PISC 2024

16th Pannonian International Symposium on Catalysis

Program and Abstracts

MONTAN
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Catalysis is the art of transforming the impossible into the inevitable, with nothing but the gentlest of nudges. It teaches us that even the smallest force, when applied wisely, can unleash profound change. In the world of reactions, the catalyst is the silent architect, shaping outcomes without ever becoming part of the story.

Marta T. P. R. Stroverner,
Chief Data Engineer*

*The organizers do not claim that this person is real. In fact, it is an anagram of ChatGPT.

THE SYMPOSIUM WAS ORGANIZED WITH THE KIND SUPPORT OF

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Julia Roll

Günther Rupprechter

Dear Participants,

it is our great pleasure to welcome you to this meeting traditionally connecting people and minds. Even in times of the iron curtain, there have been close bonds between the catalysis societies of Austria and Hungary, with meetings held in Hungary near the border. In 1990, after restrictions had been lifted, the 1st Pannonian Meeting was held at Burg Schlaining (Austria), once more close to the border to enable easy travel. The success of this meeting then stimulated other national societies to join, with the second meeting in Valtice (Czech Republic). The “Pannonian Club” now includes six countries, each organizing the conference in a “catalytic cycle”. Apart from renowned plenary and keynote speakers, the latter nominated by each national society, the meeting´s success certainly originated from the contributions of established and upcoming researchers, well documented by well-known researchers that once presented their PhD work at the Pannonian.

As we all know, catalysis is essential for a transition of our society towards a sustainable (energy) future by enabling efficient chemical reactions and minimizing energy use and waste. Catalysts facilitate the conversion of renewable resources, such as biomass, CO_2, and water, into fuels and chemicals, reducing reliance on fossil fuels and resources. With the development of highly efficient catalysts with superior reaction rates and selectivity, processes can run under milder conditions and with less waste streams, thereby conserving energy and lowering greenhouse gas emissions. Innovation is crucial for developing clean energy technologies, such as hydrogen production, carbon capture and utilization, and biofuel synthesis, thus driving the shift towards a more sustainable and resilient chemical industry.

To achieve this innovation via successful research, we wish you a fruitful conference with many interactions, old and new, scientific and social, at this scenic spot of Burg Seggau.

Best regards,

Christoph Rameshan and Günther Rupprechter
Organizers

PROGRAM

	Sunday, 01.09.2024
18:00–19:30	**Dinner**
19:30–19:45	**Opening**
19:45–20:45	**Mayr (PL.1)**
20:45–	**Welcome Reception**

	Monday, 02.09.2024		**Tuesday, 03.09.2024**		**Wednesday, 04.09.2024**		**Thursday, 05.09.2024**
09:00–09:40	**Dvoranaová** (KN.1)		**Tuba** (KN.3)		**Lercher** (PL.2) (until 10:00)		**Pintar** (KN.6)
09:40–10:05	**Horvath** (O.1)		**Feldt** (O.2)				**Ruh** (O.3)
10:05–10:40	**Coffee Break**		**Coffee Break**		**Coffee Break**		**Coffee Break**
	Room 1 (Kongress)	**Room 2** (Styria)	**Room 1** (Kongress)	**Room 2** (Styria)	**Room 1** (Kongress)	**Room 2** (Styria)	**Closing & Awards (until 11:15)**
	Session 1a	**Session 2a**	**Session 4**	**Session 5**	**Session 1d**	**Session 6a**	
10:40–11:05	**Sobalska** (O.1.01)	**Topka** (O.2.01)	**Nowakowski** (O.4.01)	**Wisniewska** (O.5.01)	**Legutko** (O.1.10)	**Al-Zuraiji** (O.6.01)	
11:05–11:30	**Schrenk** (O.1.02)	**Berger** (O.2.02)	**Sojka** (O.4.02)	**Vajda** (O.5.02)	**Iwanek** (O.1.11)	**Stelmachowski** (O.6.02)	
11:30–11:55	**Olszowka** (O.1.03)	**Jirglová** (O.2.03)	**Genest** (O.4.03)	**Michalke** (O.5.03)	**Stawicka** (O.1.12)	**Ollár** (O.6.03)	
12:00–13:30	**Lunch**		**Lunch**		**Lunch**		
13:30–14:10	**Bulánek** (KN.2)		**Trejda** (KN.4)		**Barrabés** (KN.5)		
	Session 1b	**Session 2b**	**Poster Session 2**		**Session 1e**	**Session 6b**	
14:10–14:35	**Alves** (O.1.04)	**Danylo** (O.2.04)			**Zasada** (O.1.13)	**Keszei** (O.6.04)	
14:35–15:00	**Beresova** (O.1.05)	**Grybos** (O.2.05)			**Lónyi** (O.1.14)	**Klötzer** (O.6.05)	
15:00–15:25	**Mihet** (O.1.06)	**Amin** (O.2.06)			**Grad** (O.1.15)	**Silva** (O.6.06)	
15:25–15:50	**Slezáčková** (O.1.07)	**Zawadzki** (O.2.07)			**Tampieri** (O.1.16)	**Iqbal** (O.6.07)	
15:50–16:20	**Coffee Break**		**Hiking to a „Buschenschank" (Vineyard) with Conference Dinner (Bus transfer back at 23:00)**		**Coffee Break**		
	Session 1c	**Session 3**			**Session 1f**	**Session 6c**	
16:20–16:45	**Saha** (O.1.08)	**Benko** (O.3.01)			**Haunold** (O.1.17)	**Melcher** (O.6.08)	
16:45–17:10	**Silná** (O.1.09)	**Khan** (O.3.02)			**Lindenthal** (O.1.18)	**Lipták** (O.6.09)	
17:10–17:35	**Raab** (Award Talk)	**Wang** (O.3.03)			**Open Discussion**	**Baranska** (O.6.10)	
17:35–18:00							
18:00–19:30	**Dinner**				**Dinner**		
19:30–21:00	**Poster Session 1**				**Wine Tasting**		
21:00–	**Disco Night**				**Karaoke Night**		

Sunday, 01.09.2024, Lecture Hall 1 “Kongress-Saal”

from 12:00 **Registration**

18:00–19:30 **Dinner**

19:30–19:45 **Opening**

Chair: C. Rameshan
19:45–20:45 Plenary Lecture 1
Carbon Management R&D at BASF: projects, strategy and technology needs for a sucessful Net Zero transformation
Lukas Mayr
BASF, Ludwigshafen, Germany

from 20:45 **Welcome Reception**

Monday, 02.09.2024, Lecture Hall 1 “Kongress-Saal”

Chair: A. Tampieri
09:00–09:40 Keynote Lecture 1
Electron Paramagnetic Resonance Spectroscopy in Heterogeneous Photocatalysis
Dana Dvoranová, Zuzana Dyrčíková, Miriama Malček Šimunková
Slovak University of Technology in Bratislava, Slovak Republic

09:40–10:05
O.1 **Catalytic Methane Pyrolysis on NiMo/MgO Combined with Microcombinatorial TEM Studies**
Anita Horváth, Miklós Németh, Andrea Beck, Tamás Korányi, Dániel Olasz, György Sáfrán
Centre for Energy Research, Budapest, Hungary

10:05–10:40 **Coffee Break**

Chair: A. Tampieri
10:40–11:55 Session 1a: **Heterogenous Catalysis**

10:40–11:05
O.1.01 **UV-Vis-NIR-MIR approach for tracking methane transfor-mation on Fe-zeolites**
Julia Sobalskaa, Karolina A. Tarach, Kinga Mlekodaj, Jiri Dedecek, Edyta Tabor, Kinga Góra-Marek
Jagiellonian University, Kraków, Poland

11:05–11:30
O.1.02 **Investigating the exciting world of high-temperature dry re-forming of methane with in-situ spectroscopy**
Florian Schrenk, Lorenz Lindenthal, Raffael Rameshan, Hedda Drexler, Tobias Berger, J. Rollenitz, Christoph Rameshan
Montanuniversität Leoben, Austria

11:30–11:55
O.1.03 **Metal-support interactions controlling Ni oxidation state in dry methane reforming**
Joanna E. Olszowka, Abdul Selim, Shashikant A. Kadam, Juraj Jasik, Mykhailo Vaidulych, Karolina Simkovicova, Stanislav Valtera, Magda Zlamalova, Ladislav Kavan, Hana Tarabkova, Martin Mergl, Martin Kalbac, Jaroslava Moravkova, Muntaseer Bunian, Yu Lei, Ali Rinaldi, Nico Radde, Marc G. Willinger, Armin Kleibert, Stefan Vajda
Czech Academy of Sciences, Prague, Czech Republic

12:00–13:30 **Lunch**

Chair: N. Yigit

13:30–14:10 Keynote Lecture 2
What is behind the catalytic activity of boron-based catalysts in oxidative dehydrogenation of light alkanes?
Roman Bulánek, Mehran Sajad, Kateřina Knotková, Miroslav Rubeš
The University of Pardubice, Czech Republic

14:10–15:50 Session 1b: **Heterogenous Catalysis**

14:10–14:35
O.1.04 **Exploring synergies between MoS_2 and metal oxides: towards new catalysts for CO_2 hydrogenation to methanol**
Gustavo A. S. Alves, Karin Föttinger
TU Wien, Vienna, Austria

14:35–15:00
O.1.05 **Heterogeneous transesterification of mixed non-food and waste vegetable oils over mixed oxides to prepare biodiesel**
Miroslava Bérešová, András Peller, Lívia Izsák, Michal Horňáček
Slovak University of Technology in Bratislava, Slovak Republic

15:00–15:25
O.1.06 **Ordered porous MOF-derived catalysts for CO_2 hydrogenation**
Angela M. Kasza, Oana Grad, Monica Dan, Mihaela D. Lazar, Maria Mihet
National Institute of R&D of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

15:25–15:50
O.1.07 **Use post-fermentation corn oil for advanced bio-component production. Catalytic solution**
Martina Slezáčková, Jozef Mikulec, Andras Peller, Ladislav Danč
VÚRUP a.s., Bratislava, Slovak Republic

15:50–16:20 **Coffee Break**

Chair: F. Lónyi
16:20–17:35 Session 1c: **Heterogenous Catalysis**

16:20–16:45
O.1.08 **Modified TiO_2/SiO_2 material as a support for ester hydro-genolysis catalyst**
Sharmista Saha, Jaroslav Aubrecht, David Kubička
University of Chemistry and Technology Prague, Czech Republic

16:45–17:10
O.1.09 **Synthesis of asymmetric ethers in the presence of zeolites: a study on catalyst properties**
Zuzana Silná, Jan Přech, Martin Kubů, Petr Golis, Pavol Lopatka, Mariya Shamzhy, Tomáš Soták, Jiří Čejka
Slovak University of Technology in Bratislava, Slovak Republic

17:10–17:35
Zoltan-Award **Dr. Zoltán Paál Prize 2024 Award Talk**
Maximilian Raab
TU Wien, Vienna, Austria

18:00–19:30 **Dinner**

19:30–21:00 **Poster Session 1**

from 21:00 **Disco Night**

Monday, 02.09.2024, Lecture Hall 2 “Styriasaal”

Chair:	T. Haunold
10:40–11:55	Session 2a: **Catalysis**
10:40–11:05 O.2.01	**Transition Metal Oxide Catalysts Supported on Stainless Steel Meshes Prepared by Plasma Jet Sputtering** Pavel Topka, Květuše Jirátová, M. Čada, I. Naiko, A. Ostapenko, J. Balabánová, M. Koštejn, J. Maixner, Z. Hubička, F. Kovanda *Czech Academy of Sciences, Prague, Czech Republic*
11:05–11:30 O.2.02	**Perovskite-Type Oxides for MSR: Advancements in Oxide Synthesis Techniques** Tobias Berger, Maximalian Groiß, Lorenz Lindenthal, Tom Cotter, Mario Peyha, Christian Weiß, Christoph Rameshan *Montanuniversität Leoben, Austria*
11:30–11:55 O.2.03	**Molecular oxygen activation over binuclear iron centers in ze-olites with various topology** Hana Jirglová, Kinga Mlekodaj, Agnieszka Kornas, Mariia Lemishka, Jiří Dědeček, Štěpán Sklenák, Edyta Tabor, Dominik K. Wierzbicki *Czech Academy of Sciences, Prague, Czech Republic*
12:00–13:30	**Lunch**
Chair:	A. Genest
14:10–15:50	Session 2b: **Catalysis**
14:10–14:35 O.2.04	**Boosted Catalytic Performance via Synergistic Interaction of 2D Support and Platinum Nanoparticles** Iryna Danylo, Kristína Kissíková, Lukáš Koláčný, Tomáš Hartman, Martina Pitínová, Martin Veselý *University of Chemistry and Technology Prague, Czech Republic*
14:35–15:00 O.2.05	**Redox behavior of manganese-oxide-based catalysts ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$) – comparative TEM and DFT in-vestigations** Joanna Gryboś, Monika Fedyna, Michał Pacia, Zbigniew Sojka *Jagiellonian University, Kraków, Poland*
15:00–15:25 O.2.06	**Unlocking the potential of anatase TiO_2 for 5-HMF valor-isation by the understanding of its surface properties** Babar Amin, Jaroslav Aubrecht, Oleb Kikhtyanin, David Kubička *University of Chemistry and Technology Prague, Czech Republic*
15:25–15:50 O.2.07	**Photocatalytic activity of NiO/Vermiculite materials in hydrogen production** Bartosz Zawadzki, Marta Valaskova, Alexandr Martaus, Kamila Koci *Institute of Environmental Technology, Czech Republic*
15:50–16:20	**Coffee Break**

Chair: D. Dvoranová
16:20–17:35 Session 3: **Photocatalysis**

16:20–16:45
O.3.01 **Photoelectrocatalytic Water Oxidation by Conformal CuOx on Hematite Nanoarrays**
Tímea Benkó, Shaohua Shen, Miklós Németh, Dávid Lukács, Yufei Xu, Irfan Khan, Zsolt Czigány, Zsolt Endre Horváth, Zoltán Kovács, Jinzhan Su, József Sándor Pap
Centre for Energy Research, Budapest, Hungary

16:45–17:10
O.3.02 **Enhancing Water Oxidation Efficiency: Carbon Nanotubes Economically Integrated with Visible-Light Semiconductors**
Irfan Khan, Tímea Benkó, Anita Nagyné Horváth, Shaohua Shen, Jinzhan Su, Yiqing Wang, Miklós Németh, Endre Zsolt Horváth, József Sándor Pap
Centre for Energy Research, Budapest, Hungary

17:10–17:35
O.3.03 **Polymer carbon nitride Z-scheme heterojunction for photo-catalytic overall water splitting**
Yiqing Wang, Shaohua Shen
TU Wien, Vienna, Austria

18:00–19:30 **Dinner**

19:30–21:00 **Poster Session 1**

from 21:00 **Disco Night**

Tuesday, 03.09.2024, Lecture Hall 1 "Kongress-Saal"

Chair: J. Ryczkowski
09:00–09:40 Keynote Lecture 3
Circular Economy Powered by Olefin Metathesis
– „Open-Loop" Recycling of Polyethylene –
Robert Tuba
Centre for Natural Sciences, Budapest, Hungary

09:40–10:05
O.2 **From fully automated to fully customized –**
a review of SPECS system solutions and new developments in NAP-XPS
Christoph Feldt, Paul Dietrich, Andreas Thissen
SPECS Surface Nanoanalysis GmbH, Berlin, Germany

10:05–10:40 **Coffee Break**

Chair: R. Bulánek
10:40–11:55 Session 4: **Theory**

10:40–11:05
O.4.01 **DFT and thermodynamic investigations into molecular structure of the reconstructed (100) CeO$_2$ termination**
Leszek Nowakowskia, Filip Zasada, Zbigniew Sojka
Jagiellonian University, Kraków, Poland

11:05–11:30
O.4.02 **Intrinsic and extrinsic redox processes in cobalt spinel catalyst**
Leszek Nowakowskia, Filip Zasada, Zbigniew Sojka
Jagiellonian University, Kraków, Poland

11:30–11:55
O.4.03 **An atomistic view on energy storage materials using DFT modeling**
Alexander Genest, Parinya Tangpakonsab, Günther Rupprechter
TU Wien, Vienna, Austria

12:00–13:30 **Lunch**

Chair: K. Góra-Marek
13:30–14:10 Keynote Lecture 4
Organosilanes in the service of material science and catalysis
Maciej Trejda
Adam Mickiewicz University, Poznan, Poland

14:10–15:50 **Poster Session 2**

16:00–18:00 **Hiking to Buschenschank "Schneeberger"**

18:30–23:30 **Conference Dinner**

Tuesday, 03.09.2024, Lecture Hall 2 "Styriasaal"

Chair: E. Iwanek
10:40–11:55 Session 5: **Homogeneous Catalysis / Biocatalysis**

10:40–11:05
O.5.01 **Cerium(III) phosphate as a promising support for gold catalysts addressed to selective oxidation of glucose**
Joanna Wisniewska, Izabela Sobczak , Mariusz Pietrowski, Michal Mazur, Lukasz Wolski
Adam Mickiewicz University, Poznan, Poland

11:05–11:30
O.5.02 **Subnanometer Clusters in the Oxidative Dehydrogenation of Cyclohexene: Control of Catalytic Activity and Selectivity by Changing Cluster Size and Composition One Atom a Time**
Stanislav Valtera, P. Vitek, Juraj Jasik, Mykhailo Vaidulych, Federico Loi, Muntaseer Bunian, Yu Lei, Stefan Vajda
Czech Academy of Sciences, Prague, Czech Republic

11:30–11:55
O.5.03 **From Modeling Natural Redox Transformation Catalysts to Directly Harnessing Renewable Resources**
Jessica Michalke
Montanuniversität Leoben, Austria

12:00–13:30 **Lunch**

Wednesday, 04.09.2024, Lecture Hall 1 "Kongress-Saal"

Chair: G. Rupprechter
09:00–10:00 Plenary Lecture 2
Influencing sorption and catalysis by water and other solvents
Johannes A. Lercher
Pacific Northwest National Laboratory, Richland, WA, United States

10:00–10:40 **Coffee Break**

Chair: M. Trejda
10:40–11:55 Session 1d: **Heterogenous Catalysis**

10:40–11:05
O.1.10 **Catalytic soot removal on redox-metal-doped potassium silicate glasses**
Piotr Legutko, Michał Dziadek, Gabriela Grzybek, Patrycja Przedwojska, Mateusz Marzec, Marek Michalik, Marco Piumetti, Debora Fino, Andrzej Adamski
Jagiellonian University, Kraków, Poland

11:05–11:30
O.1.11 **Heterogeneous Silver Catalysts for Soot Oxidation: a Time-of-Flight Secondary Ion Mass Spectrometry Study**
Ewa Iwanek, Aleksandra Goździk, Zbigniew Kaszkur
Warsaw University of Technology, Poland

11:30–11:55
O.1.12 **Effect of SBA-15 doping with NbVO$_x$ and TaVO$_x$ on the ex-tractive catalytic oxidative desulfurization**
Katarzyna Stawicka, Maciej Trejda, Julia Gajewska, Maria Ziolek
Adam Mickiewicz University, Poznan Poland

12:00–13:30 **Lunch**

Chair: A. Horvath
13:30–14:10 Keynote Lecture 5
Tuning activity on nanocluster catalysts
Noelia Barrabés Rabanal
TU Wien, Vienna, Austria

14:10–15:50 Session 1e: **Heterogenous Catalysis**

14:10–14:35
O.1.13 **Interaction of ammonia with Fe-SSZ-1$_3$ zeolite – ab initio thermodynamic and TPD-NH3 investigations**
Filip Zasada, Monika Fedyna, Joanna Gryboś, Zbigniew Sojka
Jagiellonian University, Kraków, Poland

14:35–15:00
O.1.14 **Hydroconversion of γ-valerolactone over Co/γ-Al2$_2$O$_3$ and Co/H-Beta zeolite catalysts**
Gyula Novodárszki, Ferenc Lónyi*, Magdolna R. Mihályi, Anna Vikár, Róbert Barthos, József Valyon, Hanna E. Solt
Centre for Natural Sciences, Budapest, Hungary

15:00–15:25
O.1.15 **MOFs supported NPs-catalysts for selective hydrogenation of nitrobenzene**
Oana Grad, Monica Dan, Maria Mihet, Angela Kasza, Mihaela D. Lazar
National Institute of R&D of Isotopic and Molecular Technologies, Cluj-Napoca, Romania

15:25–15:50
O.1.16 **Liquid-phase catalytic oxidation of alcohols over spinel oxides**
Alberto Tampieria, Federica Romanelli, Marianne Ivkic, Thomas Lederer, Michael Pittenauer, Moritz Zelenka, Ellen Backus, Karin Föttinger
TU Wien, Vienna, Austria

15:50–16:20 **Coffee Break**

Chair: D. Dvoranová
16:20–18:00 Session 1f: **Heterogenous Catalysis**

16:20–16:45
O.1.17 **Hydroxylation of an ultrathin $Co_3O_4(111)$ film on Ir(100): *in situ* NAP-XPS and DFT studies**
Thomas Haunold, Krešimir Anić, Alexander Genest, and Günther Rupprechter
TU Wien, Vienna, Austria

16:45–17:10
O.1.18 **Sisyphus – building an elevator for CO_2**
Lorenz Lindenthal, Thomas Cotter, Merve Teber-Aksoy, Christoph Markowitsch, Marion Andritz, Markus Lehner, Christoph Rameshan
Montanuniversität Leoben, Austria

17:10–18:00 **Open Discussion**
“My biggest scientific failures. What did I learn from them?”

18:00–19:30 **Dinner**

19:30–21:00 **Wine Tasting**

from 21:00 **Karaoke Night**

Wednesday, 04.09.2024, Lecture Hall 2 “Styriasaal”

Chair: A. Szegedi
10:40–11:55 Session 6a: **Electrocatalysis**

10:40–11:05
O.6.01 **Enhanced Electrochemical Water Oxidation Efficiency and Stability by Iron on Carbon Nanotubes**
Sahir M. Al-Zuraiji, Miklós Németh, József S. Pap
Centre for Energy Research, Budapest, Hungary

11:05–11:30
O.6.02 **Post-Synthetic Surface Functionalisation of Carbon-Based Composite Electrocatalysts for Oxygen Evolution Reaction**
Magdalena Lofek, Termeh Darvishzad, Grzegorz Slowik, Gabriela Grzybeka, Andrzej Kotarba, Pawel Stelmachowski
Jagiellonian University, Kraków, Poland

11:30–11:55
O.6.03 **Pt nanoclusters on 2D MoS_2, properties and activity in hydrogen evolution reaction**
Tamás Ollár, Antal Koós, Péter Kun, Péter Vancsó, József S. Pap, Péter Nemes-Incze, Levente Tapaszto
Centre for Energy Research, Budapest, Hungary

12:00–13:30 **Lunch**

Chair: A. Tompos
14:10–15:50 Session 6b: **Electrocatalysis**

14:10–14:35
O.6.04 **Mechanistic insights into hydrogen evolution reaction driven by heteroatoms of bidentate N-heterocyclic ligands in iron(II) complexes**
Soma Keszei, Yiqing Wang, Haotian Zhou, Tamás Ollár, Éva Kováts, Krisztina Frey, Levente Tapasztó, Shaohua Shen, József Sándor Pap
Centre for Energy Research, Budapest, Hungary

14:35–15:00
O.6.05 **Polarization-induced carbon spillover from Ni to YSZ boosts carbide-mediated methane formation in solid oxide co-electrolysis**
Christoph W. Thurner, Patrick Obendorf, Kevin Ploner, Daniel Winkler, Alexander Genest, Günther Rupprechter, Simon Penner, Bernhard Klötzer
University of Innsbruck, Austria

15:00–15:25
O.6.06 **Advanced Pt/Ti$_{1-x}$Sn$_x$O$_2$-C composite supported electrocat-alyst with functionalized carbon for sustainable energy conversion technologies**
C. Silva, I. Borbáth, K. Salmanzade, A. Tompos, Z. Pászti
Centre for Natural Sciences, Budapest, Hungary

15:25–15:50
O.6.07 **Advances in Electrocatalytic Nitrogen Reduction to Ammonia: Insights from Theoretical Analysis**
Atef Iqbala, Viktor Ellingsson, Egill Skúlason, Younes Abghoui
University of Iceland, Reykjavík, Iceland

15:50–16:20 **Coffee Break**

Chair: R. Tuba
16:20–17:35 Session 6c: **Electrocatalysis**

16:20–16:45
O.6.08 **Exploring Metal-Support Interactions in Solid Oxide Electrolysis Cathodes by *in-situ* Surface Analytics**
Christian Melcher, Andreas Nenning, Kirsten Rath, Stanislaus Breitwieser, Florian Schrenk, Christoph Rameshan, Alexander K. Opitz
TU Wien, Vienna, Austria

16:45–17:10
O.6.09 **Pt- MoVWNbO$_x$ mixed oxide catalysts with reduced Pt con-tent for proton exchange membrane fuel cell application**
Kata Lipták, Emília Tálas, Irina Borbáth, Zoltán Pászti, Krisztina László, András Tompos
Research Centre for Natural Sciences, Budapest, Hungary

17:10–17:35
O.6.10 **Catalytic and electrochemical properties of CMK-3 mesopo-rous carbon nanoreplicas modified with nitrogen- and oxy-gen-containing functionalities**
Katarzyna Barańska, Sebastian Jarczewski, Anna Rokicińska, Marek Dębosz, Olaf Klepel, Piotr Kuśtrowski
Jagiellonian University, Kraków, Poland

18:00–19:30 **Dinner**

19:30–21:00 **Wine Tasting**

from 21:00 **Karaoke Night**

Thursday, 04.09.2024, Lecture Hall 1 “Kongress-Saal”

Chair: J. S. Pap

09:00–09:40 Keynote Lecture 6
Highlights of cutting-edge catalysis research in Slovenia
Albin Pintar
National Institute of Chemistry, Ljubljana, Slovenia

09:40–10:05
O.3 **Process Simulations for Membrane Capture of CO_2 – CO_2 Conversion with Citizen Scientists**
Thomas Ruh, Patrizia Bartl, Martina Messner, Andreas Jantscher, Harald Lorenz, Christian Erlebach, Horst Stangl, Christoph Rameshan
Montanuniversität Leoben, Austria

10:05–10:40 **Coffee Break**

10:40–11:15 **Closing & Awards**

LIST OF POSTERS

Poster Session 1, 02.09.2024, 19:30–21:00

P.1.01	K. Góra-Marek	*Methane and CO_2 transformation on TMI-zeolites – spectroscopic approach*
P.1.02	K. Tarach	*Carbon deposit formation during ethylene transformation over microporous and hierarchical ZSM-5 zeolites*
P.1.03	K. Tarach	*Ethanol-to-hydrocarbons process – operando FT-IR spectroscopic studies supported by MCR-ALS analysis for active species identification*
P.1.04	M. Horňáček	*Biodiesel preparation by heterogeneous transesterification of Camelina sativa oil over basic zeolites*
P.1.05	B. Horváth	*Transformation of ethanol into important chemical intermediates*
P.1.06	A. Jankowska	*Transition metals modified derivatives of 2D Ti-MWW-type zeolites – verification of catalytic activity in NH_3-SCR process*
P.1.07	A. Jaswal	*Selective Furfural Hydrodeoxygenation Through In-Situ Cu@Fe_3O_4 Formation in Cu-Fe Mixed Oxide Catalysts*
P.1.08	A. M. Kasza	*$CuO/ZnO/Al_2O_3$ catalysts modified by MOF-derived carbon for CO_2 hydrogenation to methanol*
P.1.09	D. Lemmer	*Preparation of Ni-Mn-oxide catalysts and the influence of SO_2 on their low-temperature CO-oxidation performance*
P.1.10	L. Obalová	*Transistion mixed oxides catalysts for CO and hydrocarbon oxidation as an option to reduce emissions from small combustion devices*
P.1.11	I. Paterova	*Bifunctional catalysts based on hydrotalcites for sandalwood fragrances synthesis*
P.1.12	A. Šlachtová	*Nanostructured TiO_2, Fe_2O_3, CeO_2 and CuO-based catalysts prepared using titanyl sulphate in dichloromethane oxidation*
P.1.13	R. Barthos	*Ethanol coupling reactions over MgO-SiO_2 and MgO-Al_2O_3 catalysts*
P.1.14	W. Zawadzki	*The influence of Mo and W promoters on the performance of nickel and cobalt catalysts with CeO_2 support in CO_2 methanation reaction*
P.1.15	M. Cichy	*Investigation of support effects during ethanol steam reforming over cobalt-based catalysts*
P.1.16	M. Dan	*Metallic decorated 3D graphene for glycerol oxidation*
P.1.17	F. Valentini	*Impact of treatment conditions on catalysts activity and stability in glycerol hydrogenolysis*
P.1.18	Á. Szegedi	*$Ni/Zn/CeO_2/Al_2O_3$ catalysts for the dehydrogenation of methyl cyclohexane in LOHC systems*
P.1.19	M. Pitínová	*2D materials-supported Rh catalysts for hydrogenation and hydroformylation reactions*
P.1.20	G. Rupprechter	*Imaging H2 Oxidation and Promoter Effects on a Single Rh Nanoparticle*
P.1.21	J. Ryczkowski	*Research on the mechanism of soot oxidation on the surface of Mn_3O_4-CeO_2 catalysts in tight contact conditions*
P.1.22	A. Szymaszek-Wawryca	*Natural and synthetic zeolites modified with Fe and Cu as catalysts for selective catalytic reduction of nitrogen oxides with ammonia*
P.1.23	Z. Silná	*Transformation of ethanol into important chemical intermediates*
P.1.24	K. Simkovičová	*Atomically Precise Supported CuPd Clusters: Catalysts for CO_2 Conversion*
P.1.25	X. Wang	*Advanced Thermal Management and Fluid Dynamics in Nanoscale Systems: Thermo-osmosis and Photothermal Applications*
P.1.26	M. Greluk	*Enhanced understanding of the role of alkali in ethanol steam reforming over cobalt catalysts. Operando DRIFT Studies and DFT Modeling*
P.1.27	N. Yigit	*CO Oxidation on Copper Nanoparticles on Various Supports*

Poster Session 2, 03.09.2024, 14:10–15:50

P.2.01	P. Legutko	*Ni-K/CeO2 model catalyst for dry methane reforming – optimization of potassium concentration*
P.2.02	H. Drexler	*Multi-doped perovskite-type oxides: How a combination of dopants influences exsolution*
P.2.03	G. Novodárszki	*Hydrodeoxygenation of lignin-derived guaiacol over γ-alumina supported Ni-Cu bimetallic catalysts*
P.2.04	M. Slezáčková	*Hydrotreated spent coffee grounds oil as SAF bio-component*
P.2.05	M. Bérešová	*Hydrodeoxygenation of lignin-derived guaiacol over γ-alumina supported Ni-Cu bimetallic catalysts*
P.2.06	B. Hulaj	*Bright Ideas: Designing Photocathodes for Visible Light-Driven Photoelectrochemical CO2 Reduction*
P.2.07	Y. Wang	*Polymer carbon nitride Z-scheme heterojunction for photocatalytic overall water splitting*
P.2.08	H. Haspel	*Vanadium-based Catalysts for the Electrochemical Reduction of Nitrate to Ammonia*
P.2.09	Ç. Yavuz	*MOF-derived NiO/Co3O4 composite nanoparticles for overall water splitting*
P.2.10	A. T. Tabrizi	*Effect of Annealing and Phase Transition of Atomic Layer Deposited Vanadium Oxide on Hydrogen Evolution Activity*
P.2.11	S. A. Raheem	*Electrodeposited Iron on Porous Copper Foam as Electrocatalyst for Selective Nitrate Reduction to Ammonia*
P.2.12	Y. Gherib	*Hydrogenation of Acetone to Isopropanol over Fixed-Bed Raney-Type Nickel Catalyst. A Scale-up from Laboratory to Pilot Scale*
P.2.13	G. Słowik	*Iron-modified copper catalysts for the steam reforming of methanol*
P.2.14	J. Sobalska	*Zeolites bound with alumina for polyolefin cracking*
P.2.15	A. Iqbal	*Discovering Tomorrow's Catalysts: Mapping Nitrogen-to-Ammonia Conversion Horizons*
P.2.16	M. Inger	*The effect of diffusion resistance on the effectiveness NOx selective catalytic reduction process*
P.2.17	L. Koláčný	*Electron Tomography as a Tool for Advanced Characterisation of Catalysts Microstructure*
P.2.18	K. Pacultova	*Phenolics adsorption on alumina supported HDO catalyst*
P.2.19	L. Čapek	*In-situ characterization of the thermal treatment of Zn-Al Layered Double Hydroxides leading to the mixed oxides, followed by their subsequent reconstruction*
P.2.20	W. Dubiel	*Titanium grafted MWW zeolites in the role of catalysts for selective oxidation of organic sulphides*
P.2.21	A. Gomułka	*The effect of EDTA treatment on forms of copper species deposited on the surfaces of MCM-41 and MCM-48 modified by TIE method*
P.2.22	J. Rollenitz	*Modified Pechini Synthesis of Perovskite-tpye Oxide Catalysts*
P.2.23	C. Rameshan	*How A-site cations influence the in-situ formation of metallic nanoparticles in perovskite oxide catalysts*
P.2.24	L. Atzl	*Partial oxidation of methane to syngas on perovskite catalysts*
P.2.25	M. Horňáček	*Oxidation of cyclopentanone to glutaric acid over carbon-based catalysts*
P.2.26	P. Tangpakonsab	*Single Atom Catalysts Cu/CeO2 for CO and H2 Adsorption: First-principles Study*

PLENARIES

Carbon Management R&D at BASF: projects, strategy and technology needs for a successful Net Zero transformation

Lukas Mayr

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Climate change is one of the greatest challenges of the 21st century. Swift and resolute action is needed to ensure that the targets agreed in the Paris Climate Agreement can be achieved. We stand by this responsibility. We are working hard to significantly reduce our carbon footprint. Our goal is to achieve net zero emissions by 2050. For this purpose, new process technologies, new raw material sources and new forms of energy supply are inevitable. How to cleverly combine existing assets, technologies, and infrastructure with innovative approaches to establish cost-effective, fast and sustainable transition concepts is in responsibility of the organizational unit “Net Zero Accelerator” at BASF. This transformation is an enormous undertaking, but we are making good progress.

Influencing sorption and catalysis by water and other solvents

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Water, along with other polar molecules, self-organizes on oxide catalyst surfaces and within microporous materials. Their presence and self-organization affect sorption and catalysis by modifying the chemical and thermodynamic properties of both the solid environment and the hosted molecules. Water formsfluxional hydrated hydronium ions at Brønsted acid sites in micropores of all dimensions. The sizes of these clusters depend on the environment and are constrained by the entropy loss relative to condensation outside the micropores. Notably, the remaining pore space remains predominantly vacant in the exclusive presence of water. This inhomogeneity is not the consequence of weak interactions between the zeolite pore wall and water but caused by the internal stabilization of the hydrate clusters.

