.D. Neikov, S.S. Naboychenko, N.A Yefimov, *Handbook of Non-Ferrous Metals Powders*, Elsevier (2019).
7. S.A. Solov’ev, Y.V. Gubareni, Y.P. Kurilets, et al., Theor. Exp. Chem. 4**8** (2012) 199.

O-17

CARBON NANOSPHERES: SYNTHESIS IN LIQUID PHASE, STRUCTURE AND PROPERTIES

E.V. Polunkin[1]*, S.M. Pleskun[1], V.S. Pyliavskiy[1],
A.D. Rud[2], D.P. Vinnichenko[3]

[1]*V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of N.A.S. of Ukraine, Murmanska St., 1, Kyiv, 02094 Ukraine, polunkin@i.ua*
[2]*G.V. Kurdyumov Institute for Metal Physics of N.A.S. of Ukraine, Academician Vernadsky Blvd., 36, Kyiv, 03142 Ukraine*
[3]*Institute of Pulse Research and Engineering of N.A.S. of Ukraine, Bogoyavlenskiy St., 43A, Mykolaiv, 54018 Ukraine*

For the first time, methods for the synthesis of carbon nanospheres from gas and liquid aromatic and halogenated saturated hydrocarbons by high-frequency plasma-chemical method have been developed by us.

The synthesis of spherical carbon nanoparticles is carried out by the high-frequency discharge-pulse method [1], which creates a nonequilibrium plasma due to the high frequency of short high-voltage pulses-discharges in the kilohertz range in the environment of hydrocarbon liquids, and contains organometallic, or metal-complex, or organoelement compounds in the mixture (Fig. 1). At the same time, large temperature and pressure gradients (the necessary conditions for nanocarbon syntheses) are realized as a result of the high rate of energy input into the plasma channels.

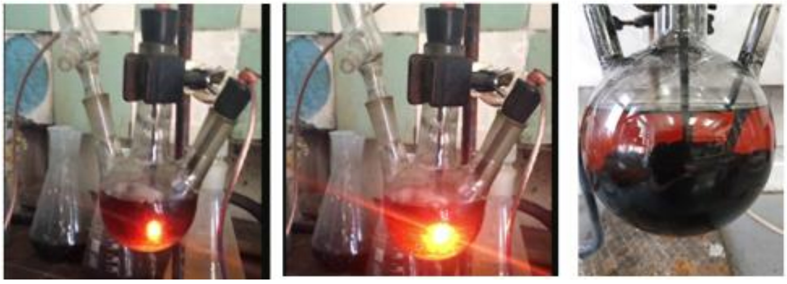


Fig. 1. Synthesis of spherical carbon nanoparticles by the high-frequency discharge-pulse method.

The synthesis of carbon nanomaterials in the liquid phase is carried out using dielectric liquids. The plasmochemical liquid-phase synthesis of carbon nanoparticles was carried out in a glass reactor. The plasma discharge in aliphatic and aromatic solvents was generated by a bipolar power source – a high-voltage high-frequency generator using tungsten gapped electrodes. Electrodes were placed in a volume of liquid, i.e., the feedstock. The frequency of the voltage pulses was 25 kHz. The generator voltage was U = 4 kV.

The modes of plasmochemical liquid-phase synthesis for the synthesis of spheroidal carbon nanomaterials were developed using individual hydrocarbon compounds in the liquid state (hexane, octane, benzene, bromethane), mixtures (hexane with bromethane), fluorinated hydrocarbons, as well as hydrocarbon solutions with organometallic compounds (in particular, ferrocene).

The synthesis products were separated from the liquid phase by centrifugation (30 min at 4000 rpm). Then the powders were further dried in vacuum and fractionated by extraction in volatile solvents and filtered on filters with a pore diameter of 250 nm and the solvent was evaporated.

High-resolution microscopic images of carbon clew-like nanospheres (CCNs) were obtained using a JEOL JEM-2100F transmission electron microscope (TEM) with an accelerating electron voltage of 200 kV. For this purpose, samples of carbon nanospheres were dispersed in dimethyl ketone medium using an ultrasonic disperser and then applied to a special grid. The obtained carbon nanomaterials are spheroidal nanoparticles with dimensions of ~10-30 nm and are characterized by a complex hierarchical structure.

To modify and change the properties of carbon nanospheres, the functionalization of these nanomaterials by adding organometallic and metal-complex compounds with different metals to the initial liquid raw material has been proposed and practically implemented. Using liquid hydrocarbons (hexane, heptane, isooctane, toluene, bromoethane) laboratory samples of carbon nanospheres, as well as nanospheres with implanted metals were developed.

The structure and nature of chemical bonds in the obtained carbon nanospheres were studied by IR (Fig. 2), NMR and Raman spectroscopy, SEM and HRTEM (Fig. 3) microscopy. It is confirmed that synthesized individual particles of clew-like nanospheres consist of woven carbin filaments with a diameter of 2.2-2.4 nm, which coincides with the diameter of the polycumulene chain. Indeed, the absorption band 1737 cm^{-1} present in the IR spectra of the obtained nanocarbon compounds is present in the IR spectrum of polycumulenes and is not observed in the spectrum of graphene or fullerenes and ideal carbon nanoonions (CNOs).

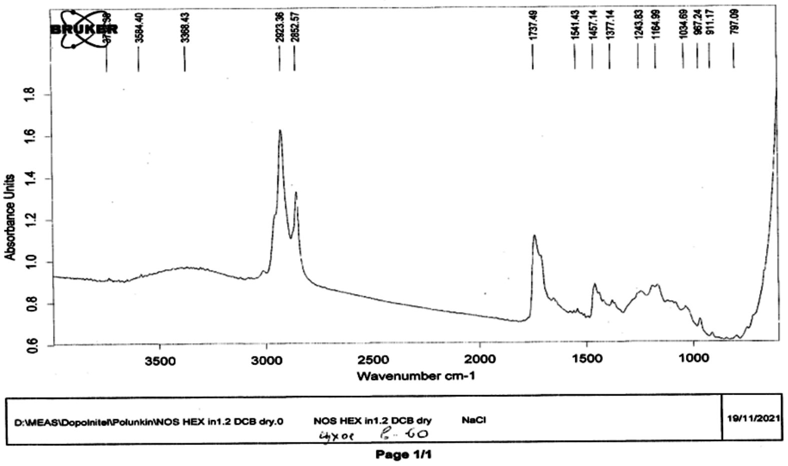


Fig. 2. IR spectre of obtained carbon nanospheres.

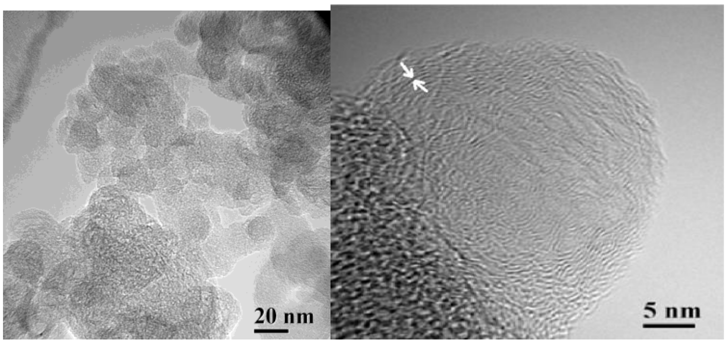


Fig. 3. HRTEM microscopy of spherical carbon nanoparticles.

We have studied the refractive indices of solutions of CCNs in various organic liquids and found an extremum - the minimum concentration at which these substances effectively change the refractive index of the solution.

References:

1. Rud, A.D., Kornienko, N.E., Polunkin, I.V. et al. Appl. Nanosci. 2023. https://doi.org/10.1007/s13204-023-02817-2.

O-18

SYNTHESIS OF NEW COMPLEX OXIDE ACID CATALYSTS AND STUDY OF THEIR PROPERTIES

N.P. Golub[1]*, Ye.O. Golub[2], A.A. Kozma[1], A.O. Kuznietsova[1],
V.I. Gomonaj[1]

[1]Department of Physical and Colloid Chemistry, Educational and Scientific Institute of Chemistry and Ecology, Uzhhorod National University, Pidhirna St., 46, Uzhhorod, 88000 Ukraine, nelya.golub@uzhnu.edu.ua
[2]Department of Pharmaceutical Disciplines, Faculty of Medicine, Uzhhorod National University, Pidhirna St., 46, Uzhhorod, 88000 Ukraine

Today, the catalytic conversion of natural gas components into valuable products is of great theoretical and practical interest and is an important area of the modern chemical industry. The relevance of this problem is particularly pronounced due to the rapid increase in the cost of natural gas as an important hydrocarbon raw material, which requires particularly rational ways of its efficient processing. This makes it possible to utilize domestic gas fields, associated petroleum gases and refinery gases efficiently and effectively. Accordingly, this requires the development of new active, highly selective and inexpensive catalysts. At the same time, the problem of developing a theory of the scientific basis for predicting the catalytic action of contacts also remains unresolved today. Therefore, it is especially important to continue to search for new approaches to targeted regulation of structural, physical and chemical parameters and to create appropriate conditions for the formation of optimal surface complexes. This makes it possible to rationally and predictably obtain new active, highly selective, and cheap catalysts for the processes of one-step partial oxidation of n-alkanes into valuable products [1].

The aim of this work was to develop new ways and methods for the synthesis and preparation of new cheap active and highly selective complex oxide catalysts with optimal structural, physicochemical, and acidic parameters and to study their properties.

As a result, we have developed new ways and methods for the synthesis of complex oxide catalysts based on d-elements with predictable structural, physicochemical, and acidic properties. New promising inexpensive active and highly selective catalysts for the one-step oxidation of n-alkanes into valuable products with optimal acidic properties were obtained. In particular, individual phosphates, aluminosilicates, zeolites and complex catalytic systems based on them. For example, metal-nickel phosphate systems such as $x\mathrm{Me}_n(\mathrm{PO}_4)_m \cdot y\mathrm{Ni}_3(\mathrm{PO}_4)_2$; catalytic systems based on aluminum phosphate modified with d-metal ions, as well as zeolite catalysts and their modified forms based on natural zeolites: mordenite and clinoptilolite from the Sokyrnytsia deposit (Zakarpattia). Their composition, structure, physical and chemical parameters were studied by modern physicochemical methods, and the value of the specific surface area, surface acidity, concentration, and distribution of active centers on it were determined. It was found that the features of all synthesized new complex oxide catalysts are the constancy of their chemical composition, high thermal stability, and a wide range of changes in the acidic properties of the surface. Also, a pronounced synergistic effect of modification on surface acidity, developed specific surface area, and low oxygen mobility of the crystal lattice. The relationship between the preparation method, composition of the obtained catalysts and their structure, physicochemical parameters, surface acidity, concentration of acid centers of the corresponding nature and their strength on the surface was established.

References:

1 V. Gomonaj, H. Toulhoat, ACS Catalysis. **8** (2018) 8263.

O-19

DEVELOPMENT OF ACID AND BIFUNCTIONAL MIXED OXIDES AS EFFECTIVE CATALYSTS FOR THE TRANSFORMATION OF RENEWABLE RAW MATERIALS

S.V. Prudius*, N.L. Hes, O.I. Inshina, V.V. Brei

Institute for Sorption and endoecology problems, National Academy of Sciences of Ukraine, General Naumov St., 13, Kyiv, 03164 Ukraine, svitprud@gmail.com

The replacement of fossil resources with renewable vegetable raw materials for obtaining fine chemicals and commodity materials is one of the promising directions of the development of chemical technology. 75 wt.% of plant biomass is made up of carbohydrates [1]. So, the sugar-based feedstock is currently considered the largest platform for the production of biomass-based chemicals [2]. Monosaccharides can be subjected to selective dehydration, decondensation, hydrogenolysis and oxidation reactions with the formation of useful products, such as lactates and glycolates, which serve as precursors for the production of bioplastics, furfurals, levulinic and formic acids, which are used in the pharmaceutical industry, C2-C3 polyols, which are widely used for the production of polyesters, as well as solvents, plasticizers, etc. [3]. The development of the most promising processes for the conversion of monosaccharides is associated with the use of mixed oxides as multifunctional catalysts of a controlled structure, which are able to catalyze complex multi-step transformations. The use of mixed oxides as solid acid catalysts is of particular interest due to their wide availability and low cost [4].

We have proposed several low acid Sn- and Ce-containing mixed oxides obtained by a simple wet impregnation method as catalysts of one-pot conversion of dihydroxyacetone, xylose and fructose into alkyl lactates. The strength and content of acid sites of supported SnO_2/Al_2O_3 oxide is $H_0 = +1.5$ and 1.6 mmol/g respectively. Doping with ZnO leads to a decrease in the content of Brönsted sites on the surface of the mixed SnO_2-ZnO/Al_2O_3 oxide, while the base sites are formed. According to the UV-*Vis* data, synthesized oxides contain isolated tetrahedral $^{IV}Sn^{4+}$ ions. Structural analysis by XRD shows that impregnation of SnO_2/Al_2O_3 with cerium ions leads to the formation of crystalline tetragonal ceria on the surface of CeO_2-SnO_2/Al_2O_3 mixed oxides. A scheme for the formation of alkyl lactates from monosaccharides on Sn-containing mixed oxides is proposed, according to which the first stage - the reaction of aldol decondensation of monosaccharides – is catalyzed by acid $^{IV}Sn^{4+}$ L-sites, which further initiate the isomerization of pyruvic aldehyde hemiacetal to methyl lactate.

Further, a binary mixed oxide of zirconium and silicon, ZrO_2-SiO_2 (Zr:Si = 1:2, at.), with high acidity (H_0 = -11.35) was synthesis by sol-gel method. For the synthesis, we used both zirconium salt and tetraethoxysilane as well as zircon concentrate, $ZrSiO_4$, from the domestic Malyshev deposit. Zirconium-silicate catalyst based on highly acid ZrO_2-SiO_2 oxide was successfully used by us for cracking of vacuum gas oil, a large-scale global processes with annual processing at the level of 109 tons of gas oil into gasoline and diesel fuel.

It was found that doping of ZrO_2-SiO_2 oxide with tin and aluminum ions leads to an increase in acid strength of ternary ZrO_2-SiO_2-Al_2O_3 and ZrO_2-SiO_2-SnO_2 oxides by three orders of magnitude to H_0 = -14.52. The highest strength ($H_0 = -14.52$) and content (1.6 mmol/g) of acid sites are achieved at the ratio of cations Si/Zr ≈ 2 and Sn^{4+} or Al^{3+} concentration within $5 \leq Sn^{4+}/Al^{3+} \leq 20$ at.%. It has been founded that the limiting band gap of 4.0–4.3 eV determined from the UV-*Vis* spectra can serve as a criterion for the superacidity of ZrO_2-SiO_2-SnO_2 oxides. The latter could be explained by the formation of coordination–unsaturated $^{VII}Zr^{4+}$ ions at the surface layer as strong Lewis sites with $H_0 = -14.52$. It is possible that strong L-sites with $H_0 = -11.35$ can form tetrahedrally coordinated $^{IV}Sn^{4+}$ ions.

The models of acid L-sites of ternary ZrO_2-SiO_2-Al_2O_3 and ZrO_2-SiO_2-SnO_2 oxides are proposed based on the XPS and ^{29}Si, ^{27}Al and ^{119}Sn NMR spectroscopy data. A combination of strong acid Brønsted and Lewis sites was found to be effective for transformation of fructose into levulinic and formic acids on superacid ZrO_2-SiO_2-SnO_2 oxide.

References:

1. Ch. Chatterjee, F. Pong, A. Sen, Green Chemistry. **17** (2015) 40.
2. Bio-Based Chemicals A 2020 Update https://www.ieabioenergy.com/wp-content/uploads/2020/02/Bio-based-chemicals-a-2020-update-final-200213.pdf
3. T.M. László, E. Cséfalvay, Á. Németh, Chemical Reviews. **118** (2018) 505.
4. A. Kokel, Ch. Schäfer, B. Török, Current Organic Synthesis, **16** (2019) 615.

O-20

PHASE COMPOSITION OF MnOx-Na_2WO_4/SiO_2 CATALYST AND THERMODYNAMICS OF THE SIZE DEPENDENT STABILITY OF MANGANESE OXIDES NANOPARTICLES IN THE OXIDATIVE CONDENSATION OF METHANE TO C_2 HYDROCARBONS

E.H. Ismailov[1]*, S.N. Osmanova[1,2], G.R. Azimova[1], A.N. Mammadov[1,3], D.B. Taghiyev[1], J.W. Thybaut[4]

[1]*Institute of Catalysis and Inorganic Chemistry,113, H. Javid Ave., AZ1143, Baku, Azerbaijan, etibar.ismailov@gmail.com*
[2]*Khazar University, 41, Mahsati St., AZ1096, Baku, Azerbaijan, sevinj.nasib.osmanli.26@gmail.com*
[3]*Azerbaijan Technical University, 25, H. Javid Ave., AZ1073, Baku, Azerbaijan*
[4]*Ghent University, Laboratory for Chemical Technology, Technologiepark 125, 9052, Ghent, Belgium*

Over the past 10-15 years, a fairly large number of works have been published on the preparation of MnNaW/SiO_2 catalysts, their structural and catalytic features in oxidative coupling (condensation) of methane (OCM). MnNaW/SiO_2 is considered a promising catalyst for this reaction. At the same time, very few studies have been published on the effect of reaction conditions on the phase composition of this catalyst and the stability of these phases under OCM conditions [1, 2].

This report presents the results based on the using of scanning electron microscopy (SEM, ThermoFisher Phenom Pro G6 with BSD detector), X-ray diffraction (Bruker D2 PHASER), electron magnetic resonance (EMX_{micro}), measurements of N_2 adsorption-desorption (Belsorp Mini II from BEL, Japan Inc) and catalytic activity (integrated mass spectrometer-microreactor system from Hiden Analytical, UK) to characterize the elemental and phase composition, magnetic particles, textural properties (specific surface area, pore size and volume) and catalytic activity of MnNaW/SiO_2 samples in the OCM reaction depending on the reaction conditions (temperature, CH_4/O_2 ratio, contact time, duration).

XRD data show that the MnNaW/SiO_2 catalyst consists of MnOx, Na_2WO_4, $MnWO_4$, and SiO_2 phases. It is assumed that, under the reaction conditions (750-850°C), one of these phases, Na_2WO_4 is in the molten state (696 ^oC), contains the products of the interaction of molten sodium tungstate with MnOx, and covers the SiO_2 surface. EMR and SEM/EDS data indicate a noticeable effect of reaction conditions on the surface structure and distribution of catalytically active components in the catalyst structure, the presence of superparamagnetic particles of manganese oxides. Calculation of the dependence of the melting temperature of oxide particles on their size shows a noticeable decrease for Mn_2O_3 particles smaller than 10 nm in size. It is assumed that a decrease in the melting temperature of manganese oxide nanoparticles can lead to their melting at typical OCM reaction temperatures. The possibility of reduction of Mn_2O_3 particles to mixed oxide Mn_3O_4, formation of $NaMnO_2$, $MnWO_4$, and $(MnO)x{*}(Mn_2O_3)y{*}(SiO_2)z$ particles under the OCM reaction conditions was also evaluated. It is assumed that catalytically active particles are formed as a result of the reversible reaction of Na_2WO_4 with Mn_2O_3 and more complex structures of the type, for example, Mn_7SiO_{12}, in the conditions of the OCM reaction, accompanied by phase transitions and melting.

Acknowledgements. This work is funded by the European Union's Horizon 2020 research and innovation program under grant agreement No.814557.

References:

1. D. Matras, A. Vamvakeros, S. D.M. Jacques, N. Grosjean, B. Rollins, et al. Faraday Discussions, 229, (2021)176.
2. E. Ismailov, D. Taghiyev, S. Zulfugarova, et al., Theor Exp Chem, **58** (2022) 61.

O-21

POLYFUNCTIONAL CATALYSTS FOR TANDEM PROCESSES OF $C_{2,4}$ BIO-ALCOHOL CONVERSION INTO INDUSTRIALLY IMPORTANT ORGANIC COMPOUNDS

O.V. Larina

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, olga.larina@ukr.net

Development of heterogeneous catalytic processes of $C_{2,4}$ bio-alcohol conversion into industrially important hydrocarbons (1,3-butadiene, butene isomers) and oxygenates (1-butanol, 2-ethyl-1-hexanol) is becoming increasingly relevant, since it allows producing fuel components and polymeric materials from renewable feed. The processes of ethanol conversion into 1,3-butadiene and 1-butanol (and further conversion of 1-butanol into 2-ethyl-1-hexanol) are multistage and include a number of sequential reactions (dehydrogenation, aldol condensation, MPV reduction, dehydration and/or hydrogenation) for the acceleration of which certain types of active sites are necessary on the catalyst surface [1].

Mg(Zr)-Si oxide systems doped with *d*-metal compounds are widely studied in the process of converting ethanol into 1,3-butadiene (ETB process) [2]. A simultaneous presence of the catalyst components: for ethanol dehydrogenation (Zn, Cu, Ag) and subsequent aldol condensation (Mg, Zr) is shown to provide high ETB process indices. Rare-earth elements, namely yttrium, lanthanum, and cerium, and alkali metals are considered to be effective modifying additives of the multicomponent catalysts [3-5]. Enhanced catalyst efficiency is achieved by adjusting acid-base properties of the catalyst surface. In particular, the selectivity for ethanol dehydration by-products could be declined by decreasing in the concentration of strong acid sites, whereas the formation of active sites of aldol condensation (the key stage) promotes the target process.

Considerable attention of researchers is paid to Mg-Al oxide hydrotalcite-derived and Ca-P hydroxyapatite systems as promising catalysts for Guerbet condensation of alcohols. Based on the study of oxide systems with various Mg/Al atomic ratio, the volume and surface area of mesopores, and also the concentration of weak and medium base sites are found to be regulated by varying time of mother liquor maturation during the preparation of hydrotalcite [6]. The highest 1-butanol selectivity of 64% and yield of 23.4% is achieved over the best sample of Mg-Al-oxide series at 548 K.

The effect of carbonaceous materials as a catalyst carrier on acid-base characteristics and catalytic properties of Mg-Al oxide and hydroxyapatite systems are considered. Enhanced catalytic activity and operation stability of the carbon-supported catalysts are achieved using both rectified and aqueous ethanol [7]. Redistribution of the active sites of Mg-Al oxide phase over the highly dispersed support and increasing their availability for the reagents were suggested to be the causes of the enhanced catalytic performance.

References:

1. P.I. Kyriienko, O.V. Larina, S.O. Soloviev et al. Theor. Exp. Chem. **56(4)** (2020) 213.
2. P.I. Kyriienko, O.V. Larina, D.Yu. Balakin et al. Catal. Letters **152** (2022) 921.
3. P.I. Kyriienko, O.V. Larina, D.Yu. Balakin et al. Mol. Catal. **518** (2022) 112096.
4. O.V. Larina, P.I. Kyriienko, O.V. Morozov et al. Theor. Exp. Chem. **57(6)** (2022) 443.
5. O.V. Larina, O.V. Zikrata, L.M. Alekseenko et al. Appl. Nanosci. (2023) https://doi.org/10.1007/s13204-023-02876-5.
6. K.V. Valihura, O.V. Larina, P.I. Kyriienko et al. Appl. Nanosci. (2023) https://doi.org/10.1007/s13204-023-02801-w.
7. O.V. Larina, P.I. Kyriienko, N.D. Shcherban et al. Ind. Eng. Chem. Res. **60(32)** (2021) 11964.

O-22

STRUCTURAL BACKGROUND OF THE SYNERGETIC BIMETALLIC EFFECT OF NiMo/MgO CATALYSTS IN METHANE PYROLYSIS

A. Beck[1]*, M. Németh[1], T.I. Korányi[1], Gy. Sáfrán[1], L. Borkó[1],
Zs.E. Horváth[1], I. Rigó[2], A. Horváth[1]

[1]*Centre for Energy Research, Konkoly-Thege M. street 29-33, H-1121 Budapest, Hungary*
[2]*Wigner Research Centre for Physics, Konkoly-Thege M. street 29-33, H-1121 Budapest, Hungary,*
beck.andrea@ek-cer.hu

As a temporary but essential link between fossil and renewable energies to establish H_2 economy, the pyrolysis of the abundant methane, producing “turquois”, carbon oxides free, fuel cell grade H_2 and solid carbon ($CH_4 \rightarrow C+2H_2$) should be considered. The cost of high energy demand of the reaction can be partly overcome by reducing reaction temperature and formation of precious carbon nanotubes, fibers using appropriate catalysts. The highly active, but fast deactivating nickel when alloyed with other metals can exhibit synergetic effect in the reaction as reported already also for the Ni-Mo couple. In the present work, we aimed to find correlation between structural details of MgO supported NiMo catalysts and their catalytic efficiency, stability and morphology of the carbon product.

The catalysts were prepared by deposition of metal precursor ions via adsorption-precipitation at 80 °C on commercial MgO, followed by washing, drying, calcination at 550 °C and reduction at 800 °C. The bimetallic catalysts designated by *MoNi0.4* and *MoNi1.2* contained 7 wt% Ni and 4 or 13 wt% Mo (Mo/Ni=0.4 or 1.2), the loading of the reference monometallic samples was 7wt% Ni and 13wt% Mo. Structural characterization by Temperature Programmed Reduction (TPR), Transmission Electron Microscopy (TEM) with STEM-EDS, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) were performed. The catalytic properties were investigated in (i) 1% CH_4/He stream under temperature ramping and (ii) at isothermal 700 °C in a MIC AutoChem instrument with QMS analysis and (iii) in 50% CH_4/Ar flow at 800 °C in a horizontal pyrolysis reactor attached to a GC. The amount of coke was determined after pyrolysis and its structure was analysed by Raman Spectroscopy (I_G/I_D) or High Resolution TEM.

According to TPR the bimetallic samples could be fully reduced up to 800 °C, while the monometallic ones only partially. The mean metal particle sizes were below 8 nm in all cases (TEM). Alloyed particles of different compositions were detected by STEM-EDS in both bimetallic samples, the larger particles were typically richer in Ni. XRD of *MoNi0.4* was in agreement with this, but *MoNi1.2* did not give any metal reflections indicating high dispersion. In situ XPS of the reduced samples measured a surface Mo excess for *MoNi1.2* and Ni excess for *MoNi0.4* (compared to the bulk Mo/Ni ratios). All three types of methane decomposition experiments showed synergetic effect of the bimetallic samples. These produced at 800 °C moderately irregular, graphitic MWCNTs (I_G/I_D:3) of lower than 10 nm in diameter with higher yield on *MoNi1.2* (300%). The monometallic *Ni* and *Mo* deactivated quickly after forming only several layers of well-ordered graphene (I_G/I_D:7.7) around Ni and not complete, highly defective carbon shells (I_G/I_D:0.4) around Mo particles (basically encapsulating type carbons).

The superiority of *MoNi1.2* catalyst in terms of activity, stability and carbon yield was explained by the high dispersion and stable equimolar alloyed NiMo particles that did not seem to segregate during the carbon nanotube growth process unlike the ones in *MoNi0.4* catalyst. The interaction of Ni with sufficient Mo partners creates new active sites that allow the methane dissociation with continuous carbon dissolution and nanotube formation, thus good catalytic performance during CH_4 decomposition.

O-23

METHYL ACETATE PRODUCTION FROM METHANOL IN VAPOR-PHASE TANDEM PROCESS ON Ni-Cu BASED CATALYSTS

A.Yu. Kapran*, L.M. Alekseenko, V.I. Chedryk

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, ayukapran@ukr.net

Methanol carbonylation (MC), based on homogeneous Monsanto and BP Chemicals Cativa^{TM} processes using Rh(Ir) catalysts and halide promoters, is of industrial importance as a large-scale route to acetic acid MeOH + CO → HOAc (ΔH^{o}_{298K} = -137.4 kJ/mol) [1]. Besides, as a carbonylation product, is also of interest methyl acetate 2MeOH + CO → MeOAc + H_2O (ΔH^{o}_{298K} = -138.2 kJ/mol). Despite the high yields of acetyls, obvious are such shortcomings of the homogeneous systems as the complexity of separation of the catalyst and the reaction products, the high cost of catalysts based on the platinum group metals (PGM), and highly corrosivity of carcinogenic halogen-containing reaction medium. As an alternative, the halide-free MC process in the vapor phase on solid catalytic compositions has several advantages including easy separation and reusability of catalysts.

Methanol decomposition (MD) MeOH → CO + $2H_2$, which is applied in the producing hydrogen for solid oxide fuel cells [2], can also be considered as a source of carbonylation agent (CO) of MeOH itself – so-called "self-carbonylation". This approach makes possible the elimination of carbon monoxide from the starting reaction mixture thereby producing HOAc/MeOAc by combining the reactions of MD and MC over appropriate catalysts placed sequentially in one or two reactors.

In [3], a purely methanolic tandem process (TP) of combining MD and MC reactions in the vapor phase using a Pd/CeO_2 catalyst (to generate CO in situ) placed upstream of the Cu-Mordenite in a flow-through reactor was used for acetic acid synthesis.

In our work, a similar approach is employed to produce methyl acetate. For generating CO, a PGM-free catalyst $CuO\text{-}ZnO\text{-}NiO/Al_2O_3$ supported on a honeycomb structure cordierite monolith was used [4], whereas the MeOH carbonylation was performed over $NiCl_2\text{-}CuCl_2$ compositions deposited on activated carbon (AC) and cordierite. It should be mentioned that the activity of carbon-supported nickel and copper chlorides toward MC was shown in [5].

As the result of the preliminary studying the effect of carbon supports (BAU-A, SKT, SUGS grades) of nickel-copper chloride compositions on the halide-free vapor-phase MC, it was shown that the 18% yield of methyl acetate, Y_{MeOAc}, over a $NiCl_2\text{-}CuCl_2$/BAU-A catalyst (S_{BET}= 690 m^2/g) is facilitated by the optimal combination of its porous structure (mesopores with an average diameter of ~7 nm) and the acidity of the surface, which are favorable for the activation of reagents' molecules [6]. At the same time, in the presence of $NiCl_2\text{-}CuCl_2$ compositions on cordierite monoliths of honeycomb structure with a specific surface area of ~0.5 m^2/g, the Y_{MeOAc} value reaches 15%. Achieving Y_{MeOAc} indices, commensurate at temperature ~633 K with those for $NiCl_2\text{-}CuCl_2$/AC, can be caused by advantages of structured systems, compared to granular ones, including more efficient mass transfer and heat removal as well as an increased degree of using the supported active components in the target process.

The combination of the MD and MC reactions was performed by passing a gas stream of MeOH–Ar through catalysts placed sequentially in two flow-type reactors or in a single reactor with two temperature zones. Such an approach, in contrast to the layered arrangement [3], makes it possible to use the catalysts of MD and MC steps of tandem "self-carbonylation" process, differing in their activity.

The obtained results are presented in the Table.

Table. Methyl acetate production indices in tandem process of decomposition and carbonylation of methanol

No.	C°_{MeOH}*, vol%	Catalyst, wt%	T, K	MeOH conversion, %	MeOAc			
					Selectivity, %	Yield in MC step, %	Output, $g_{MeOAc}\cdot kg^{-1}_{NiCl2-CuCl2}\cdot h^{-1}$	Yield in tandem process, %
1	2.1	11%$NiCl_2$-32%$CuCl_2$/AC	623	35	59	21	11.5	16.5
2	2.05	3% $NiCl_2$-9% $CuCl_2$/cordierite	618	43	40	17	4.2	13.2

P = 0.1 MPa, RM: 4 vol% MeOH – Ar, GHSV = 600 h^{-1};

*MeOH residual concentration after decomposition on 10%CuO-7%NiO-9%ZnO/Al_2O_3/cordierite catalyst at 433 K (No. 1) and 438 K (No. 2)

The methyl acetate yields in the tandem process (17% and 21% – at the MC step of TP, 13.2% and 16.5% – Y^{TP}_{MeOAc}, 618–623 K), achieved under conditions close to the equimolar MeOH/CO ratio, commensurate with those (18% and 15%) in the production of MeOAc on $NiCl_2$–$CuCl_2$/AC(cordierite) samples in the methanol carbonylation using the starting reaction mixture of 4 vol% MeOH–50 vol% CO–Ar [6]. The Table includes the outputs of the MC step catalysts of the tandem process per active components loadings within the initial samples. These values indicate a higher degree of efficiency of nickel-copper chlorides, deposited on cordierite monoliths, towards the formation of methyl acetate, as compared with those supported on activated carbon, which is due to the aforementioned advantages of structured systems compared to granular ones.

It should be noted that by our results [6], as well as the literature data including [3], an important condition for the formation of acetyl compounds in the vapor phase methanol carbonylation is a multifold excess of CO. We believe that the achievement of comparable yields of methyl acetate under the tandem process (MeOH/CO~1) and, in fact, vapor-phase MC when using the reaction mixture with the reagents ratio of MeOH/CO =4/50, can be attributed to hydrogen promoting effect (at a ratio of CO/H_2=2/1 corresponding to the stoichiometry of the MD reaction), which is leveled under conditions of multiple carbon monoxide excess.

References:

1. 1. A. Haynes, Advances in Catalysis. **53** (2010) 1.
2. N. Laosiripojana, S. Assabumrungrat, Chemical Engineering Science. **61** (2006) 2540.
3. G. Ormsby, J. Hargreaves, E.J. Ditzel, Catalysis Communications. **10** (2009) 1292.
4. A.Yu. Kapran, S.N. Orlyk, S.O. Soloviev, Reaction Kinetics, Mechanisms and Catalysis. **114** (2015) 135.
5. F.Peng, F. Xiao-Bao, Catalysis Today. **93–95** (2004) 451.
6. A.Yu. Kapran, V.I. Chedryk, L.M. Alekseenko, S.M. Orlyk, Catalysis Letters. **151 (**2021) 993.

O-24

EFFECT OF TEMPERATURE CYCLING ON Ni-M (La-, Mg-) CATALYSTS IN CO_2 CONVERSION OF METHANE

A.M. Manabayeva[1,2]*, S.A. Tungatarova[2,3], D.Yu. Murzin[4]

[1]*Kazakh-British Technical University, Tole bi str., 59, 050000 Almaty, Kazakhstan*
[2]*D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Kunayev st., 142, 050010 Almaty, Kazakhstan, manabaeva_2018@mail.ru*
[3]*al-Farabi Kazakh National University, Almaty, al-Farabi ave., 17, 050038 Kazakhstan*
[4]*Abo Akademi University, Process Chemistry Centre, Tuomiokirkontori st., 3, 20500 Turku, Finland*

The increasing global concerns over climate change and the need for sustainable energy sources have stimulated research into the utilization of greenhouse gases for the production of valuable chemicals and fuels [1]. The dry reforming of methane represents a promising avenue to address these challenges, as it enables the conversion of two major greenhouse gases, methane and carbon dioxide, into syngas, a mixture of hydrogen (H_2) and carbon monoxide (CO) [2]. Syngas serves as a versatile platform for the synthesis of various value-added products, such as liquid hydrocarbons generated during Fischer–Tropsch method [3].

Nickel has been widely studied as a catalyst for DRM due to its excellent activity in methane reforming reactions. The high catalytic activity of Ni is attributed to its ability to dissociate both CH_4 and CO_2, facilitating the formation of H_2 and CO. However, Ni catalysts suffer from carbon deposition and sintering, leading to catalyst deactivation. Therefore, the addition of promoters is crucial to enhance the catalytic performance and stability of Ni-based catalysts. Lanthanum (La) and magnesium (Mg) have been recognized as effective promoters for Ni-based DRM catalysts. La-containing promoters can enhance the dispersion and reducibility of Ni species, improve the resistance to coke formation, and increase the catalytic activity. Mg-containing promoters, on the other hand, facilitate the formation of a stable Ni-MgO solid solution, leading to enhanced resistance to sintering and coking [4].

The Ni-based catalysts with La- and Mg-containing promoters were prepared using the solution combustion synthesis (SCS) method.

The prepared catalysts were characterized using various techniques, including X-ray diffraction (XRD), CHNS analysis, temperature-programmed reduction (TPR) and thermogravimetric analysis (TGA). These techniques were employed to analyze the catalyst structure, composition, particle size, reducibility and type of carbon.

XRD analysis revealed the presence of cubic Ni^o in both 15Ni15Mg20Al and 15Ni15La20Al catalysts. The 15Ni15Mg20Al catalyst showed the presence of crystalline MgO phase and small peaks of $MgAl_2O_4$ spinel. The amount of $MgAl_2O_4$ and Ni^o increased during DRM. In the fresh 15Ni15La20Al catalyst, no significant crystalline phases were observed, except for a few possible perovskite structures of $LaAlO_3$. The XRD data indicated that the $LaAlO_3$ phase remained stable during DRM at 600 – 900°C, while the relative amounts of crystalline phases significantly increased compared to the amorphous content.

The TPR peak in the temperature range of 400–500°C can be explained by the reduction of NiO species strongly interaction with the support occurred, although NiO phase was not identified in XRD pattern due to its high dispersion. For 15Ni15Mg20Al much lower hydrogen consumption was obtained in the temperature range of 280 – 600°C most probably due to the presence of aluminum species, which strengthens the interaction between Ni and support, thus, improves the catalytic activity. However, due to the presence of La the reduction of 15Ni15La20Al was more difficult because more hydrogen was consumed at 384ºC and 542°C.

The carbon amount of 15Ni15Mg20Al and 15Ni15La20Al are 1 wt%/g_{Ni} and 0.19 wt%/g_{Ni}. It means that the carbon formation rate of the 15Ni15Mg20Al catalyst is lower than that of latter. Coke was deposited more on surface of catalyst with lower weight, as in the case of 15Ni15La20Al. According to TGA, the type of carbon is filamentous (medium active) for 15Ni15Mg20Al and 15Ni15La20Al.

At 600°C, 15Ni15Mg20Al exhibits higher conversions of CH_4 and lower conversion of CO_2 compared to 15Ni15La20Al. The H_2 yield for 15Ni15Mg20Al is 8% higher than for 15Ni15La20Al due to possible CH_4 decomposition, while the CO yield is higher in latter. In this regard filamentous carbon formed during CH_4 decomposition can be oxidized further, being active. Thus, the H_2/CO ratio is lower in 15Ni15Mg20Al being 0.6, whereas H_2/CO in 15Ni15La20Al was 0.9. At 850°C, both materials show significant improvements in conversions. 15Ni15Mg20Al achieves higher conversions of CH_4 and CO_2 compared to 15Ni15La20Al. The conversion of CO_2 was higher than CH_4 conversion for both catalysts due to reverse water-gas shift reaction. Therefore, for H_2 yield is higher than CO yield. At 900°C, 15Ni15Mg20Al achieves slightly higher conversions of CH_4 and CO_2 compared to those results obtained at 850°C. The H_2 yield of 15Ni15Mg20Al was increased slightly, while the rise of H_2 and CO yields for 15Ni15La20Al was more obvious from 54% to 61% and from 52% to 66%, respectively. The H_2/CO ratio was close to 1 for both catalysts. During the second cycle at 600°C, 15Ni15Mg20Al exhibits higher conversions of CH_4 and CO_2 compared to 15Ni15La20Al. Thus, 15Ni15La20Al underwent slight deactivation. Based on the literature, it can be assumed that $MgAl_2O_4$ is very active phase, and it mainly enhances the catalytic activity of Ni-Mg-Al, whereas $LaAlO_3$ is not completed spinel type, being unstable during DRM, thus conversion of initial gases was lower than that for former catalyst.

