2nd Forum of Young Researchers on Heterogeneous Catalysis

BOOK OF ABSTRACTS

YOURHETCAT 2024

14 – 16th of November, 2024

Szeged, Hungary

2nd Forum of Young Researchers on Heterogeneous Catalysis

Fighting climate change, most industrial technologies will not work without heterogeneous catalytic reactions. Understanding the catalytic processes, transferring and developing knowledge is essential. With this goal in mind, the 1st Forum of Young Researchers on Heterogenous Catalysis 2022 (YOURHETCAT 2022) was organized in Szeged, Hungary on July 11-13, 2022, hosted by ***the Hungarian Catalysis Society (HCS)*** with the help of ***The Secretariat of the Regional Committees of the Hungarian Academy of Sciences at Szeged (MTA SZAB)*** and the ***European Federation of Catalysis Societies (EFCATS)***.

Our main goal has remained since then to support and link talented young researchers working in the field of catalysis by organizing a high-quality international event free of charge, without any registration fees.

The presenters of the YOURHETCAT 2024 are Graduate and Postgraduate Students, Postdocs as well as Senior Researchers of National and ***European Catalytic Societies*** and the ***Young European Catalysis Network (YEuCAT)***. The program includes 5 plenary lectures, 25 student presentations, 29 posters and an extraordinary “pitch” presentation session by 7 brave students. Social activities are just as important, thus we organized a tour of Szeged, coffee breaks, dinners and a lunch to foster networking. We are expecting over 70 young researchers and Senior Researchers from all over Europe, trusting in the exchange of experience, knowledge transfers and the creation of new cooperation opportunities, building networks, which will lead to the strong connection of international catalysis research.

Best wishes for all Colleagues by the Organizing Committee,

András Sápi – Szeged

József S. Pap – Budapest

Tímea Benkó – Budapest

Ágnes Filep – Szeged

Published by the Hungarian Catalysis Society of the HAS
2nd Forum of Young Researchers on Heterogeneous Catalysis.
Book of Abstracts [PDF]

ISBN 978-963-7351-36-5

Our SPONSORS:

- **Hungarian Academy of Sciences (MTA)**
- **Hungarian Catalysis Society (HCS)**
- ***The Secretariat of the Regional Committees of the Hungarian Academy of Sciences at Szeged (MTA SZAB)***
- ***Hungarian Zeolite Association***
- ***European Federation of Catalysis Societies (EFCATS)***
- ***Young European Catalysis Network (YEuCat)***
- ***Equtechnik Ltd.***
- ***HUN-REN Centre for Energy Research***
- ***Bodri Wines***

PLENARY LECTURES

Jeroen van Bokhoven
Professor for Heterogeneous Catalysis at Institute for Chemical
and Bioengineering ETH Zurich, Switzerland

Head of Laboratory for Catalysis and Sustainable Chemistry
(LSK) Swiss Light Source, Paul Scherrer Institute

PL 1 - Catalysts under pressure

E-mail: jeroen.vanbokhoven@chem.ethz.ch

Introduction - *Jeroen A. van Bokhoven completed a degree in chemistry at Utrecht University (Netherlands) in 1995 and went on to obtain a PhD in inorganic chemistry and catalysis from the same university in 2000 (with honours). From 1999 until 2002 he was head of the XAS (X-ray absorption spectroscopy) users – support group at Utrecht University. In 2002, he moved to the ETH, where he worked as researcher in the group of professor Prins. In 2006 he obtained an SNF assistant professorship in the Department of Chemistry and Applied Biology. He was the 2008 recipient of the Swiss Chemical Society Werner Prize. Since 2010, Jeroen A. van Bokhoven has a Chair in Heterogeneous Catalysis at the Institute for Chemical and Bioengineering at ETH Zurich and is Head of Laboratory for Catalysis and Sustainable Chemistry at Paul Scherrer Institute. Van Bokhoven works in the field of heterogeneous catalysis aiming at producing better catalysts and processes that allow sustainable development. Goal is the determination of structure-performance relationships, which aid the design and construction of better catalysts for cleaner and more efficient processes. His main interests are heterogeneous catalysts and developing advanced tools in X-ray spectroscopy and scattering to study the catalyst structure under catalytic relevant conditions.*

Emanuele Moioli
Associate Professor of Chemical Plants at Politecnico di Milano,
Italy – Chairman of the Young European Catalysis Network

PL 2 - Catalysis and reaction engineering: A coupling across the scales to enable the energy transition

E-mail: **emanuele.moioli@polimi.it**

Introduction - *Emanuele Moioli is associate professor of chemical plants at politecnico di Milano, Italy, and guest scientist at the Paul Scherrer Institute, Switzerland. He holds a PhD degree in chemical reaction engineering from the FAU Erlangen-Nurnberg. He then moved to Switzerland for postdocs at the EPFL and at PSI. After a couple of years in industry at Hitachi Zosen Inova, he moved back to PSI after obtaining an Ambizione fellowship from the Swiss National Science Foundation. He received several awards for his research in the field of chemical reaction engineering, including the Hanns-Hofmann prize from DECHEMA and the innovation award from Hitachi Zosen Corporation (Japan).*

Brigitta Kocsis-M.
Television host, coach, trainer

PL 3 - Presentation and Pitch – How to Be Convincing in a Short or Even Shorter Time!

E-mail: **kbrbrigi@gmail.com**

Introduction - *Academic Journalist Award-winning television host, coach, trainer, former president of the Club of Hungarian Science Journalists. Her main field of expertise is STEM communication and the sphere of innovation and startups. For more than 10 years, she has been working as the editor-host of the weekly science magazine, called Novum in the Hungarian Public Television; acting as a host of events focusing on innovation; conducting career, business, executive and innovation coaching sessions; holding science communication and soft skills trainings.*

Juha Lehtonen
Research Professor
VTT Bioruukki Pilot Centre in Espoo, Finland

PL 4 - Production of sustainable aviation and marine fuels by catalytic technologies

E-mail: **juha.Lehtonen@vtt.fi**

Introduction - *Juha Lehtonen (D.Tech.) is a research professor of Sustainable Chemical and Catalytic Conversion Processes at VTT. He has a long career in industrial research organizations as a specialist of chemical reaction engineering, catalysis and development of biofuels, oil refinery and specialty chemicals processes. Before starting at VTT in 2016 he worked for four years as a professor of Industrial Chemistry at Aalto University (Espoo, Finland) concentrating on catalytic and thermochemical conversion of* CO_2 *and biomass to value added chemicals and fuels and catalyst development for these processes. He is an author or co-author of 101 peer-reviewed scientific publications.*

Csaba Janáky
Principal Investigator of the Photoelectrochemistry Research Group at the Department of Physical Chemistry and Materials Science at University of Szeged

PL 5 - Electrochemical processes for energy conversion: catalysts, electrodes, cells, and systems

E-mail: **janaky@chem.u-szeged.hu**

Introduction - *Csaba Janáky graduated as a chemist (2007) and economist (2009) at the University of Szeged, and obtained his PhD degree (2011) from the same university. He was a Marie Curie was a fellow at the UT Arlington (USA), and his project was selected as one of the program's success stories. In 2014, with the support of the MTA Momentum Program, he founded a research group at the University of Szeged. He has successfully built up a research group at the border of materials orientated electrochemistry and photoelectrochemistry, which carries out cutting-edge activities in both basic and applied research topics. This is indicated by 90 prestigious publications (full IF>800), 15 patent applications in the past 10 years, as well as foreign (e.g. ERC Starting, Consolidator and Proof-of-Concept Grant) and domestic grants. Fifteen of his papers were highlighted on the covers of prestigious journals (JACS, ACS Energy Letters, Advanced Energy Materials, Advanced Functional Materials, Chemistry of Materials Journal of Physical Chemistry C, Journal of Physical Chemistry Letters, ChemPhysChem). He is a member of several international scientific committees (e.g., ACS Energy Letters Editoral Advisory Board).*

ORAL CONTRIBUTIONS

OL 1 - Room temperature in situ hydrogenation of furfural over a nanocatalyst

Chand Adarsh Ashwani[1], Palanivel Subha[1], Putla Sudarsanam[*1]

[1]*Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana, India – 502284*

Corresponding author: Putla Sudarsanam, Sudarsanam.putla@chy.iith.ac.in

Abstract

The necessity of converting biomass waste into value-added materials, chemicals, and fuels is essential for a sustainable future[1]. Non-edible lignocellulosic biomass (e.g., wood, corn stover, bagasse, and forestry residues) majorly comprises three components, namely cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are composed of carbohydrates, and lignin is a functional aromatic polymer, which is also obtained as waste from the pulp/paper industry and 2G ethanol biorefinery[2]. In particular, furfural is a hemicellulose-derived platform compound that can be valorized into various chemicals and fuels having widespread industrial importance. This project involves the catalytic transfer hydrogenation of biomass-derived furfural to furfuryl alcohol at room temperature over a synergistic PdCu/TiO_2 nanoalloy catalyst.

Compared with homogeneous liquid catalysts, heterogeneous solid catalysts have numerous advantages, such as easy synthesis, outstanding hydrothermal stability, and efficient reusability[3]. Most biomass valorization reactions involve hydrogenation and hydrodeoxygenation in the presence of a hydrogen source. Using hydrogen gas requires harsh reaction conditions such as high pressure and temperature. In addition, it poses several disadvantages, such as cost-ineffectiveness, safety ambiguities, and economic barriers that limit the sustainability aspects of the process. Hence, this work aims to use a liquid hydrogen carrier as a hydrogen source, which can release hydrogen in situ and canbe utilized for biomass hydroprocessing[4].

The catalyst must possess both the acid sites and redox sites to facilitate the aforementioned hypothesis. This involves the synthesis of TiO_2 nanorods, which provide the necessary acid sites for the reaction and serve support, as well as the alloying of PdCu (redox sites) on the surface of the TiO_2 nanorods[5]. The TiO_2 nanorods, and then alloying of PdCu on TiO_2 nanorods are achieved by the hydrothermal andsolvothermal methods, respectively[6]. The as-synthesized PdCu/TiO_2 nanoalloy is used as the heterogeneous catalyst for hydrogenating biomass-derived furfural into furfuryl alcohol at room temperature using a liquid hydrogen carrier.

The PdCu/TiO_2 nanoalloy catalyst gave higher yields of furfuryl alcohol at room temperature and ambient pressure compared with the monometallic counterparts. The hot filtration studies confirm the heterogeneity of the reaction. The catalyst showed excellent reusability till 5 cycles. The optimum catalytic activity is owing to the alloying and synergistic effect of Pd-Cu and the significant hydrogen spillover effect of TiO_2. The structure-activity relationship is derived by powder XRD, N_2 adsorption-desorption analysis, XPS, TEM-EDAX, in situ pyridine FT-IR, CO-sweep chemisorption, and H_2-TPR.

Keywords: Nanoalloy catalyst, Biomass valorization, Synergistic effect, In situ hydrogenation.

References

(1) Sudarsanam, P.; Zhong, R.; Van den Bosch, S.; Coman, S. M.; Parvulescu, V. I.; Sels, B. F. *Chem Soc Rev* **2018**, *47* (22), 8349–8402.
(2) Sudarsanam, P.; Peeters, E.; Makshina, E. V.; Parvulescu, V. I.; Sels, B. F. *Chem Soc Rev* **2019**, *48* (8), 2366–2421.
(3) Gupta, N. K.; Reif, P.; Palenicek, P.; Rose, M. *ACS Catal* **2022**, *12* (16), 10400–10440.
(4) Sharma, D.; Choudhary, P.; Mittal, P.; Kumar, S.; Gouda, A.; Krishnan, V. *ACS Catal* **2024**, *14* (6), 4211–4248.
(5) Sudarsanam, P.; Köckritz, A.; Atia, H.; Amin, M. H.; Brückner, A. *ChemCatChem* **2021**, *13* (8), 1990–1997.
(6) Zhang, W.; Wang, Y.; Gu, B.; Tang, Q.; Cao, Q.-E.; Fang, W. *ACS Sustain Chem Eng* **2023**, *11* (34), 12798–12808.

OL 2 - CO_2 Hydrogenation to C_{5+} hydrocarbons using Na-Fe_3O_4/Fe_5C_2

Sara Najari[1], Samrand Saeidi[1,2], András Sápi[1], Zoltán Kónya[1]

[1]Department of Applied and Environmental Chemistry, Interdisciplinary Excellence Centre, University of Szeged, Rerrich Béla tér 1, Szeged 6720, Hungary
[2]Department of Technologies and Installations for Waste Management, Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland

Corresponding Author: Sara Najari, sara.najari@chem.u-szeged.hu

Abstract

Short Introduction

Fe-based catalysts are promising for CO_2 hydrogenation, particularly in producing C_2−C_4 olefins and C_{5+} hydrocarbons. Fe_5C_2 is recognized as the active phase in Fischer-Tropsch synthesis, making it crucial to understand how active phases affect product distribution. Additionally, factors like the oxide/carbide ratio, spatial distance, and reduction treatment can be adjusted to enhance the catalysts efficiency in generating valuable hydrocarbons.

Hypothesis and aim

In this study, Fe_5C_2, known as the active phase in CO_2 hydrogenation, is synthesized separately and physically mixed with Na-Fe_3O_4. This approach aims to investigate how key parameters influence product distribution when the active phase is present in the initial catalyst.

Methodology

Iron carbide was synthesized by carburizing iron oxalate dihydrate, while Fe_3O_4 was prepared via coprecipitation method and impregnated with $NaNO_3$. The reactor was pressurized to 3-5 MPa with a gas hourly space velocity (GHSV) of 4000-5000 mL h^{-1} $gcat^{-1}$ with a H_2/CO_2 feed (3:1 ratio) at 320-340°C, and the products were analyzed online using a gas chromatograph.

Results and main advancements

It was found that mixing iron carbide (Fe_5C_2) with iron oxide (Na-Fe_3O_4) increased CO_2 conversion and reduced CO selectivity, attributed to better oxide phase reduction and CO_2 adsorption. The ratio of Na-Fe_3O_4 to Fe_5C_2 in the initial catalyst significantly influenced the carbide content and CO_2 hydrogenation performance. Closer proximity between the two components enhanced selectivity for C_2-C_4 olefins and C_{5+} hydrocarbons, while separate stacking led to more hydrogenated products. Reduction treatment improved catalytic performance by altering carbon structures, while non-reduced samples favored light paraffins and CH_4. Overall, adjusting the oxide/carbide ratio, proximity, and reduction treatment can optimize CO_2 hydrogenation for valuable hydrocarbon production [1].

Keywords: CO_2 hydrogenation, iron oxide, iron carbide, C_{5+} hydrocarbons

Acknowledgments

Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

References

[1] S. Najari, S. Saeidi, A. Sápi, Á. Szamosvölgyi, Á. Papp, A. Efremova, H. Bali and Z. Kónya, *Chemical Engineering Journal, 485,* **2024**, 149787.

OL 3 - Utilizing aqueous-phase reforming to extract value from biorefinery residual waters

J. Palo[1], M. Reinikainen[1], J. Lehtonen[1]

[1] *VTT Technical Research Centre of Finland Ltd, P.O. Box 1000, FI-02044 Espoo, Finland*

Corresponding Author: J.Palo, jasmiina.palo@vtt.fi

In the middle of global energy crisis, novel technologies are needed. Biorefineries reply to this challenge in terms of converting biomass into biofuels. As a downside, those facilities produce a significant amount of unutilized process water with dissolved organic compounds. Catalytic aqueous-phase reforming (APR) can convert these compounds into added-value products, hydrogen and alkanes. Nickel and other base metal catalysts are often studied in APR for their cheaper price and good H_2 selectivity, while noble metal catalysts like platinum or palladium offer improved stability [1]. For their content of organic residues, biorefinery waters are ideal for APR, but the challenging environment requires catalysts to endure hot, compressed water. In addition, limited information exists on APR of aromatic oxygenates like phenols, as most literature focuses on easily reformed molecules like alcohols, sugars, and polyols [1].

This work studied the APR of compounds present in biorefinery waters, including less explored aromatics. The studied components were methanol, acetic acid, phenol, and 4-methylcatechol. The experiments were conducted over three Cu- or Co-doped Ni catalysts and one Pt catalyst at 230 °C and 32 bars. Initially, the selected materials were screened with model compound solutions, each containing only one organic component at a time with a concentration of 5 wt.%. Following this, the best catalysts in terms of stability and productivity were selected to be studied with solutions containing all four components with an organic concentration of 10 wt.% total.

The Ni catalysts were not suitable for acidic solutions such as phenols and acetic acid due to severe leaching of active metals. However, the Pt catalyst showed good stability and conversion (10%) with methanol and acetic acid but no activity with phenol. For 4-methylcatechol, the initial conversion was high, up to 30%, but dropped to less than half of the original value after 60 minutes on stream. The commercial Pt/AC and $NiCo/ZrO_2$, the best base metal candidate, were then studied with the 4-component mixture. Similarly to the 1-component experiments, the nickel catalyst deactivated, albeit at a slightly lower rate. The Pt/AC catalyst showed a reasonably high conversion with all compounds, ranging from 10% to 70%. Interestingly, a synergistic effect was found in experiments with the mixture as also phenol, which had no activity when tested individually, now had a conversion up to 30%. The H_2 and CO_2 selectivity was 23.8% and 34.0%, respectively. Additionally, a small fraction of methane was detected in the gas phase. In the liquid stream, mostly liquid products from phenol hydrogenation and hydrodeoxygenation of 4-methylcatechol were detected, with a corresponding selectivity of 40.7%.

Keywords: Aqueous-phase reforming, hydrogen, phenolic compounds

References

(1) G. Pipitone, G. Zoppi, R. Pirone, and S. Bensaid, *Int. J. Hydrogen Energy*, *“A critical review on catalyst design for aqueous phase reforming,”* vol. 47, **2022**, pp. 151–180.

OL 4 - From industrial CO_2 emissions to light olefins

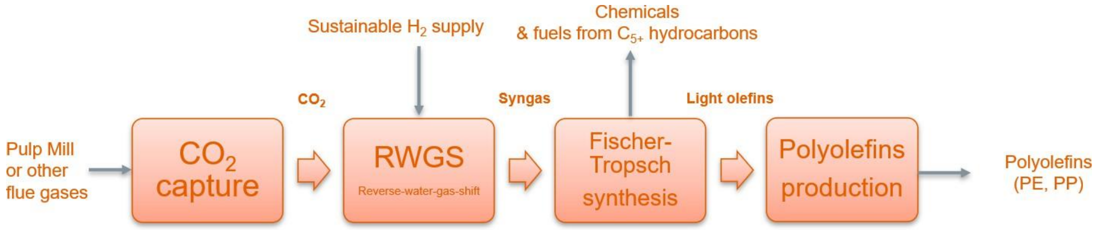
Eveliina Mäkelä[1], Niko Heikkinen[1], Ida Uotila[1*], Antero Laitinen[1], Matti Reinikainen[1], Juha Lehtonen[1]

[1]VTT Technical Research Center of Finland, Tietotie 4E, 02150 Espoo, Finland

Corresponding author: ida.m.uotila@vtt.fi

Light olefins (C_2-C_4) are among the most important industrial chemicals as being intermediates for poly- or co-olefins. Currently, they are almost merely produced by steam cracking of fossil feeds.[1] There is a global need to both renew the feedstock base for plastics production as well as to reduce the overall CO_2 emissions.

The main objective of this research project (Business Finland's Forest CUMP) is to provide a proof-of-concept of the bench scale production of light olefins from industrial pulp mill CO_2 emissions and green hydrogen produced by water electrolysis (Scheme 1). VTT's Mobile Synthesis Unit,[2] which combines reverse water-gas shift (RWGS) and Fischer-Tropsch (FT) technologies, is applied for maximizing either the direct production of light olefins or heavier products, such as naphtha, intended as a steam cracker feed.



Scheme 1. The approach for producing light olefins and steam cracker feed from CO_2.

To study the naphtha steam cracking route, the produced FT crude (final boiling point 361 °C) was distilled to a naphtha range product (final boiling point 212 °C). Both the oil and the naphtha contained roughly 10-15 wt.% olefins and 6 wt.% oxygenates with the rest being mainly linear paraffines. Hydrotreatment of both feeds was conducted at VTT's high-throughput reactor system utilizing a self-prepared, sulfide free supported metal catalyst. At first, a low reaction temperature was applied to saturate >99 wt.% of the olefins after which a higher reaction temperature was applied to remove majority of the oxygenates (<100 ppm O) without isomerization. In total, 6-10 kg of each high-quality steam cracker feed was produced to demonstrate the production of biobased light olefins.

Keywords: Light olefins, CO_2 utilization, Fischer-Tropsch synthesis

References

(1) Amghizar, I.; Dedeyne, J. N.; Brown, D. J.; Merin, G. B.; van Geem, K. M. *React. Chem. Eng.* **2020**, 5, 239-257.