Other molecules are adsorbed in the space among hydronium clusters, and small polar molecules may partially substitute for water in the cluster, either forming the hydrated hydronium ion or clustering around metal cations. The concentration and thermodynamic state of adsorbed and reacting molecules are influenced by the characteristics of the interacting sites, the steric environment, and the density of charged species. This complex environment leads to a pronounced (de)stabilization of both ground and transition states, thereby both augmenting and impeding the rates of catalytic pathways. This results in a maximum of catalytic activity with increasing charge density, a phenomenon absent on open surfaces and associated with the energy required to reorganize charges within the confined spaces of narrow pores.

Water layers on metal particles on the other hand induce changes by influencing the electronic surface properties and influencing binding of hydrogen on these metal surfaces. In turn, the strength of this binding determines rates of hydrogen addition reactions. Changing the binding of hydrogen by external electric potentials opens additional new pathways to enhance these reactions and also facilitates pathways involving coupled transfer of H^+ and electrons.

For both acid-base and metal catalyzed reactions, the lecture will show the links between these underlying physicochemical causes for the observed changes induced by water in sorption and catalysis and will discuss opportunities and limitations for developing new catalytic pathways for a circular carbon-neutral catalysis.

KEYNOTES

KN.1

The EPR Spectroscopy in the Heterogeneous Photocatalysis

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Electron paramagnetic resonance (EPR) spectroscopy represents a unique technique in the detection and identification of species with an unpaired electron. It is especially useful in the field of catalysis, because many catalytic processes are associated with the formation of radical intermediates, and here EPR spectroscopy can be helpful not only in the identification of these species, but also in a better understanding of the ongoing reactions, as well as the characterization of the catalyst. In the heterogeneous photocatalytic systems, the photocatalyst plays a dominant role, and its precise characterization and determination of its photocatalytic activity are crucial for the further utilization of the photocatalyst in real application. The EPR measurements in solid state particularly at low temperatures bring us unique insight into the geometric and electronic structure of the paramagnetic sites relevant within the (photo)catalytic processes. Due to the transient character of paramagnetic intermediates, mostly reactive oxygen species, generated upon exposure of photocatalytic dispersed systems, we are often forced to apply the indirect techniques to observe their generation, such spin trapping, spin scavenging, oxidation of sterically hindered amines or photoreduction. These techniques possess a valuable tool for the detection and characterization of nonpersistent species and the proper choice of suitable experimental conditions is crucial for their successful application in heterogeneous semiconductor systems. This approach can help us to gain a comprehensive picture of the photoinduced processes undergoing upon light exposure of the photocatalysts in suspensions. The lecture is oriented on a short overview of the application of direct and indirect cw-EPR spectroscopy in heterogeneous photocatalysis [1-4].

Keywords: electron paramagnetic resonance, reactive oxygen species, photocatalyst, photoinduced processes

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What is behind the catalytic activity of boron-based catalysts in oxidative dehydrogenation of light alkanes?

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The catalytic activity of boron particles supported on various supports has been extensively investigated in the context of oxidative dehydrogenation (ODH) or partial oxidation of light alkanes, specifically ethane and propane, in the early 1990s [1]. After a period of waning interest, boron-based catalysts experienced a resurgence in 2016 when Grant et al. reported a ground-breaking study showing that hexagonal boron nitride (h-BN) exhibits remarkable selectivity (91%) toward olefins (propene + ethene) at 14% propane conversion [2]. Notably, h-BN demonstrated higher selectivity towards olefins than V/SiO_2, which was considered a benchmark ODH catalyst. Consequently, boron has emerged as an active species in the catalysts for ODH reactions. Researchers have explored various binary compounds containing boron to gain insights into reaction mechanisms, identify boron species present on diverse catalyst surfaces, and determine the active form of boron species. In all cases, partial oxidation of the catalysts occurs, leading to the formation of BOx groups on the surface. These functionalities are believed to be responsible for the observed catalytic activity [3,4]. However, despite the great effort and attention devoted to this topic, a number of fundamental questions are still not satisfactorily answered, including the nature of the active center, the role of boron speciation, the influence of the support material, and the interrelationship of the processes taking place on the surface of the catalyst and in the gas phase.

Our research on this catalytic system focused on the study of the chemical attack of the h-BN surface, the mechanism of formation of BOx groups on its surface, and the function that BOx particles play in the reaction. An experimental study containing a combination of a number of characterization techniques (including Raman, FT-IR, and XPS spectroscopies, UHV TPD, EELS-TEM, etc.) was supplemented by molecular dynamic simulations at the DFT level.

This contribution summarizes the characteristic features of the catalytic behavior of boron-based materials and critically discusses various views on the reaction mechanism and the nature of active centers.

Keywords: oxidative dehydrogenation, propane, boron, olefins.

Acknowledgements: Financial support of Grant Agency of Czech Republic 22-23120S is highly acknowledged

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Circular Economy Powered by Olefin Metathesis
– „Open-Loop" Recycling of Polyethylene –

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From sustainability point of view, the scientific challenge currently receiving much attention is the catalytic conversion of non-biodegradable polymers into a variety of "green" platform molecules. As a model upcycling chemical process, olefin metathesis catalytic systems have been developed to decompose persistent polyethylene plastic waste to valuable chemical intermediates, which can be transformed into environmental benign materials.

Based on the concept of a multidimensional circular economy, with this approach, persistent plastic wastes can catalytically be converted into chemically recyclable and biodegradable polymers. In the first step, a mild pyrolysis of polyolefin consumer products yields oils with high olefin content. Then, for the next, in an isomerization metathesis (ISOMET) transformation step, tailored (BI)CAAC-Ru olefin metathesis catalysts are used in combination with a ruthenium based molecular isomerization catalyst for the highly selective conversion of the pyrolysis oil to propylene. Eventually, propylene can be readily converted into biodegradable plastics such as polybutylene succinate (PBS). Upscaling to a 900 ml reactor system and repetitive batch experiments proofed long-term stability of the catalyst system and paved the way to large-scale applicability of the polyethylene wastes as potential raw material sources for sustainable plastic production.

Keywords: olefin metathesis, green chemistry, polymer recycling, sustainable catalysis.

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Organosilanes in the service of material science and catalysis

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The important role of catalysis for modern society in undisputable. It is estimated that ca. 90% of industrial chemical processes are carried out by using at least one catalyst. Moreover, ca. 20% of world economy directly or indirectly depends on catalysis. In this light, the continuous interest in research related to catalytic processes is not surprising. One of the directions of studies in the area is heterogenization of processes aimed at designing and application of new solid catalytic materials.

Silica is commonly used as a support for different active species in catalysis. One of the advantages of silica application is the ease of synthesis of silica of various structures, including ordered mesoporous ones. These materials, that are usually catalytically inert, can be modified in order to generate active species. Among different possible modifiers, organosilane species proved to be very effective.

An important asset of organosilane species is the ease of its incorporation on the silica surface, which can be performed during the silica synthesis or by post-synthesis modification procedures. Moreover, depending on the kind of organosilane species, it can serve as a source of acidic or basic centres, that can be used e.g. in esterification [2], oxidative desulfurization [3] or Knoevenagel condensation [4,5]. Furthermore, as a result of incorporation of organosilanes species, the hydrophilic/hydrophobic character of pristine silica can be modified. In addition, the organosilane species previously incorporated on silica surface can be sacrificed in order to obtain a high dispersion or lower crystal size of another modifier, like Au or Ag. The above-mentioned aspects of application of organosilane species in material science and catalysis will be presented and discussed.

Keywords: acidity, esterification, desulpurization

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KN.5

Tuning activity on nanocluster catalysts

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Catalysis is a key enabler of progress towards a sustainable society, and nanoclusters offer a promising route to exploit this potential. To fully benefit from nanoparticles in catalytic processes, a comprehensive understanding of their behaviour at the molecular level is essential but challenging. This requires the development of novel nanostructures with precise control over size, composition and surface properties. Metallic nanoclusters are ideal candidates for this purpose, offering unique opportunities to study surface chemistry and catalysis at the atomic scale.

In our studies, we investigate how various factors—such as cluster structure, metal composition, ligand types, and ligand populations around the metal core—along with their interactions with supports, influence catalytic performance and reaction pathways. We have identified strong ligand-support interactions, including ligand migration to oxide surfaces, which can create new active sites. These interactions are significantly affected by the metal composition of the clusters, which, in turn, impact bond interactions and the development of the cluster-ligand-support interface.

In our recent work we explored the reactivity of platinum- and copper-doped gold clusters in hydrogenation processes. Using in situ/operando XAFS and IR spectroscopy, we have correlated the evolution of metal atoms with their catalytic behavior. We found that ligand removal induces significant structural changes, creating diverse active sites. To further investigate, we studied reactions with intact ligand shells and non-interacting support materials, particularly in electrocatalytic reduction processes. We examined two gold clusters with different staple motifs (Au25 and Au144) doped with silver or copper, uncovering the interplay between composition and catalytic performance. Spectroscopic studies combined with DFT simulations revealed the importance of dynamic ligand removal in understanding the roles of dopants, cluster curvature, and staple structure.

Our ongoing research includes studies on unsupported clusters, focusing on how ligand evolution influences the activity and selectivity of hydrogenation processes, such as the hydrogenation of ketones. Additionally, we explored the impact of ligands on the chirality of nanoclusters, successfully achieving the enantiopure synthesis of three chiral nanoclusters using a novel chiral ligand. By integrating chiral spectroscopy and theoretical simulations, we linked chiral properties to the cluster's structure and ligand configuration. Notably, we demonstrated the selective preparation of enantiopure, intrinsically chiral, and highly stable thiolate-protected gold nanoclusters, with evidence of “super” chirality in the Au144 cluster, highlighting the complex interplay of hierarchical chirality in ligands, staple configuration, and core structure.

These findings highlight the critical role of ligands in tailoring the structural, catalytic and chiral properties of gold nanoclusters, opening the way for the design of advanced materials with precise and enhanced functionalities.

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Highlights of cutting-edge catalysis research in Slovenia

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In Slovenia, the field of catalysis is flourishing, driven by a community of dedicated researchers organized in the Catalysis Division of the Slovenian Chemical Society. This division serves as a platform for the exchange of knowledge, experience and international cooperation, as well as for the organization of national and international scientific conferences and other events. The national representatives of the division actively participate in the activities of the European Federation of Catalysis Societies.

Recent advances in catalysis research in Slovenia include several innovative and impactful areas: (i) heterogeneous catalysis: Slovenian researchers, especially from the National Institute of Chemistry, have made significant progress in the development and synthesis of novel heterogeneous catalysts. Intensive research has been carried out in the field of CO_2 utilization and its conversion into fuels and value-added chemicals, involving thermal and photothermal catalysis approaches as well as the use of *in situ* and *operando* spectroscopic techniques. A notable success is the development of highly efficient and stable catalysts for the conversion of biomass into valuable chemicals and fuels. These catalysts show excellent performance and thus contribute to the progress of sustainable chemical processes; (ii) homogeneous catalysis: Scientists from the University of Ljubljana, the University of Maribor and the Jožef Stefan Institute are researching new catalytic systems for organic synthesis. A breakthrough has been achieved in the development of transition metal-based catalysts that enable highly selective and efficient transformations, including C-H activation and cross-coupling reactions; (iii) environmental catalysis: Environmental catalysis is another important area of research in which the National Institute of Chemistry and the University of Nova Gorica are significantly involved. Recent studies have led to the development of catalysts that effectively remove harmful pollutants from industrial emissions and wastewater. These catalysts are crucial for mitigating the environmental impact and promoting clean industrial processes; (iv) photocatalysis: Researchers from the University of Ljubljana and the National Institute of Chemistry are making progress in the field of heterogeneos photocatalysis. They are designing and optimizing photocatalysts based on plasmonic metals, graphitic carbon nitride and macromolecular foams for applications in solar energy conversion and environmental remediation. Comprehensive characterization techniques are used to clarify the complex relationships between the structure, composition and activity of photocatalysts. An important milestone is the development of photocatalysts that efficiently utilize sunlight to drive chemical reactions, offering promising solutions for renewable energy production and environmental sustainability; (v) biocatalysis: Research into biocatalysts, enzymes and other biological molecules for catalysis is gaining momentum at the University of Maribor and the University of Ljubljana. Researchers are developing biocatalysts to achieve improved stability and activity under industrial conditions. These biocatalysts have great potential for the production of pharmaceuticals, fine chemicals and biofuels and emphasise the importance of the principles of green chemistry.

Several research groups across the country are at the forefront of these advances. These groups are not only contributing to basic research, but are also translating their findings into practical applications, driving innovation and technological advancement in the field of catalysis. To summarize, the vibrant catalysis research community in Slovenia is making remarkable contributions to various areas of catalysis. Through continuous collaboration and innovation, these researchers are able to significantly influence both the scientific understanding and practical applications of catalysis.

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ORALS

Catalytic Methane Pyrolysis on NiMo/MgO Combined with Microcombinatorial TEM Studies

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Methane pyrolysis ($CH_4 \rightleftharpoons C+2H_2$) yields extremely clean hydrogen gas (called turquoise hydrogen) and only solid carbon without the production of any CO_2. However, the process is not industrialized yet. Application of proper catalysts can decrease the temperature requirement of the reaction and produce valuable nanostructured carbon beside hydrogen [1].

Catalyst sample preparation in the present work was done by i) chemical deposition of Ni and Mo precursors over the MgO support or ii) a novel microcombinatorial TEM method [2] using DC magnetron sputtering over a TEM grid. This latter method is able to produce thin layers of two components with linearly changing composition across a TEM grid, and these layers upon high temperature reduction transform into metallic particles or islands. Supported NiMo/MgO catalyst samples (7 wt% Ni and 4% or 12% Mo loading designated by MoNi0.4 and MoNi1.2 atomic ratios, respectively) were reacted in 50% CH_4/Ar using a horizontal reactor at 800 °C. The supported fresh or spent samples were investigated by XRD, TPR, XPS, Raman spectroscopy, HRTEM and STEM-EDS [3]. The microcombinatorial Ni-Mo samples were investigated by XPS, TEM and STEM-EDS before and after a reduction treatment and a further carbonization step in methane stream.

The bimetallic NiMo/MgO samples produced carbon nanotubes with 50-320% yield, while monometallic Ni/MgO or Mo/MgO deactivated fast. This suggested a strong synergetic effect. The superiority of the MoNi1.2 catalyst in terms of activity, stability and carbon yield was explained by the presence of the equimolar alloyed NiMo particles. The novel microcombinatorial TEM method resulted NiMo alloy particles with different compositions. It was ascertained that the Ni/Mo~1 alloy composition did not seem to segregate during the carbonization process. The most prominent novelty of our work was the disclosure of the nanoscale segregation of bimetallic MoNi particles during carbon deposition process depending on the Mo/Ni atomic ratio and affecting the catalyst lifetime. In addition, the microcombinatorial TEM method was first applied for catalytic purposes.

Acknowledgment: The financial support of the Hungarian Scientific Research Fund is acknowledged (OTKA K143216 and K146032).

Keywords: methane decomposition, hydrogen, nickel, molybdenum

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From fully automated to fully customized – a review of SPECS system solutions and new developments in NAP-XPS

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Over the last decades, XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential for numerous applications and made new fields of research accessible. Especially in operando studies on catalysts [1], studies on solid-liquid interfaces [2] and liquid jets [3] as well as for in-situ electrochemistry like dip-and-pull experiments [4] and battery material research [5], NAP XPS became an indispensable method for modern research. On the other hand, an increasing number of industrial applications benefit from the possibility to study systems under environmental conditions which increases the significance of this method for industrial customers.

For a variety of different research questions in both academia and industry, we have developed various system concepts and individual solutions in close collaboration with our customers. While fully automated, turn-key systems rather focus on requirements like high throughput, standardization and ease of use, our fully customized systems address very specific research questions.

In this presentation, we will give a brief review on different NAP-XPS solutions, demonstrate new developments and will show examples, how NAP-XPS systems have contributed to an understanding of new material systems, catalysis and electrochemical processes at solid liquid interfaces.

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Process Simulations for Membrane Capture of CO_2: CO_2 Conversion with Citizen Scientists

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Atmospheric carbon dioxide (CO_2) levels have rapidly increased to over 400 ppm since the industrial revolution. To achieve the main goal of the "European Green Deal" (climate neutrality by 2050), ways must be found to slow down this increase. One way to do this is to close the CO_2 cycle via chemical CO_2 conversion: This uses renewable energy to transform CO_2 from industrial exhaust into chemical feedstocks or fuels that can be stored or used, e.g. in the transportation sector. Three main steps are necessary: First, methods are needed to activate chemically very stable CO_2 and turn it into valuable chemicals or fuels. Second, CO_2 must be captured from industrial waste gases for use further downstream. Third, it is necessary to raise awareness that carbon dioxide is not only a waste gas, but also a valuable resource that can help address the problem of climate change.

Our Sparkling Science project "CO_2 conversion: From harmful waste gas to resource – CO_2 as a valuable raw material" approaches all three steps working with HTL students and teachers as well as partners from local industry: (i) For the conversion of CO_2, perovskite oxides are used, which have great potential as catalysts in various reactions such as reverse water gas shift reaction or methane dry reforming. These materials will be produced, characterized and tested in a catalytic reactor built at the HTL Kramsach as part of the project. (ii) Separation of CO_2 from industrial waste gases poses a challenge especially for smaller companies with relatively low CO_2 concentrations in the waste gas, since established separation processes such as gas scrubbing and adsorption processes cause high investment costs. Alternative processes, e.g. using membranes for CO_2 separation, are already being developed, but are not yet technologically mature. Within the framework of the project, process simulations with real concrete parameters (exhaust gas composition, temperature...) will be carried out using Aspen Plus or Aspen HYSYS to compare the ecological and economic suitability of different CO_2 capture processes. (iii) Public awareness about the climate crisis on the one hand and possible solutions on the other hand will be raised directly through cooperation with students and partners from local industry within the framework of the project. Students of the HTL Innsbruck design infographics on the topic (with different target groups in mind) and will graphically prepare the upcoming results. In addition, workshops will be organized, and lectures held at schools to sensitize young people to this topic as early as possible.

In this presentation we will focus on the process simulation part of the project: Initial results (with real flue gas compositions) have shown that membrane processes for CO_2 capture do have great potential – they are particularly beneficial in terms of environmental friendliness. However, what capture results can be achieved in an economical way (How much of the CO_2 in the flue gas can be recovered? How pure is the product?) strongly depends on the exact process design. We will discuss these questions for lower flue gas concentrations and present our findings for three different real industry examples.

Keywords: Citizen Science, Process Simulation, Carbon Capture and Utilization

O.1.01

UV-Vis-NIR-MIR approach for tracking methane transformation on Fe-zeolites

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Low-temperature activation of molecular oxygen is a pivotal step in developing environmentally friendly catalysts for selective oxidation reactions. The direct oxidation of methane with O_2 represents a highly favorable pathway for methanol production, mainly when using Fe-exchanged zeolites like Fe-FER and Al-rich Fe-*BEA. Using molecular oxygen as oxidantion agent for methane transformation offers a compelling alternative to the temporary use of H_2O_2 or N_2O. The process involves the splitting of the O_2 molecule by two Fe(II) sites, resulting in the formation of active α-oxygen species ($Fe^{(III)}$-$O^{-\bullet}$ and $[Fe^{(IV)}=O]^{2+}$ denote commonly used notations). These species are already capable of oxidizing methane at room temperature. We aimed to catalyze methanol formation from CH_4 and O_2 at low temperatures using Fe binuclear centers stabilized within commercially available MOR zeolite.

The application of a novel operando 2D COS UV-Vis-NIR-IR spectroscopy combined with the detection of oxidation products via mass spectrometry (operando) has provided new insights into the nature of active centers involved in oxygen splitting and the subsequent conversion of methane to methanol. Results obtained from in-situ time-resolved IR and UV-Vis spectroscopy significantly contribute to understanding catalyst properties and the definition of the reaction pathway under realistic conditions. The study presented here for the first time, demonstrate that methane oxidation in the continuous regime can be achieved using mordenite accommodating binuclear iron centers. The α-O stabilized on $[Fe^{(IV)}=O]^{2+}$ ion are exclusively located in 8-MR channels. They efficiently perform the continuous selective oxidation of methane to methanol. The presence of O_2 and CH_4 in the reaction mixture does not hinder selective oxidation; we did not observe spontaneous total oxidation of CH_4 to CO. The UV-Vis-NIR-IR-MS studies enabled the simultaneous observation of structural changes on the iron active sites and the time-dependence between intermediates and products of methane oxidation stabilized on the catalysts. The catalyst surfaces was monitored by analyzing a single spectrum simultaneously collected within the IR-NIR-Vis region. The 2D COS analysis of FT-IR results confirmed that the O_2 splitting occurred over iron ions in 8-MR on the bottom of 8-MR pockets. Operando UV-Vis-NIR-IR results revealed that $[Fe^{(IV)}=O]^{2+}$ complexes formed by O_2 splitting over binuclear sites are curtail species for methane oxidation. Reaction products, including CH_3OH, HCHO, formates, and CO_x, were detected by the FT-IR method. Unlike Fe-FER and Fe-*BEA, in the case of Fe-MOR, due to the matrix geometry, α-oxygen species formed from O_2 splitting are located in different MOR side pockets. Fe-FER and Fe-*BEA oxidation involves two cooperating α-O facing the zeolite channel. The MOR structure offers the possibility to perform oxidation reactions that require only one α-O species.

Keywords: transition metal cations, zeolites; methane oxidation to methanol; IR spectroscopy.

Acknowledgment: The work was financed by NSC, Poland - Grant No. 2021/41/B/ST4/00048 and by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Commenius, call Excellent Research.

Investigating the exciting world of high-temperature dry reforming of methane with in-situ spectroscopy

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The fight against global warming is one of the defining challenges of our time. Possible ways to combat the rising levels of greenhouse gases in our atmosphere include CO_2 utilizing reactions. One of these reactions is Dry Reforming of Methane (DRM). In this reaction, CO_2 is directly converted with CH_4 into a mixture of H_2 and CO, which is also known as synthesis gas and is one of the building blocks of modern industrial chemistry. However, thermodynamical limitations at lower temperatures and therefore harsh reaction conditions are still a hurdle on the way to large-scale applications. In previous work [1] we showed the applicability of perovskite-type oxides for this reaction as they show outstanding stability even at high temperatures. These materials achieve this by forming nanoparticles on their surface, which are anchored there and have very low surface mobility in a process known as exsolution.

Recently, a lot of research focused on the control of the shape and size of these nanoparticles. To further uncover the effects of nanoparticle size on catalytic activity we studied our established catalyst $Nd_{0.6}Ca_{0.4}Fe_{0.97}Ni_{0.03}O_3$ after treating it to three different reduction temperatures. The temperatures were chosen in a way to not enable nanoparticle exsolution (550 °C), enable it (625 °C), and an additional temperature where bigger particles are formed (700 °C), which we confirmed by XRD and SEM measurements. Catalytic data shows that the middle reduction temperature outperforms the lowest temperature, most likely due to the formation of nanoparticles. However, the highest pre-treatment temperature also leads to a decrease in catalytic activity. To investigate this further, we performed in-situ XRD measurements during temperature ramps at DESY. This revealed that a FeNi phase is forming at roughly the temperature of the middle reduction temperature. However, also a CaO phase forms, which leads to a decrease in catalytic activity as it reduces the active surface area.

Further investigations into the reduction process at different temperatures revealed that after around 100 seconds at 625 °C the nanoparticle growth was finished. Afterwards, the crystallite size of the nanoparticle phase remains constant indicating that the nanoparticles are indeed stable in size even in harsh conditions. On the other hand, the CaO phase is increasing in crystallite size as this phase is not anchored to the surface. A reduction temperature of 700 °C led to further decomposition of the material as phases such as $CaCO_3$ and Fe_2O_3 formed. In additional in-situ XRD measurements during DRM we uncovered that these decomposition phases disappear during elevated temperatures forming again a perovskite-like phase. This demonstrates a previously unknown self-healing effect of perovskite oxides under reaction conditions.

Keywords: dry reforming of methane, perovskite oxides, heterogeneous catalysis, in-situ XRD

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O.1.03

Metal-support interactions controlling Ni oxidation state in dry methane reforming

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In dry methane reforming (DMR), the two greenhouse gases CO_2 and CH_4 are simultaneously converted to the syngas (CO and H_2). Highly active Ni-based catalysts are often used for this reaction, yet their application is hampered due to susceptibility to sintering as well as deactivation caused by coke formation [1]. The modulation of the metal-surface interactions offers control of the oxidation state, stability and performance of the catalyst over time. In this study, well-defined model catalysts are investigated to identify structure-function relationships derived from support effects to leverage the gained insights for the design of real-world catalysts. Vital information about the oxidation state of the catalyst components under working conditions was acquired with synchrotron-based XPEEM (X-ray Photoemission Electron Microscopy) and XPS (X-ray Photoelectron Spectroscopy) with single particle resolution under a flow of CO_2 or CH_4 and their mixture to mimic conditions of DMR [2]. Distinct behavior in the reducibility of Ni-containing nanoparticles, initially in the form of NiO and $Ni(OH)_2$, is observed when on different supporting materials under DMR conditions. During sequential experiments, a reoxidation of Ni nanoparticles on ZrO_2 is observed by CO_2, followed by subsequent reduction by CH_4. In-situ experiments under DMR conditions reveal a reduced Ni and in-situ XPS C1s spectra suggest different distribution of the C impurities on the Ni nanoparticles and support material before the reaction, which unifies under high-temperature conditions. SEM images collected on various catalysts after the reaction often reveal a formation of additional carbon deposit on the interface between Ni nanoparticles and the support. Microscopic analysis reveals that in the case of TiO_2 deposited on SiO_2, the thin oxide film can restructure under reaction conditions into islands and depending on the composition of the reactant gas mixture a reduction of TiO_2 to metallic Ti can take place. The presentation will detail correlations between particle size, and the effect of the support and Ni oxidation state as main parameters for balancing and optimizing performance and stability.

Keywords: Ni oxidation state fluctuations; dry methane reforming; catalytic assembly; role of the support

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O.1.04

Exploring synergies between MoS_2 and metal oxides: towards new catalysts for CO_2 hydrogenation to methanol

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One of the key building blocks in the chemical industry, methanol has been mostly produced from fossil feedstocks over the last decades. With the growing necessity of developing sustainable alternatives, the catalytic production of methanol from CO_2 is a promising strategy to utilize carbon derived from biomass and industrial emissions from hard-to-abate sectors. [1] In this context, we investigate Molybdenum Sulfide (MoS_2) as an emerging catalyst for CO_2 hydrogenation reaction in virtue of its high stability, selectivity and tolerance to sulfur impurities. More specifically, the effects of combining MoS_2 with a variety of metal oxides are studied with the help of catalytic testing and material characterization via XRD, XPS, SEM, TEM, EPR, H_2-TPR and XAS, seeking to identify synergistic mechanisms and structure-property relations which drive CO_2 hydrogenation to methanol in these catalysts.

Although most formulations of MoS_2 catalyze the hydrogenation of CO_2 into methane, the formation of methanol can occur if the compound contains abundant basal plane sulfur vacancies [2]. More recently, a similar effect has also beMeten shown to arise due to the combination of MoS_2 with promoter materials. In our work, Mn-promoted MoS_2 prepared by a hydrothermal method has shown considerable selectivity for CO_2 hydrogenation to methanol under mild conditions (180 °C, 20 bar) in comparison with pure MoS_2 and other promoters such as K and Co. Although the Mn promoter is initially present in the form of $MnCO_3$, this phase is converted to MnO_x upon H_2 treatment, in order that the MoS_2/MnO_x system is suggested to be the key feature associated to catalytic activity. [3]

In our current research, MoS_2 has been alternatively impregnated into ZnO, leading to the formation of an intermediate layer consisting of ZnS and MoO_x at the support surface, which promotes high dispersion of MoS_2 and remarkable selectivity to methanol during CO_2 hydrogenation. Even though H_2 treatment may activate the catalyst by creating surface S-vacancies, here the total bulk density of S-vacancies in MoS_2 is shown to decrease during this step, possibly indicating partial suppression of these defects. In view of these findings, the formation of sulfides and oxides during calcination and pretreatment may contribute to catalytic activity, as these phases could preferentially grown on the less coordinated edge sites of MoS_2, thereby suppressing methane production on edge S-vacancies and enhancing methanol selectivity in basal plane S-vacancies at the surface of ZnO-supported MoS_2.

Keywords: catalyst; MoS_2; CO_2; methanol

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O.1.05

Heterogeneous transesterification of mixed non-food and waste vegetable oils over mixed oxides to prepare biodiesel

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As the population continues to grow and the demand for new energy sources increases, it is necessary to seek alternatives to replace fossil fuels. One such alternative is biodiesel. Currently, biodiesel is mainly produced from edible oils such as rapeseed or sunflower. One possible alternative is the use of non-food, like Camelina sativa oil (CSO) and waste oils [1]. However, its main disadvantage is its high content of nonsaturated bonds, which is reflected in its high iodine number. This high iodine number affects the low oxidative stability, which raises concerns about long-term storage. One possible solution is blending it with waste oil with a low degree of saturation. For example, coffee oil (CO) has been tested as a suitable blend.

Various blends of CSO with refined CO obtained from coffee waste were tested in a batch reactor. The CSO (IN= of 150 gI_{2}/100 g, was mixed in different weight ratios with the CO, which had an IN =92 gI_{2}/100 g).

The reactions were carried out under the same conditions in a reactor at a temperature of 140°C, in a two-stage process on a heterogeneous catalyst (mixed oxide with the addition of lanthanum/nickel).

As can be seen in Figure 1, the blend of oils achieved different results when observing the content of FAME in biodiesel. A significant difference was observed in the iodine number and oxidative stability of the biodiesel.

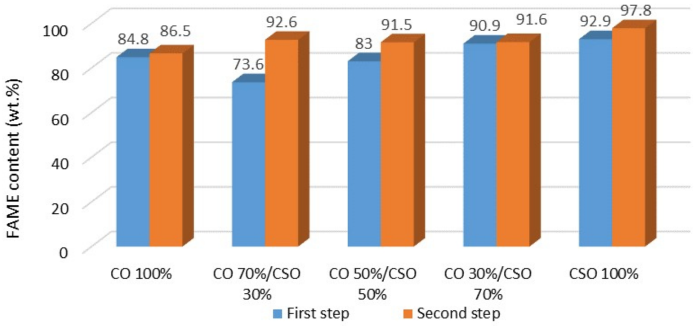

Fig. 1 FAME content after transesterification of mixed Coffee oil(CO) and Camelina sativa oil (CSO)

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Keywords: Mixed oxide, coffee oil, biodiesel, transesterification

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O.1.06

Ordered porous MOF-derived catalysts for CO_2 hydrogenation

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Carbon dioxide utilization technologies through conversion to added-value products are a straightforward approach for CO_2 recycling [1]. However, the chemical stability of the CO_2 molecule is a great challenge, requiring highly active and selective catalysts for its efficient activation. Among the various investigated catalysts for CO_2 hydrogenation to methane, Ni-based ones are the most attractive, due to their high activity and lower cost. On the other hand, the structural and textural properties of the catalytic support largely contribute to the extent of active phase dispersion, the metal-support interaction, and the extent of CO_2 activation. Therefore, catalytic supports with high surface area and controlled porosity play an important role in fulfilling these requirements. Owing to their exceptional structural and textural properties (structural diversity, large surface area, ordered porosity, etc), metal-organic frameworks (MOFs) have attracted a lot of scientific interest for various applications (gas storage, sensors, supercapacitors, catalysis, etc). However, their low stability when exposed to higher temperatures or different solvents, limits their use on a larger scale. In this context, the calcination of MOFs to produce either the corresponding metal-oxides (oxidizing atmosphere) or carbon structures (inert or reducing atmosphere), largely inheriting the properties of the initial MOFs, is regarded as a viable alternative to obtain stable MOF-derived materials. This work aims to report on the catalytic performance of MOF-derived Ni-based catalysts in the methanation of CO_2. For this purpose, MIL-53(Al), an Al-based microporous and flexible MOF, was prepared by a mild and cost-effective approach (only water as a solvent, reduced reaction temperature and time) as compared to the classical route [2]. The MOF-derived catalysts were prepared following two strategies: (1) thermolysis in air of the MIL-53(Al) structure to give the corresponding ordered porous Al_2O_3, followed by deposition of Ni [$Ni/Al_2O_{3(MIL)}$]; and (2) deposition of Ni in the parent MIL-53(Al), followed by thermolysis in air [$Ni@Al_2O_{3(Ni@MIL)}$]. The as-prepared samples were characterized by XRD, BET, TPR, SEM/TEM/EDX, H_2-TPD, CO_2-TPD, and the catalytic performance in the CO_2 methanation was evaluated under temperature-programmed reactions and stability runs for 24 h time-on-stream. It was found that the synthetic strategy for the MOF-derived Ni catalysts leads to different structural and textural properties, strongly influencing the catalytic performance in the methanation of CO_2. Additionally, the form of MIL-53(Al) used as starting material, either the as-synthesized form (as) or the activated low-temperature form (lt), plays an important role, especially with regards to the H_2 and CO_2 interaction with the catalytic support.

Keywords: MOF-derived Ni catalysts, ordered porosity, H_2/CO_2-TPD, CO_2 methanation.

Acknowledgement: This work was financially supported through Nucleu Program, PN 23 24 01 01.

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O.1.07

Use post-fermentation corn oil for advanced bio-component production. Catalytic solution

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Post-fermentation corn oil (PFCO) has a different composition than the corn germ oil. Extracted oil contains more free fatty acids than commercial corn germ oil. This corresponds to the high acid number. PFCO contains the highest proportion of linoleic acid, oleic acid and palmitic acid. Although the absolute values vary, the ratio of oleic acid to linoleic acid is in a narrow range of values from 0.49 to 0.52. The palmitic acid content is higher, and PFCO may be a suitable feedstock for bio-jet fuel production via hydrodeoxygenation. The catalytic transformation of triacylglycerides (TAG) on a hydrotreating catalyst and in a hydrogen atmosphere is one of the possible sources of renewable middle distillates. For aviation fuel, isomerisation of linear alkanes to branched alkanes is critically important to improve low-temperature properties, as linear alkanes crystallise at temperatures encountered at the operating altitudes of most commercial aircraft.