In conclusion, both catalysts displayed different behaviors in temperature cycling experiment. The 15Ni15Mg20Al exhibited higher catalytic activity than 15Ni15La20Al due to highly active $MgAl_2O_4$ phase and strong metal-support interaction. The low amount of filamentous coke with medium strength could be oxidized and form CO, therefore being active during DRM, while coke in 15Ni15La20Al was not so active, because of its high amount and blockage of pores and active centers.

References:

1. R.-Y. Chein, Y.-C. Chen, W.-H. Chen. Catalysts, 2021, 11, 777.
2. E. Akiki, D. Akiki, C. Italiano, A. Vita, R. Abbas-Ghaleb, D. Chlala, G. Drago Ferrante, M. Laganá, L. Pino, S. Specchia. International Journal of Hydrogen Energy, 2020, 45, 41, 21392
3. M.S. Lanre, A.E. Abasaeed, A.H. Fakeeha, A.A. Ibrahim, A.S. Al-Awadi, A.b. Jumah, F.S. Al-Mubaddel, A.S. Al-Fatesh. Catalysts, 2022, 12, 715.
4. Z. Abdelsadek, H. Köten, S. Gonzalez-Cortes, O. Cherifi, D. Halliche, P.J. Masset. Ournal of the Minerals 2023, 75, 3, 727.

O-25

INFLUENCE OF NICKEL AND COPPER ADDITIVES ON CATALYTIC PROPERTIES OF Mg-Al-Y OXIDE CATALYST IN THE GUERBET CONDENSATION OF ETHANOL AND 1-BUTANOL

K.V. Valihura[1,2]*, O.V. Larina[2], S.O. Soloviev[2], B. Alonso Fariñas[1], A.L. Villanueva Perales[1], J.F. Vidal Barrero[1]

[1]*Departamento de Ingeniería Química y Ambiental, Escuela Técnica Superior de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos s/n, 41092 Sevilla, Spain*
[2]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, karina.valigura@ukr.net*

The development of heterogeneous catalytic process of the production of higher alcohols, in particular 1-butanol (BuOH), from the universal building block molecule of ethanol (EtOH) via Guerbet condensation is becoming more and more relevant. The promising catalysts for this are systems based on MgO-Al_2O_3 mixed oxides obtained by thermal decomposition of hydrotalcites (layered double hydroxides). In the L.V. Pisarzhevskii Institute of Physical Chemistry of the National Academy of Sciences of Ukraine, there was conducted systematic research of vapor phase condensation of EtOH in laboratory flow reactor aimed to crate effective catalysts based on MgO-Al_2O_3 systems for this process. Based on the previous studies, all the selected as best modifying additives and methods of preparation were used to create new Ni(Cu)-Mg-Al-Y oxide catalysts to achieve better performance in EtOH to BuOH conversion. The study of their catalytic behavior in the process of Guerbet condensation of EtOH to BuOH was carried out at the experimental facility at Departamento de Ingeniería Química y Ambiental, Escuela Técnica Superior de Ingeniería, Universidad de Sevilla.

Samples of Ni(Cu)-Mg-Al-Y oxide catalysts were prepared by thermal decomposition of Ni(Cu)-Mg-Al-Y hydrotalcites with the atomic ratio of Ni-Mg-Al-Y (0.02:1.98:0,9:0.1), Cu)-Mg-Al-Y (0.02:1.98:0.9:0.1), Ni(Cu)-Mg-Al-Y (0.01:0.01:1.98:0.9:0.1), as well as Mg-Al-Y (2:0.9:0.1) for comparison. Hydrotalcites were obtained using a rapid method of co-precipitation from nitrates, the sediment was kept in the mother liquor for 1 h.

On the diffractograms of catalyst precursors, there are reflexes of planes, which are characteristic of hydrotalcite crystal structures with brucite-like layers. After calcining the samples at 600 °C, there are weak broad reflexes at 35°, 43°, 63°, which indicate the formation of mixed oxides, which are actually solid solutions based on MgO-periclase. No additional reflexes of individual Ni, Cu, Mg, Al or Y-containing phases were detected.

TEM micrographs of Ni(Cu)-Mg-Al-Y oxide systems indicate a developed layered structure. The samples are formed by aggregates of quite similar size and shape, consisting of thin small lamellar crystals with a size of 15-50 nm. The uniform homogeneous distribution of Ni, Cu, Mg, Al and Y on the surface of the samples was confirmed by elemental mapping (EDX).

Analysis of the results of low-temperature nitrogen ad(-de)sorption measurements shows that the studied Ni(Cu)-Mg-Al-Y-oxide systems are characterized by a relatively close total surface area and are mainly mesoporous materials with an average pore diameter in the range of about 30 nm. Samples modified with Ni and Cu are characterized by a slightly larger external specific surface and higher porosity (121-133 m^2/g and 1.14-1.27 cm^3/g) compared to Mg-Al-Y.

Using the thermoprogrammed CO_2 desorption it was established that with the introduction of modifying additives Ni and Cu in the composition of catalysts, the total concentration of the base surface sites increases: Mg-Al-2 - 271 μmol/g, Mg-Al-Y - 421 μmol/g, Ni-Mg-Al-Y - 428 μmol/g, Cu-Mg-Al-Y - 432 μmol/g, Ni-Cu-Mg-Al-Y- 431 μmol/g.

By means of the method of thermoprogrammed reduction with H_2, it is shown that with the introduction of modifying additives Ni and Cu, hydrogen consumption in the process of reduction of Ni^{2+} and Cu^{1+}/Cu^{2+} cations embedded in the mixed oxide structure is expected to increase. There are low-temperature peaks on the TPR profiles that can be associated with the inclusion of Ni, Cu in the structure of the solid solution, while the high-temperature peaks can be attributed to the recovery of the structural forms of NiO and CuO.

The catalytic properties of Ni,(Cu)-modified Mg-Al-Y oxide catalysts in the process of condensation of ethanol into 1-butanol were studied in a flow reactor at the temperature range of 200-450 °C under atmospheric pressure, as well as under higher pressure of 20 bar, mass flow of ethanol 0.2-1.0 $g/h_{cat} \cdot h$.

For Ni(Cu)-Mg-Al-Y oxide systems at low temperatures of 200-350 °C, the ethanol conversion decreases markedly during the first 4-6 h on the stream, and then remains fairly stable during the next 18 h, which is typical for catalysts based on Mg-Al-oxides obtained from hydrotalcites. At high temperatures of 375-450 °C, the ethanol conversion is stable over time and has high values of 60-80%, however, as the temperature increases, the selectivity for 1-butanol significantly decreases due to the active formation of by-products of ethanol dehydration, esterification and condensation of intermediate aldehydes and ketones.

Increasing the pressure at low process temperatures has little effect on the catalytic performance, while at high temperatures mainly higher alcohols/ketones/esters and possibly aromatic compounds are formed, which are difficult to separate and identify.

The introduction of Cu additive at the stage of hydrotalcite synthesis contributes to a significant increase in ethanol conversion (from 31 to 65%, T = 250 °C, P = 1 bar) and selectivity to the formation of aldehydes, mainly acetaldehyde (48%).

In turn, the addition of Ni and Cu together provides a similar increase in conversion and intensifies the formation of acetaldehyde, hydrocarbons, ethers and esters. Therefore, the selectivity for 1-butanol does not exceed 30% (T = 250 °C, P = 1 bar), however, taking into account the high conversion of 65%, a relatively high yield of 20% of 1-butanol is achieved.

The use of Ni as a modifying additive for the Mg-Al-Y oxide system helps to increase the catalytic performance of the process. It was found that the highest 1-butanol selectivity of 54% and yield of 17% is achieved for the Ni-Mg-Al-Y sample at 250 °C (P = 1 bar). In addition, Ni-Mg-Al-Y shows the most stable selectivity for 1-butanol during 18 h TOS.

All the obtained catalysts are suitable for reuse by regeneration in an air stream at 500 °C after ten catalytic cycles. Thus, Ni-modified Mg-Al-Y oxide systems obtained by rapid synthesis are a promising catalyst for the production of 1-butanol. Possible ways of improvement: changing the amount of additive, adding hydrogen during the process to prevent the formation of unwanted by-products, using catalyst circulation (in "boiling" layer) to implement rapid regeneration.

O-26

EFFICIENT SUGAR HYDROGENATION OVER Ru NANOPARTICLES DEPOSITED ONTO MESOPOROUS MOLECULAR SIEVES

N. Shcherban[1]*, G. Araujo-Barahona[2], I. Kopa[1], T. Salmi[2], D. Murzin[2]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, nataliyalisenko@ukr.net
[2]Åbo Akademi University, Henriksgatan 2, 20500, Turku/Åbo, Finland

Biomass valorization seems to be the most attractive and promising option for the production of value-added chemical compounds in an environmentally friendly way [1]. In particular, catalytic hydrogenation of hemicellulose-derived sugars allows to obtain corresponding sugar alcohols finding wide application in the alimentary, pharmaceutical and cosmetics industries [2]. The most common heterogeneous catalysts industrially applied for sugar hydrogenation are Ni based, such as Raney nickel. Poisonous, leaching, and formation of harmful by-products are among the obvious disadvantages of nickel catalysts. Application of supported Ru particles not only allows to overcome these problems, but also provides an opportunity for the operating in fixed bed reactors.

MCF, MCM and SBA type mesoporous molecular sieves (MMS) were applied as supports for Ru deposition. Uniformly distributed Ru nanoparticles with an average size of 3 nm were prepared using wet impregnation followed by reduction with hydrogen. The catalysts exhibited a developed surface area (235 – 665 m^2/g) and the pore volume (up to 1 cm^3/g), being, however, lower compared to the initial supports, which is obviously related to micropore blocking. Adsorption of pyridine monitored by FTIR spectroscopy demonstrated an increase in the acid sites concentration (up to 44 and 76 μmol/g of Brønsted and Lewis acid sites, respectively) of the supported Ru samples compared to the initial aluminosilicates.

Hydrogenation of D-xylose over the prepared Ru catalysts resulted in both high conversion and selectivity (> 99%). As can be seen from the kinetic data (Fig. 1), Ru-Al-MCM-41 followed by Ru-Al-MCF achieved complete substrate conversion during a shorter time compared to other tested materials, as well as a commercial Ru-C catalyst.

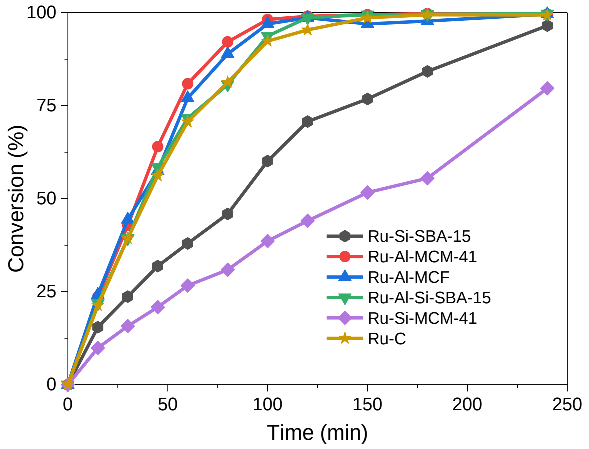


Fig. 1. Dependence of D-xylose conversion (90°C and 40 bar of hydrogen pressure) on the reaction time over the tested supported Ru catalysts.

References:

1. H. Zhang, W. Yang, I.I. Roslan, S. Jaenicke, G.K. Chuah, Journal of Catalysis. **375** (2019) 56.
2. G. Araujo-Barahona, K. Eränen, J.P. Oña, D. Murzin, J. García-Serna, T. Salmi, Industrial & Engineering Chemistry Research. **61** (2022) 2734.

O-27

AIR-STABLE NICKEL CATALYSTS FOR HYDROGENATION OF ORGANIC COMPOUNDS

M.O. Ivanytsya[1,2]*, V.V. Subotin[1,2], A.V. Terebilenko[1,3], P.S. Yaremov[1],
O.O. Pariiska[1], Y.M. Akimov[3], I.E. Kotenko[1], T.M. Sabov[4], M.M. Kurmach[1],
S.V. Ryabukhin[2,5,6], D.M. Volochnyuk[2,5,6], S.V. Kolotilov[1]

[1]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, ivanytsya.mykyta@gmail.com*
[2]*Enamine Ltd., Winston Churchill St.,78, Kyiv, 02094 Ukraine*
[3]*Laboratory of Electron Microscopy, M.G. Kholodny Institute of Botany, National Academy of Sciences of Ukraine, Tereshchenkivska St., 2, Kyiv, 01601 Ukraine*
[4]*V. Lashkaryov Institute of Semiconductors Physics, National Academy of Sciences of Ukraine, Prosp. Nauky, 41, Kyiv, 03028 Ukraine*
[5]*Institute of High Technologies, Taras Shevchenko National University of Kyiv, Volodymyrska St., 60, Kyiv, 01601 Ukraine*
[6]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Acad. Kukharia St., 5, Kyiv, 02660 Ukraine*

Hydrogenation of organic compounds is widely employed in lab-scale organic synthesis and the chemical industry. In most cases, a catalyst is required for such process. Typically, the catalyst is composed of platinum group metals (PGM). PGM catalysts offer high activity and selectivity, but their high cost hinder their wide-scale application, particularly in large-scale chemical production. Catalysts based on 3d metals, specifically groups 8–10 (Fe, Co, Ni), serve as promising alternatives, with recent reports showcasing efficient systems for hydrogenation and related processes. However, finding a cost-effective and efficient hydrogenation catalyst based on inexpensive 3d metals still remains a challenging task [1-3].

A series of composites containing nanoparticles of NiO (Fig. 1a), deposited on NORIT charcoal, was prepared by the decomposition of the Ni^0 complex $Ni(cod)_2$ (cod = cis,cis-1,5-cyclooctadiene). Ni content varied from 0.9 to 9.1 %. Characterization involved powder XRD, TEM, XPS, and adsorption techniques. Only one wide reflection was found on the powder XRD patterns of the composites; this reflection was centered at $2\theta = 44.1–44.4$ °; this position was between the positions of the most intense reflections for NiO ($2\theta = 43.1°$ for (200) reflection of NiO, Fm3m space group) and Ni ($2\theta = 44.5°$ for (111) reflection of Ni, Fm3m space group), evidencing for possible presence of both Ni and NiO in the samples. At the same time it could be concluded from the analysis of the high-resolution X-ray photoelectron spectra of the O1s and Ni2p peaks that the composites contained only NiO or $Ni(OH)_2$. Thus, the composites exhibited catalytic activity due to the *in situ* generation of active sites through NiO reduction, allowing them to maintain their catalytic performance even when stored in air.

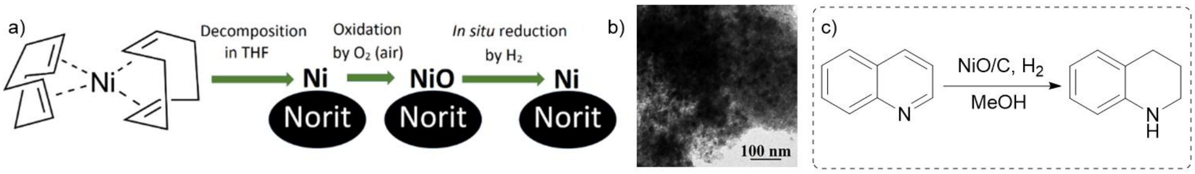


Fig. 1. a) Scheme of the preparation and use of Ni/C-X composites; b) TEM image of the mist efficient composite (3 % Ni loading); c) quinoline hydrogenation reaction scheme

It was found by CO chemisorption experiments, that the increase in the Ni loading in the row of composites from 0.9 to 9.1 % led to the growth in the size of Ni nanoparticles, which formed upon reduction with H_2, and their size changed from 0.7 nm to 7.4 nm, and significant decrease of accessible surface of metallic Ni from 935 to 91 m^2 per 1 gram of Ni, however, due to counter-balance with increased Ni content the composites containing 3 and 5 % of Ni had the highest accessible area of metal per 1 g of the catalyst (11 and 15 m^2 per 1 g of the catalysts, respectively).

The hydrogenation of quinoline served as a reference reaction to investigate the effects of temperature, $p(H_2)$, and catalyst loading on product yield, leading to the identification of the most efficient composite with 3% Ni loading. This composite demonstrated high efficiency in the hydrogenation of compounds containing unsaturated carbon bonds, nitro- and keto-groups, substituted quinolines, and analogs (30 examples). In the case of the aromatic substrates, which contained amino- or hydroxy groups (the amino-group occurred after hydrogenation of the nitro-group) the yield of the products was generally lower compared to similar compounds. Such lower yields can be explained by the passivation of Ni due to the adsorption of amines or phenols. The hydrogenation of bromoquinoline led to complete debromination, even in the case when Br was in the carbocyclic ring, which did not undergo hydrogenation. However, the hydrogenation of nitro-bromobenzene resulted in the formation of the respective aminobromobenzene; preservation of the C–Br bond in this case can be explained by the passivation of Ni by amino-groups. The hydrogenation of 6-chloroquinoline resulted in the formation of 6-chloro-1,2,3,4-tetrahydroquinoline with high yield, along with the dechlorinated product. The hydrogenation of nitro-compounds bearing a nitrile function resulted in the transformation of the NO_2 group to NH_2 and the hydrolysis of nitrile to amide, instead of the expected reduction to benzylamine.

It was found that repeated use of the same catalyst six times resulted in a decrease in the 1,2,3,4-tetrahydroquinoline yield from 100 to 86%, but in all cases, the hydrogenation selectivity was 100%. The studied composites exhibit air-stability and represent effective catalysts for the hydrogenation of a broad range of organic compounds.

V.V.S., M.M.K. and S.V.K. thank to the National Academy of sciences (the project “The development of heterogeneous catalytic processes for the production of liquid synthetic motor fuels from domestic raw for the energy independence of the state”).

References:

1 M.O. Ivanytsya, S.V. Ryabukhin, D.M. Volochnyuk; S.V. Kolotilov, Theoretical and Experimental Chemistry, **56** (2020) 283–308.

2. V.M. Asaula, A.S. Lytvynenko, A.M. Mishura, K.S. Gavrilenko, S.V. Ryabukhin, D.M. Volochnyuk, S.V. Kolotilov, Inorg. Chem. Comm. **121** (2020) 108203.

3. V.V. Subotin, M.O. Ivanytsya, A.V. Terebilenko, P.S. Yaremov, O.O. Pariiska, Y.M. Akimov, I.E. Kotenko, T.M. Sabov, M.M. Kurmach, S.V. Ryabukhin, D.M. Volochnyuk, S.V. Kolotilov, Air-Stable Efficient Nickel Catalyst for Hydrogenation of Organic Compounds, Catalysts **13** (2023) 706.

O-28

CATALYTIC CYCLE AND DEACTIVATION: KINETICO – THERMODYNAMIC INTERPLAY

G.S. Yablonsky[1]*, Z.J.G. Gromotka[2], N.M. Ostrovskii[3], D. Constales[2]

[1]Department of Energy, Environmental & Chemical Engineering, McKelvey School of Engineering, Washington University, St. Louis, MO 63130, USA, gy@wustl.edu
[2]Department of Electronics and Information Systems, Ghent University, 9000 Ghent, Belgium
[3]Euro Gas, 24000 Subotica, Serbia

The dynamic behaviour of the complex catalytic gas-solid reaction accompanied by catalyst deactivation, both reversible and irreversible, was studied. In this case, two "small parameters" determine the temporal properties of the system:

- the small parameter which is caused by the difference between the number of catalyst active sites and number of gaseous molecules.
- the small parameter caused by the difference between the deactivation parameters and parameters of the main catalytic cycle.

Different scenarios of the interplay, both transient kinetic and thermodynamic, between the main cycle and deactivation processes are presented. Using the semi-phenomenological three-factor kinetic equation of catalyst deactivation [1], different domains of the quasi-steady-state behaviour have been distinguished for the single-route reversible catalytic reaction accompanied by the deactivation reaction.

The developed approach is applied to the classical two-step mechanism by Temkin-Boudart accompanied by irreversible deactivation for typical kinetic devices (batch reactor, CSTR, and PFR reactors). Also, it was illustrated by industrial examples of catalytic dehydration of acetaldehyde and crotonaldehyde dehydrogenation. In the typical situation, there was found the relationship for the total reactant consumption during the complex catalytic reaction over the deactivated catalyst:

$$A_{\mathrm{lim}} = \lim_{t\to\infty} A(t) = N_S\left(1-\frac{1}{K}\right)\frac{k_{app}}{k_{irr}} \qquad (1)$$

where $A(t)$ is the integral reactant consumption per catalyst unit (mol cm^{-2} or mol g_{cat}^{-1}) at time t; A_{lim} is the total reactant consumption per catalyst unit (mol cm^{-2}, or mol g_{cat}^{-1}); N_S is the total number of active sites (mol cm^{-2}, or mol g_{cat}^{-1}) of the fresh catalyst; K is the apparent equilibrium constant of the main catalytic reaction; k_{app} is an apparent kinetic parameter (s^{-1}) of the main catalytic cycle; k_{irr} is an apparent kinetic parameter (s^{-1}) of the irreversible deactivation. Therefore, the total consumption of the reactant is proportional to the number of active sites of the fresh catalyst multiplied by the ratio of the apparent kinetic parameters of the main cycle and the deactivation process. This ratio $\frac{k_{app}}{k_{irr}}$ illustrates the competition between the main catalyst cycle and deactivation process for some active intermediate. The reversible deactivation case was analysed as well and illustrated by literature data [2].

The main conclusion is formulated as follows: the catalyst lifetime can be enhanced by decreasing the steady-state (quasi-steady-state) concentration of free active sites. In some domains of parameters, it can also be achieved by increasing the steady-state (quasi-steady-state) reaction rate of the fresh catalyst. This conclusion can be presented conceptually: under some conditions, an elevated fresh catalyst activity protects the catalyst from deactivation. These theoretical results are illustrated with the use of computer simulations. Previously, this was indicated experimentally by Kagan et al. [3].

References:

1. Z.J.G. Gromotka, G.S. Yablonsky, N.M. Ostrovskii, and D. Constales, Three-factor kinetic equation of catalyst deactivation. Entropy, 23(7):818, 2021.
2. N. Essayem, Y. Ben Taârit, C. Feche, P.Y. Gayraud, G. Sapaly, and C. Naccache, Comparative study of n-pentane isomerization over solid acid catalysts, heteropolyacid, sulfated zirconia, and mordenite: dependence on hydrogen and platinum addition. Journal of Catalysis, 219(1), 97-106, 2003.
3. Y. Kagan, A. Rozovskij, E. Slivinskij, and G. Korneeva, Autoregulatory effect in the hydroformylation reaction of olefins. *Kinetika I Kataliz* 1987, *28*, 1508–1511.

O-29

NOVEL MATERIALS - EFFICIENT CATALYSTS FOR METHANE DECOMPOSITION AND ITS OXIDATIVE CONVERSION TO HYDROGEN AND/OR SYNTHESIS GAS

K. Dossumov[1,2]*, M. Mambetova[1,2], G. Yergaziyeva[2], M. Anissova[2],
N. Makayeva[2], N. Khudaibergenov[2]

[1]The Center of Physico-Chemical Methods of Research and Analysis, Almaty, Kazakhstan
[2]Institute of Combustion Problems, Almaty, Kazakhstan, dossumov50@mail.ru

The efficiency of catalysts in the oxidative conversion and decomposition of methane is influenced by a number of factors, including the nature of the active phase, carrier, catalyst preparation method and the pretreatment conditions of the catalyst and reaction. This work is aimed at developing a new generation of polyoxide catalytic systems prepared by special methods that regulate the process of methane decomposition or oxidation in the desired direction for the production of hydrogen and/or synthesis gas and contributes to the creation of one-stage "green" technology. The influence of preparation methods of polyoxide modified catalysts on their activity has been investigated. The catalysts were characterized by XRD, TPR-H_2, TEM, Raman spectroscopy and SAXS-small angle X-ray scattering and other.

The properties and catalytic activity of polyoxide NiO, CoO, MoO_3, Fe_2O_3 and other containing catalysts were found to vary depending on the synthesis method used and the presence of promoters such as La_2O_3, ZrO_2, CeO_2. For the process of partial oxidation of methane it was determined that among the investigated oxide catalysts the most active one was 5% Ni-La/Al_2O_3 [1]. 5%Ni-La/Al_2O_3 was prepared by capillary impregnation method according to the moisture capacity of the carrier. At optimum technological parameters of the process ($CH_4 : O_2 = 2 : 1$, T = 750 °C, W = 1000 h^{-1}) methane conversion in the presence of 5%Ni-La/Al_2O_3 was 95%, and carbon monoxide and hydrogen selectivity was 44 and 52%, respectively. The method of capillary impregnation on the carrier moisture capacity by metal salts of variable valence allows to increase the efficiency of the catalyst due to the distribution of nanostructured impregnated active components on the outer surface of the carrier granule in the form of a "crust". The main reason for the improvement of the properties of the modified nickel catalyst according to TPR, SEM and XRD data is the decrease of its reduction temperature due to the increase in the dispersity of nickel particles. This process, although yielding a good H_2/CO ratio, requires special precautions due to its explosive behavior and is still under laboratory testing.

Monometallic and bimetallic nickel-containing catalysts have been developed for the dry reforming of methane (DRM). DRM is of particular interest because it allows utilization of two greenhouse gases - methane and carbon dioxide - simultaneously. For monometallic catalysts, the oxide content on the carrier varied from 1 to 20 wt.%[2]. The optimum composition of effective monometallic catalysts with the content of nickel oxide - 3 wt.%, cobalt oxide - 15 wt.% and molybdenum oxide - 10 wt.% on the carrier was determined. For the most active 3 wt.%NiO/γ-Al_2O_3, prepared by capillary impregnation method, under the reaction conditions CH_4:CO_2 = 1:1, T- 800°C,W=1500 h^{-1} the values of conversion, products yield and selectivity are: X_{CH4}- 89 %, X_{CO2} - 93 %, Y_{H2}- 45.4 %, Y_{CO} – 42.4 %, S_{H2}-50 % и S_{CO} – 47.5 %. According to the results of electron microscopy (SEM, TEM) it was determined that nickel nanoparticles (6.4-10 and 50-150 nm) are formed on the catalyst 3 wt.%NiO/γ-Al_2O_3, which are uniformly distributed on the carrier surface, which positively affects the activity of the catalyst in the process of carbon dioxide conversion of methane into synthesis gas. Bimetallic 5%Ni-Co/γ-Al_2O_3 and 4 %Ni-Mo/Al_2O_3 catalysts were synthesized by capillary impregnation of the carrier and solution combustion methods with the addition of a dispersing agent [2]. It is shown that the method of preparation plays an important role in regulating the textural and morphological properties of the catalysts and provides a difference in the indices of their catalytic activity in the DRM process. According to the results of SEM, TPR-H_2, XRD, SAXS synthesis of Ni-Co/γ-Al_2O_3 catalyst by the solution combustion (SC) method, in comparison with the capillary impregnation, leads to the formation of $NiCo_2O_4$ solid solution with the size of 21 nm, increase in the proportion of metal ions (Ni, Co) recovered in the region of 400-700°C. In the SC method, a dispersing agent is used to produce an active nanophase of applied metal salts, which is uniformly distributed on the carrier surface. These changes affect favorably the activity of Ni-Co/γ-Al_2O_3 catalyst in the studied process. At relatively low reaction temperature (600°C) on the sample synthesized by the solution combustion method the methane conversion is higher (X_{CH_4}-69 %) in comparison with the method of capillary impregnation of the carrier (X_{CH_4}- 65 %). Ni-Mo/Al_2O_3 catalyst was also prepared by SC. It is shown that the introduction of 1 wt.%MoO_3 into the composition of 3%NiO/Al_2O_3 leads to an increase in the efficiency of the catalyst in the DRM reaction, due to an increase in the dispersity, specific surface area of the catalyst and due to a decrease in the active phase-carrier interaction, which leads to an increase in the mobility of oxygen on the catalyst surface. These changes favorably affect the activity of Ni-Mo containing catalyst in DRM to synthesis gas. It is determined that MoO_3 modification leads to increase of stability of 3 wt.% NiO/γ-Al_2O_3 to carburization, under condition: CH_4:CO_2=1:1, W=1500 h^{-1}, Tp=700°C on 4%Ni-Mo/Al_2O_3 the conversion of X_{CH4} = 86,5 %, X_{CO2} = 79%, H_2/CO = 1.1. SC provides an efficient way to develop an active catalyst for DRM at low temperatures (600-750°C).

For the thermocatalytic decomposition of methane (TDM), Ni-Foam and Ni-xFe composites obtained electrochemically by potential cycling on the surface of Ni-Foam have been investigated [3]. Thermocatalytic decomposition of methane is characterized by the lowest carbon monoxide emissions among all investigated alternatives. The synthesized catalysts were tested in the TDM in temperature range of 650-850°C, in the flow regime. The effect of cycles (75, 150 and 250) of iron deposition on Ni-foam on its activity for methane decomposition was investigated. The catalysts were investigated at a reaction temperature of 850°C in TDM for 540 minutes. It was determined that the highest catalytic activity is observed for the catalyst where the cycle of iron deposition on nickel foam is 150.The Ni-Fe150 catalyst showed an initial methane conversion of 91 %, which increased from 60 minutes to 96.7 % and from 180 minutes to 98.6 %, and was stable during the tested 540 minutes. As the methane conversion increased, the hydrogen yield of the reaction products increased, with an initial hydrogen yield of 71 %, which increased from 60 minutes to 74 % and from 180 minutes to 76 %. According of BET, TPR-H_2 and XRD results, the increase in TDM activity of Ni-Fe composites compared to Ni-foam is due to the increase in the textural characteristics of the composite as well as the formation of Ni-Fe alloy. Increase of activity of Ni-Fe150 in comparison with Ni-Fe75 and Ni-Fe250 - with the increase in the recoverability of iron cations in the composition of nickel-iron alloy. Raman studies of spent composites showed that on the composite that showed the most increased activity and stability in TDM formed graphite with higher defectivity, which favours the passage of methane decomposition on the uncovered carbon areas of Ni-Fe150.

Thus, the influence of the method of catalyst preparation on their activity and selectivity in the reactions of methane decomposition and its oxidative conversion to hydrogen and/or synthesis gas is an important direction in catalysis. The preparation of catalytic systems of highly dispersed nanostructured, carrier-applied catalysts on the basis of new methods should allow for a more in-depth evaluation of the effects of deposition and promotion.

Acknowledgements. The work was carried out with the financial support of the Ministry of Science and Higher Education of the Republic of Kazakhstan № AP15473268.

References:

1. K. Dossumov, G.Ye. Yergaziyeva, L.K. Myltykbayeva, N.A. Asanov. Theoret. Experim. Chemistry, 2016, vol. 52, p. 119-122.
2. G. E. Ergazieva, M. M. Telbayeva, A. N. Popova, et al., Chem. Pap., 2021, v. 75, p. 2765–2774.
3. G. Yergaziyeva, N. Makayeva, A. Abdisattar, et al., Chem. Pap. 2022, 76, v. 12, p. 7405–7417.

O-30

INFLUENCE OF OXYGEN EVOLUTION OVERVOLTAGE ON SELECTIVITY OF OXYGEN TRANSFER REACTIONS

O. Shmychkova*, T. Luk’yanenko, A. Velichenko

Physical Chemistry Department, Ukrainian State University of Chemical Technology, Gagarina Ave., 8, Dnipro, 49005 Ukraine, o_shmychkova@ukr.net

The high background current of the oxygen evolution reaction is recognized as one of the main challenges in managing electrocatalytic reactions in aqueous solutions at high anodic potentials. In most cases, the presence of a large amount of water prevents the realization of processes that would proceed with 100% efficiency. Despite the fact that their implementation is only possible with the participation of oxygen-containing species and all of them are related to oxygen transfer reactions. One of the traditional assumptions states that the necessary increase in the current efficiency of the target product is possible only by increasing the overpotential of oxygen evolution. As a result, electrode materials with high oxygen evolution overpotential, such as lead dioxide, have become widely used.

However, the validity of the aforementioned assumption is seriously questioned because depending on the nature of the process, oxygen-containing species with varying degrees of binding strength to the electrode surface are consumed. It should be noted that the surface of any polycrystalline material cannot provide the same binding strength for oxygen-containing species. For platinum, five different forms of oxygen-containing species have been identified, all simultaneously existing on the electrode surface [1].

To test the existing hypothesis, we used lead dioxide as a base material, which was modified with small amounts of ion additives that have a significant impact on the oxygen evolution overpotential [2].

For the O1s spectrum of lead dioxide, a well-defined peak is observed in the binding energy range of 527.0 – 529.5 eV, and a broad, blurred peak is observed in the range of 530.0 – 534.0 eV. The first peak characterizes the amount of inert (strongly bounded to the surface) oxygen-containing species, while the second peak represents labile species. Upon modification of PbO_2 with fluorine, a significant decrease in the quantity of labile oxygen-containing species on its surface is observed, whereas the influence of iron-group metal ions heavily depends on the nature of the ion.

At low polarizations, the Tafel slopes are within the range of 130-140 mV in $HClO_4$ and 160-170 mV in H_2SO_4, with intermediate values in CF_3SO_3H. The second linear region of polarization curves occurs at high anodic polarization and is characterized by Tafel slopes of 70 mV in $HClO_4$ and 75 mV in H_2SO_4 [3]. Observed effect is due to the concurrent occurrence of two parallel reactions. Transitioning to the high anodic polarization region leads to the overall process behavior being determined by one of the stages of ozone evolution reaction. Maximum ozone current efficiencies were observed in the case of Fe-PbO_2 and F-PbO_2 systems, while the minimum was for Ni-PbO_2. It should be noted that the sequence in which the electrocatalytic activity of materials with respect to the ozone evolution process increases (Ni-PbO_2 < PbO_2 < Co-PbO_2 < F-PbO_2 < Fe-PbO_2) coincides with the sequence in which, according to XPS (O1s spectrum) data, the binding strength of adsorbed oxygen-containing species to the electrode surface increases. This serves as additional confirmation of the involvement of strongly bound oxygen-containing species in the O_3 evolution reaction.

References:

1. A. Gomez-Marin, J. Feliu, T. Edson, ACS Catalysis **8** (2018) 7931.
2. A.B. Velichenko, T.V. Luk’yanenko, O.B. Shmychkova et al., Theor Exp Chem **57** (2021) 331.
3. R. Amadelli, L. Armelao, A.B. Velichenko et al., Electrochimica Acta **45**(1999) 713.

O-31

INFLUENCE OF THE PLATINUM SURFACE STATE ON THE ELECTROCATALYTIC SELECTIVITY OF THE ELECTROCHEMICAL SYNTHESIS OF SODIUM HYPOCHLORITE

D.V. Girenko*, A.B. Velichenko

Ukrainian State University of Chemical Technology, Department of Physical Chemistry, Dnipro, 49005 Ukraine, dvgir1970@gmail.com

The synthesis of sodium hypochlorite solutions by electrolysis of low-concentration and isotonic NaCl solutions using the most available Dimensionally Stable Anodes from platinized titanium is promising from the point of view of the economics of the process. However, during the electrolysis of low-concentrated (< 0.3 M) NaCl solutions on platinized titanium, the current efficiency (CE) of hypochlorite does not exceed 40%. In addition, platinum promotes the oxidation of hypochlorite to chlorite and chlorate. The CE of chlorate on Ti/Pt anodes during the electrolysis of such NaCl solutions is more than 20%.

The current-voltage curves recorded under galvanostatic conditions on Ti/Pt in concentrated 1 M NaCl are shown on Fig. 1. Curve 1 was obtained on a pre-oxidized platinum surface after anodic polarization in 1 M NaCl at a current density of 60 mA/cm^2 for 40 minutes. Curve 2 was obtained after cathodic polarization of electrode with a current density of -20 mA/cm^2 for 1 min. At the same time, the polarization of the electrode decreased by 420 mV, and in the region of small polarizations (at current densities up to 5 mA/cm^2), a linear dependence with a characteristic Tafel slope of 34 mV/dec and an exchange current density of j_o = 1.1 A/m^2 is observed in the Tafel coordinates. The Tafel slope is characteristic for the oxidation of Cl^- on most oxide catalysts, if the chemical stage that follows the transfer of the second electron is slow. This may indicate a slowed down stage of chlorine desorption from the anode surface. A high exchange current indicates a high reversibility of the process. The demonstrated behavior of platinum is a classic example of electrocatalysis. After recording Curve 2, the electrode was polarized with an anodic current of 40 mA/cm^2 for 300 seconds, and following this, Curve 3 was obtained already on a partially oxidized surface. After recording Curve 3, the electrode was further polarized with an anodic current of 40 mA/cm^2 for 300 seconds, and following this, Curve 4 was obtained on an almost completely oxidized surface. It should be noted that the state of the surface of the Ti/Pt electrode after reduction by the cathodic current is completely reproduced, and the current-voltage curve recorded after that coincides with Curve 2.

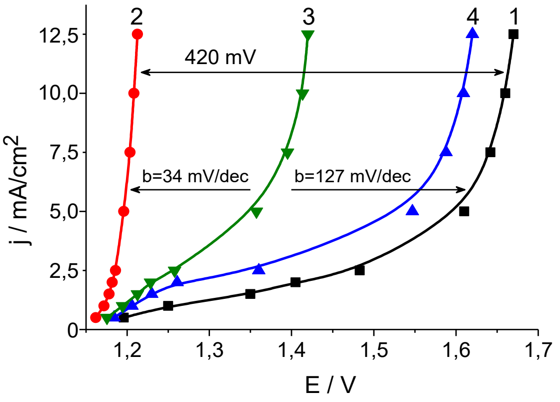


Fig. 1. Galvanostatic current-voltage curves on Ti/Pt in 1 M NaCl.