(2) Vázquez, F. V.; Koponen, J.; Ruuskanen, V.; Bajamundi, C.; Kosonen, A.; Simell, P.; Ahola, J.; Frilund, C.; Elfving, J.; Reinikainen, M.; Heikkinen, N.; Kauppinen, J.; Piermartini, P. Power-to- X technology using renewable electricity and carbon dioxide from ambient air: SOLETAIR proof-of-concept and improved process concept, *J. CO2 Util.*, **2018**, *28*, 235–246.

OL 5 - The catalytic activity of waste-derived biochar towards trimethoprimdegradation by Peroxymonosulfate activation

Dinesh Chandola[1], Gábor Kozma[2], Zsuzsanna László[3] and Tünde Alapi[1]

[1]Department of Molecular and Analytical Chemistry, University of Szeged
[2]Department of Applied and Environmental Chemistry, University of Szeged [3]Department of Biosystem Engineering, Faculty of Engineering, University of Szeged

Dinesh Chandola: dinesh.chandola@chem.u-szeged.hu

Abstract

Biochar is traditionally known for its use as an adsorbent in water purification. Still, recent studies reveal its potential as a catalyst for activating persulfate ions (PS) and generating reactive species for the elimination of organic trace pollutants. The chemical-free modification techniques like ball milling (BM) are essential to enhance the catalytic activity of biochars. However, the underlying mechanism is unclear and further investigation is needed for a comprehensive understanding. This study aims to synthesize biochar catalysts from waste materials, modify them with ball milling, and examine the catalytic activity for peroxymonosulfate (PMS) activation and degradation of trimethoprim (TMP), a widely used antibiotic.

Poplar wood (PW), corn cob (CC), and grass pellets (GP) were pyrolyzed at 400°C to 800°Cand modified through ball milling and characterized with FTIR, Raman, BET specific surface area (SSA), TGA, and XPS before and after modification. The catalyst and PMS dose were optimized during the decomposition of TMP. The effect of radical scavengers was studied to determine the role of various reactive species. Additionally, the bio-catalysts were tested in biologically treated domestic wastewater as a matrix, and the reusability of the biochar was assessed for durability.

Enhanced degradation efficiency with decreased adsorption capacity was observed as pyrolysis temperature increased from 400°C to 700 °C. The degradation efficiency of TMP depended on the raw material and varied in this order GP-BC (93.3%) > CC-BC (78.25%) > PW-BC(71.51%) using 2 mM PMS and 3 g/L biochar (700 °C) dose, respectively. Ball milling highly enlarged the specific surface area, enhanced the adsorption efficiency, accelerated the degradation, and reduced the required dose of PMS to 0.2 mM and 0.5g/L. This suggests that ball-milling has led to surface modification and the creation of new active sites, enhancing the performance of biochar. The radical scavenger study confirmed radical ($SO_4^{\bullet-}$ and $\bullet OH$) and non-radical species ($^1O_2$) involvement in TMP degradation. Biologically treated wastewater as amatrix decreased the efficiency; however, the higher dose of biochar and PMS can compensate for the negative effect.

In conclusion, bio-catalysts derived from waste biomass can be effective in AOPs and BM modification can enhance their catalytic efficiency. Radical pathways can be generated by BM modification, unlike non-milled bio-catalysts. The negative impact of water matrices can be mitigated by enhancing the dose of catalyst and PMS. The biochar demonstrated sufficient durability for up to three cycles, although regeneration may restore its efficiency.

Keywords: water treatment, antibiotic, adsorption, advanced oxidation process

Acknowledgments *This work was sponsored by the National Research, Development, and Innovation Office-NKFI Fund OTKA, project number FK132742.*

OL 6 - Catalytic valorization of Ulvan polysaccharide toward biochemicals in the presence of Nb@zeolite catalysts

Magdi El Fergani, Natalia Candu, Iunia Podolean, Simona M. Coman

Department of Inorganic Chemistry, Organic Chemistry, Biochemistry and Catalysis, Faculty of Chemistry, University of Bucharest, 4-12 Regina Elisabeta Av., 030018 Bucharest, Romania

Corresponding Author: Magdi El Fergani, magdi.belkassim@drd.unibuc.ro

Abstract

There is growing recognition of increased research efforts aimed at developing new biomass-based processes for bio-production that are environmentally acceptable in the chemical industry. These processes are considered carbon-neutral, as they do not add extra carbon dioxide to the atmosphere [1]. In this context, green algae of the order Ulvales are frequently associated with algal blooms in nutrient-rich coastal areas, leading to the accumulation of significant biomass that is currently underutilized. Nevertheless, the complex sulfated polysaccharides called ulvans present in their cell walls could be a promising source of novel biomolecules because of their unique composition and structural characteristics [2].

This study aims to advance the marine bio-economy by valorizing U. lactuca and its polysaccharide ulvan to biochemical. In this context, innovative and efficient Nb@zeolite catalysts were developed and applied in the one-pot conversion of Ulvan extracted from Ulva lactuca into furoic acid (FUR) and rhamnose (Rha) in a biphasic system.

The synthesized Nb@Beta18 and Nb@Y30 nanostructured catalysts were comprehensively characterized using XRD, BET, DRIFT, NH_3-, CO_2-TPD, and XPS techniques. The catalytic tests were conducted in batch mode as follows: 0.06 g of catalyst was added to 0.05 g of ulvan in water. After sealing, the reactor was heated to 140-180°C, under stirringfor 6-24 h. Under comparable conditions, additional catalytic tests were performed in a biphasic solvent consisting of an aqueous solution of 20% NaCl and an organic solvent, methyl-isobutyl-ketone (MIBK). Characterization of the prepared catalysts confirmed that the NbO_x nanoparticles were effectively formed onto the support. The preliminary results at 12h and 180°C demonstrated that the Nb@Beta18 catalysts achieved a conversion of 46.5% ulvan, with a selectivity of 23.5% in FUR. In contrast, the Nb@Y30 catalysts resulted in a selectivity of 37.1 in Rha for a conversion of 35.5% for ulvan. A comprehensive analysis of the optimal catalytic features and reaction conditions, as well as the correlation between the catalytic performance and properties, will be provided.

Keywords: Ulvan, HMF, rhamnose, Nb@zeolite, biphasic system

Acknowledgments: The Romanian Ministry Research and Digitalization is acknowledged for funding within the grant PNRR-III-C9-2022-I5-18, *ResPonSE* - Project, No. 760010/2022.

References

[1] P. Sudarsanam, R. Zhong, S.V.D. Bosch, S.M. Coman, V.I. Parvulescu, B.F. Sels, *Chem. Soc. Rev.* 47, **2018**, 8349−8402.

[2] A. Robic, D. Bertrand, J.-F. Sassi, Y. Lerat, M. Lahaye. *J. Appl. Phycol.* 21, **2009**, 451–456.

OL 7 - Visible light Photocatalytic CO_2 Hydrogenation with Hierarchically Conjugated and Porous Polyacetylene Networks

Harshita Chawla[1], Andras Sapi[1]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Hungary*

Corresponding Author: Andras Sapi, sapia@chem.u-szeged.hu

Abstract

Herein a series of functionalized hierarchically porous network of polyacetylene catalysts were implemented for visible light driven photocatalytic CO_2 hydrogenation, using hydrothermally fabricated ZnO photocatalyst as reference. Characteristic studies reflected polymeric structure containing highly porous structure, π-conjugation and various functional group that led to better interaction with CO_2 molecules, higher surface adsorption, and further better hydrogenation on catalytic surface. The TK-166 catalyst exhibited production rate of 14.2 $\mu molg^{-1}h^{-1}$ for CO and 3.2 $\mu molg^{-1}h^{-1}$ for CH_4.

Keywords: CO_2 hydrogenation, Polyacetylene network, visible light photocatalysis, π-conjugation

References

[1] Šorm, D., Brus, J., Pintar, A., Sedláček, J., & Kovačič, S. (2024). Hierarchically Porous Polyacetylene Networks: Adsorptive Photocatalysts for Efficient Bisphenol A Removal from Water. ACS Polymers Au.

[2] Yadav, M., Gyulavári, T., Kiss, J., Ábrahámné, K. B., Efremova, A., Szamosvölgyi, Á., ... & Kónya, Z. (2023). Noble metal nanoparticles and nanodiamond modified strontium titanate photocatalysts for room temperature CO production from direct hydrogenation of CO2. Journal of CO2 Utilization, 78, 102621.

[3] Armaković, S. J., Armaković, S., & Savanović, M. M. (2024). Photocatalytic Application of Polymers in Removing Pharmaceuticals from Water: A Comprehensive Review. Catalysts, 14(7), 447.

[4] Hasan, M. B., Parvez, M. M., Abir, A. Y., & Ahmad, M. F. Conducting Organic Polymer: Concept, Applications and Role in Controlling Environmental Pollution. Applications and Role in Controlling Environmental Pollution.

[5] Zhang, J., Jiang, J., Lei, Y., Liu, H., Tang, X., Yi, H., ... & Gao, F. (2024). Photocatalytic CO2 reduction reaction: influencing factors, reaction pathways and dominant catalysts. *Separation and Purification Technology*, *328*, 125056.

OL 8 - Persulfate ions assisted heterogeneous photocatalysis of zinc oxide to eliminate harmful organic compounds

Bence Veres, **Tünde Alapi**

Department of Molecular and Analytical Chemistry, University of Szeged,
H-6720 Szeged, Dóm tér 7, Hungary

Corresponding Author: Bence Veres, veres.bence@chem.u-szeged.hu

Abstract

In wastewater treatment, the removal of non-biodegradable, biologically active trace pollutants is an urgent problem, to which the use of advanced oxidation processes (AOPs), including heterogeneous photocatalysis, offers a solution. On the surface of a photoexcited semiconductor photocatalyst, the photogenerated charge carriers (holes (h^+_{vb}) and electrons (e^-_{cb})) can react with adsorbed substances, resulting in the formation of radicals that can initiate the transformation of organic materials. The efficiency of this process can be enhanced by adding additional oxidizing agents to the system, such as persulfate ions (peroxymonosulfate (HSO_5^-, PMS) and peroxydisulfate ($S_2O_4^{2-}$, PDS)), due to the formation of the highly reactive $SO_4^{\bullet-}$.

The effect of PMS and PDS were investigated in the case of ZnO, a UV active photocatalyst (i.e. ZnO/PMS and ZnO/PDS processes) to remove organic substances (trimethoprim antibiotic (TRIM), nitrobenzene (NB) and 1,4-hydroquinone (HQ)) from water. The suspensions were irradiated with LED light sources emitting 367 and 398 nm photons.

First, the effect of photocatalyst loading, PMS/PDS dose, and photon flux were investigated and optimized. PMS and PDS significantly increased the photocatalytic efficiencies, even in O_2-free suspensions due to the excellent electron acceptor properties of the persulfate ions. The addition of various radical scavengers proved that $SO_4^{\bullet-}$, $^{\bullet}OH$, and $^1O_2$ had a significant role in the transformations, however, their relative contribution depended on the target substance. Furthermore, the role of emerging H_2O_2 and the transformation of the oxidant (PMS/PDS) were also investigated. The effect of PDS, and H_2O_2 on the surface of ZnO was investigated by XPS method.

The effect of biologically treated communal wastewater (BTWW) was tested and found to drastically decrease the photocatalytic efficiency of ZnO. Both organic and inorganic components can influence the surface properties of a photocatalyst, where the main processes take place, creating a competition between the organic substances and inorganic ions for adsorption sites and photogenerated charges. Furthermore, matrix components, like inorganic ions, can react with $^{\bullet}OH$ and $SO_4^{\bullet-}$ and change the radical set. Examining the individual effects of Cl^- and HCO_3^- showed that mainly HCO_3^- was responsible for the lower efficiency, probably due to the hindered transformation of PDS on the ZnO surface. Additionally, changes in mineralization were also investigated through total organic carbon (TOC) measurements.

Keywords: heterogeneous photocatalysis; persulfate ion; trimethoprim; nitrobenzene; zinc oxide

Acknowledgments This work was sponsored by the National Research, Development, and Innovation Office-NKFI Fund OTKA, project number FK132742.

OL 9 - Mechanism of Oxygen Electrocatalytic Reactions in External Magnetic Field

Áron Klonka[1], Gergő Ballai[1], Henrik Haspel[1,2], Zoltán Kónya[1,2]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Abstract

Reducing the global carbon-dioxide emission could play a major role in mitigating the effect of the anthropogenic climate change. To this end, the decarbonization of large chemical industries using hydrogen as raw material (the production of ammonia and fertilizers, steel etc.) is essential. Nowadays, hydrogen is produced from natural gas by steam-methane reforming (SMR) and the water-gas shift reaction (WGSR) resulting in massive greenhouse gas emission; hence the name ‘grey hydrogen’. The future will be the so-called “green” hydrogen, produced via a carbon-neutral way, preferably electrochemical water splitting. One of the main drawbacks of the latter is the high overvoltage of the anodic water oxidation reaction (oxygen evolution reaction, OER), which can be reduced by applying a strong external magnetic field at the electrode surface. The realization of a hydrogen economy, however, also needs the development of utilization technologies. Fuel cells can transform hydrogen and oxygen into water, where the liberated electrons can be used in an external electrical circuit. Here, the cathodic oxygen reduction reaction (ORR) can generate either hydroxide or peroxide ions, whereas the latter could be detrimental to the carbonaceous catalyst supports. It is known from the literature, that external magnetic field can affect the reaction path and alter the product distribution at the cathode. An essential tool for investigating the reaction mechanism of electrochemical reactions is the rotating disc electrode (RDE). Here, we designed and fabricated an RDE setup for studying magnetic electrochemistry, a method not commercially available to this date. The constructed RDE tip encased a strong NdFeB magnet bar and can be used with the conventional rotator. The RDE setup was tested and validated on benchmark electrocatalysts, which were proven active in magnetically enhanced oxygen evolution and reduction reactions.

Keywords: Oxygen evolution reaction, oxygen reduction reaction, electrocatalysis, magnetic electrochemistry

OL 10 - Titanium-molybdenum mixed oxide-carbon composites from mixtures of graphite oxide (GO) and graphene nanoplatelets (GNP) as novel supports of Pt electrocatalysts

Ilgar Ayyubov[1], Emília Tálas[1], Irina Borbáth[1], Zoltán Pászti[1], László Trif[1], Ágnes Szegedi[1], Tamás Szabó[2], Kadosa Sajdik[2], András Tompos[1]

[1]Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, ELKH, Magyar Tudósok körútja 2, H-1117 Budapest, Hungary [2]Department of Physical Chemistry and Materials Science, University of Szeged, H- 6720 Szeged, Rerrich Béla tér 1, Hungary

Corresponding Author: **Ilgar Ayyubov, ilgar.ayyubov@ttk.hu**

Abstract

Polymer Electrolyte Membrane Fuel Cells (PEMFCs) are promising electrochemical devices to convert chemical energy of H_2 into electrical energy directly. Since one of the main components of PEMFCs, the traditional carbon supported Pt catalyst (Pt/C) can suffer from degradation, one of the main directions of studies remains the development of new supports providing stability.

In this work 75wt.%$Ti_{0.8}Mo_{0.2}O_2$-25wt.%$GNP_{1-x}GO_x$ (x=0.25; 0.5; 0.75) type composite supported Pt catalysts were synthesized by using graphite oxide (GO) and graphene nanoplatelets (GNP) mixture as a carbon component. The goal was to combine the corrosion resistance and nanoparticle-stabilizing ability of TiO_2, the good co-catalytic properties of Mo, the large surface area and high conductivity of non-traditional carbon [1]. Previously we showed that the stability of the Pt catalyst supported on composites with GNP derived carbon was less than that of the GO derived one [2]. Therefore, it was aimed to improve the properties of the GNP containing composite by using GO since it is known from the literature that GO behaved as stabilizer of GNP slurry. It has also allowed to obtain lower costed catalyst compared to GO-derived carbon containing catalyst since costly GO is partially replaced with cheaper GNP. For characterization of the samples XRD, XPS, TEM, TG-MS, N_2 adsorption, cyclic voltammetry, rotating disc electrode (RDE) tests were performed.

The electrocatalyst synthesized with the GNP/GO ratio of 1:1 had much higher electroconductivity which reflected itself on other parameters as well, such as the highest ECSA and the highest ORR activity compared to the other analogues. In a long-term stability test of 10,000 polarization cycles, this catalyst was the most stable one with an ECSA loss of 21.2%, while all synthesized catalysts outperformed Pt/C (Figure 1).

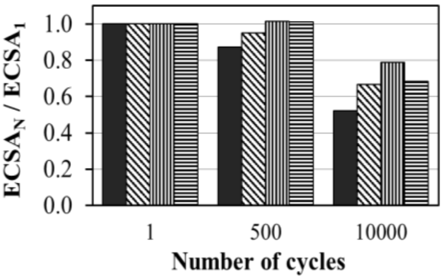


Figure 1. ECSA change during 10,000 cycles stability test for Pt/$Ti_{0.8}Mo_{0.2}O_2$–$GNP_{1-x}GO_x$ catalysts: x=0.25 (diagonal stripes), x=0.5 (vertical stripes) x=0.75 (horizontal stripes), 20 wt.% Pt/C (solid fill)

Keywords: graphene nanoplatelets, graphite oxide, carbon, PEMFC, cathode catalyst

Acknowledgments Project no. RRF-2.3.1-21-2022-00009, National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

References

[1]Borbáth, I. et al. *Appl. Catal. A* 620, **2021**, 118155.

[2]Ayyubov, I. et al. *Nanomaterials* 14 (12), **2024**, 1053.

OL 11 - Improving the reliability of electro catalysis studies with accurate flow and pressure control

Pieter Brouwer[1], Attila Kürti[2]

[1]Market Developer Renewable Energy at Bronkhorst High-Tech B.V.
[2]Equtechnik Kft Budapest

Corresponding Author: P. Brouwer, p.brouwer@bronkhorst.com

Abstract

In research projects, one should focus on the core of the project. Experiments are part of the research. In practice, setting up a reliable experiment is time consuming. Nevertheless, the effect of measurement uncertainty of a setup is often underestimated.

In electro catalysis, e.g. in fuel cells or electrolyzers, accurate measurement of gas and liquid flows is essential. However, instrumentation is not perfect and could introduce uncertainties that you do not see immediately. Especially when you are looking for small changes in results, it could be disturbed by those effects.

Examples of research topics in electro catalysis where reliable flow measurement and control is difficult to realize are: measuring Faradaic efficiency, measuring cross over effects in electrolyzers, stabilizing differential pressure over a membrane, back pressure control, measuring humidified hydrogen flow.

Some of these examples are presented and solutions are considered.

A deeper look is taken at specifications such as accuracy, repeatability and uncertainty. What do they mean and how can you deal with them?

Bronkhorst is a specialist in flow control and a well-known partner for research projects. Our sales partners around the world can help you improve your measurement setup.

Keywords: flow control, experiments, electrolysis, fuel cells, catalysts

OL 12 - Critical aspects on the etherification of glycerol with ethanol using Amberlyst-15

M. Samperi[1*], S. Donato[1], S. Todaro[1], M. Santoro[1], F. Randazzo[1], A. Cajumi[2], F. Arena[2], G. Bonura[1], C. Cannilla[1]

[1] *CNR-ITAE, via S. Lucia sopra Contesse 5, 98126 Messina, Italy.*
[2] *Università degli Studi di Messina, Dip. Ingegneria, c.da Papardo, 98166 Messina, Italy.*

***Corresponding Author: Mario Samperi, mario.samperi@itae.cnr.it**

Abstract

Biofuels are gaining significant recognition as a crucial renewable energy source, especially for their potential to mitigate greenhouse gas emissions and reliance on fossil fuels. In the field of biodiesel production, the valorisation of glycerol, main by-product of the process, has become a prominent research area for enhancing biofuels quality, efficiency, and environmental impact[1]. By means of etherification reaction, glycerol can be transformed into oxygenated poly-substituted ethers that improve combustion and stability, reduce viscosity, making biodiesel easier to blend with petroleum diesel. Moreover, they contribute to reduce pollutants emission like particulate matter and unburned hydrocarbons. In the glycerol etherification process, various alkylating reagents, i.e. alkenes or alcohols, and solid catalysts, as sulphonic resins or acidic zeolites can be employed[2] influencing reaction efficiency, selectivity, glycerol ethers yield and the overall cost of a large-scale production[3]. In this work, the etherification of glycerol has been studied in presence of ethanol, an alcohol readily available on the market and less expensive compared to other alkylating agents, to make sustainable the entire biofuel production process. However, primary alcohols have the drawback of requiring harsher reaction conditions for their activation. The etherification has been carried out in a batch reactor in a wide temperature range using Amberlyst-15, a well-known commercial ion-exchange resin widely used for this reaction. Main results show that glycerol conversion, yield and selectivity to di- and tri- ethers are mostly dependent on temperature rather than the other parameters analysed (pressure, reaction time, catalyst amount, ethanol/glycerol ratio), increasing up to 86% of conversion @ 220°C. On the other hand, irrespectively of what is generally not highlighted in recent literature[1], experimental data show that the catalyst performance and stability are negatively affected by temperature, leading to a drastic deactivation after a few catalytic runs already at 180°C. On this account, an in-depth physico-chemical characterization of the used catalyst, specifically by hyphenated TGA-MS experiments, has been carried out. Results obtained disclose important information on the deactivation process, thus revealing operative limits of Amberlyst-15 for this reaction. On this regard, a detailed understanding of deactivation pathways represents a crucial step for the design of better performing catalysts, the individuation of optimal reaction conditions and the definition of a regeneration protocol.

