Young Scientist Forum in Catalysis 2025

4.4.2025, University of Jyväskylä

Book of Abstracts

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About

Young Scientist Forum

YSF is an annual event showcasing the contemporary research of the Finnish Catalysis Society. The event provides an opportunity for students and young researchers in the field to network and present their work.

The tradition was initiated in 2016 with the following description: *The symposium has the goal to present on-going and recently finished PhD thesis works in catalysis and to promote the interaction between the key players in catalysis in our country. Contributions from all sub-fields of catalysis are very welcome: homogeneous, heterogeneous, enzymatic and polymer catalysis; presentations covering aspects from theoretical chemistry to material science and chemical engineering.*

Invited Speakers

The YSF2025 seminar program has two invited speakers: Professor Jero Ahola (LUT) and Assistant Professor Daniel Martín-Yerga (Aalto). In addition, we can enjoy 10 talks and presentations of 18 posters. 65 people will participate in this year's event.

Organizing committee

CompCatJYU Group, Department of Chemistry / Nanoscience Center

Karoliina Honkala	Marko Melander	Minttu Kauppinen	Toni Kiljunen
Bhumi Baraiya	Hanan Ibrahim	Rasmus Ikonen	Ville Korpelin
Shalini Mishra	Kayvan Moradi	Kuber Rawat	Timo Weckman

Timetable

11:00–11:15	**Coffee**		
11:15	**Welcome Remarks**		
11:20–11:50	IS	**Daniel Martín-Yerga** Aalto University	Bimetallic electrocatalysts for electro-oxidation of alcohol-based chemicals
11:50–12:05	CT	**Kayvan Moradi** University of Jyväskylä	The phase diagrams of Au(100) and Au(111) as function of pH and potential in aqueous solutions
12:05–12:20	CT	**Olha Yevdokimova** Åbo Akademi	Aldol condensation of cyclopentanone and furfural on Ce-based catalysts for production of sustainable aviation fuel precursors
12:20–12:35	CT	**Florian Rathmann** VTT	Harnessing plasmonic effects in Au@Ru core-shell catalysts for light-enhanced CO_2 methanation
12:35–12:50	CT	**Jennyfer Martinez Quimbayo** University of Oulu	Impact of Pt impregnation on P25 for visible light photocatalytic applications
12:50–13:05	CT	**Buse Bilbey** Tampere University	Comparative assessment of proton-conducting electrolytes for solid oxide cells
13:05–14:15	**Lunch**		
14:15–14:45	IS	**Jero Ahola** LUT University	How can technology research contribute to making green hydrogen more cost-effective
14:45–15:00	CT	**Margot Huerta-Flores** University of Oulu	Redox materials for sustainable hydrogen production
15:00–15:15	CT	**Enrico Marchi** Åbo Akademi	Sorption enhanced carbon dioxide methanation
15:15–15:30	CT	**Laura Laverdure** Luleå Tekniska Universitet	Effects of pH and potential on Pt-catalyzed glycerol oxidation
15:30–15:45	CT	**Abhinash Singh** VTT	Non-thermal plasma assisted catalytic oxidation of methane
15:45–16:00	CT	**Christoph Schmidt** Åbo Akademi	New bi-functional catalysts for a novel continuous production of propylene oxide with in-situ generated hydrogen peroxide
16:00	**Closing Words**		
16:30–17:30	**Poster Session**		
17:30–19:00	**Annual Meeting of the Finnish Catalysis Society**		
19:30	**Dinner**		

IS: Invited Speaker, **CT**: Contributed Talk

Talks

Invited Speakers

IS

Bimetallic electrocatalysts for electro-oxidation of alcohol-based chemicals

D. Martín-Yerga

Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, 02150 Espoo, Finland
e-mail: daniel.martinyerga@aalto.fi

Transitioning from fossil fuels to renewable resources is essential for advancing clean energy technologies and building a sustainable chemical industry. Renewable feedstocks, particularly those derived from inedible biomass, are abundant in oxidizable hydroxyl groups found in alcohols, hydroxyacids, and carbohydrates. In this context, electrocatalytic oxidation of alcohols offers a powerful green chemistry strategy: using electrons from renewable electricity under mild conditions to transform these feedstocks into value-added chemicals. This approach not only provides a sustainable route for chemical synthesis but also holds promise for renewable energy applications such as fuel cells and energy-efficient green hydrogen production. However, our fundamental understanding of electrocatalytic interfaces for these reactions remains limited, with many aspects of activity, selectivity, and stability still to be elucidated.

In this contribution, I will present our research on the electro-oxidation of alcohols using bimetallic electrocatalysts that combine non-noble and noble metals to overcome the limitations of traditional monometallic systems. I will discuss the multifaceted challenges of these reactions and explore the prospects for bimetallic catalysts. In particular, I will highlight how tailoring catalyst composition, structure, and process conditions can enhance activity and modify reaction selectivity [1-4]. Our findings pave the way for the rational design of advanced catalysts and interfaces optimized for specific applications in renewable energy conversion and green chemical synthesis.

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How Can Technology Research Contribute to Making Green Hydrogen More Cost-Effective?

Jero Ahola[a]

[a] LUT University
e-mail: jero.ahola@lut.fi

The demand for green hydrogen in the decarbonization of sectors such as industry, shipping, and aviation will be significant. To accelerate the transition, it is essential that the cost of green hydrogen becomes economically viable. Our primary objective is to develop and optimize green hydrogen production systems in order to significantly reduce the cost of producing green hydrogen. This presentation examines the key factors and research questions affecting the cost of green hydrogen using a systems approach. These factors include system investment cost, electricity cost, electrolyzer dynamic performance, energy efficiency, and the integration of hydrogen production with variable wind and solar electricity.

Contributed Talks

Young Scientist Forum 2025

The phase diagrams of Au(100) and Au(111) as function of pH and potential in aqueous solutions

Kayvan Moradi,[a] Marko. M. Melander[a*]

[a] Department of Chemistry, University of Jyväskylä
e-mail: kayvan.k.moradi@jyu.fi, marko.m.melander@jyu.fi

Environmental hazards and climate change resulting from industrial fossil fuel consumption present significant challenges, necessitating a transition to clean energy sources [1-2]. The oxygen reduction reaction (ORR) plays a crucial role in electrochemical energy conversion technologies, particularly in fuel cells, hydrogen peroxide production, and metal-air batteries. Among the numerous materials used as electrodes for the ORR, gold surfaces are recognized as exemplary electrocatalysts owing to their adjustable activity and selectivity. [3-5] In this study, we employ grand canonical ensemble density functional theory (GCE-DFT) to investigate the potential-dependent surface coverage of oxygenous species on Au(111) and Au(100) in alkaline media. Our results reveal that both surfaces exhibit moderate OH coverage under ORR conditions. Notably, our findings challenge previous hypotheses by demonstrating that OOH species are not among the thermodynamically most stable intermediates at any electrode potential, suggesting that alternative factors drive ORR selectivity. Additionally, we explore the impact of surface coverage on the potential of zero charge (PZC), local electric field, and surface stability, uncovering distinct trends that influence the degradation and restructuring of Au electrodes. These insights refine our understanding of ORR mechanisms on gold surfaces and provide a foundation for the rational design of more efficient electrocatalysts.

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Aldol Condensation of Cyclopentanone and Furfural on Ce-Based Catalysts for Production of Sustainable Aviation Fuel Precursors

O. V. Yevdokimova[1*], K. Eränen[1], N. Kumar[1], P. Mäki-Arvela[1], D. Yu. Murzin[1]

[1] Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, Turku/Åbo, Finland
e-mail: olha.yevdokimova@abo.fi

The use of renewable and sustainable fuels is crucial for the transition towards cleaner energies and to address the growing climate crisis. The aviation industry seeks innovative fuel synthesis methods to reduce carbon emissions, meet regulations, and work with existing engines. An advantage of the aldol condensation reaction of biomass-derived compounds is a possibility of obtaining products with an increased carbon number, which could ultimately be used to obtain hydrocarbons in the jet fuel range [1].

Screening of the catalysts in aldol condensation between furfural (FF) and cyclopentanone (CP) was performed at 130 °C and the CP:FF ratio of 15:1 for 6 h in a stainless-steel batch reactor. A series of catalysts bearing ceria supported on different materials (H-Y-80, H-Beta-300, H-Beta-150, H-Beta-25 (the number denotes Si/Al ratio), TiO_2, MCM-41) were prepared using cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 * 6H_2O$) as the precursor. The catalysts were extensively characterized by TEM, SEM-EDX, nitrogen physisorption, CO_2-TPD, NH_3-TPD and FTIR pyridine adsorption-desorption.

Screening of the catalysts (Figure 1) revealed that Ce-MCM-41 was the most optimal for the aldol condensation between furfural and cyclopentanone at 130 °C, resulting in 64% furfural conversion, a relatively high yield of the desired product (34% for product FC) and a mass balance closure of 74% at 6 hours of the reaction. Furthermore, selectivity towards FC was 54% at 64% FF conversion. The experiments demonstrated high repeatability and reproducibility, providing consistent and reliable results. In the final work, the performance of the catalysts will be correlated with their characteristics.

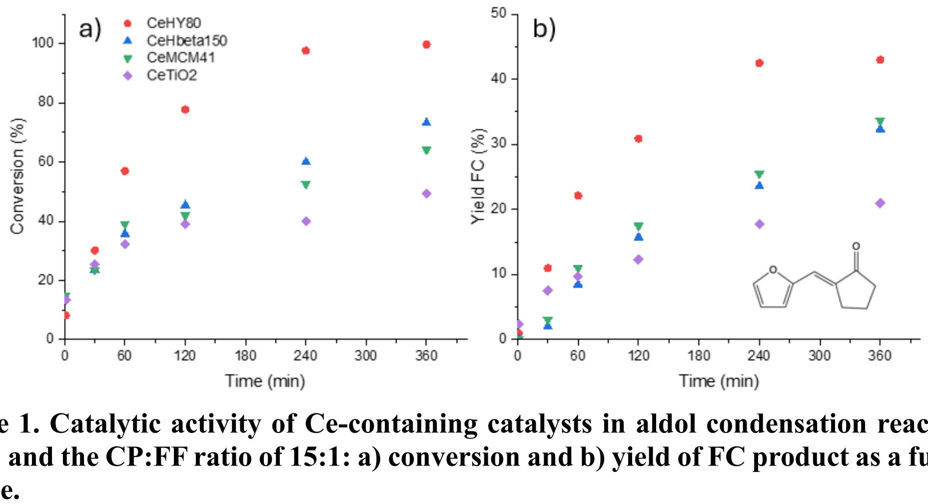

Figure 1. Catalytic activity of Ce-containing catalysts in aldol condensation reaction at 130°C and the CP:FF ratio of 15:1: a) conversion and b) yield of FC product as a function of time.

References

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Harnessing Plasmonic Effects in Au@Ru Core-Shell Catalysts for Light-Enhanced CO_2 Methanation

F. Rathmann[a*], I. Abdelsalam[b], A. L. Reznichenko[a], M. Reinikainen[a], P. H. C. Camargo[b]

[a]VTT Technical Research Centre of Finland Ltd
[b]Department of Chemistry, University of Helsinki
[*]Florian.Rathmann@VTT.fi

Background and Motivation

Mitigating CO_2 emissions via catalytic conversion into valuable products is essential for sustainable energy strategies. CO_2 methanation, utilizing hydrogen as a reducing agent, offers a viable route to generate methane, a storable and transportable energy carrier. While thermocatalytic systems are commercially deployed, light-assisted approaches can enhance reaction efficiency and enable lower operating temperatures.[1] Plasmonic nanoparticles, particularly noble metals, are known to amplify reaction rates via localized surface plasmon resonance (LSPR).[2] In this study, Au@Ru core–shell catalysts are evaluated for their plasmonic contribution to light-enhanced CO_2 methanation, with a focus on performance gains under mild conditions compared to traditional thermal catalysts.

