20th Nordic Symposium on Catalysis

3-5 June 2024, Stavanger, Norway

Program and Book of abstracts

Nordic Catalysis Society

20th Nordic Symposium on Catalysis

Catalysis for Green Transition
Catalysis in the Nordic Countries

3-5 June 2024, Stavanger, Norway

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Welcome to the 20th Nordic Symposium on Catalysis

The Norwegian Catalysis Society cordially invites you to attend the 20th Nordic Symposium on Catalysis in Stavanger Norway, 3-5 June 2024. The NSC conference series is a biennial event organized within the Nordic Catalysis Society framework. The Symposium will be organized with plenary lectures, Berzelius lecture, Nordic Keynote lectures, and parallel sessions with oral contributions as well as poster sessions. The aim of the Symposium series is to create a breeding ground for ideas by ensuring meetings between researchers and catalyst developers, from academy as well as industry.

We look forward to seeing you all in Stavanger!

Prof. Zhixin Yu,
On behalf of the organizers

Local Organising Committee

Prof. Zhixin Yu, University of Stavanger, Norway

Prof. Edd Anders Blekkan, Norwegian University of Science and Technology, Norway

Prof. Sachin Chavan, University of Stavanger, Norway

Prof. Petra Ágota Szilágyi, University of Oslo, Norway

Dr. Bjørnar Arstad, SINTEF, Norway

Dr. Ljubiša Gavrilović, Institute for Energy Technology, Norway

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Daily Program

Time	**Monday 3rd June**		
12:00-14:00	**Registration**		
14:00-14:10	**SYMPOSIUM OPENING, Room Rygekongen 1&2** **Zhixin Yu, Chair of the local organizing committee** **Sissel Knutsen Hegdal, Mayor of Stavanger**		
14:10-15:00	**Plenary 1, Room Rygekongen 1&2** **Manos Mavrikakis, University of Wisconsin at Madison** Reaction-driven formation of novel active sites on catalytic surfaces **Chair: Zhixin Yu**		
15:00-15:30	**Coffee break**		
	Catalysis for biomass and waste valorization Room: Rygekongen 1&2 Chair: De Chen	**Catalyst synthesis and characterization** Room: Rygekongen 3 Chair: Bjørnar Arstad	**Computational catalysis** Room: Axel Chair: Petra A. Szilagyi
15:30-15:50	**ORAL A-1** **Yongdan Li, Aalto University**: The dissolution and catalytic solvolysis of enzymatic hydrolysis lignin in alcohols	**ORAL B-1** **Rasmus Y. Brogaard, Topsøe A/S**: Upscaling production of tandem catalyst for single-step CO2-to-hydrocarbons conversion	**ORAL C-1** **Yuqi Yang, Chalmers University of Technology**: The Effect of Strained Ru Nanoparticles in Ammonia Synthesis Reaction
15:50-16:10	**ORAL A-2** **Albert Miró i Rovira, NTNU**: Influence of Metal Support Interaction on Product Selectivity during Anisole Hydrogenation	**ORAL B-2** **Mika Huuhtanen, University of Oulu** LOHC dehydrogenation catalyst synthesis by ball milling	**ORAL C-2** **Torstein Fjermestad, UiO**: Coupling kinetics and transport in a fixed-bed reactor from first-principles modelling
16:10-16:30	**ORAL A-3** **Tove Kristensen, Lund University**: Tuning Performance of Ni–Mo Catalysts for the HDO of Lignin Oils to Fuels	**ORAL B-3** **Jerrik Mielby, DTU**: Selective Catalysis using Metal Nanoparticles Confined in Porous Materials	**ORAL C-3** **Paulina Pršlja, Aalto University**: Machine Learning Assisted Discovery of Electroactive Catalysts
16:30-16:50	**ORAL A-4** **Aitor Arandia, VTT Research**: ZSM-5 zeolite-catalyzed aromatization of bio-oil model compounds to produce green chemicals	**ORAL B-4** **Mikkel Kock, DTU**: Unravelling a solid Mn-based catalyst for Reverse Water-Gas Shift reaction by modulation excitation	**ORAL C-4** **Matej Huš, Kemijski inštitut**: How first-principles simulations helped explain ethylene epoxidation on silver
17:00-18:00	**POSTER SESSION 1, Room Rygekongen**		
18:00-19:30	**WELCOME RECEPTION: Sverre & Mountroyal Hall**		