Thus, three states of the platinum surface can be conditionally distinguished: reduced, oxidized, and intermediate. On the reduced platinum surface, Cl^- oxidation proceeds with minimal polarization (E=1.21 V at 10 мA/cm^2), the Tafel slope of 34 mV/dec, characteristic of the delayed stage of chlorine desorption, and the large exchange current. Under these conditions, potentials are realized at which phase oxides do not form on the surface of metallic platinum or oxides with a low oxygen-metal bond energy are formed [1]. On the oxidized surface with formed phase oxides, which is observed at potentials more positive than +1.55 V, the exponential growth of the current is due to the oxygen evolution reaction (E=1.66 V at 10 mA/cm^2). Here the weak current wave can be observed, which precedes the intensive release of oxygen (Fig. 1, Curves 1, 3, 4). Thus, it can be assumed that the active surface corresponds to platinum free from phase oxides, covered with a layer of adsorbed oxygen-containing particles or phase oxides with a stoichiometry close to PtO, and the passive state corresponds to platinum covered with a layer of PtO_2.

In background solutions free of Cl^-, the formation of phase surface oxides occurs quickly and is accompanied by a potential shift to the anodic region (1.6 V and higher). At the same time, the reaction of oxygen release takes place on the oxidized surface with the formed layer of phase oxide PtO_X. The presence of Cl^- in the solution slows down the process of formation of phase oxides, and the higher the concentration of Cl^-, the longer the surface remains in a reduced or partially reduced state. Chloride ion acts as a depolarizer, discharging on the surface, and interacts with surface oxygen-containing particles, thereby slowing down oxidation of the surface. At the same time, a rather slow parallel process of dissolution of the platinum surface is possible, which occurs in the presence of chloride ions in the solution.

If the pre-reduced surface of the Ti/Pt electrode is polarized with an anodic current, the chronopotentiogram will have an S-shaped character with an induction period during which the potential in 0.1-2.0 M NaCl solutions does not exceed 1.3-1.4 V. After the induction period, during which the surface is in an active state, there is an increase in the potential to values higher than +1.7 V, which corresponds to the transition of the surface to the oxidized passive state. The duration of the reduced surface being in the active state depends on the current density, chloride concentration and hydrodynamic conditions. When polarized by the anodic current of 20 mA/cm^2 in 0.15 M NaCl under conditions of natural convection, the induction period on the pre-reduced electrode is 100 s, and at 40 mA/cm^2 – 15-20 s. In 1.0 M NaCl, the duration of being in the active state increases significantly and is, at these current densities, 3600 and 1500 s, respectively. Thus, with an increase in the concentration of chloride ions, which play the role of a depolarizer, the oxidation rate of the platinum surface in the solution significantly decreases.

The series of short-term accumulative electrolysis was carried out in low-concentrated 0.15 M NaCl on the Ti/Pt anode at a current density of 20 mA/cm^2. The electrolysis duration of 5 minutes does not exceed the time the surface remains in the active state, which for the given conditions of the process is 400-500 seconds. Thus, the entire electrolysis took place on the active surface of the anode. Before the first electrolysis, the electrode was previously reduced with a cathodic current of -20 mA/cm^2 (2 min), before the second - was oxidized at +40 mA/cm^2 (10 min). On the reduced surface, the integral CE of NaClO was 88%, and on the oxidized surface it was 39%. At the same time, CE($NaClO_3$) was 6% on the oxidized surface, and no chlorate was detected on the reduced surface. Thus, during electrolysis of a low-concentrated NaCl solution on a reduced Ti/Pt anode, the observed CE(NaClO) can be compared with electrolysis on the best TiO_2-IrO_2 catalysts. If the duration of electrolysis is increased to 60 min, the difference in current outputs on the reduced and oxidized surface becomes insignificant, and CE(NaClO) does not exceed 31%, and CE($NaClO_3$) is more than 21%. Thus, in these conditions, without prior reduction of the anode, Cl^- oxidation occurs on the fully oxidized (passive) surface of platinum.

References:

1 Cai Y and Anderson AB, Calculating reversible potentials for Pt−H and Pt−OH Bond Formation in basic solutions. *J Phys Chem B* **109**:7557–63 (2005).

O-32

METHANOL PRODUCTION FROM BIOGAS

L. Rodin[1]*, V. Kharitonov[1], A. Jakovičs[2]

[1]*Chemical Technological Company LLC, Shveykiv, Chortkivskyi Dst., Ternopil Rgn., Dobrovodivsky Cheremkhiv Str. 15, 48314 Ukraine, leonid.rodin@chtc.com.ua*
[2]*University of Latvia, Riga, Jelgavas Str. 3, Latvia, LV-1586*

Biogas is a byproduct of agricultural waste processing, primarily composed of methane and carbon dioxide [1]. The rapid development of the biogas industry over the past decades [2] is associated with an increase in the cost of traditional, fossil raw materials and an intensification of the fight against climate change caused by greenhouse gas emissions. Biogas is utilized in electricity and biomethane production, which unfortunately results in the emission of carbon dioxide [3][4]. Roughly 40 million tons of CO_2 are released into the atmosphere as a result of biogas processing in Europe.

We believe that producing methanol (CH_3OH) from biogas is the solution to the problem of CO_2 emissions during biogas combustion. This approach is more effective for two reasons:

- It is environmentally efficient as it reduces CO_2 emissions.
- It is economically efficient as it produces a high-tech product with a higher added value.

Currently, the investigation of methanol production technology from biogas is focused on two issues. The first concern is the presence of up to 50% CO_2 in biogas, which can affect the conversion and synthesis processes. The second challenge is developing innovative solutions to address the block-modular design of the BioMethanol unit.

The results of the mathematical modelling of steam-oxygen conversion of biogas and methanol synthesis processes are presented in this study. Methanol synthesis is considered in circulation and flow cases.

The methanol from biogas production technological schemes, and the main technological equipment characteristics for the stages of reforming, synthesis and rectification are presented. The technology economic aspects, in particular the raw materials and energy resources cost factors are discussed.

The study provides calculated data and technological solutions that can aid scientific research on the process and catalysts of methanol synthesis from biogas. Additionally, the proposed technology for producing methanol from biogas can be useful in engineering applications.

This work was funded by the European Regional Development Fund under the contract "Development of Syngas Production Method for Innovative Methanol Obtainment in Compact Plant Using Mathematical Modelling of Technological Processes" (project number: 1.1.1.1/20/A/110).

References:

1. P. Ghosh, G. Shah, S. Sahota, L. Singh, V. K. Vijay Biogas production from waste: technical overview, progress, and challenges. In: Bioreactors, Sustainable Design and Industrial Applications in Mitigation of GHG Emissions. – Amsterdam : Elsevier, 2020.
2. H. Singh, T. Padhi, A. Kashyap, S. Taneja Recent advances in biogas production using various bio-waste's and its potential application: An overview. Mater. Today: Proc. May 2023. In press. doi: 10.1016/j.matpr.2023.04.484.
3. A. Dahiya Bioenergy: Biomass to Biofuels and Waste to Energy, Edition 2d., Elsevier, 2020.
4. R. Feiz, M. Johansson, E. Lindkvist, J. Moestedt, S.N. Påledal, F. Ometto J. Clean. Prod. 2022. 378: Art. 134536

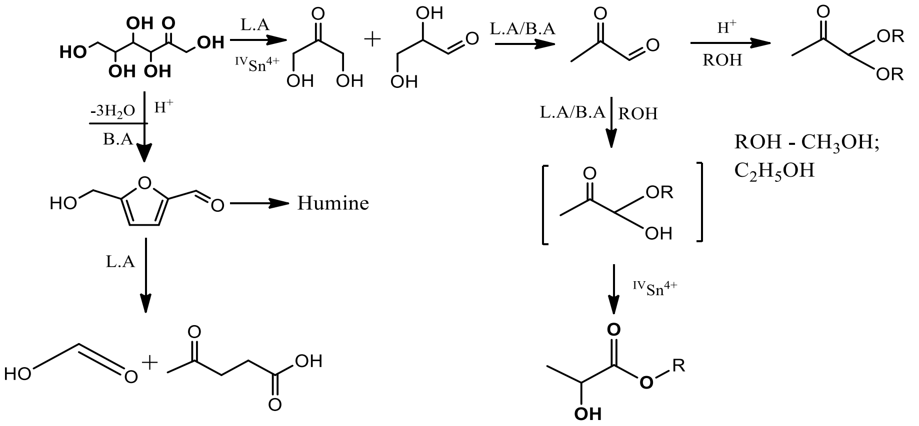
O-33

THE CONVERSION OF FRUCTOSE TO ALKYL LACTATES AND LEVULINIC ACID ON Sn-CONTAINING CATALYSTS

N.L. Hes*, S.V. Prudius, A.M. Mylin, V.V. Brei

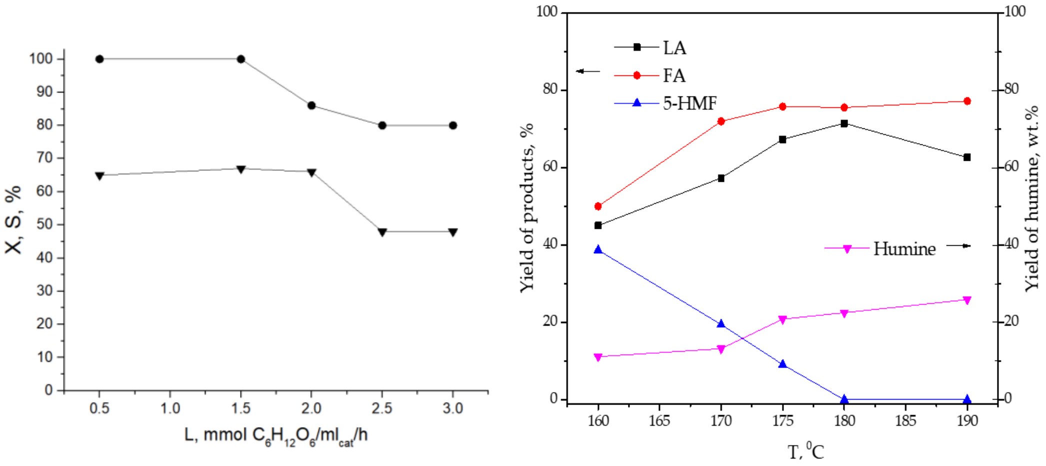
Institute for Sorption and endoecology problems, National Academy of Sciences of Ukraine, General Naumov St., 13, Kyiv, 03164 Ukraine, natalya2938@gmail.com

Fructose is a natural monosaccharide used as a starting material for the production of commodity chemicals such as: lactic acid and its esters, levulinic and formic acids, 5-hydroxymethylfurfural (5-HMF), and others. The direction of the fructose conversion reaction, as well as the generation of the desired reaction products without the formation of by-products, depends on the nature of active sites on the surface of catalyst [1] (Scheme 1). For the conversion of fructose to alkyl lactates a catalyst with moderate Lewis acid sites is required. Strong Brønsted acid sites lead to the dehydration of sugars to 5-HMF [2], which further converts to levulinic acid on strong Lewis sites [3]. Therefore, the combination of Brønsted and Lewis sites is effective for the transformation of carbohydrates to levulinic and formic acids [3].



Scheme 1. Conversion pathways of fructose depending on nature of acid sites of catalyst.

For the conversion of fructose to alkyl lactates (ethyl and methyl lactate), a SnO_2/Al_2O_3 catalyst was used. The $^{IV}Sn^{4+}$ ions act as Lewis acid sites, facilitating the retro-aldol decondensation of fructose and further isomerization of the intermediate methyl ester of glyceraldehyde hemiacetal to methyl lactate. A high selectivity for the desired ethyl lactate (51-56%) is observed on the $20SnO_2/Al_2O_3$ catalyst with > 90% conversion of concentrated 13% fructose solution in 98% ethanol in batch process. However, during this process the Brønsted acid sites on the surface of SnO_2/Al_2O_3 catalyze the dehydration of fructose predominantly to 5-HMF (26%). Two approaches were employed to reduce the number of Brønsted acid sites: the addition of potassium carbonate to the initial solution and the addition of zinc oxide (ZnO) to the SnO_2/Al_2O_3 catalyst. The addition of a small amount (0.03 wt.%) of potassium carbonate to the initial ethanol solution increased the selectivity for ethyl lactate to 61% on the $20SnO_2/Al_2O_3$ catalyst. As a result of fructose conversion on the $10SnO_2$-$5ZnO/Al_2O_3$ catalyst, the yield of ethyl lactate increased to 56%, accompanied by a significant reduction in the amount of by-product 5-HMF (14%) at 160 °C, 3 h. The fig. 1a shows the conversion of a 1.6-9.5% fructose solution in a methanol:water system (80:20) and the selectivity of methyl lactate at different load on the $5ZnO$-$10SnO_2/Al_2O_3$ catalyst in flow reactor. The use of 4.8% solution of fructose in 80% methanol and the reaction in flow mode at 180°C, 3.0 MPa under load on a catalyst of 1.5 mmol $C_6H_{12}O_6/ml_{cat}/h$ (contact time 11 min) allows to obtain methyl lactate with a yield of 65 mol% at 100% conversion of fructose.



a b

Fig. 1. a - Conversion (●) of fructose and selectivity (▼) for methyl lactate at different load on $10SnO_2$-$5ZnO/Al_2O_3$ (180 °C/3.0 MPa, $\tau = 11$ min);
b - yield of reaction products depending on temperature. Reaction conditions: fructose (2 g, 11.1 mmol, 20 wt.%), H_2O (10 mL), (Zr:Si:Sn = 1:2:0.4) catalyst (0.1 g).

For the dehydration reaction of 20 wt.% water solution of fructose into 5-HMF, levulinic and formic acids the superacid ZrO_2-SiO_2-SnO_2 (H_0=-14.52) catalyst was utilized. Fig. 1b presents the results of product yields at different reaction temperatures for the ZrO_2-SiO_2-SnO_2 catalyst. It should be noted that for this catalyst, fructose conversion exceeds 99% across the entire temperature range. The yields of both acids increase with higher reaction temperatures, while 5-HMF is not observed above 180 °C. With longer reaction durations selectivity towards the acids increases, but the yield of 5-HMF decreases, and after 3.5 h it was not detected in the ^{13}C NMR spectra. Under optimal conditions of 180 °C, 3.5 h and fructose to catalyst weight ratio 20:1, levulinic and formic acids yields were 80% and 90%, respectively, at complete fructose conversion.

References:

1. C. Megías-Sayago, S. Navarro-Jaén, R. Castillo, S. Ivanova, Current Opinion in Green and Sustainable Chemistry. **21** (2020) 50.
2. V.V. Ordomsky, J. Schaaf, J.C. Schouten, T.A. Nijhuis, ChemSusChem. **5** (2012) 1.
3. R. Weingarten, W.C. Conner, G.W. Huber, Energy Environmental Science. **5** (2012) 7559.

O-34

CATALYTIC PROPERTIES OF N-DOPED REDUCED GRAPHENE OXIDE IN HYDROGENATION OF ETHYLENE AND ACETYLENE AND DIRECT ETHANE DEHYDROGENATION PROCESSES

A.A. Abakumov*, I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, abakumov0aa@gmail.com

Reduced graphene oxide (RGO) shows catalytic activity in reduction processes in liquid phase using such agents as sodium borohydride, hydrazine or lithium aluminium hydride. Hence, one may hypothesize catalytic activity of RGO in gas-phase reactions of hydrogenation with molecular hydrogen and reverse reaction of dehydrogenation in gas phase. Present report discusses the effects of functional groups and structural parameters on catalytic properties of nitrogen-containing RGO materials in hydrogenation of acetylene and ethylene with molecular hydrogen and dehydrogenation of ethane.

Increase of hydroxylic and etheric groups surface concentration leads to the increase of surface concentration of adsorption sites of hydrogenation reactions. Carbonyls may lower of apparent activation energy (E_a^{app}) of hydrogenation process. Effect of oxygen groups may consist in facilitation of molecular hydrogen adsorption on carbon atoms located nearby oxygen functional groups. Increase of concentration of nitrogen-containing groups such as pyrazoles, pyrroles or graphitic nitrogens causes decrease of E_a^{app}, hence, leading to increase of catalytic activity in hydrogenation. However, presence of pyridinic cycles in RGO eliminates the catalytic activity in ethylene hydrogenation reaction while preserving high activity in acetylene hydrogenation. Collectively, nitrogen groups with electron-donating effect may decrease E_a^{app}, while nitrogen groups with the opposite electronic effect increase E_a^{app}. Doping of RGO with nitrogen groups allows to increase selectivity for ethylene in acetylene hydrogenation.

Increase of lateral sizes of graphene domains may facilitate ethylene adsorption resulting in increase of catalytic activity in ethylene hydrogenation. Such an effect may be caused by π-π interactions between ethylene and graphene domains whose energy increases with the increase of domain size. Defect abundance leads to increase of acetylene adsorption sites in acetylene hydrogenation.

Analysis of obtained data allows to propose structure of adsorption sites in hydrogenation reactions. Ethylene preferably adsorbs on graphene domains. Acetylene and hydrogen may adsorb on both graphene domains and graphene domains.

Catalytic activity of nitrogen doped RGO in dehydrogenation of ethane was demonstrated for the first time. Products of ethane dehydrogenation are presented by hydrogen, ethylene and methane. Increase of oxygen-containing groups concentration results in decrease of E_a^{app} of dehydrogenation and selectivity for ethylene. Doping of RGO with nitrogen atoms increases E_a^{app} and selectivity for ethylene. Such effect of nitrogen atoms may be due to electronic density rearrangement that concentrates electronic density nearby nitrogen dopant atoms. Increase of defect concentration leads to increase of catalytic activity in dehydrogenation. Hence, increase of nitrogen content may also lead to blocking of defect regions due to functionalization with nitrogen-containing groups. Ethane adsorption sites in dehydrogenation over RGO are proposed to be carbonyl groups and defects.

S-1

COMPOSITE COATING WITH PHOTOCATALYTIC PROPERTIES

I.S. Makyeyeva*, N.B. Gruschak, M.I. Gook

Faculty of Chemical and Biopharmaceutical Technologies, Kyiv National University of Technology and Design (KNUTD), Mala Shyianovska (Nemyrovycha-Danchenka) St., 2, Kyiv, 01011 Ukraine, irenmakeeva05@gmail.com

Nanosized TiO_2 is widely used as a photocatalyst for the decomposition of organic pollutants [1]. The widespread use of TiO_2 is based on its efficient photocatalytic activity and high chemical stability. TiO_2 must be synthesized under certain conditions and have a nanoscale structure to impart photocatalytic properties. TiO_2 particles 10 to 50 nm in size have the highest photocatalytic activity.

Nanosized titanium dioxide was synthesized by direct oxidation of powdered metallic titanium according to the procedure [2]. As a result, a mixture of two polymorphic modifications of titanium dioxide, anatase and rutile, was obtained, with a particle size of 30–50 nm. TiO_2 nanoparticles were used as an inert phase for nickel-tin coating [3]. Nickel-tin alloy has high corrosion resistance and does not irritate human skin.

The introduction of nanosized titanium dioxide into the alloy structure made it possible to impart a number of unique properties to the metal surface. In this work, the antibacterial effectiveness of a composite coating under the action of UV radiation was studied. The antibacterial properties of the coatings were studied against Gram-positive Staphylococcus aureus (S. Aureus) and Gram-negative Escherichia coli (E. Coli) bacteria. Before antibacterial studies, the surface of the samples was sterilized in ethanol (70%) for 2 h and dried at room temperature under UV irradiation.

Composite coatings with nanosized metal oxides are highly effective against resistant bacteria by inhibiting the activity of the pathogen as a result of slowing down the metabolic process specific to microorganisms. The antibacterial properties of the resulting Ni–Sn and Ni–Sn–TiO_2 coatings with respect to S. aureus and E. coli bacteria were studied. The presence of titanium dioxide in the coating significantly reduces the number of bacterial colonies on the surface of the samples. This trend is observed for both S. aureus and E. coli.

The concentration of viable bacteria S. aureus on the surface of the samples upon irradiation with UV radiation at an intensity of 0.01 mV/m^2 for 1 h decreases from 130 to 70 cfu/mL. Upon irradiation of coatings obtained from an electrolyte with 1 g/dm^3 of titanium dioxide, the number of cells decreases from 100 cfu/mL to 20 cfu/mL. This indicates the presence of an antibacterial effect of titanium dioxide, especially when exposed to UV. For samples obtained in electrolytes with 2 g/dm^3 titanium dioxide, the antibacterial effect increases by a factor of 1.5 compared to the control sample. This behavior of the samples is due to the photocatalytic antibacterial activity of the Ni–Sn–TiO_2 composite electrochemical coating in the presence of UV radiation due to damage to bacterial cell membranes due to the absorption of radiation by intracellular chromophores. The resulting composite coating is characterized by high biocidal activity against S. aureus and E. coli bacteria.

References:

1. X. Chen, S. Mao. Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications. Chemical Reviews. (2007). V.107. № 7. P. 2891-2959.
2. I.V. Kovalenko, L.V. Chernenko, S.A. Khaynakov, V.I. Lisin, A.A. Andriiko. Synthesis and electrochemical properties of nanosized titan dioxide. Ukr. Chem. J. (2008). V. 74. № 3–4. p. 52-54.
3. A.V. Pyanko, I.V. Makarova, I.V. Kharitonov, I.S. Makeeva, O.A. Alisienok, A.A.Chernik Tin–Nickel–Titania Composite Coatings, J. Inorg. materials (2019), 55(6), p. 568–575.

S-2

VAPOR PHASE DEALLOYING METHOD FOR FABRICATING POROUS METALLIC MATERIALS

O.S. Roik[1]*, O.M. Yakovenko[1], V.E. Sokolskii[1], M.D. Akulcheva[2], N.V. Kotova[1], N.V. Golovataya[1], P. Švec[3], V.P. Kazimirov[1]

[1]Faculty of Chemistry, Taras Shevchenko National University of Kyiv, Hetman Pavlo Skoropadskyi St., 12, Kyiv, 01033 Ukraine, oleksandr_roik@knu.ua

[2]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine

[3]Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 5807/9, 845 11 Bratislava, Slovakia

Nanoporous (np) metallic materials have attracted considerable attention as new electrocatalysts due to their open porous structure, large surface area with numerous active sites, high electrical/thermal conductivity, and mechanical properties. To date, most porous electrocatalysts are based on noble metals like Au, Ag, Pt, and Pd due to their high stability during chemical/electrochemical dealloying. The development of np-materials based on 3d-transition metals (TM), which are abundant and substantially cheaper in comparison with noble metals, is highly desirable for electrocatalyst applications. A promising electrocatalysis material class is high-entropy alloys (HEAs) where five or more elements are statistically distributed in a single-phase complex solid solution (CSS). The multielement active sites of the CSS with suitable binding energy could be appropriate for each cascade step involved in complex electrochemical reactions [1]. A very important challenge is designing suitable synthesis routes for fabricating porous TM-based HEAs.

Porous metallic materials regardless of their chemical activity can be fabricated by the vapor-phase dealloying (VPD) method [2], which is based on the selective removal of a component with a high partial vapor pressure (usually Zn) from an alloy precursor. This method can be applied to fabricate np-metals and (more important) np-HEAs. For example, a porous Cu ribbon was fabricated using VPD equipment at the Department of Physical Chemistry from an as-quenched Cu_5Zn_{21} ribbon as a precursor [3]. The dealloyed Cu has a macro/mesoporous structure with a specific surface area of up to 1.75 m^2/g.

The VPD method was applied to fabricate porous multicomponent TM-based alloys using as-quenched TM_7Zn_{93} and TM_4Zn_{96} (where TM – a mixture of the Mn, Fe, Co, Ni, and Cu) ribbons. It may be noted that the as-quenched ribbons are very brittle in contrary to the resulting porous alloys which demonstrate considerably better ductility. The SEM micrographs of the fabricated HEAs revealed a spongy microstructure with bimodal pore size. The larger pores were in the range of around 1 μm and the small pores exhibited size dispersion of around 100 - 200 nm. XRD and TEM analysis of the precursor ribbons showed that their microstructure is very complex based on many intermetallic compounds and corresponding solid solutions. XRD and TEM investigations indicate the formation of a single-phase TM-based solid solution with FCC structure during VPD treatment. The XRD analysis has also revealed that the surface of fabricated porous HEAs is covered by MnO.

References:

1. T. Löffler, A. Ludwig, J. Rossmeisl, W. Schuhmann, Angew. Chem. Int. Ed. **60** (2021) 26894–26903.
2. Z. Lu, C. Li, J. Han, F. Zhang, P. Liu, H. Wang, Z. Wang, C. Cheng, L. Chen, A. Hirata, T. Fujita, J. Erlebacher, and M. Chen: Nat. Commun. **9** (2018) 276-283
3. O. Yakovenko, V. Sokolskii, N. Golovataya, T. Kulik, G. Cieslak, O. Roik, Mater. Lett. **331** (2023) 133486

S-3

CATALYTIC ACTIVITY OF AN OPTIMIZED ALUMINIUM-NICKEL-MOLYBDENUM CATALYST

D.S. Kamenskyh[1,2], T.V. Tkachenko[1]*, O.V. Markitan[3], V.O. Yevdokymenko[1]

[1]V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Acad. Kukhar St., 1, Kyiv, 02094 Ukraine, ttv13ttv@gmail.com
[2]V. Bakul Institute for Superhard Materials, National Academy of Sciences of Ukraine, Avtozavids'ka St., 2, Kyiv, 04074 Ukraine
[3]Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov St., 17, Kyiv, 03164 Ukraine

Importance of improving traditional granular catalysts, which are widely used in industry, it is necessary to know their shortcomings: incomplete use of the catalytic mass, mechanical instability, the presence of diffusion inhibition during the chemical reaction, etc. [1].

Our work aimed to study the course of hydrocracking processes of isopropylbenzene depending on the shape and composition of the aluminium-nickel-molybdenum catalyst (ANM), which is similar in composition to the industrial hydrocracking catalyst KGP-1 (70% Al_2O_3, 20% MoO_3, 10% NiO). To study the optimized catalyst catalytic activity a model isopropylbenzene hydrocracking reaction was chosen. It was performed at elevated temperatures and pressures on the installation given in [2]. Process conditions: temperature 200–300 °C, pressure 4.0 MPa, mass rate of isopropylbenzene supply to the reaction zone 12 h-1. Comparative studies of the hydrocracking process of isopropylbenzene in the presence of an ANM catalyst in the form of granules, in the form of a membrane based on porous ceramics, both without and with the addition of a carbon polymer with conjugated multiple bonds in the chain - a product of the oxidative dehydropolycondensation of acetylene (DHPCA) - were performed. Physico-chemical characteristics of the obtained catalysts are given in [2]. Studies of the hydrocracking reaction of isopropylbenzene on granular and membrane catalysts showed that the main products of the reaction are benzene, propane, propene, and cyclohexane and cyclohexene when adding DHPCA. A comparison of the data in Fig. 1 shows that the transition from granular to membrane catalysts allows to increase the conversion of isopropylbenzene by 1.5-2 times and the introduction of a carbon polymer with conjugated multiple bonds in the chain into the composition of the hydrocracking catalyst by 2-3 times.

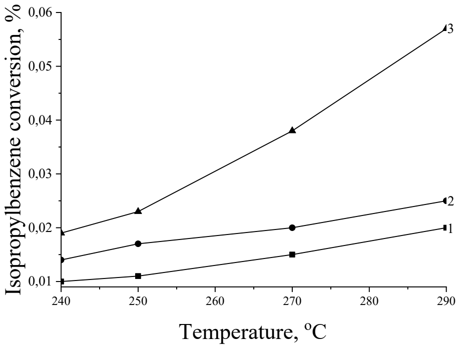


Fig. 1. Temperature dependence of the isopropylbenzene conversion on granular (1), membrane (2) and membrane with the addition of DHPCA (3) catalysts.

References:

1 S.A. Treese, D.S. Jones, P.R. Pujado (Ed), Handbook of Petroleum Processing, Springer Cham: Switzerland, 2015.
2. D. Kamenskyh, T. Tkachenko, Y. Sheludko et al., Appl Nanosci. **13** (2023) 4891.

S-4

REGENERATION OF POISONED Pd/C CATALYSTS IN THE SODIUM FORMATE DEHYDROGENATION REACTION AS PART OF THE "FORMATE/BICARBONATE" CYCLE

V.M. Melnychuk*, I.B. Bychko

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, vadymmelnychuk5@gmail.com

The prospective method for hydrogen accumulation involves the utilization of the formate/bicarbonate cycle, wherein hydrogen release is achieved through the dehydrogenation of formate utilizing supported palladium catalysts. The sodium formate dehydrogenation process occurs in an aqueous solution upon heating and follows two paths: yielding either CO_2 or CO. However, the formation of CO leads to the blockage of active Pd centers, resulting in decreased catalytic activity and catalyst lifetime. Consequently, catalyst poisoning is a significant challenge hindering the implementation of a closed cycle without hydrogen capacity loss.

The literature discusses mechanisms of deactivation of palladium catalysts for formate dehydrogenation. Deactivation pathways involving the formation of inactive β-Pd hydride, irreversibly adsorbed CO_2, and accumulation of reaction intermediates around active centers are considered. However, the major part of the results indicates surface poisoning through irreversible CO adsorption.

According to this, a series of experiments were conducted concerning the dehydrogenation of a 1 M sodium formate solution for 11 commercial Pd/C catalysts. It was determined that 100% conversion was not achieved for any catalyst, and two catalysts showed 0% conversion. It is demonstrated that catalyst poisoning occurs in all cases. The highest H_2 selectivity in the catalyst series reached 99.9%, and the initial conversion-related rate for this catalyst was 3000 ml $H_2/(g(Pd)\cdot min)$, which is comparable with previous results reported literature [1]. Therefore, CO poisoning is unavoidable for all catalysts, necessitating resolution for portable systems' (hydrogen accumulators) application through catalyst regeneration.

Hydrogen reduction represents one method for Pd reactivation. However, experiments with previously poisoned catalysts showed that bubbling a water suspension with an H_2/Ar mixture, as well as restoration in an autoclave filled with H_2 at 10 atm pressure, does not lead to catalyst reactivation.

Consequently, an alternative approach could involve conducting the process under conditions that prevent Pd surface poisoning. Particularly, a method is considered in which oxidants, such as an O_2/Ar mixture, are introduced into the reaction mixture, with their function being the oxidation of adsorbed CO on the palladium surface [2]. Following this strategy, the exploration of oxidants such as O_2, H_2O_2, CaO_2, MgO_2, ZnO_2, $2Na_2CO_3\cdot 3H_2O_2$ could be proposed. The application of the presented oxidants could extend the catalyst's operational lifespan within the closed dehydrogenation/hydrogenation reaction cycle.

References:

1. Su, J., Yang, L., Lu, M. and Lin, H. (2015), ChemSusChem, 8: 813-816.
2. Xu, Pengyu & Bernal-Juan, Fernando & Lefferts, Leon. (2020). Journal of Catalysis. 394.

S-5

CHEMOSELECTIVE PHOTOREDOX CATALYZED FLUOROALKYLCYCLIZATION OF *N*-ALLYL-4,5-DIHYDRO-3*H*-BENZO[*b*]AZEPIN-2-AMINES

I.Yu. Danyliuk*, M.V. Vovk

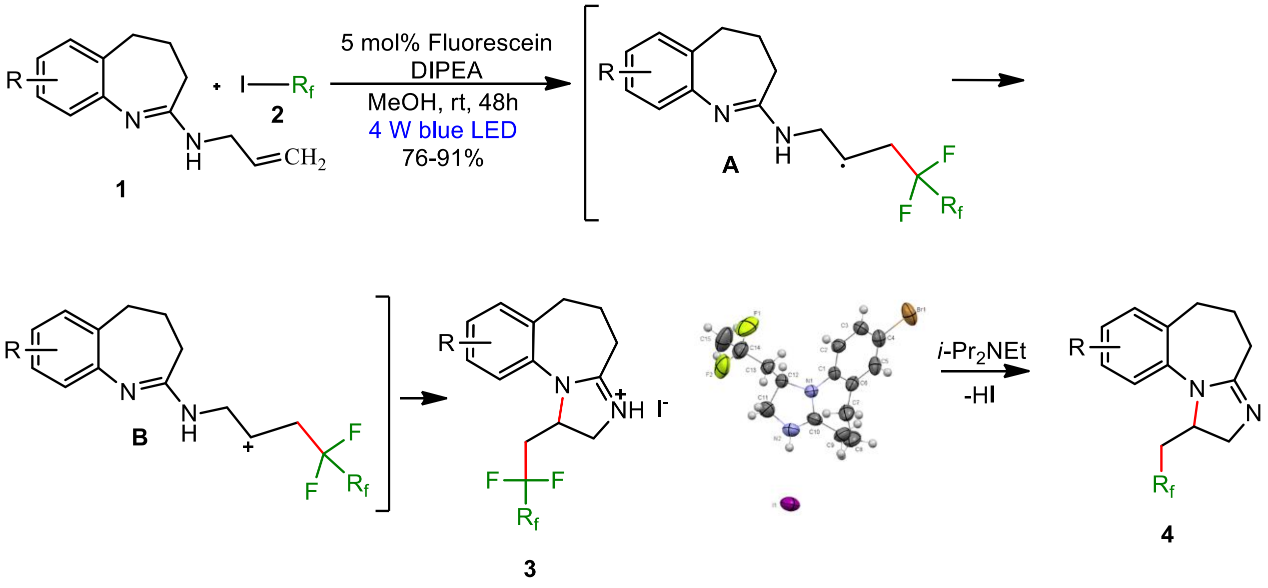
Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Akademika Kuharya St., 5, Kyiv, 02094 Ukraine, ivannayu@ukr.net

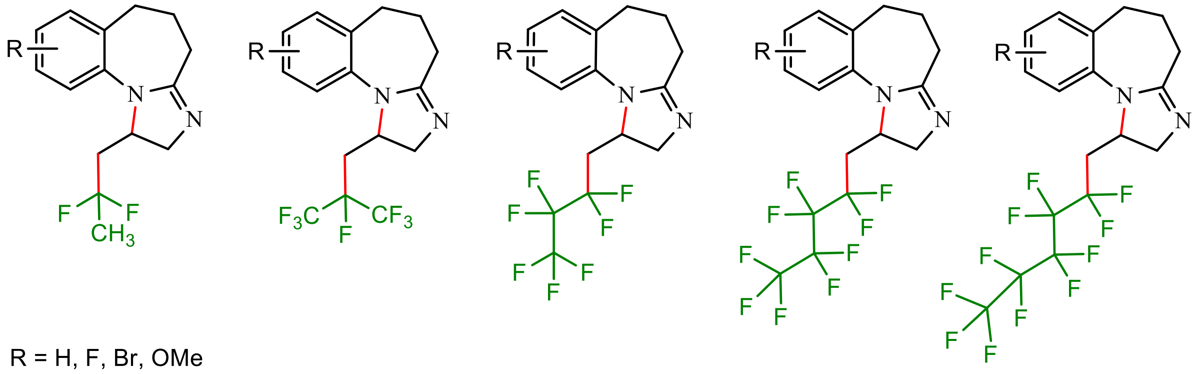
Over the past decade, visible light-induced photoreduction catalysis, due to its mild reaction conditions, high efficiency, and preparative simplicity, has come to the forefront of fine organic synthesis as a powerful tool for transforming simple substrates into complex functional molecules with a wide structural diversity. This effective technology, using commercially available and cheap fluoroalkylation reagents such as perfluoroalkyl iodides (IR_f), has contributed to the efficient design of structurally complex molecules with various polyfluorinated substituents. In recent years, many elegant methods for the fluoroalkylation-cyclization of functionalized olefin structures have been developed, and with the realization of most of them using transition metal complexes as catalysts. However, such catalysts have a number of significant drawbacks: they are expensive, difficult to access, and sensitive to air oxygen. That is why the use of organic dyes as photoinitiators, which are characterized by similar photocatalytic activity, has become a cheap, convenient and environmentally friendly alternative.

Previously, using examples of photoinitiated tandem reaction of fluoroalkylation-cyclization of N-substituted acrylamides with alkenylcarboxylic acids, the formation of a carbon-carbon bond was observed at the final stage of the process. At the same time, such transformations, which are realized through the formation of a carbon-heteroatom bond, remain virtually unexplored. According to the information available to us, the literature describes only examples of ambient light-promoted cyclization of β,γ-unsaturated hydrazones to perfluoroalkylated pyrazolines [1] and photoredox-fac-$Ir(PPy)_3$-catalyzed oxy(amino)fluoroalkylative cyclization of alkenes to fluoroalkylated 2,3-dihydrobenzofuran and indoline derivatives [2].

We propose a new drug-friendly approach to the synthesis of biopromising 1-fluoroalkylated-2,4,5,6-tetrahydro-1*H*-imidazo[1,2-*a*][1]benzazepines **4** based on the chemoselective photoredox-catalyzed fluoroalkylation cyclization of *N*-allyl-4,5-dihydro-3*H*-benzo[*b*]azepin-2-amines **1** in the presence of an organocatalyst. The use of relatively inexpensive perfluoroalkyl iodides (IR_f) **2** as a source of fluorinated fragments, mild reaction conditions and a wide range of substituents makes this method very attractive for the preparation of imidazobenzazepines with various fluorinated fragments. It is worth noting that the proposed approach is a synthetic realization of the organophotoredox catalyzed fluoroalkylation cyclization of *N*-allyl-4,5-dihydro-3*H*-benzo[*b*]azepin-2-amines through the tandem construction of two bonds: carbon-carbon and carbon-nitrogen, the formation of which is often quite difficult to access using classical protocols, and in some cases impossible.

Taking into account the above experimental results and literature data, a probable reaction mechanism was proposed. It involves the formation of an intermediate radical **A**, which is oxidized to cation **B**. The intramolecular 5-*exo*-trig-cyclization of the latter by attacking the benzazepine nitrogen atom leads to the formation of a new C-N bond and the formation of imidazolium salt 3. Its further deprotonation under the action of DIPEA results in the target product **4**.





R = H, F, Br, OMe

The structure of the synthesized intermediates and target compounds was reliably proved by X-ray, ^{1}H- and ^{13}C-NMR spectroscopy and chromatography-mass spectrometry.

References:

1. 1. J.-M. Yu, C. Cai, Eur. J. Org. Chem. **40**, (2017) 6008.
2. J. Liao, L. Ouyang, Y. Lai, R. Luo, J. Org. Chem. 85 (2020) 5590.

S-6

ELECTROCHROMIC AND GASOCHROMIC PROCESSES OF OXIDE FILMS OF TRANSITION METALS

S.S. Fomanyuk*, V.O. Smilyk, I.A. Rusetskyi, M.O. Danilov, G.Ya. Kolbasov

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Palladina Avenue, 32/34, Kyiv, Ukraine, foma7@ukr.net

Electronic information display technologies required and currently require new physico-chemical approaches and materials for controlled color change. Together with other indicator materials, electrochromic materials are also used [1]. Energy efficiency, ease of manufacture and use of these materials are currently increasingly attracting the attention of scientists and manufacturers. The color change in electrochromic materials occurs due to the flow of electrochemical reactions, so the research of the electrochemical processes of their colouring is relevant.