Materials and Methods

Au@Ru nanoparticles were synthesized via a two-step approach: Au cores were prepared using the Turkevich method,[3] and Ru shells were deposited using $RuCl_3$ as the precursor without an additional reducing agent. The resulting nanoparticles were supported on TiO_2 and ZrO_2, targeting Ru loadings of 6.7, 2.9, and 1.4 wt%. The Ru content on Au varied, leading to different particle structures. Catalytic tests were conducted in a fixed-bed reactor at 190 °C under a 4:1 H_2:CO_2 flow (WHSV = 15 h^{-1}), with light irradiation at 545 nm 545 nm (0-0.87 W/cm^2) and additional wavelengths for specific tests. CO_2 conversion was analyzed by GC, with full selectivity toward methane.

Results and Discussion

Initial screening of Au@Ru catalysts on TiO_2 and ZrO_2 with varying Ru loadings revealed notable light-induced enhancement in CO_2 methanation across all samples. Among them, the 1.4 wt% Ru catalyst exhibited the highest light-driven activity, increasing from 616 mmol/g_{Ru}/h in the dark to 2679 mmol/g_{Ru}/h at 0.87 W/cm^2, representing a 4.4-fold enhancement. Further in-depth investigations focused on this best-performing sample. Light intensity-dependent tests demonstrated that catalytic activity increased with higher irradiation power. Additionally, temperature-dependent studies under both dark and irradiated conditions, using a fixed power output at 545 nm (LSPR excitation), were conducted to determine the apparent activation energy and assess potential changes induced by light. Furthermore, wavelength-dependent tests at constant power output are being performed to evaluate the influence of LSPR excitation on catalytic performance by comparing the LSPR wavelength with off-resonance wavelengths at equal power and clarify the spectral specificity of the light-enhanced effect.

Conclusion

This work demonstrates the potential of Au@Ru core–shell catalysts for efficient light-driven CO_2 methanation under visible light irradiation at low temperatures. It offers insights into support effects and LSPR excitation in optimizing catalytic performance.

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Impact of Pt impregnation on P25 for visible light photocatalytic applications

J. S. M. Quimbayo,[a,b] S. Khesali,[a] J. F. Catala,[c] A. Sasikala,[d,e] J. Ahola,[f] R. Sliz,[g] M. Huttula,[a] S. Urpelainen,[a] S. Ojala [b]

[a] Nano and Molecular Systems Research Unit (NANOMO), University of Oulu.
[b] Environmental and Chemical Engineering, University of Oulu.
[c] Department of Inorganic Chemistry and Materials Institute, University of Alicante.
[d] Sustainable Chemistry and MME, University of Oulu.
[e] School of physics, Durham University, United Kingdom.
[f] Chemical Process Engineering Research Unit, University of Oulu.
[g] Optoelectronics and Measurement Techniques Laboratory, University of Oulu.
e-mail: jennyffer.martinezquimbayo@oulu.fi

The detection of herbicides like diuron (DIU) and atrazine (ATZ) in water bodies is concerning scientists related to their environmental and health risks [1]. The potential risks are rising, since current water treatment techniques are not effective with these kinds of pollutants. Photocatalysis is a promising method that can be used for water treatment [2,3]. Titanium dioxide (TiO_2) is a photocatalyst with good performance under UV range, and its commercial form is commonly known as P25 that is a combination of 80 % anatase and 20 % rutile phase. However, to use the solar spectrum better, it is necessary to have photocatalysts that are active under visible range, as in solar spectrum 42 % is visible light and only 5% is UV. In this case we doped P25 with Pt nanoparticles to reach better light absorption, and to analyze the interaction of their atoms and evaluate their photocatalytic activity for degradation of herbicides. P25 was impregnated with different percentages of Pt (0.2%, 0.5% and 1%). XRD showed that Pt with 1% loading contains Pt_3O_4 and most probably the Pt particles are also entering in the P25 lattice. For all the samples it was possible to identify a band gap and Valence band that correspond with TiO_2 and PtO_x, supporting a heterojunction behavior. Photocatalytic activity was evaluated under visible light using white LED light. The best photocatalytic DIU removal was observed for the sample impregnated with 0.2%PtP25 reaching ~20% degradation in comparison with ~7 % removal of the P25 in 5 h irradiation time. While for ATZ degradation during 5 h irradiation 0.2%PtP25 sample made ~7% degradation in comparison with ~1% removal of the P25. Based on experiments, the photocatalysts are stable and can be reused. Pt impregnation on P25 creates a heterojunction structure that improves their photocatalytic performance under visible light making these photocatalysts useful for water treatment applications.

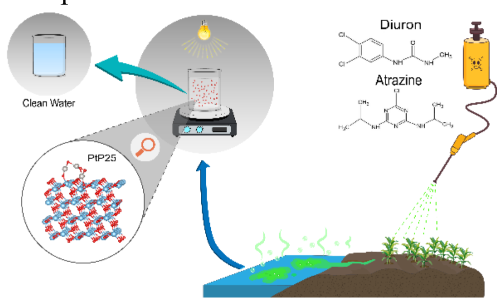

Figure 1. Graphical abstract

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Comparative Assessment of Proton-Conducting Electrolytes for Solid Oxide Cells

Buse Bilbey,[a] and M. Imran Asghar,[a]

[a] Renewable Energy Technologies Group, Engineering Materials Science, Faculty of Engineering and Natural Sciences, Tampere University, PO Box 33014, Tampere, Finland.

e-mail: buse.bilbey@tuni.fi

Solid Oxide Cells (SOCs) are promising candidates for sustainable energy conversion. However, their commercialization is challenged by high fabrication costs and performance degradation at high temperatures (800-1000°C). Proton Conducting Solid Oxide Cells (PC-SOCs) have emerged as a promising alternative, operating efficiently at lower temperatures (400–600°C) due to their reduced activation energy (~0.5-0.7 eV). This study investigates PC-SOCs for green hydrogen production and electricity generation, with a focus on reducing fabrication temperatures to lower manufacturing costs. The objective is to determine the optimal material composition for electrolyte that minimizes both fabrication and operational expenses in PC-SOC applications. Proton-conducting electrolyte materials—$BaZr_{0.7}Ce_{0.2}Y_{0.1}O_3$, $BaZr_{0.2}Ce_{0.7}Y_{0.1}O_3$, $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_3$, and $BaCe_{0.5}Zr_{0.35}Y_{0.15}O_3$—were sourced from different manufacturers and subjected to diverse sintering conditions. Their thermal properties were analyzed by simultaneous thermal analysis (STA) and dilatometry, while structural and electrochemical characteristics were assessed through X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area analysis, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Electrolyte densification was successfully achieved at 1450°C and 1500°C. Among the tested compositions, $BaCe_{0.5}Zr_{0.35}Y_{0.15}O_3$ attained approximately 97% of its theoretical density when sintered at 1450°C for 5 hours. Other materials required either prolonged sintering (10 hours) or an increased temperature of 1500°C. The highest electrochemical performance was recorded for $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_3$ sintered at 1450°C for 10 hours. The starting powder's surface area varied between suppliers, with one measuring 13.44 m²/g and another 8.39 m²/g. Activation energy calculations conducted in an air atmosphere revealed two distinct trends among the samples. A transition point appeared at 550°C, with activation energy values ranging from 0.175 to 0.610 eV. For $BaZr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1}O_3$ processed at 1450°C for 10 hours, the activation energy at lower temperatures was 0.488 eV, while at higher temperatures, values from different suppliers varied between 0.175 and 0.265 eV.

B. Bilbey et al., A Comparative Study of Proton-Conducting Electrolyte Materials for Solid Oxide Cells (SOCs) J. Mater. Chem. A (under preperation).

Redox Materials for Sustainable Hydrogen Production: Exploring Crystalline Structures, Surface Characteristics, and Advancements in Mechanistic Insights

A.M. Huerta-Flores, Z. El Assal, V. Srivastava, and U. Lassi

Research Unit of Sustainable Chemistry, University of Oulu, P.O.Box 4300, FI-90014, Oulu Finland.

e-mail: ali.huertaflores@oulu.fi

Photocatalytic and thermochemical water splitting have been studied as potential technologies to produce clean hydrogen(H_2) from water, using metal oxides as active redox materials, and energy input in the form of solar light or heat [1,2]. To ensure the scalability and sustainability of these processes, there is a need for stable, abundant, and efficient materials, preferably sourced from side streams or renewable sources. The development of effective and stable catalysts is essential for advancing the H_2 energy transition. This study examines key properties that significantly impact the reactivity and efficiency of materials used in hydrogen production. Factors such as surface area (1-200 m^2/g), crystalline and electronic structure, morphology, oxygen vacancies, and stoichiometry are examined in alkaline earth metal-perovskites and iron-based spinels. Finally, the latest findings in reaction mechanisms research are examined, highlighting the challenges and future opportunities for materials development.

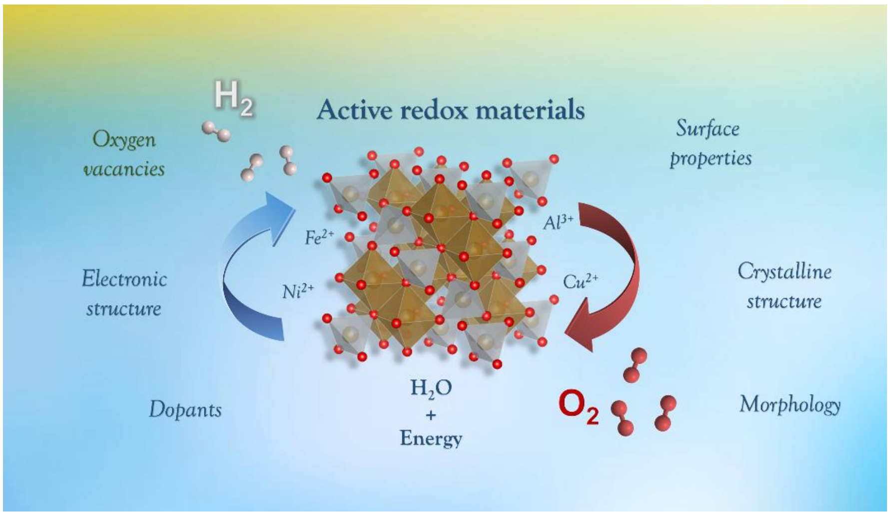

Figure 1: Characteristics of active redox materials that influence their hydrogen production capacity.

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Sorption Enhanced Carbon Dioxide Methanation

Enrico Marchi[a], Pablo Gangotena[b], Christian Frilund[b], Pekka Simell[b], Henrik Grénman[a]

[a] Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Turku, Finland

[b] VTT Technical Research Centre of Finland, Espoo, Finland

e-mail: enrico.marchi@abo.fi

Abstract: Methane obtained through the Sabatier reaction represents a renewable way to obtain a fuel and a platform molecule for the chemical industry. Carbon dioxide methanation is hampered by thermodynamic limitation. Therefore, a conversion far from 100% is obtained, yielding an impure methane stream. The equilibrium can be efficiently shifted towards the products by removing water from the reactive site as soon as it is formed using a bifunctional material.