Time	Tuesday 4th June		
8:50-9:00	**Berzelius Prize Ceremony, Room Rygekongen 1&2**		
9:00-9:50	**Plenary 2, Berzelius Lecture, Room Rygekongen 1&2** **Chair: Hilde J. Venvik**		
9:50-10:20	**Keynote Lecture - Finland, Room Rygekongen 1&2** **Henrik Grénman, Åbo Akademi University** Process technological view on catalysis and catalyst development **Chair: Hilde J. Venvik**		
10:20-10:50	**Coffee break**		
	Catalysis for biomass and waste valorization Room: Rygekongen 1&2 Chair: Yongdan Li	**Catalyst synthesis and characterization** Room: Rygekongen 3 Chair: Sachin M. Chavan	**In-situ and operando study** Room: Axel Chair: Unni Olsbye
10:50-11:10	**ORAL A-5** **Kishore Rajendran, NTNU**: Influence of TiO2 Oxygen Vacancies on Hydrodeoxygenation and Carbon-Carbon Coupling during Beech Wood Pyrolysis Gas Upgrading	**ORAL B-5** **Ellen Järvinen, Aalto University**: Characterization of Unmodified and Zn-modified ZSM-5 Zeolites with Temperature-programmed Desorption of Ammonia and Isopropylamine – An Initial Study	**ORAL C-5** **Mariam L. Schulte, KIT**: Operando X-ray absorption spectroscopy on Cu/ZnO/ZrO2 during methanol synthesis by CO2 hydrogenation in a reactor made by additive manufacturing
11:10-11:30	**ORAL A-6** **Zhihui Li, NTNU**: Unveiling the Co-Pyrolysis Mechanisms of Biomass and Plastic Wastes for Sustainable Fuel Production	**ORAL B-6** **Simon I. Hansen, DTU**: Investigating the mechanism of the iron-catalyzed ammonia synthesis	**ORAL C-6** **Ilia Kochetygov, Paul Scherrer Institut**: In situ ATR-IR spectroscopy and fast high-energy X-ray diffraction uncover the mechanism of aqueous, room-temperature synthesis of MOF-74 catalysts
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Time	**Tuesday 4th June continued**		
13:00-13:30	**Keynote Lecture – Sweden, Room Rygekongen 1&2** **Mathilde Luneau, Chalmer University of Technology** Fundamental insight into the enhanced activity of Pd/CeO2 electrocatalysts for hydrogen oxidation in alkaline media **Chair: Juha Lehtonen**		
13:30-13:35			
	Catalysis for biomass and waste valorization Room: Rygekongen 1&2 Chair: Juha Lehtonen	**Catalyst synthesis and characterization** Room: Rygekongen 3 Chair: Anker Degn Jensen	**Methane and methanol conversion** Room: Axel Chair: Henrik Grénman
13:35-13:55	**ORAL A-8** **Yushuai Sang, Aalto University**: The reaction pathways of catalytic solvolysis of enzymatic hydrolysis lignin with Ni catalyst	**ORAL B-8** **Shivangi Singh, Chalmers University of Technology**: Effect of copper on the hydrothermal stability of Cu-CHA	**ORAL C-8** **Youri van Valen, NTNU**: Silver Catalysed Partial Oxidation of Methanol to Formaldehyde and its Sub-reactions
13:55-14:15	**ORAL A-9** **Mariana M. Campos Fraga, KIT**: Sugarcane residues for bio-fuel production: catalytic hydrodeoxygenation of sugarcane bagasse and sugarcane straw fast-pyrolysis oils	**ORAL B-9** **Emil Kowalewski, DTU**: Probing the reactive intermediates in catalytic CO2 hydrogenation with Ni/Al2O3 catalysts by Modulation Excitation Spectroscopy	**ORAL C-9** **Florian Rathmann, VTT Research**: Effect of lanthanum and zinc as ceria dopants for the synthesis of dimethyl carbonate from methanol and carbon dioxide
14:15-14:35	**ORAL A-10** **Paresh S. Butolia, University of Groningen**: Catalytic conversion of lower olefins to BTX range of aromatics using zeolite-based catalysts	**ORAL B-10** **Danial Farooq, University College London**: Chemical imaging of Carbide formation and its effect on Alcohol selectivity in Fischer Tropsch Synthesis on Mn-doped Co/TiO2 pellets	**ORAL C-10** **Gordon Zhuo, DTU**: Preventing Deactivation during Dry-Reforming of Methane
14:35-14:55	**ORAL A-11** **Petter Tingelstad, NTNU**: Conversion of acetic acid over metal deposited TiO2 catalysts	**ORAL B-11** **Vladyslav Shostak, UiO**: Avoiding reactions to quantify diffusion of alkenes in zeolites: a new benchmark set by Temporal Analysis of Products (TAP)	**ORAL C-11** **Peter Njoroge, UiO**: Tuning the amount of Aluminum pairs in the Mordenite Zeolite to improve Oxidation of Methane to Methanol
14:55-15:30	**Coffee break**		