Keywords: glycerol etherification, ethanol, oxygenated additives, amberlyst-15, catalyst deactivation

Acknowledgments This research was funded by PRIN 2022 - Missione 4 Componente 2 investimento 1.1 - D.D. 104 del 02-02- 2022 Progetto AGROMET - 2022EX89KF CUP: B53D23005950006 - Next Generation EU - Bando FIS 2021 – Fondo Italiano per la Ricerca – FIS00002427 SUPERBIO

References

[1] N. Yadav, G. Yadav, M. Ahmaruzzaman, *Industrial Crops and Products* 210, **2024**, 117999.
[2] C. Cannilla, G. Bonura, S. Maisano, L. Frusteri, M. Migliori, G. Giordano, S. Todaro, F. Frusteri, *Journal of Energy Chemistry* 48, **2020**, 136-144.
[3] C. Cannilla, G. Giacoppo, L. Frusteri, S. Todaro, G. Bonura, F. Frusteri, *Journal of Industrial and Engineering Chemistry* 98, **2021**, 413-424.

OL 13 - Catalyst preparation through atomic layer deposition: Diffusion–reaction modeling and comparison with experimental data

Niko Heikkinen[1], Jihong Yim[2], Jänis Järvilehto[2], Saeed Saedy[3], P. Brüner[4], T. Grehl[4], Eero Haimi[2], Jorge Velasco[2], Christine Gonsalves[2], J. Ruud van Ommen[4], Juha Lehtonen[1], Riikka L. Puurunen[2]

[1]VTT Technical Research Centre of Finland, P.O. Box 1000, FIN-02044 VTT,
Espoo, Finland.
[2] Aalto University School of Chemical Engineering, Kemistintie 1, Espoo, Finland.
[3] IONTOF GmbH, Heisenbergstraße 15, 48149 Münster, Germany
4 TU Delft, Van der Maasweg 9, 2629 HZ Delft, The Netherlands

Corresponding Author: Niko Heikkinen, niko.heikkinen@vtt.fi

Abstract

Atomic layer deposition (ALD) is a gas phase thin film preparation method for many practical applications from planar surface microelectronics to porous and tortuous structures, such as catalysts. The precise control of precursor deposition inside a catalyst particle is achieved with a self-limiting chemisorption, where in-stead of the amount of introduced reactant, the surface itself controls the deposition process. At full reactant saturation, the thin film formation is limited by the number of surface reaction sites and all excess reactants and by-products are removed from the surface prior to next chemisorption cycle. Therefore, ALD is an interesting technology to introduce active metals and promoters to heterogeneous catalyst support.

Here, we present a diffusion–reaction (DR) model for ALD to estimate precursor travel and deposition in an alumina-based catalyst support. [1] The model considers for the porous material properties, such as average pore size, tortuosity and porosity, and particle shape. We compare modeling results to experimental studies on high-surface-area alumina spheres. Two case examples are presented: zinc deposition on alumina using gaseous $Zn(acac)_2$ precursor [2] and platinum deposition on alumina using MeCpPtMe3 precursor (5 cycles with oxygen as counter-reactant). Alumina spheres with diameters of 1, 1.8 and 2.5 mm were employed, with a specific surface area on the order of 200 m^2/g. Modelling results are found to agree reasonably well with the experimental data.

Keywords: Atomic layer deposition, diffusion-reaction modelling

References

[1] N. Heikkinen, J. Lehtonen, R. L. Phys. Chem. Chem. Phys., 2024, 26, 7580–7591. DOI: 10.1039/d3cp05639b

[2] J. Yim, E. Haimi, M. Mäntymäki, V. Kärkäs, R. Bes, A. Arandia Gutierrez, K. Meinander, P. Brüner, T. Grehl, L. Gell, T. Viinikainen, K. Honkala, S. Huotari, R. Karinen, M. Putkonen, R.L. Puurunen, Chemistry of Materials 35 (2023) 7915–7930.

OL 14 - Reactivity and stability of zeo-type materials during conversion of dimethyl ether into light olefins

S. Todaro[1], C. Cannilla[1], M. Santoro[1], S. Donato[1], M. Samperi[1], M. Failla[1], A. Cajumi[2], F. Arena[2], G. Bonura[1,]*

[1] CNR-ITAE, via S. Lucia sopra Contesse 5, 98126 Messina, Italy
[2] Università degli Studi di Messina, Dip. Ingegneria, c.da Papardo, 98166 Messina, Italy

***Corresponding Author: Giuseppe Bonura,** giuseppe.bonura@cnr.it

Abstract

Light olefins are important building blocks in the petrochemical industry, resulting as essential materials for the production of a wide range of plastics [1]. On the knowledge gained about the methanol-to-olefines (MTO) process, an increasing interest is being now arising on usingdimethyl ether (DME) instead of methanol as the starting compound for the production of light olefins (i.e., $C_2^=$-$C_4^=$ fraction of unsaturated hydrocarbons) due to thermodynamic and economic reasons [2,3]. Considering that most of research efforts are currently focused on zeolite materials,already claimed as effective catalysts in MTO conditions, in this work we synthesized four silico-aluminates of MFI-type at a progressive dealumination extent (Si/Al mol ratio of 100/9, 100/4, 100/1 and 100/0), to assess their specific reactivity and stability during conversion of DME into light olefins. The samples were tested in a tubular fixed bed reactor by feeding 20 vol.% DME inN_2 at 300 °C and atmospheric pressure, then imposing a space velocity of 2,200 *N*mL/g_{cat}/h.

Catalytic screening of the samples evidenced how the activity-selectivity pattern results to be depressed by a composition completely Al-free, while taking advantage from a relatively low Al concentration (Si/Al, 100/1) with total conversion of DME and an initial formation of light olefines as high as 48.19% in the first 20 min on stream. What is interesting is that, by monitoringthe catalytic performance over time, the product distribution changes as a function of the Si/Al ratio, only remaining substantially unaffected for the SIAL-100/1 sample. Moreover, while samples at lower Si/Al ratios exhibited significant deactivation, those at higher Si/Al ratios maintained an almost stable performance.

Overall, the study demonstrates the importance of compositional, textural and surface effects in determining the catalytic performance and stability of zeolite-based catalysts in DTO conditions.Once balanced the catalyst features with a suitable experimental strategy for maximum productionof light olefines, it is fundamental to evaluate the catalyst durability as a key indicator for efficientprocess operativity.

Keywords: DTO process; coke formation; zeolites; dealumination; surface properties.

Acknowledgments This research was funded by the European Union – NextGeneration EU through the programme POR H_2 AdP MASE-ENEA with involvement of CNR and RSE, PNRR − Mission 2, Component 2, Investment 3.5 “Ricerca e sviluppo sull’idrogeno”, CUP: B93C22000630006.

References

[1] A. Sardesai, S. Lee, *Energy Sources* 27, **2005**, 489–500.
[2] E. Catizzone, C. Freda, G. Braccio, F. Frusteri, G. Bonura, *J. Energy Chem.* 58, **2021**, 55-77.
[3] M.R. Gogate, *Petrol. Sci. Technol.* 37, **2019**, 559-565.

OL 15 - Zeolites as efficient catalysts for synthesis of cyclopentyl ethyl ether

Zuzana Silná, Pavol Lopatka, Tomáš Soták

Department of Organic Technology, Catalysis and Petroleum Chemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, Bratislava, Slovakia

Corresponding Author: Zuzana Silná, zuzana.silna@stuba.sk

Abstract

One of the main sources of chemical industrial waste stems from the use of solvents. It is therefore crucial to utilize solvents which perform well in the desired reactions, are safe to use, and can be easily recycled and disposed of. One such potential solvent is cyclopentyl methyl ether (CPME), belonging to the class of unsymmetric ethers. It is considered a green solvent thanks to its favorable physicochemical properties, such as hydrophobicity, high boiling point, narrow explosion range, and slow peroxide formation.[1,2] It has performed well in multiple organic syntheses.[3]

Hereby, we developed a method for gas-phase synthesis of unsymmetric ethers from alcohols in the presence of heterogeneous zeolite-based catalysts. This synthesis can be considered green, as it utilizes biomass-derived alcohols. It is based on dehydration of a mixture of two alcohols in the presence of a zeolite. The main challenge is the optimization of technological parameters and catalyst properties towards the best selectivity to unsymmetric ether formation. The competing reactions in this system result in two possible symmetric ethers and cyclopentene as a product of dehydration.[4]

Catalytic tests were carried out in a fixed-bed flow reactor in the presence of nitrogen. In a model experiment, a mixture of ethanol (EtOH) and cyclopentanol (CYpOH) in mass ratio of 5:1, was fed into the reactor at WHSV of 0.25 $g_{CYPol}\cdot g_{cat}^{-1}\cdot h^{-1}$. The reaction was performed at 100 °C under atmospheric pressure. Hourly samples of reaction mixture were analyzed by gas chromatography.

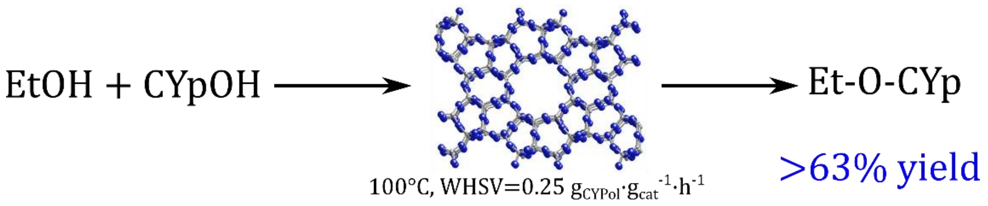


Fig. 1 Etherification of two alcohols to an unsymmetric ether

The best results were obtained using ZSM-5 (Si/Al = 40) – cyclopentyl ethyl ether (CPEE) yield and CYpOH conversion of over 63 % and 88 % respectively at optimized reaction conditions. This method of CPEE synthesis is promising thanks to its mild reaction conditions.

Keywords: zeolites, unsymmetric ethers, biomass processing, solvents

Acknowledgments The authors gratefully acknowledge the financial support from the Ministry of Education, Science, Research and Sport of the Slovak Republic (project VEGA 1/0374/23).

References

[1] S. Sakamoto, *Chim. Oggi* 31 (6), **2013**, 24-27.
[2] K. Watanabe, N. Yamigawa, Y. Torisawa, *Org. Process. Res. Dev.* 48, **2007**, 136-144.
[3] U. Azzena et al., *ChemSusChem.* 125, **2019**, 40-70.
[4] T. Soták et al., *Appl. Catal. A-Gen.* 618, **2021**, 118122

OL 16 - Prins reaction of limonene with formaldehyde catalyzed by Sn-BETA

Eva Vrbková[1], Michaela Hlinková[1], Eliška Vyskočilová[1]

[1]*Dpt. of Organic Technology, University of Chemistry and Technology Prague, Technická 5, Prague, Czech Republic*

Corresponding Author: Eva Vrbková, eva.vrbkova@vscht.cz

Abstract

Prins reaction is an acid catalyzed reaction between aldehyde and alkene during which C-C or C-O bond is formed. Limonene is renewable feedstock, which can be obtained e.g from citrus essential oil, turpentine or by pyrolysis of waste tires. Reaction of limonene with formaldehyde provides homolimonenol (Fig. 1), which serves as intermediate in synthesis of many compounds with biological activity (antibiotics, insect hormones) or as intermediate in synthesis of fragrance cyclomethylenecitronellol.

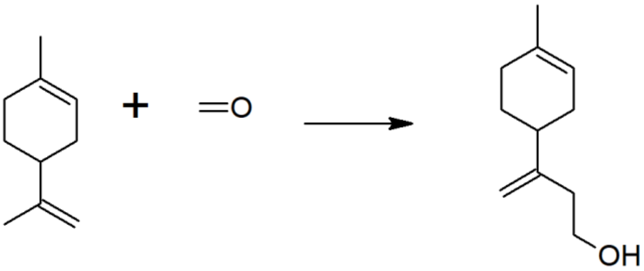


Figure 1. Prins reaction of limonene with formaldehyde giving homolimonenol

Within this work several materials based on tin-modified zeolite BETA were prepared. These materials were characterized using different techniques (e.g. XRD, XRF, nitrogen physisorption) and their catalytic activity in Prins reaction of limonene with formaldehyde in batch reaction arrangement was monitored. One selected material was used for optimization of reaction conditions (influence of temperature, solvent type, catalyst amount) and a high selectivity at 55% conversion was obtained using room temperature. Possibility of catalyst reuse was confirmed.

Keywords: homolimonenol, zeolite BETA, Prins reaction, acid catalysis

OL 17 - Kinetics of carvacryl ester synthesis using clay-based catalyst

Martin Zapletal[1], Eva Vrbková[1]

[1]*Dpt. of organic technology, University of Chemistry and Technology Prague, Technická 5, Prague, Czech Republic*

Corresponding Author: Martin Zapletal, martin.zapletal@vscht.cz

Abstract

Carvacryl acetate (5-isopropyl-2-phenyl acetate) is monoterpenoid ester which possesses similar or higher pharmacological properties as its precursor – carvacrol. Lower toxicity and higher stability of carvacryl acetate compared to carvacrol is probably caused by substitution of hydroxyl group with acetyl group. Carvacryl acetate is described to have a significant biological activity – anti-inflammatory, antibacterial and antinociceptive effects were described[1,2].

Traditional synthesis of carvacryl acetate is by reaction of carvacrol with acetyl chloride or acetic anhydride. This homogeneous reaction arrangement suffers from necessity of ester isolation together with formation of a significant amount of chlorinated waste (in case of acetyl chloride use).

In our work we present solvent – free synthesis of carvacryl acetate with acetic anhydride (Fig. 1) using a cheap and available heterogeneous catalyst – montmorillonite K10.

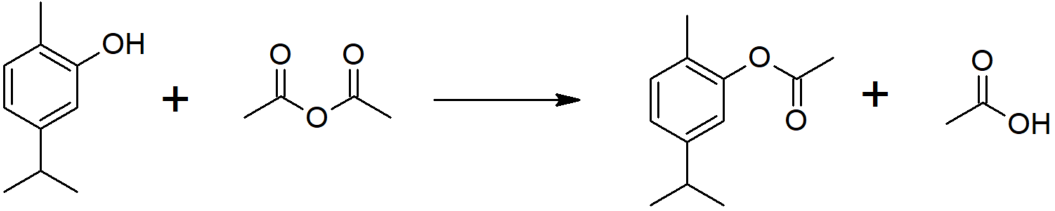


Figure 1. Reaction of carvacrol with acetic anhydride giving carvacryl acetate and acetic acid

In case of using montmorillnite treated with sulfuric or nitric acid as catalyst total conversion of carvacrol after 20 minutes of reaction at room temperature was observed (100 % selectivity to desired ester). Reaction kinetic parameters were evaluated using ERA3.0 software package[3].

Keywords: carvacryl acetate, montmorillonite, reaction kinetics

References

[1] E.M. Alvarenga, N.A. Sousa, S. de Araújo, J.L.P. Júnior, A.R. Araújo, B. Iles, D.M. Pacifíco, G.A.C. Brito, E.P.Sousa, D.P.Sousa, J.V.R. Medeiros, *Journal of Pharmacy and Pharmacology* 69 (12), **2017**, 1773-1785.

[2] C.S. Mathela, K.K. Singh, V.K. Gupta, *Acta Poloniae Pharmaceutica* 67(4), **2010**, 375-380.

[3] P. Zámostný, Z. Bělohlav, *Computers & Chemistry* 23(5), **1999**, 479-485.

OL 18 - Magnetic nanoparticles as a promising photocatalyst and antibacterial agent

Ahmed M. El-Khawaga[1], Mohamed Ayman[1], Omar Hafez[1] & Rasha E. Shalaby [1,2]

[1]*Department of Basic Medical Sciences, Faculty of Medicine, Galala University, New Galala City, Suez, Egypt*
[2]*Department of Microbiology and Immunology, Faculty of Medicine, Tanta University, Tanta, Egypt*

Corresponding author: Ahmed M. El-Khawaga, Ahmed.Elkhawaga@gu.edu.eg

Abstract

Introduction: water pollution has become a global threat to mankind due to accelerated pace of global industrialization[1]. According to sustainable development goal (SDG) 6.3, the provision of uncontaminated water and the development of safe and sustainable water purification methods are of paramount importance from environmental, industrial, and societal, and perspectives[2].
Aim of the work: In this study, we aim to contribute to the development of more effective, sustainable, and safe solutions for water treatment and antimicrobial applications, thereby addressing the pressing global issue of water contamination and antibiotic resistance.
Methodology: $MgFe_2O_4$ NPs were successfully synthesized through a co-precipitation methodology and subjected to comprehensive structural and optical characterization. The photocatalytic performance of the resultant $MgFe_2O_4$ nanocatalyst was evaluated using CF dye as the target pollutant. Additionally, a thorough exploration of various factors affecting the degradation efficacy, including pH levels during CF degradation, initial CF concentration, and the dosage of $MgFe_2O_4$ NPs as photocatalysts, was conducted.
Results and main advancement: Figure 1 illustrates the suggested mechanism of the interaction between the produced $MgFe_2O_4$ nanoparticles and CF.

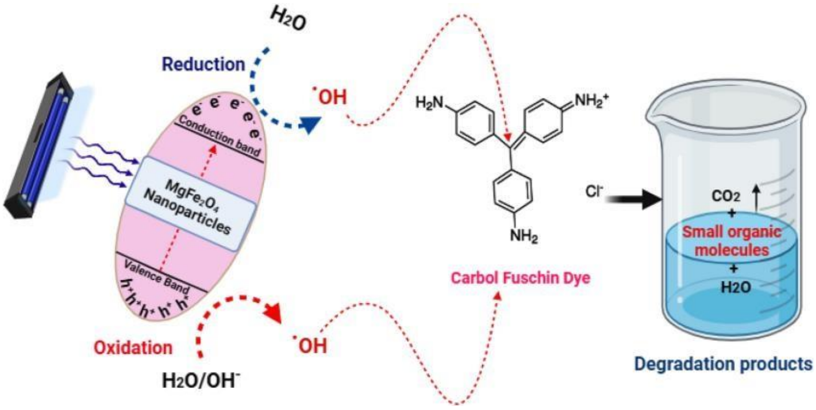


Figure 1: Potential photocatalytic reaction mechanism for CF photodegradation by $MgFe_2O_4$ NPs.

The $MgFe_2O_4$ NPs demonstrated notable photocatalytic efficiency in the removal of CF from aqueous solutions. Remarkably, under conditions of pH 9 and utilizing 15 mg of $MgFe_2O_4$ NPs, approximately 96% of a 10 ppm CF solution was effectively photodegraded after 135 min. In vitro assessments further corroborated the antimicrobial potential of $MgFe_2O_4$ NPs, as evidenced by zone of inhibition (ZOI) and minimum inhibitory concentration (MIC) results. Specifically, $MgFe_2O_4$ NPs exhibited significant antimicrobial activity against *E. coli* (ZOI: 26.0 mm, MIC: 1.25 µg/ml) and *S. aureus* (ZOI: 23.0 mm, MIC: 2.5 µg/ml). The synthesized $MgFe_2O_4$ nanocatalyst holds promise for applications in antimicrobial treatments and wastewater purification processes.

References

[1] B. Malmqvist, S. Rundle, *Environmental conservation*, 29 **(2002)** 134-153.
[2] G. Mujtaba, M.U.H. Shah, A. Hai, M. Daud, M. Hayat, *Journal of Water Process Engineering*, 57 **(2024)** 104691.