The use of green hydrogen produced from renewable sources and the valorization of carbon dioxide collected from industrial flue gasses allow the production of a platform chemical and a consolidated fuel that can be directly fed into the gas grid.

The Sabatier reaction (Equation 1) is exothermic and thermodynamically hampered.

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O; \qquad \Delta H^0_{298} = -165 \text{ kJ/mol} \qquad (1)$$

High pressures and low temperatures favor the CO_2 conversion. However low temperatures cause the kinetics to slow down excessively. Zeolite 13X demonstrates good water adsorption at high temperatures (200-300ºC) while offering a support for the active metal deposition. Nickel deposited on zeolite 13X was used to study the behavior of sorption-enhanced methanation. In Figure 1, the concentration profiles of the reaction between H_2 and CO_2 in the stoichiometric ratio are displayed. In the first period, lasting about 20 minutes, sorption of water on the zeolite takes place, the CO_2 conversion reaches 100% as well as the selectivity towards methane. When the zeolite saturates with water, methanation reaction is carried out without equilibrium shift, and a lower conversion is obtained in steady state. The experiments performed at different temperatures showed logical behavior, good repeatability and stability of the catalyst. Regeneration is required to desorb water after each sorption-enhanced period. Hence, a process composed of multiple reactors to operate in series should be utilized to obtain a continuous stream of pure methane.

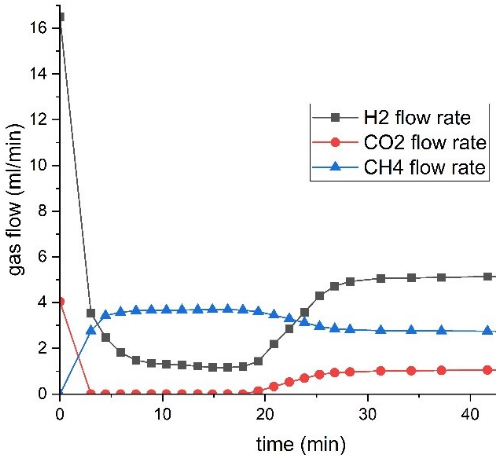

Figure 1, Sorption-Enhanced Methanation experiment. Stoichiometric ratio of H_2/CO_2, 280C, Ni-based 13X zeolite.

Conclusion: The use of a bifunctional material containing catalytically active sites and water adsorbing sites has demonstrated that is possible to shift the equilibrium of the Sabatier reaction to obtain a pure stream of methane. This process can help to reach the aim of carbon-neutral emissions and obtain energy independence for countries without access to fossil fuels. Sorption-enhanced catalysts could also find application also in other processes where the shift in equilibrium is necessary to obtain high-purity products.

Effects of pH and Potential on Pt-Catalyzed Glycerol Oxidation

L. B. Laverdure,[a] K. Honkala[a]

[a] Department of Chemistry, University of Jyväskylä
e-mail: laura.laverdure@associated.ltu.se

Electrocatalytic oxidation (ECO) of biomass-derived polyols on platinum (Pt) catalysts is a promising route clean energy and chemical production. Experimental data indicate that the activity and selectivity depend on pH, electrode potential, and catalyst choice; however, widely used Pt electrocatalysts typically yield the same major products across pH conditions.[1]
Here, we present a comprehensive thermodynamic analysis of glycerol (GLY) electro-oxidation on Pt(111), explicitly accounting for coadsorbed oxide species and the formation of conjugate bases under varying pH and electrode potentials. Although experiments report similar major products, our results reveal distinct mechanistic behaviors across differently oxidized Pt(111) surfaces. On the bare Pt(111) surface, GLY oxidation thermodynamically favours dihydroxyacetone (DHA) rather than glyceraldehyde (GLD), though keto-enol tautomerization from DHA to GLD has previously been proposed.[2] Moderate oxidation of the Pt(111) surface significantly enhances GLY adsorption and favors GLD formation, aligning with the increased activity observed under these conditions. Conversely, a more oxidized surface weakens GLY adsorption, and multiple reaction pathways have comparable energetics.[3] Early oxidation steps also set limiting potentials, suggesting that kinetics inhibit later-stage products.
These findings underscore the need to include pH, potential, and surface coverage effects to accurately predict electrocatalytic performance. Our study provides valuable insights for designing advanced catalysts that optimize both activity and selectivity in glycerol electro-oxidation processes.

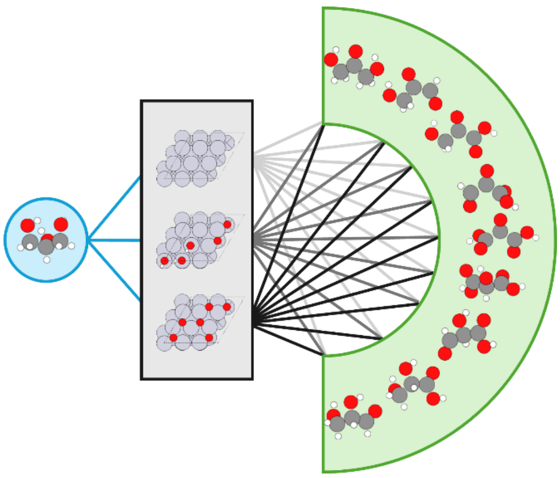

Figure 1: Schematic representation of the possible C3 products resulting from glycerol oxidation on experimentally relevant surfaces.

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Non-thermal plasma assisted catalytic oxidation of methane

Abhinash Kumar Singh[a,b], Jasmiina Palo[a], Johanna Kihlman[a], Pekka Simell[a], Mika Suvanto[b], Niko Kinnunen[b].

[a] VTT Technical Research Centre of Finland, Espoo, Finland.
[b] University of Eastern Finland, Joensuu, Finland.
e-mail: Abhinash.singh@vtt.fi

Keywords: methane oxidation, non-thermal plasma, DBD reactor, catalysts.

Background and motivation.

Methane (CH_4) is a potent greenhouse gas and converting methane to carbon dioxide is a promising strategy. Nevertheless, the catalytic oxidation of methane to CO_2 requires elevated temperature (above 400°C) to activate the strong carbon-hydrogen (C-H) bonds, making it energy intensive [1]. Non-thermal plasma employs electrical energy to generate highly energetic electrons and reactive species, initiating diverse chemical reactions at ambient conditions, making it a suitable solution for methane oxidation [2]. However, non-thermal plasma itself lacks selectivity and may lead to the formation of undesirable by-products [2,3]. Hence, the incorporation of a catalyst within the reactor can induce a synergistic effect, enhancing the selectivity of desired products [3].

Materials and methods.

The objective of this study was to investigate methane oxidation in two reactor configurations: an empty dielectric barrier discharge (DBD) reactor and a packed-bed DBD (PB-DBD) reactor containing various oxidation catalysts (1% Co/Al_2O_3, 1% Cu/Al_2O_3, 1% Fe/Al_2O_3, 1% Pt/Al_2O_3, and 1% Pd/Al_2O_3). The oxidation of methane was studied from 20 to 40 W plasma power and feed (1 vol.-% methane in air) flow rate of 200 mL/min. To assess the impact of plasma on the catalysts, several characterization techniques were employed, including N_2 physisorption, ICP-OES, XRD, and SEM.

Results and discussion.

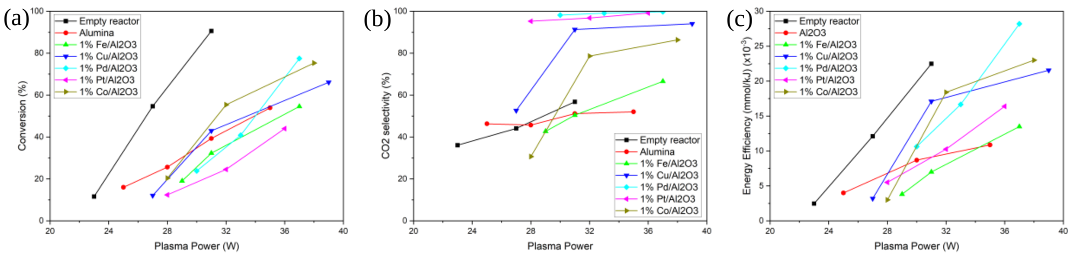

Figure 1: Effect of plasma power on (a). methane conversion, (b). CO_2 selectivity, and (c). energy efficiency of empty DBD reactor and packed bed DBD reactor with various catalysts.

Acknowledgments

Funded by the European Union

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New bi-functional catalysts for a novel continuous production of propylene oxide with in-situ generated hydrogen peroxide

Christoph Schmidt[a], Matias Alvear[a], Francesco Sandri[a], Seo Mandon[b], Satu Ojala[c], Tiina Laitinen[c], Mika Lastusaari[d], Ilari Angervo[e], Tapio Salmi[a]

[a] Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi University
[b] École des métiers de l'environnement, UniLaSalle Rennes, France
[c] Laboratory of Environmental and Chemical Engineering, University of Oulu
[d] Intelligent Materials Chemistry Group, University of Turku
[e] Wihuri Physical Laboratory, University of Turku
e-mail: christoph.schmidt@abo.fi

Combined direct synthesis of hydrogen peroxide (DSHP) and epoxidation of propene with hydrogen peroxide to propylene oxide (HPPO) was carried out first time continuously in a laboratory-scale trickle bed reactor under mild reaction condition of 8 bar and 10 °C. The reaction was performed on bimetallic gold-palladium catalysts supported on titanium silicalite 1 (TS-1). Three series of catalysts were synthesized from two different lots of TS-1 and by using different heating rates in calcination. The catalysts were extensively examined using XRD, SEM-EDS, TEM-SAED, STEM-EDS, ICP-OES, XPS, UV-vis DRS, nitrogen-physisorption and ammonia-TPD. In both commercial TS-1 materials, anatase was found as impurity, which was the preferred site for the deposition of the bimetallic nanoparticles. Titania was present in different amounts in the commercial materials, and a higher content decreased the AuPd nanoparticle size. An increasing heating rate in the calcination resulted in an additional reduction of the AuPd nanoparticle size. In catalytic experiments, a propylene oxide production of 0.71 mol·kg_{cat}^{-1}·h^{-1} was reached with a selectivity of 26.5 % and 43.4 % propene conversion using catalysts of the first series. The propylene oxide selectivity increased to 55.7 % using catalysts of the third series whereas the propylene oxide production decreased to 0.17 mol·kg_{cat}^{-1}·h^{-1} with 19.2 % propene conversion. In switch experiments, the competing side reactions hydrogenation of propene and H_2O_2 were confirmed, while the dismutation of H_2O_2 was disproved.