Transition metal oxide films are promising materials for use in indicators, energy-converting and sensors devices. Research influence of the chemical composition, structure and morphology of the surface on the oxide films electrochromic properties is relevant for understanding the mechanisms of colour change in such objects. Films of tungsten, nickel, and niobium oxides obtained by the method of cathodic electrodeposition [2, 3] were selected as objects of research. The use of tungsten oxide as a cathode material, and nickel oxide as an anode, can allow effective use of their mutually complementary electrochromic properties in indicator devices. The interest in niobium oxide films is that they have high electrochromic efficiency in the visible region of the spectrum. At the same time, the use of a simple method of electrodeposition compared to other methods allows you to control the thickness and physico-chemical properties of the films, which is a necessary requirement for the manufacture of indicator, energy-converting and sensor devices. In addition to electrochromic properties, some of the oxide films when using catalysts are sensitive to such gases as hydrogen and chlorine, which allows them to be used for visual and hardware control of these gases in the air. We found similarities between the mechanisms of gasochromic reactions to hydrogen in tungsten trioxide films and to chlorine in nickel hydroxide with electrochromic processes occurring in a liquid electrolyte. But in contrast to electrochromic processes, here the nature of the catalytic layer on the surface of the oxide film, which depends on the course of the gas-phase reaction, plays a significant role. We determined the effectiveness of electrochromic and gaschromic processes for these films, and showed reason for use in indicator and sensor devices.

References:

1. C. G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier in Amsterdam, 1995.
2. С.С. Фоманюк, Ю.С. Краснов, Г.Я. Колбасов, В.Н. Зайченко, Науковий вісник Чернівецького університету. 401 (2008) 188.
3. S.S. Fomanyuk, Yu.S. Krasnov, G.Ya. Kolbasov, Journal of Solid State Electrochemistry. 17 (2013) 2643.

S-7

OXYGEN RECOVERY CATALYSTS IN MODELS OF LITHIUM-AIR BATTERIES

D.V. Patlun[1]*, I.S. Makyeyeva[1], V.G. Khomenko[1], V.Z. Barsukov[2]

[1]Kyiv National University of Technology and Design, Mala Shyianovska St., 2, Kyiv, 01011 Ukraine
[2]Institute of Sorption and Problems of Endoecology,National Academy of Sciences of Ukraine, General Naumov St., 13, Kyiv, 03164 Ukraine, dimapatlun@gmail.com

Li–air batteries have been intensively investigated in recent decades for their application in electric vehicles [1,2]. In this work, we presented practical result of developing Li–air batteries that are using non-Pt catalysts and liquid electrolyte. In recent years, non-Pt-based catalysts have been developing rapidly and offering new possibilities for Li–air batteries. In current work we presents application in Li–air batteries of non-Pt-based catalysts which was designed for oxygen reduction reaction [3,4]. Today, prototypes with a liquid electrolyte are more promising for their use in electric transport when solving the problems of cathode passivation and electrolyte pollution. The prototype of the lithium-air battery with an aprotic electrolyte was developed in the framework of the international project LABOHR. A prototype of a lithium-air battery consisting of an anode that uses metallic lithium, a porous cathode, and an electrolyte. During discharge, the metal lithium anode is oxidized to lithium ions. Atmospheric oxygen is discharged at the porous cathode to form Li_2O_2 and other products like Li_2O, but in smaller quantities. These reactions are reversible only in the case of the formation of lithium peroxide.

The working electrode of the lithium-air battery prototype was made from a mixture of the investigated active material and the binding component (PVDF) in a ratio of 95 : 5%, respectively. Active materials were prepared by method of direct functionalize of the carbon support (graphitized carbon black) with $NiCo_2O_4$ or MnO_2 catalysts. The gas diffusion electrode was installed in a two-electrode cell with the possibility of electrolyte circulation between the electrodes. 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR14TFSI) with 0.3 M Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was used as the electrolyte. The cell fabrication operations were performed in a dry box filled with argon. Before researching laboratory prototypes of lithium-air batteries, the electrolyte was separately saturated with oxygen and then fed into the cell using a peristaltic pump. Electrochemical studies were performed in the galvanostatic mode at a current density of 0.1 mA/cm^2 in the potential range from 2.0 up to 4.1 V relative to the lithium electrode.

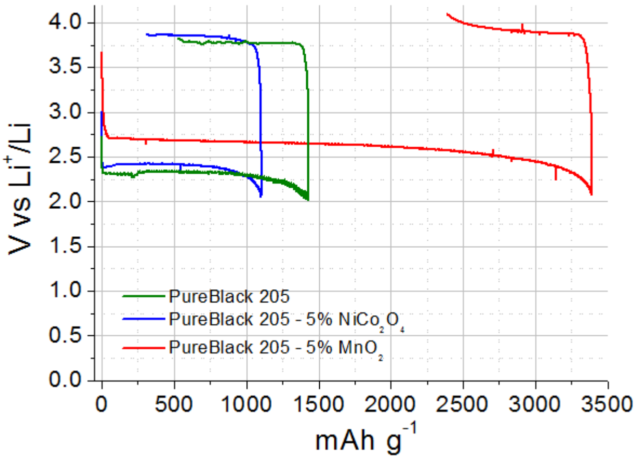


Fig. Voltage profiles upon galvanostatic discharge/charge prototype of Li–air batteries that are using non-Pt catalysts: the PB (green line), PB-$NiCo_2O_4$ (blue line) and PB-MnO_2 (red line).

The figure shows the first charge-discharge cycle of three samples of cathode material.

For the electrode based on graphitized carbon black (PB) modified by MnO_2, the charge voltage was increased up to 4.1 V relative to the lithium electrode. The table shows the calculated charge-discharge characteristics of the electrodes of the lithium-air battery prototype.

Table. The specific discharge capacity of the cathode (Q), the efficiency of the charge-discharge cycle (η), the average values of the charge (U_{charge}) and discharge (U_{charge}) voltages.

Sample	Q, $mA \cdot h \cdot g^{-1}$	η %	$U_{dicharge}$, V	U_{charge}, V
PB	1426	63	2.3	3.8
PB-$NiCo_2O_4$	1100	73	2.4	3.9
PB- MnO_2	3400	30	2.6	3.9

The sample with the MnO_2 catalyst has the highest specific capacity and power values.

The sample functionalized with MnO_2 shows specific capacity of 3400 $mA \cdot h \cdot g^{-1}$. For composite electrodes based on graphitized carbon black with a spinel-type $NiCo_2O_4$ catalyst, stable cycling characteristics were obtained and a capacity of 1100-1400 $mA \cdot h \cdot g^{-1}$ was achieved during testing of lithium-air battery prototypes.

From the results shown in the figure and in the table, it can be concluded that the $NiCo_2O_4$ catalyst does not significantly affect the polarization of the charge-discharge process but reduces the specific discharge capacity of the cathode material primarily due to the weight of the catalyst, which has a density ten times greater than carbon material.

The electrochemical performance of designed Li–air batteries was limited at a current density of 0.1 mA/cm^2. The high initial resistance of Li–air batteries and the low-rate process at the porous cathode to form Li_2O_2 reduced the power rate of designed prototypes.

Battery-supercapacitor hybridization helps overcome the limitations of Li–air batteries with ionic liquids. The hybridization of both energy storage systems provides improving power capability and service life of Li–air batteries. The battery-supercapacitor system is the subject of current work because such systems meet the demands of both higher energy and power densities for multifunctional electronics, hybrid electric vehicles, and industrial equipment.

Acknowledgements. F. Soavi, S. Monaco, M. Mastragostino are acknowledged for their assistance in the electrochemical investigation of Li–air batteries with ionic liquids.

References:

1. 1. M.Z. Kufian, Z. Osman. Prospects and challenges in the selection of polymer electrolytes in advanced lithium–air batteries, Energy Materials, 2021, p. 313-333. https://doi.org/10.1016/B978-0-12-823710-6.00009-1.
2. Oi Lun Li, T. Ishizaki. Development, Challenges, and Prospects of Carbon-Based Electrode for Lithium-Air Batteries, Emerging Materials for Energy Conversion and Storage, 2018, p. 115-152. https://doi.org/10.1016/B978-0-12-813794-9.00004-1
3. V. Barsukov, V Khomenko, O Chernysh. On the processes of migration and diffusion in the systems with solid-state reagents, J. of Electrochemical Science and Engineering, 2020, V. 10(2), P. 219-227. https://doi.org/10.5599/jese.753
4. A. S. Katashynski, V. Z. Barsukov, V. G. Khomenko. Reduction of molecular oxygen on the surface of transition metal complex oxide, Mat.-wiss. u. Werkstofftech, 2016, V. 47, P. 112-119. https://doi.org/10.1002/mawe.201600478

S-8

CATALYTIC CONVERSION OF ETHANOL TO ETHYLENE ON Ce-IMPREGNATED MESOPOROUS SILICA WITH FUNCTIONAL SULFONIC AND PHOSPHONIC GROUPS

N.G. Kobylinska[1]*, V.V. Tomina[2], O.A. Dudarko[2], D. Duraczyńska[3], K. Pamin[3], E. Serwicka[3]

[1]*A.V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Akad. Vernadsky Blvd., 42, Kyiv, 03142 Ukraine, nkobilinskaya@gmail.com*
[2]*Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov St., 17, Kyiv, 03164 Ukraine*
[3]*Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland*

The conversion of ethanol to commodity chemicals can be a chemical or fermentative process. The only product currently synthesized through ethanol fermentation is acetic acid, but many other chemicals could be produced by using catalysts. Typically, ethylene is produced in a steam hydrocarbon cracker from fossil naphtha, ethane, propane and liquid-petroleum-gas as raw materials. Due to efforts to reduce carbon emissions, the alternative ethanol dehydration route gains more and more importance. The industrial production of ethanol from biomass, particular in Brazil, has made it an available commodity for introduction as a fuel additive or hydrocarbon substitute. Thus, ethanol dehydration seems to be feasible as a workable route to make the olefins in certain locations and in this case the selectivity could be more than 99%.

The catalytic performance of Ce-containing mesoporous materials in the catalytic dehydration of ethanol in gas phase in the temperature range of 125 to 500°C was studied. Mesoporous silica SBA-15 type were functionalized with phenyl (SBA/Ph), phenylsulfonic (SBA/$PhSO_3H$) and phosphonic acid (SBA/$PhSO_3H$/PO_3H_2) groups, and then impregnated with Ce^{3+} ions. The initial functionalized silica and Ce-containing catalysts were characterized by X-ray diffraction, transmission and scanning electron microscopy (SEM) couple with energy dispersive X-ray analysis, zeta potential measurement, etc.

From the SEM images of SBA-15-based materials (**Fig. 1**), it can be observed that they possess rod-like or spherical shape without significant changes in the morphology upon the Ce-incorporation process.

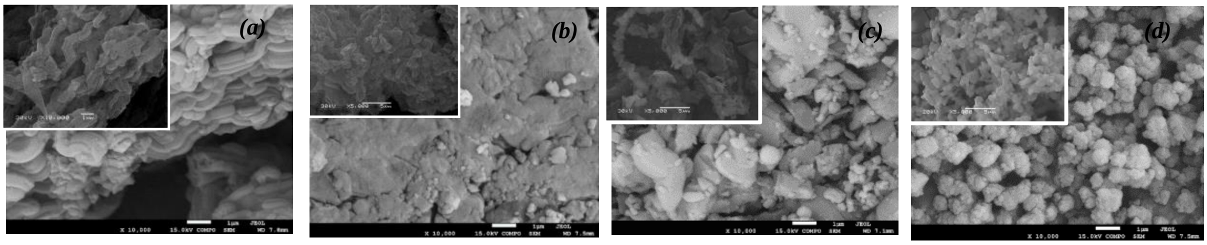


Fig. 1. SEM images of the samples (*insert*) and their Ce-containing derivatives: SBA-15 (*a*), SBA/Ph (*b*), SBA/$PhSO_3H$ (*c*) and SBA/$PhSO_3H$/PO_3H_2 (*d*)

It was found that the most important parameter influencing catalytic properties appears to be the relationship between Ce^{3+} ions and the functional groups of the mesoporous supports. The dispersion of the metal ions inside the silica matrix of SBA-15 has a direct influence on its surface acidity. Ethanol conversion and ethylene selectivity were found to increase with increasing reaction temperature. The best catalytic effect was achieved for the sample with phenylsulphonic groups that indicated ethanol conversion values and ethylene yield of ca. 93% and 68%, respectively, at 400°C.

S-9

DEHYDRATION OF BIO-ISOBUTANOL INTO LINER BUTENE ISOMERS OVER ZEOLITES OF DIFFERENT FRAMEWORK TYPES (FER, MFI, FAU AND BEA)

O.V. Zikrata[1]*, O.V. Larina[1]

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, oksanazikrata@ukr.net

Isobutanol (i-BuOH) derived by fermentation of renewable biomass sources is one of the promising starting materials for the manufacturing of valuable chemicals and intermediates. Butene isomers commonly used for synthesis of polymers, fuel additives and various specific compounds can be obtained by i-BuOH dehydration over acidic oxides and zeolites. Alumina and FER-type zeolites are the most investigated catalysts in this process [1,2]. While alumina is highly selective to branched isobutene, FER zeolite directs the process mostly to linear butenes, namely 1-butene (1-Bu), trans-2-butene (t-Bu) and cis-2-butene (c-Bu). The mechanistic aspects of i-BuOH dehydration over zeolite catalysts is still debated [3].

Zeolites of different framework types (FER, MFI, FAU and BEA) were studied as catalysts for i-BuOH conversion. The zeolite samples were characterized by XRD, N_2-ad/desorption, FE-SEM, ^{1}H, ^{27}Al, ^{29}Si MAS NMR, ^{1}H-^{29}Si CP MAS NMR, FT-IR of adsorbed pyridine, potentiometric titration, TPD-NH_3/CO_2/H_2O with MS control. Catalytic experiments were carried out at atmospheric pressure in the temperature range of 448-573 K using quartz reactor of flow type with chromatographic analysis.

Obtained results of the catalyst investigation at similar indices of i-BuOH conversion (X ~ 33 %) shows that the process selectivity highly depended on zeolite framework type and acidic characteristics of the samples directly reliant on it (see Table). FER-10 and MFI-40 catalysts are the most selective towards butenes in general (99 and 98 %, respectively) and to linear isomers ($S_{lin.\ Bu}$ = 78 and 37 %) in particular.

Table. Acid characteristics, product selectivity in i-BuOH dehydration over zeolites

[1]Sample	[2]C_{NH3}, µmol/g	[2]C_{strong}, µmol/g	[2]E_a, kJ/mol	[3]BAS/ LAS	[4]Selectivity, %					
					i-Bu	1-Bu	t-Bu	c-Bu	$\Sigma_{lin.Bu}$	Oth.
FER-10	1730	528	125	15	21	10	45	23	78	1
MFI-40	647	232	122	18	61	5	20	12	37	2
FAU-15	424	166	116	5	44	3	6	6	15	41
BEA-19	670	166	116	3	55	5	8	9	22	23
BEA-68	135	19	115	6	57	4	11	10	25	18

[1]Number in the sample name means Si/Al ratio; [2]TPD-NH_3 data; [3]Ratio of Brønsted and Lewis acid sites calculated based on FT-IR of adsorbed pyridine after desorption at 423 K; [4]T = 473 K, time-on-stream = 45 min, X ~ 33 %.

A larger amount of strong (NH_3 desorption activation energy (E_a) of ~ 125 kJ/mol) acid sites, mainly Brønsted ones, on the FER-10 and MFI-40 surfaces is considered to be decisive in the production of linear butenes.

References:

1. J.-L. Dubois et al., Catalysis Today. **418** (2023) 114126.
2. S. Van Daele et al., Applied Catalysis B: Environmental. **284** (2021) 119699.
3. M. Gešvandtnerová et al., Journal of Catalysis. **413** (2022) 786.

S-10

GAS PHASE SYNTHESIS OF CARBON NANOSPHERES, STRUCTURE AND PROPERTIES

S.M. Pleskun*, E.V. Polunkin, V.S. Pyliavskiy

V.P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry, National Academy of Sciences of Ukraine, Murmanska str., 1, Kyiv, 02094 Ukraine, sp@ktka.com.ua

There are different methods of carbon nanospheres (CNSs) synthesis: pyrolytic deposition from the gas phase, hydrothermal synthesis, templated synthesis. However, despite a significant number of publications on the methods of synthesis of carbon nanospheres, they mainly concern large-sized nanospheres. The number of publications on the synthesis of CNSs with sizes less than 100 nm is limited [1].

Basic methods to obtain such nanospheres include arc discharge between carbon electrodes in the gas phase and in a liquid, such as water or benzene, with a particle size of 5-100 nm, and high-temperature transformation of detonation nanodiamonds, which allows to obtain spheroidal particles with well-defined shells and a particle size range of 2-10 nm [2].

In previous studies, carbon nanospheres were modified by treating carbon black with various chemical reagents [3]. For the first time, we performed high-frequency high-voltage synthesis in the gas phase from freons. The use of freons in the plasma-chemical synthesis process made it possible to replace the halogenation stage of CNSs with a one-step synthesis of fluorinated hydrocarbons.

Powders were dried in a vacuum and fractionated by extraction in volatile solvents and filtered on filters with a pore diameter of 250 nm and the solvent was removed.

High-resolution microscopic images of CNS were obtained using a JEOL JEM-2100F transmission electron microscope (TEM) with an electron accelerating voltage of 200 kV. For this, samples of carbon nanospheres were dispersed in a medium of dimethyl ketone using an ultrasonic disperser, after which they were applied to a special grid. Typical electronic images are shown in fig. 1 (left). The obtained carbon nanomaterials are spheroidal nanoparticles with sizes ~ 10-30 nm and are characterized by a complex hierarchical structure.

Laser Raman spectroscopy was used to reveal the structural features, degree of orderliness, and homogeneity of the obtained carbon nanomaterials. Raman spectroscopic studies of the samples of synthesized nanomaterials were carried out at the V.E. Lashkarev Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine (senior scientific assistant Kolomys O.F.). The Raman spectra were recorded in a wide range of wavenumbers 150-3500 cm^{-1} using a LabRAM laser spectrometer (YobinYvon) with a 632.8 nm He-Ne laser excitation line (fig. 1 (right)).

Raman spectroscopy is one of the vibrational spectroscopy methods that does not require sample destruction for analysis and is widely used in the study of various allotropic modifications of carbon. A characteristic feature of Raman spectra of carbon materials is the presence of a G-band in the range of 1500-1600 cm^{-1}. Oscillations reflected in the spectrum by the G (graphite) line are considered to be associated with vibrations of carbon atoms in the plane of graphene cycles (tangential vibrations).

The effect of additives of synthesized CNSs on the anti-wear properties of liquid motor fuels was evaluated by changing the fuel bearing capacity.

The load-bearing capacity of fuels determines the range of loads at which, under specified standard conditions, the liquid friction mode is realised without direct metal contact of friction surfaces with their macro-damage - scoring. The comparative bearing capacity of the fuels without the proposed additive and with the recommended additive content was determined according to ASTM D2783 using a four-ball tribometer by the critical load value.

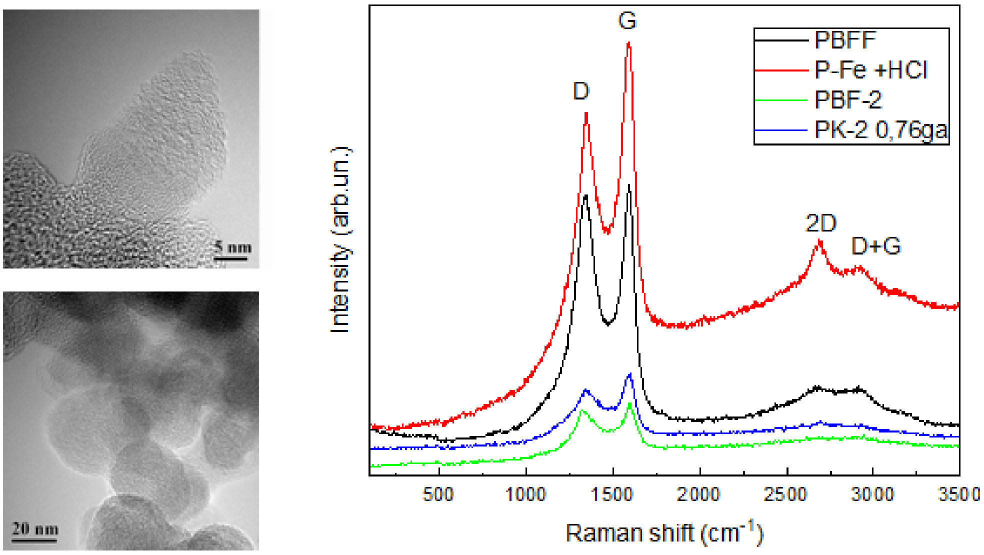


Fig. 1. TEM image of carbon nanospheres (left); Raman spectrum of carbon nanoclusters obtained by plasmochemical synthesis in the liquid phase from (from top to bottom): hexafluorobenzene, ferrocene in benzene, tetrafluoroethane (gas), cyclohexane with xylene (right).

The values of the critical load before scoring were measured in accordance with ASTM D 2783 for motor fuels on the example of ethanol and blended biodiesel (80 % commercial petroleum diesel fuel DSTU 7688:2015 + 20 % ethyl esters of vegetable oils), at different concentrations of the CNSs additive are given in Tables 1, 2.

Table 1. Critical load before ethanol scoring at various CNS contents

Concentration of CNSs, 10^{-4} % mass	0	48,8	61	97,6	162	244	488
Critical load, N	50	90	90	100	120	80	75

Table 2. Critical load before scuffing of blended biodiesel at different content of CNSs

Concentration of CNSs, 10^{-4} % mass	0	1	2	5	10
Critical load, N	372	416	441	372	372

Tribological studies have been carried out and the prospects of using synthesised small-sized CNSs to improve the anti-wear properties of liquid motor biofuels have been shown.

References:

1. 1. Kroto H.W., Heath J.R., O’Brien S.C. et al. C60: Buckminsterfullerene. Nature. 1985. – 318. – P. 162–163.
2. Ugarte D. Curling and closure of graphitic networks under electron-beam irradiation. Nature. 1992. – 359. – P. 707–709.
3. Rud, A.D., Kornienko, N.E., Polunkin, I.V. et al. Structure of carbon nanospheres modified with oxygen-containing groups and halogens. Applied Nanoscience. 2023. https://doi.org/10.1007/s13204-023-02817-2.

S-11

BINARY AND TERNARY ELECTROLYTIC RHENIUM ALLOYS AS ELECTROCATALYSTS OF HYDROGEN EVOLUTION REACTION

Yu.S. Yapontseva*, T.V. Maltseva, V.S. Kublanovsky

V.I. Vernadsky Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Prosp. Palladina, 32/34, Kyiv, 03142 Ukraine, juliya_yap@ukr.net

The increase in energy consumption in the world and the desire to use renewable energy sources puts the production, storage and use of environmentally friendly hydrogen fuel into a number of important and urgent technical problems. The electrolytic method for hydrogen producing is a highly efficient but expensive method due to the cost of electrocatalysts. Thin-layer coatings with base metal alloys can solve this problem by the surface modifying of existing nickel and steel electrodes in order to increase the electrocatalytic activity and reduce the energy consumption for hydrogen production.

Rhenium is a catalyst for many chemical and electrochemical reactions in the form of metal, alloys, oxides and composite materials. When electrodeposited with iron subgroup metals rhenium forms electrolytic alloys. The composition, structure and electrocatalytic activity of such alloys is controlled and reproduced by changing the electrolytes composition and electrodeposition modes.

The paper presents a study of the electrodeposition process of binary and ternary rhenium alloys (CoRe, CoWRe) in connection with the dependence of electrocatalytic activity in the hydrogen evolution reaction and corrosion resistance in a solution of 1.0 $mol \cdot l^{-1}$ KOH on the chemical composition and structure of coatings.

n order to obtain electrolytic alloys with different rhenium content (12–78 at.% Re in binary CoRe alloys; 13–41 at.% Re and 3–11 at.% W in ternary CoWRe alloys), we developed monoligand citrate and polyligand citrate pyrophosphate electrolytes. The deposition was carried out in a galvanostatic mode in the range of current densities of 5–40 $mA \cdot cm^{-2}$ at a temperature of 50°C under conditions of intensive mechanical stirring.

Voltammetric studies of hydrogen evolution process on the obtained coatings show that all coatings have a significantly lower hydrogen evolution overvoltage than the base metal cobalt. The alloy exhibits a synergistic effect of the two types of surface. Metals on which an electrochemical reaction occurs at a high rate (Volmer reaction), in this case, are refractory metals W and Re. These atoms should be sufficient for the spillover of the formed hydrogen adatoms to cobalt atoms, on which the stage of electrochemical desorption (Heyrovsky reaction) rapidly occurs. The use of rhenium alloys makes it possible to reduce the hydrogen evolution overvoltage by 90-170 mV and increase -logj0 from 4.08 to 2.6 A cm-2 compared to cobalt. However, a large number of refractory metal atoms leads to a decrease in the number of cobalt atoms and a decrease in the rate of hydrogen removal from the surface, and hence the entire process. Therefore, the best characteristics are obtained for alloys containing up to 30 at.% of refractory metals.

A feature of ternary alloys is higher corrosion resistance than binary alloys and very high current efficiency during their electrodeposition, which is not typical for alloys of refractory metals with iron-subgroup metals. These characteristics are also directly related to the electrocatalytic activity of the alloys. On the surface of alloys with a high content of refractory metals, the hydrogen evolution reaction is inhibited both in the process of obtaining an alloy and in the process of corrosion with hydrogen depolarization.

S-12

SIZE DEPENDENCE OF THE FERMI LEVEL POSITION IN ZnO NANOPARTICLES AND ITS EFFECT ON THE CATALYTIC ACTIVITY IN THE CO OXIDATION

O.Z. Didenko, G.R. Kosmambetova, P.E. Strizhak

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, o.z.didenko@gmail.com

The relation between the size, electronic and catalytic characteristics of the magnesia-supported ZnO nanoparticles in the CO oxidation is considered within the framework of Th. Wolkenstein's electron theory of catalysis on semiconductors. This theory offers an explanation of the elementary (microscopic) mechanism of the catalytic act as an electronic process and establishes a connection between the electronic and catalytic properties of the semiconductor. In particular, the catalytic activity of a semiconductor material depends on the Fermi level position, which affects the chemisorption type of reactants and reaction products on its surface [1, 2].

A series of the ZnO/MgO solids were prepared by a two-step method including the synthesis of the ZnO nanoparticle colloidal solutions from zinc acetate and sodium hydroxide in isopropanol followed by their deposition over MgO powder [3]. The 1%ZnO/MgO samples with a different average diameter of ZnO nanoparticles in narrow range of 4.0-4.6 nm were prepared by varying the conditions of the colloidal solution synthesis (reagent concentrations, aging temperature, and aging time).

The quantum confinement effect in ZnO nanoparticles was identified by the appearance of a shift in the ultraviolet-visual diffuse reflectance (UV-Vis DR) onset toward shorter wavelengths compared with bulk ZnO. A widening of the band gap with a decrease in the ZnO nanoparticles size indicates a narrowing of the conduction band, a decrease in the electron affinity energy, and a shift of the Fermi level to the bottom of the conduction band. According to Wolkenstein's theory, the approach of the Fermi level to the conduction band increases the rate of acceptor reactions accelerated by electrons, and the shift to the valence band leads to an increase in the rate of donor reactions accelerated by holes. Thus, a decrease in the average size of ZnO nanoparticles is accompanied by a shift in the Fermi level to the conduction band and acceleration of the acceptor stage of the CO oxidation reaction - CO adsorption on oxygen radical ions that accepted an electron from the catalyst surface. Accordingly, the donor stage - neutralization of the CO_2^- intermediate by donating electron to the catalyst followed by CO_2 desorption from the surface - is the limiting stage of the reaction. Opposite processes occur as the Fermi level approaches the valence band with an increase in the size of ZnO nanoparticles: the acceptor stage of CO adsorption on the catalyst surface is limiting. It is the competition between the acceptor and donor stages of the CO oxidation reaction and the change in the ratio of their rates with a shift in the Fermi level in ZnO nanoparticles that explains the bell-shaped size dependence of the rate of the CO oxidation reaction.

References:

1. Th. Wolkenstein, The electron theory of catalysis on semiconductors, Adv. Catal. **12** (1960) 189. doi:10.1016/S0360-0564(08)60603-3
2. N. Turaeva, H. Krueger, Wolkenstein’s model of size effects in CO oxidation by gold nanoparticles, Catalysts **10** (2020) 288. doi:10.3390/catal100302888
3. O.Z. Didenko, G.R. Kosmambetova, P.E. Strizhak, Size effect in CO oxidation over magnesia-supported ZnO nanoparticles, J. Mol. Catal. A Chem., 2011, Vol. 335, No. 1-2, P. 14-23. doi:10.1016/j.molcata.2010.12.005

S-13

SELECTIVE HYDROGENATION OF POLYFUNCTIONAL ORGANIC COMPOUNDS USING CATALYSTS BASED ON RHENIUM SULPHIDE

A.S. Poturai[1]*, V.V. Subotin[2,3], S.V. Ryabukhin[1,3,4], D.M. Volochnyuk[1,3,4], S.V. Kolotilov[2]

[1]*Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska St., 5, Kyiv, 02660 Ukraine, poturayas@gmail.com*
[2]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine*
[3]*Enamine Ltd., Winston Churchill St., 78, Kyiv, 02094 Ukraine*
[4]*Institute of High Technologies, Taras Shevchenko National University of Kyiv, Volodymyrska St., 60, Kyiv, 01601 Ukraine*

The interest in platinum-group-metal-free catalytic systems for hydrogenation or organic compounds drastically increased in recent decade due to the constantly growing shortage of palladium worldwide. Besides high price, the catalysts based on platinum group metals are toxic and their use (at metallic nanoparticles) unavoidably leads to dehalogenation of halogenated arenes. Search of new catalysts for the hydrogenation of the aromatic compounds is still a crucial problem of modern physical and organic chemistry.

The aim of this work was to develop the catalytic system for reduction of substituted heteroaromatic scaffolds based on rhenium sulfide, which possessed unique selectivity in hydrogenation of halogen-containing species. Unlike one of the most popular catalysts in organic synthesis - palladium on carbon [1], rhenium does not take part in metallization reactions with aryl halides. Also, it was supposed that Re-based catalysts would allow to perform hydrogenation of thiophenes, because no sulfur poisoning of the metallic phase occurs in this case in contrast to Pd-containing systems [2].

The method for obtaining finely dispersed rhenium sulfide from ammonium perrhenate in multigram quantities was developed. The composition of rhenium sulfide corresponds to Re_2S_7, however samples contain significant quantity of sulfur. Carrier-free Re_2S_7 and its composites with activated carbon were prepared and characterized by XRD, TEM, SEM and XPS techniques.

Rhenium sulfide forms "fish scales" on activated carbon of *ca*. 50 nm size (Fig. 1). It was found by XPS that Re atoms in the sample mainly have oxidation state +4, with insignificant quantity of Re +6 and +7. Respectively, peaks of S atoms on XPS could be assigned to S^{2-} and bridging S_2^{2-}.

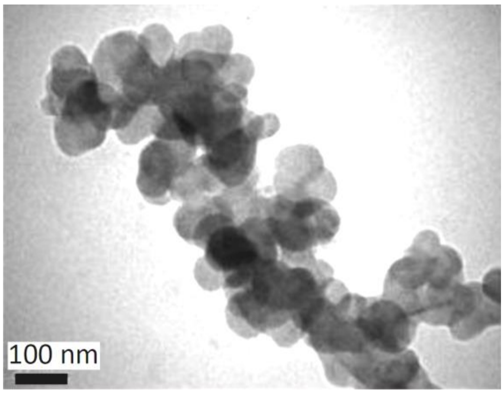


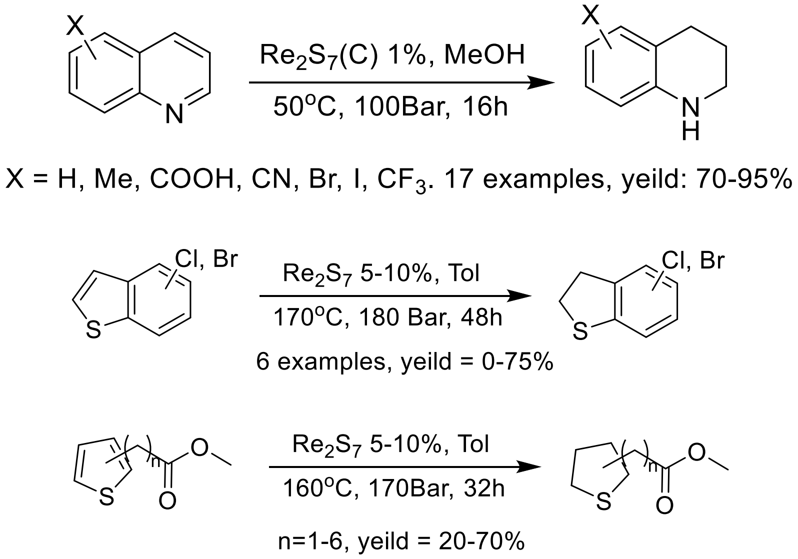
Fig. 1. TEM image of pure Re_2S_7

Rhenium sulfide and its composites showed high catalytic activity in hydrogenation reactions of substituted quinolines and thiophenes. It was found that hydrogenation of substituted quinolines occurred with more than 90 % yield already at 50 °C, p(H_2) = 50 bar in 4 hours at 6 mol % loading of the catalyst. Though consumption of Re is significantly higher compared to Pd in similar processes, the cost of use of Re-containing systems is still lower due to significant difference in prices of these metals. It was shown that the kinetics of the reaction of quinoline hydrogenation corresponded to zero order on concentration of quinoline at p(H_2) = 50 and 100 bar.

The main specific feature of rhenium sulfide is its unprecedented selectivity. Hydrogenation of compounds containing C-Br and C-I bonds leads to formation of the respective products, bearing Br and I atoms. For example, hydrogenation of 5- and 6-iodoquinoline could be performed leading to 5-iodo-1,2,3,4-tetrahydroquinoline and 6-iodo-1,2,3,4-tetrahydroquinoline in preparative scale with 35-45 % yields.

Hydrogenation of substituted thiophenes and benzothiophenes could be performed with preservation of S-containing ring. The reactions were scaled up to 20 grams per autoclave load.

The optimal conditions for hydrogenation of quinolines and thiophenes are shown on the scheme:



Thus, rhenium sulfide catalysts can be proposed for hydrogenation of organic compounds as a good alternative to Pd-based systems. Moreover, use of rhenium sulfide allow to perform hydrogenation of heterocycles preserving C-Br and even C-I bonds, as well as to prepare tetrahydrothiophenes and dihydrobenzothiophenes preserving S-containing ring in preparative scale.

References:

1. A. Biffis, M. Zecca, M. Basato, Eur. J. Inorg. Chem. **5** (2001) 1131.
2. L.J. Hoyos, M. Primet, H. Praliaud, J. Chem. Soc., Faraday Trans. **88** (1992) 113.

S-14

MODELLING THE CPE PHENOMENON FOR METHANE REFORMING

M.O. Vilboi[1]*, V.R. Trishch[1], G.S. Yablonsky[2], D. Constales[3]

[1]National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Peremohy Avenue, 37, Kyiv, 03056 Ukraine, mvilboy@gmail.com
[2]Washington University in St. Louis, St. Louis, MO 63130, USA
[3]Ghent University, Sint-Pietersnieuwstraat 25, Gent, Ost-Flandern, Belgium

Conservatively Perturbed Equilibrium (CPE) is a new phenomenon in chemical kinetics first distinguished by Yablonsky et al. [1]. This phenomenon is described as dynamic behavior of complex chemical reactions in closed or some open systems at the fixed temperature and given amounts of any chemical element and at initial/inlet concentrations which are equal to the equilibrium ones. In transient regimes, CPE results in unavoidable passing of a reacting system from initial partially equilibrated state through a point of concentration extremum of initially equilibrated components to a full chemical equilibrium. Model examples of cyclic and acyclic mechanisms representing CPE-effect are presented in articles [2,3]. Experimentally this phenomenon was justified by Peng and Zhu [4]

In this paper, CPE-phenomenon will be illustrated taken as example reactions of the known catalytic process of tri-reforming. This process is still in infancy, but potentially it can be considered important for chemical industry. The reversible ‘block’ of reactions is chosen as the subject of studying, i.e. dry reforming of methane(1) and steam reforming of methane(2):

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \qquad (1)$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (2)$$

According to Wei and Iglesia [5], these reactions have very similar kinetic parameters, such as forward rate constants and equilibrium constants.

For achieving the CPE effect, it is necessary first to calculate the equilibrium composition for a given set of conditions, such as the temperature, pressure and initial element amounts. This was done for a range of temperatures from 973 to 1123 K with intervals of 50 K. After this initial calculation it is possible to conduct CPE experiment itself. To do this it is necessary to set one (or multiple) of initial concentrations to its equilibrium value, and set other ones to not be equal to equilibrium, but do this in such a way to not change overall amount of each chemical element in the mixture. Temperature and pressure must be held the same too.

Fig.1 depicts one of possible scenarios in which CO concentration was set initially as its equilibrium value, and other ones were not.

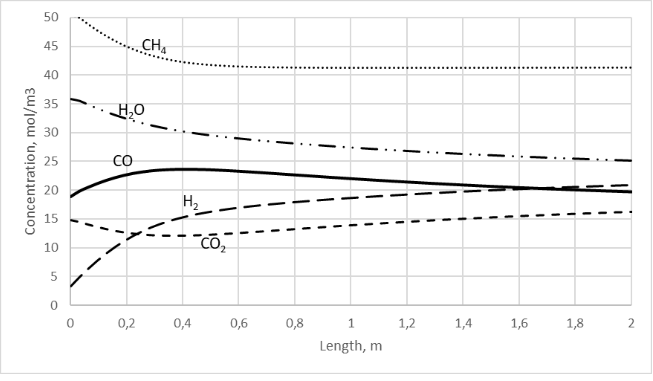


Fig. 1. Concentration profile for computer experiment with CPE effect, T = 973 K, P = 10 bar. CO initial = CO equilibrium.

It is clear that CO concentration profile experienced a maximum at 0,4 meters into the reactor, which is a much shorter length that is needed to reach equilibrium, and value of concentration at this maximum is, obviously, greater that equilibrium one. It is possible to evaluate this by calculating over-equilibrium, which, in this case, is 36,8 %.

This was done for a range of temperature from 973 to 1123 K, and for H_2 as well as for CO, as these are products of methane reforming reactions. Results are present in Table.