Before the hydrogenation process, PFCO refining was done to remove unwanted phospholipids and reduce the metal cations in the oil. A 30% citric acid solution was used for degumming. The degummed oil was dried and refined on silica gel. Hydrotreating of PFCO was carried out in a continuous flow tubular reactor, with a temperature range of 360-380 °C, pressure 4-5 MPa, LHSV 1 h^{-1} and ratio hydrogen to feedstock form 450-600 NL/L. h in a co-processing regime with n-decane or kerosine solvent. The catalysts used in the present study were catalysts $NiMoP/Al_2O_3$ and NiW/Al_2O_3-zeolite (sulfidic form). The decarboxylation reactions were predominant over hydrodecarboxylation. When a sulfidation - $NiMoP/Al_2O_3$ catalyst was used, the n-C_{17}/n-C_{18} ratio was high at 2.4 due to the high free fatty acid content of 13.2 wt.%. The yield of the C_{5+} fraction was 96.0 wt.%, and the n-alkane content was 96 wt.% due to the high free fatty acid content of 13.2 wt.%. The reaction pathway involves hydrogenation of the C=C bonds of the PFCO followed by alkane production by three different pathways: mainly decarboxylation, hydrodeoxygenation, and decarbonylation. Hydrotreating of PFCO and hydroisomerisation were tested in one reactor with a stacked catalyst bed. When hydrotreating of PFCO and hydroisomerisation were tested in one reactor with a stacked catalyst bed, the content of n-alkanes in the liquid product was 60% (m/m), the content of mono-methylated alkanes was 23.48 wt.% and 15.28 wt.% of unidentified iso alkanes.

Keywords: post-fermentation corn oil; advanced biofuels; hydrodeoxygenation; catalyst; co-processing.

Acknowledgement: The Slovak Research and Development Agency has financially supported this research under contracts APVV-18-0348, APVV-18-0255 and APVV-20-0348.

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O.1.08

Modified TiO_2/SiO_2 material as a support for ester hydrogenolysis catalyst

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The anchoring of titanium alkoxide on the hydroxyl-rich SiO_2 surface has caught the attention due to the covalent interaction between these two oxides resulting in the highly dispersed TiO_2. However, the surface morphology of this TiO_2/SiO_2 material largely depends on the preparation method [1]. Previously reported impregnation typically gives agglomeration and poor oxide dispersion and the precipitation deposits the TiO_2 on the silica's external surface [2]. On the contrary, the grafting method ensures controllable deposition and thus, predictable surface properties that are desired for further metal deposition and use. It has been testified that the efficiency of the grafting method depends either on the length of alkyl chain of the titanium alkoxide or the abundance of the surface silanol groups [3]. Considering all the factors, we used the grafting method for the preparation of modified TiO_2/SiO_2 that ensures both high dispersion and the smallest crystalline size. To use modified TiO_2/SiO_2 material in a model reaction, Cu nanoparticles were deposited and catalysts were tested over the ester hydrogenolysis to evaluate the catalyst activity. It was assumed, that the modified TiO_2/SiO_2 might increase the Cu active sites and improve the sintering effect during the reaction.

In this work, 1-10 wt% of modified TiO_2/SiO_2 was prepared by the grafting method and afterward 8-16 wt% of Cu was loaded by chemisorption hydrolysis. The prepared catalysts were characterized using XRD, XRF, BET, FTIR, RAMAN, and TPR. The TiO_2 deposition was successfully identified by FTIR confirming the SiO-Ti bond while reducing Si-OH. When XRD was employed, no crystalline titania phase and agglomeration of clusters were detected. Together with Raman, the presence of an amorphous phase is concluded. The TPR data confirms that the addition of titania improved the reducibility and suggested homogeneous dispersion of copper. Finally, all $Cu/TiO_2/SiO_2$ catalysts were tested on the conversion of dimethyl adipate (DMA) as a model reaction of ester hydrogenolysis by aiming for hexane-1,6-diol as a core product. The catalysts were reduced at 220°C before testing in the autoclave at 250°C in the presence of H_2 at 100 bar for 3 hr. The products were analyzed using GC-FID. From the conversion and selectivity data, it was concluded that the best interaction between the TiO_2/SiO_2 support and influence on copper metal was when 8%Cu was loaded on 5% TiO_2/SiO_2.

Keywords: modified TiO_2/SiO_2, grafting method, dimethyl adipate, hexane-1,6-diol.

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O.1.09

Synthesis of asymmetric ethers in the presence of zeolites: a study on catalyst properties

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Use and recuperation of solvents in chemical industry is one of the main contributors to waste production and energy requirements. Some conventionally used solvents, such as diethyl ether, also pose a significant occupational safety hazard due to their unstable nature. Such reasons justify the need for alternative solvents that could provide the desirable physico-chemical properties for industrial processes, as well as increase workplace safety and minimize energy demands for solvent recycling.

A group of chemicals intensively studied in this context are unsymmetric ethers. Cyclopentyl methyl ether (CPME), being a "flagship" in these compounds, possesses multiple favourable properties, such as hydrophobicity, high boiling point, slow generation of volatile explosive peroxides, and narrow explosion range. There are possibilities for its production from green biomass-derived chemicals [1,2]. Its incorporation into routine organic syntheses has been successfully demonstrated in multiple reactions [3].

A method for CPME synthesis, utilizing a heterogeneous acid zeolite-based catalyst, has been developed [4]. In this method, a mixture of methanol (MeOH) and cyclopentanol (CYPol) undergoes a gas-phase dehydration. The initial research focused on evaluation of a series of commercially available zeolites for this reaction under the following optimized conditions: a mixture of MeOH and CYPol in a mass ratio of 5:1 was fed into the reactor at weight hourly space velocity of 0.25 $g_{CYPol}\cdot g_{cat}^{-1}\cdot h^{-1}$ and a temperature of 100 °C.

We further aim to expand the knowledge of various zeolite properties effecting the outcome of this reaction. A series of catalysts prepared by varying temperatures of activation has been synthesized to demonstrate the effect of Brønsted to Lewis acid sites ratio. The effect of crystal size has also been determined. For this purpose, a series of targeted syntheses of zeolites with various crystal sizes was carried out.

Acknowledgment: This work was supported by the Slovak Research and Development Agency under Contract no. APVV-17-0302 and VEGA no. 1/0374/23.

Keywords: zeolites, unsymmetric ethers, green chemistry, solvents

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O.1.10

Catalytic soot removal on redox-metal-doped potassium silicate glasses

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From both environmental and technological perspectives, soot emission is one of the most challenging problems to be solved. Catalysis provides several alternative solutions to tackle this problem, however, searching for cheap, active, and stable catalysts is still far from its maturity. The usage of alkali metals seems to be a promising way, however, such dopants have to be immobilized in the matrix [1]. Our work aimed to investigate the effects induced by doping of potassium glasses with redox metals on their catalytic performance in soot combustion.

Potassium silicate glass was synthesized by melting (1345°C/1h). Doping by aliovalent redox metal was processed by remelting (1340°C/0.5h) of the parent glass with the corresponding dopant (Ti, V, Mn, Fe, Co, Ni, Cu, Zr, Ce, Pb, Bi) in oxide form. The obtained samples were characterized by XRD, RS, FTIR, XRF, DRIFT, UV/Vis-DR, XPS, SEM, and SR-TAD. Catalytic activity in soot combustion was tested in *tight* and *loose contacts*, in the atmosphere of 10%O_2/He and 0-500 ppm NO [2].

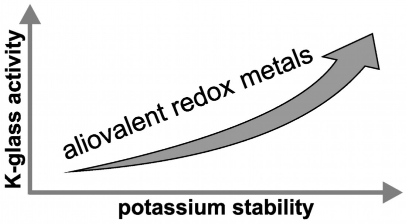

Fig. 1. Correlation between catalytic activity of the investigated glass samples and thermal stability of potassium.

Structural verification confirmed the amorphous character of all investigated samples. Their chemical composition remained as expected. The determined oxidation states of the introduced dopants resembled those in their parent oxides. The surface was found to be very sensitive to the presence of both CO_2 and H_2O and in the case of some samples, surface carbonates were identified by SEM. Based on the obtained results, it was inferred that potassium thermal stability can be controlled by the addition of redox metals, however, the presence of these dopants usually led to the lowering of the K-stability. Redox-metal-doped glasses showed high activity in soot combustion, regardless of catalytic test conditions. However, Co, Cu, Zr, and Pb can be considered as promising dopants for future optimization. Moreover, the correlation between the observed catalytic activity of potassium glasses and potassium stability was found (Fig. 1). It can be stated that the higher activity of the investigated glasses can be achieved by the higher stability of potassium in glassy structures.

Keywords: catalytic soot combustion, glasses, structural modifications, redox metals, potassium stability.

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O.1.11

Heterogeneous Silver Catalysts for Soot Oxidation: a Time-of-Flight Secondary Ion Mass Spectrometry Study

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A series of alumina-supported silver catalysts for soot combustion was studied using Time-of-Flight Secondary Ions Mass Spectrometry (ToF SIMS). Although the application of silver catalysts in this reaction is quite common, and different structural polymorphs of alumina have been used [1,2], there has been no systematic study of the effect of the alumina structure on the activity of the silver catalysts in soot oxidation. Since our preliminary studies have shown that the activity of a catalyst supported on the low-surface-area, alpha alumina was substantially superior to that with other forms of alumina, a series of alumina supports calcined within the temperature range 550-1300°C was synthesized. The Scanning Electron Microscopy imaging of the supports showed a progressive change in the topography of the samples with increasing calcination temperature. The results of the X-Ray Diffraction studies revealed how the calcination temperature of the supports influenced their structure, and that all of the supports obtained at or above 1000°C contained alpha-alumina. The change in the activity in soot combustion was not gradual, but step-wise, with a sharp increase noted between the alumina calcined at 900°C and 1000°C. This indicated that the change is most likely caused by a difference in the type of active sites found on the surface. Hence, apart from typical methods of catalyst investigation, an attempt to delve into the nature of the active sites using ToF SIMS was made. The reason for the selection of this particular technique is the fact that the matrix effect is an important contributor to the intensity and type of signals obtained in these measurements [3]. Because the composition/presence of contaminants also influences the results of ToF SIMS experiments, making a series of supports from the same precursor synthesized via the same method and with the same silver deposition technique is beneficial, as it eliminates most of the other variables which normally complicate the obtained MS spectra.

Keywords: soot combustion; silver catalysts; active site; time-of-flight mass spectrometry; alumina structure

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Effect of SBA-15 doping with $NbVO_x$ and $TaVO_x$ on the extractive catalytic oxidative desulfurization

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Due to the environmental aspects still one of the main issues is the decrease in sulfur content for petroleum products to a very low level. Thus, new strategies for the removal of sulfur compounds from gasoline have to be developed. One of the efficient methods used for this purpose is an extractive catalytic oxidative desulfurization (ECODS). This method allows for instance to remove dibenzotiophene (DBT) more efficiently by its oxidation to sulfoxides or sulfones under mild reaction conditions and simultaneous extraction of products [1]. The efficient catalysts for this process require the presence of strong Brønsted acid sites (BAS).

The objective of our study was to obtain an efficient catalyst for ECODS process. For this purpose SBA-15 was synthesized according to the procedure described in [2], and then doped with $NbVO_x$ or $TaVO_x$ using two methods: i) wetness impregnation with Nb or Ta and V precursors; ii) mechanical mixing of silica with $NbVO_x$ or $TaVO_x$ metal oxides. The catalysts obtained were examined by N_2 ads./des. isotherms, XRD, XPS, UV-vis, FTIR combined with pyridine adsorption. 2-propanol decomposition and 2,5-hexanedione dehydration and cyclization were applied as test reactions, and finally catalysts were applied in the ECODS process.

The mesoporous structure of SBA-15 support and amorphous nature of its walls were confirmed by N_2 ads./des. isotherm and XRD. For $NbVO_x$ and $TaVO_x$, the isotherms were of type II, which is typical for porous materials with a wide PSD. The XRD pattern of $NbVO_x$ confirmed the successful synthesis of mixed oxide phase, i.e. $Nb_{10.7}V_{2.38}O_{32.7}$, with some addition of Nb_2O_5, while for $TaVO_x$ the two phases were obtained: $TaVO_5$ and $Ta_{18}V_4O_{55}$**.** Modification of SBA-15 with metal oxides did not affect the mesoporous structure of the support, as confirmed by XRD and N_2 ads./des. The XRD patterns of mechanically mixed SBA-15 with metal oxides showed reflexes previously observed for $NbVO_x$ and $TaVO_x$ prior to incorporation, while for SBA-15 impregnated with both metal sources no reflexes appeared. The latter feature can be explained by the good dispersion of modifiers on the support. Both test reactions confirmed the acidic character of the catalysts. The highest number and strength of BAS was detected for samples obtained by impregnation method. The catalytic activity of the materials obtained was examined in ECODS in the presence of H_2O_2. The highest efficiency in the removal of DBT (ca. 98% within 15 minutes) and stability up to the fifth reaction runs were obtained in the presence of SBA-15 modified by Nb and V or Ta and V sources with impregnation. Superior catalytic performance of these materials was in line with a high number and strength of BAS.

Keywords: niobium, tantalum, vanadium, SBA-15, ECODS.

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O.1.13

Interaction of ammonia with Fe-SSZ-13 zeolite – ab initio thermodynamic and TPD-NH_3 investigations

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NH_3-SCR (Selective Catalytic Reduction using Ammonia) is an important technology for mitigating harmful environmental emissions, particularly in automotive and industrial exhaust treatment. Among the SCR catalysts, copper-iron-exchanged Cu-Fe-SSZ-13 zeolites exhibit remarkable activity and selectivity in NO_x reduction with NH_3. This catalytic system is characterized by higher activity and selectivity towards N_2 at elevated temperatures compared to zeolites containing single Cu or Fe cations. In the case of Cu-SSZ-13 co-catalyst, thanks to extensive research, it was possible to delve into the nature of copper active centers, estimate the impact of segregated CuO on reactivity, and propose a reliable mechanism of the SCR reaction [1]. Much more remains to be elucidated about the fundamental chemistry of Fe-SSZ-13, including the speciation of Fe cations, the identification of active sites, and the underlying reaction mechanisms. This is largely because a wide variety of iron species, including isolated Fe^{3+} or Fe^{2+} ions, dinuclear Fe-O-Fe oxo-cations, larger oligomeric Fe-oxo species with a wide range of nuclearity, and segregated Fe_2O_3 nanoparticles, very often coexist in the same catalyst, making their precise recognition difficult [2].

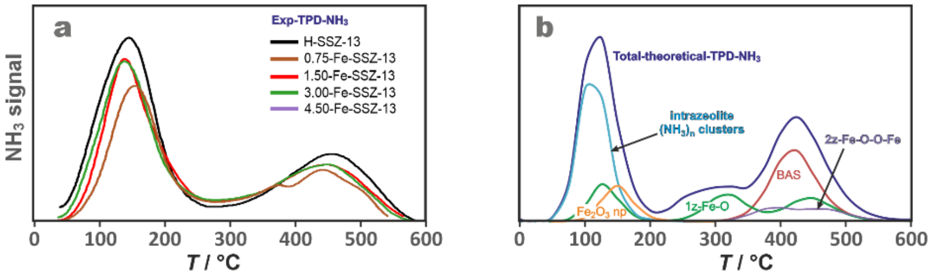

Figure 1: Experimental (a) and simulated (b) NH_3-TPD over Fe-SSZ-13 profiles

To probe the nature of the Fe active sites (in addition to spectroscopic techniques) the NH_3-TPD can be employed. The interpretation of the desorption peaks can be significantly improved thanks to the atomistic thermodynamics calculations [3]. In this study, our goal was to provide a comprehensive understanding of the temperature-guided NH_3 adsorption and desorption processes and to unravel the origin of NH_3-TPD peaks recorded for Fe-SSZ-13 zeolite of various iron loading (**Figure 1a**). We achieved this by conducting systematic DFT+D calculations and complementing them with first-principles thermodynamic modeling of NH_3 adsorption/desorption on single and dimeric intrazeolite Fe sites (Fe^{2+} , $[FeO]^{+}$, $[Fe\text{-}OH]^{2+}$, $[Fe\text{-}O\text{-}Fe]^{2+}$, $[Fe\text{-}O\text{-}O\text{-}Fe]^{2+}$), Brønsted centers, Fe_2O_3 nanoparticles, as well as extra framework Al-O Lewis centers (**Figure 1b**). In this way, we established a rational foundation for interpreting the intricate nature of NH_3-TPD profiles.

Keywords: Fe-SSZ-13 zeolite, NH_3-SCR, NH_3-TPD, DFT, atomistic thermodynamics

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O.1.14

Hydroconversion of γ-valerolactone over Co/γ-Al_2O_3 and Co/H-Beta zeolite catalysts

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Biomass, particularly the non-food and non-feed lignocellulose is an abundant source of renewable carbon for the chemical industry. Levulinic acid (LA) is one of the most important platform chemicals, which is already produced from lignocellulose at industrial scale [1,2]. From LA γ-valerolactone (GVL) can be derived via consecutive catalytic dehydration and hydrogenation reactions [3]. GVL has the potential to be blended with gasoline, or to be used as commodity of alkenes, polymers, and a number of value-added chemical products [1]. By catalytic GVL hydroconversion mainly 2-methyltetrahydrofuran (2-MTHF) and/or pentanoic acid (PA) is obtained. The reaction can be directed by applying catalyst and reaction conditions to favor the formation of one or the other product [3].

The present study concerns the GVL hydroconversion activity of zeolite H-Beta and γ-Al_2O_3-supported Co catalysts. Co/γ-Al_2O_3 and Co/H-Beta catalysts were found to direct the reaction to get selectively 2-MTHF and PA, respectively, at 200–250 °C, though the acidic and hydrogenation functions of the catalysts were found to be hardly different. Operando DRIFT spectroscopic investigations revealed that acid sites of γ-Al_2O_3 and zeolite H-Beta induces the ring opening of GVL at the [CH_3CH-O] bond giving pentenoate carboxylate, bound to Lewis acid sites, and pentenoic acid. Introduction of Co hardly influenced the Lewis acidity of γ-Al_2O_3, whereas the Lewis acid sites in H-Beta were partly converted to new type of Lewis acid sites represented by Co lattice cations. Over these latter sites no carboxylate species were formed, thus the concentration of surface carboxylates was significantly lower on Co/H-Beta than on the H-Beta support. The Brønsted acid sites did not take part in carboxylate formation. In the presence of hydrogenation function (Co^0) and H_2, the unsaturated carboxylate species were hydrogenated to saturated surface carboxylates, while the hydrogenation of the carbonyl group leading to intermediate of 2-MTHF formation was also initiated. The strong bonding of monodentate carboxylates to the Lewis sites of γ-Al_2O_3 prevented the acid catalyzed ring opening reaction at temperatures below about 250 °C, thus the 2-MTHF formation prevailed due to the dominating hydrogenation activity. In contrast, carboxylate formation did not block the Brønsted acid sites of H-Beta thus the ring opening reaction leading to PA formation prevailed over the hydrogenation reaction above about 175 °C. This study shows that the steady-state GVL hydroconversion activity of these bifunctional catalysts is generated in the interaction of the catalyst, the reactants, and the products.

Keywords: GVL hydroconversion; Co/γ-Al_2O_3; Co/H-Beta, 2-MTHF; pentanoic acid; DRIFTS-MS.

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O.1.15

MOFs supported NPs-catalysts for selective hydrogenation of nitrobenzene

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The selective hydrogenation of nitrobenzene and its derivatives is a crucial industrial reaction used to produce their corresponding amines. These amines are versatile intermediates and precursors in the synthesis of various organic compounds, including pharmaceuticals, pigments, dyes, polymers, and other fine chemicals [1]. In the chemical industry, the catalytic hydrogenation of nitrobenzene (NB) is the primary method for synthesizing aniline (AN) using various catalytic systems in both vapor and liquid phases [2]. Selecting the right catalysts and ensuring optimal hydrogenation reaction conditions are crucial in achieving high yields and superior selectivity for AN [3]. Apart from other porous materials, MOFs offer clear advantages for use in heterogeneous catalysis. Recently, MOF-supported nanoparticles have exhibited exceptional catalytic activity in the liquid-phase catalytic hydrogenation of nitrobenzene [4]. The objective of this study was the preparation, characterization, and exploration of the catalytic performance of MOF-supported NPs catalysts: Pt/MIL-101(Cr) (2 wt.% Pt loading) and Au-Pt/MIL-101(Cr) (1 wt.% Au and 1 wt.% Pt loading) in the selective hydrogenation of nitrobenzene, under mild reaction conditions. The monometallic Pt NPs and bimetallic Au-Pt NPs were successfully immobilized inside the pores of the MIL-101(Cr) support by employing the double-solvent method (DS), followed by thermal H_2 reduction. The characterization results demonstrated that the small metal nanoparticles were uniformly distributed (2.9 nm for the Pt catalyst and 2.7 nm for the Au-Pt catalyst) while maintaining the crystalline structure of the MIL-101(Cr) support. The results of the catalytic activity test showed that the Pt(2%)/MIL-101(Cr) catalyst exhibited outstanding catalytic performance and recycling stability under mild reaction conditions (30 °C, 2 bar H_2). The catalyst was able to convert NB completely with a selectivity towards AN of >99% within 2 hours. The composite's high efficiency was attributed to the homogeneous deposition of small Pt nanoparticles, as well as the large pore size and surface area of the MIL-101(Cr) catalytic support, which facilitated the adsorption of NB at the catalyst's active sites. In comparison to the monometallic Pt(2%)/MIL-101(Cr) catalyst, the bimetallic Au(1%)-Pt(1%)/MIL-101(Cr) catalyst was investigated for the first time for the selective hydrogenation of NB in the liquid phase. It showed improved hydrogenation activity due to the synergistic effect between the two metals.

Keywords: MIL-101(Cr), Au-Pt nanoparticles, nitrobenzene, liquid phase hydrogenation.

Acknowledgments: This work was financially supported by the Ministry of Research, Innovation, and Digitalization, Nucleu Program within the National Research Development, and Innovation Plan 2022-2027 [PN 23 24 01 01].

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O.1.16

Liquid-phase catalytic oxidation of alcohols over spinel oxides

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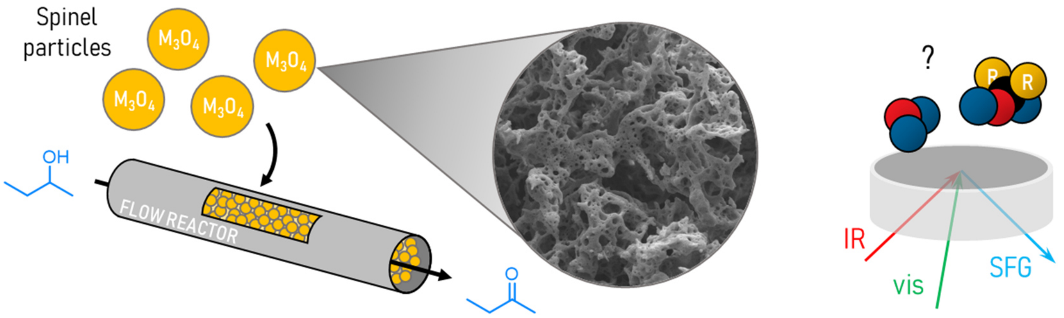
The selective oxidation of alcohols is an important synthetic tool in the portfolio of the chemical industry. Even though the oxidations of small alcohols such as methanol to formaldehyde are established processes, the selective transformation of higher alcohols is more challenging; moreover, the mechanistic understanding of these reactions over heterogeneous catalysts is still poor, especially about the phenomena taking place at the solid-liquid interface [1]. Besides, the most active catalysts are based on noble metals [2]; metal oxide catalysts are more complex and comprise less defined active sites, but they are based on more earth-abundant metals and are less susceptible to leaching. Therefore, the surface study and design of more active and selective oxide catalysts are important matters in light of the green transition. In this regard, oxides of the spinel type proved to be outstanding catalysts in liquid-phase aerobic oxidations [3]. Co-based spinels doped with Mn, Fe, Ni, and Zn were prepared using the combustion method followed by calcination. The obtained porous solids were characterised by XRD, FT-IR, SEM-EDX, TEM, N_2-physisorption, and XPS. The catalysts were tested for the liquid-phase oxidation of 2-butanol to methylethylketone in a flow reactor, in the presence of water and O_2, to study the effect of the catalyst composition on the activity and selectivity, the stability of the catalyst to water and to the reaction conditions was also assessed. The liquid and gas streams were separated, and both were analysed by GC-FID. The optimised reaction conditions for kinetic testing were 200 °C and 40 bars of O_2 pressure. The doping resulted in a boost of activity for Mn, with $MnCo_2O_4$ being the most active catalyst. The reaction was also performed in batch using an autoclave reactor to compare the performance of the catalyst in the different regimes and corroborate the activity trends obtained in flow. Finally, Co_3O_4 thin films were prepared by thermal decomposition, and were used to study the interaction of alcohols with the oxide surface by SFG spectroscopy.

Keywords: Spinel oxides, alcohol oxidation, flow reactor, SFG spectroscopy.



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O.1.17

Hydroxylation of an ultrathin $Co_3O_4(111)$ film on Ir(100): *in situ* NAP-XPS and DFT studies

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Spinel cobalt oxide (Co_3O_4) is a promising inexpensive functional material for many applications including heterogeneous oxidation catalysis (e.g., low-temperature CO oxidation[1,2], preferential oxidation of CO (PROX)[3], oxidation of hydrocarbons[4], etc.). Despite its outstanding catalytic performance, several studies[1,5,6] report rapid deactivation related to lowest levels of humidity in the reactant feed gas. Since the formation of OH groups at the oxide surface has already been demonstrated in ultrahigh vacuum (UHV)[7,8], the present study focuses on the mbar pressure range relevant for applied catalysis.

Within a model system approach, a $Co_3O_4(111)$ thin film (thickness: 2.4 nm) was prepared by oxidative physical vapor deposition (PVD) on the bulk-truncated surface of an Ir(100) single crystal substrate (10´2 mm). After heating to 570 K in 0.5 mbar O_2 to remove carbonaceous contaminants as well as OH due to H_2O traces in the UHV background, and brief cooling to RT, 0.5 mbar H_2O vapor was dosed and the OH signal monitored *in situ* in the XPS O 1s region (NAP-XPS was performed at the MAX synchrotron laboratory). For surface modeling, DFT+U was applied in its implementation published in the Vienna *ab initio* simulation package (VASP, ver. 6.4.1)[10,11]. Based on corresponding results and quantification of oxidic and OH signals in the O 1s region, the OH coverage was calculated and its evolution with time determined by Langmuir pseudo-second order kinetics. The present work contributes to the understanding of H_2O interaction with Co_3O_4 surfaces, which is discussed in the context of catalytic deactivation.

Keywords: Co_3O_4, water interaction, NAP-XPS, DFT

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Sisyphus – building an elevator for CO_2

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Addressing climate change is a pressing issue, and while reducing global CO_2 emissions is crucial, some economic sectors, such as aviation, marine transport and chemical production, heavily depend on carbon based products and are at the same time extremely difficult to abate. In such cases, establishing a circular carbon economy – utilising captured CO_2 – offers a sustainable alternative to decarbonisation. However, the large-scale conversion of CO_2 to valuable products needed to meet this challenge is still too expensive due to the significant efficiency losses associated with the multi-step process routes.

Sisyphus, a spin-off project at the Montanuniversität Leoben in Austria, has taken it upon themselves to tackle one of the critical steps in the utilisation of CO_2: the efficient production of renewable synthesis gas (syngas) via the reverse water-gas shift reaction. Syngas is a key building block for e-fuels and green chemicals, placing Sisyphus at the heart of several larger value chains for sustainable products. Our technology is based on a catalyst material showing highly promising performance under industrially relevant conditions.

In order to establish a successful business, we are targeting future producers of e-fuels, methanol producers shifting to sustainable feedstocks, and operators of biomass fermentation and conversion processes. These segments will be growing tremendously in the coming years and decades, offering a great market opportunity. The benefits of our more efficient process include increased productivity and reduced cost, leading to quicker technology adoption.

Join us to learn more about our progress, as well as the challenges we meet trying to uncover the potential pathways towards sustainable syngas-based products. We are looking forward to share our experiences and visions for the coming years.

Keywords: CO_2 Utilisation, Renewable Syngas, University Spin-off.

O.2.01

Transition Metal Oxide Catalysts Supported on Stainless Steel Meshes Prepared by Plasma Jet Sputtering

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Low-temperature plasma sputtering is one of the most important methods used in industry to deposit thin films on various substrates. Recently, an alternative deposition method based on sputtering using a metal nozzle with a flowing gas has attracted attention. Transition metal oxides are suitable for the abatement of harmful volatile organic compounds by total oxidation [1]. We decided to study Ni-Co-Cu-Mn oxides supported on stainless steel meshes and their performance in gas-phase total oxidation of ethanol and toluene as model VOCs.

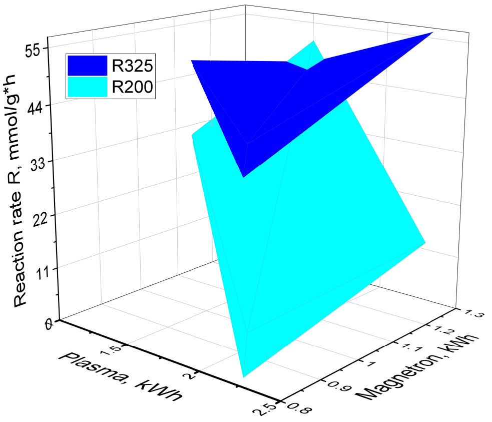

Figure 1. Dependence of ethanol (R200) and toluene (R325) oxidation rate on plasma and magnetron energy.

The Raman spectroscopy proved crystallization and oxidation process during calcination. The XRD showed the formation of NiO-like oxides in the calcined catalysts. The XPS spectroscopy revealed the enrichment of the catalyst surface by Mn. The effect of energy delivery on the performance of the catalysts in ethanol and toluene oxidation was studied. In ethanol oxidation, the specific reaction rate at 200 °C was the highest at mild delivered plasma energy (1.6 kWh) and high magnetron sputtering energy (1.3 kWh). In toluene oxidation, the specific reaction rate at 325 °C was the highest when both plasma jet and magnetron sputtering delivery of energy were high (2.3 and 1.3 kWh, respectively). Thin-film catalysts supported on meshes are promising due to high catalytic activity at low content of active phase and low pressure drop in the catalytic reactor.

Keywords: low-temperature plasma jet sputtering, transition metal oxides, stainless steel meshes, VOCs.

Acknowledgement: This work was supported by the Strategy AV21 (project Food for Future).

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O.2.02

Flame-Forged Perovskite-Type Oxides: Advancements in Oxide Synthesis Techniques

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This research examines the novel application of Flame Spray Pyrolysis (FSP) for synthesising complex oxides such as perovskite-type oxides, a class of materials with a vast potential as catalysts for the global energy transition. FSP's continuous and scalable production process ensures reproducibility and product standardisation, which is crucial in industrial applications. Our investigation focused on the influence of various parameters for the successful synthesis of perovskite-type oxides, including flow rates, flame composition, and precursor solution. The comparison between FSP and well-established modified Pechini synthesis for complex oxides was of particular interest, as it offers enhanced control over particle size, composition, and specific surface area (SSA), thereby addressing the limitations of traditional methods. [1–3] A proof of concept could be demonstrated for synthesising complex oxides, such as perovskite-type oxides, with high control over their morphology. Our findings demonstrate the practical implications of using FSP as a synthesis approach over the Pechini route, as it allows for the deliberate tailoring of the material´s properties. By controlling the flow rates of the gas streams (fuel gas, dispersion gas, sheath gas) and the flow rate of the liquid injection, the surface of the oxides can be selectively modified to meet specific requirements, opening up new possibilities in materials science and energy conversion.

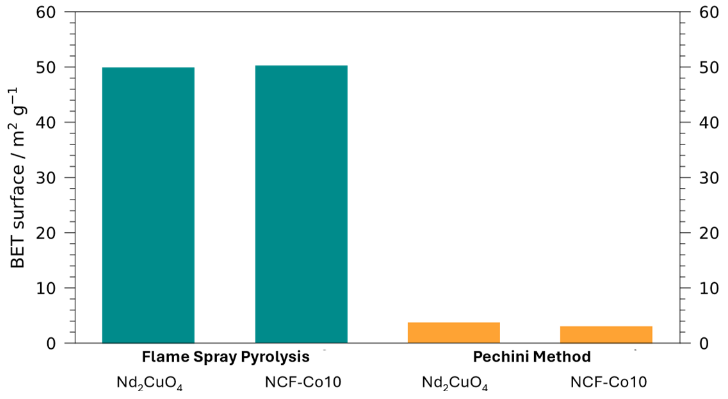

Figure 1 – Differences in the specific surface area of perovskite-type oxides using two different synthesis approaches.

Keywords: energy conversion, catalysis, synthesis method, flame spray pyrolysis

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O.2.03

Molecular oxygen activation over binuclear iron centers in zeolites with various topology

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The employment of molecular oxygen as an oxidizing agent for methane oxidation represents one of the challenges of current catalysis. [1,2] Recently, it was shown that binuclear divalent transition metal ions embedded in zeolite matrices cooperate in O_2 splitting and formation of an active oxygen form called α-O.[1] This α-O can be subsequently used for methane to methanol oxidation at ambient conditions. In this work, we are focused on the structural analysis of iron active sites in the ferrierite and Al rich *BEA matrices that are responsible for activation of O_2 and methane to methanol transformation. This work compares the O_2/ CH_4 redox behaviour of binuclear Fe(II) sites in *BEA and FER monitored by in-situ XAS, FTIR and Mössbauer spectroscopies and subsequent interaction with methane as a testing reaction.

Two zeolites of FER (Si/Al 8.5, Tosoh Corp.) and *BEA (Si/Al 5, laboratory made [2]) topology were used as parent materials for preparation of Fe -FER and Fe-*BEA with Fe/Al ~0.05. The Mössbauer and XAS spectral features of the evacuated Fe-FER and Fe-*BEA confirmed the presence of atomically dispersed Fe(II) cations in both samples. Interaction of studied zeolites with O_2 at RT, generate α-O species, which confirm the activity of binuclear iron sites presence in both Fe-FER and Fe-*BEA in O_2 splitting. In-situ XAS spectra collected after the interaction of α-O species formed over Fe-FER and Fe-*BEA with CH_4 confirmed the occurrence of a redox cycle, and the regeneration of Fe(II) active sites. Activity tests with FTIR and MS detection, revealed the presence of methanol and CO_2 in the gas stream. Fe-FER zeolite exhibited high catalytic performance at lower temperature ranges compared to Fe-*BEA, with the latter showing higher activity above 160 °C. Moreover, both samples displayed stability over three consecutive redox cycles.