Time	Tuesday 4th June continued		
	CO2 conversion and utilization Room: Rygekongen 1&2 Chair: Richard H. Heyn	**Environmental catalysis** Room: Rygekongen 3 Chair: Kim Daasbjerg	**Hydrotreating** Room: Axel Chair: Søren Kegnæs
15:30-15:50	**ORAL A-12** **Elif Tezela, UiO**: UiO-67(Zr)/Pd(Zn) composite catalysts for CO2 hydrogenation to methanol	**ORAL B-12** **S. Mossin, DTU**: Understanding Water-Induced Deactivation of Palladium Based Methane Oxidation Catalysts	**ORAL C-12** **Jacob Venuti Björkman, KTH**: Evaluating hydrotreating catalysts for dynamic operations
15:50-16:10	**ORAL A-13** **Jakob Munkholt Christensen, DTU**: Influence of pre-treatment on the support effect in catalytic methanol synthesis	**ORAL B-13** **Vasco A. C. Saltão, University of Turin**: Effect of hydrothermal aging on Cu-CHA catalysts for NH3-SCR	**ORAL C-13** **Tiina Laitinen, University of Oulu**: Activity of vanadia based catalysts in methanol and methanethiol dehydrogenation
16:10-16:30	**ORAL A-14** **Elżbieta Truszkiewicz, Warsaw University of Technology**: Catalytic CO2 methanation over modified carbon–supported Ruthenium: The influence of the support type on the properties and activity of the catalyst	**ORAL B-14** **Miia Kokkonen, University of Oulu**: Na-jarosite based catalysts for water treatment applications	**ORAL C-14** **Joakim Kattelus, Aalto University**: Hydrodeoxygenation and hydrodenitrogenation of n-hexadecanamide with NiMo sulfide catalysts
16:30-16:50	**ORAL A-15** **Lorena Baumgarten, KIT**: Identifying the Active Species in Ga-promoted Cu Catalysts for CO2-Hydrogenation	**ORAL B-15** **Teuvo Maunula, Dinex A/S**: Catalytic aftertreatment systems for combustion exhaust gases from hydrogen, ammonia and e-HC engines	**ORAL C-15** **Naiara C. Telis, KIT**: Scalability and Performance of Niobium Pellet Catalysts in HDO Reactions
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Time	Wednesday 5th June		
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9:50-10:20	**Keynote Lecture - Denmark, Room Rygekongen 1&2** **Kim Daasbjerg, Aarhus University** Advancements in the Electroreduction of Carbon Dioxide using Manganese Bipyridine Complexes and Single-Atom Catalysts **Chair: Edd Anders Blekkan**		
10:20-10:50	**Coffee break**		
	Electro/photocatalysis Room: Rygekongen 1&2 Chair: Sara Bloomberg	**Homogeneous catalysis** Room: Rygekongen 3 Chair: Anders Riisager	**Computational catalysis** Room: Axel Chair: Ljubisa Gavrilovic
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11:10-11:30	**ORAL A-17** **Neethu Kochukunnel Varghese, University of Genoa**: Electrochemical characterization of NiFe nanoparticles on colloidal CeO2 for Anion Exchange Membrane Electrolysers	**ORAL B-17** **M. Abu Rasheed, UiO**: Homogeneous catalytic peroxidation of cyclohexane over Cu-N,N,N,N complexes: Mechanistic insight by copper intermediates characterization	**ORAL C-17** **Joachim D. Bjerregaard, Chalmers University of Technology**: Effect of Aluminum Distribution on the Diffusion and Pairing of [Cu(NH3)2]+ Complexes in Cu-CHA
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11:50-12:10	**ORAL A-19** **Ingeborg-Helene Svenum, SINTEF Industry**: Operando AP-XPS investigations of Ta3N5-based electrodes during photoelectrochemical water splitting	**ORAL B-19** **Véronique Dufaud, University of Lyon**: Carbonatation of ethylene - glycidyl methacrylate based polymers using carbon dioxide as reagent: from batch to reactive extrusion	**ORAL C-19** **Nawras Abidi, IFPEN**: Unveiling closed and open site stability of Sn-, Ti-, Hf-, and Zr-Beta zeolites: A DFT investigation for biomass sugar conversion
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Time	**Wednesday 5th June continued**		
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13:35-13:55	**ORAL A-20** **Prabin DHAKAL, Chalmers University of Technology**: Depolymerization of nylon-6 over supported ruthenium catalyst to ε-caprolactam	**ORAL B-20** **Michael T. Nikolajsen, DTU**: Direct syngas to light olefins using supported ZnO and acidic CHA catalysts	**ORAL C-20** **Sam Taylor, Lund University**: In situ AP-XPS in a Plasma Environment
13:55-13:15	**ORAL A-21** **Moritz Böhme, DTU**: Catalytic upgrading of fast pyrolysis oils of biomass and residual waste with calcium-based catalysts towards alternative fuels for marine engines	**ORAL B-21** **Laura Keskiväli, VTT Research**: Highly selective production of isobutene from syngas – Isosynthesis over zirconia	**ORAL C-21** **Izar Capel Berdiell, UiO**: Exploring ZSM-5/alumina Shaped Objects with X-ray Diffraction Computed Tomography after Methanol-to-Hydrocarbons reaction
14:15-14:35	**ORAL A-22** **Derek Creaser, Chalmers University of Technology:** Catalytic Reductive Liquefaction of Bark into Biofuel using Ni-based Catalysts: Char Formation Prevention Strategies	**ORAL B-22** **Zouhair El Assal, University of Oulu**: Effect of the support and active phase loading in the production of H2 and high-quality carbon in the thermocatalytic decomposition (TCD) of methane	**ORAL C-22** **Morsal Babayan, University of Oulu**: Low-pressure, isomer-selective kinetic characterization using PEPICO
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Poster-3	**Nora Corneliussen, NTNU**: Bimetallic catalysts for catalytic upgrading of biomass pyrolysis vapors
Poster-4	**Ana Oberlintner, National Institute of Chemistry**: Acetylation of Cellulose Nanomaterials: Ab Initio Mechanisms, Reaction Microkinetics, and Experimental Structural Insights
Poster-5	**Aqsa Noreen, Chalmers University of Technology**: Pentaerythritol synthesis through a heterogeneous catalysis route
Poster-6	**Agnieszka Seremak, UiO**: Flexibility of MFI zeolite upon adsorption of guest species: DFT study
Poster-7	**Joanna Pierchala, SINTEF Industry**: Production of C3 hydrocarbon from GaInOx with addition of SAPO-34
Poster-8	**Guido de Reijer, Chalmers University of Technology**: Modified Zeolites for Catalytic Valorisation of Furans to Aromatics
Poster-9	**Amalie Paarup Krebs, DTU**: Investigating Stabilization – A Model Compound Study of Catalytic Stabilization of Pyrolysis Bio-Oi
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Poster-11	**Sašo Gyergyek, Jožef Stefan Institute**: Dynamically responsive ammonia cracking for H2 release utilizing magnetically-heated catalyst
Poster-12	**Dimitra Iltsiou, DTU**: Design of Cu-zeolites for the selective hydrogenation of CO2
Poster-13	**Rishav Chand, DTU**: Catalytic Reduction of N2O by NH3+NO over Fe-CHA, -BEA and -FER catalysts
Poster-14	**Alvaro Posada-Borbon, Chalmers University of Technology**: Exploration of Liquid Organic Hydrogen Carriers using First-Principles Calculations: Dehydrogenation of methylcyclohexane on Pt(111) and Pd(111)
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Poster-16	**Sajad Ahmadi, University of Oulu**: Bismuth-rich photocatalysts for the removal of paracetamol
Poster-17	**Velma Beri Kimbi Yaah, University of Granada**: One-pot hydrothermal synthesis of tungsten-based photocatalysts for the photocatalytic degradation of 5-Fluoruoacil under solar-LED