Table. Over-equilibrium percent

Temperature, K	Over-equilibrium for CO, %	Over-equilibrium for H_2, %
973	36,8	21,56
1023	25,44	15,79
1073	17,71	12,64
1123	11,17	10,53

The fact the time for achieving the over-equilibrium in the CPE-region is much shorter than the time for achieving the vicinity of the final equilibrium can be considered as an advantage for industrial applications of this phenomenon. Also, the CPE-point can be used for more precise estimating of kinetic parameters of the chosen scheme. It can be a subject of our further studies.

References:

1. G.S. Yablonsky, P.D. Branco, G.B. Marin and D. Constales, Vol. 196, pp. 384-390, 2019.
2. V.R. Trishch, Y.O. Beznosyk, D. Constales and G.S. Yablonsky, Journal of Non-Equilibrium Thermodynamics, Vol. 47, pp. 103-110, 2022.
3. V.R. Trishch, Y.O. Beznosyk, G.S. Yablonsky and D. Constales, Bulletin of NTUU "Igor Sikorsky Kyiv Polytechnic Institute". Series: Chemical Engineering, Ecology and Resource Conservation, Vol. 3, pp. 39-55, 2021.
4. Baoxiang Peng, Xilei Zhu, Denis Constales, Gregory S. Yablonsky, Chemical Engineering Science, Volume 229, 2021.
5. Junmei Wei, Enrique Iglesia (2004), Journal of Catalysis, Vol. 224, Issue 2, 370-383..

S-15

CATALYSIS OF HYDRODEHALOGENATION, C-C- AND C-N-COUPLING REACTIONS OF HALOARENES BY CARBENE COMPLEXES OF PALLADIUM CHLORIDE

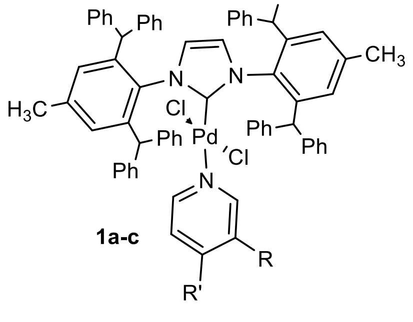
V.Sh. Saberov[1]*, O.S. Avksentiev[1], V.I. Yenya[1], G.F. Rayenko[2], N.I. Korotkikh[1]

[1]Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Acad. Kukhar St., 5, Kyiv, 02660 Ukraine, nkorotkikh@ua.fm
[2]L.M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Kharkiv road, 50, Kyiv, 02160 Ukraine

Carbene complexes of transition metals are increasingly included in the arsenal of organic reaction catalysts, and palladium complexes occupy a special place among them in terms of efficiency [1]. Recently, such compounds have been used to solve the problems of disposal of toxic halogen-containing industrial products by the hydrodehalogenation reaction of haloarenes.

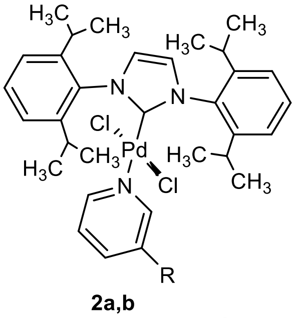
In order to find new highly effective and technologically available catalysts for the reaction of hydrodehalogenation, C-C and C-N coupling of haloarenes, a number of carbene PEPPSI complexes of palladium chloride **1a-c**, **2a,b**, **3**, **4** (LPdCl$_2$· L′) were synthesized by interactions of sterically shielded imidazolium salts LHX (L – carbene ligand, L′ – pyridine-containing ligand, X = Cl, ClO$_4$) with palladium chloride in the presence of potassium carbonate in pyridines or in acetonitrile in the presence of the corresponding pyridines (4-dimethylaminopyridine, phenanthroline) at room temperature [2]. The obtained complexes **1a-c**, **2a,b**, **3**, **4** are colorless or pale yellow substances stable upon storage, which have certain advantages over analogous complexes without pyridine ligands (LPdCl$_2$), because they are obtained without the use of carbenes, have increased stability in atmospheric conditions. Similarly, the nickel chloride complex **5** was synthesized, which, despite carrying out the reaction in pyridine, does not contain a pyridine ligand in its structure. The structure of the compounds was proved by the methods of ^{1}H and ^{13}C NMR spectroscopy.

The catalytic efficiency of complexes **1**–**4** in the reactions of hydrodehalogenation of *p*-dichlorobenzene and hexachlorobenzene in isopropanol under the action of potassium *tert*-butoxide at 80 °C for 24 h was studied. It was established that most complexes catalyze the reaction effectively, but carbenophenanthroline (**2c**), carbeno-4-dimethylaminopyridine (**1c**), triazolylidene (**3**) and cetyl-substituted carbene (**4**) complexes are less effective. To complete the reaction of *p*-dichlorobenzene, 0.01 mol% of the most effective and available catalyst **1a** is sufficient under the indicated conditions, and 0.04 mol% with the addition of PEG-2000 is sufficient for the reaction of hexachlorobenzene. Catalyst **2a** is somewhat less effective compared to **1a**, but it is also very suitable for technological purposes and, moreover, is more accessible. The nickel complex **5** turned out to be ineffective in the reaction.



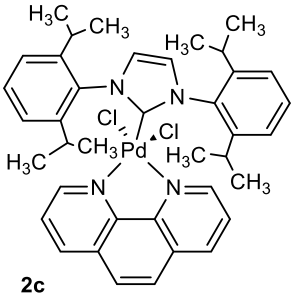
1a-c

7 R = R' = H (**a**); R = Cl; R' = H (**b**);
R = H, R' = NMe$_2$ (**c**).



2a,b

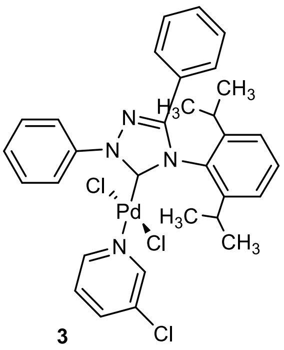
R - H (**a**), Cl (**b**)



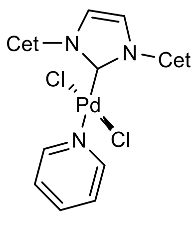
2c

In the reaction with potassium formate, the efficiency of catalysis by the analog complex **1a** without pyridine ligands ($LPdCl_2$) [3] is much lower (conversion of *p*-dichlorobenzene 65–79% with 0.1 mol% of the catalyst).

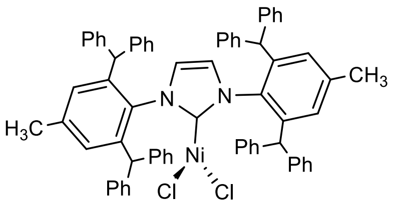
Compound **1a** ($LPdCl_2$.Py) also effectively catalyzes the Suzuki-Miyaura C-C cross-coupling reaction of bromobenzene with phenylboronic acid, allowing high yields of diphenyl (80–90%) to be obtained at a catalyst amount of 1 mol%. The reaction was carried out in the presence of potassium *tert*-butoxide in isopropanol at room temperature.



3



4



5

In the reaction of bromobenzene with phenylacetylene according to Sonogashira, PEPPSI-complex **1a** ($LPdCl_2$·Py) was used, which in the amount of 0.1 mol% provides high yields of diphenylacetylene (up to 95%). The reaction was carried out in the presence of potassium carbonate in dimethylformamide at room temperature.

Complex 1a ($LPdCl_2$) even in the amount of 0.002 mol% provides quantitative yields of diarylamine (TON 50000) in the Buchwald-Hartwig reaction of chlorobenzene with 2,6-dimethylaniline. The reaction was carried out in the presence of sodium *tert*-butoxide in dioxane at room temperature.

References:

1. N.I. Korotkikh, O.P. Shvaika. Organic reactions catalysis by carbenes and metal carbene complexes. LAP Lambert Academic Publishing, 2015, 385 p.
2. V.Sh. Saberov, A.V. Avksentiev, G.F. Rayenko, A.B. Ryabitsky, V.I. Yenya, M.M. Nechitaylov, N.I. Korotkikh, Ukr. Chem. J. 1 (2022) 67–81.
3. V. Sh. Saberov, D. A. Evans, N. I. Korotkikh, A. H. Cowley, T. M. Pekhtereva, A. F. Popov, O. P. Shvaika, Dalton Trans. **43 (**2014) 18117 – 18122.

S-16

KINETICS AND MECHANISM OF METHANOL DEHYDRATION ON ACID SITES OF COMPOSITE CATALYSTS H-ZSM-5–Al_2O_3

A.I. Trypolskyi*, N.V. Vlasenko, O.O. Zhokh

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, atripolski@gmail.com

Heterogeneous catalytic dehydration of methanol proceeds through the intermediate formation of dimethyl ether (DME), with subsequent loss of water and formation of olefins (MTO process). Zeolites are usually used as catalysts. The choice of their structural type and porosity depends on the desired target product. One of the most active catalysts for methanol conversion is H-ZSM-5.

In addition to the zeolite itself, the composition of industrial catalysts includes a matrix, that also exhibits catalytic activity. The kinetics of the process are significantly affected by physical and chemical characteristics of catalyst, which are determined by the conditions both of its synthesis and subsequent operation.

he kinetics of the transformation of methanol into DME has been studied over H-ZSM-5 zeolite, alumina, and their composites prepared by precipitation of aluminium hydroxide in the presence of finely ground HZSM-5 zeolite, followed by calcination at 500 °C. The mass ratio of H-ZSM-5/Al_2O_3 in the obtained composites was 3/1, 1/1 and 1/3. The acid characteristics of the catalysts has been studied by the method of quasi-equilibrium thermal desorption (QE-TD) of ammonia [1] in the temperature range of 50–500°C, in a vacuum thermogravimetric setup with McBean balances. The total concentration of acid sites was determined by ammonia sorption at 50ºC. The concentrations of acid sites of different types were determined by ammonia adsorption in the corresponding temperature ranges. The ammonia adsorption heat has been calculated by the method [2]. The nature of acid sites has been investigated using FTIR spectroscopy of adsorbed pyridine. Kinetic experiments were carried out in a flow unit at atmospheric pressure in the temperature range of 140–190 °C, WHSV = 2–43 h^{-1} in the absence of diffusion limitations.

A number of kinetic models allowing for different reaction mechanisms based on the Langmuir-Hinshelwood or Eley–Ridel formalism have been developed and experimentally verified. Within the Langmuir-Hinshelwood formalism, both dissociative and associative mechanisms of methanol adsorption were considered. Using the developed models, as well as the models described in the literature, calculations were made to match the given mechanisms of the obtained experimental kinetic data.

It was established that two kinetic models, based on dissociative and associative mechanisms of methanol adsorption, adequately describe the entire set of experimental kinetic data for all studied catalysts. Kinetic parameters of dimethyl ether synthesis for two mechanisms (both associative and dissociative) were calculated: activation energy, adsorption heat, adsorption entropy, pre-exponential factors, and entropy of the activated complex. Analysis of the calculated kinetic parameters of the process for all the studied catalysts showed that the full correspondence of the values of constants to their physical meaning is observed only for the dissociative mechanism.

The correlation of DME formation rate with a total concentration of acid sites in studied catalysts (Fig. 1) indicates the participation of the entire set of acid sites, regardless of their nature, in the conversion of methanol into DME. This agrees with the literature data [3] that both Lewis and Brønsted acid sites participate in the methanol dehydration.

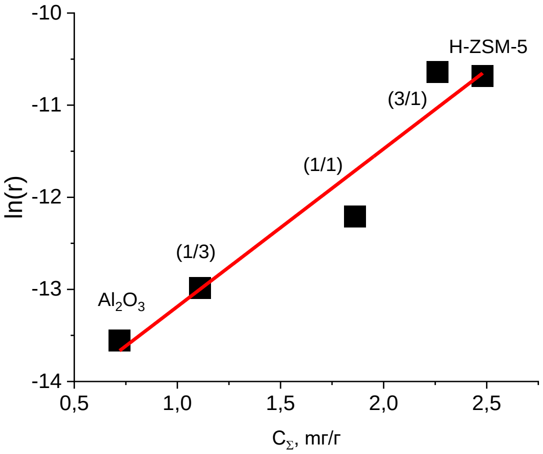


Fig. 1. Dependence of the catalytic activity of studied catalysts on the concentration of acid sites

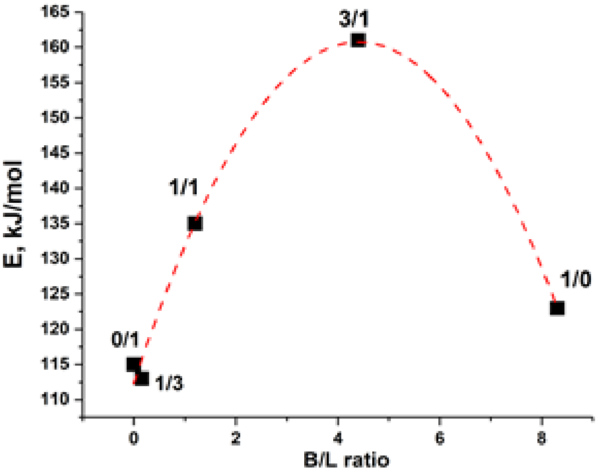


Fig. 2. Dependence of activation energy of methanol dehydration on the ratio of Brønsted and Lewis sites in HZSM-5–Al_2O_3 catalysts

It was founded that the activity of catalysts increases with an increase in the concentration of Brønsted sites. That is due to the difference in the nature of activated complexes of methanol that are formed with the participation of Brønsted and Lewis acid sites. The activation of methanol over Brønsted sites occurs by the addition of a proton from an acidic hydroxyl with the formation of an oxonium ion $CH_3OH_2^+$. Meanwhile, on the Lewis sites, methanol is adsorbed in molecular form [4]. Since the activation of methanol on the acid sites of catalyst is the limiting stage of the reaction, it is obvious that energy of activated complex will determine the rate of this stage. This is manifested as an extreme dependence of the energy parameters of the process on the ratio of Brønsted and Lewis sites (Fig.2).

References:

1. 1. N.V. Vlasenko, Yu.N. Kochkin, G.M. Telbiz, et al., RSC Advances. 9 (2019), 35957.
2. G.I. Kapustin, T.R Brueva, Thermochem. Acta. **379** (2001), 71.
3. J. Spivey, Chern. Eng. Comm. **110** (1991), 123.
4. M.T. Aronson, R.J. Gorte, D W. E. Farneth, J. Catal. **98** (1986), 434.

S-17

MESOPOROUS PHOSPHATE-STABILIZED TUNGSTEN-ZIRCONIUM OXIDE COMPOSITION AS A CATALYSTS FOR GLYCEROL DEHYDRATION

E.V. Senchylo*, N.V. Vlasenko, G.R. Kosmambetova

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, Jane_Senchylo@ukr.net

Acrolein and its derivatives are used to obtain acrylic acid, pyridine, medicines, herbicides, etc. The industrial method of production is based on the reaction of partial vapor phase oxidation of propylene in the presence of multicomponent catalysts. Today, one of the promising ways to obtain acrolein is the dehydration of glycerol, large amounts of which are formed during the production of biodiesel.

This work is devoted to developing catalysts based on mesoporous tungsten-containing zirconium dioxide. The advantage of WO_3-ZrO_2 compositions is the combination of acidic properties with high thermal stability. The activity and selectivity of WO_3-ZrO_2 compositions significantly depend on the surface acidity, which, in turn, is determined by the method of preparation, component content and modifying additives. It is known that Brønsted protonic sites are responsible for the conversion of glycerol into acrolein [1]. Therefore, our task was to synthesize a catalyst possessing a mesoporous structure, that ensures accessibility of acid sites for glycerol molecules, and Brønsted acidity.

The phosphate additives stabilize mesoporous structure of oxides and also surface hydroxyls, which represent Brønsted acid sites. Phosphated $WO_x{\cdot}ZrO_2$ oxide systems with WO_x content from 10 to 25 wt. % were synthesized by template synthesis. $Zr(SO_4)_2{\cdot}4H_2O$ and $(NH_4)_2WO_4$ were used as the starting compounds, and CTMAB was used as a template. The obtained air-dried solids were treated with 0.87M H_3PO_4 followed by drying and calcination at 500°C for 5h.

An increase in the WO_3 content in the samples from 10 to 25% the specific surface area of the samples increases from 140 to 280 m^2/g. The average pore size varies slightly and equals 2–3 nm which does not prevent the penetration of glycerol molecules with a kinetic diameter of 0.61 nm into the catalyst structure.

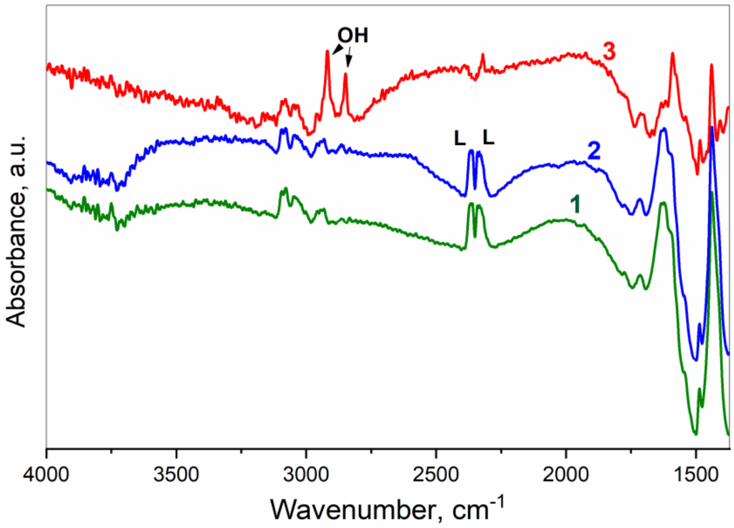


Fig. 1. FTIR- spectra of pyridine adsorbed on samples 10WO_x-ZrO_2-P (1); 19WO_x-ZrO_2-P (2) and 25WO_x-ZrO_2-P (3).

FTIR spectra of adsorbed pyridine for WO_x-ZrO_2-P samples (Fig. 1) show that when WO_x content increases from 19 to 25%, the acid spectra of samples changes significantly.

There are only bands due to the coordination of pyridine with Zr^{4+} and W^{6+} Lewis acid sites in the spectra of $10WO_x$-ZrO_2-P and $19WO_x$-ZrO_2-P. Meanwhile, the spectrum for $25WO_x$-ZrO_2-P contains absorption bands in the region of about 2800–3000 cm^{-1} corresponds to OH groups [2]. This is the result of the formation of surface polytungstate complexes $[\equiv Zr_6^{1/2+} W_6^{6+} O_{20}^{2-}]^{-}H^{+}$ which are characterized by increased Brønsted acid strength due to their reduced Coulomb interactions with protons. On low WO_x content catalysts, where tungsten oxide exists in the form of monomer particles, Brønsted sites are practically absent [3].

All studied samples showed catalytic activity for glycerol conversion. The conversion of glycerol in the temperature range of 280–340 °C was from 7 to 65%. However, the formation of acrolein was observed only over $25WO_x$-ZrO_2-P (Fig. 2), for which, according to the FTIR spectroscopy, the Brønsted hydroxyls are present. When the content of tungsten oxide decreases to 19 wt. %. the composition of the products changes dramatically, and allyl alcohol becomes the only product of glycerol conversion. It is likely that in this case, surface sites Zr^{4+} and W^{6+} play the role of redox centers, which causes hydrogenolysis of some hydroxyl-containing intermediate and/or glycerol. For the $10WO_x$-ZrO_2-P catalyst, along with allyl alcohol, the reaction products contain acetaldehyde.

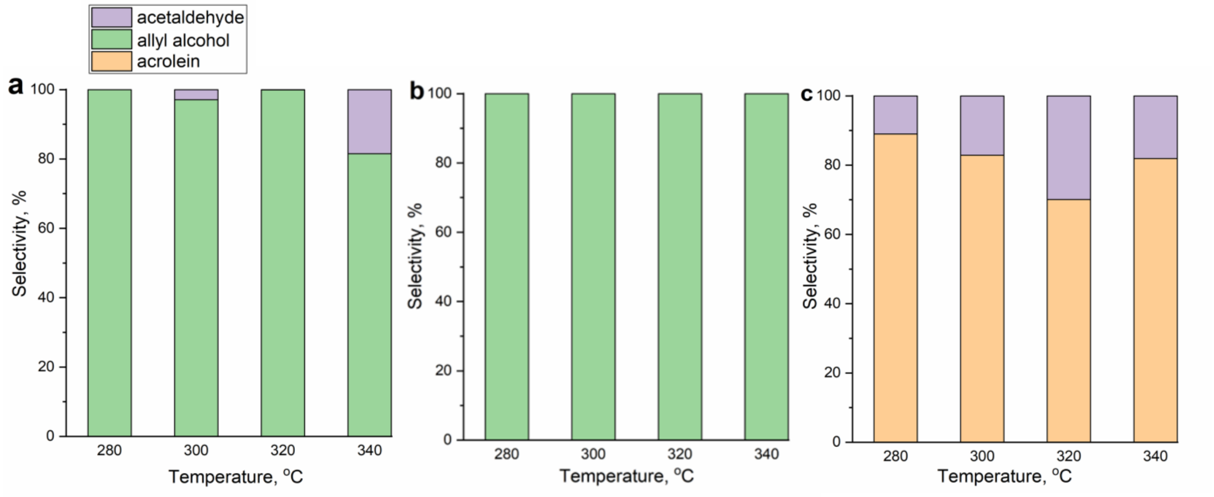


Fig. 2. Products selectivity for: $10WO_x$–ZrO_2-P (a); $19WO_x$–ZrO_2-P (b) and $25WO_x$–ZrO_2-P (c).

Thus, the composition of phosphate-stabilized tungsten-zirconium oxide catalysts determines the nature of the surface functional groups that are the active sites responsible for the direction of glycerol conversion. Catalysts with a low content of WO_x possess strong Zr^{4+} and W^{6+} sites which play the role of redox sites, that lead to the formation of allyl alcohol. Increased (more than 20 wt.%) concentrations of tungsten oxide contribute to the formation of surface polytungstates, which are strong Brønsted acid sites. This changes the process selectivity towards the formation of acrolein.

References:

1. A. Alhanash, E. F. Kozhevnikova, I. V. Kozhevnikov, Appl. Catal. A: Gen. **378** (2010) 11.
2. K. I. Hadjiivanov, D. A. Panayotov, M. Y. Mihaylov, et al., Chem. Rev. **121** (2021) 1286.
3. F. Can, X. Courtois, D. Duprez, Catalysts **11**(2021) 703.
4. F. Di Gregorio, V. Keller, J. Catal. **225** (2004) 45.

S-18

HETEROGENEOUS PHOTOELECTROCATALYSIS OF POROUS ZnO PLATE WITH MICRO- AND NANO ELEMENTS

L. Hrytsak*, V. Vasil’ev, B. Turko

Ivan Franko National University of Lviv, Dragomanova St., 50, Lviv, 79005 Ukraine, liliatoporovska@gmail.com

Photocatalysis provides a potential offer to purify water with a low expense, high working efficiency in removing pollutants and reusable ability. In recent years, increasing attention among semiconductor materials in heterogeneous photocatalysis has been paid to ZnO [1]. ZnO nanostructures have been shown promising photocatalytic activities due to their non-toxic, inexpensive, and highly efficient nature [2].

Methyl orange (MO) dye served as model organic pollutant was used in our expirements. Photocatalytic, photoelectrocatalytic and electrocatalytic studies were carried out for zinc oxide porous plate with micro- and nanoelements. The method of synthesis of obtained sample is described in detail in our previous work [3]. The influence of the electric field on the photocatalytic parameters of ZnO microstructures was investigated.

On Fig. 1 was shown that the best values of efficiency of dye decomposition were obtained during photoelectrocatalysis – 66.67%, in comparison with photocatalysis (48.8%) and electrocatalysis (56.6%)(Fig.1). It was found that the higher value of the catalyst efficiency in photoelectrocatalysis compared to photocatalysis is associated with a more efficient redistribution of charges when applying a voltage of 1.5 V and a higher concentration of hydroxyl radicals on the catalyst surface.

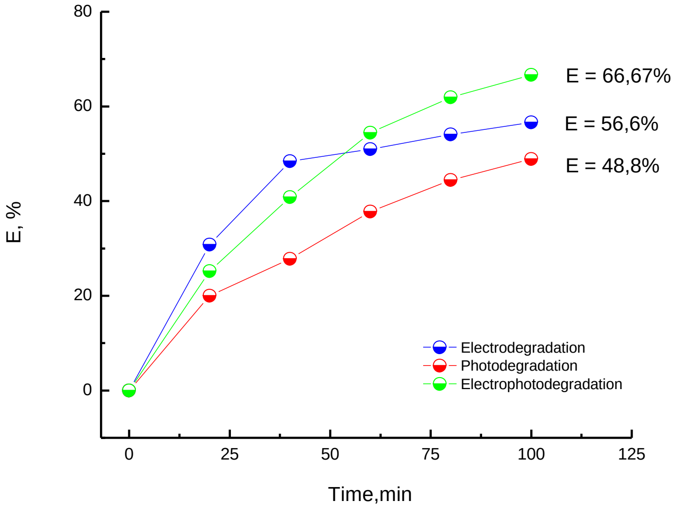


Fig. 1. Dependence of MO degradation efficiency on irradiation time during electrocatalysis (blue dots), photocatalysis (red dots), and electrophotocatalysis (green dots) using a catalyst based on a porous ZnO plate.

References:

1. A. A. Yaqoob, T. Parveen, K. Umar, I. Mohamad, N. Mohamad, Water, **12** (2020) 495.
2. M. Samadi, M. Zirak, A. Naseri, E. Khorashadizade, A. Z. Moshfegh, **605** (2016) 2.
3. L. Hrytsak, B. Turko, V. Vasil’yev, R. Serkiz, A. Kostruba, J. Phys. Stud, **26**, (2022) 3401.

S-19

REMOVAL OF HARMFUL EMISSIONS FROM ELECTRODE PRODUCTION IN A CATALYTIC REACTOR WITH A FERRITE LOADING

O.I. Ivanenko[1]*, S.D. Dovholap[1], A.I. Trypolskyi[2], P.E. Strizhak[2],
T.A. Overchenko[1]

[1]Faculty of Chemical Engineering, Igor Sikorsky Kyiv Polytechnic Institute, Beresteiskyi Avenu, 37/4, Kyiv, 03056 Ukraine, olenka.vasaynovich@gmail.com
[2]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine

In the context of a military conflict, supporting the operation of an enterprise for the production of carbon-graphite electrode products, which is used mainly in the metallurgical industry, is a necessary component of victory. It is known that the processes of heat treatment of carbon materials generate significant emissions of toxic pollutants, one of which is carbon monoxide. Therefore, the development of an accessible highly efficient system for the catalytic oxidation of harmful components of industrial flue gases and its design features in accordance with the parameters of furnace equipment will eventually increase the environmental safety of carbon-graphite production and reduce the man-made load at the regional level, which is under constant artillery and missile attacks.

In the studies of the CO oxidation process, a composite ferrite catalyst was used as the loading of the catalytic reactor, and the zeolite rock of the Sokyrnytsky deposit of the Transcarpathian region with a predominant content of clinoptilolite was used as a particle fixator. To obtain a catalyst, a dried batch of zeolite was brought into contact in a static mode with regeneration solutions of ion-exchange processing of electroplating waste of a machine-building enterprise, containing iron, copper, and chromium ions, with subsequent precipitation of ferrites with an alkaline solution according to [1].

The calculation of the catalytic CO oxidation reactor was performed for the real flow rate of flue gases of PJSC "Ukrainian Graphite" (Zaporizhzhia) of multi-chamber furnaces for baking electrode blanks with the temperature 270−390 ºC, coming from the "first fire" furnace chamber heated by flue gases. The flue gas passed through 7 fire channels of the furnace chamber. For such medium exothermic processes, the mass and heat transfer between the gas flow and the outer surface of the catalyst grains is quite intense. In this case, it is sufficient to use a quasi-homogeneous single-phase model to describe the catalytic process in the reactor [2, 3]. To calculate the catalytic oxidation of CO, the technological scheme presented in Fig. 1.

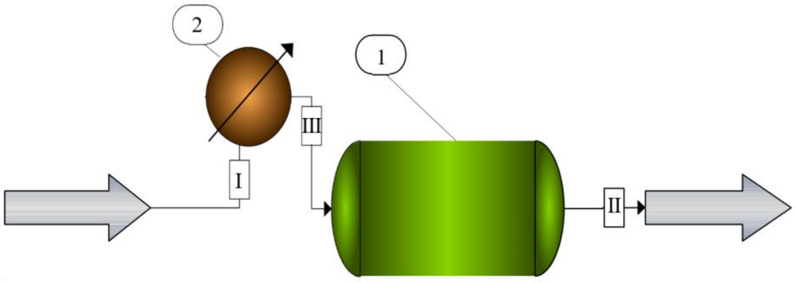


Fig. 1. Process diagram of catalytic oxidation: 1 − kinetic reactor; 2 − heat exchanger; I – gas composition at normal conditions before feeding into kinetic reactor;
II – gas composition after the catalyst; III − gas composition at the outlet of heat exchanger at the temperature 350ºC

Using a model of a plug-flow catalytic fixed-bed reactor, the parameters of the gas mixture flow through a reactor loaded with a zeolite-based ferrite composite catalyst during the catalytic oxidation of CO are calculated. A feature of the proposed solution was the use of the developed catalytic reactor for processing a large volume of flue gases with CO concentrations of about 0.13% vol., at enterprises producing electrode carbon graphite (Fig. 2).

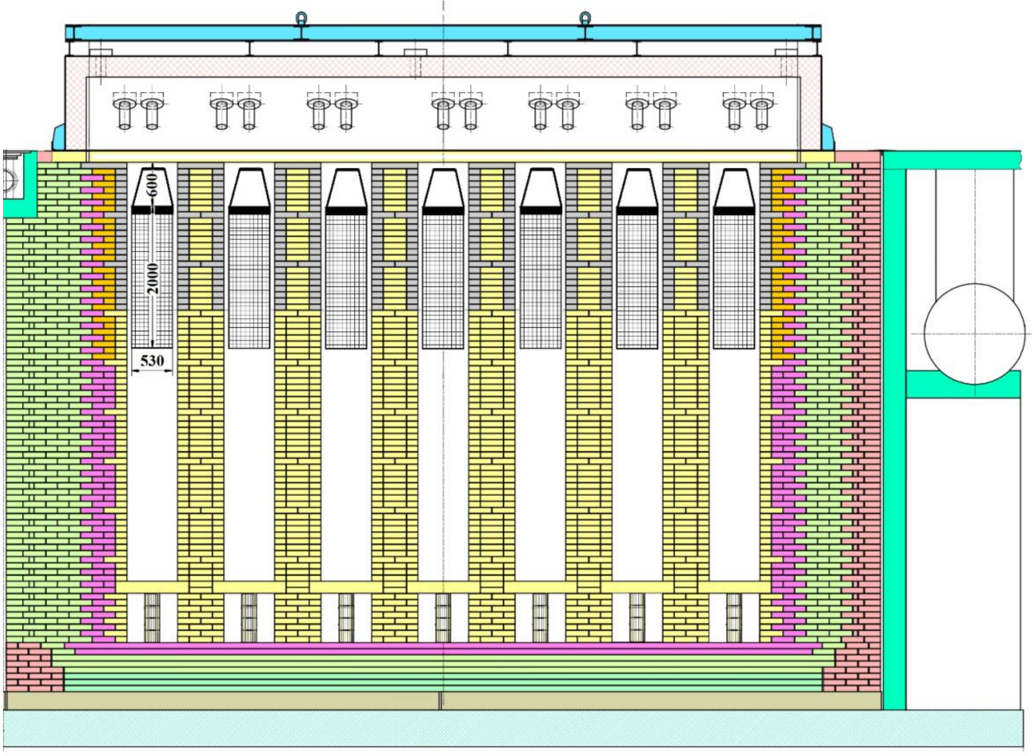


Fig. 2. Side view of Riedhammer furnace chamber with catalyst containers installed in the fire channels

The proposed calculation and design solutions, in addition to the production of carbon electrodes, can be used in environmental technologies at other environmentally hazardous facilities to neutralize harmful emissions.

References:

1. O. Ivanenko, A. Trypolskyi, N. Gomelya, A. Karvatskii, A. Vahin, O. Didenko, V. Konovalova, P. Strizhak, Development of a Catalyst for Flue Gas Purification from Carbon Monoxide of Multi-Chamber Furnaces for Baking Electrode Blanks, Journal of Ecological Engineering, 2020, 22(1), 174–187.
2. O. Ivanenko, A. Trypolskyi, O. Khokhotva, P. Strizhak, S. Leleka, I. Mikulionok, The kinetic parameters of the smoke gases purification process from carbon monoxide on a zeolite-based manganese oxide catalyst, Eastern-European Journal of Enterprise Technologies, 2020, 6/6(108), 50-58.

O. Ivanenko, A. Trypolskyi, O. Khokhotva, I. Mikulionok, A. Karvatskii, V. Radovenchyk, S. Plashykhin, T. Overchenko, S. Dovholap, P. Strizhak, The development of carbon monoxide oxidation reactor for multi-chamber furnaces for baking electrode blanks, EUREKA: Physics and Engineering, 2023, 1, 13-23.

S-20

DETERMINATION OF THERMOCHEMICAL PROPERTIES OF DIVALENT METAL ORTHOPHOSPHATES BY SEMI-EMPIRICAL METHODS

A.A. Kozma[1]*, N.P. Golub[1], Ye.O. Golub[2], D.V. Davyda[1], V.I. Gomonaj[1]

[1]Department of Physical and Colloid Chemistry, Educational and Scientific Institute of Chemistry and Ecology (Faculty of Chemistry), Uzhhorod National University, Pidhirna St., 46, Uzhhorod, 88000 Ukraine, Anton_Kozma@uzhnu.edu.ua

[2]Department of Pharmaceutical Disciplines, Faculty of Medicine, Uzhhorod National University, Pidhirna St., 46, Uzhhorod, 88000 Ukraine

In this work, a number of thermochemical properties of orthophosphate catalysts [1] of the general formula $Me_3(PO_4)_2$ (Me – Be, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Ge, Sr, Pd, Cd, Sn, Ba, Eu, Hg, Pb) were determined using semi-empirical methods.

The main calculations were performed using three different methods: by Kapustynskyi, by Fersman, and by Yatsymirskyi. The obtained values of the crystal lattice energies U were used in the Born–Haber cycle to calculate the enthalpy of formation ΔH_f of these compounds. The Shannon's ionic radii, heat of formation of gaseous ions, energy coefficients of cations and orthophosphate anion were used as auxiliary quantities [2].

The results were compared with known experimental and theoretical data. It turned out that the Kapustynskyi's method gives the smallest deviations from known values, and the Fersman's method gives the largest deviations. However, both approaches can be combined. The combined use of these methods allowed us to significantly minimize the magnitude of errors. In particular, for the vast majority of $Me_3(PO_4)_2$ phosphates, the maximum deviations from the literature data did not exceed ±(1-6) %. The optimal methods were used to determine previously unknown values of ΔH_f for five compounds: $Be_3(PO_4)_2$ (-3378 kJ/mol), $Fe_3(PO_4)_2$ (-2689 kJ/mol), $Cd_3(PO_4)_2$ (-2612 kJ/mol), $Eu_3(PO_4)_2$ (-4605 kJ/mol), $Hg_3(PO_4)_2$ (-1816 kJ/mol) [2]. In addition, from the thermochemical point of view, the possibility of formation of two new orthophosphates $Ge_3(PO_4)_2$ and $Pd_3(PO_4)_2$, the existence of which is not reported in the literature, was predicted.

The determined values of ΔH_f, in combination with the initial data from [3, 4], were used to calculate other thermochemical functions of $Me_3(PO_4)_2$: the Gibbs energy of formation ΔG_f, the entropy of formation ΔS_f, and the logarithm of the equilibrium constant of formation reaction $log[K_f]$.

The obtained results can be used for thermochemical analysis of promising catalytic systems formed on the basis or with the participation of the considered divalent metal orthophosphates.

References:

1. V. Gomonaj, H. Toulhoat, ACS Catalysis. **8** (2018) 8263.
2. A.A. Kozma, N.P. Golub, Ye.O. Golub, D.V. Davyda, N.V. Rusaniuk, V.V. Barna, The 75th Final Scientific Conference of the Teaching Staff of the Faculty of Chemistry of the Uzhhorod National University. Uzhhorod, Ukraine. 2021, P. 50-52, and references cited therein.
3. I. Barin, Thermochemical Data of Pure Substaces, John Wiley & Sons, Weinheim (1995).
4. M.W. Chase Jr., NIST-JANAF Thermochemical Tables, 4th edn., Journal of Physical and Chemical Reference Data, Monograph 9, American Institute of Physics (1998).

S-21

CATALYTIC OXIDATION OF SULFIDES AT PRESENCE OF Co^{II}, Fe^{III} AND Mn^{II} COMPLEXES

Yu.L. Lishchenko[1,2]*, S.O. Sotnik[1,2], A.S. Poturai[2,3], S.V. Ryabukhin[2,3,4],
D.M. Volochnyuk[2,3,4], S.V. Kolotilov[1]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, yuliyl908@gmail.com
[2]Enamine Ltd., Winston Churchill St., 78, Kyiv, 02094 Ukraine
[3]Institute of Organic Chemistry, Murmanska St., 5, Kyiv, 02660 Ukraine
[4]Institute of High Technologies, Taras Shevchenko National University of Kyiv, Volodymyrska St., 60, Kyiv, 01601 Ukraine

Complexes of metals with polydentate N-containing ligands have been widely studied as catalysts of wide range of organic reactions. Such systems have good outlook of use for catalytic oxidation of organic sulfides to chiral sulfoxides, which as widely used in drug design and medicinal chemistry.

In this work, new complexes with Salen fragments (Co^{II}(salen1) and Co^{II}(salen2), Fig 1(a)), Fe^{III}(salen1), as well as previously reported complex Mn^{II}(L) [1], containing derivative of valine (Fig. 1(b)), were studied.

It was shown that complexes (Co^{II}(salen1), Co^{II}(salen2), Fe^{III}(salen1)) had high catalytic activity in oxidation of thioanisole by H_2O_2 in water. The reaction mixtures and isolated products were studied by NMR and GCMS. Phenylmethylsulfone formed at presence of Fe^{III}(Salen1) with 95 % yield. Unexpectedly, in the case of Co(II)-Salen complexes oxidation process stopped on the stage of sulfoxide formation, and its yield exceeded 95 %. Oxidation of thioanisole by H_2O_2 without catalyst leads to formation of phenylmethylsulfone as a sole product.