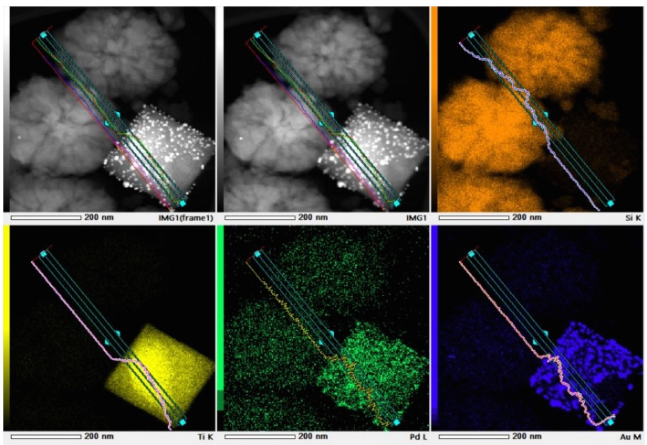

Figure 1: STEM-EDS with line scans of fresh AuPd-TS1-10-3 (a, b STEM image, c Si, d Ti, e Pd and f Au).

Posters

P-1

Electro-methanol synthesis for marine engines

M. Reinikainen, P. Aakko-Saksa, C. Frilund, C. Söderström, T Hangasmaa, and, M. Westerholm

VTT Technical Research Centre of Finland, Espoo
e-mail: paivi.aakko-saksa@vtt.fi

Methanol is a promising alternative fuel for shipping, especially electro-methanol produced from captured carbon dioxide (CO_2) and hydrogen or from bio-based materials. Ambitious targets are established to reduce the greenhouse gas (GHG) emissions from shipping, and hence carbon-neutral or carbon-negative fuels are needed. Within the EU UP-TO-ME project, methanol synthesis is developed to produce e-methanol from the CO_2 point-sources by a fully autonomous, self-optimizing, and compact technology. The e-methanol from the autonomous production plants is targeted for smaller vessels.

In this project the emphasis of reactor development has been in applying new 3d printing technologies for the manufacture of efficient reactors for highly exothermic methanol synthesis. Parallel to reactor development different methods for depositing the catalytic coating on the printed reactor surfaces was studied. We present the direct methanol synthesis process and efficiency of the exhaust aftertreatment system to reduce harmful emissions from retrofitted marine methanol engine.

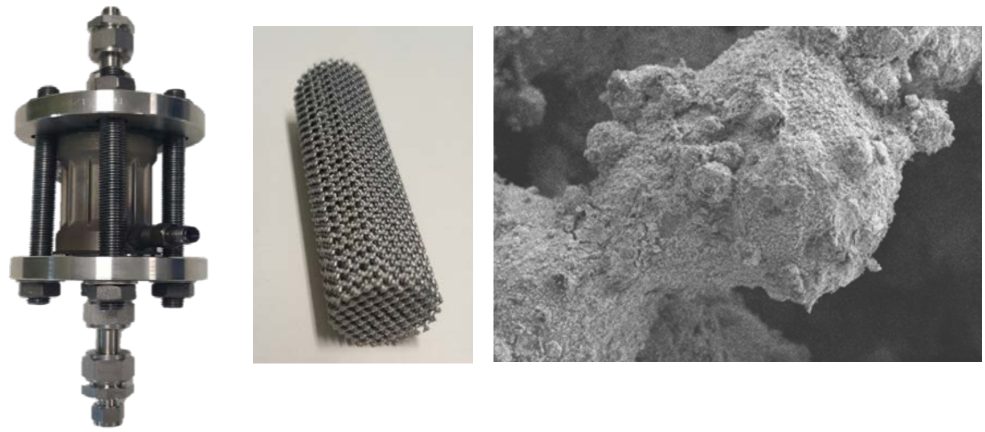

Figure 1. 3D-printed test reactor, aluminum insert and catalyst deposited on anodized aluminum.

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P-2

Photocatalytic degradation of pharmaceuticals with Bi_3O_4Br/TiO_2

Sajad Ahmadi,[a] Velma Beri Kimbi Yaah,[b] Sergio Botelho de Oliveira,[c] Satu Ojala[a]

[a] Environmental and Chemical Engineering, Faculty of Technology, University of Oulu. Oulu, Finland.
[b] Nano and Molecular Systems Research Unit, University of Oulu, P.O. Box 4500, FI, 90014, Finland.
[c] Department of Chemistry, Federal Institute of Goiás, Goiania 74055 110 Brazil.
e-mail: Sajad.ahmadi@oulu.fi

The presence of pharmaceuticals, such as paracetamol in wastewater has become a significant issue, exacerbated by a 198% increase in paracetamol consumption during the COVID-19 pandemic [1]. Photocatalysis is effective for removing paracetamol, with titanium dioxide (TiO_2) being a common photocatalyst due to its unique properties. However, the wide band gap of TiO_2 limits its activation [2]. BiOBr exhibits great photocatalytic potential owing to the particular layered structure, facilitating efficient separation of electron-hole pairs [3]. Despite its visible light activity, BiOBr's light absorption is limited to a narrow range (less than 450 nm). Bismuth-rich oxybromides exhibit visible light activity, and Bi_3O_4Br, identified as one of the most effective photocatalysts in our previous study [3]. Bi_3O_4Br demonstrated better performance compared to BiOBr, achieving 80% paracetamol degradation versus 35% for BiOBr. PL and EIS analyses confirmed the factors contributing to enhanced effectiveness. It was then selected to form a heterojunction with TiO_2 nanobelts to enhance photocatalytic performance. Prepared TiO_2 nanobelts have monoclinic structure. Raman and XPS analyses confirm strong interactions between Bi_3O_4Br and TiO_2 NB, with shifts in binding energies and spectral overlaps supporting the formation of a heterojunction. UV-Vis DRS results show improved visible light absorption and narrower bandgaps in Bi_3O_4Br/ TiO_2 NB composites compared to pure TiO_2 NB. The composite with the ratio of 2:1 ($Bi_3O_4Br:TiO_2$) was the most effective in paracetamol removal. This was due to the enhanced charge carrier separation, efficient charge transfer, and slower electron-hole recombination, as confirmed by PL, EIS, and time-resolved PL. The neutral pH of paracetamol (6.5) was optimal for degradation and 89 % removal efficiency was obtained. Increasing photocatalyst dosage up to 0.4-0.5 g/L improved removal efficiency to 96 % without hindering light penetration. However, higher initial pollutant concentrations decreased efficiency, resulting in 89 % removal at 10 mg/L and 55 % at 20 mg/L. Temperature increase enhanced degradation, with optimal performance reached at 35 °C (97 % removal efficiency). The results of stability and recyclability experiments showed that the composite retained 66% removal efficiency after four cycles, and structural stability was maintained as confirmed by XRD and FTIR analyses. The mineralization degree of paracetamol was tested by total organic carbon (TOC) analysis. It was found that around 54 % and 70 % of TOC was eliminated when the 0.2 g and 0.4 g of Bi_3O_4Br/ TiO_2 NB was used. The TOC experiments were done at neutral pH of paracetamol, 10 mg/L of paracetamol, room temperature, and without presence of any scavengers. The performance of the composite in diluted wastewater treatment was also tested. Approximately 21% TOC removal was achieved within 24 hours when 0.2 g of the composite was used.

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P-3

Novel Raney-type solid foam catalyst for xylitol production

G. A. Barahona[a, b], M. De Simone[a, c], C. Brunberg[a], K. Eränen[a], A. Reinsdorf[d], M. Roos[d], J. García-Serna[b], V. Russo[c], D. Yu. Murzin[a], and T. Salmi[a, c]
[a] Laboratory of Industrial Chemistry and Reaction Engineering (TKR), Åbo Akademi University
[b] Grupo de Tecnologías a Presión (PressTech), Universidad de Valladolid
[c] Chemical Sciences Department, Università di Napoli "Federico II"
[d] Evonik Operations GmbH, Business Line Catalysts
e-mail: garaujob@abo.fi

Sponge nickel, commonly known as Raney nickel, is a heterogeneous catalyst developed in the 1920s, widely employed in hydrogenation of carbonyl groups and double bonds due to its high hydrogen storage capacity. Despite its effectiveness in biomass valorization, its traditional finely dispersed form is limited to batch operation due to high pressure drop [1]. In this work, the performance of novel activated nickel foam catalysts from Evonik's Metalyst® MC 9 series was investigated for the selective hydrogenation of xylose to xylitol under continuous and semi-batch conditions, with a focus on a molybdenum-promoted variant of the catalyst. Catalyst deactivation mechanisms were examined, particularly the impact of poisoning compounds such as aldonic acids.

The catalysts were characterized using thermogravimetric analysis (TGA), pulse hydrogen chemisorption, X-ray photoelectron spectroscopy (XPS), and inductively coupled plasma optical emission spectroscopy (ICP-OES) to assess stability, surface properties, and metal leaching. Hydrogenation experiments of xylose were conducted in a rotating bed reactor (semi-batch) and a parallel screening tubular reactor (continuous) under varying temperatures (90–120 °C) and flow rates (0.25–0.75 mL min^{-1}). The effect of xylonic acid on catalyst deactivation was evaluated, too, and advance kinetic modeling was applied to describe the reaction rates and the deactivation behavior.

The results demonstrated the strong potential of solid Raney-type Ni foam catalysts for selective xylose hydrogenation, with the molybdenum-promoted variant outperforming the unpromoted catalyst in activity, stability, and selectivity. Continuous operation exhibited reduced deactivation, attributed to lower accumulation of poisoning species. The decrease of the catalyst activity was primarily linked to the adsorption of strongly bound organic species and metal leaching via chelating effects, both mitigated by the role of molybdenum in stabilizing the active sites and enhancing the hydrogen and xylose adsorption-desorption processes. Advanced kinetic modeling effectively described reaction and deactivation behaviors, reinforcing the superior performance of the Mo-promoted catalyst and providing valuable insights into catalyst design and process optimization in biomass valorization.

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P-4

Cross-aldol Condensation of Aldehydes on *m*-$ZrO_2(\bar{2}12)$ surface: A DFT Study

Bhumi A. Baraiya,[a] Ville Korpelin,[a] Toni Kiljunen,[a] and Karoliina Honkala[a]

[a] Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014, Finland
E-mail: bhumi.a.baraiya@jyu.fi

Selective syngas (a mixture of CO and H_2) conversion into isobutene over zirconia has been recognized as *isosynthesis reactions* and has regained attention by the 'hard-to-electrify' aviation industry due to the vital role of *isobutene* in the production of jet fuel range hydrocarbons [1]. For *isosynthesis*, the aldol condensation type reactions have been proposed to promote the chain growth for C_2 to C_3 species and the subsequent chain branching to iso-C_4 compounds [2]. On monoclinic zirconia, the role of coordinatively unsaturated Lewis acid-base sites lacks clarity in the selective C_1–C_n (n=2,3) coupling mechanism of isosynthesis. Hence, the aldol condensation reactions of acetaldehyde and propionaldehyde with formaldehyde were carried out over a stepped *m*-$ZrO_2(\bar{2}12)$ model catalyst. The vdW-corrected GGA-DFT method was used to investigate the thermodynamics of reactant and intermediate species; the CI-NEB method was used to calculate the activation energies of elementary reactions using the GPAW simulation code [3]. The enolization (extraction of α-H) of aldehydes is facilitated by the coordinatively unsaturated edge base site (O^{2-}) while the edge acid site (Zr^{4+}) stabilizes the enolates and activates carbonyl groups for further C–C coupling reactions with available formaldehyde on the adjacent acid site. In the subsequent steps of aldol condensation, proton transfer to O of the aldol intermediate is the rate-limiting step, while C–OH cleavage is facile on the edge-acid site and forms α,β-unsaturated aldehydes such as acrolein and methacrolein. This DFT study demonstrates the active and selective role of coordinatively unsaturated Zr^{4+}–O^{2-} sites in chain growth and branching of compounds through cross-aldol condensation.