OL 19 - Ethanol coupling reactions over noble metal (Pt, Pd) promoted $MgO-Al_2O_3$mixed oxide-based catalysts

Amosi Makoye[1,2], Anna Vikár[1], Tibor Nagy[1], József Valyon[1], Ferenc Lónyi[1,*]

[1]Renewable Energy Research Group, Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, Magyar tudósok körútja 2, Budapest 1117, Hungary

[2] Hevesy György Doctoral School of Chemistry, Eötvös Loránd University (ELTE), Pázmány Péter sétány 1/A, Budapest 1117, Hungary

[*]Corresponding Author: Ferenc Lónyi, e-mail: lonyi.ferenc@ttk.hu

Abstract

Conversion of bioethanol to biobutanol via Guerbet coupling reaction attracted significant interest of chemical industry, because 1-butanol could be used as renewable fuel or blending component of gasoline, as well as precursor for the production of other valuable chemicals [1-3]. Catalytic conversion of ethanol to1-butanol was studied over hydrotalcite-derived $MgO-Al_2O_3$ mixed oxide-based catalysts and their noble metal (Pt, Pd) promoted derivatives. Relationships between acid-base and catalytic properties and the effectof active metal on the hydrogen transfer reaction steps were investigated. The acid-base properties were studied by temperature-programmed desorption of CO_2 and NH_3, and by the FT-IR spectroscopic examination of adsorbed pyridine. Dispersion of the metal promoter was determined by CO pulse chemisorption. The ethanol coupling reaction was studied using a flow-through microreactor system, He orH_2 carrier gas, and at WHSV= 1 $g_{EtOH} \cdot g_{cat.}^{-1} \cdot h^{-1}$ space velocity, 21 bar total pressure, and 200 – 350 °C reaction temperature. Formation and transformation of surface species under catalytic conditions were studied by in situ DRIFT spectroscopy.

The highest butanol selectivity and yield was observed when the $MgO-Al_2O_3$ catalyst contained relatively high amount of strong base and medium-strong Lewis acid sites. The presence of metal, especiallyPd promoter improved the activity both in He and H_2, however the butanol selectivity significantly decreased at temperatures ≥300 °C due to acceleration of undesired side reactions. DRIFT spectroscopic results showed that the active metal promoted H-transfer from H_2 over the narrow temperature range of 200-250 °C, where the equilibrium allowed significant concentrations of both dehydrogenated and hydrogenatedproducts. Also, detailed microkinetic modelling of the packed bed reactor was employed to help the interpretation of the results.

Keywords: ethanol coupling to butanol; $MgO-Al_2O_3$ mixed oxide-based catalysts; in situ DRIFT spectroscopy

Acknowledgments The authors thank the financial support provided by the Ministry of Innovation and Technology of Hungaryfrom the National Research, Development and Innovation Fund, under the 2019-2.1.13-TÉT_IN funding scheme (Project No. 2019-2.1.13-TÉT_IN-2020-00043). The support from the European Regional Development Fund and the National Research, Development and Innovation Office, under the Interreg V- A Slovakia - Hungary Cooperation Program, SKHU/1902, (Project No: SKHU/1902/4.1/001) is also acknowledged.

References

[1]Dagle, R.A.; Winkelman, A.D.; Ramasamy, K.K.; Lebarbier Dagle, V.; Weber, R.S., *Ind. Eng. Chem. Res.* 59(11), **2020**,4843–4853.

[2]Gabriëls, D.; Hernández, W.Y.; Sels, B.; Van Der Voort, P.; Verberckmoes, A., *Catal. Sci. Technol 5(8)*, **2015**, 3876–3902.

[3]Wu, X.; Fang, G.; Tong, Y.; Jiang, D.; Liang, Z.; Leng, W.; Liu, L.; Tu, P.; Wang, H.; Ni, J., *ChemSusChem11(1)*, **2018,** 71–85.

OL 20 - Boosting the Photocatalytic Performance of Swiftly Produced Carbon Nitride: Impact of Cyano Group and Oxygen Doping within the Matrix

Ragesh Nath R [1], Shyue Chu Ke [1*]

[1] *Physics Department, National Dong Hwa University, Hualien, Taiwan, 971*

Corresponding Author: Shyue Chu Ke, e-mail: ke@gms.ndhu.edu.tw

Abstract

Graphitic carbon nitride (g-C_3N_4) stands out as a promising photocatalyst due to its eco-friendly nature, cost-effectiveness, chemical stability, and optimal energy levels for efficient water splitting under visible light. However, conventional furnace methods for producing bulk g-C_3N_4 are time-consuming, typically requiring at least a day, and often fall short in achieving the desired structure. Recent research has shifted focus towards enhancing the photocatalytic performance of g-C_3N_4 by introducing defects into its framework, either intentionally or unintentionally. [1-3]

In response to these challenges, we have developed a rapid and efficient synthesis method for defect-rich carbon nitride (CN) tailored for photocatalytic water splitting and toxic dye degradation under both visible light and natural sunlight. The resulting material, designated as U10, features increased porosity and a semi-scrolled structure with a thickness of 2.1 nm. To validate the robustness and reliability of our approach, we tested two additional precursors, analyzing their hydrogen production rates. The exceptional photocatalytic performance of U10 can be attributed to its unique structural characteristics and the synergistic effects of oxygen doping (O-doping) and cyano (-C≡N) functional groups introduced during the rapid synthesis process. The charge transfer dynamics was studied by EPR method.

This innovative synthesis strategy not only saves time and energy but also significantly reduces production costs, making it a viable method for large-scale production of carbon nitride materials. The development of U10 demonstrates a leap forward in photocatalyst design, offering enhanced efficiency and practicality for sustainable energy applications.

Keywords: Photocatalysis, Carbon nitride, Fast-synthesis method, Defect rich.

Acknowledgments: This work was financially supported by the Ministry of Science and Technology, Taiwan under the grant No. NSTC 112-2112-M-259-008-MY3.

References

1. S. Dyjak, W. Kiciński, A. Huczko, *J. Mater. Chem. A*, **2015**, 3(18), 9621- 9631
2. V.-z.Y. VW-h Lau, F. Ehrat, T. Botari, I. Moudrakovski, T. Simon, V. Duppel, E. Medina, J. Stolarczyk, J. Feldmann, V. Blum, *Adv. Energy Mater.* **2017**, 1602251.
3. D. Zhao, C.L. Dong, B. Wang, C. Chen, Y.C. Huang, Z. Diao, S. Li, L. Guo, S. Shen, *Adv. Mater.* **2019**, 31(43) 1903545.

OL 21 - Green and environmentally friendly approach towards MXene as a novel bifunctional electrocatalyst for Hydrogen production

Shahid Bashir[1], Jeyraj Selvaraj[1], Nasrudin Abd Rahim[1], K. Ramesh[2], S. Ramesh[2]

[1] Higher Institution Centre of Excellence (HICoE), UM Power Energy Dedicated Advanced Centre (UMPEDAC), Level 4, Wisma R&D, Universiti Malaya, Jalan Pantai Baharu, Kuala Lumpur 59990, Malaysia

[2] Centre for Ionics Universiti Malaya, Department of Physics, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Corresponding Author: Shahid Bashir, shahidbashirbaig@um.edu.my

Abstract

Environmental pollution caused by excessive use of fossil fuels to fulfill the energy demands of the rapidly growing population around the globe is a serious concern. Hydrogen is considered the carbon-free clean energy source having several advantages such as high energy density, zero carbon emission, zero greenhouse effect and so on. Electrocatalytic water splitting is the most used technique for hydrogen production, however, it only contributes 4% of the total hydrogen production. Water electrolysis comprises hydrogen evolution reaction (HER) and oxygen evolution (OER) half-cell reactions responsible for generating Hydrogen and Oxygen, respectively. Various rare earth elements have been tried as a catalyst but due to their prohibitively high cost and scarcity, the elements cannot be sustainably employed. The introduction of two-dimensional MXenes made tremendous progress in the development of electrolyzer due to high conductivity, high charge mobility, high mechanical strength, large surface area, hydrophilicity, stability, and rich surface chemistry. Therefore, MXenes attained significant interest in heterogeneous catalysis. Herein, we developed double transition metal based MXene as a bifunctional electrocalatyst decorated with active sites to achieve stability at higher current densities and lower the overpotential compared to theoretical potential. Coupling of HER and OER reactions in the same medium is a big challenge. Therefore, bifunctional layered MXene was developed using environmentally friend deep eutectic solvent for etching of Aluminum from MAX phase. The developed MXenes were characterized using numerous techniques such as Raman spectroscopy, XRD, SEM, EDX, and XPS. The MXene as an electrocatalyst significantly reduced the overpotential value to 200 mV at 50 mA/cm^2 compared to the reported catalyst. Moreover, the Tafel slope of 43 and 54 mV/dec was achieved for HER and OER along with high electrochemical stability up to 60 h at high current density. It is realized that the redox activity of MXenes is quite impressive due to a high surface area and electric conductivity. The newly discovered 2D MXenes, owing to high conductivity and rich surface chemistry, have shown potential to overcome the stability problem as a catalyst in an electrolyzer.

Keywords: MXene, bifunctional electrocatalyst, green synthesis, electrolyzer

Acknowledgments: We acknowledge the support from Universiti Malaya, Malaysia

References

1. S. Ponnada, *et al.*, *Cat. Sci. Technol.*, *12*(14), **2022**, 4413-4441.
2. T. Rasheed, *et al.*, *Fuel*, *346*, **2023**, 128305.
3. M. Saquib, *et al.*, *Int. J. Hydr. Energy*, *59*, **2024**, 1132-1142

OL 22 - Sustainable Heterogeneous Catalysis: A perspective from the nanoscale

Cederick Cyril Amoo[1], Andras Sapi[1]

[1]*University of Szeged, Department of Applied and Environmental Chemistry*

Corresponding Author: Andras Sapi, sapia@chem.u-szeged.hu

Abstract

Sustainability driven process are opted in efforts targeting the '**sustainable development goals'** which strongly encourages the implementation of green chemistry. The concept of green chemistry encompasses the use of sustainable materials with no hazards in the overall process, considering every step, involved in the Chemical processes. Catalysis is recognized a foundational pillar of green chemistry with the benefits of lower energy requirements and improved efficiency of process.[1, 2] Heterogeneous catalysis, in particular, tackles the goals of green chemistry by easing product separations, thereby eliminating the need for separation through complex processes such as distillation or extraction.[3]

Improving the nature of reactions require thorough understanding of materials and processes to encourage the design of more robust catalysts. This has driven research towards nanoscale chemistry. Nanoscale chemistry benefits theoretical, experimental, and simulation tools. The design of sustainable heterogeneous catalysts using knowledge from the nanoscale eases control of the active phases to improve the reaction.[4]

In this work, the developments on the design, synthesis and characterization of various heterogenous catalysts are reported, skewed towards precise control of catalyst interface at nanoscale. The work mainly focuses on catalytic materials for energy conversion and conservation. further emphasis is placed on the breakthroughs in the techniques for structural analysis. The work is concluded with a summary and a outlook for future research.

Keywords: nanomaterials, heterogeneous catalysis, energy conversion.

Acknowledgments A.S. gratefully acknowledges the support of FK 143583. The Ministry of Human Capacities through the 20391-3/2018/FEKUSTRAT, as well as Project No. TKP2021-NVA-19 under the TKP2021-NVA funding scheme of the Ministry for Innovation and Technology.

References

[1] D. Wang, Z. Xie, M.D. Porosoff, J.G. Chen, Recent advances in carbon dioxide hydrogenation to produce olefins and aromatics, Chem, 7 (2021) 2277-2311.
[2] J.R. Ludwig, C.S. Schindler, Catalyst: Sustainable Catalysis, Chem, 2 (2017) 313-316.
[3] I. Pálinkó, Chapter 3.12 - Heterogeneous Catalysis: A Fundamental Pillar of Sustainable Synthesis, in: B. Török, T. Dransfield (Eds.) Green Chemistry, Elsevier2018, pp. 415-447.
[4] S. Mitchell, R. Qin, N. Zheng, J. Pérez-Ramírez, Nanoscale engineering of catalytic materials for sustainable technologies, Nature Nanotechnology, 16 (2021) 129-139.

OL 23 - Anchoring Pd nanoparticles to zeolite surface silanols to developheterogenous Tsuji-Trost allylation catalysts

Adéla Olšovská[1], Martin Kamlar[2], Jan Veselý[2], Jiří Čejka[1] and Michal Mazur[1]

[1]*Department of Physical and Macromolecular Chemistry, Faculty of Science, CharlesUniversity, Hlavova 2030/8, 128 43, Prague, Czech Republic*
[2]*Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova2030/8, 128 43, Prague, Czech Republic*

Corresponding Author: Adéla Olšovská, olsovska@natur.cuni.cz

Abstract

Homogeneous catalysts are used in industry due to their high activity and excellent contact with reactants. However, homogeneous processes are usually limited, *e.g.* to batch reactors due to challenging separation of products. In contrast, heterogeneous catalysts are straightforward to separate and reuse, making them economically advantageous.[1] A common approach in developing heterogeneous catalysts involves anchoring active species onto supports, *e.g.* zeolites, valued for their high surface areas, porosity, and excellent chemical and thermal stability.[2] Zeolites can also be modified, *e.g.* by dealumination, to remove framework aluminumand introduce surface silanol groups that were found to stabilize metal nanoparticles.[3]

The aim of our study was to prepare heterogeneous catalysts for the Tsuji-Trost allylation,a reaction typically catalyzed by Pd(0) species in homogeneous systems. Our goal was to developa heterogeneous catalyst as a potential alternative to its homogeneous counterpart. To achievethis, we impregnated various USY zeolites with Pd nanoparticles. We used PXRD to confirm crystallinity of samples, argon sorption to investigate their texture, ICP-MS to confirm loading ofPd, and electron microscopy to analyze crystal morphology as well as nanoparticle dispersion andsize distribution. TPR was used to determine the reduction conditions for activation of catalysts.

We studied the size and distribution of anchored nanoparticles in relation to the presenceof silanols in the support. Commercial USY zeolites were impregnated with Pd producing nanoparticles of about 1.5 nm in diameter. We show that use of zeolite supports with introducedstructural defects, such as mesopores and silanol nests, leads to formation of nanoparticles of approx. 3.0 nm in diameter. Materials with smaller nanoparticles showed the highest activity of diethyl malonate allylation, likely because they more closely resemble homogeneous catalysts. However, nanoparticles anchored to silanol-poor zeolites sintered substantially during activation,resulting in their lower activity over multiple catalytic cycles. We show that silanol-rich supportsthat initially contain larger nanoparticles are more resistant to sintering during activation and regeneration of the catalysts, leading to greater stability and sustained activity. Furthermore, thesematerials can potentially be investigated towards utilization of the acid sites in zeolites. This mightcreate bifunctional catalysts for synergic metal- and acid-catalyzed reactions.

Keywords: zeolites, Pd nanoparticles, impregnation, Tsuji-Trost allylation

Acknowledgments The work was supported from ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587) and by the Czech Science Foundation (project 23- 08031K).

References

[1] A. Corma, H. Garcia, *Advanced Synthesis and Catalysis* 384(12-13), **2006**, 1391-1412.

[2] R. E. Morris, et al., *RSC Catalysis Series*, **2017**.

[3] L. Ang, et al., *Angewandte Chemie International Edition* 62(1), **2023**.

OL 24 - Mechanochemical Strategies for Effective Impregnation of MFI Zeolitewith Metal Nanoparticles

Samuel Kolesár, Paul A. Diddams, and Michal Mazur

Department of Physical and Macromolecular Chemistry; Faculty of Science,Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Corresponding author: Samuel Kolesár, samuel.kolesar@natur.cuni.cz

Abstract

Metal nanoparticles on zeolite supports represent an important group of heterogeneous catalysts. These catalysts possess advantageous properties, such as a favourable mass-to-surface ratio caused by the small size of metal species.

The main post-synthesis strategy for incorporation of metal nanoparticles onto supports is by incipient wetness impregnation, which may be accomplished manually, using a mortar and a pestle. However, this procedure does not always lead to uniform distribution of small metal species within the zeolite support. A possible solution to overcome these issues and avoid manual labour is to use a mechanochemical approach[1]. The application of mechanochemistry in wet impregnation can automize and scale-up synthesis processes while enhancing the properties of a catalyst, especially an increase in the homogeneity of dispersion of nanoparticles and their size distribution.

We utilized a gallosilicate – MFI zeolite nanosponge, obtained by hydrothermal synthesis, as a support. Its architecture comprises of interconnected, disordered network of MFI nanolayers[2] that have immense potential as a support for metal nanoparticles. The gallosilicate was post-synthesis modified by degallation to generate silanol nests[3] – surface hydroxyl groups that can anchor nanoparticles. To compare impregnation methods, we immobilized Pt species at the zeolite support both manually – using mortar and pestle, and mechanochemically – using ball mill, the source of high energy impacts with anadjustable frequency.

The structure and texture of the degallated MFI nanosponge support, size, location and distribution of metal nanoparticles, were characterized in nanocomposites prepared by both methods. Powder X-ray diffraction (PXRD) confirmed that the zeolite nanolayers were preserved after milling. Preservation of zeolite structure and the incorporation of nanoparticles were also confirmed by scanning transmission electron microscopy (STEM) and EDS mapping. Application of powerful high-frequency ball milling led to more uniform nanoparticle size distribution of ball milled samples than when using a mortar and the pestle. Moreover, we observed a slight decrease in the average zeolite crystallite size. We demonstrated that a rational choice of the impregnation method allows tuning the nanoparticle size and space distribution. Prepared catalysts will be tested in various hydrogenation reactions, such as the conversion of eugenol – a model molecule for lignin valorisation[4].

Keywords: mechanochemistry, impregnation, zeolites, metal nanoparticles, size distribution

Acknowledgement Authors would like to acknowledge the support from ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587) and the support of the Czech Science Foundation for the project 23-08031K.

References

[1] D. N. Rainer, R. E. Morris, Dalton Trans., 50, **2021**, 8995–9009

[2] C. Jo et al., Chem. Commun., 50, **2014**, 4175–4177

[3] A. Li et al., Angew. Chem. Int. Ed., 62, **2023**, e202213361

[4] A. Sreenavya et al., Ind. Eng. Chem. Res., 59, **2020**, 11979–11990

OL 25 - Homogeneous vs. heterogeneous transesterification: How refinement steps of different types of oil affect biodiesel production

Miroslava Mališová Bérešová[1], András Peller[1], Michal Horňáček[1]

[1]Slovak University of Technology in Bratislava, Faculty of Chemical and Food Technology, Radlinského 9 812 37 Bratislava, Slovakia

Corresponding Author: Miroslava Bérešová, miroslava.beresova@stuba.sk

Abstract

The refining process of vegetable oils for biodiesel preparation consists of several steps. In the first step, it involves the removal of hydratable and non-hydratable phospholipids, commonly known as gums[1]. Their removal is essential, especially in heterogeneous transesterification, due to the deactivation of the catalyst and, not least, issues with fuel injection into the engine. Another important step of the refining process is the neutralization of free fatty acids using KOH. This process is particularly important for homogeneous transesterification, where basic catalysts are significantly more susceptible to neutralization. The impact of each step on heterogeneous and homogeneous transesterification can be different. The choice of vegetable oil could also cause different catalyst activity in case of different refining steps. This work is focused on the influence of individual refining process steps and their influence on catalyst activity in homogeneous and heterogeneous transesterification to prepare biodiesel from different types of oils[2].

As a studied heterogeneous catalyst mixed oxides obtained from hydrotalcites by calcination were tested. Hydrotalcites were prepared by co-precipitation with the addition of different metal cations during precipitation. Several methods for hydrotalcite physicochemical properties measurement were used (XRD, TPDA, TPD-CO, XRF, SBET, TG, FTIR, XPS). As tested oils, Camelina sativa as a non-food oil and coffee oil as a waste oil were used to compare with commonly used food oils. Each oil was pretreated by refining treatment. To compare the impact of each raffination step, different steps were excluded from the raffination process. Heterogeneous transesterifications of oils were performed in a batch reactor at the same conditions. In prepared biodiesel, the content of FAME, the content of phosphor, sulfur, FFA, and other components was analyzed.

Results showed a significant influence of refining steps to catalyst activity. While during homogeneous transesterification of fully refined Camelina sativa oil, it was possible to obtain more than 99 wt.% of FAME, in case of excluding the acid degumming step from the refining process, the FAME content decreased to less than 90 wt.%. In the case of heterogeneous transesterification, excluding the KOH step had the most significant impact on heterogeneous catalyst activity in transesterification, where the content of FAME decreased to less than 64 wt.%.