Poster-18	**Paavo Auvinen, University of Eastern Finland**: Ni/Al2O3 catalyst for efficient debromination of brominated flame retardants from water phase
Poster-19	**Eerika Olkkonen, University of Eastern Finland**: Exploring the reaction network in the catalytic debromination of tetrabromobisphenol A
Poster-20	**Jie Wang, DTU**: CO2 Hydrogenation using Mn-based Catalysts
Poster-21	**Sahra Ahmed, UiO**: Towards a MOF-based Single-Atom Catalyst: Investigating the Effects of Immobilized Pd Single Atoms in UiO-66
Poster-22	**Aitor Arandia, VTT Technical Research Centre of Finland**: Preparation of bimetallic nickel-palladium catalysts on various supports for an efficient hydrotreatment of waste plastic pyrolysis oil
Poster-23	**Claudia Fabris, UiO**: Modification of zeolite Y for the upcycling of polypropylene waste: A systematic study
Poster-24	**Alexander Søgaard, DTU**: Advanced reactor designs for continuous pyrolysis oil conversion into renewable hydrocarbon fuels through hydrodeoxygenation catalysis
Poster-25	**Olha Yevdokimova, Åbo Akademi University**: Aldol Condensation of Cyclopentanone and Furfural on Different Metal Organic Frameworks for Synthesis of Jet-Fuels from Renewable Biomass