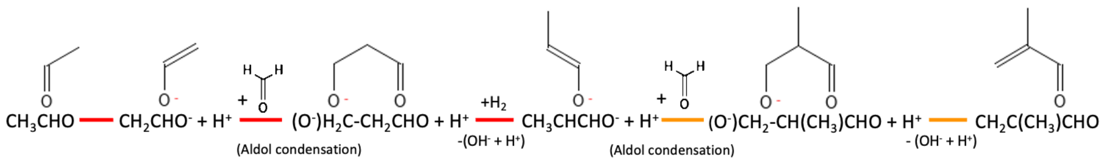

Figure 1: Mechanism of two consecutive cross-aldol condensation.

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P-5

Kinetics of isosynthesis over monoclinic ZrO_2

K. Chen,[1] B. Baraiya,[2] V. Korpelin,[2] N. Heikkinen,[1] M. Reinikainen,[1] K. Honkala,[2] and J. Lehtonen[1]

[1] VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Espoo, Finland
[2] Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014, Jyväskylä, Finland
e-mail: kristian.chen@vtt.fi

Introduction. Isosynthesis is a process to produce branched hydrocarbons from a mixture of carbon monoxide and hydrogen utilizing a heterogeneous ZrO_2 catalyst [1]. The primary reaction product is isobutylene which can then be used in the production of fuels, chemicals and elastomers. Currently isobutylene is produced solely from fossil sources which makes isosynthesis an attractive sustainable route to isobutylene. Scale up of the process, however, requires more information on the chemical kinetics of isosynthesis than is currently available. In this work, three kinetic models were developed to evaluate the kinetic parameters of the isosynthesis process over monoclinic ZrO_2 catalyst.
Experimental/Methodology. The kinetic parameters refer to the pre-exponential factors and activation energies. Model 3 of this work includes equilibrium constants as well. The kinetic parameters associated with each model were calculated using numerical optimization in Matlab, utilizing non-linear least squares analysis with data acquired from kinetic experiments. The reactor model was a pseudo-homogeneous plug flow model. The rate equation for the isosynthesis was derived using quasi-equilibrium hypothesis from an elementary step reaction mechanism developed based on literature information. Furthermore, side reactions for significant by-products were considered. The reaction network used in this work is shown in Figure 1.
Results and discussion. Three kinetic models were compared. Model 1 was based on power law rate equations for main and all side reactions. Model 2 followed a similar structure except most of the side reactions were lumped to one reaction. In model 3, the rate equation derived from the reaction mechanism was applied for the main reaction and all side reactions were accounted for by modelling them using Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism or power law equation depending on the reaction. All three models produced reasonably accurate results when compared to experimental data, with model 3 having the best results. However, as model 3 contained the highest number of parameters to be calculated there is also a possibility of overparameterization.

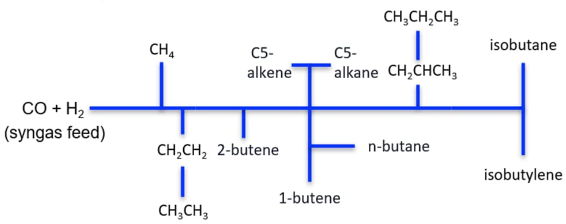

Figure 1: A simplified version of the reaction network used to derive the rate of the RDS in isosynthesis. Although not shown, oxygen is assumed to leave the process as CO_2.

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P-6

Synthesis of monoterpene epoxides over dendritic ZSM-5 zeolites

Luis A. Gallego-Villada,[a] Jennifer Cueto,[b] María del Mar Alonso-Doncel,[b] Päivi Mäki-Arvela,[a] Edwin A. Alarcón,[c] David P. Serrano,[b] and Dmitry Yu. Murzin,[a]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Henriksgatan 2, 20500 Turku/ Åbo, Finland
[b] Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra, 3, 28935, Móstoles, Madrid, Spain
[c] Environmental Catalysis Research Group, Chemical Engineering Faculty, Universidad de Antioquia, Medellín, Colombia
e-mail: luis.gallegovillada@abo.fi

The valorization of renewable feedstock is a key area in chemistry for producing valuable chemicals while aligning with the principles of Green Chemistry [1]. Among these feedstocks, terpenoids are structurally diverse natural products with broad applications. The synthesis of monoterpene epoxides, such as limonene-1,2-epoxide (LE), is crucial for bio-based polymer production and the fragrance, cosmetic, and pharmaceutical industries [2]. However, there is a research gap in selective heterogeneous catalysts for the isomerization of LE (Figure 1) to dihydrocarvone (DHC). Zeolites, particularly ZSM-5, have attracted significant interest due to their exceptional properties and versatility [3]. In this work, dendritic ZSM-5 zeolites with a 3D branched, radially oriented nanoarchitecture were synthesized to enhance catalytic performance. These materials feature a highly interconnected pore network, improving accessibility and overcoming diffusional limitations in reactions involving bulky molecules. The catalysts were characterized using XRD, Ar physisorption, pyridine-FTIR, TEM, FTIR/DTBPy, and ^{27}Al MAS NMR. Among various ZSM-5 materials, the dendritic zeolite synthesized with a 4-day crystallization time exhibited the highest activity, achieving a turnover frequency (TOF) of 4.4 min^{-1}. Additionally, this material provided a remarkable 63% yield of DHC at 70 °C in 2 h. Its superior performance was attributed to an increased mesopore/external surface area (360 m^2 g^{-1}) and a narrow mesopore size distribution. A direct correlation was observed between TOF values and the concentration of external Brønsted acid sites, highlighting the role of steric and diffusional constraints, which are significantly mitigated by the dendritic structure.

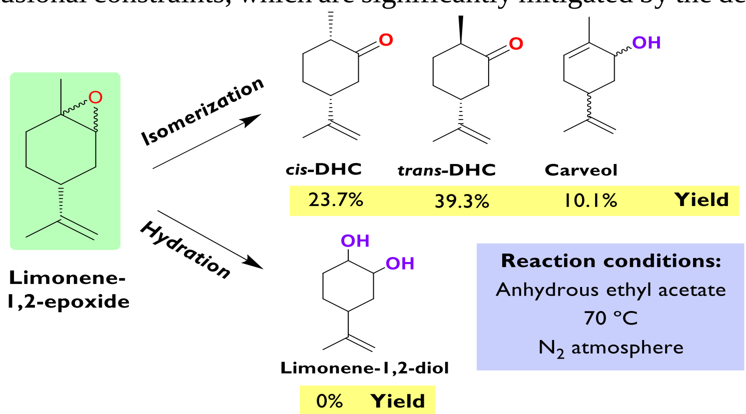

Figure 1: Limonene-1,2-epoxide isomerization over dendritic ZSM-5 zeolite. Adapted from [3].

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P-7

Eugenol Hydrodeoxygenation: The Effect of Hydrogen Source

Liinu M. Hämäläinen, A.Juntunen, A. Haapala and Niko M. Kinnunen

Department of Chemistry and Sustainable Technology, University of Eastern Finland, Joensuu, Finland
e-mail: Liinu.Hamalainen@uef.fi

Lignin as a biopolymer with natural renewable and aromatic structures is of particular interest as a starting material for future bio-based aromatics and plastic industry products. The availability of lignin as a by-product of the forest industry is currently excellent and the low price increases its interest. The structure of lignin is complex, consisting of three different building blocks: p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol. These lignin monomers contain allyl-, hydroxide-, and methoxy groups bonded in various ways. This study investigates the role of hydrogen source with RuW/zeolite catalyst in HDO reaction with model compound. To study catalytical removal of allyl-, hydroxide-, and methoxy groups, one option is the use of model compound, such as eugenol. The purpose is to find optimal parameters for removal of allyl-, hydroxide-, and methoxy groups to produce monomeric aromatic hydrocarbons. Finally, optimized reaction parameters were tested in the depolymerization of organosolv lignin. Model reactions were performed under mild conditions at 1 bar pressure and 180 degrees using water as a solvent. Paraformaldehyde, formic acid and isopropanol were tested as the hydrogen source. The use of a hydrogen source prevented the polymerization of the model compound. Isopropanol was the most efficient hydrogen source among the sources studied in HDO reaction. Decreasing reaction time increases carbon balances in the reaction.

P-8

Computational insights into the role of tetragonal zirconia in isosynthesis

R. Ikonen,[a] B. Baraya,[a], V. Korpelin,[a] and K. Honkala [a]

[a] Department of Chemistry, University of Jyväskylä
e-mail: rasmus.l.o.ikonen@jyu.fi

Isosynthesis is a selective catalytic process to convert syngas, a mixture of CO and H_2, into isobutene.[1] This process is catalyzed by zirconia (ZrO_2), but the product distribution is highly sensitive to the polymorph of the zirconia catalyst. While monoclinic zirconia (m$-ZrO_2$) exhibits relatively good selectivity towards isobutene, tetragonal zirconia (t-ZrO_2) converts syngas predominantly to methane and other C_1 compounds. [2,3]

In this computational study, we shed light on the polymorph sensitivity in isosynthesis by investigating the energetics of methanation and CO insertion on t$-ZrO_2$ (Figure 1), and m$-ZrO_2$ surfaces. Investigated surfaces include both defect-free flat surfaces and stepped structures. DFT + U calculations show distinct behavior for every investigated surface model, and highlights the important role of unsaturated sites for the chain growth in isosynthesis.

101

134

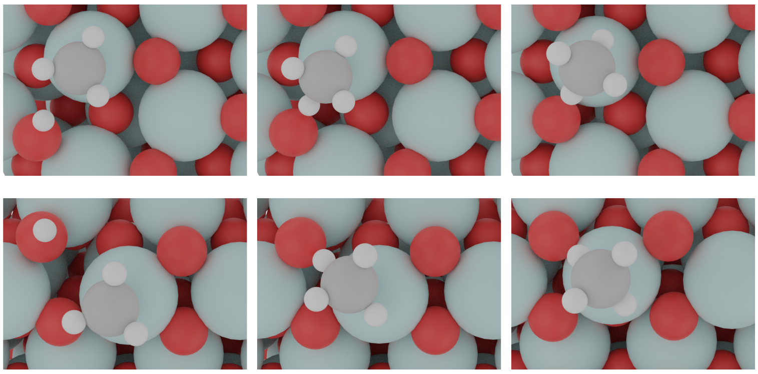

Figure 1: Methane formation on t$-ZrO_2$ (101) and (134) surfaces.

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P-9

Effect of the acidic properties of zeolite catalysts on glycerol aromatization

E. Järvinen [a], J. A. Velasco [a], R. Karinen [a], R. L. Puurunen[a]

[a] Department of Chemical Engineering and Metallurgy, Aalto University
e-mail: ellen.jarvinen@aalto.fi

Due to increased availability, crude glycerol has become a favorable raw material for the manufacture of renewable chemicals [1,2]. Chemicals that can be derived from glycerol include benzene, toluene, and xylene (BTX) [1], which are widely used in the manufacture of plastics, resins, and synthetic fibers and currently have few renewable commercial alternatives [2–4]. The glycerol-to-BTX reaction is typically carried out over an acidic zeolite catalyst. This work examined the effect of catalyst acidic properties on the aromatization activity.