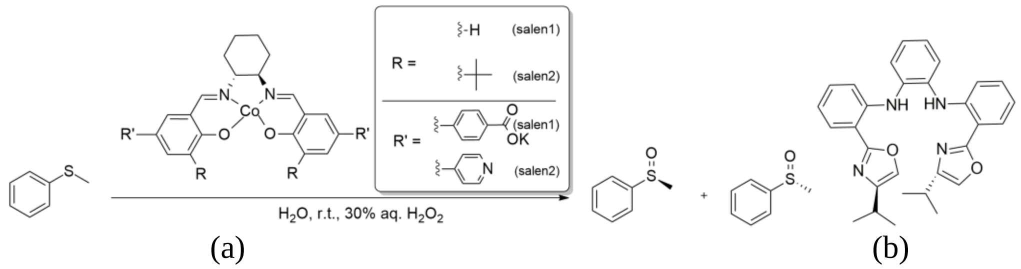


Fig. 1. Structural formulas of complexes Co^{II}(salen1) and Co^{II}(salen2) along with scheme of thioanisole oxidation (a) and structural formula of Mn^{II}(L) (b)

Oxidation of the non-cyclic sulfides by H_2O_2 at presence of Mn^{II}(L) resulted in formation of chiral sulfoxides with up to 94 % enanthiomeric excess of one of the enantiomers, while oxidation of the substituted dihydrobenzothiophenes gave the asymmetric sulfoxides with up to 93 % enantiomeric excess. The methods of sulfides oxidation at presence of Mn^{II}(L), proposed in [1], were optimized for oxidation of different functionalized derivatives and scaled-up for preparation of chiral compounds (0.5-1 g scale).

The studied complexes have outlook of application for catalytic preparative asymmetric transformation of organic sulfides into sulfoxides and sulfones.

References:

1. W. Dai, J. Li, B. Chen, G. Li, Ying Lv, L. Wang, S. Gao, Org. Lett 15 (2013) 5658.

S-22

FABRICATION OF ELECTROCATALYSTS FOR GREEN HYDROGEN PRODUCTION USING DEEP EUTECTIC SOLVENTS

V.S. Protsenko*, D.O. Makhota, O.D. Sukhatskyi, L.S. Bobrova,
T.E. Butyrina, F.I. Danilov

Ukrainian State University of Chemical Technology, Gagarin Ave., 8, Dnipro, 49005 Ukraine, Vprotsenko7@ukr.net

The development of high-performance electrocatalysts for water electrolysis in green hydrogen production is considered as an urgent and pivotal task in modern science [1]. Although various techniques for the preparation of electrocatalysts are known, electrochemical methods (electrochemical deposition and electrochemical anodic and cathodic surface treatment) seem to be the most promising since they have great potential to flexibly adjust the chemical composition, microstructure, and functional properties of the produced electrocatalytic materials [2]. Recently, electrochemical systems based on the so-called deep eutectic solvents (DESs) have been proposed for the electrochemical synthesis of electrocatalysts, offering a versatile alternative to both aqueous solutions and electrolytes based on organic solvents.

Deep eutectic solvents (DESs) are eutectic mixtures of Lewis or Brønsted acids and bases, typically containing relatively large asymmetric ions (for instance, choline cation). Due to the interactions between the components, the melting point of the mixture is appreciably reduced as compared to the melting points of individual constituents, and electrolytic dissociation occurs. Thus, in contrast to "conventional" ionic liquids, which consist of discrete cations and anions, DESs are ionic eutectic mixtures of several components [3, 4].

The significant interest in utilizing DES-assisted systems for the production of electrocatalysts is driven by the following advantages and positive attributes of this novel class of ionic liquids: a broad electrochemical window enabling the cathodic deposition of highly electronegative metals, high solubility of salts and oxides in DESs, relatively high electrical conductivity, cost-effectiveness, availability, non-flammability, non-toxicity, and biodegradability [5]. Importantly, the physicochemical and operational properties of DESs can be flexibly tuned by altering the nature and concentration of components, as well as by introducing controlled amounts of water and surfactants. It should also be noted that transitioning from "traditional" aqueous electrolytes to DES-based solutions substantially alters the nature and structure of the double layer at the electrode/electrolyte interface, thereby opening up fundamentally new possibilities for controlled manipulation of the mechanisms and rates of both charge transfer at the electrode surface and electrocrystallization stage. As a result, materials with a unique set of properties can be obtained, which are markedly distinct from those deposited in "conventional" aqueous electrolytes.

We have explored the possibilities of electrochemical synthesis of electrocatalysts for cathodic hydrogen evolution by using DES-assisted electrolytes. In particular, the electrodeposition of nickel, iron and nickel-iron alloy from a DES based on the eutectic mixture of choline chloride and ethylene glycol (known as "ethaline") has been investigated [6]. It has been demonstrated that the iron content in the coatings increases with the rise in the concentration of Fe(II) ions and added water in the electrolyte, as well as with an increase in cathodic current density. Uniform nanocrystalline coatings containing up to 10–15 wt.% iron in the Ni–Fe alloy have been successfully deposited. The electrocatalytic activity of the coatings towards the hydrogen evolution reaction in an aqueous alkaline solution can be significantly improved even at relatively low iron content (~2–7 wt.%).

Composite nanocrystalline Ni–TiO_2 coatings were electrochemically deposited from a DES-based electrolyte [7, 8]. It has been found that the addition of extra water to the colloidal electrolyte not only reduces viscosity and enhances electrical conductivity but also significantly increases the content of the dispersed phase in the composite (up to 10 wt.%). The augmentation of the nanodispersed TiO_2 phase content in the coating contributes to the improvement of its corrosion resistance [9] and substantial enhancement of electrocatalytic activity in the hydrogen evolution reaction [7, 8]. A novel theoretical model for the electrodeposition of composite coatings has been developed, implying the irreversible adsorption of dispersed phase particles on the electrode surface [10].

The possibility of significant improvement in electrocatalytic activity towards the hydrogen evolution reaction was demonstrated through the alloying of a nickel matrix, electrodeposited from DES, with molybdenum, cerium, and lanthanum [11–13]. The electrodeposition of electrocatalytic chromium-carbide coatings from an electrolyte containing trivalent chromium salt dissolved in a DES was also investigated [14]. The electrocatalytic activity of Cr–C coatings in the hydrogen evolution reaction can be flexibly tuned by altering the chemical composition and surface morphology, achieved by varying the content of added water in the electrolyte.

It has been established that the electrocatalytic activity of copper-nickel alloy towards cathodic hydrogen evolution can be enhanced through anodic electrochemical treatment (etching) in a DES (ethaline) [15].

Thus, the obtained results indicate the remarkable potential of using deep eutectic solvents for the electrochemical synthesis of electrocatalysts, which could be effectively employed in green hydrogen energy technology.

References:

1. C.B.B. Farias, R.C.S. Barreiros, M.F. da Silva, A.A. Casazza, A. Converti, L.A. Sarubbo, Energies. **15** (2022) 311.
2. R. Li, Y. Li, P. Yang, D. Wang, H. Xu, B. Wang, F. Meng, J. Zhang, M. An, Journal of Energy Chemistry. **57** (2021) 547.
3. E.L. Smith, A.P. Abbott, K.S. Ryder, Chemical Reviews. **114** (2014) 11060.
4. B.B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J.M. Klein, A. Horton, L. Adhikari, et al., Chemical Reviews. **121** (2021) 1232.
5. C. Zhang, Y. Fu, W. Gao, T. Bai, T. Cao, J. Jin, B. Xin, Molecules. **27** (2022) 8098.
6. F.I. Danilov, D.A. Bogdanov, O.V. Smyrnova, S.A. Korniy, V.S. Protsenko, Journal of Solid State Electrochemistry. **26** (2022) 939.
7. V.S. Protsenko, T.E. Butyrina, L.S. Bobrova, F.I. Danilov, Materials Today: Proceedings. **62** (2022) 7712.
8. V.S. Protsenko, T.E. Butyrina, D.A. Bogdanov, S.A. Korniy, F.I. Danilov, Surface Engineering and Applied Electrochemistry. **58** (2022) 440.
9. V.S. Protsenko, T.E. Butyrina, L.S. Bobrova, S.A. Korniy, F.I. Danilov, Coatings. **12** (2022) 800.
10. V.S. Protsenko, F.I. Danilov, Journal of Electroanalytical Chemistry. **918** (2022) 116463.
11. V.S. Protsenko, L.S. Bobrova, T.E. Butyrina, A.S. Baskevich, S.A. Korniy, F.I. Danilov, Heliyon. **9** (2023) e15230.
12. V.S. Protsenko, L.M. Pavlenko, L.S. Bobrova, S.A. Korniy, F.I. Danilov, Journal of Solid State Electrochemistry. (2023) in press. https://doi.org/10.1007/s10008-023-05499-6.
13. V.S. Protsenko, L.M. Pavlenko, L.S. Bobrova, S.A. Korniy, T.E. Butyrina, F.I. Danilov, Voprosy Khimii i Khimicheskoi Tekhnologii, (**3**) (2023) 103.
14. V.S. Protsenko, L.S. Bobrova, S.A. Korniy, F.I. Danilov, Materials Letters. **313** (2022) 131800.
15. V.S. Protsenko, T.E. Butyrina, D.O. Makhota, S.A. Korniy, F.I. Danilov, Portugaliae Electrochimica Acta. **41** (2023) 29.

S-23

INSIGHT INTO STRUCTURAL AND PHYSICOCHEMICAL PROPERTIES OF ZrO_2-SiO_2 MONOLITHS WITH HIERARCHICAL PORE STRUCTURE. EFFECT OF ZIRCONIUM PRECURSOR

A. Ciemięga[1], K. Maresz[1], M. Sitarz[2], M. Krzywiecki[3], J. Mrowiec-Białoń[1]*

[1]*Institute of Chemical Engineering Polish Academy of Sciences, Bałtycka 5, 44-100 Gliwice, Poland, j.bialon@iich.gliwice.pl*

[2]*AGH University of Science and Technology, Faculty of Materials Science and Ceramics, A. Mickiewicza 30 Avenue, 30-059, Cracow, Poland*

[3]*Institute of Physics, CSE, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland*

Zirconia-silica mixed oxides, due to unique properties, are widely applied as advanced ceramics, catalysts, catalyst carriers, adsorbents, coatings, support for controlled release of drugs and others [1-3]. Synthesis of monolithic materials with hierarchical pore structure, large specific surface area, and high dispersion of zirconia is still a challenge. In particular, such materials are required for continuous-flow catalytic processes.

In this work, we present the impact of a type of zirconium salt on the structure and physico-chemical properties of zirconia-silica monoliths obtained using modified sol-gel process combined with phase separation. Three inorganic zirconium salts i.e. oxychloride (Cl), oxynitrate (N) and sulfate (S), were used in the synthesis of zirconia-silica monoliths with hierarchical pore structure and a Zr:SiO_2 mass ratio of 0.02 (Figure 1). The influence of TEOS prehydrolysis was also studied. The structural parameters of the monoliths: macro- and micropore size distribution, pore volume, and specific surface area were determined from nitrogen adsorption and mercury porosimetry. The dispersion of zirconium atoms in the silica skeleton and surface acidity were studied by spectroscopic methods (FTIR, XPS, UV-Vis). Flow properties of the monoliths were also investigated.

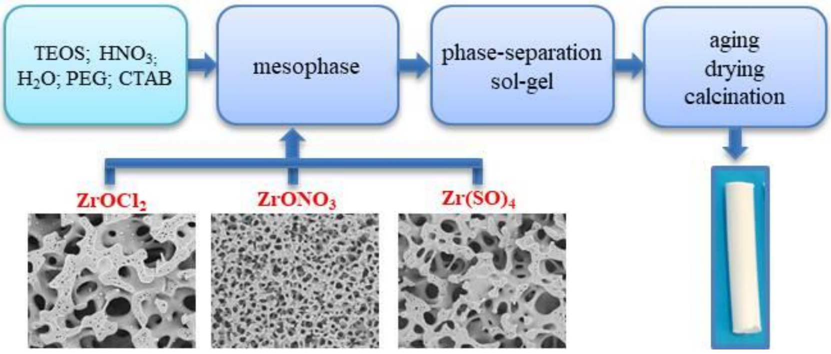


Figure 1. Scheme of zirconia-silica monoliths fabrication.

Detailed analysis of the SEM images and porosimetry data showed a complex relationship between the structural properties of materials and the type of salt and synthesis method applied. The size of the macropores depended significantly on the type of zirconium salt and an increase in the pore diameter was observed in the following order: oxynitrate<sulphate<oxychloride. A similar relation was observed for the dispersion (D) of zirconium in the skeleton of the monoliths and the surface acidity of the materials. This was influenced by the different structure of the zirconium species present in the aqueous reaction mixture.

Table 1. Properties of zirconia-silica monoliths

Sample	S_{BET} [m^2/g]	V_{micro} [cm^3/g]	V_t [cm^3/g]	d_{micro} [nm]	d_{macro} [μm]	D (Zr-O-Si)	Surface acidity	
							Lewis	Brönsted
Zr/Si-Cl-h	547	0.26	0.84	1.5	10.2	26.4	85	103
Zr/Si-N	592	0.29	0.77	1.5	1.8	24.1	35	71
Zr/Si-N-h	574	0.28	0.67	1.5	2.5			
Zr/Si-S	559	0.27	0.81	1.5	7.5	20.7	33	72
Zr/Si-S-h	564	0.27	0.68	1.5	5.0			

V_{micro} - micropores volume; V_t - total pore volume; d_{micro} - micropore diameter; d_{macro} - macropore diameter; D - dispersion of Zr.

The inspection of structural and physico-chemical properties of synthesized materials have clearly indicated that the use of oxychloride and prehydrolysis of TEOS (h) allowed to obtain material with the largest volume and diameter of macropores, the thickest skeleton walls, and thus the lowest flow resistance. Moreover, these materials featured significantly higher surface concentrations of the Brönsted and Lewis acidic centres. The presence of micropores with a diameter of 1.5 nm in the skeleton provided a large surface area of 550 m^2/g. Fabrication of these new materials paves the way for application in flow-catalytic processes which require strong acidic centres.

Acknowledgements. This work was financed by the National Science Centre, Poland, project No 2021/43/D/ST8/01727.

References:

1. M. Catauro, F. Barrino, G. Dal Poggetto, M. Milazzo, I. Blanco, S.V. Ciprioti, Ceram. Int., **46** (2020) 29459-29465.
2. I.M. El-Naggar, E.A. Mowafy, Y.F. El-Aryan, M.G. Abd El-Wahed, Solid State Ion., **178** (2007) 741-747.
3. F. Ciesielczyk, J. Gościańska, J. Zdarta, T. Jesionowski, J. Colloid Surf. A., **545** (2018) 39-50

S-24

USE OF SPENT ALUMINA IN THE PRODUCTION OF AN ADSORBENT FOR DRYING NITROGEN AT A CATALYTIC REFORMER

Kh.A. Nasullaev[1]*, I.S. Abdurakhmanova[2], Sh.T. Gulomov[1], R.G. Khadjiev[3], D.P. Turdieva[1]

[1]*Uzbek Research Chemical-Pharmaceutical Institute, Tashkent, Uzbekistan, kh.a.nasullayev@gmail.com*
[2]*National University of Uzbekistan, Tashkent, Uzbekistan*
[3]*Bukhara Oil Refinery Ltd., Bukhara, Uzbekistan*

In the conditions of an acute shortage of natural resources, the vector of development of modern industry should be aimed at the development of waste-free technologies, minimizing the impact on the environment, energy and material consumption, which is one of the main provisions of sustainable development. One of the options for solving this problem is the recycling of waste aluminum-containing waste by synthesizing fresh adsorbents. Adsorption drying of various process gases is a necessary element of their preparation of gases for subsequent processing, transportation, use as a target product, etc. Each adsorption process, depending on the characteristics of the gas to be purified and the required degree of purification from harmful impurities, requires the use of an adsorbent of a strictly defined nature. As a rule, for deep drying of gases, the best effect is achieved on finely porous adsorbents.

Nitrogen entering the adsorption drying contains drop moisture, water vapor, hydrogen chloride and sodium chloride aerosol. It is known that for deep drying of gases, the best effect is achieved on finely porous adsorbents. Therefore, we carried out the processing of large-tonnage waste - the spent adsorbent, which is formed at the Shurtan gas chemical complex in the process of cleaning a solution of polyethylene in cyclohexane from deactivated polymerization catalysts, HCl, acetylacetone and pelargonic acid residues.

The composition of the spent adsorbent after drying at 100°C, according to electron microscopy (SEM) and chemical analysis, varied within the limits (wt. %): Al_2O_3- 75.0-85.8; V_2O_5 - 0.5-2.5; TiO_2- 0.3-1.2; Na_2O - 1.0-1.7; CaO- 0.5-1.3; Cl- - 0.8-2.5 and burnable organic deposits - the rest.

The spent adsorbent was crushed in a ball mill, then dissolved in sulfuric or nitric acid. The resulting solutions of aluminum sulfate and nitrate were concentrated by evaporation. The precipitation of aluminum hydroxide was carried out with a 25% ammonia solution, maintaining the pH of the suspension at about 7.5. After maturation, the precipitate was washed, dried and molded into granules by extrusion.

A combination of X-ray phase SEM analysis revealed that pseudoboehmite obtained by precipitation from an aluminum sulfate solution included the $Al_4SO_4(OH)10.5\ H_2O$ phase as an impurity. The content of impurity elements was in the range: S - 0.5-0.9% wt., and Na and Cl less than 0.5% wt. In the composition of pseudoboehmite precipitated from an aluminum nitrate solution, no impurities of sodium, chlorine, vanadium, and titanium compounds were found within the sensitivity of SEM analysis. Optimal conditions have been found to ensure the maximum yield of aluminum monohydroxide of pseudoboehmite modification with a particle size of about 2.5 nm. Granules of the optimal sample of aluminum oxide had a specific surface area of 330 m^2/g, crushing strength of 3.3 kg/granule.

The adsorption capacity before "breakthrough" when tested in laboratory conditions reached 23.3 g H_2O/100g, and 22.7 g H_2O+HCl/100g. The adsorbent obtained from production waste has been successfully tested at the naphtha reformer at the Bukhara Oil Refinery.

S-25

EFFECTS OF CERIUM OXIDE ON THE ACTIVITY OF Fe-Ni/Al_2O_3 CATALYST IN THE DECOMPOSITION OF METHANE

N. Makayeva[1,2]*, G. Yergaziyeva[1,2], S. Soloviev[3], N. Khudaibergenov[4],
M. Annisova[1], M. Mambetova[1,2], K. Dossumov[1]

[1]Institute of Combustion Problems, Almaty, Kazakhstan, nursaya.1996.mk@mail.ru
[2]Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Technology, Almaty, Kazakhstan
[3]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine
[4]Satbayev University, Almaty, Kazakhstan

In association with the move to “green” innovation, seriously work is underway all through the world to discover elective vitality sources and vitality carriers. One of the most promising cutting edge vitality carriers is hydrogen, which is decided by its biological immaculateness, flexibility and tall productivity of vitality transformation forms with its interest. The most common technologies for hydrogen production are steam reforming of methane (SRM), catalytic decomposition of methane (CDM), partial oxidation of methane [1], gasification of coal and other hydrocarbons [2], electrolysis of water, photocatalytic splitting of water, etc.

The catalytic decomposition of methane is a promising technology for the production of hydrogen and nanocarbon without emissions of carbon oxides (CO, CO_2), and at the same time is a promising replacement for steam reforming of methane to produce hydrogen [3].

In this work the influence of cerium oxide on the activity of Fe-Ni/γ-Al_2O_3 oxide catalyst in the reaction of methane decomposition to hydrogen and nanocarbon is shown. The synthesized catalysts were dried at 300 °C (2 hours) and calcined at 500 °C for three hours. The activity of the synthesized catalysts in the decomposition of methane was tested in a laboratory flow-through unit. Determination of the concentration of the starting reagents and analysis of the methane decomposition reaction products were carried out on a chromatograph (Chromos-1000) on columns: a CaA molecular sieve column for the determination of N_2, H_2 and O_2, an HP/Plot Q column for CH_4, CO_2 and CO. It was determined that the introduction of cerium oxide into the composition of Fe-Ni/γ-Al_2O_3, leads to an increase in stability and activity of the catalyst at high temperatures. At 750 ^{o}C, for 300 minutes the Fe-Ni-Ce/γ-Al_2O_3 catalyst remains stable, methane conversion is 96 %, hydrogen productivity is 2.8 mmol/g^{-1}.

According to XRD, SEM and Raman data, the decomposition of methane on the Fe-Ni/γ-Al_2O_3 catalyst forms a 1-2-layer graphene, the growth center of which may be aggregated particles of Fe or Ni oxides. Single-layer nanotubes are formed on the Fe-Ni-Ce/γ-Al_2O_3 catalyst. The introduction of cerium oxide into the composition of Fe-Ni/γ-Al_2O_3 promotes the dispersion of active phases, thereby creating conditions for the nucleation and growth of free carbon in the form of nanotubes, which positively affects the activity and stability of the catalyst system in methane decomposition.

References:

1. Dossumov K., Ergazieva G.E., Ermagambet B.T., Telbayeva M.M., Mambetova M.M., Myltykbayeva L.K., Kassenova Z.M., Chemical Papers, 2020, vol. 74, p. 373.
2. Dossumov K., Ergazieva G.E., Ermagambet B.T., Mambetova M.M., Kassenova, Z., Russian Journal of Physical Chemistry 2020, vol.4, p. 880.
3. H. Roh, K. Jun, W. Dong, J. Chang, S. Park, I. Joe, J MolCatal A Chemical 2002, vol. 42, p. 181.

S-26

CATALYSIS FOR CO_2 UTILIZATION USING BIO-RESOURCES

M. Zabochnicka[1]*, P.E. Strizhak[2], G.R. Kosmambetova[2], S. Szufa[3],
R. Bhosale[4], G. Piechota[5], G. Kumar[6]

[1]*Faculty of Infrastructure and Environment, Czestochowa University of Technology, Brzeźnicka 60a, 42-200 Czestochowa, Poland, magdalena.zabochnicka@pcz.pl*
[2]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine; pstrizhak@hotmail.com*
[3]*Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland*
[4]*Department of Chemical Engineering,University of Tennessee, Chattanooga, TN, 37421, USA*
[5]*GPCHEM, Laboratory of Biogas Research and Analysis, ul. Legionów 40a/3, 87–100 Toruń, Poland*
[6]*Institute of Chemistry Bioscience and Environmental Engineering, University of Stavanger, Norway*

In recent years we have seen the emergence and rapid growth of new areas in catalysis, such as heterogeneous, homogeneous-, electrochemical-, photo-, photoelectro-, and plasmocatalysis. Therefore, catalysis will play a key role in enabling both the short-term and longer-term emerging strategies for CO_2 utilization and the development of new ways for the conversion of CO_2 still represents a great challenge. Catalysis allows the utilization of CO_2 to obtain various products. Synthetic motor fuels and methane can be obtained from CO_2 using hydrogen. Platform molecules, e.g., methanol, formaldehyde, and formic acid, are another example that leads to the production of more complicated organic compounds, including polymeric materials. Many chemicals may be obtained by the carboxylation of alcohols, esters, epoxides, etc. The corresponding processes require not only the development of effective catalysts but also the application of different catalytic approaches.

Reaching net-zero carbon emissions is the main driving force for developing technologies targeted at CO_2 capture, storage and utilization. Catalysis plays a crucial role in CO_2 utilization by activating CO_2 molecules to be involved in redox or acid-base reactions with another reagent. Catalysis eventually transform CO_2 into valuable products. The development of catalytic technologies is one of the main factors in the sustainable development of the society, aimed at a transition from an extensive and rational utilization of the natural resources using modern catalytic approaches. Numerous studies have shown progress in this way by means of various chemical reagents for CO_2 utilization for instance, hydrogen, ammonia, alcohol, *etc*. The utilization of bio-resources for CO_2 activation seems fairly attractive because that approach also utilizes wastes those produced by the wood, agriculture, food industry, *etc*. However, much less attention is paid to CO_2 utilization using bio-resources. In this view, this article describes different heterogeneous catalytic processes for CO_2 utilization, using various bio-resources *viz*. biogas, lignocellulose, lignin, cellulose, bio-ethanol, bio-butanol and glycerol. Such an approach is an element of the sustainable circular carbon economy.

Summarizing the results of current studies, Fig. 1 presents the pathways of CO_2 utilization using biogas, lignocellulose, bioethanol, and bio-glycerol. All these bioresources give the possibility to convert CO_2 into a synthesis gas. Regardless of the type of renewable raw materials, the most active and selective catalysts for that process are noble metals, nickel, and cobalt. Biogas may also be used for CO_2 conversion to methane which is effective over nickel-, iron-, and cobalt-containing catalysts. Alcohol-based bioresources, e.g., bioethanol and glycerol, may be effectively used for CO_2 utilization producing organic carbonates and polycarbonates over catalysts with amphoteric properties. A recent study also showed that ethanol and acetic acid may be produced by the conversion of lignin with CO_2**.** Contrary to using traditional regents like hydrogen and ammonia, the use of bioresources significantly limits possible products of CO_2 transformations. On one hand, that is associated with the specific chemistry of biogas and lignocellulose. On the other hand, that may be associated with low attention paid to the possibility of using bioresources for CO_2 utilization.

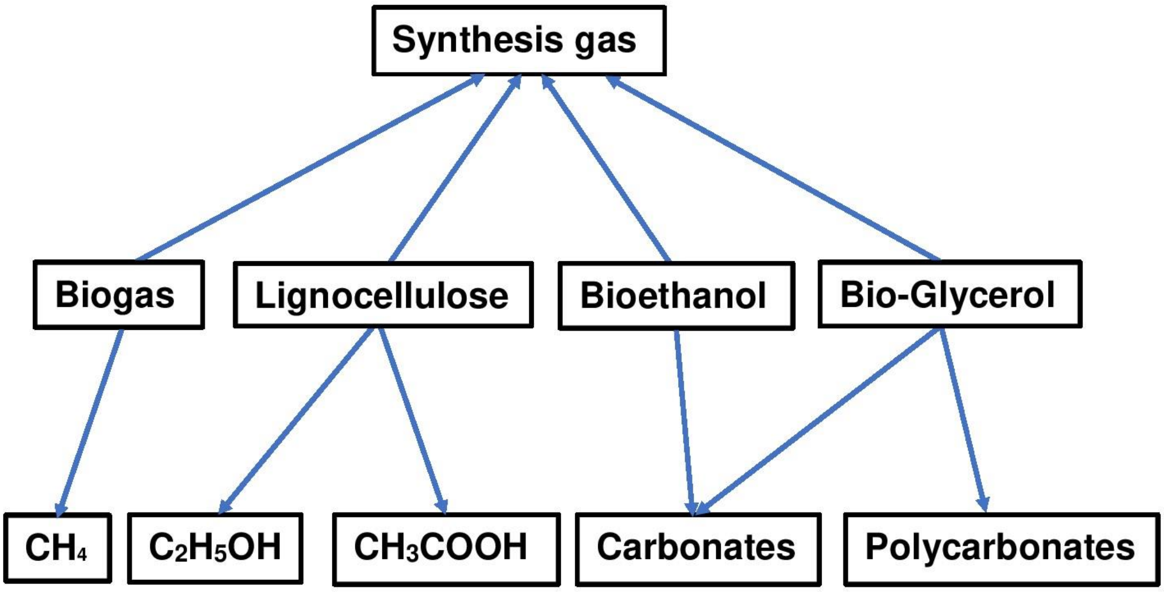


Fig.1. Heterogeneous-catalytic conversion of renewable bioresources with CO_2

All these processes are far from commercial implementation. The main reason for that is the need for thorough cleaning and preparation of raw materials and the development of catalysts with stable work under the conditions of the process. The main advantage of heterogeneous catalytic technologies is related to the large-scale utilization of CO_2 and utilization of by-products of agricultural, household, livestock, and woodworking waste. These processes do not require complex factory equipment and can be implemented in small enterprises.

Application of heterogeneous catalysis seems to be reliable for CO_2 transformations to valuable chemical products using several types of bioresources, e.g., biogas, lignocellulose, lignin, cellulose, bioethanol, biobutanol, and glycerol. The most studied process is the production of synthesis gas that can be realized for all types of bioresources. Biogas also may help to produce methane from CO_2 whereas alcohols are mainly used for production of organic carbonates and polycarbonates. Except synthesis gas production, other pathways of using bioresources for CO_2 utilization are far from their technological realization and require further studies that may open a new avenue for CO_2 utilization. Such an approach is an element of the sustainable circular carbon economy.

S-27

ETHANOL CONVERSION ON COPPER CATALYSTS

M. Mambetova[1,2]*, G. Yergaziyeva[2,3], K. Dossumov[1,2]

[1]*Center of Physico-Chemical Methods of Research and Analysis, Almaty, Kazakhstan*
[2]*Institute of Combustion Problems, Almaty, Kazakhstan, mambetova_manshuk@list.ru*
[3]*Al-Farabi Kazakh National University, Faculty of Chemistry and Chemical Technology, Almaty, Kazakhstan*

The increase in the use of mineral resources and the limited amount of resources have prompted extensive research into renewable energy. Among the numerous products obtained from biomass, ethanol is of particular interest because of its high productivity, versatility and also great mobilization value [1]. In addition, ethanol is a key platform chemical suitable for upgrading to value-added chemicals such as acetaldehyde, ethylene, butanol, 1,1-diethoxyethane, hydrogen, and aromatics [2, 3].

During the processing of ethanol, the resulting acetaldehyde is an important raw material for the production of other valuable substances [4], for example, acetic acid, acetic anhydride, cyanohydrin, followed by its processing into acrylonitrile, acrylic acid esters, and lactic acid. In general, acetaldehyde is produced by the Wacker process by the direct oxidation of ethylene to acetaldehyde using palladium chloride or copper chloride catalysts. This technology is characterized by the formation of a number of toxic organochlorine by-products, as well as acetic acid and crotonaldehyde dissolved in large quantities of water.

The literature describes two gas-phase processes for the conversion of ethanol to acetaldehyde: selective catalytic oxidation with oxygen or air and thermal catalytic dehydrogenation [5, 6]. Compared to the oxidative method, thermal catalytic dehydrogenation has clear advantages, for example, excessive oxidation to acetic acid and carbon dioxide is eliminated, the formed acetaldehyde is easily separated from the reaction by-products, and an equimolar amount of hydrogen is obtained as a valuable by-product [7-8]. In addition, the non-oxidative dehydrogenation of ethanol is inherently safe, while the mixture of ethanol and oxygen presents a serious problem due to its explosive nature for large-scale industrial processes [9]. The main problem in the development of ethanol processing technologies is the low selectivity of the process. Therefore, it is necessary to create a new efficient catalytic system for obtaining the target product - acetaldehyde by non-oxidative dehydrogenation of ethanol.

The aim of this work is to develop copper-containing catalytic systems with desired properties of selective action for the dehydrogenation of ethanol to obtain a valuable product - acetaldehyde. In the framework of the presented work, the effect of modifying additives - oxides of cerium, lanthanum and nickel on the activity and selectivity of 1 wt.% CuO/Al_2O_3 catalyst in the nonoxidative dehydrogenation of ethanol was studied. The content of modifying additives was 0.5 wt.%. Copper oxide-based catalysts were prepared by capillary impregnation of supports with a solution of copper nitrate ($Cu(NO_3)_2 \cdot 5H_2O$) according to their moisture capacity. The activity of the synthesized catalysts was studied in the temperature range of 200-400 °C, at a space velocity of 0.5 h^{-1}. To study the physicochemical properties of the samples, methods such as BET, SEM, XRD, TPD-NH_3 and TPR-H_2 were used.

The results of TPD-ammonia showed that the catalysts have weak, medium and strong acid sites. According to the SEM and BET data, the modification of the copper catalyst with nickel and lanthanum oxides leads to an increase in the dispersity of the catalyst particles. The highest selectivity for acetaldehyde, 35%, was obtained for the $CuO\text{-}NiO/\gamma\text{-}Al_2O_3$ catalyst, which has the highest acidity, 372 μmol/g.

References:

1. H.P. Finger., T.A. Osmari, M.S. Costa, J. Maria, C. Bueno, R. Gallo, Applied Catalysis A: General, 2019, p.1-25.
2. S. Tayrabekova, P.M. Arvela, M. Peurla, P. Paturi, K. Eränen, G.E. Ergazieva, A. Aho, D.Yu. Murzin, K. Dossumov, Comptes Rendus Chimie, 2018, vol. 21, p.194-209.
3. Z. Wang, J. Pang, L. Song, X. Li, Q. Yuan, X. Li, M. Zheng, Industrial Engineering Chemistry Research, 2020, vol. 59(51). p. 22057-22067. doi.org/10.1021/acs.iecr.0c04649
4. Han S., et al, ACS Catalysis, 2019, vol. 9(5), p. 4360-4368. doi.org/10.1021/acscatal.9b00079
5. V.V. Dutova, G.V. Mamontova, V.I. Soboleva, O.V. Vodyankina, Catalysis Today, 2016, vol. 278, p. 164-173. doi.org/10.1016/j.cattod.2016.05.058.
6. G. Carotenuto, R. Tesser, M.D. Serio, E. Santacesaria, Catalysis Today, 2013, vol. 203, p. 202-210. doi.org/10.1016/j.cattod.2012.02.054.
7. T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa, K. Kaneda, Angewandte Chemie International Edition, 2008, vol. 120, p. 144-147. doi.org/10.1002/anie.200703161
8. T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa, K. Kaneda, Catalysis Communications, 2008, vol. 39, p. 4804-4806. doi.org/10.1039/b809012b
9. E.W. Ping, Topics in Catalysis, 2010, vol. 53(15-18), p. 1048-1054. doi.org/10.1007/s11244-010-9530-8.

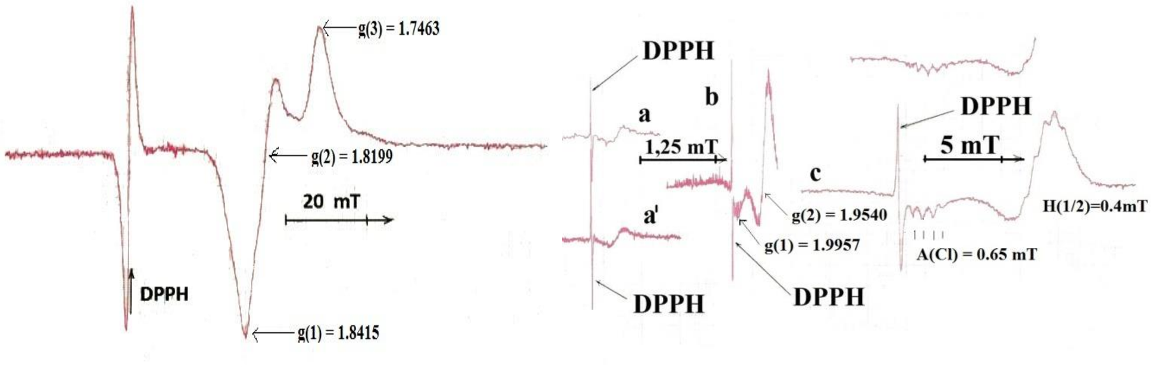
S-28

INTERMEDIATES IN CATALYTIC SYSTEMS FOR METATHESIS OF OLEFINS BASED ON WCl_6 AND ORGANOALUMINIUM COMPOUNDS ACCORDING TO DYNAMIC LIGHT SCATTERING AND ELECTRON PARAMAGNETIC REZONANCE DATA

S.N. Osmanova[1,2]*, S.A. Suleymanova[1], T.G. Zeynalova[3], E.H. Ismailov[1]

[1]Institute of Catalysis and Inorganic Chemistry, 113, H.Javid Ave., AZ1143, Baku, Azerbaijan
[2]Khazar University, 41, Mahsati St., AZ1096, Baku, Azerbaijan, sevinj.nasib.osmanli.26@gmail.com
[3]Azerbaijan University of Architecture and Construction, 11, A. Sultanova St., AZ1073, Baku, Azerbaijan

Electron paramagnetic resonance (EPR) and dynamic light scattering (DLS) methods have been used to identify the products of the interaction of organoaluminum compounds (OAC) with WCl_6 in an ethanol medium. It has been shown that the interaction of WCl_6 with ethanol is accompanied by the formation of a colloid whose particle sizes vary from several units to hundreds of nanometers. By adding OAC (Et_2AlCl, Et_3Al) the colloid becomes completely transparent. There are no lines in the DLS spectra indicating the presence of particles larger than one nm; the impact of OAC on a colloidal solution leads to the destruction of colloidal particles and the formation of a molecular / molecular-ionic solution. It has been established that the interaction of WCl_6 with OAC leads to the formation of intermediate, metastable organic radicals with $g = 2.0037$, $\Delta H = 1.7$ mT, W^{5+} complexes with $g_1 = 1.83$, $g_2 = 1.74$ at 77 K, and stable paramagnetic products with $g_1 = 1.9957$, $g_2 = 1.9540$, $g_3 = 1.9465$ at 77 K and $g_0 = 1.9583$ at 300K and with $g_1 = 1.9957$, $g_2 = 1.9540$, $g_3 = 1.9465$ at 77K and $g_0 = 1.9583$ at 300 K with an additional hyperfine structure from two chlorine nuclei $^{35.37}Cl$, most likely belonging to paramagnetic metal-carbene type tungsten complexes (Fig. 1). The formation of these products is accompanied by the release of only ethane, which was established on-line by chromato-mass spectrometry.



a) b)

Fig.1. EPR spectra at: a) 77K after defrosting for 10 minutes of a frozen at 77K $WCl_6/EtOH$ colloid system with added $AlEt_3$ (in n-heptane with 40% toluene), b) 77 and 300 K of the $WCl_6/E_{t2}AlCl/C_2H_5OH$ system after keeping it at room temperature for 2 days.

The mechanism of formation of tungsten-carbene structures in these systems and the role of tungsten-carbene structures in the catalysis of the metathesis of lower olefins are discussed.

S-29

NICKEL PHOSPHIDES BASED COMPOSITE MULTIFUNCTIONAL ELECTROCATALYSTS FOR OXYGEN REDUCTION, OXYGEN AND HYDROGEN EVOLUTION REACTIONS

O.O. Pariiska*, D.O. Mazur, Ya.I. Kurys, V.G. Koshechko, V.D. Pokhodenko

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, pariiska@ukr.net

We have proposed a facile and environmentally friendly approach for obtaining composites of N,P-doped carbon with nickel phosphides particles (Ni_xP_y/N,P-C). The proposed approach involves the pyrolysis (800-1000ºC) of H_3PO_4-doped polyaniline together with $NiCl_2·6H_2O$ and does not provide for the use of expensive and toxic reagents. The obtained hybrid materials were characterized by SEM, TEM, EDX, Raman spectroscopy, X-ray diffraction, XPS, and also studied as platinum-free electrocatalysts for hydrogen evolution (HER), oxygen evolution (OER), and oxygen reduction (ORR) reactions.