The study presented here has demonstrated that O_2 can be activated over binuclear iron centres stabilized in FER and *BEA topology. This research has provided valuable insights into the interplay between the structural and functional aspects of FER and *BEA in the creation of active oxygen species, that can be further used for hydrocarbons oxidation.

Keywords: zeolites, binuclear iron centers, molecular oxygen, methane, redox cycle

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O.2.04

Boosted Catalytic Performance via Synergistic Interaction of 2D Support and Platinum Nanoparticles

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Graphene and its derivatives are widely used in the catalytic field due to their physical and chemical properties, such as high electrical conductivity, large specific surface area, excellent catalytic activity and selectivity. Although contemporary two-dimensional (2D) materials beyond graphene, such as germanene and silicene [1], have provided great potential as promising supports for metal nanoparticle-based catalysts. In these 2D material-supported catalysts, the strong binding of metal nanoparticles (NPs) to 2D supports ensures superior catalytic performance owing to the interaction between NPs and 2D supports. Furthermore, the NP-support interaction affects selectivity and catalytic activity [2]; therefore, the catalytic performance of 2D material-supported catalysts may strongly depend on the physical-chemical properties of 2D support. However, understanding the NP-support interaction is scientifically challenging because of various system parameters such as morphology, composition, and structure of the 2D supports and supported NPs.

One possibility to investigate the NP-support interaction consists of the necessity to exclude the effect of the NPs in order to evaluate the specific influence of the 2D support. For this, the same uniform pattern of NPs with a fixed size and spatial distribution needs to be obtained on different types of 2D supports. Electron beam lithography (EBL) is an ideal technique for the precise controlled nanofabrication of metal NPs. This technique is able to prepare patterns with a precision of 10 nm. The advantage of this method is the direct and target deposition of metal NPs on the selected 2D sheet with the known size and spatial distribution.

In this study, we have focused on understanding the NP-support interaction distinguished from the determination of catalytic activity based on 2D material-supported catalysts prepared by EBL and chemical deposition. As a 2D support for platinum (Pt) NPs, several types of 2D materials were used: functionalized graphene oxide, hydrogenated germanane, modified germanane and silicane. The macroscopic catalytic activity and selectivity of 2D material-supported Pt catalysts with varying electronic properties were explored in a model reaction of cinnamaldehyde hydrogenation. Our findings validated a proposed mechanism of interaction between the support and Pt NPs, which was gained from the analysis of microscopic catalytic activity on 2D material-supported Pt catalysts prepared via EBL. The catalytic characterization of these catalysts advanced the understanding of the interaction between NPs and 2D supports.

Keywords: 2D Materials, Platinum Nanoparticles, Metal-Support Interaction, Catalytic Activity

Acknowledgments: This project was supported by the Czech Science Foundation (GACR No. 23-08083M) and the grant of Specific university research – grant No A2_FCHT_2024_056

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O.2.05

Redox behavior of manganese-oxide-based catalysts ($K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$) – comparative TEM and DFT investigations

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This contribution presents a detailed analysis of thermally induced redox processes occurring in manganese-oxide-based catalysts, $K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$, using a combination of in-situ transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), and DFT molecular modeling. The structure of $K_2Mn_8O_{16}$ consists of the edge-shared double 2×2 MnO_6 chains with some corner-shariAnang octahedra, leading to the appearance of one-dimensional tunnels. Potassium ions (K^+) are inserted into these tunnels to stabilize the lattice, resulting in mixed valence states of manganese ions (Mn^{4+}, Mn^{3+}, and Mn^{2+}). The $Na_2Mn_3O_7$ structure is featured by the Mn_3O_7 2-layers separated by sodium ions, occupying different sites (the prismatic sites above and below the vacant manganese sites, and the octahedral sites). This structural disparity is crucial for understanding the diverse redox behavior of the catalysts.

The examined manganese catalysts were prepared via hydrothermal and solid-state syntheses, using different precursors (manganese acetate, manganese sulphate, manganese nitrate) and reducing agents (e.g. glucose). Subsequently, only those exhibiting well-defined morphologies were selected for further analysis.

Ex-situ microscopic characterization of the catalysts revealed differences in the redox state of manganese ions, depending on their location within the catalysts. For the $K_2Mn_8O_{16}$ catalyst, the ELNES spectra analysis (**Fig. 1,** *left*) showed a chemical shift of the Mn energy loss towards lower values, indicating changes in the Mn valency state on passing from the core (Mn^{4+}) to the tip/surface (Mn^{2+}/Mn^{3+}). In-situ TEM and EELS experiments focused on thermally-induced redox changes demonstrated discrepancies in redox properties and stability between nanorods and layered manganese catalysts (**Fig. 1**, *right*). The EELS analysis was complemented by DFT modeling, which provided insights into oxygen vacancies formation and their migration within the atomic structure of the $K_2Mn_8O_{16}$ and $Na_2Mn_3O_7$ catalysts. Through a combination of ex-situ and in-situ experiments with the DFT results, it was possible to identify a temperature window where both catalysts exhibited fully reversible redox behavior, as well as stable structure and morphology. This comprehensive approach contributes to a deeper understanding of the redox processes occurring in the manganese-oxide-based catalysts and their potential applications in thermochemical cycles.

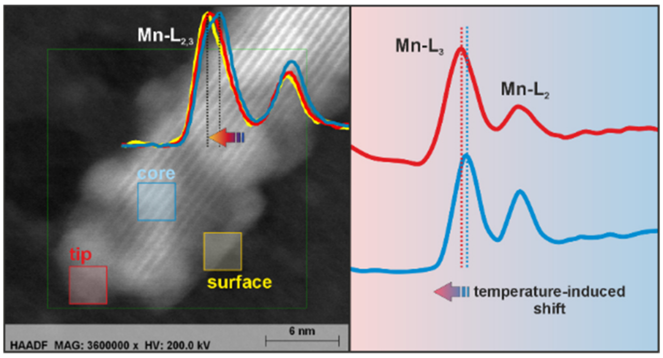

Fig. 1. ***left***: ELNES Mn-$L_{2,3}$ lines measured in different positions at the $K_2Mn_8O_{16}$ nanorod: surface (yellow), tip (red), core (blue).

right: ELNES Mn-$L_{2,3}$ lines collected and room temperature and at 900 °C.

Keywords: manganese oxides-based catalysts, DFT, in-situ TEM, EELS.

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O.2.06

Unlocking the potential of anatase TiO_2 for 5-HMF valorisation by the understanding of its surface properties

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Throughout the past century, fossil resources have been the main supply of chemicals and transportation fuels, which has increased the economic growth [1]. Currently, more than 85% of energy is taken from fossil resources; however these resources are scarce and associated with emission of CO_2 resulting in climate change and global warming [2, 3]. To overcome these problems, lignocellulose biomass is considered as one of alternative sources of energy and chemicals because of its low price and good availability [4]. Lignocellulose can be hydrolysed into platform chemicals like 5-hydroxymethylfurfural (5-HMF). 5-HMF is considered the most promising chemical because it consists of three different functional groups, C=O, C=C and C-O. Catalytic hydrogenation or hydrogenolysis of any of these groups gives us value-added components like 5-methylfurfural (5-MF), 2,5diformylfuran (2,5-DFF) and many more [5]. TiO_2 is a well-known material used for a design of supported catalysts, due to its low cost, high surface area provides high number of Lewis sites. People have reported anatase TiO_2-supported metallic catalysts [6] for the hydrodeoxygenation of 5-HMF without understanding the behaviour of pure anatase TiO_2 in conversion of 5-HMF.

In this research work, we comparatively tested three different anatase TiO_2 including two commercial materials named as TiO_2-S and TiO_2-A and one laboratory-made by hydrolysis of titanium butoxide named as TiO_2-B. To elucidate changes in structural and textural properties of titania, we treated them at 400 and 800 °C. The composition and structural-textural properties including also acid-base characteristics were determined using XRF, XRD, BET, TEM, pyr-TPD, CO_2-TPD IPA-TPD and *in situ* pyr-FTIR. Then, all supports were tested in a batch reactor at 220 °C with 70 bar H_2 pressure in THF as a solvent for 3 hours in 5-HMF conversion. Reaction mixtures were analysed using GC-FID. Surface acid sites play a critical role in 5-HMF conversion, that varied with changing the surface areas. We found that 5-HMF can be converted into 5-MF and 2,5-DFF through the intermolecular hydride (^{-}H) transfer which take place over the Lewis acid sites through disproportionation reaction. From the correlation results we found that increasing pretreatment temperature from 400 to 800 ^{O}C has dramatically disturbed the catalytic activity by increasing the crystallite sizes directly decreased the surface area and number of acid sites resulting in lower 5-HMF conversion. Our work provides insightful information about the exploitation of the potential of anatase-TiO_2 intrinsic properties in valorisation of biomass derived chemicals.

Keywords: 5-hydroxymethylfurfural (HMF), 5-methylfurfural (5-MF), 2,5-diformylfuran (2,5-DFF), anatase TiO_2, disproportionation reaction

Acknowledgements*:* Financial support from Czech Science Foundation (project No. GF21-45648L) is greatly acknowledged.

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O.2.07

Photocatalytic activity of NiO/Vermiculite materials in hydrogen production

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Due to global problems with increasing energy consumption, depletion of fossil fuels, and environmental pollution caused by human activity, it is extremely important to seek new ways to obtain and store pure energy sources. Hydrogen production appears to be a very promising possibility to replace fossil fuels with minimal impact on the environment, as well as to be used as a key chemical compound in many branches of industry like for the synthesis of ammonia or hydrorefining processes [1,2].

Clay base materials, as vermiculites, are classified as good photocatalysts for hydrogen production and wastewater degradation due to their structure, relatively high surface area and high adsorption properties [2]. Vermiculite 2:1 layer phyllosilicate structure consists of two tetrahedral silica sheets and one octahedral magnesium sheet between. Aluminum or iron substitutions in the tetrahedra and octahedra cause a layer charge imbalance, providing unique features to the material [2].

Metal oxide semiconductors have attracted widespread attention due to their high sensitivity, good thermal stability, easy control over composition and structure, and low cost. Nickel oxide (NiO), a typical p-type semiconductor is considered as a promising candidate with a wide band gap (3.6–4.0 eV). Vermiculite can acted as two dimensional layer support of NiO nanoparticles for enhancing photocatalytic reactions [1,2].

The aim of this study was synthesis of NiO/Vermiculite photocatalysts through various methods, aiming to create stable, low-cost, environmentally friendly and efficient materials for photocatalytic hydrogen generation. The photocatalytic activity was examined in the stirred batch photoreactor under 254 nm light irradiation for hydrogen production from methanol–water mixture. Detailed investigations were conducted to analyse the correlations between structural, textural, optical, and electrical properties and the photocatalytic activity. The results revealed that the different methods of photocatalyst preparation significantly influenced photocatalytic efficiency of hydrogen generation.

Keywords: Hydrogen production, heterogeneous photocatalysis, nickel oxide, vermiculite.

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O.3.01

Photoelectrocatalytic Water Oxidation by Conformal CuOx on Hematite Nanoarrays

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Photoelectrochemical (PEC) water splitting, promising for efficient hydrogen production, relies on hematite (α-Fe_2O_3) as an ideal photoanode material due to its favorable band gap, band edge positions, and cost efficiency. Challenges like low conductivity, high surface state density, short hole lifetime, and sluggish oxygen evolution at the electrode/electrolyte interface limit its catalytic potential. Loading co-catalysts is crucial to overcoming these hurdles. The specific effects of these co-catalysts, particularly in promoting water oxidation on hematite, especially regarding surface states S1 and S2, are still uncertain. Herein, we engineered two structurally similar hematite nanoarrays – undoped and Ti-doped α-Fe_2O_3 – with a thin layer of amorphous copper oxide (CuOx), using a gentle electrodeposition of the Cu-triglycine complex. [1] The resulting hybrid nanostructures, CuOx/α-Fe_2O_3 and CuOx/Ti:α-Fe_2O_3 were characterized by XRD, XPS, TEM-EDX, SEM, electro- and photoelectrochemcial techniques, such as LSV, fast cathodic CV, PEIS.

Interestingly, our findings reveal that in undoped hematite (α-Fe_2O_3), the S2 state plays a crucial role in activating the CuOx ad-layer for water oxidation. At lower external biases (around 0.9-1.1 V_{RHE}), CuOx acts as a charge reservoir in equilibrium with the S2 state. Notably, beyond 1.1 V_{RHE}, when the high-energy holes of the S1 state become accessible, CuOx is indirectly activated through its equilibrium with the S2 state, leading to a significant increase in photocurrent. Conversely, in the case of Ti-doped hematite (Ti:α-Fe_2O_3) lacking the S2 state, the presence of CuOx leads to a decrease in charge transfer efficiency. Instead of facilitating water oxidation, CuOx negatively impacts the S1 surface sites and reduces the density of charge carriers in Ti:α-Fe_2O_3. The fabricated photoanode materials highlight the importance of the S2 state in transferring holes to CuOx for enhancing the OER. Our research emphasizes that developing co-catalyst/semiconductor HUcombinations without understanding the nature of the surface states could lead to ineffective systems. Conversely, more efficient co-catalyst deposition suggests the presence of surface states capable of facilitating charge transfer between the co-catalyst and the semiconductor, thus supporting efficient catalytic reactions. [2]

Keywords: copper-oxide, co-catalyst, hematite, nanostructures, solar water splitting

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O.3.02

Enhancing Water Oxidation Efficiency: Carbon Nanotubes Economically Integrated with Visible-Light Semiconductors

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This study focuses on developing a highly efficient photoanode system for photoelectrochemical (PEC) water oxidation through the utilization of green chemical techniques. Hematite (α-Fe_2O_3) emerges as a promising material for this purpose owing to its photocatalytic properties, low band gap energy, and photochemical stability. Herein, α-Fe_2O_3 nanorods were synthesized and surface-modified with boron-doped g-C_3N_4 (B-C_3N_4), followed by the economical integration of carbon nanotubes obtained from methane pyrolysis, and utilized as prepared (pCNT). This process involved a facile two-step dip-coating method followed by post-heat treatment. The resulting α-Fe_2O_3/B-C_3N_4/pCNT heterojunction effectively modulated interface charge properties, thereby enhancing spatial charge separation within the anode.

Characterization through X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV-visible spectroscopy, and PEC measurements revealed disti`nctive features. XRD patterns confirmed the presence of α-Fe_2O_3 peaks, while the absence of B-C_3N_4 peaks indicated its low proportion and crystallinity. XPS analysis validated the chemical environment of all elements, with characteristic peaks observed for Fe $2p_{3/2}$ and Fe $2p_{1/2}$ at 710.7 eV and 723.4 eV, respectively, in the α-Fe_2O_3 nanorods.

Notably, the α-Fe_2O_3/B-C_3N_4/pCNT composite exhibited a significant enhancement in PEC water splitting performance, achieving a photocurrent density of 1.2 mA cm^{-2} at 1.23 V_{RHE} at pH 7, approximately 3.2 times higher than pristine hematite under visible light irradiation. This enhancement is attributed to the synergistic interfacial coordination between B-C_3N_4 and pCNT nanoparticles on the α-Fe_2O_3 nanorods, facilitating bandgap-dependent interfacial charge transfer. The development of such cost-effective, highly active, and surface-modified α-Fe_2O_3 anodes presents an avenue for fabricating tandem photoelectrochemical devices aimed at low-cost solar fuel production.

Keywords: Photoelectrochemical water oxidation, Hematite, Carbon nanotubes, Z-scheme pathway

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O.3.03

Polymer carbon nitride Z-scheme heterojunction for photocatalytic overall water splitting

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Z-scheme heterostructure artificial photocatalytic systems are optimal for the achievement of photocatalytic overall water splitting.[1] The system emulates natural photosynthesis by connecting disparate semiconductors in a series configuration.[2] However, the coupling of components that facilitate H_2 evolution and O_2 evolution remains a challenging area of research.[3] Recently, polymer photocatalysis with tunable band structures (e.g., polymer carbon nitride (PCN)) has attracted wide interest from researchers.[4] Firstly, we fabricate a Z-scheme system for photocatalytic overall water splitting based on boron-doped, nitrogen-deficient carbon nitride two-dimensional (2D) nanosheets. We prepare ultrathin PCN nanosheets with varying levels of boron dopants and nitrogen defects, which leads to nanosheets that can act as either H_2 or O_2 evolving photocatalysts.[5] An electrostatic self-assembly strategy was employed to couple the nanosheets, resulting in the formation of a 2D/2D polymeric heterostructure. The heterostructure exhibited stoichiometric H_2 and O_2 evolution in the presence of Pt and $Co(OH)_2$ co-catalysts, with a solar-to-hydrogen (STH) efficiency of 1.16% under one-sun illumination.[6] However, heterojunctions are often identified by chance. To facilitate the design of Z-scheme heterojunctions based on limited data, we propose an active learning strategy that integrates machine learning with high-throughput theoretical calculations, thermodynamic calculations, and experiments. The STH efficiency of the photocatalyst, which was designed using rational methods, was 1.59% under one-sun illumination in the presence of Pt/Cr_2O_3 and $Co(OH)_2$ co-catalysts. Furthermore, a numbering-up reactor system was developed for large-scale photocatalytic overall water splitting. The STH efficiency of the unit module was found to be 1.92% when operated steadily for 72 hours under natural sunlight. A large-area reactor comprising nine units (light-exposed area 324 cm^2 and reactive area 1,296 cm^2) demonstrated a high STH efficiency (1.86%) under natural light irradiation. The results of this study indicate a clear need for the development of large-scale integrated photocatalytic overall water splitting technologies.

Keywords: Polymer carbon nitride; Z-scheme heterojunction; Photocatalytic; Overall water splitting

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O.4.01

DFT and thermodynamic investigations into molecular structure of the reconstructed (100) CeO_2 termination

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In recent years, there has been a growing interest in catalytic aplications of oxide heterojunctions. As an example strong, synergistic catalytic effects were observed in reactions such as O_2 isotopic exchange [1], N_2O decomposition or CH_4 oxidation for (100)CeO_2|(100)Co_3O_4 n-p junctions. The structure of the (100) surface of the cerium oxide component, due to its polar termination undergoes significant reconstruction. The most thermodynamically stable surface, with a hybrid Ce and O termination structure, was recently discovered and named CeO_4-t [2]. However, it is still relatively poorly understood, especially regarding its geometric relaxation, electronic structure and defect formation controling its reactivity. An in depth understaning of the CeO_4-t structure and electronic properties is essential for elucidation the redox function of this phase in the (100)CeO_2|(100)Co_3O_4 junctions in catalytic reactions involving small molecules. The surface geometry of CeO_4-t was optimized using DFT modeling (**Figure 1a**) implemented in the VASP program, employing the PBE functional with Hubbard correction. Periodic calculations utilized slab models of the (100) surface with CeO_4-t termination, proposed earlier in the literature based on experimental studies [2]. The optimized surfaces were further perturbed by introducing defects (anionic and cationic vacancies). Interaction with gaseous oxygen was investigated by ab initio thermodynamic modeling and temperature and pressure stability of the produced surface oxygen reactive species was established and discussed using the 2D $\Theta_O(p,T)$ diagrams (**Figure 1b**). The electronic structure of the cationic and ionic vacancies was determined (**Figure 1c**), and their role in O_2, N_2O and CH_4 ractants capture was discussed.

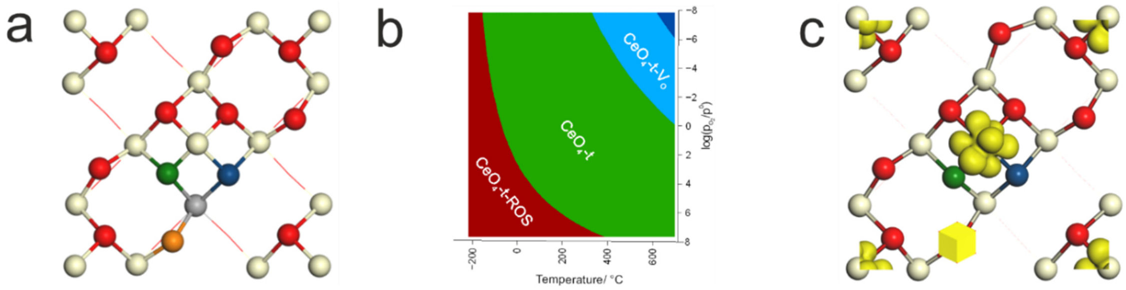

Figure 1. CeO_4-t termination of (100) ceria slab (a) together with 2D FPT diagram of $\Theta_O(p,T)$ for the reconstructed CeO_4-t (100) ceria plane (b) and spin density repartition plotted for the reduced CeO_4-t termination with the V_O defects.

Keywords: DFT molecular modeling, ceria, ab initio thermodynamics, surface reconstruction

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O.4.02

Intrinsic and extrinsic redox processes in cobalt spinel catalyst

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Heterogeneous redox catalysis on oxides is a rapidly developing research area of vital importance for establishment of new synthetic technologies and environment protection. In this context cobalt spinel (Co_3O_4) is one of the most attractive materials with remarkable record of important applications. It has received a great deal of theoretical and experimental interest owing to the spectacular activity in many redox processes that are vital for photo/electro/catalysis, chemical sensor devices or as a promising substitute for PGM in VOC, CH_4 or NH_3 oxidation processes and oxygen reduction reaction (ORR), in particular. The key redox properties of nanostructured cobalt spinel materials depend on the dimensionality, size and shape of the crystallites. Euhedral Co_3O_4 nanocrystals expose well defined facets, allowing for sensible investigations into structure-reactivity relationships at real catalytic conditions, providing a straightforward one-to one connection into theoretical modeling.

In this presentation periodic spin unrestricted gradient DFT-PW91+U and hybrid HSE06 modeling of morphology and electronic properties relevant for redox behavior of cobalt spinel nanocrystals is described. The ab initio thermodynamics was also applied to elucidate stability of different terminations of cobalt spinel under surface various redox conditions imposed by different oxygen partial pressure and temperature and the structure of the generated defects (anionic and cationic vacanices). Three types of surfaces, containing under-stoichiometric, stoichiometric, and over-stoichiometric amount of cobalt ions, were analyzed in detail. For the most stable stoichiometric facet, formation of cationic and anionic vacancies was examined, and a surface redox state diagram of the possible terminations in the wide stoichiometry range was constructed. Intrinsic charge transfer processes involving electron (*n*-conductivity) and hole (*p*-conductivity) transfer between the octahedral and tetrahedral cobalt cations were modeled using a small polaron approximation (Marcus-Dupuis model), and compared with the results of the contactless electronic conductivity, work function, and XAS measurements. For Li-doped Co3O4 the effect of the lithium locus on the valence pining of the cobalt cations was determined. DFT calculations together with the ab initio thermodynamic modeling were used to study the electronic structure of the created defects, and the associated electronic and spin relaxation processes were discussed as well. Extrinsic redox processes, triggered by interfacial electron transfer (reductive activation of O_2 and N_2O) and back electron transfer (oxidative evolution of dioxygen) were factorized and molecularly resolved. The key role of the Fermi level energy and orbital line-up between MO of the reactants and DOS features of the active site for redox redox behavior of the catalyst was established.

Keywords: spinel, redox, Fermi level, O_2 and N_2O activation.

O.4.03

An atomistic view on energy storage materials using DFT modeling

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Storing energy in chemical bonds is among the densest variants available in terms of material and space required, such that it is routinely used by nature. Most important is the efficiency of energy storage, equivalent to the ratio of energy released on demand vs. the energy required to make the bonds. Usually this corresponds to the reaction barrier to make these bonds. Effective catalysts lower these barriers by leading the reaction path to an alternative route. Using DFT calculations on slab models we will shed light on the underlying energetics of such systems to function as energy material.

Metal surfaces such as Rh(111) can be used to activate small molecules such as H_2, O_2, H_2O. These metals work as they bind intermediates just with appropriate strength, neither too weak nor too strong, according to Sabatier's principle. In this case we study the effect of La as a promoter and how it affects the binding strength of oxygen atoms at the surface, providing an additional option to tune this catalyst [1]. This overview is continued with Co_3O_4(111) as typical example of a metal oxide that activates water in rather specialized fashion [2]. Finally, we shed light on a combined system, where clusters are supported on a mixed metal oxide [3].

Keywords: DFT, Metal Oxide, Nanoparticle, Catalysis, Kinetics

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Cerium(III) phosphate as a promising support for gold catalysts addressed to selective oxidation of glucose

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Glucose is the most abundant unit in cellulosic biomass and the most widely distributed monosaccharide in nature. Its catalytic oxidation to gluconic acid and its derivatives has become one of the key topics of concern. Over the last 20 years, gold catalysts based on carbons or metal oxides (e.g. TiO_2, CeO_2, etc.) have been widely used in this process because of their excellent selectivity and high reactivity. However, reports related to the application of gold catalysts supported on inorganic metal salts (e.g. phosphates), which possess several unique properties, are sparse in the field of selective oxidation processes. Therefore, the main goal of this study was the preparation and characterization of new gold catalysts supported on cerium(III) phosphate as well as evaluation of their catalytic activity in base-free glucose oxidation. For comparison purposes, gold supported on ceria (Au/CeO_2) was applied as a reference material.

The supports for gold, namely $CePO_4$ and CeO_2, were synthesized via facile hydrothermal method [1]. Gold nanoparticles were loaded on the surface of the as-prepared materials using a grafting procedure described elsewhere [2]. All materials were characterized by ICP-OES, elemental analysis, XRD, NH_3-TPD, CO_2-TPD, STEM with EDS analysis, N_2 adsorption/desorption, zeta potential measurements as well as UV-Vis, FT-IR, and XPS spectroscopies. Catalytic activity of the prepared materials was evaluated in base-free glucose oxidation in a batch reactor with the use of molecular oxygen as an oxidant. Products of glucose oxidation were identified and quantified by means of UHPLC.

According to the results of XRD measurements, cerium dioxide crystallized in cubic CeO_2 phase, while cerium(III) phosphate had a hexagonal structure. Crystalline structure of these samples was preserved after anchoring of gold species. It was found that Au/CeO_2 and $Au/CePO_4$ exhibited similar surface area (ca. 80 m^2/g) and comparable gold loading (ca. 1.8 wt.%). Despite of these similarities, gold species supported on cerium(III) phopshate were approximetely three times more active in glucose oxidation than these loaded on cerium dioxide. Both catalysts exhibited also 100% selectivity to gluconic acid. The origin of the highly enhanced reactivity of gold species supported on $CePO_4$ will be explained and widely discussed during the presentation based on experimental data obtained from various characterization techniques.

Keywords: gold, cerium(III) phosphate, glucose oxidation, gluconic acid

Acknowledgements*:* M.M. acknowledges the Czech Science Foundation for the project no. 23-08031K and OP VVV “Excellent Research Teams” project no. CZ.02.1.01/0.0/0.0/15_003/0000417-CUCAM for funding.

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O.5.02

Subnanometer Clusters in the Oxidative Dehydrogenation of Cyclohexene: Control of Catalytic Activity and Selectivity by Changing Cluster Size and Composition One Atom a Time

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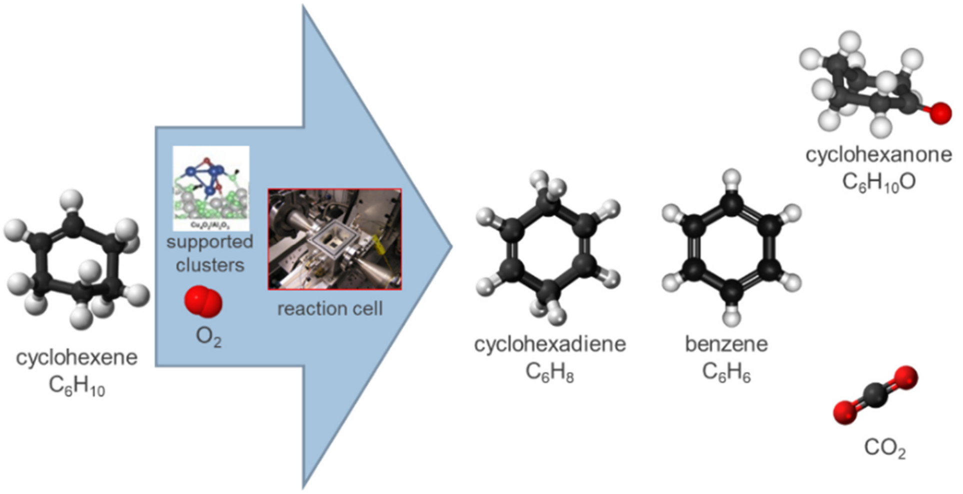
The focus of the presentation will be on catalysts by supported monodisperse subnanometer clusters made of a handful of atoms, supported on technologically relevant oxide- and model carbon-based supports.



The performance of Cu, Pd and CuPd clusters in the oxidative dehydrogenation of cyclohexene will be discussed [1-3], where the atomic precision design of mono- and bimetallic clusters allows for the fine-tuning of their activity and selectivity by varying the composition of the clusters in an atom-by-atom fashion and by support effects.

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O.5.03

From Modeling Natural Redox Transformation Catalysts to Directly Harnessing Renewable Resources

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This work bridges the gap between advanced catalyst design and the direct harnessing of renewable resources. In the initial phase, the focus was placed on exploring heteroatom-doped catalysts with exceptional activity in both reductive amination and nitroarene reduction, prepared using air-stable, non-precious molecularly defined precursors applied to support materials via wet impregnation followed by pyrolysis.[1-3] These catalysts exhibit significant activity for both batch and continuous-flow processes, with a strong emphasis on material recyclability and stability. The study then progressed to harnessing the intrinsic redox capabilities of the Amanita muscaria (fly agaric mushroom), renowned for its remarkable ability to accumulate vanadium at concentrations as high as 1000 mg V kg^{-1} in its bulb section.[4,5] Without the need for labor-intensive extraction steps, the mushroom is pyrolyzed directly to produce vanadium-containing materials. The resulting bio-derived catalysts leverage the inherent redox potential of the natural vanadium complex, amavadin, which is present in high concentrations within the mushroom. This approach highlights the possibility of utilizing renewable biological resources as direct sources of catalytic materials, advancing our understanding of natural redox transformations and their practical applications in catalysis.

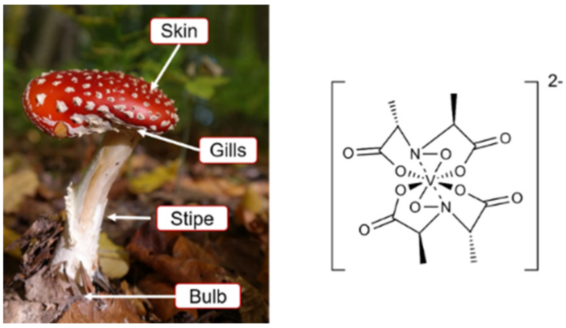

Figure 1: Depiction of the fruit body of Amanita muscaria and its parts (left), Structure of Amavadin, the most prominent Vanadium-containing species in Amanita muscaria.(right).

Keywords: catalysis, heterogeneous, renewable ressources, vanadium

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O.6.01

Enhanced Electrochemical Water Oxidation Efficiency and Stability by Iron on Carbon Nanotubes

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Efficient, low-cost, and robust electrocatalysts are urgently needed to address the energy and environmental crisis. Newly developed carbon nanotubes (CNTs) are in focus as substrates for immobilizing metal nanoparticles and molecular components due to enhanced robustness that stems from passivation by surface oxygen functions. First-row transition metals (TM) abundant in nature and their various compounds have been researched as hydrogen and oxygen evolution (HER and OER) catalysts due to their partially vacant d-orbitals allowing rich redox chemistry. However, TM-based electrocatalysts may show low conductivity, corrosion, dissolution, and aggregation issues that diminish their cost-effectiveness and efficiency during water oxidation [1]. Combining highly conductive carbon nanomaterials (CNMs) with TMs creates stable TM/CNM hybrid electrocatalytic materials with improved efficiency and improved stability by exposing more active sites and facilitating efficient electron transfer [2].

We present two methods for attaching Fe onto CNTs with different initial oxygen coverage (pristine MWCNT and MWCNT-C rich in carboxylic functions) to improve stability and OER reactivity. The modified anodes were characterized by electrochemical and spectroscopic techniques. In general, Fe on the MWCNTs significantly improved the OER performance. However, notable differences were found depending on the Fe precursors. MWCNT and MWCNT-C have been modified using $Fe(NO_3)_3$ (**1**), and two water-insoluble Fe(II) complexes made with the non-symmetric, bidentate ligands, 2-(2'-pyridyl)benzimidazole (PBI) in $[Fe(PBI)_3](OTf)_2$ (**2**, OTf^- = trifluoromethyl sulfonate anion) and 2-(2'-pyridyl)benzoxazole (PBO) in $[Fe(PBO)_2(OTf)_2]$ (**3**) [3]. When deposited using MWCNT-C, substances **1** and **2** exhibited sustained electrocatalysis, while substance **3** decomposed after only 10 minutes. The electrode modified with substance **1** regained its activity after several reloading cycles with Fe, making it suitable for longer term applications. Our results imply that proper precursors like simple complexes or salts, and designs for deposition make Fe-utilizing OER catalysts viable with respect to performance and stability, but new approaches like reloading cycles must be implemented in contrast to classical, noble metal-based catalysis.

Keywords: electrochemical water splitting, carbon nanotubes-supported, electrocatalysts, iron, water-insoluble ligands

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O.6.02

Post-Synthetic Surface Functionalisation of Carbon-Based Composite Electrocatalysts for Oxygen Evolution Reaction

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Oxygen evolution reaction (OER) is a bottleneck of hydrogen production via electrolysis. Anion exchange membrane (AEM) electrolysers combine the benefits of proton exchange membrane and alkaline electrolysers. From the catalytic point of view, developing cheap electrocatalysts for OER is crucial for their large-scale application. While abundant and cheap transition metals, such as iron, cobalt, and nickel, allow for satisfactory electrocatalytic activity, cobalt oxides are the most stable in alkaline conditions. The electrocatalysts for application in the AEM electrolysers are often deposited onto the carbon supports to increase their compatibility with the carbon gas diffusion layer and usage efficiency. Various strategies are adopted to optimise the catalytic activity of carbon-supported OER catalysts, such as phosphidisation, nitridation, or doping.[1] We propose a simple and fast way to boost the OER activity by oxygen plasma treatment of the otherwise ready composite carbon-cobalt catalyst. The reported post-synthetic functionalisation with oxygen plasma significantly enhances their oxygen evolution reaction. This effect is much more substantial for the materials with well-dispersed cobalt phase, irrespective of their initial activity. The applied post-synthetic plasma oxidation allows for obtaining highly active electrocatalysts with overpotentials of 340 mV@10 mAcm^{-2} for the Co_3O_4 loading of 12 wt% and 340 mV@10 mAcm^{-2} for 8 wt% of Co_3O_4, determined in the 3-electrode RDE setup. The plasma activation of a non-supported cobalt spinel is relatively small. At the same time, the oxidation of the bare carbon support substantially improves its OER reactivity, but the overall activity is much lower than that of cobalt/carbon catalysts. The oxidation of the carbon support before the active phase deposition enhances the cobalt oxide dispersion, especially when abundant COO-type groups are present.[2] The X-ray photoelectron spectroscopy studies indicate that the applied post-synthetic plasma oxidation creates additional C=O and C–O-type surface groups on carbon but does not modify the state of cobalt. Therefore, we hypothesise that a synergistic effect between the cobalt phase and the oxidised carbon support endows the composite electrocatalytic system with improved oxygen evolution reaction activity.