Keywords: biodiesel, transesterification, hydrotalcite, mixed oxide, FAME

Acknowledgments (This work was supported by the call for doctoral students and young researchers of the Slovak University of Technology in Bratislava to start a research career (Grant 23-04-03-B) and by the Slovak Research and Development Agency No. APVV-20-0348

References

[1] M.Mališová et al., *ACS Omega* 5(49), **2020**, 32040-32050.
[2] M.Mališová et al., *Petroleum and Coal* 65(4), **2023**, 1280-1285

PITCH PRESENTATIONS

Pi 1 - Mechanochemical Strategies for Effective Impregnation of MFI Zeolite with Metal Nanoparticles

Samuel Kolesár, Paul A. Diddams, and Michal Mazur

Department of Physical and Macromolecular Chemistry; Faculty of Science,
Charles University, Hlavova 8, 128 43 Prague 2, Czech Republic

Corresponding author: Samuel Kolesár, samuel.kolesar@natur.cuni.cz

Highlights

- A rational choice of the impregnation method allows tuning the nanoparticle size and space distribution.
- Mechanochemistry in wet impregnation enhances the properties of a catalyst and reduces the size of crystallites.
- The ball milling is effective in a controllable impregnation of noble metals and metallic promoters X: La, Ce, and Y.
- First experiments of the hydrogenation of eugenol showed a catalytic activity of Pt@MFI and Pt-X@MFI catalysts.

Keywords: mechanochemistry, impregnation, metal nanoparticles, size distribution

Acknowledgements Authors would like to acknowledge the support from ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587) and the support of the Czech Science Foundation for the project 23-08031K.

Pi 2 - Production of Aromatic Hydrocarbons from Long Chain Unsaturated Used Cooking Oil Over a Hierarchical Imidazole Supported Zeolite

Omvir Singh[1]

[1]*Rajiv Gandhi Institute of Petroleum Technology, Jais, Amethi, Uttar Pradesh India-229304*

Corresponding Author: R*ajiv Gandhi Institute of Petroleum Technology, Jais, Amethi, Uttar Pradesh India-229304, email:* omvirs@rgipt.ac.in

Highlights

- Unlike coal, oil, or natural gas, waste cooking oil (WCO) acts as a renewable source of carbon. It can be converted into energy, fuels, and fine chemicals, instead of being disposed of.
- Aromatics are the most important petrochemical building blocks widely used in making products for improving quality of our modern living.
- WCO can be viewed as a potential feedstock for the production of petrochemicals, particularly critical aromatic platform molecules for high-value chemicals.
- The study examined, the direct conversion of WCO into aromatic hydrocarbons on an imidazole-supported zeolite (ISZ) catalyst was investigated.

Keywords: Sustainable chemistry, Catalytic upgradation, Tree-borne oils,Aromatics, Biobased feedstock.

Acknowledgements OS acknowledges the Department of Science and Technology for providing the funding. also thank the YOURHETCAT 2024 and the Hungarian Academy of Sciences, for allowing presenting the work

Pi 3 - Anchoring Pd nanoparticles to zeolite surface silanols to develop heterogenous Tsuji-Trost allylation catalysts

Adéla Olšovská[1], Martin Kamlar[2], Jan Veselý[2], Jiří Čejka[1] and Michal Mazur[1]

[1]Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 43, Prague, Czech Republic
[2]Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 2030/8, 128 43, Prague, Czech Republic

Corresponding Author: Adéla Olšovská, olsovska@natur.cuni.cz

Highlights

- The influence of supporting zeolitic material on the final Pd nanoparticle size, distribution and stability.
- Different catalytic performance of Pd@USY and Pd@deAl-USY catalysts due to their different Pd nanoparticle size.
- Performance of catalysts over multiple cycles, decrease in activities.

Keywords: zeolites, Pd nanoparticles, impregnation, Tsuji-Trost allylation

Acknowledgments The work was supported from ERDF/ESF project TECHSCALE (No. CZ.02.01.01/00/22_008/0004587) and by the Czech Science Foundation (project 23-08031K).

Pi 4 - Green and environmentally friendly approach towards MXene as a novel bifunctional electrocatalyst development for Hydrogen production

Shahid Bashir[1], Jeyraj Selvaraj[1], Nasrudin Abd Rahim[1], K. Ramesh[2], S. Ramesh[2]

[1] Higher Institution Centre of Excellence (HICoE), UM Power Energy Dedicated Advanced Centre (UMPEDAC), Level 4, Wisma R&D, Universiti Malaya, Jalan Pantai Baharu, Kuala Lumpur 59990, Malaysia

[2] Centre for Ionics Universiti Malaya, Department of Physics, Faculty of Science, Universiti Malaya, 50603 Kuala Lumpur, Malaysia

Corresponding Author: Shahid Bashir, shahidbashirbaig@um.edu.my

Highlights

- Green synthesis
- MXenes
- Bifunctional electrocatalyst
- Hydrogen production

Keywords: MXene, bifunctional electrocatalyst, green synthesis, electrolyzer

Acknowledgments We acknowledge the support from Universiti Malaya, Malaysia

Pi 5 - Coordination Polymer-Derived Ag Catalysis: In-Situ Investigation of the Formation and Decomposition

Henrik Haspel,[1,2,*] Henrik Fülöp,[2] Gergő Ballai,[2] Dániel Sebők,[2] Imre Szenti,[1,2] Dorina Gabriella Dobó,[3] Ákos Kukovecz,[2] Zoltán Kónya[1,2]

[1]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*
[2]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[3]*Institute of Pharmaceutical Technology and Regulatory Affairs, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Highlights

- Coordination polymers (CPs) and metal organic frameworks (MOFs) as potential catalysts and catalyst precursors
- Synthesis and thermal decomposition of a silver coordination polymer (Ag-CP) into silver nanostructures
- In-situ diffraction and spectroscopy study of the structural and morphology evolution of the AG-CP during decomposition
- Applications of MOF-derived catalysts in thermal and electrocatalysis

Keywords: Coordination polymers, metal organic frameworks, silver nanoparticles, thermal catalysis, electrocatalysis

Acknowledgments H.H. acknowledges the financial support of the János Bolyai Research Grant of the Hungarian Academy of Sciences (BO/682/22/7). Project no. RRF-2.3.1-21-2022-00009 (National Laboratory for Renewable Energy) has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus. This project has received funding from the HUN-REN Hungarian Research Network.

Pi 6 - Sustainable Heterogeneous Catalysis: A perspective from the nanoscale

Cederick Cyril Amoo[1,2], Andras Sapi[1,2]

[1]*University of Szeged, Department of Applied and Environmental Chemistry*

Corresponding Author: Andras Sapi, sapia@chem.u-szeged.hu

Highlights

- Nano-catalysis in energy chemistry, with progress from academia to industry are reported
- Nano-catalysts demonstrate better performance in energy processes over larger sized catalysts
- Advances in ***QENS, NMR, SPTs*** and other ***techniques*** unravel mysteries in nanoscale catalysis
- Industrial demand keeps increasing and expanding for nano-catalysis with a forecast growth > 6%

Keywords: green chemistry, nanotechnology, industrial catalysis

Acknowledgments A.S. gratefully acknowledges the support of FK 143583. The Ministry of Human Capacities through the 20391-3/2018/FEKUSTRAT, as well as Project No. TKP2021-NVA-19 under the TKP2021-NVA funding scheme of the Ministry for Innovation and Technology.

Pi 7 - Waste to value: The future dimension

Palanivel Subha[1], Putla Sudarsanam*[1]

[1]*Department of Chemistry, Indian Institute of Technology Hyderabad, Telangana, India.*

Corresponding Author: Putla Sudarsanam, sudarsanam.putla@chy.iith.ac.in

Highlights

- Converting biomass wastes into valuable products (fuels and chemicals) is the most renowned and thriving field of catalysis to overcome the dependence on fossil resources.
- Plastic waste recycling is one of the hot topics among researchers currently.
- In general, the synthesis of bio-based N-containing compounds relies mostly on primary amines that are cost-ineffective.
- However, such amines can be successfully produced from plastic wastes and can be utilized for the production of bio-based amines and amides, which are potential drug precursors.
- Combining both biomass and plastic waste can lead to a sustainable pathway to produce bio-based amines and amides.

Keywords: Biomass valorization, Plastic waste recycling, In situ hydrogenation, sustainable catalysts, acid-redox synergy.

Acknowledgments
1. University Grants Commission (UGC)
2. SERB-CRG
3. Indian Institute of Technology Hyderabad.

POSTER CONTRIBUTIONS

P 1 - Electronic Synergy of Ni & Ni_2P in Mimicking Pt for CO Selectivity in the Reverse Water-Gas Shift Reaction

Haythem S Basheer[1], Janos Kiss[1], András Sápi[1*], Ákos Kukovecz[1], Zoltán Kónya[1,2]

[1]Department of Applied and Environmental Chemistry, Interdisciplinary Excellence Centre, University of Szeged, H-6720, Rerrich Bela ter 1, Szeged, Hungary
[2]ELKH-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Rerrich Béla tér 1, Szeged 6720, Hungary

Corresponding Author: Haythem Basheer, haythemsuliman@gmail.com

Abstract

In this study, the catalytic behavior of nickel (Ni) and nickel phosphide (Ni_2P) in the Reverse Water-Gas Shift (RWGS) reaction was investigated, with a focus on understanding how Ni_2P mimics platinum (Pt) in selectively producing CO, rather than CH_4, which is typically the main product in the presence of pure Ni. This shift in selectivity is believed to arise from changes in the electronic properties of Ni upon the formation of Ni_2P, making its catalytic performance resemble that of Pt.

To explore the underlying electronic factors contributing to this synergistic effect**,** Density Functional Theory (DFT) calculations were carried out using the Quantum ESPRESSO package. The DFT analysis provided insights into the electronic structure, charge distribution, and adsorption energies of the relevant intermediates on Ni, Ni_2P, and Pt surfaces, helping to elucidate how Ni_2P alters the electronic environment of Ni to enhance CO production.

Keywords: Electronic properties, synergetic effect and selectivity.

Acknowledgments Department of Applied and Environmental Chemistry, Interdisciplinary Excellence Centre, University of Szeged, Hungary, Ministry of Innovation and Technology of Hungary and stipendium hungaricum scholarship.

References

[1] Lentz, Claudia, Sara Panahian Jand, Julia Melke, Christina Roth, and Payam Kaghazchi. "DRIFTS study of CO adsorption on Pt nanoparticles supported by DFT calculations." *Journal of Molecular Catalysis A: Chemical* 426 (2017): 1-9.

[2] Al Ali, Latifa, Sara Alkhoori, Omer Elmutasim, Khalid Al-Ali, and Kyriaki Polychronopoulou. "Computational insights into the deoxygenation reaction of biomass-derived phenolic compounds over Ni2P (001) catalysts." *Materials Chemistry and Physics* (2024): 129926.

P 2 - Valorizing biomass waste glycerol to fuel additive at room temperatureusing a nanostructured mixed oxide catalyst

Suresh Babu Putla[1], Palanivel Subha[1], Bhattu Swapna[1], Nittan Singh Putla[2]
Sudarsanam*[1]

[1] Department of Chemistry, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana, India – 502284
[2] Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune,India – 411008

Corresponding Author: Putla Sudarsanam, Sudarsanam.putla@chy.iith.ac.in

Abstract

The necessity of converting waste into value-added materials, chemicals, and fuels is essential for a sustainable future[1]. Non-edible lignocellulosic biomass (e.g., wood, corn stover, bagasse, and forestry residues) majorly comprises three components, namely cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are composed of carbohydrates, and lignin is a functional aromatic polymer, which is also obtained as waste from the pulp/paper industry and 2G ethanol biorefinery[2]. This project involves acetalizing biomass-derived glycerol into solketal at room temperature over a synergistic WO_3/Nb_2O_5 nanocatalyst.

Glycerol is a major byproduct of biodiesel production and is available to a large extent. Thus, valorizing glycerol into value-added chemicals and fuels is very important to boost the biodiesel industry and foster the concept of waste-to-wealth.[3] The primary objective of this study was to convert glycerol into solketal (a valuable fuel additive) via acetalization.[4] Among all the available techniques, heterogeneous catalysis is one of the most important and reliable tools in valorizing glycerol and all types of biomass into various functional molecules and drop-in chemicals.

In this catalytic approach, we found an interesting pathway to produce solketal from glycerol with acetone at room temperature using a nanostructured WO_3/Nb_2O_5 solid acid catalyst. The catalyst must contain acid sites to activate the acetone, as glycerol and acetone are immiscible at room temperature. Thus, we found that WO_3 and Nb_2O_5 are suitable acid catalysts among other available metal oxides andare prepared by the hydrothermal method followed by the incipient wet-impregnation method.

The catalyst was characterized and investigated by various characterization techniques such as powderXRD, pyridine-adsorbed FT-IR spectra, Raman spectroscopy, TEM, STEM-EDAX, and BET surface area.[5] The efficiency and stability of the catalysts for glycerol acetalization with acetone were supportedby several catalytic activity studies, such as catalyst screening, time on stream studies, hot-filtration test, and catalyst reusability. In summary, we found an efficient method to convert glycerol into solketalusing acetone in the presence of solid acid catalysts at room temperature. Interesting observations fromthis study will be elaborated in the poster presentation.

Keywords: Acid catalysis, Biomass Valorization, Nanocatalysts, Acetalization.

References

[1] P. Sudarsanam, R. Zhong, S. Van den Bosch, S. M. Coman, V. I. Parvulescu and B. F. Sels, *Chem Soc Rev*, 2018, **47**, 8349–8402.
[2] P. Sudarsanam, E. Peeters, E. V. Makshina, V. I. Parvulescu and B. F. Sels, *Chem Soc Rev*, 2019, **48**, 2366–2421.
[3] A. F. Lee, J. A. Bennett, J. C. Manayil and K. Wilson, *Chem. Soc. Rev.*, 2014, **43**, 7887–7916.
[4] C. A. Akinnawo, L. Mosia, O. A. Alimi, C. O. Oseghale, D. P. Fapojuwo, N. Bingwa and R. Meijboom, *Catal Commun*, 2021, **152**, 106287.
[5] N. Singh, P. N. Kalbande, S. Umbarkar and P. Sudarsanam, *Molecular Catalysis*, 2022, **532**, 112742.

P 3 - Biomass carbon-assisted soft oxidative dehydrogenation of ethylbenzene to styrene *via* CO_2 as soft oxidant

Rohit Rangnath Nikam[1], B. M. Nagaraja[1*]

[1] *Centre for Nano and Material Sciences (CNMS), Jain (Deemed-to-be-University), Jain Global Campus, Bangalore-562112, India.*

Corresponding Author: B. M. Nagaraja, bm.nagaraja@jainuniversity.ac.in

Abstract

The increasing concern for the excessive usage of fossil fuels and the increase in energy demand has led to the industrial sector along with the effect of global warming. [1, 2] The emission of greenhouse gases majorly includes the emission of CO_2 and is considered to be the primary cause of global warming. [2] The vapour-phase catalytic dehydrogenation of ethylbenzene was studied using a bio-derived carbon synthesized by the pyrolysis process. [3,4] The different carbon materials were also tested for the effective conversion of ethylbenzene to styrene wherein the effect of temperature was studied to optimize the studied materials. [4] The catalyst was characterized by different spectroscopic and analytical techniques to study the physiochemical properties. Better catalytic results were obtained at 560 °C with a feed flow of 0.5 mL/h, catalyst amount of 0.5 g, and 40 mL/min CO_2 gas flow. The literature revealed that the acidic sites in the catalyst played a vital role in the higher catalytic activity of the optimized catalyst.

Keywords: Biocarbon, MWCNT, Carbon Granules, Activated Carbon, Ethylbenzene, Styrene, Carbon dioxide

References

[1] Sancheti, Sonam V., and Ganapati D. Yadav. "Highly selective production of styrene by non- oxidative dehydrogenation of ethylbenzene over molybdenum-zirconium mixed oxide catalyst in fixed bed reactor: Activity, stability and kinetics." Catalysis Communications 154 (2021): 106307.

[2] Pochamoni, Ramudu, Murali Kondeboina, Mohan Varkolu, David Raju Burri, and Rama Rao Kamaraju Seetha. "Modification of Al2O3 by activated carbon-supported vanadia catalyst studies for ODH of ethylbenzene in presence of CO2 as a soft oxidant." Emergent Materials 5, no. 6 (2022): 1767-1777.

[3] Pan, Dahai, Yu Ru, Tonglian Liu, Yongjie Wang, Feng Yu, Shuwei Chen, Xiaoliang Yan, Binbin Fan, and Ruifeng Li. "Highly efficient and stable ordered mesoporous Ti-Al composite oxide catalyst for oxidative dehydrogenation of ethylbenzene to styrene with CO2." Chemical Engineering Science 250 (2022): 117388.

[4] Kainthla, Itika, Jayesh T. Bhanushali, Rangappa S. Keri, and Bhari Mallanna Nagaraja. "Activity studies of vanadium, iron, carbon and mixed oxides based catalysts for the oxidative dehydrogenation of ethylbenzene to styrene: a review." Catalysis Science & Technology 5, no. 12 (2015): 5062-5076.

P 4 - Graphitic carbon nitride(g-C_3N_4)/ZnO perovskite-based interface for sustainable decontamination of Pollutants from wastewater using Visible-lightdriven photo-catalysis

SahimaTabasum[1], Alok Kumar Rai[2]

[1]*Department of Environmental Sciences, School of Climate Change and Sustainability, Institution of Eminence, University of Delhi, Delhi, India*
[2]*Department of Chemistry, University of Delhi, Delhi, India*

Corresponding Author: Sahima Tabasum Sahimatabasum1997@gmail.com

Abstract

Per- and poly-fluoroalkyl substances (PFASs) and Pesticides are an emerging group of persistent organic pollutants in aquatic environments with high toxicity levels and bioaccumulation. Therefore, advanced, effective methods need to be developed to minimize or neutralize the environmental harm of these pollutants. Photo/electrocatalytic heterogeneous AOPs, with the assistance of nanostructured catalysts andexternal energy in the form of light/electricity, has emerged as one of the most powerful techniques, overcoming the difficulty associated with defluorination and achieving the effective and complete degradation of PFASs and Pesticides in water. Graphitic carbon nitride(g-C_3N_4), is a polymeric material consisting of C, N, and some impurity H, due to the special semiconductor properties of carbon nitrides, they show unexpected catalytic activity for a variety of reactions, and the catalytic activity of the g-C_3N_4 can be improved by the doping with the transition metals such as V_2O_5, ZnO, perovskite, The g-C_3N_4 doped with La_2O_3 photocatalyst shows enhanced visible-light photocatalytic activities for the mineralization of Chlorpyrifos.

The nanocomposite is synthesized using hydrothermal and microwave techniques. The powder X-ray diffraction technique is employed to identify the crystal structure of a ternary nanocomposite material, specifically focusing on the crystallite size, phase, and defects. The surface morphologies and functional groups are assessed using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FT-IR). The FTIR analysis reveals the presence of C–N and C=N stretching modes in the heterocycle, characterized by bands ranging from 1200 to 1650 cm^{-1}. The experiment aimed to study the effects of several experimental factors, including pH, time, H_2O_2 concentration, and Catalyst Dose, on the breakdown of Chlorpyrifos. The results suggest that PFOA degrades in the presence of g-C_3N_4)/ZnO perovskite via a hole-initiated reaction pathway similar to the TiO2 case and involves superoxide/hydroperoxyl and hydroxyl radicals. These findings offer new possibilities for designing materials and re-evaluating alternative wide band gap semiconductors to break PFAS and pesticides by photocatalysis.

Keywords: *Solar-catalyst; mineralization; g-C_3N_4; Pesticides; PFASs;*

Acknowledgments This work is supported by the Institution of Eminence, University of Delhi.

References

[1] Das, S., Paul, T., Maiti, S., & Chattopadhyay, K. K. (2020). Ambient-processed CsPbX3 perovskite cubes for photocatalysis. *Materials Letters*, *267*, 127501.
[2] Olatunde, O. C., Kuvarega, A. T., & Onwudiwe, D. C. (2020). Photo-enhanced degradation ofpolyfluoroalkyl and perfluoroalkyl substances. *Heliyon*, *6*(12).

P 5 - Ceria-alumina based hydrogenation/dehydrogenation catalysts for LOHC systems

Yuting Shi[1,2], Ferenc Lónyi[1], Tibor Nagy[1], József Valyon[1], Ágnes Szegedi[1]

[1]HUN-REN Research Centre for Natural Sciences, Institute of Materials and Environmental Chemistry, 1117 Magyar tudósok krt. 2, Budapest, Hungary
[2]Doctoral School of Environmental Sciences, Eötvös Loránd University, 1053 Egyetem tér 1-3, Budapest, Hungary

Corresponding Author: Yuting Shi , shi.yuting@ttk.hu

Abstract

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.

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/γ-Al_2O_3 support containing 20 wt.% cerium was prepared by 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 CeO_2-Al_2O_3 supports were loaded with 10 wt.% metal (Ni only, or 6 wt. % Ni and 4 wt.% Zn) by incipient wetness impregnation. The NiCe and NiZnCe catalysts were much more active and stable in dehydrogenation reaction compared to 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 has high specific surface area and pore volume, and that finely dispersed, crystalline ceria homogenously covered the surface of alumina. By this preparation method a high surface area ceria support could be produced, 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 at lower temperatures 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.