It was found that an increase in the pyrolysis temperature leads to the formation of nickel phosphides with a lower phosphorus content in the composition of the composites. The relative content of phosphides is 20.6% NiP, 65.9% $Ni_{12}P_5$ and 13.5% Ni_2P in the composite obtained at 800ºC (Ni_xP_y/N,P-C_800), 39.5% $Ni_{12}P_5$ and 60.5% Ni_2P – in the composite obtained at 900ºC (Ni_xP_y/N,P-C_900) and 11.1% $Ni_{12}P_5$ and 88.9% Ni_2P – in the composite obtained at 1000ºC (Ni_xP_y/N,P-C_1000).

It was shown that all the obtained composites are multifunctional electrocatalysts capable of exhibiting sufficiently high activity in HER in 0.5 M H_2SO_4 and 1.0 M NaOH, as well as in OER and ORR in 1.0 M NaOH (Table). The trends of electrocatalysts activity in ORR and OER (in an alkaline electrolyte) is the opposite to that found for in HER, which may be due to different sites that are involved in these processes.

Table. Main parameters of HER, OER, and ORR performance (b – Tafel slope; η_{10} and η_{20} –overpotential at current density 10 and 20 mA/cm^2; $E_{1/2}$ – half-wave potential; n - the number of electrons transferred during ORR), that were obtained in the indicated electrolytes on Ni_xP_y/N,P-C catalysts

Каталізатор	HER				OER		ORR	
	0.5 M H_2SO_4		1.0 M NaOH		1.0 M NaOH			
	b, mV/dec	η_{10}, mV	b, mV/dec	η_{10}, mV	b, mV/dec	η_{20}, mV	$E_{1/2}$, mV	n
Ni_xP_y/N,P-C_800	64	182	100	176	236	400	790	2.8
Ni_xP_y/N,P-C_900	58	150	109	191	162	370	830	3.5
Ni_xP_y/N,P-C_1000	62	190	108	237	161	400	850	3.6

S-30

TITANOSILICATE ZEOLITES AS CATALYSTS FOR EPOXIDATION OF CYCLIC OLEFINES WITH H_2O_2

M.M. Kurmach[1]*, A.O. Samotoi[1], S.O. Sotnik[1,2,3], P.S. Yaremov[1],
O.V. Shvets[1], N.D. Shcherban[1]

[1]*L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, mazinator3710@ukr.net*
[2]*Taras Shevchenko National University of Kyiv, Volodymyrska St., 60, Kyiv, 01601 Ukraine*
[3]*Enamine Ltd, Chervonotkatska St., 78, Kyiv, 02094 Ukraine*

Epoxides are quite important materials which have wide use as precursors for production of different valuable polymers, in particular, cyclic carbonates [1] or epoxy resins. Mild oxidation of olefines is one of the important methods to produce epoxides. Ti-containing zeolites are known to be effective catalysts for olefin epoxidation process [2]. However, in process involving “bulky” cyclic olefines molecules, such as cyclohexene or cyclooctene, the activity of microporous "zeolites" is extremely low, due to their diffusion and steric limitations [2]. The creation of materials with a developed external surface (hierarchical zeolites), and a high concentration of active sites on the external surface is aimed at significantly improving the catalytic activity of these materials.

In the work, a number of Ti-containing hierarchical zeolites were obtained using Gemini-type surfactants as structure-directing agents. AlTi- and BTi-BEA and Ti-MTW zeolites were obtained using bromide form of zeolite in the presence of Na cations. Both AlTi- and BTi-BEA after SDA removal contain a certain amount of Brønsted acid sites (BAS) which results irreversible chemosorption of alkenes. To decrease an amount of BAS ion exchange H^+ to Na^+, Cs^+, K^+ ions was performed. Formed Na-, K-, Cs- AlTi-BEA tested as catalyst for alkene epoxidation reaction. Hierarchical Ti-BEA without Al or B source were obtained using OH-form of Gemini-type surfactant in highly concentrated media (dry-gel method) containing F^- source. Ti-MFI were obtained using $C_{16\text{-}6\text{-}6}OH^-_2$ without fluoride media.

Such materials are characterized by a developed external surface and a high proportion of active centers available for bulk molecules. In case of all groups of titanosilicate materials, a set of samples with Si/Ti = 200 ÷ 33 was obtained. Pyridine adsorption shows that all Na-, K-, Cs- AlTi-BEA do not contain BAS which provides high selectivity in relation to the target product for the styrene oxidation with hydrogen peroxide at a temperature of 100 °C. Ti-BEA provide high activity (up to 96%) in epoxidation of cyclohexanone at 60 ºC using H_2O_2 as an oxidant. However, high catalytic activity in this process, selectivity towards the main product decreased after 24 h of catalytic tests wearying between 40 and 90%.

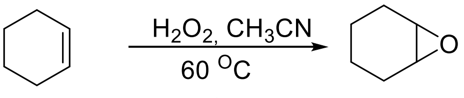


Fig. 1. Scheme for epoxidation of cyclohexene by hydrogen peroxide

References:

1. A. A.Marciniak, K. J. Lamb, L. P. Ozorio, C. J. A. Mota, M. North, Curr Opin. Green Sust. Chem. (2020) 26.
2. K. Na, C. Jo, J. Kim, W.-S. Ahn, R. Ryoo, ACS Catal. **1** (2011) 901-907.

S-31

ON THE POSSIBILITY OF USE OF WASTE ZEOLITE ADSORBENTS OF TYPE A

Sh.T. Gulomov*, A.R. Sultanov

Uzbek Research Chemical-Pharmaceutical Institute, Tashkent city, shuhratrich@gmail.com

Zeolite adsorbents are widely used for drying and removing sulfur compounds from natural and liquefied gas [1].Wastes from the oil and gas processing industry - spent zeolite adsorbents - are mostly coked due to incomplete removal of gradually accumulating carbon, and exchange forms of zeolite A that have lost their original activity. These are mainly zeolite adsorbents CaA, NaA and its stabilized forms, as well as KA. We have shown that the complete removal of coke deposits from the spent KA zeolite adsorbent occurs at a high temperature with the participation of atmospheric oxygen and leads to a strong decrease in the adsorption capacity and water absorption.

When developing the technology for the synthesis of type A zeolite adsorbents based on Angrenkaolins somewhat depleted in kaolinite, we used the seed synthesis method, where fractions of regenerated sodium, potassium, and calcium forms of zeolite adsorbents were tested as seed crystals. The studied waste samples, in particular, NaA and KA from the processes of purification of natural gas and pyrolysis gases in the production of ethylene, have a fairly preserved crystalline structure. After heat treatment in an oxygen-free environment, the samples have an equilibrium dynamic activity during the adsorption of water from air of 14.8%, under static conditions the capacity is 19–21%, and water absorption is 21–34%.

Adsorbent granules containing residual carbon in an amount of 0.6 - 3.6% wt. have a water absorption of ~ 34% wt. The specific gravity of the KA adsorbent sample containing residual carbon after a single heat treatment was 2.247 g/cm3 (volumetric liquid - water). The pH value of the water extract (exposure in distilled water for 1 month of a fraction less than 0.5 mm) is 8.5.

As a result of a 2-month experiment using X-ray fluorescence analysis, it was found that for a fraction of 1.0 - 0.315 mm of the heat-treated adsorbent KA, kept in loess soil with periodic irrigation with tap water, the content of Na + ions practically did not change (11.3 and 11.0% wt., respectively), while the content of K2O decreased from 6.2 to 4.27% wt. We can make a preliminary conclusion that Na+ cations, located in positions less accessible for exchange for K+ cations, do not transfer into the soil composition during repeated watering.

The zeolite adsorbents NaA and KA used in the processes of purification of natural gas and separation of ethylene from pyrolysis gases have a sufficiently preserved crystalline structure until their deep regeneration and complete removal of coke deposits from them. Complete removal of coke deposits from the spent zeolite adsorbent KA leads to a decrease in adsorption capacity and water absorption.

The presence of elemental potassium in the composition of the treated zeolite adsorbent in an amount of more than 4.2 wt %, with a small amount of remaining carbon, and the water-retaining properties of KA adsorbents heat-treated in a certain way suggest the possibility of their use in the agricultural direction after appropriate processing, and, possibly, ion exchange.

References:

1 Degnan T. F. Recent progress in the development of zeolitic catalysts for the petroleum refining and petrochemical manufacturing industries // Studies in Surface Science and Catalysis. 2007. Vol. 170. P. 54–65.

S-32

PLASMA-CATALYTIC DRY REFORMING OF PROPANE WITH CHROMIUM (III) OXIDE BASED CATALYSTS IN DIELECTRIC BARRIER DISCHARGE REACTOR

D.E. Samoylenko[1]*, V.I. Kornaha[2], P.I. Kyriienko[1]

[1] *L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, d.samoylenko96@gmail.com*
[2] *V.E. Lashkaryov Institute of Semiconductor Physics, National Academy of Sciences of Ukraine, Prosp. Nauky, 41, Kyiv, 03028 Ukraine*

Reducing greenhouse gas emissions, producing energy from renewable sources and improving energy efficiency are imperative to limiting the global warming. Dry reforming (DR) can potentially be perspective solution due not only consumption of greenhouse gas in the process, but additionally obtaining syngas [1]. DR is usually carried with methane, however, propane DR can offer some benefits like lower reagent activation temperature [2]. In this research dry reforming of propane was carried under non-thermal plasma conditions in dielectric-barrier discharge reactor with catalyst.

Process of plasma-catalytic propane dry reforming was performed at temperature of 140 °C and atmospheric pressure on such catalysts: 5% Cr_2O_3/SiO_2 (ZrO_2; ZnO; MgO). Catalysts were prepared by impregnating the support with required quantities of aqueous $Cr(NO_3)_3 \cdot 9H_2O$, then dried and calcined in air at 550 °C.

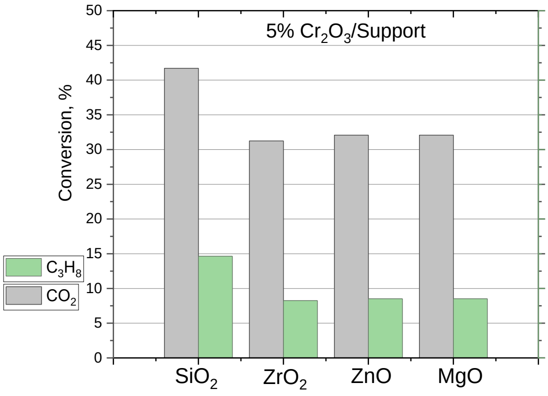


Fig. 1. Conversion of C_3H_8/CO_2 over different catalyst samples under non-thermal plasma conditions at T = 140 °C, discharge heating (feed gas (C_{vol}) 25% C_3H_8, 30% CO_2, Ar balance, flow rate 20 mL/min).

Conversion of C_3H_8 and CO_2 over different samples is presented on Figure 1. Along with main products of plasma-catalytic dry reforming of propane (syngas), such product as propylene was registered during experiment over Cr_2O_3/SiO_2 sample.

Thus support of catalyst affects catalytic activity during dry reforming of propane in non-thermal plasma. Additionally, presence of propylene indicates that CO_2-assisted dehydrogenation of propane also occur under plasma condition.

References:

1. H. Wang, J. Han, Z. Bo, L. Qin, Y. Wang and F. Yu, Molecular Catalysis 475 (2019).
2. A. Siahvashi, A.A. Adesina, International Journal of Hydrogen Energy, 43 (2018).

S-33

HYDROGENATION OF CARBON DIOXIDE TO METHANOL AT ATMOSPHERIC PRESSURE BY BENTONITE-BASED CATALYSTS WITH SUPPORTED MONO-, BI-, AND TRI-NUCLEAR FERROCENE DERIVATIVES

A.I. Rustamova[1]*, S.N. Osmanova[1,2], Z.M. Mammadova[1], E.H. Ismailov[1]

[1]*Institute of Catalysis and Inorganic Chemistry, 113, H. Javid Ave., AZ1143, Baku, Azerbaijan, aygun.rustamova1601@gmail.com*
[2]*Khazar University, 41, Mahsati St., AZ1096, Baku, Azerbaijan*

The hydrogenation of carbon dioxide into methanol is one of the most efficient ways of utilizing CO_2 [1, 2]. Due to the low equilibrium conversion of CO_2 to methanol at high temperature, it is extremely important to develop efficient processes for the catalytic hydrogenation of CO_2 operating at low temperature and atmospheric pressure [3]. This report presents the results of a study of the catalytic activity of one-, two- and three nuclear derivatives of ferrocene - $C_5H_5FeC_5H_4\text{-}C(CH_3)_2OH$ (I), $[C_5H_5FeC_5H_4]_2C(CH_3)OH$ (II), $[C_5H_5FeC_5H_4]_3C\text{-}OH$ (III), supported on mesoporous bentonite in the reaction of carbon dioxide hydrogenation to methanol. I-III with an iron content of 1-5 wt.% at atmospheric pressure, deposited on mesoporous bentonite, promote the hydrogenation of CO_2 with a selectivity for methanol of 80-85% at a reaction temperature of 145 °C. Mesoporous bentonite was obtained by treating bentonite first with alkali (NaOH), followed by repeated washing with bidistilled water, and then with acid (HCl). air at 400 ° C for 4 hours and reduced at the same temperature in a stream of hydrogen for half an hour. As bentonite, bentonite of the Dash-Salakhli deposit of the Republic of Azerbaijan was used. Ferrocene derivatives I-III were supported on bentonite from organic solutions. The elemental and phase composition of the catalysts before and after treatment, deposition of active components, calcination, and reduction was determined using an XRF Tiger S8 X-ray fluorescence spectrometer and an XRD D2 PHASE X-ray diffractometer, Bruker. The surface morphology of the catalysts and the distribution of elements in the structure of the catalysts were studied using a scanning electron microscope in combination with a Hitachi S 3400N/EDS energy-dispersive elemental analyzer. The textural parameters (specific surface area, volume, pore size) were determined from N_2 adsorption–desorption measurements using Belsorp Mini II from BEL, Japan Inc. device. Before measurements, the samples were degassed at 200°C in a vacuum ($\sim 10^{-2}$ Torr) for 12 h. The infrared and electronic magnetic resonance spectra of the samples were recorded, respectively, using an Alfa FTIR Fourier spectrophotometer, Bruker in KBr pellets, and an EMX_{micro} radiospectrometer, Bruker, Germany. The dependence of activity and selectivity with respect to the target reaction product, distribution of iron in the catalyst structure, phase composition of catalysts, FTIR and EMR spectra on the composition of ferrocene derivatives and the temperature of preliminary reduction of catalysts with hydrogen has been studied. The structure-activity relationship for these catalytic systems has been studied. It is assumed that nanometer-sized iron particles formed during the reduction of iron compounds I-III are catalytically active centers of the methanol formation reaction.

References:

1. S. De, A. Dokania, A. Ramirez, J. Gascon, ACS, **10** (2020), 14147.
2. J. Zhong, X. Yang, Z. Wu, B. Liang, Y. Huang, T. Zhang, (2020), Chem Soc Rev, **49** (2020), 1385.
3. T. Toyao, S. Kayamori, Z. Maeno, S.M.A.H. Siddiki, K. Shimizu, ACS Catalysis, **9** (2019), 8187.

S-34

ON THE THERMODYNAMICS OF ETHANOL CONVERSION INTO HYDROGEN AND PROPYLENE

Y.I. Pyatnitsky*, L.Yu. Dolgikh, I.L. Stolyarchuk, L.M. Senchylo

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, yupyat@gmail.com

Bioethanol is considered as promising raw materials for use in bioenergy and for the production of chemicals [1-3]. Nowadays bioethanol is mainly used as a biofuel being safe, easy to transport, handle, and store [1], but it is believed that more important the use of bioethanol for the production of hydrogen, a promising friendly environmental fuel, and for production of higher value-added products, in particular, propylene.

Many reviews are devoted to the processes of producing hydrogen by ethanol steam reforming (ESR) and propylene by ethanol-to-propylene (ETP), in particular [1, 2, 4-6].

The main initial reactions in the processes of ESR and ETP are as follows:

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2 \qquad (R1)$$

$$2\ CH_3CHO + H_2O \rightleftarrows CH_3COCH_3 + CO_2 + 2\ H_2 \qquad (R2)$$

Acetone in the ESR process is converted to produce hydrogen by reaction:

$$CH_3COCH_3 + 5\ H_2O \rightleftarrows 3\ CO_2 + 8\ H_2 \qquad (R3)$$

and in the ETP process, hydrogen and propylene are produced by reactions:

$$CH_3COCH_3 + H_2 \rightleftarrows \text{iso-}C_3H_7OH \qquad (R4)$$

$$\text{iso-}C_3H_7OH \rightleftarrows C_3H_6 + H_2O \qquad (R5)$$

Thermodynamic calculations were carried out for these reaction pathways (Fig.1). The yields of hydrogen, $Y_{H2,m}$, and propylene selectivity, S_{C3H6}, were calculated by the formulas:

$$Y_{H2,m} = \frac{m_{H2}}{\Sigma(\frac{n_{Cn}}{2} m_{Cn})} X_{Et} \qquad (1)$$

$$S_{C3H6} = \frac{1{,}5\ m_{C3H6}}{\Sigma(\frac{n_{Cn}}{2} m_{Cn})} \qquad (2)$$

where X_{Et} is ethanol conversion, m_{H2} and m_{Cn} are mole fractions of hydrogen and carbon-containing compounds Cn, respectively; n_{Cn} is a number of carbon atoms in the Cn molecule.

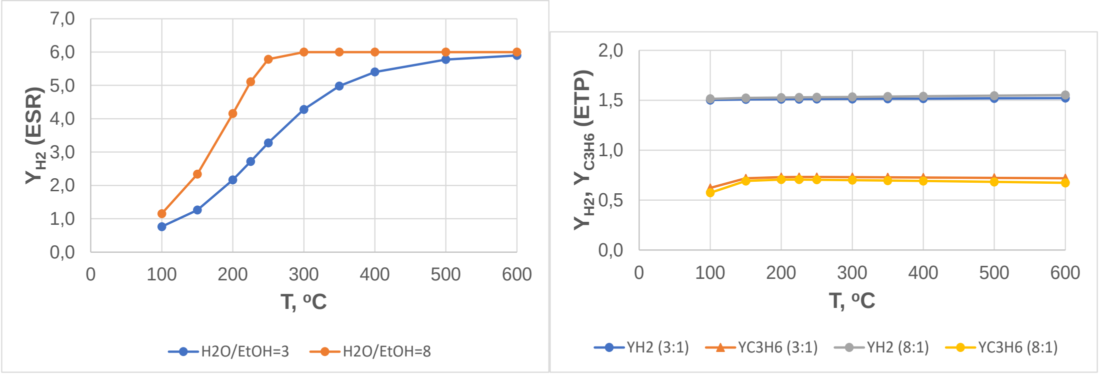


Fig. 1. Temperature dependences of equilibrium hydrogen yield in the ESR process, reactions (R1)-(R3), and equilibrium yields of hydrogen and propylene in the ETP process, reactions (R1), (R2), (R4), (R5).

Fig.1 shows the following patterns:

- the equilibrium yield of hydrogen in the ESR process increases with increasing temperature, and the greater the ratio of H_2O/C_2H_5OH in the initial mixture, the earlier the hydrogen yield close to its maximum value is achieved;
- the equilibrium yield of hydrogen in the ETP process depends little on both temperature and the concentration of ethanol; besides, in the equilibrium reaction mixture, there is a ratio of concentrations close to stoichiometric: H_2:C_3H_6:CO_2 = 3:1:1.

Qualitatively, the same patterns are observed for a wider range of products, namely, acetaldehyde, acetone, ethyl acetate, acetic acid, *iso*-propanol, methane, CO, and CO_2.

Using the approach proposed in the works [7, 8], it is possible to obtain for the ESR and ETP processes the common alternative equation for calculating the hydrogen yield, as a function of carbon compound selectivity:

$$Y_{H2,S} = \left(S_{CH3CHO} + \left(\frac{2}{3}\right) S_{CH3COCH3} - 2\,S_{CH4} + 4\,S_{CO} + 2\,S_{CH3COOH} + S_{CH3COOC2H5} + 6\,S_{CO2}\right) X_{Et} \tag{3}$$

From the equation $Y_{H2,m} = Y_{H2,S}$, one can obtain a simple, albeit non-trivial, formula that relates the concentration of hydrogen to the concentrations of carbon compounds:

$$m_{H2} = m_{CH3CHO} + m_{CH3COCH3} - m_{CH4} + 2\,m_{CO} + 2\,m_{CH3COOH} + m_{CH3COOC2H5} + 3\,m_{CO2} \tag{4}$$

This formula provides auxiliary capabilities for in-depth analysis of experimental data, in particular, to assess their reliability.

In conclusion, we note the following. The main difference between the ESR and ETP processes is the difference in the conversion of acetone into final products. In the ETP process, this transformation occurs with the preservation of the carbon skeleton of the molecule, whereas in the ESR process, a complete break in the C-C bonds occurs. It cannot be ruled out that improvements in the ESR process can be achieved by applying a two-step process with different catalysts in the steps, similar to what was proposed for the ETP process [9].

References:

1. C.R.V. Matheus, E.F. Sousa-Aguiar, Main catalytic challenges in ethanol chemistry: A review. Catal. Rev. (2022) DOI: 10.1080/01614940.2022.2054554.
2. Z. Liu, S.D. Senanayake, J.A. Rodriguez, in: A.Basile, A. Iulianelli, F. Dalena, T.N. Veziroglu (Eds), Ethanol Science and Engineering, Elsevier, 2019, chapter 5, p. 133.
3. K.Ulonska, A. König, M. Klatt, A. Mitsos, J. Viell, Optimization of Multiproduct Biorefinery Processes under Consideration of Biomass Supply Chain Management and Market Developments. Ind. Eng. Chem. Res. **57** (2018), (20), 6980.
4. M. Iwamoto, M (2015) Selective catalytic conversion of bio-ethanol to propylene: a review of catalysts and reaction pathways. Catal. Today **242** (2015) 243.
5. Y.I. Pyatnitsky, L.Yu. Dolgykh, I. L.Stolyarchuk, P. E. Strizhak, Production of hydrogen by steam reforming of ethanol. Theor. Exp. Chem. 49 (2013) 277.
6. Y.I. Pyatnitsky, L.M. Senchylo, L.Yu. Dolgikh, P.E. Strizhak, Processes of propene production from ethanol: catalysts, reaction pathways and thermodynamic aspects: a review. Theor. Exp. Chem. **58** (2022) 15.
7. Y.I. Pyatnitsky, L.Yu. Dolgykh, I.L. Stolyarchuk, P.E. Strizhak, Relationship between yield of hydrogen in steam reforming of ethanol and selectivity with respect to carbon containing products. Theor. Exp. Chem. **49** (2013) 109.
8. Y. Pyatnitsky, L. Dolgykh, I. Stolyarchuk, P. Strizhak, Analysis of the hydrogen yield for the ethanol steam reforming. Biomass Convers. Biorefin. (2023) DOI: 10.1007/s13399-023-04544-8.
9. Y. Pyatnytsky, L. Dolgykh, L. Senchilo, A two-step strategy for the selective conversion of ethanol to propene and hydrogen. Chem. Papers, **75** (2021) 5773.

S-35

CATALYTIC METHODS OF DECONTAMINATION AND PROTECTION OF THE SURFACE OF DIFFERENT MATERIALS FROM CONTAMINATION WITH RADIOACTIVE DUST

S.A. Kurta*, I.F. Myroniuk

Chemistry Department of Vasyl Stefanyk Precarpathian National University, Institute of Natural Sciences, Galytska st, 201, Ivano-Frankivsk, 76008 Ukraine, sergiykurta@pnu.edu.ua

Every year on April 26, we in Ukraine commemotare our sad date - the disaster at the Chornobyl NPP on April 26, 1986. Before the disaster on April 26, 1986, the power of 4 units of the Chornobyl NPP was 4 million kilowatts. After the disaster, 8 tons of radioactive fuel were released from the reactor area, 190 tons of radioactive substances into the atmosphere, and 700 tons of radioactive graphite debris and 40,000 m3 of soil were removed from the nuclear power plant. The scale of the level of contamination corresponded to 200-300 explosions on Hiroshima, Japan. All residents were evicted from 118 settlements in the 30-kilometer zone of the Chernobyl nuclear power plant in Ukraine.

The Chernobyl disaster is a man-made ecological and humanitarian disaster caused by two thermal explosions followed by the nuclear destruction of the fourth unit of the Chernobyl nuclear power plant in Ukraine (in the former USSR) on April 26, 1986. The radioactive cloud formed by the accident passed through the European part of the USSR, most of Europe, and the eastern part of the USA. About 60% of radioactive substances settled in Ukraine. About 300,000 people were evacuated from the contaminated territories of Pripyat, Chornobyl and all villages within a 30 km zone.

By this time, my head of the laboratory, prof. Myronyuk I.F. worked at the research production of the Institute of Physical Chemistry of the National Academy of Sciences of Ukraine in Kalush, and the director of our Surface Institute, academician of the National Academy of Sciences of the National Academy of Sciences, Oleksiy Chuyko, gathered us all in Kyiv and offered to go to the Chernobyl zone to take part in the liquidation of the consequences of the disaster. That's how I got to the special processing station of PUSO equipment. Rosokh, Kyiv region. 5 km from the Chernobyl Nuclear Power Plant.

Before the trip to the territory of the Chernobyl nuclear power plant, we were checked in a special department of the KGB in Kyiv and issued special plastic passes. We were forbidden to photograph, film and film, and to report on our work and everything we see and hear there for 25 years, that is, from 1986 to 2011, which we signed in a special document. We lived in the villages of Stari Sokoly and Rosokh, located on the border of the zone 30 km from the Chernobyl NPP, where all transit transport, including military, was checked with radiometers and dosimeters. Our task was to improve old and create new methods of decontamination and surface protection of various materials from contamination by radioactive particles and dust. We checked the degree and dimensions of radioactive contamination of car surfaces using DP-5A radiometers. The radioactive dose obtained by us was measured with a DP-22 individual dosimeter. The measurement range for gamma radiation is from 0mR/h to 0.05mR/h and from 0.05mR/h to 200P/h in the energy range from 0.084 MeV (170Tu) to 1.25 MeV (60Co). Since dosimeters are designed mainly to detect strong sources of radiation pollution (mR/h and P/h), the standardized measurement range of these devices starts at only 50 μR/h. During our stay at the Chernobyl nuclear power plant for two months in the summer of 1986, we only dealt with vehicles, especially buses, that were evacuating people from the 30-kilometer zone near the Chernobyl nuclear power plant, but in 1986 there were hundreds of them. These LAZ buses were perfectly roadworthy, could go anywhere, but were heavily contaminated with radioactive particles, the so-called radioactive dust and dirt.

So I had a military profession at the time, a senior lieutenant of the reserve of chemical troops of radioactive and chemical protection, and I knew very well and was prepared to work in the zone of radiation contamination of the Chernobyl nuclear power plant. At that time, in 1986, the main equipment for decontamination, disinfection and deratization of equipment was special automotive equipment, such as the ARS-12U machine, which can work as a regular irrigation or fire engine. Now, more advanced equipment is used for decontamination - a special vehicle with a TMS-500 jet engine.At that time, it was recommended to use a surfactant (SF-12U) for the decontamination of equipment from radioactive contamination. It is a washing powder for contact disinfection and deactivation of all types of surfaces painted with chemically resistant enamels (concrete, plaster, wood, tool and stainless steel, mass of plastics) from alpha- and beta-radioactive active pollutants in the form of dispersion aerosols in an aqueous environment. But in 1986, in Chernobyl, the use of this powder was completely ineffective, because after processing the surface of the equipment contaminated with radioactive dust and drying, the level of radioactive contamination decreased by only 1-2%. This means that the equipment must be washed up to 60 times to reach the permissible level of radiation contamination of 50 μR/h.

Therefore, my partner and I used a new method of cleaning the surface from radioactive dust, by treating the contaminated surface with an organic solvent and adsorbent, brand PLIK-4, which was used for dry cleaning of clothes. Highly dispersed hydrophobized silica of various brands AM-1-175, AMS, AMD was used as an adsorbent, the characteristics of which are presented in Table 1. For the production of modified silica in laboratory conditions, such classes of substances as organic alcohols are used, but the best hydrophobization of aerosols was carried out with organosilicon compounds, in particular alkoxy and haloidosilanes, siloxanes, and silazanes. On Fig. 1. IR-spectra of pyrogenic silica "Asil 300" (a) and hydrophobized with organic silicon (DMDHC) AMS brand aerosil, or produced after modification of PMS 400 aerosil, are presented. Since we used partially (no more than 60-80%) hydrophobized silica of the AMS brand as an adsorbent of radioactive dust particles on the surface of vehicles, therefore. then we washed it with water, but the radioactive dust particles were tightly adsorbed on the surface to the AMC absorbent and were removed together and, dispersing in the water, floated to the top of the water. At the same time, the level of radioactive contamination of the surface decreased by 10-20 times to the then acceptable norms of 30 microns/ h. And automobile equipment could be reused for the evacuation and transportation of people from the Chernobyl zone in 1986.

References:

1. Заявка СССР №4135521/05. Способ получения органоминеральных сополимеров. /Курта С.А.. Чуйко А.А., Хома М.И. – 1986, не подлежит публикованию, положит. решение 28.04.87.
2. Авт. св.№ 1396532 "Спосіб одержання привитих органомінеральних сополімерів" авт. Курта С.А., Чуйко А.А., Хома М.І., Сушко В.В., Хабер М.В., заяв. 15.10.1986 р., опубл. 15.01.1988р., кл. С 08 Р 29/00, 2/44.
3. Авт. св. №273146 "Спосіб дезактивації техніки і дезактивуючий розчин" авт. Миронюк І.Ф., Чуйко А.А., Огенко В.М., Курта С.А., Морєв А.В., Пикалов В.К., Кунцевич А.А., Климкуш О.Д., Лахно Ю.А., Гамоцький Р.П., Гуняєв А.А., заяв. 29.07.1987р., опубл. 01.04.1988р.
4. Авт. св. №281935 "Захисний полімерний розчин" авт. Курта С.А., Чуйко А.А., Огенко В.М., Миронюк І.Ф., Пикалов В.К., Кунцевич А.А., Климкуш О.Д., Лахно Ю.А., Гамоцький Р.П., Гуняєв А.А., заяв. 06.11.1987 р., опубл. 01.09.1988р.

S-36

TERNARY NANOSTRUCTURES Ni(Co)/Pd AS CATALYSTS FOR THE REDUCTION OF *p*–NITROPHENOL

L.I. Bazylyak[1]*, A.R. Kytsya[1,2]

[1]Department of Physical Chemistry of Fossil Fuels of the Institute of Physical Organic Chemistry and Coal Chemistry named after L.M. Lytvynenko, National Academy of Sciences of Ukraine, Naukova St., 3a, Lviv, 79060 Ukraine, bazylyak.liliya@gmail.com
[2]Physico-Mechanical Institute named after G.V. Karpenko, the National Academy of Sciences of Ukraine, Naukova St., 5, Lviv, 79060 Ukraine

Bi– and trimetallic nanostructures are promising materials for solving a wide range of applied problems in the chemical industry, in particular in catalysis, as well as in nanomaterials science. The applied applications of such materials in reactions with the participation of hydrogen, in particular in the processes of hydrogen generation (chemical and electrochemical) for hydrogen energy, as well as in the reactions of the reduction of organic substances to practically important products deserve a special attention. The use of metal nanoparticles based on *d*–elements as catalysts of chemical processes, in particular in the reactions of the reduction of organic substances to practically important products, has a number of advantages, since the catalysis by such nanoparticles is heterogeneous, which allows the reuse of the catalyst; at the same time, the large surface area of the catalyst and the high activity of metal atoms on the surface of nanoparticles allow to achieve a significant acceleration of the process with a low metal content in the system. In view of the increasingly widespread use of nanocatalysis in chemical transformations, special attention should be paid to the prospects of using of the nanocatalysts for the important reaction of the reduction (hydrogenation) of nitroaromatic substances with an aqueous solution of sodium borohydride in order to obtain industrially important aminoaromatic substances that are widely used in the production of polymers and dyes. On the other hand, when using nanocatalysts, improving the methods of their separation and regeneration remains a problem. The use of magnetic nanoparticles provides the possibility of combining known procedures of heterogeneous catalysis with the methods of magnetic separation [1]. Magnetic separation of the catalyst is cost-effective, as it allows less effort to be spent on filtering and centrifuging the mixture after the reaction. Therefore, an urgent problem is the development of methods of effective immobilization of metal nanocatalysts on the surface of magnetic media. The aim of the work is to synthesize polymetallic Ni(Co)/Pd nanostructures with magnetic properties and to investigate their catalytic activity in reduction processes on example of *p*–nitrophenol.

Ni(Co)/Pd nanosized ternary composite materials were synthesized by the method of galvanic replacement. The structure and phase composition of the obtained Ni(Co)/Pd nanostructures were investigated using SEM, EDX and X–ray powder diffraction (X–ray analysis). Using the X–ray powder diffraction method, it was established that the palladium is crystallized in the form of a cubic phase, space group Fm-3m. There are no unidentified peaks on the diffraction pattern of the Ni(Co)/Pd nanocomposite (Fig. 1), which could indicate the presence of another impurities. At the same time, the presence of anisotropy of peaks was noted for the Pd phase. Such anisotropy, namely the abnormally low intensities of the (200) and (311) reflex peaks compared to (111) and (220) (the latter are indicated by arrows on Fig. 1), may be an indirect confirmation of the formation of lamellar 2D palladium nanostructures in the obtained nanocomposite.

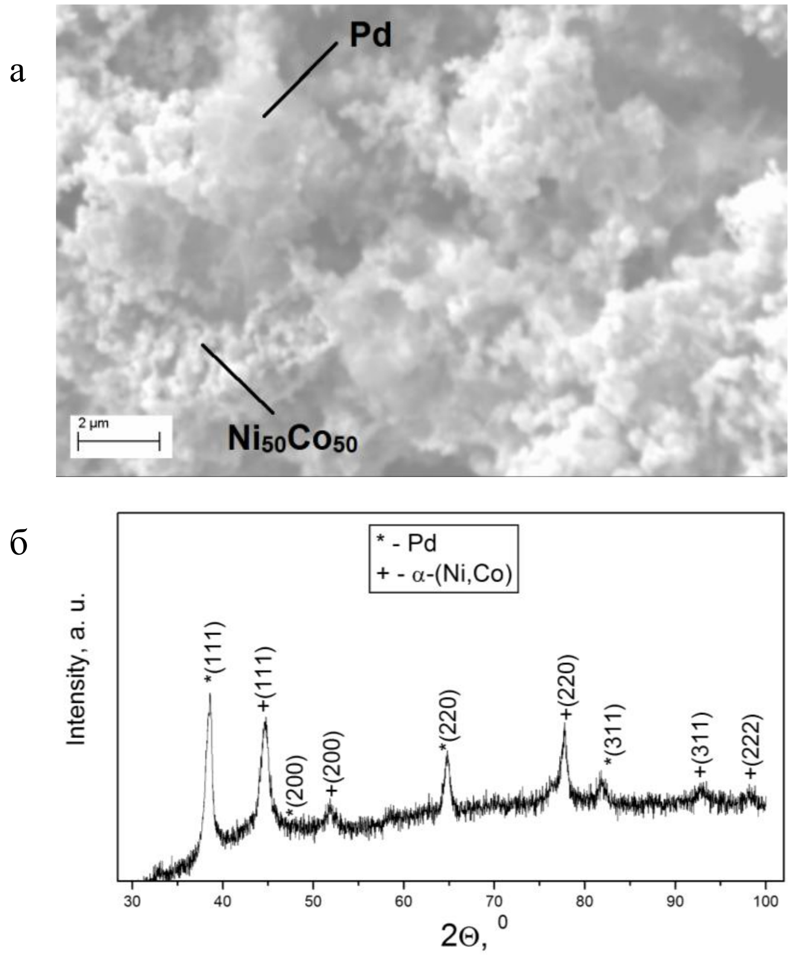


Fig. 1. SEM-image (a) and XRD pattern (b) of Ni(Co)/Pd nanocomposite

The catalytic activity of the synthesized polymetallic Ni(Co)/Pd nanoparticles was studied using the example of the reduction reaction of *p*–nitrophenol with $NaBH_4$ solution. It was found that in all cases the process of reduction of *p*–nitrophenol $NaBH_4$ in the presence of Ni(Co)/Pd nanoparticles as a catalyst is described by the first-order kinetic equation for *p*–nitrophenol. The catalytic activity of the studied nanoparticles based on nickel (Ni) is varied in the following order: **Ni** < **Ni(Co)** < **Ni(Pd)** < **Ni(Co)/Pd**. It was shown that the decoration of nanoparticles based on d–elements (Ni, Co) with palladium (Pd) significantly increases of their catalytic activity. Moreover, the reduction rate of *p*–nitrophenol in the presence of Ni(Co)/Pd is almost three times higher, compared to effecttive catalytic systems known from the references, i. e., such nanosystems can be considered as promising material for the development of new types of magnetically separable catalysts for the production of aminoaromatic compounds.

The work was carried out with the partial financial support of the National Research Fund of Ukraine (NFSU) (grant No. 2020.02/0309).

References:

1. Shylesh S., Schunemann V., Thiel W. (2010). Magnetically separable nanocatalysts: bridges between homogeneous and heterogeneous catalysis. *Angewandte Chemie International Edition*, *49*(20), 3428–3459.

S-37

ELECTROCATALYTIC CONVERSION OF CARBON DIOXIDE TO FORMALDEHYDE AND METHANOL

V. Viazovyk*, A. Kamensky

Cherkasy state technological university, Shevchenko Blvd., 460, Cherkasy, 18006 Ukraine, v.viazovyk@chdtu.edu.ua

In our time, the problem that fossil energy sources are being depleted, and their use leads to the formation of unnecessary greenhouse gas CO_2, has become very relevant. Emissions of carbon dioxide into the atmosphere are considered the main cause of global warming, in 2021 they exceeded the mark of 37 billion tons [1]. The average concentration of CO_2 as of the end of July 2023 was 421.9 ppm, while at the end of July 2022 this value was about 419.08 ppm [1]. We observe an increase 0.67 %. And this increase worries.

Carbon dioxide CO_2 is the most significant of anthropogenic greenhouse gases. Although this gas is of natural origin, thanks to human activity it is formed in the largest amount. Industrialization has led to an increase in the use of organic fuels extracted from the Earth's interior: coal, oil, gas, and burned with the formation of a large amount of CO_2. The largest emissions of carbon dioxide occur in transport and production of electricity and heat. It is known that the source of CO_2 emissions into the atmosphere is the flue gases of power plants of various types, capacities and purposes. In addition, about 39 Gt CO_2 is in the atmosphere [1].