Acknowledgements: This study was financially supported by the National Science Centre, Poland, project number 2020/37/B/ST5/01876.

Keywords: OER; water splitting; hydrogen production; electrocatalysis; carbon materials

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Pt nanoclusters on 2D MoS_2, properties and activity in hydrogen evolution reaction

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While platinum is the most efficient and widely studied catalysts, for hydrogen evolution, further improving its activity and stability is still needed, to enable large-scale applications, such as the cost-efficient, mass-production of green hydrogen. Transition metal chalcogenides are broadly investigated catalysts, limited by the relative inertness of their pristine basal plane MoS_2 single layers modified by substitutional oxygen can harvest the synergistic benefits of stably anchored single-atom sites and activated MoS_2 basal planes. [1] These oxygen sites lower the hydrogen adsorption barrier and also act as vertical electron channels. MoS_2 single-layer substrates with embedded non-metal heteroatoms also offer the benefit of site densities that are much higher than generally reported in the literature for metal SACs on various substrates [2] These sites might be suitable not only for hydrogen evolution, but also for anchoring metal atoms. We have shown that small Pt clusters (1 nm) anchored to MoS_2 defect sites shown orders of magnitude higher intrinsic activity in HER than Pt nanoparticles (5-10 nm) or even Pt single atom catalysts

By optimizing the deposition conditions, we were able to achieve a high-density decoration of the whole MoS_2 basal plane with small Pt clusters. The interaction of Pt atoms and MoS_2 creates ultra-fine (~1nm), bilayer (~3 A height), semiconductor (Eg~250 meV) Pt clusters. The observation of ultra-fine Pt clusters by STM indicates a remarkable stability, since the aggregation of Pt clusters is suppressed, even though the average distance between the clusters is only a few nanometres, a clear indication of strong support adhesion. Due to enhanced Pt/MoS_2 interactions, we were able to resolve the fine details of the local density of states (LDOS) of small Pt clusters by tunneling spectroscopy. The most striking feature, is a sizeable energy gap of about 300 meV, with fully suppressed Pt LDOS near the Fermi energy (0 V), evidencing the semiconducting nature of bilayer Pt clusters. These 2D MoS_2 supported Pt clusters have an exceptionally high hydrogen production efficiency (>1000 H_2 s^{-1} per Pt atom @ 100 mV). The high intrinsic activity emerges from the strongly enhanced interaction of small Pt clusters with MoS_2, affecting about every aspect, related to their catalytic performance: hydrogen adsorption, charge transfer, lattice distortions, and stability.

Keywords: 2D MoS_2, Pt clusters. Pt, Hydrogen Evolution Reaction

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Mechanistic insights into hydrogen evolution reaction driven by heteroatoms of bidentate N-heterocyclic ligands in iron(II) complexes

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While Pt remains the most efficient catalyst for the electrocatalytic hydrogen evolution reaction (HER), its price and limited availability make the investigation of alternative non-noble metals mandatory. In this context, electrocatalytic hydrogen production – an attractive solution to meet the rising global energy demand – should rely on new, cost-effective and highly active catalysts that utilize inexpensive metals.

In our study, we set out as goal to understand the catalytic activity of organoiron compounds and examine how their activity is influenced by non-coordinating heteroatoms (S, O, N, or none) of the simple, heterocyclic ligands. The selected ligands form stable homolog complexes with ferrous ions that also model potential binding sites in various carbon nitrides, and the situation, when different heteroatoms are found near the metal center. Thus, our study focused on the structure-activity relationships of Fe(II) complexes with bidentate 2-(2′-pyridyl)benzoxazole ($\mathbf{L}^{\mathbf{O}}$), 2-(2′-pyridyl)benzthiazole ($\mathbf{L}^{\mathrm{S}}$), 2-(2′-pyridyl)benzimidazole ($\mathbf{L}^{\mathbf{NH}}$) and 2-2′-bipyridyl ($\mathbf{L}^{\mathrm{py}}$) ligands in elechemical HER uder homogeneous conditions in acetonitrile, utilizing trifluoroacetic acid (TFA) as a proton source.

Within the ligand series, the electronic environment of the heterocyclic N-donor group was systematically changed by the non-coordinating heteroatoms that was expected to affect the stabilisation of the reduced complex form. We observed that the catalytically relevant reduction potentials in the presence of TFA correlated with the basicity of the ligand. Kinetic studies and controlled potential electrolysis using TFA as proton source revealed HER activities for the complexes with $\mathbf{L}^{\mathbf{NH}}$, $\mathbf{L}^{\mathbf{O}}$ and $\mathbf{L}^{\mathrm{S}}$ of k_{cat} = 0.03, 1.1 and 10.8 s^{-1} at overpotentials of 0.81, 0.76 and 0.79 V, respectively. The activity has been associated with the $[Fe(\mathbf{L}^{\mathrm{S/O/NH}})_2(S)_2]^{2+}$ form (S = solvent or substrate molecule), while the rate determining step with the formation of $[Fe(H\text{-}H)]^{+}$, during the weakening of Fe-H and CF_3CO_2-H bonds, according to experimental and DFT results. In contrast, the $\mathbf{L}^{\mathrm{py}}$ based complex is inactive in catalysis, due to the persistence of $[Fe(\mathbf{L}^{\mathrm{py}})_3]^{2+}$ in the reaction mixture. In conclusion, the non-coordinating heteroatoms in aromatic systems may strongly influence the HER reactivity of the iron center.

Keywords: hydrogen evolution reaction, iron complex, electrocatalysis.

O.6.05

Polarization-induced carbon spillover from Ni to YSZ boosts carbide-mediated methane formation in solid oxide co-electrolysis

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The high-temperature co-electrolysis of CO_2 and H_2O in solid oxide cells is a promising avenue for climate change mitigation, converting greenhouse gases into renewable energy carriers. This study focuses on electrochemical pathways toward methane and investigates the reactivities of the involved carbon species. The study employs a Ni/8 mol% yttria stabilized-zirconia thin-film model electrode, combining operando near ambient pressure X-ray photoelectron spectroscopy with electrochemical electrolysis control and mass spectrometric product detection. Results reveal a hitherto unknown methane-gene rating mechanism under strongly cathodic co-electrolysis conditions. Mechanistic details offormation, accumulation, and dissolution of electrochemically induced carbon species on Ni are revealed/rationalized. Furthermore, polarization-induced carbon spill-over triggers ZrC_x formation at the triple phase boundary, demonstrating the complexity of carbon-related processes in co-electrolysis. The study provides critical insights into the reactivity of carbon species and their impact on methane selectivity, advancing our understanding of high-temperature CO_2-H_2O co-electrolysis for renewable energy storage.

Advanced Pt/$Ti_{1-x}Sn_xO_2$-C composite supported electrocatalyst with functionalized carbon for sustainable energy conversion technologies

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In the previous works of our research group $Ti_{1-x}M_xO_2$–C (M: Mo, Sn) mixed oxide – carbon composites were identified as promising multifunctional supports for Pt electrocatalysts, in which strong metal-support interactions at the Pt-oxide boundary ensure high stability for the Pt nanoparticles [1,2].

The main objective is to systematically investigate the effect of the functionalization of the carbonaceous component on the properties of Pt/$Ti_{(1-x)}Sn_xO_2$–C catalysts as a strategic approach for enhancing stability. We will explain why the formation of Pt-oxide-carbon triple junctions can contribute to improved stability.

The composition and structure of the samples were investigated using XRD and TEM. The diffraction patterns demonstrated the exclusive presence of a rutile-type oxide, Pt loading caused no obvious change in the rutile reflections. TEM micrographs revealed a relatively uniform coverage of both carbon materials by 10-20 nm rectangular or somewhat rounded oxide particles and homogeneous distribution of 2-3 nm Pt particles. Elemental mapping revealed the proximity of Sn species with Pt particles. Notably, electrochemical results indicated enhanced activity in CO electrooxidation for both catalysts. Nevertheless, a significant improvement in the long-term stability of the catalyst prepared using functionalized carbon was evident compared to the untreated carbon-containing catalyst or Pt/C. This study provides valuable insight into the design and optimizing of mixed oxide–carbon composite catalysts supports by modifying the functionality of the carbonaceous component, since through synergistic effects, functionalized carbon can improve the dispersion and utilization of Pt catalysts, and enhance the properties of the Pt-oxide-carbon junctions.

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Keywords: $TiSnO_x$, composite material, functionalized carbon, Pt electrocatalyst.

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O.6.07

Advances in Electrocatalytic Nitrogen Reduction to Ammonia: Insights from Theoretical Analysis

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The electrochemical reduction of nitrogen to ammonia holds significant promise for sustainable ammonia synthesis, but finding efficient catalysts remains a challenge. In this study, we employ density functional theory (DFT) calculations to conduct a comprehensive exploration of potential catalysts under ambient conditions. Specifically, we investigated the different texture orientations of rocksalt structures of transition metal carbides and carbonitrides, assessing their catalytic activity, stability, and selectivity across diverse reaction mechanisms. Our analysis identifies VCN and NbCN as stable and active catalysts, demonstrating low onset potentials conducive to efficient nitrogen reduction at ambient conditions [1, 2]. Furthermore, we explore the potential of transition metal carbides (TMCs) as catalysts for nitrogen reduction. Initially, pristine TMC surfaces exhibit limited nitrogen adsorption and selective protonation capabilities; however, the introduction of a carbon vacancy significantly enhances these properties, boosting nitrogen adsorption and improving selectivity towards ammonia. Among the TMCs investigated, WC and VC emerge as particularly promising materials for experimental exploration [3]. Overall, this study contributes valuable insights to the ongoing quest for sustainable and efficient electrochemical nitrogen reduction catalysts, providing a foundation for the design of future catalysts tailored for ammonia synthesis

Keywords: DFT, Heterogenous catalysis, TMC, TMCN, Electrochemical ammonia synthesis

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O.6.08

Exploring Metal-Support Interactions in Solid Oxide Electrolysis Cathodes by *in-situ* Surface Analytics

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High-temperature electrolysis is a compelling choice for efficient renewable energy storage, with electrochemical CO_2 and H_2O splitting serving as key reactions. Solid Oxide Electrolysis Cells (SOECs), known for their stability at elevated temperatures, stand out for such applications. Perovskite-type and fluorite-type oxides functioning as Mixed Ionic and Electronic Conductors (MIECs) prove to be well-suited materials for SOEC cathodes. Crucial properties for these materials include catalytic activity, electronic and ionic conductivity, redox-cycling stability, and resilience against graphitic carbon deposition during CO_2 splitting. However, many available materials combine only some of these properties, or degrade in the course of operation.

In order to enhance the efficiency and stability of SOEC cathode materials, it is imperative to attain a fundamental understanding regarding the mechanisms of degradation processes and surface reactions. A prominent example of degradation is the dewetting of metallic nickel on metal oxide cathodes under electrolyzing conditions. Monitoring such changes in morphology and surface chemistry, while they are happening, can be achieved by the utilisation of *in-situ* X-ray Photoelectron Spectroscopy (XPS) and *in-situ* Auger Electron Microscopy (AEM). By combining these techniques with precisely crafted model electrodes, fabricated using Pulsed Laser Deposition (PLD) and magnetron sputtering, changes to the surface morphology and the surface chemistry can be analysed.

Using electrochemical solid oxide half-cells, the oxygen activity in our Working Electrode (WE) thin-films can be varied by changing the applied voltage via the Nernst-equation. This way, *in-situ* measurements where high or ultra-high vacuum is needed become possible. Furthermore, this novel method sets the stage to distinguish effects caused by metal/oxide interfaces from effects caused by interactions with the gas phase.

In conclusion, our study on metal-support interactions on cathode materials for SOECs using *in-situ* surface-sensitive measurements provides valuable insights for enhancing the efficiency and stability of high-temperature electrolysis for renewable energy storage.

Keywords: SOEC, XPS, AEM, dewetting

Pt- $MoVWNbO_x$ mixed oxide catalysts with reduced Pt content for proton exchange membrane fuel cell application

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This work aimed the preparation of novel electrocatalysts for proton exchange membrane fuel cells (PEMFCs). Beside the activity, these catalysts have to fulfill several requirements: resistance to acidic media; enhanced surface area; good electrical conductivity and long-term durability. Commercial PEMFCs most commonly contain carbon supported Pt catalyst (Pt/C). However, it is prone to degradation and significantly loses its activity during the operation. The above phenomenon can be connected to degradation of the carbon and the changing of the supported Pt nanoparticles [1]. Therefore, a big demand exists to find a new type of support which provides stability of the Pt nanoparticles. Non-noble metal oxides are under investigation since the last century. They have several advantageous properties, like higher corrosion resistance compared with carbon materials; they are able to form strong interactions with the catalysts particles; and through their hydroxyl groups on the surface, they can participate in the reaction as co-catalysts. For our study, we considered that 1) both tungsten oxide (WO_x) and molybdenum oxide (MoO_x) have already examined in PEMFC applications and possess the above mentioned requirements [2,3]; 2) their conductivity can be improved with Nb-doping; 3) there has been a great interest of $MoVZO_x$ (Z=Nb, Te, W) type of complex mixed oxides, especially those existing in so-called M1 phase as they have already proved their activity and selectivity in gas phase alkane oxidation. Depending the conditions of their preparation, Mo_3VO_x-oxides can exist in four different phases such as amorphous, orthorhombic, trigonal and tetragonal ones [4]. Based on the literary results, a thirteen-member mixed oxide series was prepared by microwave-assisted reaction and following heat treatment. The reaction mixtures contained Mo, V, W and Nb with changing molar ratio, in order to create different mixed oxide phases. Pt was directly introduced onto the surface of the oxides by use of H_2PtCl_6 precursor. X-Ray Diffractometry (XRD) was used to identify the phases. Electrochemical experiments, such as cyclic voltammetry (CV) and oxygen reduction reaction (ORR) were performed in a three-electrode cell. Long term stability of the samples was calculated from CV measurements.

Keywords: PEM fuel cell, MoVWNbOx mixed oxides, microwave-assisted reaction, electrocatalyst

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O.6.10

Catalytic and electrochemical properties of CMK-3 mesoporous carbon nanoreplicas modified with nitrogen- and oxygen-containing functionalities

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Metal-free porous carbons exhibit several desirable properties, including environmental friendliness, which makes them suitable for many applications based on the principles of green chemistry and sustainable development [1]. The functionalization of the surface of carbon materials by nitrogen- and oxygen-containing groups has therefore been an object of growing interest. Such modifications can cause changes in acid-base and electron properties, contributing to the improvement of catalytic and electrochemical performance of carbons in various chemical processes. Hence, control of structure of the generated groups, their content and polarity becomes very important [2]. In the presented work, an influence of surface modification of CMK-3 carbon nanoreplica on its catalytic and electrochemical behavior was studied.

CMK-3 ordered mesoporous carbons modified with N- and O-containing functionalities were obtained by structural nanoreplication of SBA-15 silica template, synthesized by supramolecular, non-ionic self-assembly between a ethylene oxide/propylene oxide copolymer (Pluronic P123) and a silica precursor (TEOS) followed by calcination. The SBA-15 pores were infiltrated with sucrose or sucrose/urea solution to achieve a defined N/C molar ratio of 0, 0.14 and 0.51. The prepared materials were finally carbonized at an inert atmosphere in a temperature range of 600-1000°C. The obtained carbons were characterized in terms of their textural parameters (low-temperature nitrogen adsorption), structure and morphology (XRD, SEM), electrochemical properties (CV), surface and bulk composition (XPS, CHNO analysis), as well as tested as catalysts in the oxidation of sulfurous acid in the aqueous phase (OSA). A clear increase in the cataltyic activity in the OSA process was observed with an increase in the carbonization temperature, which confirms the promoting role of graphite structures in facilitating electron transport and activation of molecular oxygen. Additionally, these features were significantly improved in the presence of surface nitrogen groups.

Keywords: surface modifications, metal-free carbon replicas, redox catalysis, electrochemical properties

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POSTER SESSION 1

Methane and CO_2 transformation on TMI-zeolites – spectroscopic approach

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Carbon dioxide and methane represent the main gases contributing to the greenhouse effect. Their chemical recycling to methanol, dimethyl ether, and/or acetic acid makes them a renewable source of green platform chemicals (GPCs).

Both CH_4 and CO_2 can be effectively activated over transition metal-containing catalysts, which offer unique electron-donating properties, decreasing the energy barrier of their bond splitting [1-3]. One of the largest groups of industrially used heterogeneous catalysts with high thermal stability and surface area, highly tuneable to the catalytic process by synthesis procedure, are zeolites [4-5]. The transition metal ions (TMI) in extra-framework positions formed in TMI-zeolites represent catalytically active in many important redox processes [4-5]. In this contribution, the mechanism, the nature of active centers for CO_2 and CH_4 activation over *BEA, CHA, and FER zeolites exchanged with TMI, the reagent molecules activation, and their binding to the active sites were investigated by operando and in-situ rapid scan IR spectroscopy with the implementation of two-dimensional correlation analysis. Our studies showed that Fe-zeolites provide simultaneous processing of CO_2 and CH_4 to methanol, while their TMI-modified counterparts offer the production of more sophisticated compounds from the green platform chemicals (GPCs). In our studies, a special emphasis is paid to spectroscopic analysis of the siting and ligation of metal ion centers, which allows us to determine the relationship between the structure of the matrix and distribution of Al atoms in the activation of CO_2 over metal ion/oxo species.

Keywords: transition metal cations, zeolites; methane; carbondioxide, IR spectroscopy

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P.1.02

Carbon deposit formation during ethylene transformation over microporous and hierarchical ZSM-5 zeolites

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Introduction

Catalytical transformation of hydrocarbons over zeolites is always burdened by decreasing activity with time on stream. One of the reasons behind that is the formation of unwanted heavy carbon-derived species that are poisoning the catalysts. The nature of formed coke and its location affects the access to active sites by blocking the entrance to pores from an external surface or by forming soft coke inside micropores. A comprehensive assessment of coke nature and its exact location is crucial for properly designing catalysts' textural and acidic properties. Prior knowledge regarding the paths of catalyst deactivation is unequivocally crucial for designing zeolitic catalysts with targeted performance. In this respect, an important research goal is defining the relationship between coke speciation and zeolitic catalyst properties, which determine the carbonaceous deposit formation.

Materials and Methods

Coke's nature was assessed during IR and UV-vis temperature-programmed oxidation experiments supported by mass spectrometry in the temperature range of 200 to 550 °C in the synthetic air flow. For quantitative analysis, the TG experiments of total coke removal were performed. The qualitative analysis was further supported by GC-MS analysis of coke extracted from the catalyst (dissolved in HF and extracted with CH_2Cl_2). The spent catalysts were after ethylene conversion into higher hydrocarbons (ZSM-5, CBV2314E, Zeolyst, 325 °C, 5000 ml/(g·h), 15 hours). The catalysts were modified by sequential desilication (0.6 M or 0.8 M NaOH, 65°C, 30 min) and dealumination (0.1 M or 0.2 M HNO_3, 65°C, 2 h) procedures to alter their acidic and textural properties.

Results and Discussion

Parent ZSM-5 and modified analogues displayed differentiated textural and acidic properties (Table 1). Mild modification in the m-deSi&deAl sample preserved the microporosity and acidity of the sample without extensive formation of mesopores. A harsher treatment in the *s*-deSi&deAl sample developed the external surface area at the expense of micropore volume and acid site concentration.

The catalysts were used to convert ethylene to higher hydrocarbons with the preferable formation of propene. The most increased activity and fastest deactivation were found for microporous ZSM-5 catalysts (from 100% to 45% within 15 hours), while the modified *m*-deSi&deAl presented a slower deactivation rate (from 100% to 70% within 15 hours). The *s*-deSi&deAl sample gave constant conversion at a moderate level without a significant drop in activity (60%-55% during 15 hours).

The total oxidation during TG analysis of spent catalysts provided information that the lowest amount of coke was found for *s*-deSi&deAl (Figure 1). The mild dealumination did not significantly influence the coke content. The GC-MS analysis of extracted coke informed that the highest content of naphthalenes was found for the parent catalyst, which is characterised by the highest concentration of Brønsted acid centres (c_B, Table 1). It is with these centres that aromatisation reactions are mainly associated.

Table 1. Chemical composition, acidic and textural properties of micro/mesoporous zeolites

Catalyst	**Si/Al**	**S_{BET} m^2/g**	**S_{EXT} m^2/g**	**V_{micro} cm^3/g**	**c_B $\mu mol/g^{-1}$**	**c_L $\mu mol/g^{-1}$**
ZSM-5	11.3	346	27	0.16	559	111
m-deSi&deAl	11.7	387	67	0.16	509	109
s-deSi&deAl	11.1	377	157	0.11	227	228

The FT-IR spectroscopic analysis of the coke oxidation process over spent catalysts has provided information on the nature of coke species. The complex IR band around 1640-1550 cm^{-1} identifies the coke species formed during ethylene oligomerisation over a series of ZSM-5. The bands centred at 1615 and 1575 cm^{-1} are indicative of species formed by condensation reactions producing $C_6H_7^+$ olefinic cations ($CH_2{=}CH{-}CH]CH{=}CH]CH^+$ or cyclic alkenyl carbenium ions $C_6H_9^+$) and polymethyl-benzenes as coke forming compounds (e.g. 1,2,4- or 1,2,3-trimethylbenzene – the 1615 cm^{-1} band). The modified in *s*-deSi&deAl zeolite presented lower coke amount and less aromatic with higher content of olefins, thus more prone for removal. The moderate catalytic activity and low coke content of *s*-deSi&deAl can provide a proper balance between the activity and lifetime of the catalyst.

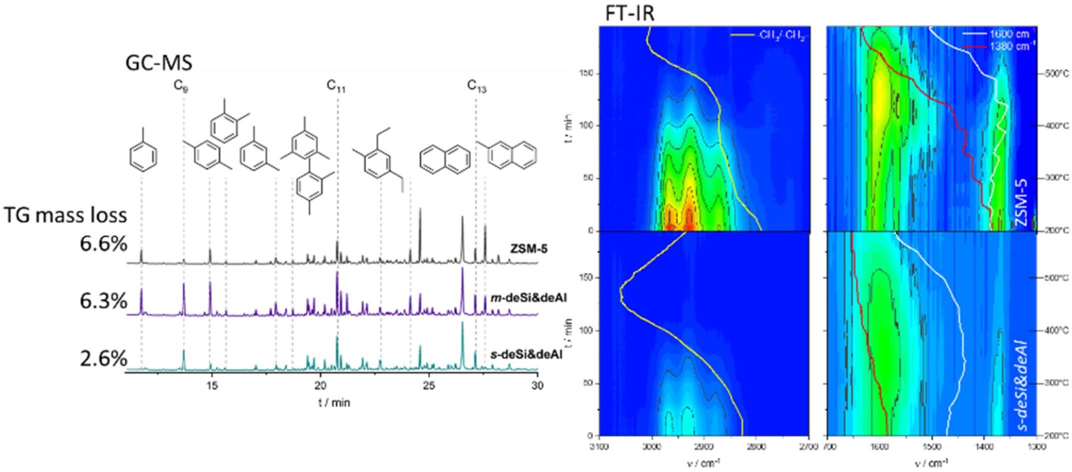

Figure 1. (right) GC-MS chromatograms of coke extracted from spent catalysts, (right) top-down view of spectra registered during coke oxidation over parent and *s*-deSi&deAl in range of C-H stretching (3100-2700 cm^{-1}) and C-C stretching (1700-1300 cm^{-1}) bands.

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Keywords: zeolites, coke nature, spectroscopy, ethylene conversion

P.1.03

Ethanol-to-hydrocarbons process – *operando* FT-IR spectroscopic studies supported by MCR-ALS analysis for active species identification

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Introduction

FT-IR spectroscopy has played a major role in the identification of reaction intermediates in catalytic processes since the first detection of surface-adsorbed species. The ethanol conversion processes were performed over protonic chabazite (Si/Al = 8) zeolite in advanced FT-IR *operando* spectroscopic studies with simultaneous mass spectroscopy and gas chromatography analysis of products. The spectroscopic investigation provided information on species formed on the surface of catalysts, while mass spectrometry and gas chromatography methods identified the desorbed products. The studies were also supported by spectroscopic, chromatographic, and thermogravimetric analysis of coke species formed over the catalyst's surface during alcohol conversion. The experimental spectroscopic data was analysed using Multivariate Curve Resolution by Alternating Least Squares (MCR-ALS) algorithms. This allowed for the identification of concentration profiles for specific species found in complex spectra.

Results and Discussion

The FT-IR spectra (Figure 1) registered during ethanol conversion showed the extensive formation of species involved in HCP in chabazite cages. This is confirmed by the rapid formation of propylene and C_{4+} hydrocarbons upon contact with the SSZ-13 catalyst and ethanol. The bands at 1602 and 1617 cm^{-1} can tentatively be attributed to aromatic compounds as highly methylated (ethylated) benzenium cations. The m/z = 70 fragmentation ion observed may come from the divinyl ether formed over the acid sites of SSZ-13 in trace amounts during the first 25 minutes of the reaction. The band observed at 1505 cm^{-1} was identified in the methanol-to-hydrocarbon process as alkyl-substituted cyclopentenyl cations.

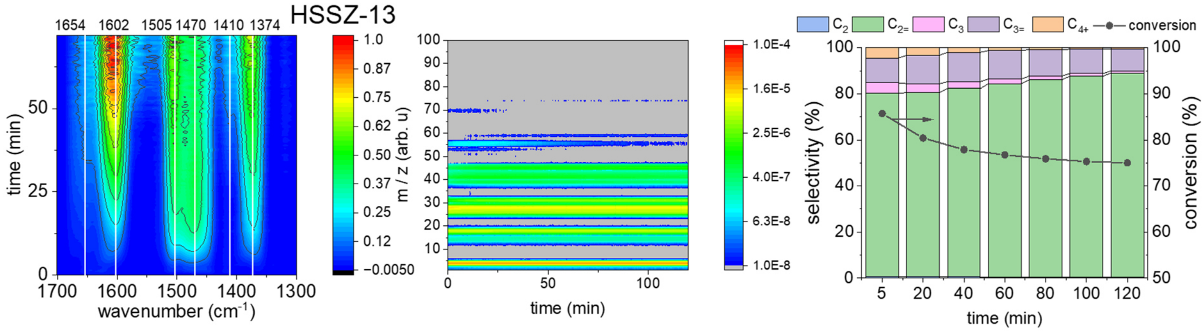

Figure 1. *(Left)* Top-down projection of FT-IR spectra, *(middle)* mass spectrometry results and *(right)* gas chromatography selectivities and conversions collected during ethanol conversion over HSSZ-13.

Further analysis using MCR-ALS of the obtained results helped in identifying three distinct species formed during the dehydration of ethanol over SSZ-13 zeolite. The concentration profiles provided information on the timing of their formation. Species A, represented by bands specific for alkyl-substituted cyclopentenyl cations (band at 1505 cm^{-1}), was identified as the one formed at the very beginning of ethanol conversion. Species B and C were formed in the later stages of the reaction. Species B is expected to be a gas phase product (ethylene) formed only in part of the reaction and then prone to oligomerise to aromatics represented by species C.

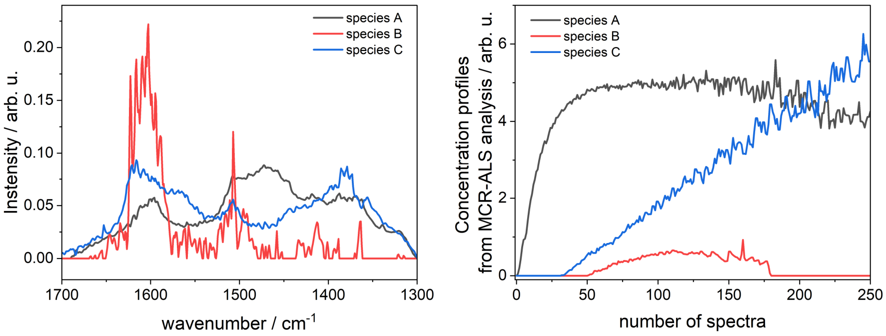

Figure 2. The MCR-ALS results analysis of FT-IR spectra registered during ethanol conversion of SSZ-13 zeolite.

Overall, the MCR-ALS allows for the resolution of complex spectra of a mixture of species into pure-component contributions. At the same time, the component profiles are constrained by physical or chemical objectives (for instance, non-negativity and unimodality).

Acknowledgement: The National Science Centre, Poland, supported the work within Grants No. 2023/49/B/ST4/02340.

Keywords: MCR-ALS, ethanol, zeolites, FT-IR spectroscopy

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P.1.04

Biodiesel preparation by heterogeneous transesterification of Camelina sativa oil over basic zeolites

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Biodiesel, a mixture of alkyl esters of fatty acids, is an alternative fuel to diesel fuel. Biodiesel is currently being prepared in technology using homogeneous transesterification, where sodium or potassium methoxide is used. The disadvantage of homogeneous transesterification remains the difficult separation of the product from the catalyst, as well as the need for washing it from the product. Due to this, it is necessary to consider alternatives related to the technological process of biodiesel preparation. One of the alternatives is heterogeneous transesterification, which brings the advantage of simple separation of products from the catalyst and its possibility of reuse [1]. Zeolites are the most common type of catalyst used in various processes. One of the possible applications of zeolites is in biodiesel preparation. However, an essential part of using zeolites as catalysts is the ion exchange process to create basic sites within the zeolite structure. Basic catalysis in transesterification is much faster compared to acidic catalysis.

Zeolites were modified by ion exchange. The ions used for the exchange were potassium and caesium. The basic zeolite used as the starting material was Zeolite X. The prepared zeolites were tested using SBET, XRD, TPDA, TPD-CO2, and FTIR. The modified zeolites were used in a transesterification reaction in a batch reactor. The oil used was Camellia sativa oil, which is a non-edible oil that was previously refined before the reaction.

Basicity measurement by TPD-CO_2 confirmed that the modified zeolite samples showed an increase in basic sites. A comparison of the textural properties (Table 1) shows a decrease in specific surface area and pore volume as a result of modification using potassium and caesium. The transesterification reactions showed that the modification of zeolites had a significant impact on the activity itself in transesterification.

Table 1. Textural properties of original Zeolite X and modified zeolites with K and Cs

Tested sample	S_{BET} (m^2/g)	V_a (cm^3/g)
Zeo-X	650	0.354
Zeo-KX	562	0.314
Zeo-CsX	389	0.225

Acknowledgment: This work was supported by the Slovak Research and Development Agency No. APVV-20-0348

Keywords: biodiesel, zeolite, transesterification, catalysis

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P.1.05

Transformation of ethanol into important chemical intermediates

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The use of renewable raw materials is the subject of a number of studies at present. Replacing fossil raw materials with renewables has the potential to address the challenges of global warming and the depletion of oil reserves. The implementation of the production of butadiene, an important monomer in the chemical industry, from ethanol can facilitate the transition to more sustainable production.

In this work, the influence of catalysts, their properties, composition and method of preparation for the transformation of ethanol into industrially significant compounds was studied. The reaction of ethanol on heterogeneous catalysts produces a mixture of hydrocarbons, mainly ethylene, propylene, acetaldehyde and C4 hydrocarbons, the most significant of which is 1,3-butadiene.

A series of catalysts based on zinc, zirconium, indium, wheat straw ash and cobalt, as well as multi-element catalysts were prepared. The structure of the catalysts has been characterized using UV-Vis, FTIR, XRD, temperature-programmed methods. Catalysts containing zinc have been found to promote the dehydrogenation of ethanol to form acetaldehyde, and with a greater content of zinc, its yield increases. A similar trend was observed for catalysts containing zirconium, which, however, promoted subsequent reactions to form butadiene.

Using the reaction in a two-reactor arrangement, where acetaldehyde was formed in the first reactor by dehydrogenating ethanol, the synergy of ZnO and ZrO_2 was refuted. On the contrary, it has been confirmed that they work together in tandem. In the IR spectra, a correlation was found between catalyst activity and mixed Zr-O-Si phase formation. The formation of mixed oxides was also promoted by further doping with magnesium. Magnesium successfully suppresses the formation of ethylene and increases butadiene yields. According to several studies, the acidobasicity of the catalyst plays a key role in the formation of butadiene from ethanol. Ideal catalysts are those with a limited amount of alkaline and medium amounts of acidic centres. This suggests that the balance between acidic and alkaline sites is critical for the efficient production of butadiene. The advantage of the acid/base ratio determination method using the isopropanol conversion test reaction – unlike most spectral methods – is that the acidobasicity is tested at the same pressure and temperature as the reaction itself (350 °C in our case).

Increasing the amount of zirconium in fumed silica support was found to increase acidity as measured by isopropanol decomposition. Surprisingly, adding magnesium to such a catalyst – in addition to increasing butadiene yields – increases the acidity of the catalyst. The best catalysts achieved ethanol conversions above 90% and butadiene yields above 40%. In addition to light alkenes, attention was paid to the formation of liquid products, where, in addition to typical oxygenates (alcohols, ketones), a significant formation of alkylaromates and alkylphenols was observed.

Acknowledgement: This work was supported by grant VEGA 01/0374/23.

Keywords: ethanol, butadiene, mixed oxides, alkenes.

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Transition metals modified derivatives of 2D Ti-MWW-type zeolites – verification of catalytic activity in NH_3-SCR process

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One of the problems that currently bothers humanity is air pollution and its environmental impact. Nitrogen oxides ($NO+NO_2$, denoted as NO_x) are considered a group of gaseous compounds, hazardous to the environment and human health and life, while their emission from anthropogenic sources is strictly defined by law [1]. The process that is most often used for the removal of NO_x emissions from stationary emitters (e.g. power plants) is their selective catalytic reduction with ammonia (NH_3-SCR). Even though this technology can be considered well-known [1], the problem that currently accompanies research on the process of eliminating nitrogen oxides is their low-temperature conversion [1]. For this reason, there is still a need for the development of new NO conversion catalysts. The interesting materials that could be used in this role are zeolites modified with transition metal cations. The 2D zeolites with MWW topology are an interesting group of materials because of their extraordinary properties allowing for modifications in the pore structure to obtain micro-mesoporous systems. Such bimodal porosity, consisting of a more open structure and smaller diffusion restrictions, is crucial in the design of modern catalytic systems [2]. Therefore, delaminated (ITQ-2) or pillared (MCM-36) MWW derivatives seem to be interesting candidates for application as catalyst carriers (Figure 1).