Pristine H-ZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 23, 50, 80, and 280 (Zeolyst International), and a Zn-modified H-ZSM-5-80 zeolite prepared with atomic layer deposition (ALD) (Zn loading ca. 2 wt.%, support Thermo Scientific Chemicals) were studied. Catalytic tests were carried out in a fixed bed flow reactor (450 °C, 1 bar, N_2 carrier gas, $WHSV_{glycerol} = 0.71\ h^{-1}$) with a model liquid feed for crude glycerol containing 40 wt.% glycerol in water. Product analysis was by gas chromatography. The acidic properties of the zeolites were characterized with the temperature programmed desorption of ammonia (NH_3-TPD) and isopropylamine (IPAm-TPD).

Complete glycerol conversion was achieved with all catalysts. At ca. 7 h, the BTX yield had decreased significantly for all pristine zeolites compared to ca. 2 h with H-ZSM-5-23 and H-ZSM-5-80 maintaining the highest yield. The ALD-made Zn/H-ZSM-5-80 catalysts maintained an even BTX yield within the time-on-stream tested. The results suggest a moderate Brønsted acidity combined with the presence of Lewis acid sites facilitates a more stable BTX production.

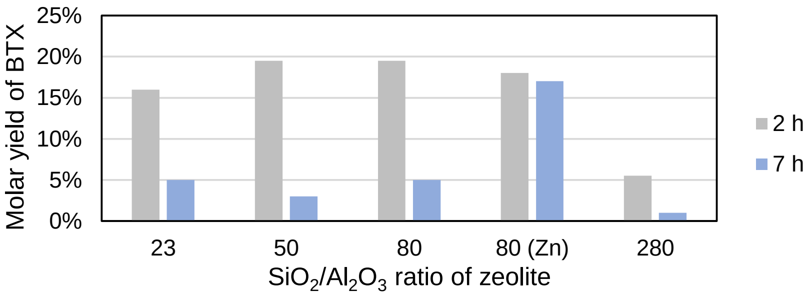

Figure 1. BTX molar yield of pristine H-ZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 23, 50, 80, and 280, and Zn/H-ZSM-5-80 at times-on-stream (TOS) of ca. 2 and 7 hours.

Acknowledgments. *This work was funded by Business Finland (GreenAro project).*

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P-10

Bimetallic alloy catalysts for syngas conversion: a machine-learning survey

T. Kiljunen, V. Korpelin, H. Ibrahim and K. Honkala

Nanoscience Center, Department of Chemistry, University of Jyväskylä
e-mail: toni.k.kiljunen@jyu.fi

We computationally investigated the conversion of synthesis gas into higher value products via heterogeneous catalysis. The catalytic interface was modelled as a stepped Cu surface at different dilutions of another metal Fe, Co or Ni. The compositions of these bimetallic alloys were discovered by using a machine-learning method based on a density-functional-theory calculator. We found that upon exposure to CO and H, both of these reagents induce a surface reconstruction, and that the preferred surface structures depend on the alloy metal and the strength of the metal–reagent bonds. On the surface, Fe was found to exist as singe-atom centres that can form tricarbonyl groups, Co appears as larger domains separated from Cu, and Ni becomes more evenly distributed and in larger degree mixed with surface Cu. Figure 1 shows a sample collection of 1:1 alloys for adsorption of six CO molecules (a–c), and a 1:17 FeCu alloy for adsorption of six dissociated H_2 molecules (c top).

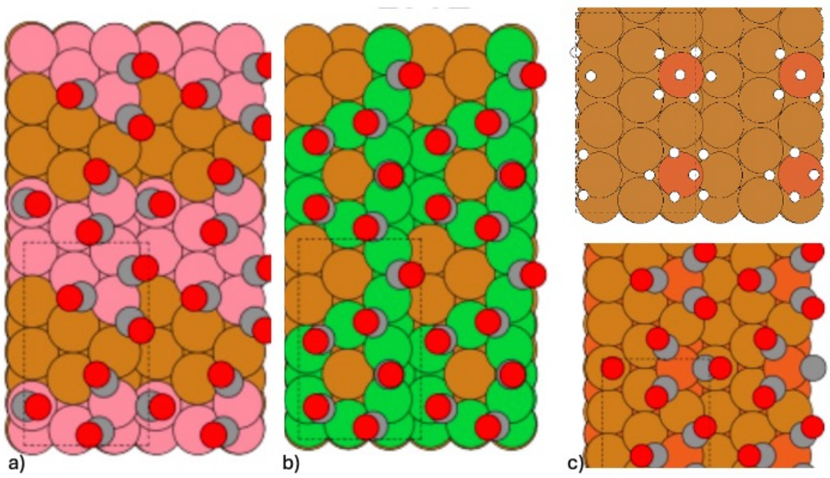

Figure 1: Alloy surface structures with adsorbed CO or H for a) CoCu, b) NiCu, and c) FeCu catalyst models (top view, $3 \times 4 \times 4$ simulation cell.). The results were obtained by the machine-learning method ICEBEACON [1,2] that was incorporated with DFT runs using GPAW code.

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P-11

Simulating iron in oxygen-containing environments: An improved Fe-O interaction for density-functional tight-binding

V. Korpelin,[a] J. Nevalaita,[b] M. M. Melander,[a] K. Honkala,[a] and P. Koskinen [b]

[a] Department of Chemistry, University of Jyväskylä
[b] Department of Physics, University of Jyväskylä
e-mail: ville.p.korpelin@jyu.fi

Iron–oxygen interactions are crucial for the description of important systems ranging from biological (heme protein) to electrocatalytic (Fe-N-modified graphene). Simulating the dynamics of such systems at extended time and length scales using standard density functional theory (DFT) is very costly, while standard classical force-field methods are unable to describe the relevant bond breaking and formation events. The density-functional tight-binding (DFTB) method can provide a suitable compromise between cost and accuracy.

DFTB requires each type of atom pair to be individually parametrized. The existing Fe–O parametrization in the trans3d set[1] has been identified as flawed, causing geometric distortions due to a spurious attractive component.[2] We have refitted the Fe–O parametrization, rectifying this issue and also generally improving the energetics of iron–oxygen systems (Figure 1). The DFTB description of water was also tuned by fitting the O–H interaction and dispersion parameters against high-quality reference data.

The parametrization was validated by simulations of aqueous Fe species and FeN_4-modified graphene. Structural properties such as pair distribution functions and the layer structure of water on graphene were well described. Dynamic properties ranging from short (vibrational frequencies) to long (diffusion coefficients) timescales were also in qualitative agreement with experiment. The parametrization therefore provides an efficient way to explore the structure, stability and dynamics of catalytically relevant iron–oxygen and iron–water systems.

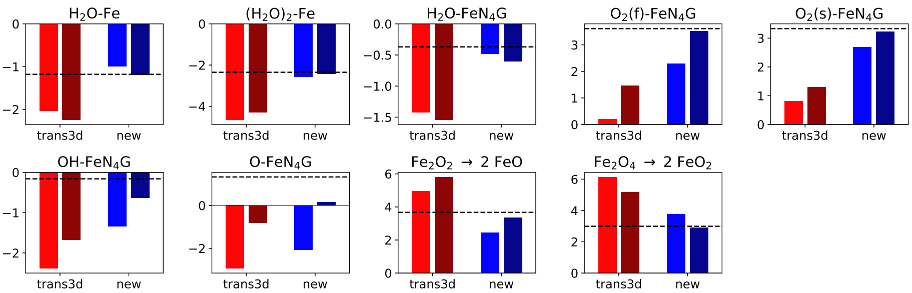

Figure 1: The new parametrization (blue bars) produces better agreement with DFT adsorption energies (dashed lines) than the existing trans3d parametrization (red bars). Orbital-dependent Hubbard parameters (dark bars) provide a further improvement over the standard atomic parameters (light bars). FeN_4G refers to FeN_4-modified graphene. Energies are given in eV.

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[2] C. Liu et al. *J. Phys. Chem.* **2020**, *124*, 9674.

P-12

Green aromatics from biomass pyrolysis oils with zinc-doped ZSM-5 zeolites

V. Lehtinen [a], A. Arandia [a], F. Sandri [b], I. Uotila [a], M. Reinikainen [a], J. Kihlman [a], J. Lehtonen [a]

[a] VTT Technical Research Centre of Finland Ltd., Espoo, Finland
[b] Johann Gadolin Process Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finland
e-mail: veikka.lehtinen@vtt.fi

Keywords: bio-oil, aromatics, zeolites

Introduction. Benzene, toluene and xylenes (BTX) are important compounds used in the synthesis of various high-value materials in the petrochemical industry, such as resins, solvents and fibers [1]. While traditionally produced from crude oil, the production of BTX from sustainable feedstocks, such as bio-oil, should be ensured in the future. One renewable route is the catalytic treatment of bio-oil and it has been investigated for the production of BTX. Zeolites are attractive catalysts to produce aromatics from bio-oil due to their ability to dehydrogenate and deoxygenate bio-oil compounds because of their favorable acidic and structural properties. In this work, the production of green aromatics was investigated using zinc doped ZSM-5 catalysts with various Si/Al ratios. The effect of temperature was tested to see its effect on BTX production. In addition, the reusability of the catalyst, a key parameter for industrial production, was investigated for two regeneration cycles.

Materials and methods. The catalytic treatment of bio-oil was investigated in a continuous catalytic reactor using H-ZSM-5 (50) and three zinc doped ZSM-5 with Si/Al ratios of 30, 50 and 80. The best performing catalyst was chosen for experimentation at different temperatures (400, 450, 500, 550 ˚C). The bio-oil had been previously treated by hydrogenation which decreased the oxygen content to 2 w-%. The gaseous products were analyzed by microGC and the liquid product was identified by GC-MS and quantified by GC-FID. The regeneration of the catalyst was done at 500 ˚C in contact with synthetic air for a duration of 4-6 hours and monitored by microGC.

Results. Zinc doped ZSM-5 was more active in the production of aromatics from bio-oil compared to parent H-ZSM-5. The mass fraction of aromatics in the liquid product was 26 and 37 w-% for H-ZSM-5 (50) and Zn-ZSM-5 (50), respectively. Decreasing the Si/Al ratio to 30 yielded similar results but deactivated faster. Temperature was also crucial to BTX production. Increasing the temperature from 400 to 550˚C improved the BTX production significantly with initial BTX mass fractions of 24 and 44 w-%, respectively. Reusability tests proved that 79 % and 81% of the initial activity to BTX were recovered in the two regeneration cycles.

Acknowledgements
We acknowledge Business Finland for the financial support of GreenAro project, and our research and industrial partners for the scientific support.

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P-13

Ozonation of Pharmaceuticals: Single APIs vs Complex Mixtures

A. F. Nuñez,[a] P. Tolvanen,[a] , N. Kumar, [a] Shey Jude Fale, [a] D. Murzin, [a] T. Salmi, [a,b]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University, FI-20500 Turku/Åbo, Finland
[b] Università di Napoli 'Federico II', Chemical Sciences, IT-80125 Napoli, Italy
e-mail: ana.nuneznunez@abo.fi

The removal of pharmaceuticals from wastewater remains a critical challenge, with ozonation being a promising treatment option. In our earlier studies, the degradation of single active pharmaceutical ingredients (APIs), such as ibuprofen, diclofenac, carbamazepine, sulfadiazine and sulfamethoxazole, under ozonation with and without catalytic enhancement was investigated [1]. Fe and Cu based zeolites were found to be effective to eliminate byproducts and increase degradation efficiency. While single-compound studies provided valuable mechanistic insights, real wastewater scenarios contain complex mixtures, necessitating further investigation of multi-API degradation. Given that pharmaceuticals often occur as complex mixtures in wastewater, understanding their combined degradation pathways and transformation products is crucial for assessing the efficiency and safety of advanced treatment processes [2]. This study expands on our previous work by examining binary and full five-component API mixtures to understand competitive reactions, transformation product formation, and potential synergies or inhibitory effects in ozonation.