Number	**Tuesday 4th June**
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Poster-27	**Anders Riisager, DTU**: Optimizing the Catalytic Production of Jet Fuel Intermediates from CO2 fermentation derived oxygenates
Poster-28	**Alicia San Martin Rueda, NTNU**: Surface analysis of LSCF perovskite anodes for solid oxide ammonia-fuel cells
Poster-29	**Zhihui Li, NTNU**: Co-pyrolysis of biomass and plastic to produce high quality liquid yield
Poster-30	**Pol Fernandez Reixach, KTH**: The impact of Cu addition on Ni-catalysts for the dehydrogenation of Liquid Organic Hydrogen Carriers
Poster-31	**Alen Rupnik, National Institute of Chemistry**: Application of Box-Behnken Design for Enhanced HCl Electrolysis
Poster-32	**Jerrik Mielby, DTU**: CO2 Conversion over Zeolite-Encapsulated Ni Nanoparticles
Poster-33	**Jonas Elmroth Nordlander, Lund University**: In situ AP-XPS reduction study of engineered NiMoO4 nanoparticles
Poster-34	**Filip Hallböök, Lund University**: In-situ reduction study of Pd-NiMo and Ru-NiMo catalysts using AP-XPS
Poster-35	**Rafael Cortez Sgroi Pupo, UiO**: Bioinspired Cu(I) MOFs for C-H activation
Poster-36	**Tuba Iftikhar, UiB**: Metallosalen tethered Polyoxometalates: Potential candidates for CO2/epoxide copolymerization
Poster-37	**Lucy Idowu Ajakaiye Jensen, Lund University**: Oxidative Depolymerization of Hardwood Lignin into Valuable Aromatics
Poster-38	**Song Lu, UiS**: Atomically dispersed Fe-Cu dual-sites on carbon black for efficient electroreduction of CO2 to CO
Poster-39	**Maria Soledad Chino Mamani, KTH**: Effect of impurities on catalytic dehydrogenation of ethanol to acetaldehyde