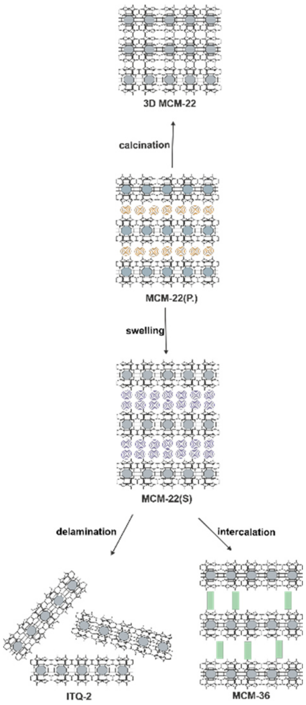

Figure 2 Structural transformations of layered MWW precursor.

In the presented studies, a modern group of heteroatomic (Ti, B and Si-containing) layered zeolites from the MWW family were functionalized with transition metal cations (e.g. copper, iron or manganese), deeply characterized and studied in the NH_3-SCR process. The obtained catalysts were characterized concerning structure (powder XRD), texture (low-temperature N_2-sorption), chemical composition (ICP-OES), surface acidity (NH_3-TPD), form and aggregation of titanium and transition metals species (UV-vis-DR) as well as their reducibility (H_2-TPR). The obtained catalysts are found to be active and selective in the process of NO conversion with ammonia. Especially zeolites functionalized with copper show high catalytic performance at a low-temperature range, below 250°C. Thus, they meet the needs of modern NH_3-SCR installations working within the operating temperature range of the electrostatic filter.

Keywords: MWW zeolites, transition metals, low-temperature NO conversion with ammonia

Acknowledgements: The studies were carried out in the frame of project 2021/41/N/ST5/03358 from the National Science Centre (Poland).

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P.1.07

Selective Furfural Hydrodeoxygenation Through In-Situ $Cu@Fe_3O_4$ Formation in Cu-Fe Mixed Oxide Catalysts

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This study explores Cu-Fe mixed oxide catalysts with varying Cu/Fe molar ratios (from 0.5 to 2), produced through a sol–gel technique for vapor-phase furfural (FFR) hydrodeoxygenation (HDO) to 2-methylfuran (2-MeF). The catalysts underwent a variety of characterization methods such as XRD, H_2-TPR, NH_3-TPD, N_2 physisorption, FESEM, and XPS to understand their properties better. The analysis highlighted the importance of the Cu/Fe ratio in affecting both the properties and the catalytic performance in FFR HDO. It was found that iron helped disperse copper oxide, with a pronounced effect at a Cu/Fe ratio of 1, indicating synergistic interactions between copper and iron. Increasing the Cu/Fe ratio boosted the reducibility of iron but reduced that of copper. The study thoroughly examined the influence of key factors, including Cu/Fe ratio, temperature, contact time, reduction temperature, and H_2/FFR molar ratio. The Cu-Fe mixed oxide catalyst with a Cu/Fe ratio of 1 emerged as the best catalyst, achieving over 99% FFR conversion and 90% selectivity for 2-MeF at a H_2/FFR ratio of 10, a temperature of 230 °C, and a flow rate of 0.5 g_{FFR} per hour per $gram_{catalyst}$. Extended tests on catalytic activity revealed consistent high performance, maintaining over 99% conversion and 90% 2-MeF selectivity over a 12-hour period. Even after 24 hours, conversion rates stayed above 90%. Following regeneration, the catalyst exhibited partial recovery, with conversion and selectivity stabilizing at around 85% and 86% respectively for a 10-hour duration. Catalyst deactivation was attributed to site and/or pore blockage due to the adsorption of FFR and furfuryl alcohol (FAL), as well as the formation of oligomeric compounds on the catalyst's surface.

Keywords: Biomass Valorization, Furfural, Hydrodeoxygenation, 2-Methylfuran, Biofuels

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$CuO/ZnO/Al_2O_3$ catalysts modified by MOF-derived carbon for CO_2 hydrogenation to methanol

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Due to the increasing scientific and technological interest in transforming CO_2 into value-added products, CO_2 hydrogenation to methanol (CO_2–MeOH) has drawn special attention lately. Thus, CO_2–MeOH is regarded not only as a potential route for CO_2 mitigation, but also as an alternative for the chemical storage of energy (the power to liquid concept, P2L) [1], and for the industrial MeOH synthesis from syngas. CO_2–MeOH is a very challenging process due to its thermodynamics (highly exothermic reaction, proceeding with decreasing number of moles), the stability of the CO_2 molecule, the possible side reactions, and catalyst deactivation problems, all these issues being closely interconnected. Current approaches to tackle these challenges mainly focus on catalysts' modification to achieve improved MeOH yields in the process. The most investigated catalyst is the commercial $Cu/ZnO/Al_2O_3$ (CZA, 50-70% Cu, 20-50% ZnO, 5-20% Al_2O_3), an untypical catalyst since the metal oxides do not play the role of supports for Cu [2]. The strategies envisaged for increasing the performances of the CO_2–MeOH catalysts are (i) enhancement of surface defects by promotion with additional oxides (Ga_2O_3, In_2O_3) [2]; (ii) improvement of Cu dispersion by confinement in the ordered porous structure of various materials (KIT-6, SBA-15) [1], and (iii) use of hydrophobic additives to limit the negative effects of water formation during the process (ZrO_2, or carbon-based materials) [3]. In this work, MOF-derived carbon (C_{MOF}) was used to modify CZA catalysts (Cu:Zn:Al = 6:3:1) aiming the enhancement of surface area and the catalysts' water resistance due to the hydrophobic character of the added C. C_{MOF} was obtained by thermal treatment under an inert atmosphere of MIL-53(Al) synthesized by a cost-effective hydrothermal procedure [4], leading to a carbon structure with channel-like porosity, and high surface area (~1500 m^2/g). The C_{MOF}-CZA catalysts were prepared by precipitation with $NaHCO_3$ at pH=7, using different amounts of C_{MOF} (3/6/12wt.%). Materials were characterized by XRD, BET, SEM/TEM/EDX, FTIR, TPR, CO_2 and H_2-TPD. It was found that catalyst components are uniformly dispersed in the matrix, with CuO particle size slightly increasing with C_{MOF} content. Also, surface area and pore volume increase with C_{MOF} loading, while pore size distribution becomes narrower. In addition, it was found that the reducibility of catalysts, as well as their interaction with both CO_2 and H_2, are strongly influenced by the type and amount of C_{MOF}, with clear perspectives towards enhanced CO_2–MeOH.

Keywords: CZA catalysts, MOF-derived carbon, H_2/CO_2-TPD

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P.1.09

Preparation of Ni-Mn-oxide catalysts and the influence of SO_2 on their low-temperature CO-oxidation performance

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Small amounts of carbon monoxide (CO) in the ppm range, eventually up to some volume percent, remain in industrial off-gas-streams as a result of incomplete combustion conditions. In light of the need to comply with environmental regulations and the economic aspects involved, a post-combustion treatment is required to abate CO emissions.

In order to perform CO-oxidation efficiently within the low gas-temperature range (in typical post-combustion scenarios at < 250 °C) a catalytic enhancement of the oxidation process is required. Besides novel metal catalysts consisting of Pt- or Pd-containing formulations, CO-oxidation catalyzed by mixed oxide based oxi-catalytic materials (MOOCs) offers an alternative path.

Good availability at comparably low prices of MOOCs offer advantages over novel metal-based catalysts. However, both material classes suffer from considerable restrictions of application in industrial off-gas-treatment due to their tendency to be severely poisoned by SO_2 from waste-gas-streams. Even in the ten ppm range, traces of SO_2 in many industrial off-gases may be critical, regarding the activity and service lifetime of MOOC-catalysts.

The present work focuses on the preparation and characterization of Ni-Mn-oxide catalysts, namely $NiMnO_3$ and $NiMn_2O_4$, as well as testing the materials regarding their CO-oxidation capability in the presence of SO_2. A typical co-precipitation method using the corresponding metal nitrates (molar ratio Ni:Mn = 1:2) combined with $(NH_4)_2CO_3$ as a precipitation agent was used to obtain the precursor. In-situ-PXRD enabled the identification of the phases present during the calcination process and was used to identify the phase transition of the ilmenite-type structure $NiMnO_3$ to the spinel structure $NiMn_2O_4$ at around 750°C. While calcination at low temperature (450 °C) resulted in a rather amorphous $NiMnO_3$ + Mn-oxide, calcination at 1000 °C yielded phase-pure crystalline $NiMn_2O_4$-powder. The catalysts were further characterized using BET-measurements, SEM/EDX, ex-situ PXRD, NH_3-TPD and catalytic activity tests under $CO/O_2/SO_2$-conditions. BET-measurements showed that the specific surface area of amorphous $NiMnO_3$ (~135 m^2/g) was significantly higher than that of crystalline $NiMn_2O_4$ (< 2 m^2/g). The results of NH_3-TPD experiments confirmed that crystalline $NiMn_2O_4$ exhibited greater acidity than amorphous $NiMnO_3$. The NH_3-chemidesorption peaks were observed at 385 °C, 435 °C and 210 °C, 340 °C, respectively. Furthermore, CO-oxidation measurements and the potential enhancement of SO_2-tolerance of the materials were conducted in a quartz-tube catalytic reactor.

Acknowledgements: The financial support of this research by the Austrian Forschungsförderungsgesellschaft (FFG) and Ceram Austria GmbH is greatly acknowledged.

Keywords: mixed oxide catalysts, spinel material, SO_2-tolerance

P.1.10

Transition mixed oxides catalysts for CO and hydrocarbons oxidation as an option to reduce emissions from small combustion devices

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The burning of wood, like the burning of other solid fuels, produces pollutants that have a negative impact on the environment and human health. In order to protect both, limits have been set for combustion plants to comply with. At present, manufacturers of small combustion plants (e.g. stoves) mainly use primary technologies to reduce emissions (change of combustion air intake, optimisation of the combustion chamber, inclusion of an afterburner, etc.), but it is expected that secondary technologies, e.g. addition of a catalyst in the flue gas path, will also be necessary [1].

The aim of this work is to study transition metal mixed oxide (MMO) based catalysts for the catalytic oxidation of CO, propane and methane as the typical gas pollutants from biomass combustion in domestic stoves. TMMOs represent an interesting alternative to currently used precious metals (mostly Au, Ag, Pd and Pt) based catalysts [1].

Six Co and Cu based MMOs have been prepared by co-precipitation method from corresponding nitrates and tested in CO, C_3H_8 and CH_4 oxidation reaction at temperature range of 100-500 °C. The catalytic experiments were performed in stainless steel fix-bed reactor and reaction products were analyzed on GC with TCD and FID. Tested samples were characterized by AAS, XRD, N_2 physisorption and temperature programmed techniques (TPD-CO_2, TPD-NH_3 and TPR-H_2).

All samples were active in CO, C_3H_8 and CH_4 oxidation reaction at studied temperature range. Co-based samples showed significantly higher activity than Cu-based samples (Fig. 1) due to better reducibility. The next step in the research will be scale-up active phase deposition on ceramic monolith and its testing in pilot plant as well as real full plant application (household stoves).

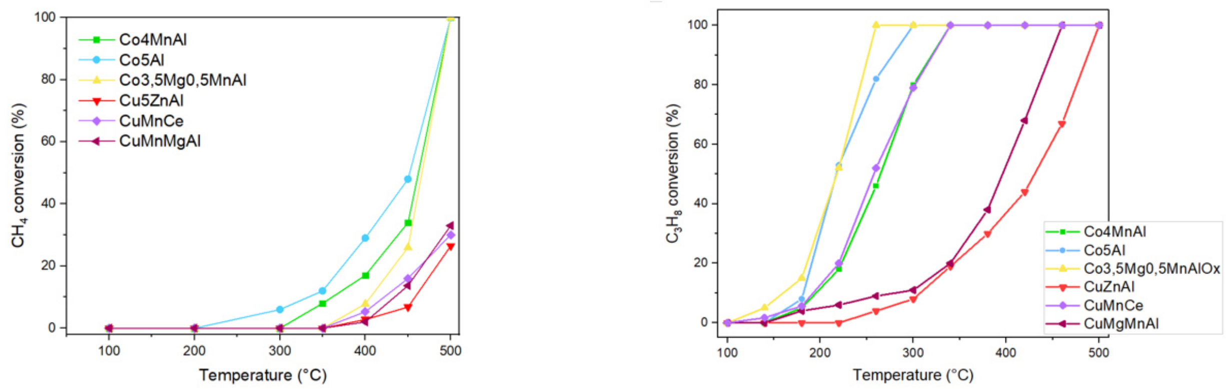

Fig. 1: Conversion curves of CH_4 and C_3H_8 over MMO catalysts. 0.2 g of catalyst, 100 ml/min, reaction mixture: 2500 ppm CO + 100 ppm C_3H_8 or 100 ppm CH_4 + 10 vol.% O_2 + N_2.

Keywords: CO, propane, methane, oxidation, mixed metal oxides.

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P.1.11

Bifunctional catalysts based on hydrotalcites for sandalwood fragrances synthesis

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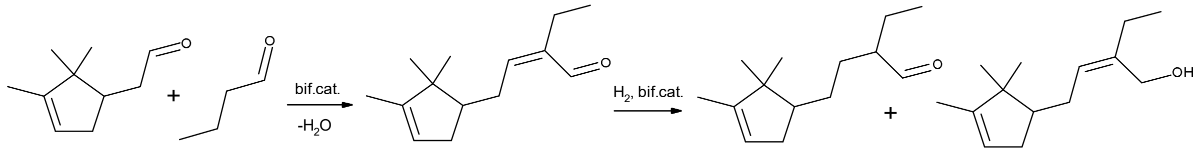
The presented study deals with the preparation of metal-modified bifunctional catalysts based hydrotalcite and their utilization for the „one-pot" synthesis of Levosandal, dihydro-Levosandal and Levosandol (Fig.1).



Levosandal **dihydro-Levosandal** **Levosandol**

Figure 1: One-pot synthesis of sandalwood fragrances over bifunctional hydrotalcite-based catalyst

The first synthesis step, aldol condensation of campholenic aldehyde with butanal results in Levosandal formation. Levosandal synthesis has been described over different catalysts such as hydrotalcites[1], or 10% aqueous NaOH solution [2]. In industrial production, alkali hydroxides are commonly employed for aldol condensation. However, homogeneous catalysis presents several drawbacks, making the adoption of heterogeneous catalysts a challenging endeavor. Hydrotalcites, known for their base properties, emerge as highly promising candidates for catalyzing the synthesis of fine chemicals through aldol condensation. The second step of sandalwood fragrances synthesis is selective hydrogenation of Levosandal. Hydrogenation of Levosandal has been described over Cu/SiO_2 [3] or ruthenium phosphine complexes [4]. Hydrotalcites can undergo modification with precious metals, resulting in the preparation of bifunctional catalysts suitable for a "one-pot" synthesis.

In the first step of sandalwood fragrance preparation, aldol condensation, the optimal reaction conditions were found as follows - temperature of 75 °C, ethanol as a solvent, 40 wt.% of hydrotalcite with a Mg:Al ratio of 3.4 and the molar ratio of reactants 1:1. Under such conditions, after 5 hours of the reaction, 55% conversion and 83% selectivity to the desired Levosandal were achieved. It was also confirmed that the hydrotalcite could be reused without loss of activity in 4 cycles. In the following, Pd or Ru bifunctional hydrotalcite-based catalysts were prepared and tested in a one-pot reaction. Such prepared catalysts are selective for hydrogenation of CC double bond on the aliphatic chain to dihydro-Levosandal.

Keywords: Levosandal, hydrotalcite, one-pot synthesis, aldol condensation, impregnation

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Nanostructured TiO_2, Fe_2O_3, CeO_2 and CuO-based catalysts prepared using titanyl sulphate in dichloromethane oxidation

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In recent years, there has been an increase in emissions of volatile organic compounds (VOCs) and chlorinated volatile organic compounds (CVOCs) from industries [1]. Dichloromethane is one of the frequently used CVOCs as a solvent, which is classified into group 2A so probable carcinogens to human by the International Agency for Research on Cancer [2] . Catalytic oxidation appears to be a promising technology for reducing VOCs and CVOCs [3].

A set of powder catalysts TiO_2-CeO_2-CuO (69:28:3 wt.%), TiO_2-CeO_2-Fe_2O_3 (69:12:19 wt.%) and TiO_2-Fe_2O_3 (71:29 wt.%) was prepared by the co-precipitation method, using titanyl sulphate as a precursor for TiO_2 and cerium (III), iron (III) and copper (II) nitrates as precursors for CeO_2, Fe_2O_3 and CuO, and subsequent calcination. Prepared powder catalysts were investigated in the oxidation of dichloromethane on a laboratory apparatus, consisting of a vertical tubular reactor with a fixed bed of catalyst. Catalytic tests were carried out over a temperature range of 100-500 °C in the SV of 71 $m^3 \cdot kg_{cat}^{-1} \cdot h^{-1}$, with an initial dichloromethane concentration of 500 ppm and 1.5 vol. % water. Gaseous products were analysed on an online FTIR analyser.

The set of prepared powder catalysts showed dichloromethane conversion in the range of 98-100 % and HCl yields ranged from 76-90 %. The TiO_2-CeO_2-CuO (69:28:3 wt.%) catalyst showed the best catalytic efficiency and HCl selectivity. It was shown that increasing the surface acidity of the catalyst by using titanyl sulphate as a precursor resulted in an increase in catalytic efficiency.

Keywords: catalytic oxidation, chlorinated VOCs, dichloromethane, titanyl sulphate

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Ethanol coupling reactions over $MgO-SiO_2$ and $MgO-Al_2O_3$ catalysts

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The formation of new carbon-carbon bonds is of great importance in chemical technologies. Bioethanol, a renewable source, can be an important raw material for hydrocarbon chain extension reactions. Recently, two types of ethanol coupling reactions are thoroughly investigated. i.e. ethanol to butadiene reaction (ETBD) is known as the Lebedev synthesis, and the ethanol to butanol coupling (ETBOL) which is referred to as the Guerbet reaction. The two reactions are thought to occur via very similar pathways. According to the more widely accepted mechanism in the first step of the reaction dehydrogenation of ethanol produces acetaldehyde, from which crotonaldehyde is formed after aldol condensation and dehydration. This is followed by a hydrogenation step in which an ethanol molecule reduces crotonaldehyde to crotyl alcohol while acetaldehyde is formed (MPV reaction). At that point the two reaction pathways separate, namely, in the ETBD reaction, crotyl alcohol is dehydrated to butadiene, while in the ETBOL reaction butanol is formed after a hydrogenation step. Less accepted mechanism is the so-called direct-coupling pathway according to which butadiene is formed through the crotyl alcohol formed by the condensation of one ethanol and one acetaldehyde molecule, while butanol is produced by the condensation of two ethanol molecules.

In present study the ETBD reaction was investigated on $MgO-SiO_2$ and the ETBOL reaction on $MgO-Al_2O_3$ catalyst. The conversion of ethanol and the main intermediate products (acetaldehyde, crotonaldehyde, crotyl alcohol, butanal) and the mixture of ethanol and the intermediate products over the two catalysts was investigated in detail. Butadiene is the main product on the $MgO-SiO_2$ catalyst. Its formation is favored by high temperatures, at 450 °C a yield of about 50% can be achieved. $MgO-Al_2O_3$ butanol is the main product, which is formed between 250-350 °C with high selectivity, at higher temperatures the dehydration of ethanol is the main reaction. The selectivity of acetaldehyde on both catalysts is more than 95% to croton aldehyde, however, the conversion is not complete, reaching a value of only 20-40%. In the reaction of pure crotyl alcohol, like ethanol, the main product is butadiene on the $MgO-SiO_2$ catalyst, and butanol on the $MgO-Al_2O_3$ catalyst. A significant amount of butanol is produced from pure crotonaldehyde on both catalysts, for which the hydrogen is supplied by the aromatization process. Pure butanal produces C_8 molecules with high selectivity. In the reaction of the ethanol-intermediate product mixtures, it was observed that the intermediate products retain their original reactivity, so, for example, in the reaction of the ethanol-acetaldehyde mixture, crotonaldehyde appears among the products. In addition, the conversion of the intermediate products is not complete, which refutes the idea that in the reaction of pure ethanol, crotonaldehyde and butanal do not appear among the products because they are rapidly further transformed. From these results, we concluded that on the butadiene is formed via the crotyl alcohol intermediate product formed by the coupling of ethanol and acetaldehyde, while butanol is formed at low temperature by the coupling of two ethanol molecules. At higher temperatures, only traces of butanol are formed from pure ethanol, but if acetaldehyde is also added to the reactant mixture, the high butanol selectivity is preserved, which can be explained by the fact that butanol is then formed via the crotyl alcohol intermediate.

Keywords: ethanol, butadiene, butanol, condensation, reaction mechanism

The influence of Mo and W promoters on the performance of nickel and cobalt catalysts with CeO_2 support in CO_2 methanation reaction

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Carbon dioxide is considered as one of the main casues of the greenhouse effect. That's why capturing and using it is one of the greatest challenges facing science and technology today. On the other hand, CO_2 is an attractive feedstock that can be converted to methane using renewable hydrogen. This can be realized by hydrogenation reaction. Numerous literature data indicate that the most active and at the same time relatively inexpensive are supported nickel and cobalt catalysts. Their properties can be modified by the use of appropriate supports and promoters [1,2].

The aim of this study was to compare the activity and selectivity of nickel and cobalt catalysts with nano-CeO_2 as support and to determine the effect of Mo and W promoters.

Two series of nickel-based and cobalt-based catalysts with CeO_2 as support were examined. The catalysts were synthesized by wet impregnation procedure using nickel or cobalt nitrates and commercial nano-CeO_2 [1]. Each series contained similar amounts (about 9 wt.%) of nickel or cobalt as the active phase and up to 2 wt.% of Mo or W promoters. The promoters were introduced using ammonium molybdate and ammonium metatungstate.

Studies indicated the complex role of Mo and W promoters in the catalysts.Temperature-programmed reduction studies showed that the addition of tungsten and molybdenum led to a decrease in reducibility of the catalysts. The activity and selectivity of the catalysts were tested and compared at various reaction temperatures ranging from 200 to 600 ºC. The higher activity was found for nickel-based catalysts. In general, the decrease in CO_2 conversion at low temperatures and increase in CO selectivity was observed with an increase in the contents of promoters.

Keywords: CO_2 methanation, nickel and cobalt catalyst, CeO_2, Mo and W promoters

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Investigation of support effects during ethanol steam reforming over cobalt-based catalysts

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Hydrogen-derived energy sources are a sustainable and environmentally friendly alternative to the utilization of fossil fuels, for which the availability of reserves is subject to high uncertainty. Bioethanol offers a promising starting material for hydrogen due to its low toxicity, its ease of handling and its availability from many different renewable sources, ranging from sugarcane to algae. In the ethanol steam reforming (ESR) process, two mechanisms can occur to convert ethanol to hydrogen and carbon dioxide, namely dehydrogenation and dehydration routes. In the dehydrogenation route, the ethanol is converted to acetaldehyde and hydrogen. Whereas in the dehydration route, the intermediate product of ethylene is first produced. Among them, the most undesired path is the ethanol conversion to ethylene as the latter is easily transformed into the carbonaceous deposit. Breaking the C–C bond of the ethanol is of immense importance and is considered a main challenge in the ESR process. The noble-metal-based catalysts such as Rh, Ru, Pt, Ir, and Au have been extensively studied for the ethanol steam reforming reaction with a high potential to break the C–C bond. However, the high cost limits their industrial application, and interest shifts to catalysts based on nonnoble metals such as Ni, and Co. Among the supports used in the ESR reaction, δ-Al_2O_3 with a high specific surface area and good textural properties is often chosen even though it is characterized by a high surface acidity which promotes ethanol dehydration path. The presence of basic sites on the surface of supports can prevent this path. Therefore, amongst the various metal oxide supports, the MnO_x seems to be a great support of cobalt-based catalysts in the ESR process because it possesses the basic sites and high oxygen storage capacity [1-3].

In this work, δ-Al_2O_3, MnO_x, 5%MnO_x-Al_2O_3, and 5%Al_2O_3-MnO_x were used as support for the cobalt active phase in the steam reforming of ethanol. The supports were synthesized by the co-precipitation method. Whereas the cobalt-based catalysts with metal loadings of 10 wt.% were prepared by wet impregnation. The catalysts were characterized by N_2-physisorption, XRF, XRD, H_2-TPR, CO_2-TPD, and TEM methods. The tests were performed in a fixed-bed reactor with a water-to-ethanol ratio of 12. Co/5%Al_2O_3-MnO_x catalysts showed much better catalytic performance than other cobalt-based catalysts.

Keywords: hydrogen, ethanol steam reforming, cobalt-based catalysts

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Metallic decorated 3D graphene for glycerol oxidation

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Transforming the glycerol through partial oxidation might be considered an example of circular economy in action, as it permits an effective utilization of a waste product to be converted into other useful compounds (aldehyde, ketones, carboxylic acids) for cosmetic, pharmaceutic or food industry [1]. The catalyst involved in this process has to be carefully considered because of their implication in different aspects of the technologies (economic nature as well as at the productivity level) [2]. In this paper, we present a series of metallic-nanoparticle catalysts that might lead to improvements in glycerol partial oxidation.

The catalysts investigated for glycerol partial oxidation are carbon-based materials with controlled mesoporous structure (3D-graphene) decorated with mono metallic nanoparticles (Au, Pt) and bimetallic particles (Au-Pt). The 3D graphene-based materials are innovative and attractive catalysts because of their structural composition having (micro, meso, and macro) pores, remarkable mechanical properties, and accelerated mass and electron transport [3]. The 3D graphene support has been prepared by self-assembly through the hydrothermal method by controlling the temperature and pressure. The deposition method has been employed for the addition of mono-metallic and bimetallic nanoparticles to 3D graphene support. The metallic concentration varies between 1-2 weight%. The 3D graphene metallic nanocomposites have been characterized by different techniques such as X-ray diffraction in order to observe the crystalline structure of the nanocomposite before and after the deposition of the metallic nanoparticles, thermogravimetric analysis (TGA) to determine the thermal stability profile of the newly synthesized metallic composite and electronic microscopy (TEM and SEM) to underline the presence and the distribution of the metallic nanoparticles.

Due to the excellent properties of synthesized material mainly the controllable pore dimension and their high stability in acid/base media the selectivity, stability and the catalytic activity of the reaction will be improved.

Keywords: 3D graphene, hydrothermal, self-assembly, partial glycerol oxidation, metallic nanoparticles

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Impact of treatment conditions on catalysts activity and stability in glycerol hydrogenolysis

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Considering all the concerns about environmental changes and the increasing demand for cleaner energies, in the last decades the production of biofuels, occurring via transesterification of vegetable oils and animal fats, is strongly increased [1]. Glycerol is the main by-product of this reaction, and its conversion via hydrogenolysis is continuously attracting the interest of many research groups due to the potential applications of different value-added chemicals that can be produced [2, 3]. High activity, selectivity towards desired products and structural resilience are all properties that have to be taken into account to select the best catalyst for the reaction. Therefore, this study wants to shine light on the consequences of diverse treatments on catalyst's integrity and efficiency. A commercial zeolite Y loaded with 2%Pt and 15%WOx (wt%) has been used to perform glycerol hydrogenolysis reactions under different conditions, aimed to test whether these treatments could play a role in structural and physico-chemicals changes. The reaction was performed at different temperatures up to the glycerol degradation limit to evaluate the influence of the reaction temperature on the reaction mechanism, the selectivity towards different products and on the stability. Furthermore, we focused on testing the catalyst's resilience against H_2O washing and O_2 treatment, two selected regeneration procedures. Finally, we studied the effect of a phase change of the zeolite detected previously in liquid hot water [4] on the catalytic performance. Extensive characterization of the catalyst before and after reaction highlighted the differences arising after each reaction. Via X-Ray Diffraction (XRD) we observed structural changes occurring from the perspective of the crystallinity of the samples. Surface area (N_2 physisorption) was strongly decreased after the reaction, and the ratio of Bronsted to Lewis acid sites, determined by IR spectroscopy of pyridine adsorption, was affected, too. The amount of coke was determined by Thermogravimetric Analysis (TGA).

Keywords: glycerol hydrogenolysis, zeolite y, treatments, stability

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$Ni/Zn/CeO_2/Al_2O_3$ catalysts for the dehydrogenation of methyl cyclohexane in LOHC systems

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Methyl cyclohexane (MCH)-toluene (TOL) couple is a potential industrial candidate for an economical and safe liquid organic hydrogen carrier (LOHC) system. Platinum based alumina catalysts are the most active and selective for the hydrogenation-dehydrogenation cycle, as hydrodemethylation side reaction leading to benzene and methane can be avoided with them. Substitution of noble metals with transition metals is a cost-effective solution, however, commonly used nickel catalysts are less selective due to their high hydrogenolysis activity. The type of supporting oxide and the use of bimetallic catalysts can play a decisive role in improving selectivity.

A series of mono- and bimetallic, nickel-zinc-ceria-alumina based catalysts were prepared and studied in the hydrogenation-dehydrogenation cycle of TOL-MCH. Ceria differs from alumina support in that it contains reducible oxide centers, influencing the metal-support interaction and mediating the spillover of hydrogen. $CeO_2/\gamma\text{-}Al_2O_3$ support containing 20 wt.% cerium was prepared by two synthesis methods. One involved impregnation of a commercial γ-alumina, which had bimodal pore size distribution, with cerium nitrate solution followed by thermal decomposition of the ceria precursor. The other method was a sol-gel procedure, combining pseudo boehmite (AlOOH) suspension with cerium nitrate solution and ammonia. Both types of supports were loaded with 10 wt.% metal (Ni only, or 6 wt. % Ni and 4 wt.% Zn) by incipient wetness impregnation. The preparation method of the support did not affect the catalytic performance of the catalysts. However, the NiCe and NiZnCe catalysts were much more active and stable in dehydrogenation reaction compared to the neat alumina supported Ni/Al_2O_3 catalyst, reaching 95/90 % conversion with 80/95 % selectivity to TOL at 375°C and WHSV=1 h^{-1}, respectively. Hydrogenation of TOL proceeded with 100 % conversion and selectivity between 125-175°C and at 30 bar H_2 pressure on both types of catalysts. Textural investigations showed that the bimodal catalyst had similarly high specific surface area and pore volume as the sol-gel type, and that finely dispersed, crystalline ceria homogenously covered the surface of alumina. Both preparation methods could actually produce a high surface area ceria support, which is more difficult to achieve by using pure ceria. Coverage of alumina by ceria particles modifies the surface favorably, inhibiting the strong interaction between nickel and alumina and thereby avoiding the formation of hardly reducible spinel structure. In fact, according to TPR measurements, the reducibility of nickel was higher on ceria catalysts. Modification of the nickel phase with zinc improved the selectivity, i.e. inhibited the hydrodealkylation activity by influencing the electronic properties of the nickel phase.

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Keywords: LOHC, dehydrogenation, methyl cyclohexane, ceria-alumina, nickel

2D materials-supported Rh catalysts for hydrogenation and hydroformylation reactions

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2D materials are defined as layered materials with minimum thickness to the physical limit [1]. Beyond graphene, the most common of 2D materials, a wide spectrum of 2D materials has been described [1-3]. They are characterized by large surface area, uniformly exposed lattice plane, adjustable electronic state, ability of surface defect formation, and possibility of controlled surface functionalization [1, 3] and therefore one possible utilization targets to the catalysis. Excellent catalytic activities with superior selectivities of 2D materials supported-metal catalysts have been described in various chemical and electrochemical reactions [1].

The hydroformylation reactions are important industrial process for the production of aldehydes, that are formed via reaction of olefins with synthetic gas (CO and H_2). Hydroformylations are still nowadays catalyzed dominantly homogeneously by conventional Rh- or Co-based catalysts. These catalysts exhibit great catalytic activity and selectivity, however the problems with recovery of expensive metals make this process less environmentally friendly and economically profitable. Therefore, an effort for replacing these homogeneous catalysts by the heterogeneous counterparts is significant.

The presented research focused on the Rh modification of various 2D materials (as graphene, MoS_2, WS_2, germanene, silicene, germanene-silicene hybrids), their deep characterization (XRF, XRD, SEM-EDS, TEM, FTIR and Raman spectroscopy), and their testing in the model reactions as hydroformylations of olefins (styrene, 1-octene) and hydrogenation of cinnamaldehyde. Additionally, conventional counterparts to the tested 2D materials as activated carbon, bulk MoS_2 or silica were modified by Rh for comparison. Different preparation methods as impregnations and chemical-reduction depositions were used for preparation of Rh/2D catalysts with different nominal Rh loading (1 – 5 wt.%).

Rh modified MoS_2 supports as well as some of germananes showed reasonably activity and selectivity in the hydroformylation of styrene. Additionally, Rh/graphene revealed relatively high activity with high selectivity toward hydrogenation products in hydrogenation of cinnamaldehyde.

Keywords: 2D supports, Rh catalysts, styrene hydroformalytion, cinnamaldehyde hydrogenation

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Imaging H_2 Oxidation and Promoter Effects on a Single Rh Nanoparticle

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The active sites of metal nanoparticles are the workhorses of heterogeneous catalysis, but factors affecting catalytic activity and selectivity are typically studied by averaging techniques summarizing over a large number of nanoparticles, thus smearing out much information [1]. In contrast, methods that can directly resolve a catalytic reaction on an individual single nanoparticle are very scarce [2]. Furthermore, in situ/operando visualization and characterization of reaction behavior on the nanoscale is also limited to few methods.

In this contribution we report a microscopy driven approach that utilizes the apex of a metal nanotip to mimic the surface of a spherical catalytic particle ($r < 20$ nm), and correlative field ion microscopy (FIM)/field emission microscopy (FEM) for real-time imaging of both the nanoparticle surface (facets) and the ongoing reaction (10^{-5} pressure range). In a certain parameter range (at constant reaction conditions), the hydrogen oxidation reaction on Rh exhibited complex self-sustained oscillatory reaction behavior [3].