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

Acknowledgments: Financial supports of HUN-REN Proof of Concept project, ELKH POC-2022-006, KSZF-16/2022, and National Research, Development and Innovation Fund project FK134332 are greatly acknowledged.

P 6 - Synthesis of metal sulfide/*g*-C_3N_4 nanocomposite for photocatalytic degradation of organic pollutant under visible light

Shoaib Mukhtar, **Erzsébet Szabó-Bárdos, Ottó Horváth**

Research Group of Environmental and Inorganic Photochemistry, Center for Natural Sciences,
University of Pannonia, H-8210 Veszprém, POB. 1158, Hungary

Corresponding Author: shoaibmukht131@gmail.com

Abstract

Graphitic carbon nitride (g-C_3N_4) is a fascinating two-dimensional (2D) material that possesses exceptional properties, including its ability to absorb visible light, excellent thermal stability, and high abundance of its constituents in the earth crust. Unlike traditional photocatalysts such as titanium dioxide (TiO_2), g-C_3N_4 is able to effectively operate under visible light, which makes up a significant portion of the solar spectrum. This makes it a more sustainable option for environmental remediation. Nevertheless, the effectiveness of pure g-C_3N_4 in photocatalysis is hindered by issues like the quick recombination of electron-hole pairs and a relatively small surface area. To address these challenges, g-C_3N_4 is modified with metal sulfides like manganese sulfide (MnS), zinc sulfide (ZnS), and bismuth sulfide (Bi_2S_3), using a simple sustainable method utilizing starch. These modifications optimize the separation of charge carriers and enhance light absorption, resulting in a substantial improvement in photocatalytic efficiency.

These composite materials have demonstrated impressive capabilities in efficiently breaking down coumarin and para-nitrophenol, when exposed to visible light. Through the combination of g-C_3N_4 and metal sulfides, the degradation rates are significantly increased, making them highly effective in environmental cleanup applications.

This development provides a powerful and environmentally friendly solution for breaking down organic pollutants found in wastewater and industrial effluents.

Acknowledgments This work was supported by the National Research, Development, and Innovation Office of Hungary in the frame of the bilateral Hungarian-Vietnamese S&T Cooperation Program (project code 2019-2.1.12-TÉT_VN-2020-00009) and by the Ministry for Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the 2021 Thematic Excellence Program funding scheme (grant number TKP2021-NKTA-21).

P 7 - Reactivity of various monoterpenic alcohols under acid-catalyzedcondition in alkyl acetates

Anna Rejzková[1], Eliška Vyskočilová[1]

[1]*Department of Organic Technology, University of Chemistry and Technology, Prague,Czech Republic*

Corresponding Author: Anna Rejzková, anna.rejzkova@vscht.cz

Abstract

Monoterpenic alcohols are very interesting compounds. They are present in several plants, especially in herbs and conifers[1]. Thus, these compounds can used as biorenewable resources. They have a characteristic scent and thanks to it they are used as fragrances in perfumery and cosmetics. Monoterpenic alcohols often possess positive biological activity (e.g., analgetic, anti-inflammatory, antioxidant, antihypertensive, and insecticidal properties).

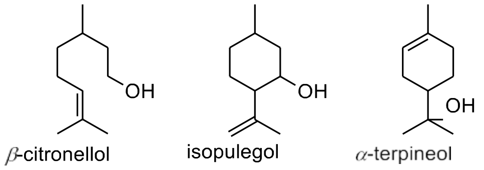


Fig. 1: Structures of studied monoterpenic alcohols

We want to study the reactivity of some monoterpenic alcohols by heterogeneous acid catalysis in various alkyl acetates, and their possibility to convert into corresponding acetates by transesterification. We chose three alcohols: primary – β-citronellol, secondary – isopulegol, and tertiary – α-terpineol (Fig. 1). Strong acid catex Amberlyst 15 was used as a catalyst.

The experiments were performed in a glass reactor with a condenser in an oil bath. The compositions of collected samples were analysed by gas chromatography with flame- ionization detection. The compounds were identified by gas chromatography with mass detection.

During our study, we observed the different behaviour of alcohols. β-Citronellyl acetate was produced at almost 100 % selectivity from β-citronellol. The secondary isopulegol provided isopulegyl acetate at 66 % selectivity. In contrast, when we used α-terpineol, we obtained the mixture of 1,8-cineol and several monoterpenes. In this case, the isomerization (and dehydration)was the main way of the conversion.

Keywords: monoterpenic alcohol, transesterification, isomerization, acid catalysis

Acknowledgments This work was supported the grant of Specific university research from Grant No.A1_FCHT_2024_004 and Grant No. A2_FCHT_2024_035.

References

[1] M. Dvořáková, I. Valterová, T. Vaněk, *Chem. Listy* 105, **2011**, 839-845.

P 8 - Bismuth oxychloride microcrystals decorated carbon foam derivedfrom waste polyurethane elastomer for enhanced removal of methylene blue

Mahitha Udayakumar[1], Zoltán Németh[2], Klara Hernadi[3*]

[1]*Department of Surface Chemistry and Catalysis, HUN-REN Centre for EnergyResearch, H-1121 Budapest, Hungary*
[2]*Advanced Materials and Intelligent Technologies Higher Education and Industrial Cooperation Centre, University of Miskolc, H-3515 Miskolc, Hungary*
[3]*Institute of Physical Metallurgy, Metal Forming and Nanotechnology, University ofMiskolc, H-3515 Miskolc, Hungary*

***Corresponding Author: Klara Hernadi**, femhernadi@uni-miskolc.hu

Abstract

Multicomponent materials containing nanoscale structures, the so-called “nanocomposites” are one of the fastest-growing areas of photocatalytic research. In this study, the nanocomposites of bismuth oxychloride (BiOCl) with porous carbon foam (CF) derived from waste polyurethane (PU) elastomer were developed by a simple hydrothermal method, and the photocatalytic performance of the as-prepared materials was investigated. The applicability of this type of waste polymer-derived CFs in photocatalytic water treatment was investigated in linewith multiple Sustainable Development Goals (SDGs) of the United Nations, e.g., Goal 6 (Clean Water and Sanitation) and Goal 12 (Responsible Consumption and Production)[1]. The structure, morphology and optical properties of the composites were characterized in detail. The photocatalytic activity of the samples was evaluated by studying the degradation of methylene blue (MB) under UV-A irradiation. Even at a high MB concentration (0.5 mmol/L), excellent photocatalytic activity was observed, with an overall removal efficiency of 99.0% in 100 min irradiation. Kinetic studies were also carried out for the degradation of MB by pristine BiOCl andCF-BiOCl. The photodegradation rate constants were evaluated by fitting the kinetic data with apseudo-first-order model, and the rate constants of CF-BiOCl composites were higher than that of pristine BiOCl. The enhanced activity of the composites was due to the well-connected heterojunction interface, improved hydrophilicity, more reactive sites, and effective separation ofphoto-generated charges. Thus, our work combines the valuable waste PU-derived CFs with BiOCl, which provides a strategy to achieve circular economy and environmental remediation objectives.

Keywords: Carbon foam, Bismuth oxychloride, Nanocomposite, Methylene blue,Photocatalytic activity

Acknowledgements Zoltán Németh would like to thank the Hungarian Academy of Sciences Bolyai JánosResearch Scholarship Program.

References

[1] Take Action for the Sustainable Development Goals - United Nations Sustainable Development. https://www.un.org/sustainabledevelopment/sustainable-development-goals/ (accessed Aug. 25, 2024).

P 9 - Photocatalytically active CdS decorated spherical and plate-like TiO_2

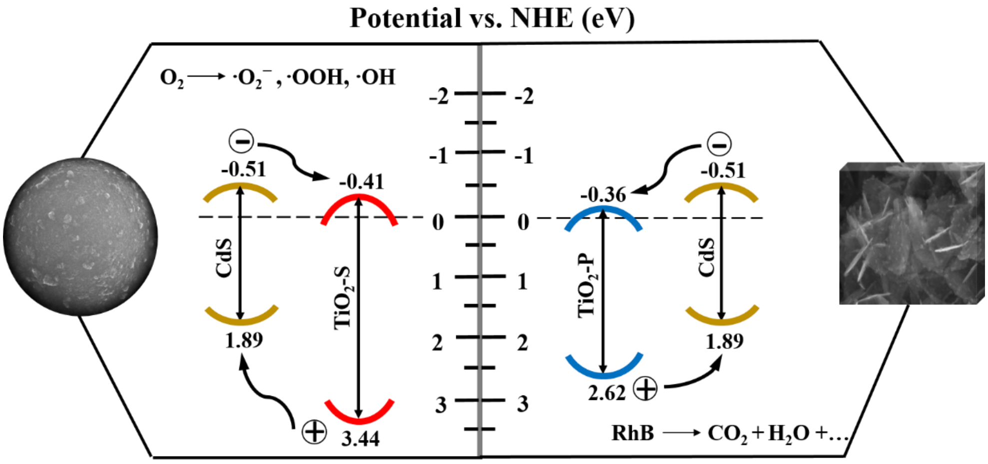
Çağdaş Yavuz[1], Henrik Haspel[1,2,*], Zoltán Kónya[1,2]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Abstract

Photocatalytic degradation is an advanced oxidation process, an effective technique for the removal of organic contaminants from wastewater, important in environmental protection and waste management. TiO_2 has long been recognized as a promising photocatalyst in the UV region with severe limitations in the visible range. Efforts have been made to overcome these drawbacks, and TiO_2 decorated by narrow band gap co-catalysts demonstrated improved photocatalytic activity in the visible spectrum. The current study compares four samples that were produced via an easy and affordable wet-chemical method. Spherical (TiO_2-S) and plate-like (TiO_2-P) TiO_2 particles were decorated by nanosized CdS, and the structure, morphology, optical properties, and elemental composition of the fabricated nanocomposites were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), UV-visible DRS and energy-dispersive X-ray spectroscopy (EDS). The photocatalytic degradation activity of the TiO_2/CdS samples was characterized in dye decolorization experiments using rhodamine B (RhB) at an initial concentration of 10^{-5} M under Xenon light exposure. Changes in morphology, crystallite size, and band alignment affected the removal efficiency of organic pollutants from water, and the TiO_2-S/CdS sample showed a pollution degradation rate of 96.8% after 180 min light exposure.



Keywords: TiO_2/CdS, composite photocatalyst, photodegradation, rhodamine B

P 10 - Comparative analyzes of tip tilting of CO-terminated tips on experimental and simulated STM setups

Ivan Abilio^{1,2}, Nicolas Néel^{3}, Jörg Kröger^{3}, and Krisztián Palotás^{1,2,4}

[1]Department of Theoretical Solid State Physics, Institute for Solid State Physics and Optics, HUN-REN Wigner Research Center for Physics, H-1121 Budapest, Hungary
[2]Department of Theoretical Physics, Institute of Physics, Budapest University of Technology and Economics, H-1111 Budapest, Hungary
[3]Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany
[4]HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, H-6720 Szeged, Hungary

Corresponding Author: Ivan Abilio, abilio.ivan@wigner.hun-ren.hu

Abstract

Tip functionalization is an important tool for STM imaging, as it can provide a series of benefits from improved spatial resolution to selective interaction, and CO functionalization has been shown to have high spatial resolution [1,2]. Most functionalizations, however, are known for bending in unpredictable manners, causing a tip tilting that can greatly affect the orbital interactions and therefore the generated images. To better understand and identify the effects of the functionalization tilting, we compared experimental STM images with simulated STM images of CO tips over CO molecule (relevant for catalysis applications) and Cu adatom adsorbed on a Cu(111) substrate, at different tip-tilt angles, tip heights, and voltages [3]. For the simulations, we employed density functional theory (DFT) calculations of the sample and the functionalized tips, as well as model tips, to produce STM images through the revised Chen method [4] that could be compared with the experimental ones. Furthermore, a novel technique allowed us to analyze the individual contributions of the atomic orbitals of the tip (and their interferences) upon the current of any specific point of the simulated STM image, allowing for a deeper understanding of the functionalization impact on the current. Through this comparison we gained further insight into the effects of tip functionalization and its tilting, allowing for easier identification of their real state on experimental setups, as well as understanding better the role of each tip-orbital, which provides insights on the sample's physical and chemical properties.

Keywords: CO tip, tip tilting, tip-orbitals, DFT, STM

Acknowledgments Financial support from the National Research Development and Innovation Office of Hungary (NKFIH, Grant No. FK124100), a Stipendium Hungaricum Scholarship of the Tempus Public Foundation, the János Bolyai Research Grant of the Hungarian Academy of Sciences (Grant No. BO/292/21/11), the New National Excellence Program of the Ministry for Culture and Innovation from NKFIH Fund (Grant Nos. UNKP-22-5-BME-282, UNKP-23-5-BME-12) and from the Deutsche Forschungsgemeinschaft through KR 2912/17-1 is acknowledged.

References

[1] P. Hapala, G. Kichin, C. Wagner, F. S. Tautz, R. Temirov, and P. Jelínek,, *Phys. Rev. B 90*(8), **2014**, 085421.
[2] L. Bartels, G. Meyer, K.-H. Rieder, D. Velic, E. Knoesel, A. Hotzel, M. Wolf, and G. Ertl, *Phys. Rev. Lett. 80*(9), **1998**, 2004.
[3] Abilio, I., Néel, N., Kröger, J., & Palotás, K., *arXiv.org*, **2024**, https://arxiv.org/abs/2406.12601
[4] Mándi, G., & Palotás, K. *Phys. Rev. B 91*(16), **2015**, 165406.

P 11 - Utilization of cutting-edge, cost-effective nanocomposites with outstanding anticorrosive properties in waterborne coatings

Walaa M. Abd El-Gawad

[1]*Polymers and Pigments Dept., National Research Centre, Dokki, Giza, Egypt*

Corresponding Author: Walaa M. Abd El-Gawad, chem.walaa@yahoo.com

Abstract

Water-borne coatings have been attracting a lot of interest lately, driven by human health and eco-system requirements due to their low toxicity, low volatile organic compounds, and low flammability. The aim of this study is to prepare anticorrosive water-borne coatings based on advanced nanocomposites. First, a thin layer of nanoZnO or nanoCuO was precipitated on the surface of silica fume waste by using the sol-gel method. Besides, pure nano-ZnO or nano-CuO was synthesized for comparison. Then, the synthesized nanocomposites and nanomaterials were integrated into the acrylic emulsion with two ratios (e.g., 5% and 25%) to form cost-effective and eco-friendly anticorrosive coatings. The performance of the anticorrosive coatings was investigated using electrochemical impedance spectroscopy and scanning electron microscopy. Throughout the test period, the results showed the resistance of coatings based on 25% nanoZnO/silica fume and 25% nanoCuO/silica fume was much greater than that of the other coatings, indicating a good barrier effect, followed by nanoZnO and nanoCuO. Therefore, it can be concluded that utilizing the modified silica fume industrial waste in water-borne coatings could achieve the eco-friendly principle, which can be regarded as an economical and green strategy.

Keywords: water-borne coatings; nanocomposites; corrosion resistance; nanoZnO; nanoCuO

Acknowledgments This work was supported by Academy of Scientific Research and Technology - ASRT in Egypt [Grant entitled Initiative to deepen local industrialization]**.**

References

[1] A.I. Hafez, H.M. Ali, R.M. Sabry, H.M. El-Masry, W.M. Abd El-Gawad, Generation of novel, hygienic, inhibitive, and cost-effective nanostructured Core-shell pigments, Progress in Organic Coatings 175, 2023, 107325.

[2] W.M. Abd El-Gawad, E.A. Mossalam, M.M. Selim, Synthesis and Application of Cost- effective Egyptian Blue Pigments for Versatile Decorative and Anticorrosive Coatings, Materials today Communications 37, 2023, 107412.

[3] N.M. Ahmed, W.M. Abd El-Gawad, E.M.R. Souaya, Evaluation of the anticorrosive performance of epoxy coatings containing new core/shell pigments, Pigment & Resin Technology 47, 2018, 116-126.

[4] N.M. Ahmed, M.G. Mohamed, W.M. Abd El-Gawad, Corrosion protection performance of silica fume waste-phosphates core-shell pigments, Pigment & Resin Technology 47, 2018, pp. 261-271.

P 12 - Evaluating the sustainability of holding glass fiber in natural rubber for various industrial applications

Mahmoud D.S[1], **El-Sabbagh S.H[1]**

[1]*Polymers and Pigments Department, National Research Centre, Giza, Egypt*
[2]*Therapeutic Chemistry Department, National Research Centre, Giza, Egypt*

Corresponding Author: Mahmoud D.S, doaa.samiir@yahoo.com

Abstract

Glass fiber is inorganic fiber to utilize in rubber technological products. The purpose of this article is to evaluate the properties of nature rubber/glass fiber composites. Glass fiber (GF) is interesting fiber reinforcement for the modern composites, to reduce the total cost and achieve improved mechanical characteristics. Variety of tests was assessed on the investigated natural rubber composites towards exploring their morphological aspects, rheological, swelling and mechanical properties. The findings showed that the GF exhibited superior interfacial interaction with the rubber chains, improving modulus at 100 and 300% strain, tensile strength, strain energy and Payne effect. The morphology of the fractured sample surfaces revealed that good adhesion between the GF, and the natural rubber chains. The NR composites contained 16 phr GF illustrated outstanding results in terms of reduced swelling features; in toluene revealing that this fiber has a lot of potential for use in rubber utilized as interior car accessories. Good safety properties were demonstrated by the cytotoxicity test findings on the produced vulcanizates against the human normal fibroblast cell line (BJ1). The car accessories industry will benefit from the study's conclusions regarding benchmarking and optimizing environmental sustainability, and consumers will find the results insightful.

Keywords: Glass fiber (GF); Natural rubber; Rheological characteristic, Mechanical properties; Swelling resistance

P 13 - Na-Fe_3O_4 catalyst for CO_2 hydrogenation to produce C_{5+} liquid fuels:Impact of catalyst pretreatment conditions

Dr. Rajib Kumar Singha, Dr. Astha Shukla, Papp Ádám, Anastasiia Efremova, Henrik Bali, Dr. András Sápi*

Department of Applied and Environmental Chemistry, Interdisciplinary ExcellenceCentre, University of Szeged, Rerrich Béla tér 1, Szeged 6720, Hungary

Corresponding Author: Dr. András Sápi, sapia@chem.u-szeged.hu

Abstract

CO_2 conversion, utilization is one of the major topics of heterogenous catalysis research, due to its impact towards environmental and climate change issues for sustainable future. Catalytic CO_2 conversion to liquid fuels is one of the potential routes to tackle this environmental challenge. Direct conversion of CO_2 to C_{5+} gasoline liquids is a potential CO_2 conversion route[1,2] which canbe applied in large scale if a suitable catalyst and process conditions can be established.

Direct CO_2 conversion to C_{5+} gasoline fuels are structure sensitive and depending on the active species properties, formation of gasoline liquids varies. Just like Fischer-Tropsch synthesis, for this case also it is found that Fe-carbide is the main active species. There are few different types of Fe-carbide possible but for this particular case, χ-Fe_5C_2 (Hagg Carbide) is the most active form.[1-4] Depending on the catalyst pretreatment conditions, the formation and phase change of χ-Fe_5C_2 is highly possible, which can alter the reaction results and effect on selectivity of the desiredC_{5+} production.

A 1wt%Na-Fe_3O_4 catalyst was prepared following a reported method.[4] This catalyst was appliedfor direct conversion of CO_2 to C_{5+} gasoline fuels via CO_2 hydrogenation process keeping H_2/CO_2ratio 3/1. Before the actual experiment, the catalyst was pre-treated in different temperature and gas environments to generate the active χ-Fe_5C_2. The pretreatment was performed at 300-450 °Cin presence of (i) hydrogen (H_2), (ii) hydrogen (H_2) and then carbon monoxide (CO), and (iii) syngas (H_2/CO=1) gas environments. Although, χ-Fe_5C_2 species can be formed in-situ (or duringthe reaction) and the catalyst can still produce C_{5+} molecules, but it was found that generation ofactive χ-Fe_5C_2 species before starting the actual CO_2 hydrogenation experiment have a positive effect on C_{5+} product formation, provided that the right conditions are applied to generate χ-Fe_5C_2species on the catalyst surface. Detailed investigation is ongoing.

Keywords: CO_2 hydrogenation; C_{5+} fuels; Na-Fe_3O_4; χ-Fe_5C_2; pretreatment conditions

Acknowledgments Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus. The authors would like to thank University of Szeged, Hungary for allowing this research to carry out.

References

[1] P. Kaiser, R.B. Unde, C. Kern, A. Jess, *Chemie Ingenieur Technik* 85(4), **2013**, 489–499.

[2] X. Shang, G. Liu, X. Su, Y. Huang, T. Zhang, *EES Catalysis* 1, **2023**, 353–368.