Poster-40	**Jon Selimi, Lund University**: Further enhancement of hydrodeoxygenated lipid oil by isomerization
Poster-41	**Simmy Rathod, UiS**: Introducing Brønsted Acidity via Sulfonic Acid Functionalization in Zr Metal-Organic Framework
Poster-42	**Ronald Mauricio Lara Prado, KTH**: Hydrodeoxygenation of Pyrolysis Oils - A Catalytic Approach for Rural Areas Sustainability
Poster-43	**Gen Li, Aalto University**: Insights into the Hydrodeoxygenation (HDO) Reaction Mechanism of Guaiacol on Ni2P Catalyst Surface: A Combined Study of Density Functional Theory (DFT) Simulation and Experimental Investigations
Poster-44	**Tor S. Haugland, SINTEF Industry**: First-principles investigation of CO adsorption on a PdAg surface
Poster-45	**Sahra Louise Guldahl-Ibouder, NTNU**: Catalytic low temperature ammonia decomposition for COx free hydrogen production
Poster-46	**Anders Riisager, DTU**: New strategies to develop low-temperature Mn-based NH3-SCR catalysts with improved water and SO2 tolerance
Poster-47	**Ljubisa Gavrilovic, IFE**: Further insights on the effect of potassium on cobalt-based Fischer-Tropsch catalysts
Poster-48	**S. S. Kazi, IFE**: Nickel alumina-based catalyst for sorption enhanced reforming - Effect of calcination temperature
Poster-49	**Thomas Krøier Rønne-Nielsen, DTU**: In-situ EPR study of the effect of sulfur poisoning and regeneration on Cu-CHA catalysts
Poster-50	**Song Lu, UiS**: Atomically dispersed Fe-Cu dual-sites on carbon black for efficient electroreduction of CO2 to CO

Abstracts: Plenary presentations

Reaction-driven formation of novel active sites on catalytic surfaces

Manos Mavrikakis

Department of Chemical & Biological Engineering

University of Wisconsin-Madison

Madison, WI 53706

USA

Adsorption of reactants and reaction intermediates on solid catalytic surfaces can lead to significant changes of the surface structure, including, as shown in high-pressure Scanning Tunneling Microscopy (STM) experiments, ejection of metal atoms and formation of metal clusters while the reaction is taking place. Depending on the specific system, these clusters provide new, more favorable reaction paths than the typically considered active sites. In this talk, we will attempt to provide a more realistic picture of the catalyst's surface and its active sites as a function of reaction conditions and the identity of reactants and that of key intermediates. Insights derived from our analysis can inform the design of new catalysts with improved activity, selectivity, and stability characteristics.