Experiments were conducted in a semi-batch ozonation reactor equipped with a laboratory-scale ozone generator. Ozone was continuously bubbled through the solution. Stability tests of the pharmaceutical mixtures were performed before ozonation to assess interactions between APIs in the absence of oxidative treatment and no notable interactions were found.

Single API ozonation followed predictable degradation pathways, consistent with our previous studies, whereas the presence of multiple APIs altered transformation product distributions and reaction rates. Competitive ozone consumption and possible transformation product interactions were observed, emphasizing the need for further pathway elucidation in multi-API systems. This study contributes to a deeper understanding of pharmaceutical oxidation in realistic wastewater conditions and provides insight into optimizing ozonation for improved contaminant removal.

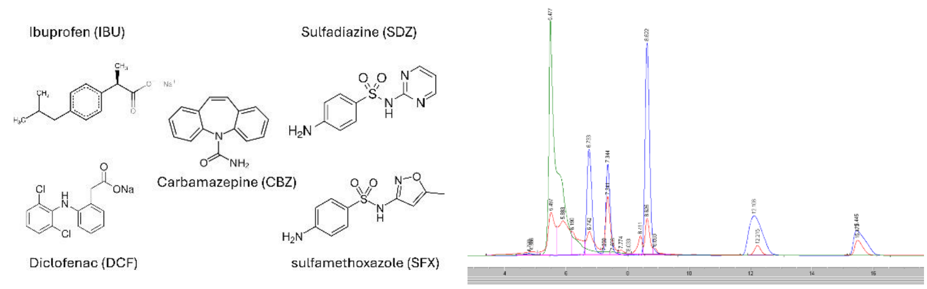

Figure 1: Molecular structure of studied APIs, and an HPLC chromatograph of an ozonated mixture with all five APIs.

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P-14

Carbon dioxide cycloaddition to limonene di-epoxide for sustainable cyclic carbonate production

Federica Orabona[a,b], Wander Y. Perez-Sena[a], Tapio Salmi[a,b] and Vicenzo Russo[a,b]

[a] Åbo Akademi, Laboratory of Industrial Chemistry and Reaction Engineering, Henrikinkatu 2, FI-20500 Turku/Åbo, Finland
[b] Università degli Studi di Napoli Federico II, Dipartimento di Scienze Chimiche, via Cintia, IT-80126 Napoli, Italy
e-mail: wander.perezsena@abo.fi

Cyclic carbonates are promising polymer precursors for the production of non-isocyanate polyurethanes [1], entirely derived from biomass feedstocks. In this context, biomass-derived molecules containing epoxides, such as lignin derived epoxides, epoxidized vegetable oils and terpenes, are particularly attractive [2]. This study investigates the production of bi-cyclic carbonates from renewable limonene di-epoxide in a 300 mL autoclave reactor. In the first stage, tetra-butyl ammonium halide salts were evaluated as homogeneous catalysts, with tetraethylammonium chloride (TEACL) emerging as the most effective in terms of both conversion and selectivity toward mono- and di-carbonate products. The solubility of CO_2 in di-epoxide and carbonate substrates was determined using Henry's law [3]. Additionally, the effects of temperature (100–170 °C), pressure (20–50 bar), and catalyst loading (4–10 wt.%) were assessed to understand the system's catalytic behavior.

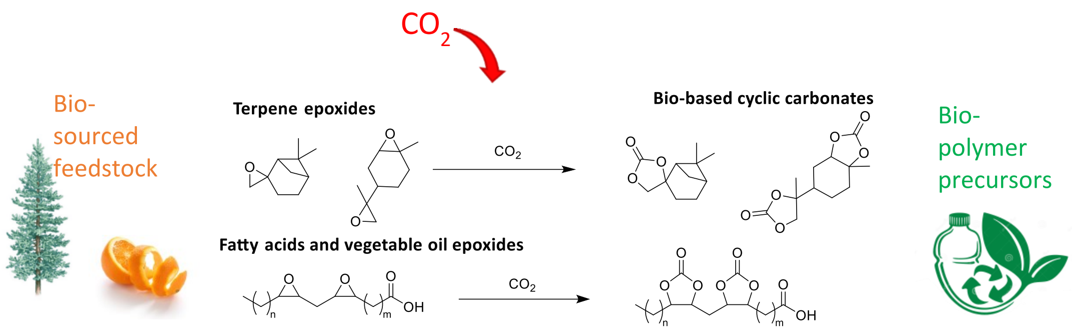

Figure 1: Carbon dioxide cycloaddition to epoxides

In the second stage, chloride-containing ionic species were immobilized onto silica gel via silane coupling techniques to develop heterogeneous catalysts for CO_2 cycloaddition to limonene diepoxide. The heterogeneous system achieved high conversion and yield for the mono-carbonate product. however, the yield of di-carbonate limonene remained low under the tested conditions.

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P-15

Catalytic decomposition of N_2O over Cu- and Fe- modified Beta, USY and ZSM-5 zeolite catalysts

Md Habibur Rahman[a], Kari Eränen[a], Jari Böling[b], Narendra Kumar[a], Dmitry Yu. Murzin[a]

[a] Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of science & engineering, Åbo Akademi University, Åbo, Finland.
[b] Automation Engineering, Department of Mechanical and Materials Engineering, University of Turku, Finland.
e-mail: habibur.rahman@abo.fi

Nitrous oxide is a greenhouse gas that is 300 times more potent than carbon dioxide, underscoring the urgency of its decomposition before atmospheric release. Metal-modified zeolites have long been of interest as catalysts for the direct and selective catalytic reduction (SCR) of nitrous oxide. However, the development of an active, selective, and stable catalyst for this reaction still remains a challenge[1] .
In this work, copper and iron were used as metals, with their acetate and nitrate forms serving as metal precursors. Beta, USY, and ZSM-5 zeolites with different acidity levels were selected as support materials. Metal promotion was carried out using evaporation impregnation (EIM), ion-exchange (IE), and deposition precipitation (DP) techniques. All synthesized catalysts were dried at 110°C for 24 hours and calcined at 400°C.
The performance of the catalysts was tested in a stainless-steel tubular reactor with a total flow of 200 ml/min, containing 1000 ppm nitrous oxide balanced with helium. The influence of oxygen was examined under an excess oxygen flow of 10 ml/min to assess its impact on catalytic performance.
The results clearly demonstrated that copper nitrate is a better precursor compared to copper acetate. Iron catalysts perform best when synthesized via the ion-exchange method, while the evaporation impregnation method was more effective for copper-based catalysts. Additionally, Beta and ZSM-5 zeolite supports outperformed USY zeolite. These findings provide valuable insights into optimizing zeolite-supported catalysts for efficient N_2O reduction.

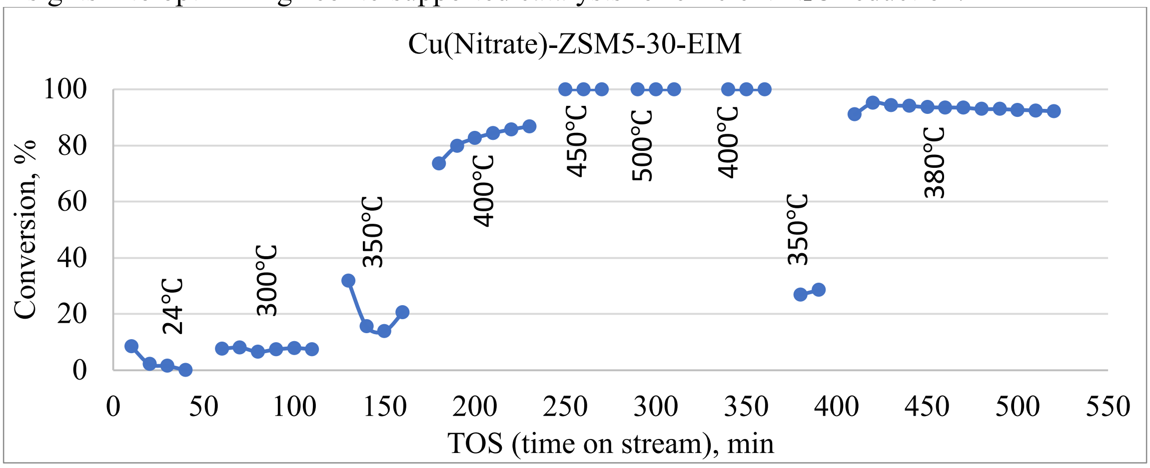

Figure 1: Conversion at different temperature for Cu (Nitrate)-H-ZSM5-30-EIM catalyst. Total gas flow 200ml/min, N_2O 1000ppm and balanced He, 0.405g 250-125µm sized catalyst.

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P-16

Zinc doped zeolites for the production of aromatics from ethanol and furfural

F. Sandri,[a] N. Narendra,[a] P. Mäki-Arvela[a] and D. Yu. Murzin[a]

[a] Johan Gadolin Process Chemistry Centre, Åbo Akademi University, Turku, Finland
e-mail: Francesco.Sandri@abo.fi

Benzene, toluene and xylenes (BTX), reached a production of ca. 143 million tons in 2025 increasing over the years[1]. Their production from renewable feedstock is of fundamental importance for the green transition of chemical industry from fossil to renewable. Recently a promising novel production route was proposed, starting from furfural and ethanol, with HZSM-5 zeolites as the catalyst [2]. This new biobased route is limited by catalyst deactivation due to coke formation. This work explores the mechanism of deactivation and its prevention/mitigation. The performance of the metal-doped zeolites was studied, following the literature where it was reported how addition of the metal can improve aromatization of similar substrates[3]. The zeolites in the acidic form were modified with either ion-exchange or evaporation methods, followed by their performance evaluation in aromatization along with testing the commercial metal-free zeolites in a fixed-bed plug flow reactor (T=500°C, P=1 atm). Fresh and spent catalysts were characterized with IPC-OES, TEM, nitrogen physisorption, TGA, XRD, solid state ^{27}Al MAS NMR and pyridine adsorption combined with FT-IR. A coke formation dependency with the acid sites amount was found, namely higher acidity resulted in higher carbon formation and subsequently lower aromatics production. Because of experiments with single reactants and characterization of the spent catalysts, deactivation could be ascribed to the influence of furfural. By using a mixture of ethanol and furfural a new reaction pathway can be unlocked, leading to a more efficient aromatic production, together with a different mechanism of carbon formation. The coke formation happens in two separate steps, the most relevant occurs at the beginning of the reaction and corresponds to the end of BTX production. Functionalization with Zn leads to promotion of BTX production or an enhancement of the coke formation, due to varying balance between Brønsted and Lewis acid sites, when compared with the metal-free zeolites (Figure 1).