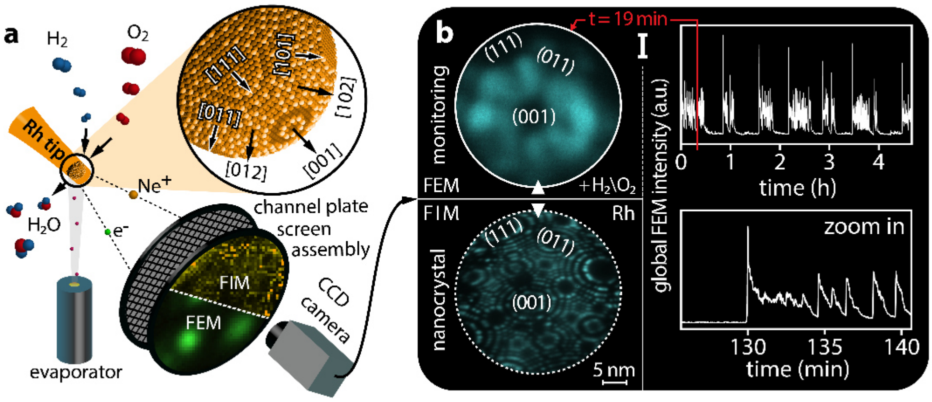

Figure 1. Resolving rhythmical reaction behavior on a single catalytic particle: (a) Schematic of the experimental approach; (b) sequences of activity in hydrogen oxidation on Rh.

By analyzing the spatio-temporal behavior of hydrogen oxidation on Rh (pure and with La adatoms), structure-activity relations, intraparticle lateral interaction and synergistic cooperation between active sites become *directly visible*, enabling to elucidate reaction mechanisms. The presence of La shifts the activity to higher p_{H2} and significantly slows down oscillations, due to La-enhanced oxygen activation on the catalyst surface.

Keywords: single particle catalysis, field emission

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Research on the mechanism of soot oxidation on the surface of Mn_3O_4-CeO_2 catalysts in tight contact conditions

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Soot removal (oxidation) from diesel engine exhaust is a crucial process in terms of environment and health. Soot, due to its size and floating time in the air, is one of the causes of several diseases (e.g. lung cancer) and also contributes to the greenhouse effect. Currently, a common method to prevent the emission of this type of pollutant is the installation of a catalytic diesel particle filter (CDPF) in the engine exhaust system. This solution is based on noble metals, in particular, platinum. To reduce the dependence on rare and expensive precious metals, other catalytic materials are being sought. One such candidate is Mn_3O_4-CeO_2 catalysts, which are very active in soot oxidation. However, the reaction mechanism on their surface is not fully understood.

Analyzed Mn_3O_4-CeO_2 catalysts were prepared by co-precipitation from aqueous solutions of acetate salts by adding ammonium carbonate. The catalyst precursors were dried at room temperature, then at 110°C for 5 hours, and calcined at 500°C for 2 hours. Physicochemical properties were tested using XRF, BET, XRD, Raman, and XPS methods. Catalytic abilities were analyzed in a gas mixture containing 10 vol.% of oxygen in tight contact conditions with the use of commercial soot (printex U). The reducibility and oxidizability of the catalyst surface were tested by TPR and TPO methods. For mechanistic studies and the mobility of oxygen under the conditions of the soot oxidation process, the isotopic transient kinetic analysis (ITKA) was used. The ITKA experiments were carried out following the test conditions and procedures for the steady-state isotopic transient kinetic analysis, but with the soot content changing with time – decreasing the concentration of the product (carbon dioxide) during the experiment.

The obtained ITKA results, among others, demonstrate that oxygen from the crystal lattice of the catalysts takes place in the process of soot oxidation and is also exchanged for oxygen from the gas phase (Fig. 1).

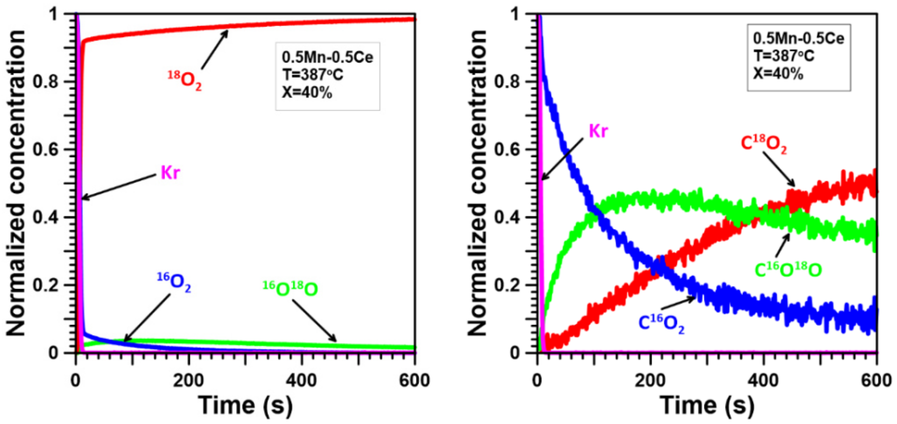

Fig. 1. ITKA results for the Mn_3O_4-CeO_2 catalyst containing equimolar amounts of Mn and Ce.

Keywords: Mn_3O_4-CeO_2, soot oxidation, ITKA

Natural and synthetic zeolites modified with Fe and Cu as catalysts for selective catalytic reduction of nitrogen oxides with ammonia

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Selective catalytic reduction with ammonia (NH_3-SCR) is one of the most effective methods for controlling the emission of nitrogen oxides. Nevertheless, the efficiency of this technology is limited by industrial vanadium-based catalysts [1]. According to general consensus, metal-modified zeolites are promising candidates for alternative NH_3-SCR catalysts [2]. However, the catalytic performance of these zeolites primarily depends on how the metals are distributed within the carrier. Many different methods have been investigated to incorporate the active phase into zeolites. Previous studies have shown that the majority of these methods required multiple deposition cycles or resulted in pore blockage. To our knowledge, no studies have yet examined the NH_3-SCR performance of catalysts supported on natural clinoptilolite and synthetic MCM-22, modified with transition metal oxides (Fe or Fe and Cu) using the solution combustion synthesis (SCS) method. We believe the greatest advantage of SCS is the rapid formation of the desired concentration of well-dispersed metal oxides, which provides outstanding low-temperature activity and high catalyst selectivity. Additionally, our study aimed to determine whether natural or synthetic zeolites served as a more beneficial support for the new NH_3-SCR catalysts. The investigated catalysts were prepared using the H-form of clinoptilolite and the Na-form of MCM-22. Typically, an aqueous solution of iron nitrate or iron and copper nitrates was mixed with sodium carbonate and urea, the latter serving as fuel to initiate the combustion reaction over 30 min. Subsequently, the mixture was transferred to a crucible containing 5 g of zeolite and introduced into a muffle furnace. Metal oxides were produced in the combustion process for approximately 5 minutes at 350 °C. Catalytic tests in the 150-450 °C range were carried out using a model gas mixture containing NO, NH_3, O_2, and He as an inert gas. Both clinoptilolite and MCM-22 were found to exhibit satisfactory NO conversion and relatively low N_2O formation during the catalytic reaction. Clinoptilolite-supported catalysts were remarkably more active than those based on MCM-22; however, the opposite trend was observed in the case of N_2O concentration in the post-reaction gas mixture. Based on the physicochemical characterization, it was concluded that the outstanding catalytic performance obtained for the materials resulted from the beneficial distribution of the active phase and the abundance of Brönsted and Lewis acid sites in the zeolitic framework.

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Keywords: clinoptilolite, MCM-22, solution combustion synthesis, iron, copper, DeNOx

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Transformation of ethanol into important chemical intermediates

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The use of renewable raw materials is the subject of a number of studies at present. Replacing fossil raw materials with renewables has the potential to address the challenges of global warming and the depletion of oil reserves. The implementation of the production of butadiene, an important monomer in the chemical industry, from ethanol can facilitate the transition to more sustainable production.

In this work, the influence of catalysts, their properties, composition and method of preparation for the transformation of ethanol into industrially significant compounds was studied. The reaction of ethanol on heterogeneous catalysts produces a mixture of hydrocarbons, mainly ethylene, propylene, acetaldehyde and C4 hydrocarbons, the most significant of which is 1,3-butadiene.

A series of catalysts based on zinc, zirconium, indium, wheat straw ash and cobalt, as well as multi-element catalysts were prepared. The structure of the catalysts has been characterized using UV-Vis, FTIR, XRD, temperature-programmed methods. Catalysts containing zinc have been found to promote the dehydrogenation of ethanol to form acetaldehyde, and with a greater content of zinc, its yield increases. A similar trend was observed for catalysts containing zirconium, which, however, promoted subsequent reactions to form butadiene.

Using the reaction in a two-reactor arrangement, where acetaldehyde was formed in the first reactor by dehydrogenating ethanol, the synergy of ZnO and ZrO_2 was refuted. On the contrary, it has been confirmed that they work together in tandem. In the IR spectra, a correlation was found between catalyst activity and mixed Zr-O-Si phase formation. The formation of mixed oxides was also promoted by further doping with magnesium. Magnesium successfully suppresses the formation of ethylene and increases butadiene yields. According to several studies, the acidobasicity of the catalyst plays a key role in the formation of butadiene from ethanol. Ideal catalysts are those with a limited amount of alkaline and medium amounts of acidic centres. This suggests that the balance between acidic and alkaline sites is critical for the efficient production of butadiene. The advantage of the acid/base ratio determination method using the isopropanol conversion test reaction – unlike most spectral methods – is that the acidobasicity is tested at the same pressure and temperature as the reaction itself (350 °C in our case).

Increasing the amount of zirconium in fumed silica support was found to increase acidity as measured by isopropanol decomposition. Surprisingly, adding magnesium to such a catalyst – in addition to increasing butadiene yields – increases the acidity of the catalyst. The best catalysts achieved ethanol conversions above 90% and butadiene yields above 40%. In addition to light alkenes, attention was paid to the formation of liquid products, where, in addition to typical oxygenates (alcohols, ketones), a significant formation of alkylaromates and alkylphenols was observed.

Keywords: ethanol, butadiene, mixed oxides, alkenes

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P.1.24

Atomically Precise Supported CuPd Clusters: Catalysts for CO_2 Conversion

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The production of value-added products (e.g., methane, methanol, etc.) from carbon dioxide and hydrogen offers a promising avenue for sustainable energy production and CO_2 utilization. However, under mild conditions, CO_2 hydrogenation presents a significant challenge due to the high stability of the CO_2 molecule. In recent years, significant research efforts have been devoted to exploring novel catalytic systems for this conversion process. Among these, subnanometer-sized supported clusters have emerged as particularly intriguing candidates. By tailoring the size and composition of clusters, the electronic and geometric properties of the clusters can be fine-tuned, thereby enabling the proper adjustment of their catalytic activity and selectivity. This can be further enhanced by the synergy of different metals within bimetallic clusters [1]. Hence, it was already shown that Cu_4 clusters are active in methanol synthesis [2]. Moreover, a recently published DFT study on bimetallic tetramer clusters predicted that the substitution of one Cu atom with an atom of Pd can efficiently tailor the catalytic properties of the cluster-based catalysts [3].

In this experimental and theoretical study, we investigate atomically precise CuPd clusters supported on ZrO_2 as a promising catalyst for low-pressure methanol synthesis from CO_2. Catalytic studies were carried out in a continuous flow reactor under atmospheric pressure conditions and temperatures ranging from 25°C to 350°C. The results of catalytic testing indicate that fine-tuning the atomic composition of the bimetallic clusters has a substantial effect on the catalytic activity and selectivity. Hence, CuPd catalysts exhibited catalytic activity in CO_2 conversion into methanol, with Cu_3Pd_1 being the most active. Our ongoing work aims to elucidate the underlying mechanisms governing the CO_2 hydrogenation reaction on these nanoscale catalysts and assess their potential as efficient and selective catalysts for CO_2 conversion.

Keywords: CO_2 conversion, methanol synthesis, bimetallic clusters, subnanometer clusters, support-cluster interactions

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Advanced Thermal Management and Fluid Dynamics in Nanoscale Systems: Thermo-osmosis and Photothermal Applications

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This study explores the impact of thermo-osmosis and photothermal applications on fluid dynamics and thermal management at the nanoscale. Through molecular dynamics simulations, we demonstrate a novel phenomenon in nanoscale thermo-osmosis, where localized heating in a nanochannel can induce multiple nanoscale convective layers, leading to net unidirectional fluid transport even without a temperature difference between reservoirs. This transport can be enhanced by precisely controlling the location of the heated region and tuning liquid-wall interactions, providing a promising strategy for chip-level cooling by utilizing heat generated by chips to create asymmetric temperature gradients, circulating coolant liquids without extra pumps. Additionally, we present a method to generate shear flows in heterogeneous nanochannels composed of parallel walls with differing wetting behaviors, without moving parts. The thermo-osmosis-induced shear flows, governed by surface excess enthalpy and nanoscale interfacial hydrodynamics, demonstrate an efficient means of generating *from temperature differences. Furthermore, we integrate photothermal water evaporation with photocatalytic microplastics upcycling in a nanofluidic thermal management system. This system utilizes electrospun nanofibers with alternately aligned photothermal and photocatalytic nanostructures, achieving high photothermal evaporation rates (2.59 kg m^{-2} h^{-1}, surpassing the limit rate) and efficient photocatalytic conversion of microplastic pollutants into valuable products. Controlled photothermal heating facilitates the selective evaporation of the main product, methyl acetate, through in situ separation. These findings offer new strategies for enhancing fluid mixing and thermal management at the nanoscale, with potential applications in chip cooling and micromechanical systems.

Keywords: Nanofluidics; Thermo-osmosis; Molecular dynamcis; Photothermal; Flow chemistry

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Enhanced understanding of the role of alkali in ethanol steam reforming over cobalt catalysts. Operando DRIFT Studies and DFT Modeling

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As the demand for cost-effective and low-emission hydrogen production methods grows, bioethanol emerges as a promising candidate for fuel generation. Among various approaches, catalytic steam reforming of ethanol (ESR) stands out as a key method for deriving hydrogen from biomass. Due to the complexity of the process and the possibility of creating multiple intermediates, it is crucial to reduce the formation of undesirable compounds through the appropriate choice of catalysts, as well as to precisely understand the reaction mechanism [1]. The study investigated how various alkali promoters influence the performance of $Co|\alpha\text{-}Al_2O_3$ catalysts. A series of alkali-doped cobalt catalysts supported on alpha-alumina oxide were synthesized through a sonochemical method for cobalt deposition and an impregnation method for alkali doping. K, Na, Cs, and Rb compounds were added at a concentration of 1wt%. Comprehensive characterization of the samples included analysis of their chemical and phase composition, reducibility, and morphology. Additionally, the surface state of the alkali metals was examined using a dedicated technique: the species-resolved thermal alkali desorption method (SR-TAD). Catalytic tests confirmed that the addition of alkali promotes the selectivity of the reaction to the desired products, namely H_2, CO_2, and methane. For all catalysts doped with alkali metals, the results were comparable. Operando DRIFT spectroscopy was employed to examine the performance difference between catalysts with and without alkali doping in ethanol steam reforming (ESR). The results shed light on the mechanism of ethanol adsorption onto the catalyst surface. Experimental data were compared with results obtained from periodic DFT-GGA+U molecular modelling conducted using the VASP package. To achieve this, slab models were created, exposing the (0001) Al_2O_3 surface (with $Al_{108}O_{162}$ stoichiometry) in contact with the cobalt cluster (Co_{26}). The modelling revealed that the presence of alkali atoms induces electron transfer to the metal cluster, significantly impacting the ethanol reforming reaction pathway. Specifically, it enhances the adsorption energy of the aldehyde intermediate and facilitates the crucial C-C bond-breaking step.

Keywords: hydrogen, ethanol steam reforming, cobalt-based catalysts

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CO Oxidation on Copper Nanoparticles on Various Supports

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Copper oxide catalysts are of great interest due to their widespread applications in a variety of chemical processes such as low-temperature CO oxidation, soot oxidation, CO_2 hydrogenation, steam reforming of methanol and preferential CO oxidation (PROX) [1]. Low temperature CO oxidation is specifically interesting in the context of avoiding automotive cold-start emissions when the noble metals of conventional three-way-catalysts (TWCs) are inactive and poisoned by strongly adsorbed CO [2].

In this work, we have synthesized different supported copper oxide catalysts, such as $CuO-CeO_2$, CuO-ZnO, and CuO-C. The catalysts were characterized using BET, XRD, TPR, pulsed adsorption and FTIR techniques and applied for CO oxidation in a tubular flow reactor. The catalytic tests demonstrated that cerium oxide was the most effective support material for CO oxidation, based on low-temperature reducibility and CO and O_2 adsorption experiments at room temperature. Although the catalyst supported by activated carbon had the largest specific surface area and smaller copper oxide crystallites than CuO/ZnO, it still exhibited the lowest catalytic activity, demonstrating the importance of a proper metal/oxide interface.

Using DFT modeling, we have further investigated the energetics of potential reaction pathways on copper oxide surfaces, revealing a typical Mars-van-Krevelen (MvK) mechanism. The adsorption and conversion of CO to CO_2 facilitated the formation of oxygen vacancies on the copper oxide surfaces, largely independent of the oxidation state of neighboring copper centers. The effect of the ceria support has also been modelled by DFT.

Keywords: CO oxidation, copper oxide, various supports, pulsed adsorption, reaction kinetics, DFT

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POSTER SESSION 2

Ni-K/CeO$_2$ model catalyst for dry methane reforming – optimization of potassium concentration

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A substantial reduction of still growing emissions of such greenhouse gases as carbon dioxide and methane belongs nowadays to the burning societal, economic, and environmental challenges. The most sustainable solution to this problem is efficient valorization of these gases. Several possible technologies can be proposed to reach this goal, including dry methane reforming (DMR). This catalytic pathway seems to be especially interesting, due to its potential to convert simultaneously CO_2 and CH_4 into a mixture of H_2 and CO (syngas). Even though DMR is a rather demanding reaction, requiring high temperature and a very stable catalyst [1], promising results were reported for many transition metal-based catalysts, including supported Ni systems. An efficient way to increase the stability of the latter catalysts is by adding various promoters, e.g., alkaline additives. This work aimed to optimize the potassium concentration in the Ni-K/CeO$_2$ model catalyst tested in DMR.

Based on our previous studies [1], 3 wt. % of nickel was chosen for the parent Ni/CeO$_2$ material. This system was impregnated with appropriate amounts of aqueous KNO_3 solutions to achieve potassium contents ranging from 0 to 10 wt. %. All synthesized catalysts were characterized by XRD, RS, SEM, N_2-BET, DRIFT, UV/Vis-DR, and XPS. The catalytic tests in DMR were performed in 2.5% CO_2 and 2.5% CH_4 in Ar. Reaction products were analyzed by the GC/TCD method. Long-term stability tests were performed at 750°C for around 20 hours.

As it was confirmed by the characterization techniques, both the bulk and surface of the investigated catalysts were not significantly affected by the potassium addition. The initial activity of the tested Ni/CeO$_2$ samples decreased with potassium loading. On the other hand, the long-term activity tests showed that the stability of the investigated catalysts increased with potassium loading. Based on both activity and stability tests, the optimal potassium concentration can be maintained (Fig. 1) at relatively low loading (0.5-1.5 wt. %).

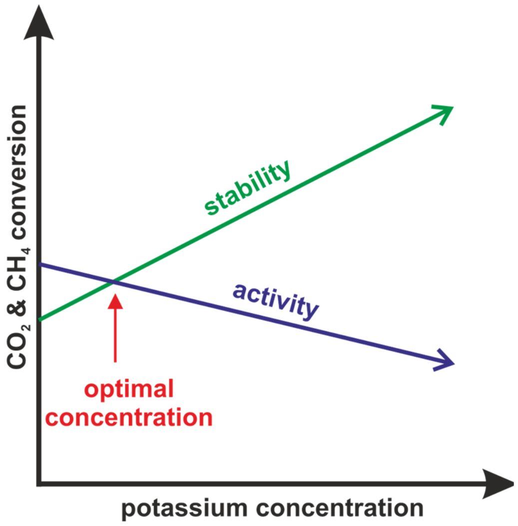

Fig. 1. Schematic way of optimization of DMR catalyst.

Keywords: dry methane reforming, syngas, catalyst stability, potassium

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Multi-doped perovskite-type oxides: How a combination of dopants influences exsolution

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Copper (Cu) containing materials play a crucial role in CO_2 hydrogenation reactions, as they support CO_2 activation and facilitate the production of value-added products like e.g. methanol or formate [1]. However, for wide-spread industrial application this activity has to be enhanced even further. This can be done by doping Cu nanoparticles with different elements, assisting the hydrogenation catalyst, thereby creating bi- and multifunctional materials.

Perovskite-type oxides are catalysts with the general structure of ABO_3, allowing for a wide variety of elemental compositions. Due to this flexibility, they are used in CO_2 utilisation reactions and can also be applied for methanol synthesis [2, 3]. Perovskite-type oxides are capable of forming nanoparticles on their surfaces, as the B-site elements migrate there under reducing conditions (= exsolution) [4]. These nanoparticles are uniformly distributed and lead to increased catalytic activity [5, 6].

This work combines these two aspects and compares different perovskite-type oxides with multi-doping on the B-site for their exsolution behaviour by triggering metallic or mixed phase nanoparticles. To enhance the catalytic activity of the Cu-dopant, it will be accompanied in small amounts by other elements, forming perovskites with the composition $Nd_{0.6}Ca_{0.4}Fe_{0.9}Cu_{0.05}M_{0.05}O_{3-\delta}$ (M = Co, In, Zr, Mn). These newly synthesised materials are checked for phase purity via X-ray diffraction (XRD) and specific surface area via Brunauer-Emmett-Teller method (BET). For the pre-treatment different exsolution temperatures are investigated, to maximize the catalytic activity in the methanol synthesis reaction.

Keywords: double-doped perovskites, methanol synthesis, CO2 hydrogenation, exsolution, bimetallic nanoparticles

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P.2.03

Hydrodeoxygenation of lignin-derived guaiacol over γ-alumina supported Ni-Cu bimetallic catalysts

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Converting lignocellulose into chemicals and fuels is of major interest to reduce dependence on fossil carbon resources. Lignocellulose is composed of polymeric saccharides (cellulose, hemicellulose) and polymeric aromatics (lignin). Lignin is a three-dimensional, amorphous polymer built from methoxylated phenylpropane monomers. Its thermochemical and/or chemical depolymerization gives liquid products (bio-oils) with a high oxygen content, which consist mainly of aromatic compounds. Due to their high oxygenate content, these bio-oils have low heating value, poor thermal stability, and are corrosive. The oxygen content of bio-oxygenates can be significantly reduced by catalytic hydrodeoxygenation (HDO) reaction [1].

Guaiacol (GUA), a representative aromatic component of bio-oils, is a preferred model feedstock to investigate the processes of bio-oil HDO. It contains a hydroxyl (–OH) and a methoxy (–O–CH_3) functional group, and three types of C–O bonds, which must be cleaved in the HDO reaction. The HDO reaction of GUA can lead to a variety of fully or partially deoxygenated products. Saturated hydrocarbons (cyclohexanes) can be used as fuels or non-polar solvents. Aromatic products like benzene, toluene, and xylenes are important precursors of many commercial chemicals and polymers, such as, trinitrotoluene, nylons, rubbers and plastics. The partially reduced products like cyclohexanone and cyclohexanol are industrial precursors of nylons, while phenol serves as a precursor to a large array of drugs, herbicides, cosmetics, and plastics.

In our previous paper, the HDO reaction of GUA was studied on monometallic Ni catalysts [2]. In the present study, we used γ-alumina supported bimetallic Ni-Cu catalysts and investigated the effect Cu on the physicochemical properties and catalytic behaviour of the bimetallic catalysts in the HDO of GUA. The reaction was carried out using a fixed-bed flow-through microreactor. Selectivity control is a major issue in designing HDO catalysts. The selectivity depends strongly on the balance of the hydrogenation and acidic functions of the catalyst and on the reaction conditions. The hydrogenation function was varied by the changing the Ni to Cu molar ratio in the catalyst. It was observed that the addition of Cu to Ni can significantly affect the activity, selectivity, and stability of the catalysts. The dispersion of the bimetallic Ni-Cu catalysts was higher than that of the monometallic Ni or Cu catalysts. The presence of Cu increased the reducibility of Ni. The effect of the reaction conditions on the catalytic activity and selectivity, such as, time-on-stream, space time, and temperature, was also studied. It will be shown how Ni-Cu loading and acidity of the catalyst affect the relative weights of the possible reaction pathways in the HDO reaction of GUA.

Keywords: lignin, guaiacol, catalytic hydrodeoxygenation, bimetallic catalyst

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P.2.04

Hydrotreated spent coffee grounds oil as SAF bio-component

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The world's annual coffee production is around 10 million tonnes per year. An average lipid content of 15 wt. % represents about 1.5 million tonnes of non-food grade spent coffee grounds oil (SCGO) per year. Therefore, the scientific literature also addresses the issue of higher and more complex use of coffee. This work presents the potential of oil extracted from spent coffee grounds for SAF biocomponent production via hydrotreating. SCGO was extracted from dried SCGs using n-hexane. The SCGO extracted with hexane has a chocolate brown colour and a characteristic coffee aroma. The crude SCGO had a high acidity (9.45 mg KOH/g) and must be degummed before hydrotreatment. After extraction, it contained P 24.53; Ca 5.1; Mg 7.31; Na 1.39; K 4.94; S 35.55 mg/kg. SCGO contain triacylglycerides (54.9 %), a high proportion of diacylglycerides (35.21 %), monoacylglycerides (0.8 %), free fatty acids (7.6 %), and sterols (1.5 %). Degummed SCGO mainly contains cis linoleic acid (45.4 wt. %), palmitic acid (33 wt. %) and oleic acid (9 wt. %).

Hydrotreating of PFCO was carried out in a continuous flow tubular reactor, with a temperature range of 360-380 deg. C, pressure 4-5 MPa, LHSV 1 h^{-1} and ratio hydrogen to feedstock form 450-600 NL/L. h in a co-processing regime with n-decane or kerosine solvent. The catalysts used in the present study were $NiMoP/Al_2O_3$ and NiW/Al_2O_3-zeolite (sulfidic form). The decarboxylation reactions were predominant over hydrodecarboxylation. The main decarboxylation products were n- and iso-alkanes C_{15}-C_{18}. PFCO is an excellent feedstock in the co-process with kerosene.

Keywords: spent coffee ground oil; SAF bio-component; hydrotreatment; NiMo catalysts; extraction

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P.2.05

Stability of different mixed oxides in heterogeneous transesterification and its influence on conversion

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One of the possible problems with heterogeneous transesterification for biodiesel preparation, which several authors have recently encountered, is the stability of catalysts. In the case of mixed oxides, the leaching of metals present in the oxides into the prepared biodiesel and glycerol has been observed. This not only causes problems with the quality of the produced products but also raises questions about the mechanism of transesterification [1]. In the case of metal leaching during reaction with methanol, the formation of a metal methanolate occurs, which is itself a homogeneous catalyst. Therefore, the question remains: to what extent is the reaction heterogeneous, and to what extent is it homogeneous when metal leaching occurs, and homogeneous reactions are significantly faster than heterogeneous reactions [2].

In the work, mixed metal oxides were tested, and prepared by co-precipitation to form hydrotalcites with different aging times. After the catalyst was precipitated, it usually stood for 24 hours. In the work, three variants of aging were tested: one was the catalyst that was washed immediately after precipitation (MO-0), i.e., did not stand for even one hour; the second was the catalyst that stood for 24 hours (MO-24); and the third was the catalyst that stood for a week (MO-168).

The testing reaction used was transesterification in a batch reactor on Camelina sativa oil. The stability of the catalysts was tested as follows. First, a reaction of heterogeneous transesterification was performed under conditions (140°C, 3 hours, Me/Oil 18/1, 3 wt.% catalyst). In the second step, the fresh catalyst was boiled in methanol under the same conditions as the reaction. This boiled methanol was then used in a reaction with oil without adding a catalyst to test the leaching and its activity in the reaction. The catalyst was also leached in oil, which was then used in a reaction with fresh methanol.

Results showed a significant amount of leached metals in oil as well as in methanol. The leaching influences transesterification and caused that by using only methanol in which the catalyst was boiled and oil without using methanol more than 30 % of FAME was produced. This fact confirms, that because of the instability of the catalyst, leaching into methanol an oil occurs and causes homogeneous catalysis instead of heterogeneous.

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Keywords: Mixed oxide, coffee oil, biodiesel, transesterification

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P.2.06

Bright Ideas: Designing Photocathodes for Visible Light-Driven Photoelectrochemical CO_2 Reduction

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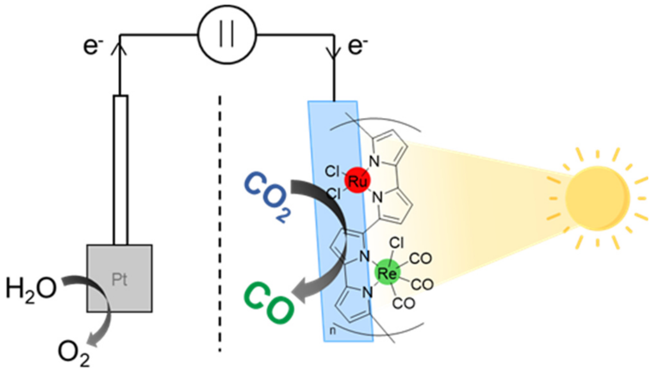

Navigating the complexities of transforming carbon dioxide into valuable chemicals is not just a scientific challenge – it's a global imperative. Achieving this goal demands efficient catalytic systems, essential for overcoming significant thermodynamic and kinetic barriers hindering the conversion of CO_2 into value-added chemicals [1].

In this study, we delve into the intricacies of designing photocathodes coated with a conductive polymer, optionally doped with the strategic addition of ruthenium and rhenium. Our objective is to develop an optimal photoelectrocatalytic CO_2 reduction framework. We prioritize simplicity in our synthesis methodology, aiming to sidestep the complexities often associated with various molecular CO_2 reduction strategies. The incorporation of ruthenium and/or rhenium introduces a synergistic enhancement of both photo- and electrocatalytic properties, resulting in increased selectivity for carbon monoxide formation with relatively low overpotentials [2].

Analytical data confirms the successful deposition of a conductive polymer layer and optional doping with ruthenium and/or rhenium. Comprehensive elemental analysis is enabled through Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS).

Keywords: CO_2 valorization, photoelectrochemistry, molecular catalyst system

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Polymer carbon nitride Z-scheme heterojunction for photocatalytic overall water splitting

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Z-scheme heterostructure artificial photocatalytic systems are optimal for the achievement of photocatalytic overall water splitting.[1] The system emulates natural photosynthesis by connecting disparate semiconductors in a series configuration.[2] However, the coupling of components that facilitate H_2 evolution and O_2 evolution remains a challenging area of research.[3] Recently, polymer photocatalysis with tunable band structures (e.g., polymer carbon nitride (PCN)) has attracted wide interest from researchers.[4] Firstly, we fabricate a Z-scheme system for photocatalytic overall water splitting based on boron-doped, nitrogen-deficient carbon nitride two-dimensional (2D) nanosheets. We prepare ultrathin PCN nanosheets with varying levels of boron dopants and nitrogen defects, which leads to nanosheets that can act as either H_2 or O_2 evolving photocatalysts.[5] An electrostatic self-assembly strategy was employed to couple the nanosheets, resulting in the formation of a 2D/2D polymeric heterostructure. The heterostructure exhibited stoichiometric H_2 and O_2 evolution in the presence of Pt and $Co(OH)_2$ co-catalysts, with a solar-to-hydrogen (STH) efficiency of 1.16% under one-sun illumination.[6] However, heterojunctions are often identified by chance. To facilitate the design of Z-scheme heterojunctions based on limited data, we propose an active learning strategy that integrates machine learning with high-throughput theoretical calculations, thermodynamic calculations, and experiments. The STH efficiency of the photocatalyst, which was designed using rational methods, was 1.59% under one-sun illumination in the presence of Pt/Cr_2O_3 and $Co(OH)_2$ co-catalysts. Furthermore, a numbering-up reactor system was developed for large-scale photocatalytic overall water splitting. The STH efficiency of the unit module was found to be 1.92% when operated steadily for 72 hours under natural sunlight. A large-area reactor comprising nine units (light-exposed area 324 cm^2 and reactive area 1,296 cm^2) demonstrated a high STH efficiency (1.86%) under natural light irradiation. The results of this study indicate a clear need for the development of large-scale integrated photocatalytic overall water splitting technologies.

Keywords: Polymer carbon nitride; Z-scheme heterojunction; Photocatalytic; Overall water splitting

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Vanadium-based Catalysts for the Electrochemical Reduction of Nitrate to Ammonia

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The so-called 'green' hydrogen can contribute to the mitigation of the effect of atmospheric carbon dioxide to the global climate change by 1) storing intermittent energy in chemical bonds and 2) providing a carbon-neutral reactant, e.g., to ammonia synthesis. Hence, expectations are high for realizing a hydrogen-based carbon-free economy, despite the series of known issues related to the lack of infrastructure for storage and distribution. Most of these drawbacks can be overcome by the use of ammonia as a hydrogen-transporting molecule, and also a high energy density energy vector with an already existing infrastructure. The current global ammonia production is, however, based on the energy- and carbon-intensive Haber-Bosch process, where elemental hydrogen and nitrogen are reacted at high temperature and pressure. The huge carbon footprint of this process mainly comes from the use of 'grey' hydrogen, i.e., hydrogen synthesized from natural gas by steam-methane reforming (SMR) and the water-gas shift reaction (WGSR). On the other hand, the direct electrochemical conversion of N-sources to NH_3 (electrochemical nitrate reduction, NO_3RR) is a promising technology still in its infancy and limited by low selectivity and yield for NH_3 production. To this date, ruthenium and palladium containing catalysts showed the highest nitrate reduction activity, whose scarcity and high cost hinder their widespread utilization. Here, we prepared vanadium-based non-noble metal NO_3RR catalysts by 1) mechanical alloying of carbon-doped boron nitride by V_2O_5, and b) electrochemical deposition of metallic vanadium onto macroporous copper foam substrate. After characterizing the structure (XRD, Raman) and morphology (SEM-EDS) of the catalysts, their electrochemical behaviour (CV, LSV, EIS) was tested in a standard three-electrode setup. The nitrate reduction activity was then studied in the same cell under alkaline conditions in 0.1 M KNO_3/1 M KOH at room temperature. Despite the obvious differences in the chemical structure of the two systems, both V-based catalysts showed high nitrate conversion (> 90%) along with high NH_3 Faradaic efficiency ($FE(NH_3) > 90\%$) and yield. Reports on NO_3RR active vanadium species (e.g., V-MoS_2 and $VN_{0.7}O_{0.45}$) are scarce in the literature, thus the differences and similarities were discussed between the two investigated systems, and their activity was ascribed to the facilitated initial NO_3^- adsorption. The mechanistic understanding of nitrate reduction on noble metal-free vanadium catalysts would forward the realization of an 'Ammonia Economy' in the near future.