[3] J. Zhu, P. Wang, X. Zhang, G.Zhang, R. Li, W. Li, T.P. Senftle, W. Liu, J. Wang, Y. Wang, A.Zhang, Q. Fu, C. Song, X. Guo, *Science Advances* 8, **2022**, eabm3629.

[4] S. Najari, S. Saeidi, A. Sápi, Á. Szamosvölgyi, Á. Papp, A. Efremova, H. Bali, Z. Kónya, *Chemical Engineering Journal* 485, **2024**, 149787.

P 14 - Scale-up of catalyst and their activities for CO_2 activation towards C_{5+}fuels

Dr. Astha Shukla, Dr. Rajib Kumar Singha, Ádám Papp, Anastasiia Efremova,
Prof. Zoltán Kónya, Dr. András Sápi*

Department of Applied and Environmental Chemistry, Interdisciplinary ExcellenceCentre,
University of Szeged, Rerrich Béla tér 1, Szeged 6720, Hungary

Corresponding Author: Dr. András Sápi, sapia@chem.u-szeged.hu

Abstract

CO_2 utilization is one of the most important topics of recent catalysis research. Converting CO_2, a greenhouse gas to C_{5+} fuels not only alleviate the CO_2 emission, but can also provide liquid fuels with high potentials to enhance energy security for sustainable future. However, CO_2 is chemically inert, thermodynamically stable and has a fully oxidized carbon atom which requireshigh energy to activate it. To produce C_{5+} fuels (i.e., long chain hydrocarbons), Fe-based catalysts are reported to be potential candidates[1]. For Fe-catalysts, not oxides or metallic Fe but Fe-carbide is established as the active species for the said purpose[1]. Scale-up of a heterogeneouscatalyst is quite challenging because it is not just producing more catalyst, rather to ensure that there is not much change in its physicochemical properties and it works efficiently in large scale. A small change in the synthesis process could lead to big change in the material property which in turn may affect the reproducibility of catalytic activity data. Here, we tried to upgrade the material synthesis from 5g to 100g in number of steps, following a reported method[2]. We kept the ratio of the chemicals fixed upto 60g batch then there was little change for 100g batch.

For CO_2 to C_{5+} fuels conversion process, we successfully upgraded a Na-Fe_3O_4 catalyst from 5g to 100g without any significant change in its property and activity. The physicochemical properties of materials were checked by analytical techniques. To compare the differences in their activities, all synthesized materials were investigated for CO_2 hydrogenation reaction to produce C_{5+} fuels. Preliminary experimental results of synthesized batches showed almostunchanged activity pattern. This study provides how we can upgrade a lab-scale catalyst synthesis process to much larger scale material synthesis process without affecting the properties and activity of it, which advances by better understanding of the scale-up process. In addition, this scale-up study will fulfill industrial demands of scaling up a lab scale catalyst to pilot scale, and the goal of bringing lab innovations to the pilot-scale.

Keywords: Catalyst Scale-up, Na-Fe_3O_4, CO_2 hydrogenation, C_{5+} fuels

Acknowledgments Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

References

[1]X.Shang, G. Liu, X. Su, Y. Huang, T. Zhang, *EES Catalysis* 1, **2023**,353-368.

[2]S. Najari, S. Saeidi, A. Sápi, Á. Szamosvölgyi, Á. Papp, A. Efremova, H. Bali, Z. Kónya, J.Chem. Eng., 485, **2024**, 149787.

P 15 - PtCo Alloy Nanoparticles for Stable Reverse Water Gas Shift Activation of CO_2

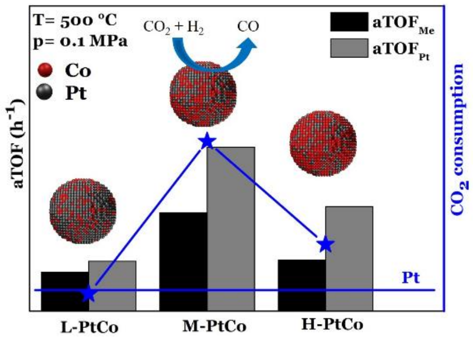
Ákos Szamosvölgyi[1], Ádám Pitó[2], Anastasiia Efremova[1], Kornélia Baán[1], Bence Kutus[2], Suresh Mutyala[1], András Sápi[1,3], Imre Szenti[1,4], Tamás Kolonits[5], Zsolt Fogarassy[5], Ákos Kukovecz[1], Zoltán Kónya[1,4]

[1]*University of Szeged, Department of Applied and Environmental Chemistry, H-6720, Rerrich Béla tér 1, Szeged, Hungary*
[2]*University of Szeged, Department of Molecular and Analytical Chemistry, H-6720, Dóm tér 7-8, Szeged, Hungary*
[3]*University of Szeged, Institute of Environmental and Technological Sciences, H-6720, Szeged, Hungary*
[4]*University of Szeged, HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, H-6720, Szeged, Hungary*
[5]*HUN-REN Centre for Energy Research, Institute of Technical Physics and Materials Science, H-1121, Budapest, Hungary*

Corresponding Author: Ákos Szamosvölgyi, szamosvolgyi@chem.u-szeged.hu

Abstract

Different Co contents were used to tune bimetallic Pt-Co nanoparticles with a diameter of 8 nm, resulting in Pt:Co ratios of 3.54, 1.51, and 0.96. These nanoparticles were then applied to MCF-17 mesoporous silica support. The synthesized materials were characterized with HR-TEM, HAADF-TEM, EDS, XRD, BET, ICP-MS, *in situ* DRIFTS, and *quasi in situ* XPS techniques. The catalysts were tested in thermally induced RWGS reaction (CO_2:H_2 = 1:4) at atmospheric pressure in the 200-700 °C temperature range. All bimetallic Pt-Co particles outperformed the pure Pt benchmark catalyst. The nanoparticles with a Pt:Co ratio of 1.51 exhibited 2.6 times higher activity and increased CO selectivity by 4 % at 500°C. Experiments proved that the electron accumulation and alloying effect on the Pt-Co particles are stronger with higher Co ratios. The production of CO followed the formate reaction pathway on all catalysts due to the ffc structure which is similar to the Pt benchmark. It is concluded that the enhancing properties of Co culminate at a Pt:Co ratio of 1.51, since decreasing the ratio to 0.96 results in lower activity despite having more Co atoms available for the electronic interaction. This is due to the fact that less electron-rich Pt is available for the reaction.



1 w/w % Pt-Co bimetal nanoparticles loaded onto MCF-17 SiO_2 support are compared in RWGS reactions. Differences in their activity are demonstrated with CO_2 consumption rate and apparent TOF specified to the Pt and cumulative metal atoms on the catalyst at 500 °C and 0.1 MPa reaction conditions. The main product of the reaction is CO, with > 98 % selectivity.

Keywords: Pt, Co, alloy nanoparticles, reverse water-gas shift reaction, carbon monoxide

P 16 - An integrated approach for biomass waste valorization: *bio*-chemicalsextraction and fuel production by catalytic gasification under supercritical water

S. Donato[1], A. Cajumi[2], S. Todaro[1], M. Santoro[1], F. Arena[2], F. Randazzo[1], M. Samperi[1], G. Bonura[1], C. Cannilla[1*]

[1]*CNR-ITAE, via S. Lucia sopra Contesse 5, 98126 Messina, Italy.*
[2]*Università degli Studi di Messina, Dip. Ingegneria, c.da Papardo, 98166 Messina, Italy*

Corresponding Author: Catia Cannilla, catia.cannilla@cnr.it

Abstract

The agro-food sector produces 400 thousand tons/year of wet waste in Sicily, which cause serious environmental pollution problems if not properly treated. For this reason, innovative technologiesare necessary to reuse and valorize wet agroindustrial waste (WAW) containing a very low organic matter (<20% by weight) with the production of biofuels and higher value products in theframe of the circular economy. On this account, the physical characteristics of water under supercritical conditions (400 °C and 22.4 MPa) make it a non-polar solvent and at the same timea reagent for gasification reaction (SCWG) of WAW to CH_4 or H_2-rich flow. In this study, a stirred reactor designed to validate the efficiency of structured catalysts has been used and to define the optimal reaction conditions for the conversion of model molecules, as representative of wastes coming from citrus industries. A customized robocasting machine represents a powerful tool to properly tune the multifunctional features of no-noble based catalysts characterized by defined multi-channel geometry and specific porosity. This could ensure the best accessibility tothe active sites and overcome plugging problems due to inorganic compounds precipitation whichtypically affect the lifetime of powdered catalysts[1]. Ni-based catalysts have been prepared and thebehaviour of structured and powdered materials have been compared in terms of biomass conversion and methane selectivity. To enhance the economic sustainability of the process, before SCWG, a preliminary extraction from WAW of added-value chemicals, for pharmaceutical or cosmetic uses, has been carried out. Up today, conventional solvents for organic extractions are based on organic compounds that have a high environmental impact, so green alternative solutionsshould be developed. A new generation of solvents based on natural deep eutectic solvent (NADES) could result a good solution for new extraction methodologies. They, coming from natural precursors, have almost no impact on the environment and their cost is relatively low. Thechemical formulation of suitable solvent could be defined on the basis of the molecule to be extracted[3]. Main results obtained with chloride-choline, glycerol, L-proline and acetic acid will be discussed in terms of extraction efficiency of some flavonoids, polyphenols and D-limonene.

Keywords: wet agroindustrial waste, SCWG, biochemicals extraction, NADES

Acknowledgments PRIN 2022 - Missione 4 Componente 2 investimento 1.1 - D.D. 104 del 02-02-2022 ProgettoAGROMET - 2022EX89KF CUP: B53D23005950006 - Next Generation EU
Bando FIS 2021- Fondo Italiano per la Ricerca – FIS00002427 SUPERBIO

References

[1] F. Frusteri, L. Frusteri, F. Costa, C. Cannilla, G. Bonura, *Applied Catalysis A* 545, **2017**, 24-32.

[2] J. Ren, Y. L. Liu, X. Y. Zhao, J. P. Cao, *Hydrogen Energy* 45, **2020**, 4223-4243

[3] N. Medina-Herrera, G. C. G. Martínez-Ávila, C. Z. Robledo-Jiménez, R. Rojas, B. S. Orozco-Zamora, *Biomass* 4, **2024**, 784-808

P 17 - Investigating Particle Size Effect on Thermal Mechanical Properties of Ceramic Composites: Empirical Design of SiC Milling Energy Map

John. W. Makokha[1, 2], **Imre Szenti**[1], **Tamas Boldizsar**[2], **Koszma Gabor**[1], **Andras Sapi**[1], **Nagy Laszlo**[2]

[1]Department of Applied and Environmental Chemistry, University of Szeged, H-6720 Szeged, Rerrich Bela ter 1, Hungary.
[2]H, K Ceramic Limited, Bese Laszlo Utican, Szentes 6600, Hungary.

Abstract

This study identifies the energy conditions required for achieving specific particle size distribution and morphology through High-Energy Ball Milling. The technique offers advantages such as scalability, ease of operation, cost-effectiveness, and the ability to work with various materials across various hardness levels. WC milling balls (diameter≈10mm and density≈ 14.95g/cm^3) were used with a constant ball-to-powder weight ratio of 15:1 and a charge volume of ≈40%. The milling speed varied from 100 rpm to 600 rpm at intervals of 60, 180, and 360 minutes. SEM analysis revealed plastic deformation at 200 rpm, cold welding between 300-500 rpm, and particle fracturing at 600 rpm. Particles milled at 100 rpm were observed to have smooth edges and enhanced sphericity. XRD characterization illustrated pronounced peak broadening and attenuation at milling speed between 300-500 rpm. A true amorphous phase was observed when SiC was milled at 600 rpm for 3 hours, while phase transformation, i.e., the milling endpoint, was observed to occur at 600 rpm for 6 hours. SEM micrograph and DLS particle size profiling linked microns, submicrons, and nanoparticles to plastic deformation, cold welding, and fracturing, respectively. TGA analysis revealed remarkable thermal integrity of milled SiC particles, exceeding 95%, at 900°C in an oxidizing environment. The designed empirical milling map reliably predicted the milling conditions to synthesize SiC particles with varying particle sizes and morphology. The particles are being investigated for their potential to enhance the thermal-mechanical properties of the ceramic composites.

Keywords: High Energy Ball Milling, Milling Map, Particle Size, SEM

Acknowledgment This Project No. TKP2021-NVA-19 has been implemented with support from the Ministry of Innovation and Technology of Hungary from the National Research, Development and Innovation Fund, financed under the TKP2021-NVA funding scheme. The authors also acknowledge HK Ceramics for providing experimental facilities and research materials.

References

[1] N. Burgio, A. Iasonna, M. Magini, S. Martelli, F. Padella, Mechanical alloying of the Fe−Zr system. Correlation between input energy and end products, Il Nuovo Cimento D 13 (1991) 459–476. https://doi.org/10.1007/BF02452130.

[2] J. Rao, G. Catherin, I. Murthy, D. Rao, B. Raju, Production of nano structured silicon carbide by high energy ball milling, Int. J. Eng. Sci. Tech 3 (2011). https://doi.org/10.4314/ijest.v3i4.68544.

P 18 - Exploring MoVWNbO$_x$ Mixed Oxides for Enhanced Fuel Cell Catalysts

K. Liptak[1,2], E. Talas[1], I. Borbath[1], Z. Paszti[1], M. Mohai jr.[1], K. Laszlo[2], A. Tompos[1]

[1]Institute of Materials and Environmental Chemistry, HUN-REN Research Centre for Natural Sciences, Budapest, Hungary
[2]Department of Physical Chemistry and Materials Science, Budapest University of Technology and Economics, Budapest, Hungary

Corresponding Author: Kata Liptak, liptak.kata@ttk.hu

Abstract

Due to their high energy conversion efficiency and environmental friendliness, fuel cells (FCs) have become a promising technology in the search of sustainable energy alternatives. The materials used for electrodes, especially those that promote electrochemical reactions, are crucial to the performance of FCs. Even though, proton exchange membrane fuel cells (PEMFCs) are already used in some applications, the improvement of their catalyst, membrane and bipolar plates is still an important task. The most commonly used, commercially available catalyst is the carbon supported platinum (Pt/C); however, it has disadvantageous properties like the corrosion of the carbon, agglomeration of the Pt[1] and the high price of the Pt. Therefore, a big demand exists to find new types of supports which provide stability of the Pt nanoparticles. Non-noble metal oxides for this purpose have been investigated 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 metal nanoparticles; and through their hydroxyl groups on the surface, they can participate in the reaction as co-catalysts. Tungsten oxide and molybdenum oxide have already been examined in fuel cells[2,3]; and their features can be changed with additional metal components. The aim of our present study was the synthesis of catalytically active mixed oxides, which provide a possibility of reduced Pt content of the catalyst and are stable in acidic media (under working conditions of PEMFCs). MoVWNbO$_x$ mixed oxides with systematically changed component composition were prepared in microwave assisted reaction. After the heat treatment where the final structure has formed, the Pt introduction (nominal Pt content: 15 wt.%) was made by a UV-light assisted ethanolic reduction. X-ray diffraction measurements revealed that all the samples had tetragonal structure. Electrochemical measurements in a 3-electrode cell, showed that despite the similar structure of the oxides, their electrochemical activity in oxygen reduction reaction (ORR) differed significantly due to the various compositions. Interestingly, the Pt/oxide composites were ORR active even without any carbon material.

Keywords: PEM fuel cell, MoVWNbO$_x$ mixed oxides, microwave-assisted reaction, electrocatalyst

Acknowledgments This research was funded by Project no. RRF-2.3.1-21-2022-00009, titled the National Laboratory for Renewable Energy, and has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

References

[1]Meier, J. C., Galeano, C., Katsounaros, I., Witte, J., Bongard, H. J., Topalov, A. A., ... & Mayrhofer, K. J. *Beilstein journal of nanotechnology 5*(1), **2014**, 44-67.
[2]Hobbs, B. S., & Tseung, A. C. C. (1969). *Nature*, *222*(5193), **1969**, 556-558.
[3]Chen, L., Cooper, A. C., Pez, G. P., & Cheng, H., *The Journal of Physical Chemistry*, *112*(6), **2008**, 1755-1758.

P 19 - 3D-iron-copper nanostructure electrocatalyst for nitrate reduction to ammonia

Saheed Abiola Raheem[1], Gergő Ballai[1], Imre Szenti[2], Henrik Haspel[1,2], Zoltán Kónya[1,2]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Abstract

The release of nitrate (NO_3^-) from industrial wastewater and agricultural activities presents a serious risk to both the environment and human health. To solve this issue, electrocatalytic nitrate reduction (NO_3RR) has gained attention as a promising approach for alleviating the nitrate pollution and converting nitrate into ammonia (NH_3)[1]. Ammonia, in contrast, serves as a crucial precursor in the chemical industry, and is the starting material for producing a range of essential products such as fertilizers, pharmaceuticals, and polymers. Furthermore, with the transition towards a hydrogen-based economy, efficient hydrogen storage remains a key challenge. Ammonia, with its hydrogen atoms chemically bound within the molecules, offers a potential solution as an energy carrier[2]. Although the NO_3RR is an established reaction, its effectiveness is hindered by low selectivity and NH_3 yield. In this study, we synthesized a non-noble metal catalyst by depositing iron (Fe) onto copper foam (CF). When evaluated in a three-electrode set up under alkaline conditions in the presence of 0.1 M KNO_3, it demonstrated > 99% nitrate conversion along with an appreciable Faradaic efficiency of 64% and a large NH_3 yield of 1910.4 $\mu g\ cm^{-2}\ h^{-1}$. The enhanced performance could be attributed to the synergistic effects between iron and copper which improves the adsorption of NO_3^-. This approach offers a promising strategy for designing electrocatalysts that selectively reduce and convert NO_3^- into NH_3.

Keywords: Electrocatalysis, non-noble catalyst, nitrate reduction, ammonia production

References

[1] X. Zhao, Q. Geng, F. Dong, K. Zhao, S. Chen, H. Yu, X. Quan, Boosting the selectivity and efficiency of nitrate reduction to ammonia with a single-atom Cu electrocatalyst. *Chemical Engineering Journal*, 466, **2023**, 143314.

[2] Z. Deng, C. Ma, Z. Li, Y. Luo, L. Zhang, S. Sun, Q. Liu, J. Du, Q. Lu, B. Zheng, X. Sun, High-efficiency electrochemical nitrate reduction to ammonia on a Co_3O_4 nanoarray catalyst with cobalt vacancies. *ACS Applied Materials and Interfaces*, 14(41), **2022**, 46595-46602.

P 20 - In-situ Investigation of the Coordination Polymer-Derived Ag Catalyst Formation Mechanism

Henrik Haspel,[1,2] **Henrik Fülöp,[2] Gergő Ballai,[2] Dániel Sebők,[2] Imre Szenti,[1,2] Dorina Gabriella Dobó,[3] Ákos Kukovecz,[2] Zoltán Kónya[1,2]**

[1]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*
[2]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[3]*Institute of Pharmaceutical Technology and Regulatory Affairs, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Abstract

Coordination polymers (CPs) and metal organic frameworks (MOFs) are highly ordered 3D structures consist of metallic nodes and organic linker molecules and could potentially be utilized as catalysts or catalyst precursors. For the latter, CPs can be transformed into supported highly dispersed metal nanoparticles at elevated temperature or in a reductive (electro)chemical environment. CP-mediated Ag nanoparticle formation trough the electro-decomposition of a gas-diffusion layer supported silver coordination polymer (Ag-CP) has already been reported. The resulted highly dispersed nanoarrays demonstrated high activity per metal atom in a CO_2RR gas diffusion electrode.[1] Despite the detailed structural studies, the mechanism of Ag nanoparticle formation remained unknown. In this work, the same Ag-CP was synthesized directly onto the microporous layer (MPL) of a carbon cloth gas-diffusion layer (GDL) and as stand-alone crystals via the reaction of Ag^+ and 2,5-Pyridinedicarboxylic acid (PYDC) as the organic linker. The decomposition of Ag-CP was followed under inert and reductive atmospheres by thermal methods (TGA, DSC), and a series of in-situ techniques, i.e., in-situ X-ray diffraction (XRD), in-situ Raman spectroscopy, and in-situ FT-IR spectroscopy. The morphology of the initial and the decomposed Ag-CP was studied by SEM and microcomputed tomography (micro-CT). The better understanding of the CP/MOF-derived catalyst formation could further advance the field of thermal and electrocatalysis.

Keywords: Coordination polymers, metal organic frameworks, silver nanoparticles, electrocatalysis, in-situ techniques

References

[1]R. Wang, H Haspel A. Pustovarenko, A. Dikhtiarenko, A. Russkikh, G. Shterk, D. Osadchii, S. Ould-Chikh, M. Ma, W. A. Smith, K. Takanabe, F. Kapteijn, J. Gascon, *ACS Energy Lett.* 4(8), **2019**, 2024-2031.