The main direction in the fight against climate change is the joint reduction of greenhouse gas emissions into the Earth's atmosphere, decarbonization - carbon capture and storage, and the conversion of CO_2 into fuel and petrochemical products. These problems could be solved if an effective way of using carbon dioxide as a carbon source in the production of fuel and chemical raw materials was found.

The transformation of CO_2 into chemicals and energy carriers with added value is considered one of the most important tasks of the 21st century. Due to the limitations of traditional thermal approaches, several new technologies are being developed.

Among them, the following can be distinguished [2-3]: biological, solar, photochemical, electrochemical and plasma methods, as well as methods using catalysts.

One of the new methods that is currently developing are plasma catalytic methods. The combination of plasma with catalytic processes gives very good results. This allows for the enhancement of plasma reactions by adding a catalyst to the reaction cycle. Inert molecules are activated by plasma under mild conditions, and subsequently the activated particles are selectively recombined on the surface of the catalyst to obtain the desired products. Plasma and catalysts can be combined in various combinations: the catalyst is spatially separated from the plasma region, or is located inside the discharge region. In a traditional experiment on thermal catalysis, molecules are dissociatively adsorbed on the catalyst with energy supplied in the form of heat. In plasma catalysis, particles are activated by the plasma due to excitation, ionization or dissociation by electrons in the gas phase or on the surface of the catalyst. The main difference between the one-stage and two-stage configuration is the type of particles to which the catalyst is exposed. In the two-step configuration, the final products and long-lived intermediates will interact with the catalyst, while in the one-step configuration, the catalyst can also interact with all short-lived species, including excited compounds, radicals, photons, and electrons. In addition, in this configuration, the catalyst can also be affected by plasma and vice versa.

To increase the efficiency of the simultaneous use of plasma and catalyst, a two-stage process can be used, but in the second stage, the catalyst can also be placed in the plasma zone. The proposed scheme of the two-stage treatment of the gas mixture is as follows: first, for the activation of chemical reactions and the formation of radicals in the primary discharger (pure plasma), and then for the direct synthesis process on the catalyst in a low-temperature environment. plasma zone in the second discharger.

The formation of methanol is affected by temperature and discharge voltage. Thus, there was an increase in the formation of methanol in the sample immediately after the experiment from 0.3419 g (for a temperature of 250°C and a voltage of 11 kV) and up to 0.9317 g (for 350°C and a voltage of 10 kV), for formaldehyde from 0.1549 (for a temperature of 250°C and a voltage of 10 kV) to 0.5589 (for 350°C and a voltage of 10 kV).

Also, significantly affects the content of formaldehyde and methanol in the sample, the exposure of the sample during the day. As a result, there is an increase in the concentration of methanol in the sample from 5.8% (at a temperature of 250°C and a voltage of 10 kV) to 49.7% (at a temperature of 350°C and a voltage of 11 kV) and formaldehyde from 4.1% (for 250 ° C and a voltage of 10 kV) up to 50.01% (for 350°C and a voltage of 9 kV). All this is explained by a sharp increase in the formation of oxygen-containing radicals HO°, and HO_2°, which are formed by the interaction of ozone formed from CO_2 in the discharge zone with aqueous solutions.

References:

1. CO_2 Earth is live!! Daily CO_2 https://www.co2.earth/daily-co2/, 2023 (accessed 12.07 2023).
2. A. Bogaerts, T. Kozak, K. Van Laer, R. Snoeckx, Faraday Discuss.. 2015, **183**, 217–232
3. A. Bogaerts, A. Berthelot, S. Heijkers, St. Kolev, R. Snoeckx, S. Sun, G. Trenchev, K. Van Laer, W. Wang, Plasma Sources Science and Technology, 2017, **26**, 063001, 1-34.

S-38

SYNTHESIS OF THE F-TiO_2/CuO PARTICLES VIA COPRECIPITATION METHOD

D.S. Sofronov[1]*, O.M. Lebedynskiy[2], M. Rucki[3], S.S. Minenko[4]

[1]Institute for Single Crystals, National Academy of Sciences of Ukraine, Prosp. Nauky, 60, Kharkiv, 61178 Ukraine, 19sofronov73@gmail.com
[2]State Scientific Institution «Institute for Single Crystals», National Academy of Sciences of Ukraine, Prosp. Nauky, 60, Kharkiv, 61178 Ukraine
[3]Kazimierz Pulaski University of Technology and Humanities in Radom, Stasieckiego St., 51, 26-600 Radom, Poland
[4]Institute for Scintillation Materials, National Academy of Sciences of Ukraine, Prosp. Nauky, 60, Kharkiv, 61178 Ukraine

Titanium oxide TiO_2 is a semiconductor suitable for photocatalysis and solar energy conversion due to its properties, such as stability against photo- and chemical corrosion), low cost, as well as high cleaning and antibacterial effects. However, the inherent limitations and high operating costs limit the practical applications of TiO_2 photocatalytic membranes, which motivates researchers to search for new approaches to enhancing their photocatalytic performance, including metal and non-metal doping, control over reaction conditions, fabrication of heterojunction structures, increase in hydrophilicity, and increase in membrane porosity. One of the most popular directions for improving the photocatalytic properties of titanium oxide particles is the creation of TiO_2-based heterostructural catalysts. Copper(II) oxide has recently attracted research interest in the area of photocatalyst formation with heterojunction structures due to its availability, good stability and its absorption in visible light spectrum. CuO is a typical p-type semiconducting compound with a monoclinic structure and a low band gap of Eg = 1.2–2.0 eV. Since Eg lays between the wide band gap of TiO_2, it is possible to form p–n junctions of CuO with n-type TiO_2.

In particular, inserting CuO into the structure of TiO_2 can cause an increase in photocatalytic activity, because it is created internal electric field, which promotes electron-hole separation and decelerates the charge carrier recombination.

The synthesis was carried out as follows: metallic titanium was placed in a fluoroplastic vessel. Its full dissolution was reached adding of distilled water and of hydrofluoric acid. Next, a weighed portion of copper nitrate was added to obtain concentrations 0.5, 1, 2, 5, and 10 wt.%, calculated in relation to CuO. Asprepared solution was heated up to boiling temperature and boiled for ½ up to 4 hours. Due to evaporation, the precursor in form of a dry powder appeared, which was then subject of calcination at temperatures 300 °C, 400 °C, 500 °C, and 600 °C in air during 1 hour. Dependent on the copper content, the as-obtained powders had colors from white to dark grey.

After evaporation, white precipitate was formed from the titanium fluoride solution with pH 1. The obtained results demonstrated that addition of copper 1 wt.% and 2 wt.%, as calculated in relation to CuO, contributed to the synthesis of a single phase $TiOF_2$ precipitates. On the other hand, the samples synthesized with 5 wt.%, as calculated in relation to CuO, consisted of two phases, namely, titanium oxyfluoride and copper fluorotitanate tetrahydrate $CuTiF_6{\cdot}4H_2O$. It should be noted that increase of the copper proportion in the precursor has also impact on the ratio between the cubic (c-$TiOF_2$) and hexagonal (h-$TiOF_2$) modifications of titanium oxyfluoride, with the amount of hexagonal modification being decreased. Noteworthy, neither pH increase up to 4, nor addition of the hydrofluoric acid during synthesis had any effect on the phase composition or on the morphological features of the obtained powder. When the copper was present in concentration of 0.5 wt.%, agglomerated particles were formed of spherical form with diameters up to 1 μm. When the proportion of the copper increased, the particles grew larger, up to 2-3 μm.

After evaporation, white precipitate was formed from the titanium fluoride solution with pH 8. It should be noted that the obtained results were identical for both neutral and alkaline environments. XRD analysis above demonstrated that right after synthesis, the samples represented a multiphase composition. The following compounds were identified: $(NH_4)_2TiF_6(H_2O)_2$, $(NH_4)_3TiF_7$ и $(NH_4)_2CuF_4(H_2O)_2$.

In order to form a CuO phase, calcination procedure of the initial precursor was performed in air for 1 hour, applying from 300 °C up to 600 °C. Calcination process at temperature Tc = 300 °C resulted with appearance of anatase and rutile phases in the titanium dioxide sample. Formation of new phases of titanium dioxide and copper(II) oxide was accompanied by the decrease of the powder particles dimensions. At low concentrations of copper up to 1 wt.%, particles size did not change substantially. However, high content of copper (10 wt.%) caused formation of fine-dispersed powder with spherical particles. The results of elemental analysis confirmed that decomposition of the titanium oxyfluoride took place at temperatures higher than 300 °C. In this temperature range, significant decrease of the fluorine was noted with the increase of oxygen in the samples. At the same time, fluorine was found in the samples calcined at 600 °C which can be attributed to the formation of fluorinated titanium dioxide F-TiO_2. Fluorine content in titanium dioxide increased with the increase of copper concentration in the samples.

Calculations Eg proved that the increase of copper content caused slight decrease of the gap energies for the samples obtained in the acid solutions. In particular, for copper dopant content of 0.5 wt.% it was 3.3 eV, for 1 wt.% it was 2.25 eV, while for 5 wt.% it was 3.2 eV. In contrast, the opposite trend was observed for the samples synthesized in the alkaline solutions. Copper dopant content up to 5 wt.% did not cause significant changes of the absorption edge, but for 10 wt.% it shifted significantly toward ultraviolet area of the spectrum. At the same time, the band gap energy Eg increased up to 5.1 eV. The calcination procedure had some effect on the diffuse reflectance spectra, as it is seen in Fig. 14. The absorption edge shifted somewhat toward visible spectrum area, which can be seen also from data provided in Table 5. At the same time, Eg decreased down to values of 3.05 eV and 3.14 eV for the particles synthesized at pH 1 and pH 6, respectively, and afterwards calcined at 600 °C. So it is quite evident that the presence of CuO in the CuO/TiO_2 nanocomposites had a favorable effect on the light absorption characteristics, making it possible to exploit effectively the visible spectral region of the solar light. The increase of light absorption can contribute to the improvement of the photocatalytic properties.

S-39

HIGHLY SENSITIVE CHEMILUMINESCENCE DETERMINATION OF CITRATE IONS BASED ON THE ENHANCEMENT OF THE LUMINOL REACTION CATALYZED BY COBALT (II)

Yu.I. Mazna, N.G. Kobylinska, O.V. Zuy*

A.V. Dumansky Institute of Colloid and Water Chemistry, National Academy of Sciences of Ukraine, Vernadsky blvd., 42, Kyiv, 03142 Ukraine, olegzuy@gmail.com

The oxidation of luminol (3-aminophthalhydrazide) is one of the most efficient chemiluminescence reactions. The produced chemiluminescence emission is strongly enhanced when metal ions such us Co(II) ions are used as an effective catalyst (Fig. 1) [1].

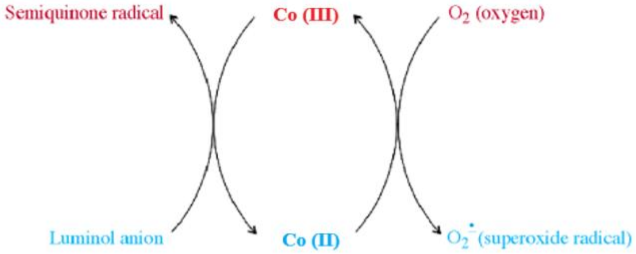


Fig. 1. Schematic diagram of the catalytic reaction luminol – Co(II) – oxygen

It is seen from Fig. 1 that catalytic oxidation of luminol anion to semiquinone radical by air oxygen proceeds through the redox cycle of cobalt ions. Then superoxide formed further oxidizes semiquinone radical to luminol peroxide which decomposes with light emission forming aminophthalate as a final product. The reaction in the luminol – Co(II) – O_2 system is accompanied by a flash-like light emission. Also, citric and glutamic acids enhance the chemiluminescence intensity of this reaction by a factor of 2-3, unlike other ligands [1]. It was found by us that chemiluminescence in the system is further increased by additions of tetradecylpyridinium bromide. This effect could be explained by formation of Co(II) – citric acid complexes [2] and then the complexes are concentrated at the surface of cationic micelles. The complex reacts with dissolved oxygen in water to form hydroxyl radicals or superoxide ions on the surface of micelles. Thus, the intensity of chemiluminescence emission is enhanced as the reaction rate increases markedly in micellar medium. In this work, we propose the first chemiluminescence method for the determination of citrate ions based on the fact that citrate activates strongly the chemiluminescence emission from luminol in alkaline medium by oxygen on the surface of tetradecylpyridinium micelles in the presence of Co(II) as a catalyst. A multivariate optimization was used for obtaining the optimum parameters for this catalyzed chemiluminescence method.

The results demonstrated that the intensity and duration of chemiluminescence emission depends on solution pH, concentration of components, and order of adding of reagents into the reaction mixture. The most intense light emission is observed at pH 12.0 – 12.5. The mixing of components is implied by following order: (*1*) luminol + NaOH; (*2*) Co(II). The lowest detection limit of Co(II) is achieved at the concentration of luminol equal to $1 \cdot 10^{-3}$ M. Micelle enhanced luminol chemiluminescence method is developed for determination of citrate ions with detection limit near 1×10^{-7} M.

The proposed method has been satisfactorily applied to the determination of citrate ions in soft drinks and different pharmaceutical formulations. In addition, this simple and sensitive method can be used for quality control of various citrate-containing products.

References:

1. A.T. Pilipenko, O.V. Zui, A.V. Terletskaya, J. Water Chem. Technol. **6** (1984) 48.
2. V.M. Nikitenko, Yu.S. Yapontseva, V.S. Kublanovsky, Ukr. Chem. J. **88** (2022) 113.

DEVELOPMENT OF THE PROCESS OF BIODIESEL SYNTHESIS USING DOMESTIC RAW MATERIALS

I.B. Bychko*, A.I. Trypolskyi

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, igorbyhko@ukr.net

The results of the work carried out under the project "Development of heterogeneous-catalytic processes for obtaining liquid synthetic motor fuels from domestic raw materials to ensure energy independence of the state" are presented under the section "Development of catalysts and technological design of processes for obtaining components of motor fuels from synthetic gas, bio-raw materials, and products with added value", which is carried out as part of a complex of scientific and experimental works on the development and scientific support of the implementation of national strategic initiatives for the development of innovative types of industrial activity during the war period and during the post-war recovery of Ukraine for 2023-2024 years.

The project is aimed at creating catalysts for transesterification of fatty acid triglycerides as the basis of biodiesel production technology. While the production of biodiesel in the world is measured in the amount of 20 million tons/year, biodiesel is practically does not manufactured in Ukraine. With the actual sunflower oil production capacity of 4 million tons per annum, and the established bioethanol production capacity of 0.3 million tons per annum, Ukraine has a raw material base to meet its own needs in motor fuel at the expense of biodiesel at the level of 1-2 million tons per annum, which is 15-30% of all diesel fuel consumption in 2021.

An experimental study of the biodiesel production process using both methanol and ethanol in the presence of homogeneous and heterogeneous catalysts was provided. It was shown that the water impurities in ethanol significantly reduces the reaction rate as well as the yield, which is a consequence of the greater acidity of the water compared to the ethanol and, as a result, the equilibrium shift towards the formation of alkali, which leads to a decrease in the concentration of the target products - alcoholates. Thus, the application of ethanol for biodiesel production is possible only in case of its absolutization.

It was shown that the use of such homogeneous catalysts as methylate or sodium ethylate allows to increase the yield of biodiesel in comparison with the use of sodium hydroxide. The low performance of sodium hydroxide is conditioned by the formation of water due to the interaction of sodium hydroxide with alcohol, which in turn leads to saponification of the reaction products and, accordingly, to a decrease in the yield of the biodiesel. It is shown that the product obtained as a result of direct interaction requires purification from sodium salts of fatty acids, impurities of glycerin and alcohol. Purification is achieved by washing the biodiesel three times with water, followed by the separation of polar and non-polar phases and their separation using a separator. The final purification of the obtained biodiesel is achieved by drying in a vacuum or using sorbents.

It was established that the use of ion exchange resins as heterogeneous catalysts for the production of biodiesel is can be provided only in the case of using ethanol. The use of methanol is complicated by the high polarity of methanol, which leads to unsatisfactory wetting of the ion exchange resin and, as a result, a small part of the catalyst surface involved in the catalytic conversion. It is shown that the catalytic activity of anion exchange resins is significantly higher than that of cation exchange resins. However, during the synthesis there was observed an irreversible swelling and destruction of anion-exchange resins particles, which hindered the repeated applying of resins for the synthesis of biodiesel.

MIDDLE DISTILLATE FUEL PRODUCTION FROM SYNTHESIS GAS OBTAINED BY GASIFICATION OF BIOMASS VIA THE FISCHER–TROPSCH PROCESS

A.I. Trypolskyi[1]*, K.Ye. Pyanykh[2], B.S. Soroka[2]

[1]L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, atripolski@gmail.com
[2]The Gas Institute, National Academy of Sciences of Ukraine, Degtyarivska st., 39, Kyiv, 03113 Ukraine

Biomass conversion to liquid transportation fuels has been a topic of significant research interest since it is a renewable and sustainable energy source [1]. There is a huge amount of biomass available, and the use of biomass as energy source can alleviate global warming because the emitted CO2 can be used for growing new biomass through photosynthesis [2].

The main methods of thermochemical transformation of biomass into synthesis gas are gasification, pyrolysis and hydrothermal liquefaction. In our work, we used gasification technology to convert biomass into syngas (mainly CO and H2) at high temperatures, for further use in Fischer-Tropsch synthesis (FTS), to produce a wide range of hydrocarbons that can be used as a liquid motor fuel. We have studied biomass gasification in combination with FTS to produce liquid fuel. A pilot plant was developed for the production of up to 10 m3/h of generator gas from solid fuels with a moisture content of up to 15% and a content of volatile substances of more than 40%. Among them are brown coal, lignite, chicken droppings, city sewage sludge, agricultural waste, and wood processing waste (Fig. 1).

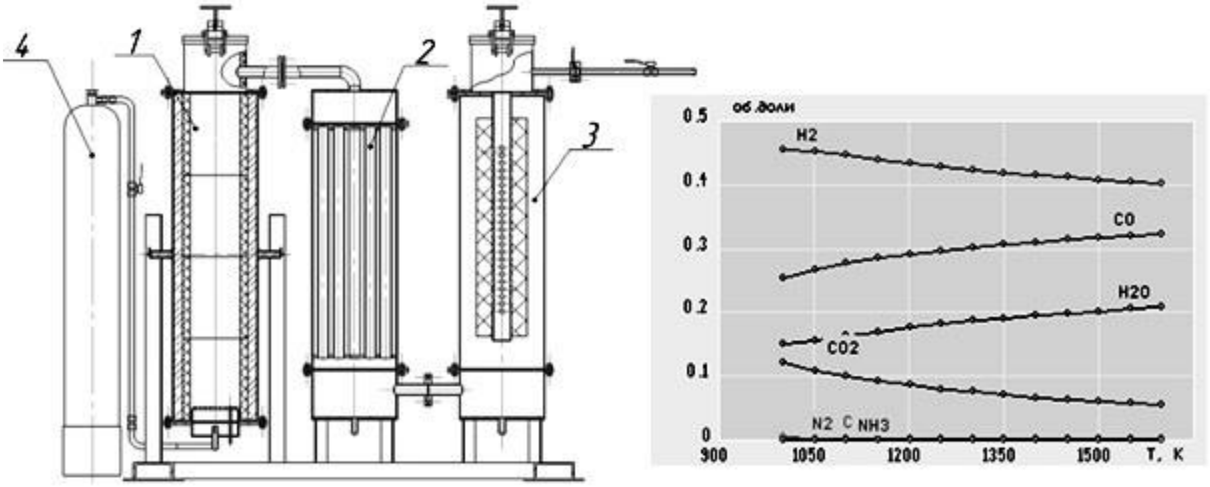
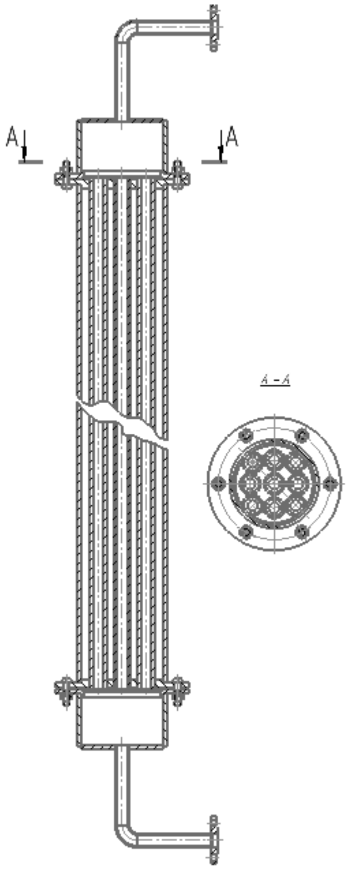


Figure 1. Equipment for gas generation and primary preparation:
1 – gas generator, 2 – heat exchanger – gas cooler; 3 – filter; 4 – oxygen supply unit.
Dependence of the composition of gasification products on temperature (fuel - lignite.
Conditional fuel composition: $C_{2,4372}\,H_{7,99}\,O_{3,4231}\,N_{0,025}\,S_{0,0615}$).

For the implementation of the FTS process, a model of a multi-tube reactor with a fixed catalyst bed was chosen. Its main advantage is easy scaling when the design and experimental data for one tube are available.

Since the syngas obtained by the gasification of bio-raw materials have a low H2/CO ratio, a relatively high concentration of CO2, and a generally unstable composition, an iron-based catalyst is optimal. We have fabricated a catalyst with the following composition: Fe-

79%, Cu-4.5%, MnO-1.5%, and Al_2O_3-15%. The catalyst showed high catalytic activity and selectivity for liquid hydrocarbons on model mixtures of syngas. Kinetic studies of the developed process carried out in laboratory conditions made it possible to create a construction of the FTS reactor (Fig. 2) based on mathematical modeling and to optimize the parameters to achieve the highest productivity in the absence of significant overheating of catalyst layer. In the mathematical modeling of the reactor, diffusion inhibition in the pores of the catalyst particles, and radial heat exchange from the backfill layer to the reactor wall and from the reactor wall to the cooling medium, which is boiling water, were taken into account.



Pressure Drop	5 Bar
Residence time	7.2 c
Temperature	280 °C
Temperature delta	50 °C
Volume	0.003 m^3
Tube Length	1.2 m
Diameter	0.1 m
Cross section area:	0.00785 m^2
Total reactor volume	0.0094 m^3
Total tube cross section area	0.0028 m^2
Total tube perimeter	0.5655 m
Net cross section area	0.005 m^2
Net reactor volume	0.006 m^3
Hydraulic diameter	0.0229 m
Catalyst loading	8000 kg/m^3
Catalyst diameter	2 mm
Catalyst void fraction	0.5
Heat load	-2.28871 kW
Tube Diameter	0.02 m
Number of Tubes	9
Carbon monoxide: Conversion	88.7544%

Figure 2. Construction of a multi-tube reactor with a fixed catalyst bed and results of model calculation.

The basis was a one-dimensional heterogeneous model in the approximation of isothermal granules, which takes into account both diffusion from the gas phase to the surface of the granules, and diffusion in the pores of the catalyst. The heat carrier (water) continuously circulates through a stationary bundle of tubes. The boiling coolant fills the reactor jacket, and due to the density difference in the drain pipe and the reactor jacket, a circulation flow is established. The temperature of the saturated steam is regulated by the pressure of the saturated steam.

References:

1. R.C. Saxena, D.K. Adhikari, H.B. Goyal, Biomass-based energy fuel through biochemical routes: A review, Renewable and Sustainable Energy Reviews, **13** (2009) 167.
2. P. McKendry, Energy production from biomass (part 1): overview of biomass, Bioresource Technology, **83**, (2002) 37.

APPROACHES TO THE FABRICATION OF EFFECTIVE ORGANIC-INORGANIC CATALYSTS FOR ETHERIFICATION OF ALCOHOLS

N.V. Vlasenko

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, nvvlasenko@gmail.com

Sulfonic resins that represent the sulfonated copolymers of styrene and divinyl benzene are well-known catalysts for acid-base heterogeneous catalysis reactions, e.g., esterification, hydration, alkylation, carbonylation and oligomerization, etc. This peculiar type of materials can be considered as an "intermediate link" between homogeneous and heterogeneous catalysts since the catalytic reaction occurs with the participation of acid sites both on the surface and inside the bulk of the catalyst. Commercial sulfonic resins belong to two main morphological types: gel-type, which are characterized by a small specific surface area and no pores, and macroporous, in which gelular polymer micrograines form macropores. Catalytically active sites of these materials are acid groups, $–SO_3H^+$.

Despite the identity of the nature of the active sites, the activity of a single acid site, characterized by the "turnover frequency" of the catalytic reaction, differs significantly for sulfonic resins of different morphological types. Thus, morphology is no less important factor in the formation of catalytic characteristics of sulfonic resins than their acidity. For the bulk commercial sulfonic resins, acid sites are not enough efficiently used in catalytic reactions. That may be caused by the localization of the majority of acid sites in the depth of the polymer matrix. As a result, they are accessible only upon swelling. The effect of morphology is multifaceted but primarily, it determines the localization of acid sites and their accessibility for reagents, and, consequently, the efficiency of their participation in the reactions of etherification of alcohols [1].

The term "accessibility" defines the portion of sites that can participate in the activation of reagents [2]. This value determines the ease of penetration of the adsorbate into the polymer structure, and can also be characterized as the ratio of the amount of sorbed substance in the polymer bulk and in a free state. Accessibility in turn, affects the catalytic activity of sulfonic resins due to various factors: energetics of acid sites, adsorption-desorption dynamics of reagents, and mass transfer efficiency [1].

The effect on the acidity of sulfonic resins is manifested in the differences in the energy of external and internal acid sites. The effect on mass transfer characteristics determines the low-temperature branch of the volcano-like temperature dependence of the catalytic activity of sulfonic resins in alcohols esterification reactions and thus determines the optimum process temperature. Thus, improving the accessibility of acid sites, allows us to significantly increase the productivity of sulfonic resin catalysts.

Increasing the number of well-accessible sites is possible by the fabrication of hybrid organic-inorganic materials. The fabrication of these type of catalysts makes it possible to eliminate the disadvantages of bulk sulfonic resins and significantly increase the productivity in catalysis. The rigid structure of these materials minimizes the contribution of swelling and mass transfer processes to the observed reaction rate. In this report, various types of hybrid organic-inorganic resin catalysts: mixed and co-precipitated composites, loaded and tailored systems are considered.

Based on a comparison of the productivity of organic-inorganic and commercial sulfonic resins, the role of acid sites localization for determining the catalytic characteristics of sulfonic resin catalysts in ethanol and *iso*-propanol etherification with *iso*-butylene is shown.

Fig. 1 presents the temperature dependences of the productivity of sulfonic resin catalysts of various types (both bulk organic and organic-inorganic) in the reactions of ethyl-*tert*-butyl (ETBE) and *iso*-propyl-*tert*-butyl (IPTBE) ethers synthesis from corresponding alcohols and *iso*-butylene:

$$\text{Alc-OH} + H_2C{=}C(CH_3)_2 \xrightarrow{H^+} \text{Alc-O-C}(CH_3)_3$$

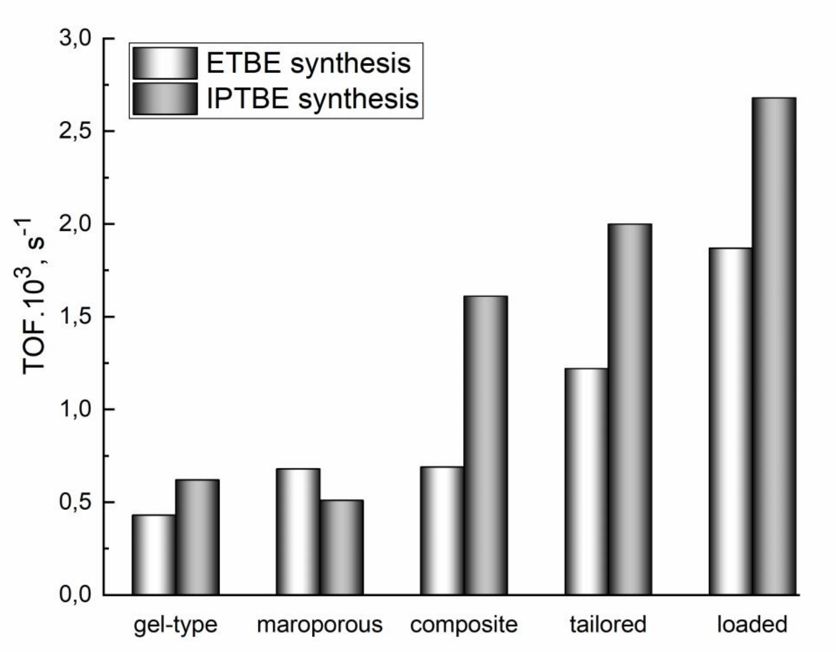


Fig. 1. Dependences of ETBE (1) and IPTBE (2) productivity on acid capacity of organic phase for sulfonic resin catalysts of various morphological types.

Studies have shown that productivity of sulfonic resin catalysts depends significantly on the accessibility of acid sites [3]. A more significant increase in productivity is achieved when creating tailored and loaded sulfonic resins. In these materials, acid sites are localized on the external surface. Loaded resins, which ensure the most effective participation of acid sites in the catalytic reaction, are characterized by the highest productivity in the etherification of alcohols.

Among the variety of types of organic-inorganic materials, the most technologically convenient are composites, owing to the simplicity of preparation, as well as the cheapness and availability of ingredients. The productivity of these catalysts in the etherification of alcohols is significantly higher than for bulk sulfonic resins. However, in this type of catalysts, some part of acid sites are inaccessible for reagents and the effect of mass transfer is not completely excluded.

References:

1. N.V. Vlasenko, P.E. Strizhak, Theor. Exp. Chem., 56 (2020) 309.
2. Ch. Butfersack, Reactive Polymers, 10 (1989) 143.
3. N.V. Vlasenko, P.E. Strizhak, J. Appl. Polym. Sci., 139 (2022) e51926.

GLYCEROL TRANSFORMATIONS OVER H-MOR CATALYSTS

N.V. Vlasenko*, G.R. Kosmambetova, O.V. Shvets

L.V. Pysarzhevskii Institute of Physical Chemistry, National Academy of Sciences of Ukraine, Prosp. Nauky, 31, Kyiv, 03028 Ukraine, nvvlasenko@gmail.com

Recently, a fundamental shift in the world of energy has stimulated the search and development of alternative energy sources, the production of which is based on the use of renewable raw materials. The attractiveness of biodiesel is due to the fact that it can be obtained both from vegetable raw materials and from spent fats of vegetable and animal origin. The economic profitability of biodiesel production depends on the rational use of a large amount of glycerol, which is a by-product of the process. Simultaneously, due to unique structure, glycerol is an attractive raw material for the production of a large number of chemicals, motor fuel additives, hydrogen-enriched mixtures, etc.

Catalytic processing of glycerol opens the way to obtaining such valuable products as acrolein, acetol, allyl alcohol, acetaldehyde, which are widely used in the production of polymer materials, medicines, and flavourings. The direction of the process depends mainly on the acid-base properties of the catalyst surface [1]. The transformation of glycerol into acrolein occurs with the participation of Brønsted acid sites and involves protonation of the secondary hydroxyl group [2]. The formation of acetol requires the participation of Lewis acid sites and occurs by direct dehydration of one of the terminal hydroxyl groups [1]. Lewis acid sites are coordinatively unsaturated metal ions. At the same time, these sites can act as redox centers [3]. In this case, instead of mild dehydration of glycerol, its hydrogenolysis occurs with the formation of allyl alcohol.

Among the large number of studied catalytic systems, one of the most active are zeolites [4]. However, the presence of strong acid sites causes their carbonization, which leads to the blocking of active sites and loss of activity [5]. Therefore, the development of effective and stable zeolite-containing catalysts that do not lose activity during operation is an urgent task. One of the ways to fabricate these catalysts is to adjust the spectrum of acidity of zeolites, aiming to increase the concentration of acid sites of moderate strength and remove strong acid sites, which are responsible for cracking and carbonization processes.

One of the requirements for catalysts of industrially important processes is their cheapness and availability. H-MOR zeolites were chosen for research due to high thermal and hydrolitic stability, and high concentration of acid sites. The initial H-MOR sample was dealuminated by acid treatment with 1 or 6 M hydrochloric acid solutions to reduce the concentration of strong acid sites, which are responsible for the side reactions of cracking, which causes carburization. The samples obtained in this way were leached with 0.25–3.0 M NaOH solutions to form a mesoporous structure and washed with a weak (0.05 M) HCl solution to remove sodium and release acid sites. In this way, a series of samples was obtained, which are listed in the Table.

Table. Research objects

Sample	Treatment procedure
catalyst 1	MOR deAl 6M HCl
catalyst 2	NH_4^+-MOR H^+, 0,1 M HCl
catalyst 3	MOR deAl 1M HCl, de Si 0,5 M NaOH, 0,1 M HCl
catalyst 4	MOR deAl 1M HCl, de Si 0,25 M NaOH, 0,1 M HCl
catalyst 5	MOR 3 M NaOH, 6M HCl + 10 % HCl

According to the FTIR data of adsorbed pyridine, all the studied samples possess mainly Brønsted acidity (B/L > 20). Acid treatment by 6M HCl leads to decrease in the concentration of Brønsted acid sites from 415 µmole/g (catalyst 1) to 250 µmole/g (catalyst 2) due to partial elimination of aluminum from zeolite framework. The following treatment procedures significantly change the concentration of Brønsted acid sites: from 100 µmole/g for catalyst 3 to 700 µmole/g for catalyst 4.

The study of catalytic characteristics was carried out in a flow reactor under atmospheric pressure at a temperature of 320 °C. To reduce the viscosity and increase the boiling point, the reagent was used as a water-glycerol mixture (10% vol. glycerol).

The products of glycerol conversion in all cases were acetaldehyde and allyl alcohol. The yield of products, calculated as the proportion of the product to the theoretically possible (by stoichiometry) amount, did not exceed ~20% and slightly decreased over time. The highest yield (21%) was achieved on catalyst 3 (the sample dealuminated with 0.1 M HCl). The selectivity of the catalysts on acetaldehyde and allyl alcohol was approximately the same, but over time the formation of acetaldehyde gained some advantages (Fig. 1).

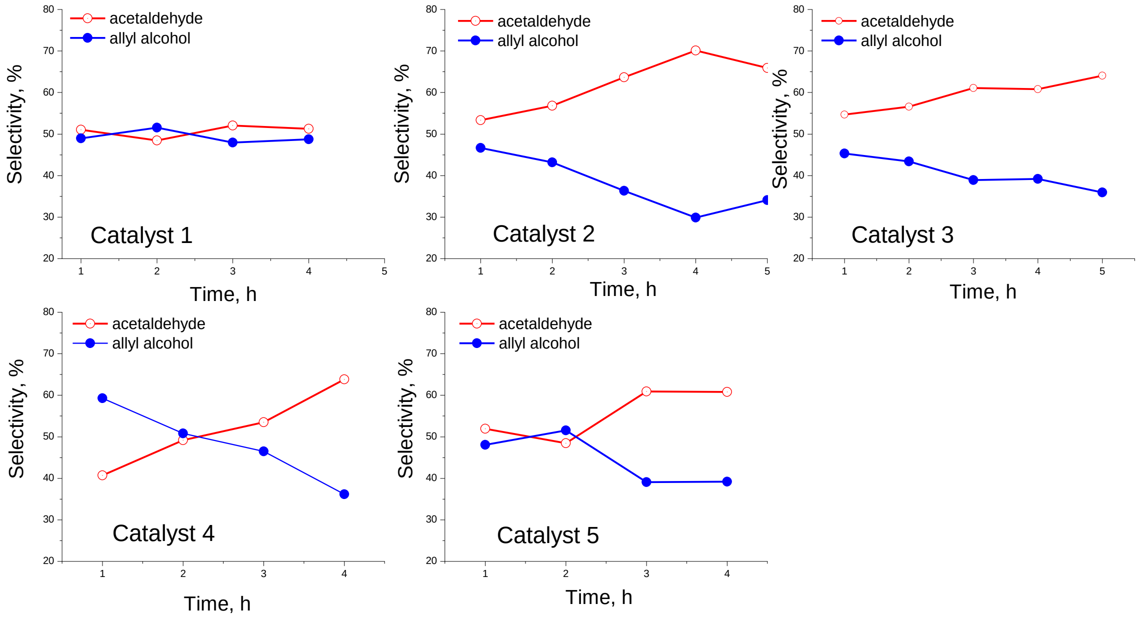


Fig. 1. Change over time in the selectivity of H-Mor catalysts for the products of glycerol conversion.

Thus, H-Mor zeolites can be promising for the creation of catalysts for the processing of glycerol into acrolein and/or allyl alcohol. Further research should be aimed at improving the stability of the catalysts' operation and to design of the active surface in order to unification the acid spectrum of zeolite, with the aim of increasing the selectivity towards the formation of the desired product acetaldehyde or allyl alcohol).

References:

1. M. Velásquez, C. Batiot-Dupeyrat, J.F. Espinal, et al., Dyna. **86** (2019), 126.
2. S-H. Chai, H-P. Wang, Y. Liang, B-Q. Xu, Green Chemistry. **9** (2007), 1130.
3. H. Zhao, Y. Jiang, H. Liu, et al, Appl. Catal. B: Environ. **277** (2020), 119187.
4. Q. Ge, Y. Huang, F. Qiu, S. Li, Appl. Catal. A **167** (1998) 23.
5. M. Migliori, E. Catizzone, A. Aloise, et al., J. Ind. Eng. Chem. **68** (2018) 196.

AUTHORS INDEX

CONTENTS

Наукове видання

НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ
ІНСТИТУТ ФІЗИЧНОЇ ХІМІЇ
ім. Л.В. ПИСАРЖЕВСЬКОГО НАН УКРАЇНИ

МАТЕРІАЛИ МІЖНАРОДНОЇ КОНФЕРЕНЦІЇ “СУЧАСНІ ПРОБЛЕМИ КАТАЛІЗУ”
CPC-2023
(м. Київ, 25—29 вересня 2023 р.)

Англійською мовою

Підп. до друку 20.09.2023. Формат 60×84/16.
Ум. друк. арк. 10,46. Обл.-вид. арк. 12,87.
Тираж 50 прим. Зам. № 7043

Видавець і виготовлювач
Видавничий дім «Академперіодика» НАН України
01024, Київ, вул. Терещенківська, 4

Свідоцтво про внесення до Державного реєстру суб’єктів
видавничої справи серії ДК № 544 від 27.07.2001 р.