Keywords: Vanadium electrochemistry, electrocatalysis, electrochemical nitrate reduction, ammonia production

MOF-derived NiO/Co_3O_4 composite nanoparticles for overall water splitting

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Water electrolysis by renewable energy will play a major role in our effort to mitigate the effect of anthropogenic climate change. Also, the produced green hydrogen is a carbon neutral energy source and an indispensable feedstock in the chemical industry at the same time. The latter means, that green hydrogen will become important in the sustainable production of chemical fertilizers and green steel in the future. To this end, it is essential to develop cost-effective nonprecious metal catalysts with catalytic performance comparable to that of the noble metal-based counterparts. Metal organic frameworks (MOFs) consist of metallic nodes held together by organic ligands or aromatic acids into a repeating coordination in 1, 2, or 3 dimensions. A series of MOFs have already been tested as catalysts or catalyst precursors in a wide range of catalytic reactions. By decomposing the highly ordered frameworks into well-dispersed nanoparticles or thin layers by thermal, chemical, or electrochemical reduction, metallic catalysts of controlled structure can be obtained. Therefore, metal organic framework-derived materials attracted great attention due to their large specific surface area, high number of active sites, structural and functional diversity, and their potential use in energy conversion. In this study, NiO/Co_3O_4 was synthesized by using a bimetallic Co-, Ni-zeolitic imidazolate framework (ZIF-67) as the metal source and sacrificial template through calcination at high temperature in air. A series of characterization techniques, such as scanning electron microscopy (SEM), in-situ X-ray powder diffraction (XRD), Raman spectroscopy, FT-IR, energy-dispersive X-ray spectroscopy (EDS), and electrochemical impedance spectroscopy (EIS) were applied to investigate the physicochemical properties of the catalysts. The formed bimetallic structure was applied in electrochemical water splitting for oxygen and hydrogen evolution in a standard three-electrode setup. Linear sweep voltammetry (LSV) was performed in 1.0 M KOH at a scan rate of 5 mV s^{-1}. The NiO/Co_3O_4 composite exhibited onset potentials of 240 and 370 mV (vs. RHE) for the hydrogen (HER) and the oxygen evolution reaction (OER) at 10 mA cm^{-2}, respectively. Our results show promise and encourage further research in the application of MOF-derived mixed metal oxides for electrochemical water splitting, and electrocatalysis in general.

Keywords: electrochemical water splitting, metal-organic frameworks, MOF-derived catalysts, cobalt-nickel bimetallic catalyst

P.2.10

Effect of Annealing and Phase Transition of Atomic Layer Deposited Vanadium Oxide on Hydrogen Evolution Activity

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Atomic layer deposition (ALD) is a unique method for the fabrication of thin layer structures. It utilizes self-terminating surface half-reactions through the repeated decomposition of multiple (usually two) reactants (the so-called precursors) on the surface of the target substrate. Due to their beneficial electronic, electrochemical, and catalytic characteristics, vanadium oxide is suitable for various applications, such as electrochemical energy storage, electrocatalysis etc. VO_x thin layers can be fabricated via ALD, however, the formation of multiple oxide phases of diverse physical properties, e.g. VO_2, V_2O_5, V_2O_3 etc., undermines their direct applicability. Certain phases can be stabilized by applying posttreatments, such as annealing. The latter impacts not only the phase transition, but also influences the morphology of the layer and its electrochemical behaviour. Thus, in this study, VO_x thin layers were fabricated by ALD, and the effect of annealing at 300, 400 and 500 °C was investigated on the phase transition in vanadium oxide. First, VO_x thin film was deposited onto nickel foam (NiF) at 150 °C through 280 cycles using tetrakis(ethylmethylamino)vanadium(IV) (TEMAV) and water as vanadium and oxygen precursors, respectively. In the second step, annealing was applied at the aforementioned temperatures for 2 h under argon atmosphere. The phase formation and phase transition in subsequent annealing were studied by X-ray diffraction (XRD), while the morphology of the as-synthesized and annealed thin layers was characterized using scanning electron microscopy (SEM), and atomic force microscopy (AFM). It is known that vanadium oxide shows electrocatalytic activity in the hydrogen evolution reaction (HER). Therefore, the as-prepared and the annealed electrodes were tested in HER by linear scanning voltammetry (LSV) in 1 M KOH solution at room temperature. Results on the annealed VO_x electrode demonstrated improved HER performance of −0.16 V (vs. RHE) onset potential, and a −62 mA cm^{-2} current density at −0.45 V (vs. RHE).

Keywords: Vanadium oxide, Atomic Layer Deposition, Hydrogen Evolution Reaction, annealing, phase Transition

Electrodeposited Iron on Porous Copper Foam as Electrocatalyst for Selective Nitrate Reduction to Ammonia

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The discharge of nitrate (NO_3^-) from industrial sewage and agricultural practices poses a significant threat to the environment and human well-being. To address this concern, electrocatalytic nitrate reduction (NO_3RR) emerges as a promising route for mitigating nitrate stress and converting nitrate to ammonia (NH_3). Ammonia, on the other hand, is an important precursor in the chemical industry, and the starting material in the synthesis of a series of commodities, like fertilizers, polymers, pharmaceuticals etc. Moreover, in the realization of a hydrogen economy, the effective storage of hydrogen itself must be solved, too. Ammonia stores hydrogen locked in the molecule by chemical bonds, and hence serves as a potential energy vector. Although NO_3RR is a well-known electrochemical reaction, the technology is currently limited by low selectivity and yield, particularly in ammonia production. In this work, we prepared a non-noble metal NO_3^--to-NH_3 electrocatalyst by depositing iron (Fe) onto porous copper foam (CF) substrate. The electrochemical behaviour of the constructed system was tested in a standard three-electrode setup under alkaline conditions (1 M KOH) at room temperature. Upon addition of 0.1 M KNO_3, the Fe/CF catalyst showed > 99% nitrate conversion along with a high Faradaic efficiency $FE(NH_3) = 91\%$ and a large NH_3 yield of 1910.4 $\mu g\ cm^{-1}\ h^{-1}$. The observed performance may be ascribed to the synergistic effect between iron and copper, which in turn facilitates the adsorption of NO_3^- in the initial steps of the reaction. Our strategy proposes an avenue for the rational development of electrocatalysts for the selective reduction of a pollutant and turning a waste stream (NO_3^-) into a valuable product (NH_3).

Keywords: Iron electrochemistry, electrocatalysis, electrochemical nitrate reduction, ammonia production

Hydrogenation of Acetone to Isopropanol over Fixed-Bed Raney-Type Nickel Catalyst. A Scale-up from Laboratory to Pilot Scale.

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The catalytic hydrogenation of acetone is an important catalytic process to produce highly demanded isopropanol used for fine chemical synthesis [1, 2]. The utilization of acetone produced from CO_2 and green hydrogen can provide an access to renewable isopropanol and other downstream products [3]. An experimental study on acetone hydrogenation was conducted by using Raney-type nickel alloy as a catalyst. Hydrogenation experiments were carried out in a fixed bed continuous flow reactor at pressures above and below the critical pressure of the acetone [4]. Experiments were carried out on a laboratory and a pilot-scale units. The effect of operating parameters such as space velocity, temperature, and hydrogen/acetone molar ratio on the catalytic performance was investigated.

The optimal conditions carried out in the laboratory were successfully reproduced in a pilot-scale production. It was found that, after multi-parameter optimization, Raney-type nickel catalyst efficiently converted acetone to isopropanol in both cases. Higher pressures led to an improvement in the conversions which exceeded 99%. A high selectivity toward the hydrogenated product (>97%) was achieved.
Significant progress has been made in scaling up high-pressure heterogeneous catalytic process to increase productivity and to provide a sustainable approach to isopropanol production.

Keywords: Hydrogenation, Raney-type nickel, Fixed-bed, High pressure

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Iron-modified copper catalysts for the steam reforming of methanol

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The increase in demand for electricity and, at the same time, the depletion of fossil resources contributes to the increased interest in obtaining energy from alternative and renewable energy sources. One of the promising renewable fuels is hydrogen, which, apart from the highest energy value per mass unit, is burned to produce only water. Hydrogen is considered the fuel of the future. It is a clean energy source that does not emit CO_2, CO, SO_2, NO_x, particulate matter or hydrocarbons, unlike fossil fuels.

More and more stringent environmental regulations mean that there is a growing interest in the use of hydrogen as a fuel for fuel cells, where it is converted into useful electricity, which could then be used in stationary applications or in electric vehicles. Among the many methods proposed for the production of hydrogen, the most common and energy efficient catalytic process is the steam reforming of methanol (SRM): $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$. During the conversion of methanol with steam, under the most favourable process conditions, as much as three moles of hydrogen can be obtained from one mole of methanol.

The production of hydrogen as a result of the conversion of methanol with water is a process that requires a properly selected catalytic system. The most commonly used catalysts in the steam reforming of methanol are mainly copper-based systems, as well as metals of groups 8-10 of the periodic table. Copper catalysts show high activity and selectivity to hydrogen in low-temperature SRM, and are also a cheaper alternative to noble metals. Nevertheless, copper-based catalysts have pyrophoric properties and are deactivated by thermal sintering. One way to improve the stability of these systems and reduce their costs is to add a second or more metals, usually from group 8-10 of the periodic table, which show better stability, good selectivity to hydrogen, but lower methanol conversion compared to a copper catalyst. Fe is demonstrated to be an effective species to improve the stability of Cu particles on the surface in the SRM. The presence of Fe species can improve the dispersion of copper by inhibiting the copper-sintering and this way improve activity of catalyst.

The aim of this work is determination of the relationship between physicochemical properties and catalytic performance of Cu-Fe/CeO_2 catalysts in the SRM process. The Fe-modified Cu catalysts with CeO_2 support, prepared by the impregnation method, were subjected to physicochemical analysis and catalytic tests in the steam reforming of methanol (SRM). The modification of the copper catalyst with iron resulted mainly in the improvement of the stability of the system and the reduction of the production of undesirable CO in the SRM process by increasing the efficiency of the WGS reaction. Different treatment conditions of Cu-Fe/CeO_2 catalysts before the catalytic process resulted in different activity of these systems in the SRM. This could be due to different SRM reaction mechanisms related to the different forms of active metals.

Keywords: Copper-iron catalysts, Ceria support, Steam reforming of methanol, Hydrogen production.

Zeolites bound with alumina for polyolefin cracking

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With industrial development, we are experiencing a rapid increase in the production of plastics. Since plastic recycling is not a sufficient solution, new ways to dispose of waste must be sought [1]. One of them is catalytic cracking of plastics using zeolites as a catalyst. Since this process involves dividing a long polymer chain into shorter ones, it seems to be a good idea to use a catalyst for fluid catalytic cracking - USY zeolite. It is known for its high thermal and hydrothermal stability, as well as high catalytic activity.

Zeolite Y (Si/Al = 2.5) and USY with different Si/Al ratios (6 and 30), their mechanical mixtures (dentoned as m-zeolite), and shaped catalysts with Al_2O_3 as a binder were tested in polypropylene (PP) cracking performed in TG-FT-IR-GC-MS and an operando FT-IR-GC-MS systems. Shaped catalysts were mildly and intensely grounded to follow the alteration of the acidic function and reagent diffusion property. The polymer to catalyst ratio was 3:1 in thermogravimetric measurements and 1:1 in FT-IR measurements.

The results show that the zeolite with the highest Si/Al ratio, USY-31, is the most active catalyst for PP catalytic cracking. This catalyst exhibits high mesoporosity, thus mass transport properties while preserving its native intercrystalline mesoporosity. Brønsted-type acid sites of the highest strength and accessibility benefit the efficient cracking of polymer chains but limited re-cracking reactions. Upon dilution with alumina, the smallest decrease in catalytic activity is observed for m-USY-31, confirming that the acidic function of the zeolite component is still effective for cracking polypropylene chains. The number of acid sites, both Brønsted and Lewis-type, detected in mildly ground samples, exceed the values expected from the extrudate composition by ca. 7-20 %. This proves that the chemical interactions between alumina and the zeolite active phase lead to the forming of new sites, mainly of protonic character. The number of acid Brønsted sites determined with pyridine in quantitative IR studies is linearly correlated with the micropore volume, evidencing the microporous origin of protonic sites. The positive effect of the binder has already been noticed in previous studies [2, 3].

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Keywords: zeolites, cracking, operando, polypropylene

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Discovering Tomorrow's Catalysts: Mapping Nitrogen-to-Ammonia Conversion Horizons

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This study presents key findings from multiple studies on the electro-reduction of nitrogen to ammonia (NH_3) using transition metal carbide and carbonitride catalysts under ambient conditions. Using density functional theory (DFT) calculations, we investigated the catalytic potential of these materials and analyzed various structural orientations. Free energy diagrams are employed to assess reaction mechanisms, with a focus on associative, dissociative, and Mars–van Krevelen mechanisms, while considering stability against poisoning and decomposition. WC, VC, VCN, and NbCN emerge as robust catalysts for NH3 synthesis, with low onset potentials [1-3]. Join us in catalytic science, where we're revolutionizing ammonia production for a sustainable future.

Keywords: DFT, Heterogenous catalysis, TMC, TMCN, Electrochemical ammonia synthesis

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The effect of diffusion resistance on the effectiveness NO_x selective catalytic reduction process

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In the heterogeneous catalytic process, apart from the kinetic features of the catalyst, the limitations related to diffusion resistance play an important role on the effectiveness of the reaction. The relationship between diffusion and kinetics for the first order reaction is described by Thiele modulus Φ [1]:

$$\Phi = V/S\sqrt{\frac{k}{D_{ef}}}$$

where: V – volume of the catalyst particles, S – surface of the catalyst particles, k- kinetic constant rate determined at the kinetic regime, D_{ef} – effective diffusion rate.

The value of the Thiele modulus indicates the nature of the process, and makes it possible to determine the effectiveness factor of catalyst particle η.

Our work led to the development of a new catalyst formula for the selective catalytic reduction of NO_x with ammonia ($SCR-NH_3$), in the form of iron-modified natural clinoptilolite [2]. When developing the catalyst formula, it was assumed that the catalyst should consist of cheap and harmless raw materials, and the manufacturing procedure should be uncomplicated. Such assumptions favor high implementation potential. The results of the activity of the developed catalyst for the $SCR-NH_3$ including the effect of reaction temperature and GHSV were shown. Another important aspect of usefulness of the catalyst is to avoid the formation of the undesirable product N_2O, so the change of its concentration in the post-reaction mixture was monitored, too.

The results obtained for the powdered catalyst ($d_{cat}\rightarrow 0$ mm, kinetic regime) and formed catalyst particle into tablets ($d_{cat} = 5$ mm, diffusion-kinetic or diffusion regime) were compared. Based on the obtained results effectiveness factor of catalyst particle was calculated.

The obtained results are of practical importance because they provide the basis for calculating the required volume of the catalyst bed for industrial use in a nitric acid plant.

Keywords: nitric acid plant; selective catalytic reduction; clinoptilolite; Thiele modulus.

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P.2.17

Electron Tomography as a Tool for Advanced Characterisation of Catalysts Microstructure

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This study focuses on the implementation and application of electron tomography techniques [1,2] at UCT Prague. It comprises two main sections: one dedicated to the methodology of electron tomography, and another focusing on case studies involving catalysts.

The methodology section outlines the whole process involved in electron tomography, including specimen preparation methods like the FIB-SEM lift-out technique [3], data acquisition within a transmission electron microscope and image processing. The image processing [4] of acquired image data undergoes analysis which leads to quantitative information [2] about materials and catalysts with resolution in nanometres.

The case studies serve to illustrate the utility and results of electron tomography in material analysis. Beyond generating 3D models, the reconstructions yield valuable quantitative insights into the material, such as particle size distribution, proximity of metallic components to the material surface, spatial porosity and the structure of porous systems. These insights enable the observation of phenomena like changes in pore connectivity, sintering, or metal migration within porous supports.

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Keywords: Electron microscopy; Tomography; SEM; TEM; Image processing

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P.2.18

Phenolics adsorption on alumina supported HDO catalyst

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Majority of the catalytic hydrodeoxygenation (HDO) studies is focused on individual components neglecting all the interactions in a multicomponent mixture of oxygenates. One of the challenges is the lack of understanding of the observed catalytic activity inhibition when working with a mixture of oxygenates caused by competitive adsorption effects. Composition, morphology and structure of the catalyst control the type of adsorption sites and the mutual interactions of adsorbed species. The use of multicomponent catalysts may increase the complexity of adsorption/desorption (ADS/DES) effects due to different interactions between catalysts constituents and the individual components of reaction mixture. Therefore, the aim was to describe the ADS/DES behavior of model organic compounds anisole (ANI) and guaiacol (GUA) and their mixture on the Ni and Cu catalysts supported on Al_2O_3. ADS/DES studies were conducted by means of the temperature programmed desorption techniques (TPD) and breakthrough curves measurements.

The number of adsorbed species of both organic compounds was much higher than that desorbed during TPD confirming chemisorption as predominant mode of adsorption. ANI and GUA adsorbed strongly on different sites. When GUA was adsorbed as the first component followed by subsequent ANI adsorption, the pre-adsorbed GUA hindered ANI adsorption resulting in lower ANI adsorption capacity. In the opposite case, both components were adsorbed in similar amounts as in the case of monocomponent adsorption. Weakly adsorbed GUA species adsorbed more strongly than ANI species that were consequently forced out / desorbed from the surface by GUA adsorption (Fig. 1a). For simultaneous adsorption (Fig. 1b), the effect of the concentration of each component was observed on its respective adsorption capacity.

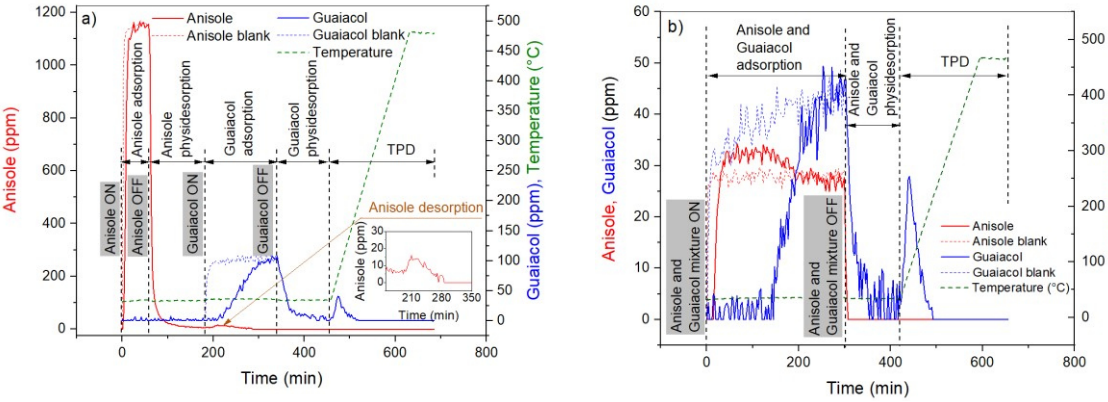

Fig. 1 Breakthrough curve and TPD for **a)** subsequent anisole and guaiacol adsorption and **b)** simultaneous anisole and guaiacol adsorption

Keywords: adsorption, phenolics, HDO catalyst, nickel, copper.

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In-situ characterization of the thermal treatment of Zn-Al Layered Double Hydroxides leading to the mixed oxides, followed by their subsequent reconstruction

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There is described the transformation of Zn-Al layered double hydroxides (LDHs) into the appropriate Zn-Al mixed oxides during their thermal treatment. In detail, the structure, composition, morphology and growth of ZnO and $ZnAl_2O_4$ phases are analysed. The obtained Zn-Al mixed oxides are attractive catalysts in the aldol condensation of furfural with acetone. Manuscript defines the region of the ZnO phase formation and their role on catalytic properties of Zn-Al mixed oxides formed. High values of the conversion of furfural well correlated with the low values of ZnO crystallite size and high values of the specific surface area. In detail, we have introduced a simple method based on diffuse reflectance spectroscopy with a potential to predict furfural conversion over Zn-Al mixed oxides in aldol condensation of furfural with acetone.

A memory effect is the ability to restore the original, lamellar layered double hydroxide structure. Herein, we have described the changes in the structural and basic properties of ZnAl mixed oxides during their transformation into ZnAl-reconstructed LDHs and the extraordinary properties of reconstructed ZnAl LDHs compared to the original ZnAl LDHs.

Keywords: layered double hydroxid, reconstructed materials, basic sites, Zn/Al based materials

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Titanium grafted MWW zeolites in the role of catalysts for selective oxidation of organic sulphides

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Nowadays catalytic materials with high hydrothermal stability, large specific surface area and the possibility to modify structure accessibility are desirable. Zeolites exhibit the above-mentioned unique features and other properties, such as crystalline microporous structure, surface acidity and ion-exchange potential ability [1]. Various transition metals have been applied to enhance catalytic activity in many chemical reactions. Titanium containing materials were found to be active in a variety of selective oxidation reactions. The content, as well as the form and aggregation of the metal species, exhibit a significant role in catalyst activity. The method of titanium complexes grafting on highly stable supports resulting in the formation of easily accessible, isolated Ti-species. The modification procedure requires support structures with the well-defined distribution of silanol groups, where Ti-species can be grafted. Layered silica zeolites of MWW topology were found to be suitable for this type of functionalisation [2].

In the studies, we performed a multi-step synthesis to obtain titanium modified 3D siliceous layered structure (Ti-ITQ-1) and its delaminated form (Ti-ITQ-2) with MWW zeolite topology. The structure of the obtained materials where examined by powder X-ray diffraction method. The chemical composition of the samples was determined by ICP-OES measurements. Textural properties were analysed using the method of low-temperature N_2 sorption. Metal form and aggregation were studied by UV-Vis-DR spectroscopy. The obtained catalysts were tested in the reactions of organic sulphide oxidation (e.g. diphenyl sulphide) with using hydrogen peroxide as an oxidant.

The obtained materials presented the desired structure and textural properties. The titanium was incorporated mainly in the form of highly dispersed tetrahedrally coordinated species. Both series of the catalysts, Ti-ITQ-1 and Ti-ITQ-2, showed promising performance in the selective diphenyl sulphide (Ph_2S) oxidation. Moreover, it has been concluded that in this type of catalytic system, the reaction takes place in two subsequent oxidation steps, where the primary product of Ph_2S oxidation is diphenyl sulphoxide (Ph_2SO), which in the next step is oxidised to the final product – diphenyl sulphone (Ph_2SO_2).

Keywords: MWW zeolites, Ti grafting, selective catalytic oxidation, diphenyl sulphide, hydrogen peroxide

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P.2.21

The effect of EDTA treatment on forms of copper species deposited on the surfaces of MCM-41 and MCM-48 modified by TIE method

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Mesoporous silicas exhibit promising capabilities in catalysis, attributed to unique properties such as evenly distributed pores, large specific surface area and high porosity. [1] However, these materials inherently do not possess ion-exchange abilities, making it difficult to deposit catalytically active components on their surfaces in a dispersed manner. Therefore, the process of applying catalytic elements uniformly and finely is intricate and costly, which severely limits their wider use. [2] Consequently, to depost uniform copper species on mesoporous silica's surfaces, a very specific functionalization procedure was used - modification by TIE method followed by a treatment with EDTA solution.

The TIE method is based on the exchange cationic surfactants bounded to the negatively charged silica surface (non-calcined materials) by Coulombic forces with metal cations. The TIE modification is performed on silica materials before calcination, as during the calcination process, the organic matrix is removed, and silanol groups, Si-OH, formed on the silica surface longer exhibit ion exchange abilities. [3] However, when modifying silica with a larger amount of copper by TIE method, the active phase is often deposited in a non-uniform form. For this reason, the samples after TIE modification were treated with EDTA solution to examine its effect on the deposited forms of copper.

Parent silica materials and copper-modified samples were characterized by XRD method (porous structure of the samples), low-temperature nitrogen sorption (textural parameters), UV-Vis-DRS (form and aggregation of deposited copper species), ICP-OES (chemical composition) and H_2-TPR (reducibility of catalysts). It has been demonstrated that EDTA acts selectively towards deposited forms of copper by removing dispersed copper cations from the silica surface, while leaving aggregated forms intact. This, in turn, can be applied in the design of catalysts for various processes where the aggregated form of the metal exhibits activity. **Keywords:** mesoporous silicas, copper, TIE method, catalysts

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Modified Pechini Synthesis of Perovskite-type oxide Catalysts

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Meeting the target of reaching net zero carbon emissions within the EU by 2050 necessitates the development of new technologies for energy storage and reduction of CO_2 emissions. One approach is the conversion of CO_2 to value added products. A key step in these processes is the reduction of the stable CO_2 molecule to CO, which can for example be achieved using the Reverse Water-Gas Shift reaction (rWGS), in which hydrogen is used as the reducing agent. The resulting synthesis gas can then be used to either produce basic chemicals (e.g.: Methanol) or sustainable aviation fuels (SAF) for energy storage.

Perovskite-type oxides have previously been found to be promising catalysts for this reaction. Their ABO_3 structure allows for a wide range of elemental compositions due to the possibility of A- and B-site doping. Furthermore B-site ions can segregate from the bulk under reducing conditions and form metallic nanoparticles on the surface. Tailoring this exsolution effect can be used for enhancing the catalytic activity for a specific reaction. A common synthesis pathway for this class of materials is the Pechini synthesis due to its simplicity and comparably higher surface areas over solid state syntheses [1]. However, the variability of the exact Pechini synthesis protocols can pose challenges when comparing results in literature. Studies have been carried out on the effect of pH on selected properties [2], but very little information can be found on how nanoparticle exsolution and catalytic activity are affected. In this work, the influence of these synthesis variations on the catalytic properties of $Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_3$, a potential rWGS catalyst [3], was investigated.

Variations in the synthesis were introduced by adding ammonia to adjust the pH of the precursor solution and adding different amounts of ethylene glycol (EG), two common modifications found in literature. Phase purity of the catalysts was determined using powder X-ray diffraction (XRD) and surface areas were measured using N_2 adsorption using the Brunauer-Emmet-Teller (BET) method. Furthermore, reducibility – particularly in regard to the exsolution behaviour – was examined using temperature programmed reduction (TPR) with 5 % H_2 in Ar. Finally, catalytic testing of the materials was performed in a reaction atmosphere of CO_2:H_2:Ar = 1:1:2 between 300 – 700 °C. The catalyst morphology and nanoparticle size were investigated before and after the reaction using scanning electron microscopy (SEM).

XRD measurements confirmed formation of a phase pure perovskite structure. Surface areas varied between different protocols and were the highest when a combination of EG addition and high pH was used in the synthesis. Results of the catalytic testing revealed differences in catalytic activity that could not be explained by surface area alone. Possible explanations are the differences in morphology that could be observed in SEM images. Additionally, TPR measurements showed two major peaks that correspond to the formation of oxygen vacancies at low temperatures and the exsolution process and subsequent material decomposition at higher temperatures. Their position and relative intensities were dependent on pH and additives especially for the low temperature vacancy formation. This indicates that the vacancy formation, which is a known driving force for the exsolution of nanoparticles, might be influenced by the choice of synthesis conditions.

Keywords: exsolution, synthesis variation, perovskite-type oxides

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How A-site cations influence the in-situ formation of metallic nanoparticles in perovskite oxide catalysts

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The fight against the steadily increasing amount of greenhouse gases in our atmosphere is one of the defining challenges of our time. A possible solution may be reducing and converting CO_2, closing the carbon cycle. Therefore, catalysts that are highly active and exhibit long-term stability are needed. A promising material class are perovskite-oxides as they can form metallic nanoparticles anchored in the surface in a process known as exsolution. It was shown that these exsolved nanoparticles are suitable for CO_2 utilization applications [1]. However, we still lack a fundamental understanding of the process and how to precisely control the shape and size of the exsolved nanoparticles. To deepen our understanding of exsolution, this study systematically varies the A-site of perovskite-oxides while observing both the effect on the catalytic activity for CO_2 reduction but also fundamental parameters like oxygen exchange kinetics and stability of the crystalline structure.

Based on previous work, the basic composition chosen for this study was $A_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_3$. with the variation of A = La, Nd, and Pr. Additionally, variants without Ca and Co were prepared to understand the effect of oxygen vacancy formation further. Based on catalytic tests using Reverse Water-Gas Shift reaction (rWGS), it becomes clear that the Pr-based material works better than the Nd and La-based materials. Additional XRD and SEM measurements after the reaction revealed that the formation of nanoparticles is promoted by Nd and Pr-based materials, respectively.

To further investigate the onset point of exsolution, we performed in-situ XRD measurements under reducing conditions, observing a clear difference in the temperature at which a metallic Co phase formed. Again, this measurement showed a preferred exsolution of the Pr-based material over its La and Nd counterparts. To fully understand this behaviour, we determined oxygen vacancy formation energy using Density Functional Theory calculations. From the experimental side, the oxygen exchange kinetics were determined using conductivity relaxation, and Pair Density Function measurements were performed.

Keywords: material design, CO_2 reduction, perovskite oxides

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Partial oxidation of methane to syngas on perovskite catalysts

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Compared to conventional steam reforming, partial oxidation of methane (POM) to synthesis gas (CO and H_2) is more energy efficient [1], furthermore yielding a H_2:CO ratio of 2 well suited for Fischer-Tropsch synthesis. Perovskites containing catalytically active elements can be used as precursors of supported metal catalysts, which form upon pretreatment in reductive environment or *in situ* via reduction of the perovskite by reaction gases. The synthesized perovskites lanthanum nickel oxide, lanthanum cobalt oxide and mixed lanthanum nickel/cobalt oxides have been characterized with XRD, SEM, BET and TPR and tested for POM reaction in a tubular flow reactor. The activation of the catalyst and the evolution of phases during the POM reaction have been monitored with *operando* XRD. Under specific conditions, cycles of activation and deactivation have been observed, which can also occur in a periodical manner, resulting in oscillations. This behaviour will be further investigated to determine the parameter space required for the oscillations and to provide insight into their mechanisms. The synthesis of the perovskites was carried out by different routes, such as the Pechini method and wet impregnation to determine the effect of the different procedures on nanoparticle morphology/composition and catalytic performance. Additional characterization methods such as XPS, UPS and *in situ* electron microscopy will be applied for more detailed understanding of the surface reactions. In the future, synchrotron-based *operando* XPS, XAS and XRD will enable to investigate the fast decomposition of the perovskite structure during the activation of the catalyst and the quick changes of the phases during oscillations.

Keywords: nickel catalyst, perovskites, partial oxidation of methane, synthesis gas, *operando* XRD

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P.2.25

Oxidation of cyclopentanone to glutaric acid over carbon-based catalysts

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Glutaric acid (GA) and its derivatives are relatively easily biodegraded and therefore it has started to be very important chemical for the production of bioplastics, and other chemicals; particularly surfactants, additives to dietary products and biologically active substances. GA was industrially produced as a side product in the production of adipic acid. Other possibility is the oxidation of cyclopentanone and cyclopentanol by concentrated nitric acid, or by the carbonylation of butyrolactone [1]. A few reports describe research on the oxidation of cyclopentanone with oxygen or air over homogeneous catalysts [2,3].
In this work, we investigated the catalytic performance of carbon-based catalysts in the liquid phase oxidation of bio-cyclopentanone to glutaric acid with molecular oxygen in a solvent-free system. The influence of the surface modification of carbon black Vulcan XC-72 (Cabot) on carbon-based catalyst activity and selectivity to glutaric acid as well as diacids with smaller carbon chains, succinic and oxalic acids, was studied. Commercial carbon black was demineralized before use with hydrochloric acid and subsequently calcined in nitrogen. Urea modified catalysts were prepared by the impregnation method as reported by Seredych [4]. Carbon supported metal catalysts were prepared by the wet impregnation method described in paper [5]. The nominal weight loading of metal was 1 wt. %. The prepared catalysts were characterized using XRD, XPS, nitrogen adsorption-desorption isotherms, acid-base titration and FTIR. The oxidation experiments were carried out in a stirred batch reactor with equipment for monitoring of oxygen consumption at temperature 90 °C and the pressure of 0.35 MPa. The reaction mixture was analyzed by GC and GC/MS.
Catalysts based on carbon black Vulcan showed high catalytic activity. Nevertheless, the selectivity on GA did not exceed 35%, neither over Vulcan itself nor after the addition of a metallic component. However, based on GCMS analyses of reaction intermediates, we believe that the reaction over-metal-free and metal-loaded catalysts proceeds by a different reaction mechanism. The advantage of these catalysts is their trouble-free recycling. The challenge remains, however, to recycle unreacted cyclopentanone and use by-products.

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Keywords: cyclopentanone, oxidation, carbon catalysts, glutaric acid.

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Single Atom Catalysts Cu/CeO_2 for CO and H_2 Adsorption: First-principles Study

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Single atom catalysts (SAC) have gained attention in heterogeneous catalysts due to their ability to reduce the use of expensive precious metal catalysts [1]. Copper-doped ceria catalysts have been reported for their activity and selectivity in oxidation of CO in H_2-rich conditions at low temperatures [2-3]. In this work we modelled single copper atoms supported on $CeO_2(111)$ for CO and H_2 adsorption, as the adsorption serves as the starting point for oxidation processes, using density functional theory (DFT) calculations. Perdew-Burke-Ernzerhof (PBE) functional together with Hubbard model using Dudarev scheme were used to treat exchange-correlation interactions (PBE+U). The adsorption energy of a single Cu atom on the $CeO_2(111)$ surface was calculated to be -3.14 eV, affecting the oxidation states of Cu^0 and Ce^{4+} when separated to become Cu^+ and Ce^{3+} in Cu/CeO_2 indicating the reducibility of Ce. The interaction of CO with the Cu adatom shows a chemical adsorption energy of -1.38 eV, more stable than that of H_2 adsorption, -0.37 eV. This clearly shows that the CO adsorption on the Cu adatom of Cu/CeO_2 is energetically preferable compared to the surfaces of CuO (-1.29 eV) or CeO_2 (>-1 eV) alone [2-4]. During H_2 adsorption, the H_2 bond slightly elongates to 0.82 Å, 9% longer than in the gas phase, demonstrating the activation of H_2 even on single atoms of noble metals deposited on the $CeO_2(111)$, as discussed by the work of Righi *et al.* [5]. These results suggest that the presence of a single Cu atom on CeO_2 surface enhances the adsorption strength of the CO molecule with the interaction distance of 1.80 Å, while for H_2 weak interaction is observed. Finally, this study shows promising potential of earth-abundant, low-cost single atom Cu catalysts on CeO_2 (Cu/CeO_2) for CO oxidation process.

Keywords: DFT, Single Atom Catalyst, Cu/CeO_2

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