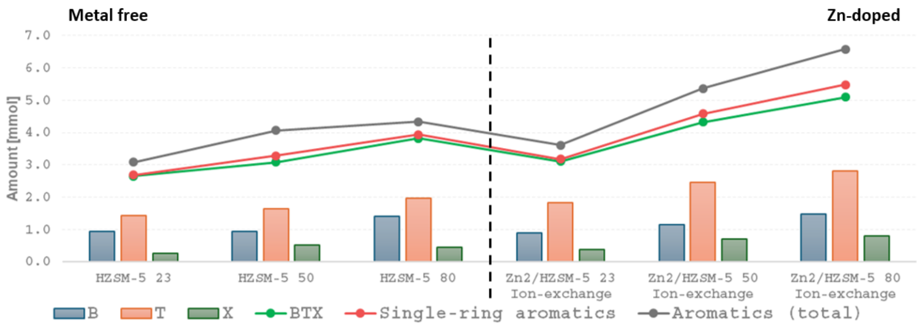

Figure 1: Comparison of aromatics formation on metal-free and zinc-doped zeolites with different SiO_2/Al_2O_3 ratios.

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[2] Gancedo et al. *ACS Sustain. Chem. Eng*. **2022**, *10*, 7752
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Characterization of zeolite catalysts for aromatization of bio-oil model compounds with operando UV/Vis diffuse reflectance spectroscopy

I. Uotila,[a] A. Arandia,[a] F. Sandri[b], X. Ye[c], B. M. Weckhuysen[c], J. Kihlman[a], J. Lehtonen[a]

[a] VTT Technical research centre of Finland, 02200 Espoo, Finland
[b] Johan Gadolin Chemistry Centre, Åbo Akademi University, Turku/Åbo, Finlandc
[c] Inorganic Chemistry and Catalysis group, Utrecht University, Utrecht, the Netherlands
e-mail: ida.m.uotila@vtt.fi

Background and motivation. There is a growing interest in the production of valuable green aromatics in a sustainable way [1]. Bio-oils can be utilized as a feedstock to produce benzene, toluene and xylenes (BTX). Insight into the aromatization surface reaction mechanism on the catalyst with operando spectroscopy methods is needed to improve the efficiency of the catalyst for bio-oil aromatization. In this work, the aromatization of bio-oil model compounds such as octane and methylcyclohexane is studied with operando UV/Vis diffuse reflectance spectroscopy (DRS), to understand the mechanisms of catalyst reaction and deactivation. The catalytic materials studied in this work are zeolite HZSM-5 with different Si/Al ratios doped with Zn or Ga, prepared with different methods such as ion-exchange, evaporation impregnation and incipient wetness impregnation. Un-doped zeolite HZSM-5:s are used as a reference/benchmark catalyst material.

Materials and methods. The characterization experiments were performed in a fixed-bed reactor with quartz-window equipped with UV/Vis AvaSpec-2048L spectrometer at temperatures of 350-500°C. During these experiments, the products were analyzed with GC-FID and UV/Vis spectra was recorded.

Results and discussion. Figure 1, shows a selection of the UV/Vis DRS data. Different bands are detected with HZSM-5 (SiO2/Al2O3=50) and (b) Zn-HZSM-5 (SiO2/Al2O3=50) zeolites at 500°C converting octane into aromatics and an increased intensity for Zn doped HZSM-5 was found to appear at ~250-350 nm, which can be assigned to alkylated aromatic reaction intermediate species [2]. More aromatic compounds are formed with the Zn doped HZSM-5 catalyst, compared to the HZSM-5 at 500°C during 1h time-onstream.

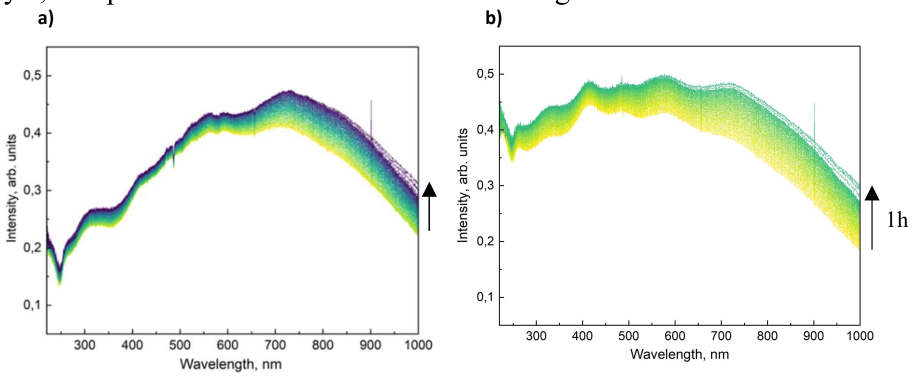

Figure 1: UV/vis absorbance spectra recorded over 1h time-on-stream converting octane at T = 500°C, WHSV = 110h^{-1} for a) HZSM-5 (SiO2/Al2O3=50) and b) Zn-ZSM-5 (Si/Al=50) catalyst prepared by ion-exchange.

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P-18

Multiple C−B Bond Cleavage Reactions at $[BAr^{F}_{4}]^{-}$ Anions Mediated by Terphenyl Phosphine Gold Catalysts

J. Miranda-Pizarro,[a,b] M. Navarro,[a,c] and J. Campos[a]

[a] Instituto de Investigaciones Químicas (IIQ), Departamento de Química Inorgánica and Centro de Innovación en Química (ORFEO−CINQA), Consejo Superior de Investigaciones Científicas (CSIC), Sevilla 41092, Spain.
[b] Present address: Department of Chemistry, University of Jyväskylä, 40500, Finland
[c] Present address: Departamento de Química Orgánica & Institute for Advanced Research in Chemical Sciences (IAdChem), Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, Madrid 28049, Spain
e-mail: jmiranda@jyu.fi

The use of weakly coordinating and low interacting counteranions has proven to be a powerful tool to access highly reactive transition metal species. Fluorinated borates, such as $[BAr^{F}_{4}]^{-}$ ($[B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4]^{-}$), occupy a prominent position due to the robustness of their C−B bonds [1]. In homogeneous gold chemistry, species of type $[LAu]^{+}$, where L is a neutral donor ligand, are considered to be the active species in the catalytic cycle, being stabilized by these weakly interacting anions. A few examples have described the activation of $[BAr^{F}_{4}]^{-}$ C−B bonds by transition metals [2], which could negatively affect their behavior in catalysis, however most of the details of such processes remain unknown. The use of bulky terphenyl phosphines (PR_2Ar', where Ar' = $C_6H_3\text{-}2,6\text{-}Ar_2$) to stabilize highly electrophilic gold intermediates, provides key information regarding the C−B bond cleavage. In addition, the stoichiometric studies have allowed us to construct a catalytic cycle for the synthesis of boranes under acidic conditions.

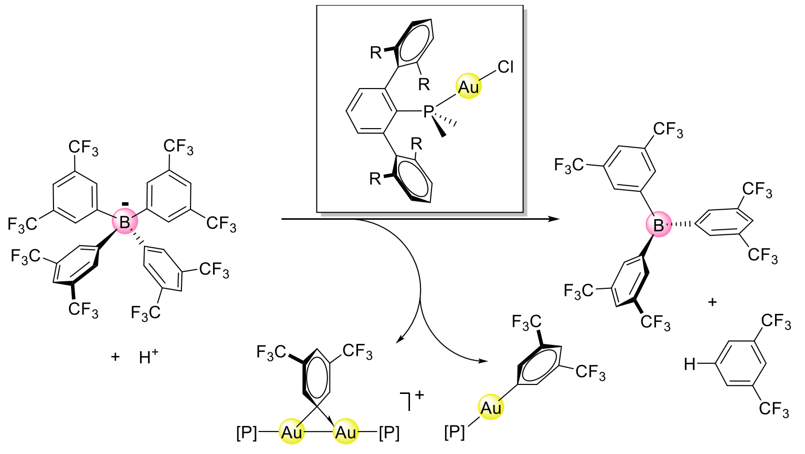

Figure 1. Schematic representation of $[BAr^{F}_{4}]^{-}$ activation with the key gold intermediates.

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List of Participants

Oral contributions

Last name	First name	Author index	Affiliation
Ahola	Jero	IS-2	LUT University
Martín-Yerga	Daniel	IS-1	Aalto University
Bilbey	Buse	CT-5	Tuni
Huerta Flores	Ali Margot	CT-6	University of Oulu
Laverdure	Laura	CT-8	Luleå tekniska universitet
Marchi	Enrico	CT-7	Åbo Akademi
Martinez Quimbayo	Jennyffer Stefania	CT-4	University of Oulu
Moradi	Kayvan	CT-1	University of Jyväskylä
Rathmann	Florian	CT-3	VTT
Schmidt	Christoph	CT-10	Åbo Akademi
Singh	Abhinash	CT-9	VTT
Yevdokimova	Olha	CT-2	Åbo Akademi

Poster contributions

Last name	First name	Author index	Affiliation
Aakko-Saksa	Päivi	P-1	VTT
Ahmadi	Sajad	P-2	University of Oulu
Araujo Barahona	German	P-3	Åbo Akademi
Baraiya	Bhumi Arunkumar	P-4	University of Jyväskylä
Chen	Kristian	P-5	VTT
Gallego Villada	Luis	P-6	Åbo Akademi
Hämäläinen	Liinu	P-7	University of Eastern Finland
Ikonen	Rasmus	P-8	University of Jyväskylä
Järvinen	Ellen	P-9	Aalto University
Kiljunen	Toni	P-10	University of Jyväskylä
Korpelin	Ville	P-11	University of Jyväskylä
Lehtinen	Veikka	P-12	VTT
Nuñez Nuñez	Ana Fernanda	P-13	Åbo Akademi
Perez Sena	Wander	P-14	Åbo Akademi
Rahman	Md Habibur	P-15	Abo Akademi
Sandri	Francesco	P-16	Åbo Akademi
Uotila	Ida	P-17	VTT
Miranda-Pizarro	Juan	P-18	University of Jyväskylä

Participants

Last name	First name	Affiliation
Adam	Ahmed	Åbo Akademi
Auvinen	Paavo	University of Eastern Finland
Biswas	Sayani	Aalto University
Capasso	Salvatore	Åbo Akademi
De Rosso	Filippo	Åbo Akademi
Di Finizio	Claudia	Åbo Akademi
Floris	Federico	Åbo Akademi University
Heikkinen	Niko	VTT
Heiskanen	Katja	VTT
Honkala	Karoliina	University of Jyväskylä
Huuhtanen	Mika	University of Oulu
Jokimies	Päivi	VTT
Kauppinen	Minttu Maria	University of Jyväskylä
Kihlman	Johanna	VTT
Kinnunen	Niko	University of Eastern Finland
Kouva	Sonja	Neste Oyj
Kumar	Narendra	Åbo Akademi
Kuutti	Krista	VTT
Latomäki	Kyösti	VTT
Lavino	Federica	Åbo Akademi
Lehtonen	Juha	VTT
Melander	Marko	University of Jyväskylä
Mishra	Shalini	University of Jyväskylä
Olatunde	Temitayo	Abo Akademi
Palo	Jasmiina	VTT
Palu	Matias	Helsinki university
Raj	Amar	University of Jyväskylä
Rawat	Kuber Singh	University of Jyväskylä
Reinikainen	Matti	VTT
Salmi	Tapio	Åbo Akademi
Sok-Sar	Yukho	VTT
Sorvillo	Eleonora	Åbo Akademi
Tolvanen	Pasi	VTT
Virkki	Niko	VTT
Vitiello	Sabrina	Åbo Akademi
Weckman	Timo	University of Jyväskylä