P 21 - Photocatalytic Hydrogenation of Carbon Dioxide on Flower-like 3D Bi_2WO_6

Aicha Elaouni[1,2] , Gergo Ballai[2], Haythem Basheer[2], Henrik Haspel[2], András Sápi[2], H. Ait Ahsaine[1], M. Saadi[1]

[1] *Laboratoire de Chimie Appliquée des Matériaux, Centre des Sciences des Matériaux, Faculty of Sciences, Mohammed V University in Rabat, Morocco*
[2] *Department of Applied and Environmental Chemistry, University of Szeged, H-6720, Hungary*

Corresponding Author: Elaouni Aicha, aicha.elaouni@um5r.ac.ma

Abstract

The growing releases of CO_2 emissions pose a serious threat to the planet's climate and its ecosystems, which brings about the serious issues of the need for emissions reduction, creation of green energy, and extraction of greenhouse gases. Among various CO_2 reduction methods, photocatalytic CO_2 reduction stands out due to its ability to utilize solar energy for CO_2 conversion reactions. In this study, bismuth tungstate Bi_2WO_6 was synthesized by the hydrothermal method using two different surfactants. The samples were characterized using an X-ray diffractometer (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM), and UV-vis diffuse reflectance spectroscopy (UV-DRS). This research investigates the effectiveness of Bi_2WO_6 as a photocatalyst for CO_2 reduction under both UV and visible light irradiation.

Keywords: Photocatalysis, Hydrogenation, Mechanism, Greenhouse gases.

P 22 - Zn content, Si/Al ratio and proximity of the active sites regulate the synthesis of C_{5+} isoalkanes via CO_2 hydrogenation over $FeZnCeO_2$/HZSM-5 composite catalyst

Henrik Bali[1], Rajib Kumar Singha[2], Ali Shan Malik[1], Anastasiia Efremova[1], Ákos Szamosvölgyi[1], András Sápi[1]

[1]*Department of Applied and Environmental Chemistry, Interdisciplinary Excellence Centre, University of Szeged, H-6720, Rerrich Bela ter 1, Szeged, Hungary*

Abstract

Utilization of CO_2 as an abundant, non-toxic and economical C_1 resource for high value synthetic fuels and chemicals has received enormous attention from academia and industry. It provides a substantial solution to the increasing concerns of global warming and dwindling fossil fuel sources by forming a carbon cycle resulting in numerous environmental and economic benefits. The enormous potential of CO_2 has already been unearthed as it could be converted to a variety of C_1 products, alcohols and liquid hydrocarbons especially gasoline/jet fuel range. In gasoline, alkene and aromatic content is restricted in order to make gasoline more environmentally benign by adding isoparaffins (C_{5+} isoalkanes) – as gasoline additives – and also to maintain high octane value of gasoline. Turning CO_2 into C_{5+} higher hydrocarbons is more challenging in general as catalytic activity of CO_2 and attaining a high selectivity of the desired product is hampered by various associated challenges such as high barrier accompanying with the C–C coupling, low selectivity due to C_1 products and poor stability.

Transformation of CO_2 into higher hydrocarbons is accomplished by two different reaction pathways – modified CO_2-FTS (Fischer-Tropsch synthesis) and CO_2-MTH (methanol to hydrocarbon) route. Usually, the catalytic systems following these routes are entirely different from each other in terms of their composition, nature of active sites, type of supports and promoters.

Herein, $FeZnCeO_2$ catalyst was synthesized for CO_2 conversion directly to C5+ products of gasoline range. Simple $FeCeO_2$ catalyst with 20wt% of Fe showed CO and CH_4 as the major products but promoting it with 5wt% Zinc (Zn) changed the reaction route and produced methanol as the major product. In-situ DRIFTS experiments were carried out to find the evidence that Zn altered the reaction pathway towards methanol. The catalysts mixed with HZSM-5 were employed for CO_2 conversion which exhibited very high selectivity to hydrocarbons (HCs) upto 53% at 340 °C, 50 bar. It was found that 57% of the total hydrocarbons were gasoline products (C5+) and of which > 99% products are C_{5+} isoalkanes with negligible aromatic content in the product distribution.

Keywords: Heterogenous catalysis, CO2 utilization, liquid hydrocarbon

Acknowledgments Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

P 23 - Unravelling synergistic effects in the Pt/Me_xO_y system to drive ambient pressure CO_2 reduction

Anastasiia Efremova[1]**, Imre Szenti**[1]**, János Kiss**[1,2]**, András Sápi**[1]**, Zoltán Kónya**[1,2]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2] *MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group Institution, Szeged, Hungary*

Corresponding Author: András Sápi, sapia@chem.u-szeged.hu

Abstract

The global challenge of excessive CO_2 release into the atmosphere necessitates catalysis as a pivotal solution for its efficient utilization which can partially replace traditional exhaustible carbon sources, such as oil and gas[1]. The catalytic CO_2 hydrogenation especially using a sustainable H_2 source not only reduces CO_2 emissions but also produces valuable components such as methane and CO.
Interfaces in catalyst systems have long been recognized as the most critical factor in controlling catalytic reaction mechanisms[2]. In this work, we propose designed catalysts consisting of controlled-size Pt nanoparticles and high surface 3D mesoporous metal oxides to generate metal/metal oxide interface and utilize its synergy to drive CO_2 reduction.
The polyol method was used to synthesize 5 nm Pt nanoparticles using $H_2PtCl_6{\cdot}6H_2O$ as Pt source, ethylene-glycol as a reducing agent and PVP as a capping agent. The hard template replica method was utilized to prepare mesoporous manganese dioxide (MnO_2) and cobalt oxide (Co_3O_4) supports. Before catalytic reactions, the catalysts were activated: in O_2 and H_2 environments at 573 K. CO_2+H_2 reaction was carried out at 1 atm in a fixed-bed continuous-flow reactor (200 mm long with 8 mm i.d.). GHSV=16 000 $mL{\cdot}g^{-1}{\cdot}h^{-1}$ with CO_2: H_2 = 1:4.
Apart from notable performance enhancement, beneficial synergy effect of supported catalysts compared to the reference Pt/SBA-15, was pronounced in distinct selectivity. Pt/CoO_x produced mainly CH_4 while Pt/MnO generated exclusively CO. The active sites responsible for the activity enhancement were established in each case. In the case of Pt/Cobalt Oxide, it was revealed that during the pre-treatment process Co-Pt alloy particles partially covered by Co_xO_y overlayer are formed. This structural rearrangement creates new basic centers, which facilitate CO_2 activation. With regards to the Pt/MnO, it was found that during the pre-treatment process the support is reduced to MnO and edge dislocations form at the Pt/MnO interface. As the result of lattice expansion, Pt-CO bond is weakened and thus CO desorption is facilitated.

Keywords: CO_2 hydrogenation, MnO, Cobalt Oxide, Platina

Acknowledgments Project no. RRF-2.3.1-21-2022-00009, “National Laboratory for Renewable Energy” has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

References

[1]M. González-Castano, React. Chem. Eng. 2021, 6

P 24 - Insights into the effect of promoters on iron-based catalyst in direct CO_2 hydrogenation

Ádám Papp[1,2], Sara Najari[1,2], Henrik Bali[1,2], Tamás Takács[1], András Sápi[1,2], Zoltán Kónya[1]

[1]*University of Szeged, Applied and Environmental Chemistry Department, Hungary*
[2]*University of Szeged, Interdisciplinary Excellence Centre, Hungary*

Corresponding Author: Ádám Papp, adam.papp@chem.u-szeged.hu

Abstract

The rapid increase in carbon-based energy consumption alongside the development of the global economy is responsible for high carbon dioxide (CO_2) emissions, which lead to severe environmental issues. To mitigate the excessive emissions of CO_2 and also reduce reliance on fossil fuels, alternative routes for producing value-added chemicals and carbon-neutral fuels from captured CO_2 have received wide interest. The direct hydrogenation of CO_2 to value-added hydrocarbons may serve as a significant process contributing to a net-zero emission.

Fe-based catalysts are promising materials to convert CO_2. Fe and its oxides are widely known being active in both, reverse water gas shift (RWGS) reaction and Fischer-Tropsch synthesis (FTS). However, the harsh reaction conditions, including high temperature, reductive atmosphere, and the formation of water vapor, often induce a dramatic change in catalyst properties during the reaction. Thus, many research efforts have been devoted to employ chemical or structural promoters for better stability and catalytic performance.

In order to enhance the catalytic activity and stability of Fe systems, the addition of metal promoters is commonly employed, such as alkali (e.g., K, Na), alkaline earth (e.g., Ca, Mg), or transition metals (e.g., Mn, Cu, Zn), which can increase the conversion of CO_2, accelerate the carbonization of iron, slow the deactivation of the catalyst, hinder the deposition of carbon etc.

We synthesized 1M-Fe_3O_4 catalysts, promoted with the most widely used and promising metals (M = Na, K, Mg, Zn, Mn) with 1 w/w % loading and tested them in direct CO_2 hydrogenation.

In order to gain information about the surface and properties of the catalysts (adsorption-desorption behavior, reducibility, observation of surface species and phase changes etc.), several instrumental analyses such as temperature programmed desorption (CO_2-TPD) and reduction (H_2-TPR), X-ray diffraction (XRD), in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) have been carried out. Noteworthy, that XRD analysis has shown, promoters have a paramount effect on the active phase's composition and on the ratio of the forming iron carbides.

Based on our catalytic measurements, it was revealed that addition of sodium, potassium and manganese respectively can enhance the performance of the CO_2 hydrogenation reaction towards production of more C_{5+}, while keeping CO selectivity below 20%. Mg-, and Zn-promoted iron-oxides were producing mostly methane and C_2-C_4 paraffins with less C_{5+}. All promoted catalyst's CO_2 conversion has surpassed 30%, reached 40% in the case of K-Fe_3O_4.

Keywords: CO_2 hydrogenation, Fe-based catalyst, promoter effect, carbide formation

Acknowledgements Project no. RRF-2.3.1-21-2022-00009, titled National Laboratory for Renewable Energy, has been implemented with the support provided by the Recovery and Resilience Facility of the European Union within the framework of Programme Széchenyi Plan Plus.

P 25 - Electrochemical Nitrate Reduction Performance of Vanadium-oxide Electrocatalysts

Arvin Taghizadeh Tabrizi[1], Gergő Ballai[1], Henrik Haspel[1,2], Zoltán Kónya[1,2]

[1]*Department of Applied and Environmental Chemistry, University of Szeged, Szeged, Hungary*
[2]*HUN-REN-SZTE Reaction Kinetics and Surface Chemistry Research Group, University of Szeged, Szeged, Hungary*

Corresponding Author: Henrik Haspel, haspel@chem.u-szeged.hu

Abstract

Development of efficient electrocatalysts is inevitable for the realization of various green energy technologies. Although highly active electrocatalysts are known for a number of electrochemical reactions, since these are predominantly noble-metal based systems, like platinum, ruthenium etc., their high cost and limited availability prevent them from widespread applications. Ammonia is one of the most important chemical feedstocks, and besides the highly carbon-intensive Haber-Bosch process, it can be synthesized through the electrochemical reduction of aqueous nitrate ions. This is the so-called Nitrate Reduction Reaction (NO_3RR). To achieve high ammonia selectivity and yield in the latter, the competing hydrogen evolution reaction (HER) needs to be suppressed with a well-structured catalyst, which can maintain an eight-electron process. Thus, highly active non-noble metal NO_3RR electrocatalysts would be of great importance in this field. Due to the several oxidation states (−3 to +5) vanadium has multiple stable phases. Since, electrochemical reduction requires electron transfer, it is possible to benefit from the different oxidation states of vanadium and the possible phase transition to improve catalytic performance of the fabricated vanadium-based electrodes. Vanadium-based electrocatalysts were fabricated via various methods. First. V_2O_5 nanoparticles were immobilized onto BCN particles through ball milling at 450 rpm for 6 h, while V_xO_y thin layers were also synthesized by atomic layer deposition (ALD). The electrochemical reduction behavior of vanadium-based electrodes was evaluated in a conventional three-electrode setup under alkaline conditions. In the latter, the effect of high-temperature calcination-induced phase transition on the electrochemical performance was also studied. The V_2O_5/carbon-doped BN heterostructure showed higher NO_3RR activity compared to that of the bare BCN, and also surpassed those of the other vanadium-oxide phases, namely VO_2 and V_2O_3. Our results proved the oxidation state dependent electrochemical nitrate reduction activity in vanadium-based systems, and hence, the importance of stabilizing the active phase in the catalyst.

Keywords: Vanadium, electrocatalysis, electrochemical nitrate reduction, Atomic Layer Deposition

P 26 - Enhanced Electrochemical Hydrogen Storage on V_2O_3-3D Graphene Nanocomposite: A Hydrothermal Synthesis Approach for Clean Energy Applications

Amir Reza Mashtizadeh [1], Shahab Khameneh Asl [1], Hossein Aghajani[2,*], Seyed Morteza Masoudpanah [2], and Marek Wojnicki [3]

[1]Department of Materials Engineering, University of Tabriz, Tabriz, Iran 1;
rezamashtizadeh@gmail.com, sh.kh.asl@tabrizu.ac.ir
[2]School of Metallurgy & Materials Engineering, Iran University of Science & Technology, Narmak, Tehran, Iran haghajani@iust.ac.ir, masoodpanah@iust.ac.ir
[3]Faculty of Non-Ferrous Metals, AGH University, Mickiewicza Ave. 30, 30-059 Krakow, Poland;
marekw@agh.edu.pl

Corresponding Author: Dr. Hossein Aghajani, haghajani@iust.ac.ir

Abstract

The escalating demand for sustainable energy solutions has driven intensive research into advanced hydrogen storage materials. In this work, a novel approach is developed for enhancing electrochemical hydrogen storage of 3D graphene foam by decorating it with V_2O_3 nanoparticles through hydrothermal method. The free-standing 3D graphene/V_2O_3 electrode was analyzed by various characterization methods as a function of V_2O_3 contents. The successful incorporation of crystalline V_2O_3 nanoparticles with sheetlike morphology onto the graphene foam is observed scaning electron microscopy. The hydrogen atoms are physically adsorbed on the surface of 3D graphene/V_2O_3 electrode in a 3-electrode setup. By adding the V_2O_3 nanoparticles, the capability of hydrogen storage increases from 0.5 to 30 mAh g^{-1} at 1A g^{-1} due to the synergistic interaction between the conductive graphene framework and the redox-active V_2O_3 nanoparticles.

Keywords: Electrochemical Hydrogen Storage; 3D Graphene Foam; V_2O_3.

References

[1] H. Wu et al., “Flexible 3D porous MnOx/rGO hydrogel with fiber reinforced effect for enhancing mechanical and zinc storage performances,” J. Alloys Compd., vol. 976, no. November 2023, p. 173363, 2024, doi: 10.1016/j.jallcom.2023.173363.

[2] C. Xu et al., “Enhanced electrochemical hydrogen storage performance upon the Pt-Co nanoparticles decorated N-doped mesoporous carbon,” J. Alloys Compd., vol. 937, 2023, doi: 10.1016/j.jallcom.2022.168370.

[3] B. Meng et al., “Three-dimensional cage-like structured VOF@CNT composite material: In situ one-step synthesis and high-performance as the anode for lithium-ion batteries,” J. Alloys Compd., vol. 952, p. 170092, 2023, doi: 10.1016/j.jallcom.2023.170092.

[4] J. Hao, R. Zhao, L. Xu, C. Chi, and H. Li, “Conversion of Coal into Graphitized Microcrystalline Carbon with a Hierarchical Porous Structure for Electrochemical Hydrogen Storage,” J. Electron. Mater., vol. 52, no. 3, pp. 2034–2043, 2023.

[5] H. Xu, Y. Lu, F. Jiang, J. Zhang, Y. Ge, and Z. Li, “3D porous N-doped lignosulfonate/graphene oxide aerogel for efficient solar steam generation and desalination,” Int. J. Biol. Macromol., vol. 233, no. December 2022, p. 123469, 2023, doi: 10.1016/j.ijbiomac.2023.123469.

P 27 - Partial oxidation of methane to syngas on perovskite catalysts

Leonard Atzl, Nevzat Yigit, Günther Rupprechter

Institute of Materials Chemistry, TU Wien, Getreidemarkt 9/BC, 1060 Wien, Austria

Corresponding Author: Günther Rupprechter, guenther.rupprechter@tuwien.ac.at

Abstract

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 common issue of catalyst deactivation by carbon deposition during partial oxidation reactions was addressed with the incorporation of lanthanum oxide, which is reported to consume carbon under the presence of CO_2 [2], and cobalt, which is less prone to carbon deposition than nickel[3].

The perovskites lanthanum nickel oxide, lanthanum cobalt oxide and mixed lanthanum nickel/cobalt oxides were investigated as catalyst precursors. The perovskite samples have been synthesized with a modified Pechini method and have been characterized with XRD, SEM, BET and TPR and tested for POM reaction in a tubular flow reactor with GC and MS for gas monitoring. The *in situ* activation of the catalyst by reduction with the reaction gas mixture was investigated with *operando* XRD[4] and MS and compared with the reduction by hydrogen during pretreatment.

It is observed that all samples can be activated by both pretreatment with hydrogen or in situ with methane resulting in the same supported metal catalyst, although the reduction pathway is different. The nickel catalyst was found to be most active, and the lanthanum oxide support effective in the suppression of carbon deposition.

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

References

[1] Y. J. O. Asencios et al., *Topics in Catalysis* 66, **2023**, 1539-1552.
[2] A. Slagtern et al., *J. Catal*. 172, **1997**, 118-126.
[3] V.R. Choudhary et al., *Fuel* 77,**1998**, 1803-1807.
[4] G. Rupprechter, *Small* 17, **2021**, 2004289 (26 pages).

P 28 - Advanced characterization methods for coke deposits on Ni-Mo/$Al_2O_3$and Ni/Al_2O_3 extrudates for the catalytic upgrading of fast pyrolysis bio-oil

Carolin C. Rieg[1], **Donia Bouzouita**[2], **Paola Gauthier-Maradei**[3], **ThomasCoustham**[2], **Bert M. Weckhuysen**[1]

[1]Inorganic Chemistry and Catalysis Group, Institute for Sustainable and CircularChemistry, Utrecht University, Universiteitsweg 99, 3584CG Utrecht, The Netherlands.
[2]TotalEnergies, TRTG –76700 Harfleur, France
[3]TotalEnergies, CRES, F-69360 Solaize, France

Corresponding Author: Bert M. Weckhuysen, b.m.weckhuysen@uu.nl

Abstract

Fast pyrolysis of biomass offers a direct route to producing bio-oil, a versatile liquid that can be further processed into transportation fuels, chemicals, and other value-added products. However, the stabilization of fast pyrolysis bio-oil (FPBO) remains a critical challenge due to the formation of carbonaceous deposits, known as coke, on the surfaces of catalysts used in the upgrading process. These coke deposits not only deactivate the catalysts but also decrease the efficiency of the bio-oil stabilization, hindering the overall economic viability of biomass as an alternative energy source. Analyzing carbonaceous deposits is crucial because it allows for the identification of factors that lead to catalyst deactivation, enabling the development of more resilient catalysts and optimization of the bio-oil stabilization process, ultimately improving the efficiency and sustainability of biomass conversion technologies. The location, the nature, and the extent of carbonaceous deposits (coke) deposited on sulfidized Ni-Mo/Al_2O_3 and Ni/Al_2O_3 trilobe catalyst extrudates during the stabilization of fast pyrolysis bio-oil (FPBO) were investigated using various characterization methods, including multi-laser confocal fluorescence microscopy (CFM), Raman spectroscopy and thermogravimetrical analysis (TGA). The CFM technique allowed for the spatial localization of fluorescent coke on the catalyst extrudates and provided detailed information on the polyaromatic nature of the coke deposits. For the Ni-Mo/Al_2O_3 catalysts, coke deposits were exclusively found on the outer surface of the extrudates, forming a 6-15 µm thick layer. In contrast, for the Ni/Al_2O_3 extrudates, coke was also located in the foils of the trefoils with a layer of ~ 11-15 µm thick. The laser emission colors indicated the size of the aromatic system, revealing that the coke on the external layer consisted of a larger number of aromatic rings compared to those in the trefoil. Raman spectroscopy provided more detailed insights into the specific nature of the coke species, whereas the overall coke content is given by the TGA method. Notably, the Ni/Al_2O_3 catalyst exhibited a lower disagree of disorder ($I_D/I_G \sim 1.2$) and a larger crystallite size ($L_a \sim 16.1$ nm) compared to the Ni-Mo/Al2O3 catalyst, which hada I_D/I_G of ~ 2.0 and a L_a of ~ 9.6 nm.

Keywords: Biomass, Catalyst Deactivation, Coke

Acknowledgments The authors gratefully thank TotalEnergies for funding.