PLEANRY LECTURE 2

Design and Construction of Catalytic Systems for Selective Transformation of C1 to C2 Molecules

Ye Wang

State Key Laboratory of Physical Chemistry of Solid Surfaces, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China
E-mail: wangye@xmu.edu.cn

Selective transformations of C1 molecules (including CO, CO_2, CH_4 and CH_3OH), which are abundant and cheap carbon feedstocks, into C2 compounds (e.g., C_2H_4, C_2H_5OH, CH_3COOH and ethylene glycol), key building blocks in the chemical industry, are highly attractive, but the selectivity control is quite challenging because these transformations usually have multiple intermediates and reaction channels that may lead to various side-reactions. The traditional method for the design of heterogeneous catalysts by optimizing the active phase/site, promoters and support becomes difficult for control of these reactions. Here, I demonstrate that the relay catalysis is a useful methodology to control the selectivity for such transformations with complicated networks. The new systems developed by the relay-catalysis method for highly selective conversion of syngas (hydrogenation of CO) to lower olefins, acetic acid and ethanol *via* methanol intermediate will be presented.[1-4] Our studies on the electrocatalytic reduction of CO_2 to C_2H_4 and C_2H_5OH as well as the photocatalytic transformations of CH_4 and CH_3OH to C_2H_6 and ethylene glycol, respectively,[5-8] will also be briefly introduced to show the potentials of electro- and photo-catalysis in selectivity control for C1 to C2 transformations.

References

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Abstracts: Keynote lectures

Process technological view on catalysis and catalyst development

Henrik Grénman
Henriksgatan 2, 20500, Turku/Åbo, Finland

The current work presents case examples from our recent research where the starting point in the catalyst development or utilization has been based on a process technological approach. The last example discusses the influence of catalysis on a non-catalytic process and its consequences on the overall process development and intensification.

The economy of synthetic natural gas production for energy carrier purposes, i.e., the Sabatier reaction, suffers from unfavorable thermodynamics in the typical operating temperatures of around 400°C-450°C. Moreover, the purity requirements of the product are typically very high, which necessitates high conversion and selectivity to avoid the costs of purification. Both low-temperature catalyst activity and equilibrium shift are required to overcome the challenges, and combining both properties in the same material is one of the promising options from a process technological point of view[1,2].

Hemicelluloses processing to valuable sugar acids or alcohols is essential in the overall economic development of many modern biorefinery concepts; however, the number of process steps should be minimized for efficiency, and on the other hand, renewable hydrogen supply can be an issue. One example describes an integrated process for the production of sugar alcohol directly from industrially based hemicellulose feedstock, in which the operational temperature window determines the requirements of the catalysts.[3] Direct electrocatalytic valorization of sugars also presents an interesting opportunity for overall process intensification.[4,5]

The last case example focuses on the influence of the water-gas and reverse water-gas shift reactions on a non-catalytic large-scale process, namely the production of sustainable steel.[6]

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Palladium supported on ceria (Pd/CeO2) has recently raised strong interest as an alternative catalyst to platinum on the anode electrode in anion exchange membrane fuel cells.

Mathilde Luneau

Chalmers University of Technology

In this work, we provide new insight into the enhanced activity of Pd/CeO2 in hydrogen oxidation reaction (HOR) in alkaline media. Using well-defined model thin films, we show that Pd/CeO2 thin films lead to enhanced activity in HOR compared to pure Pd thin films. In situ characterization using electrochemical quartz crystal microbalance provide in-depth understanding of the role of CeO2. CeO2 leads to fundamental differences in adsorption and absorption of key reaction intermediates during HOR. In combination with characterization and theoretical calculations, Pd atoms embedded in CeO2 are shown to be present on the prepared thin films and active for hydrogen activation but are not able to bind CO during CO-stripping characterization. Finally, an estimation of the source of hydroxyl intermediates provided by CeO2 - which could be directly participating in the reaction - is presented.

This work indicates that the interface between Pd and ceria must be carefully designed to provide synergies and to lead to enhanced reactivity. Fundamental understanding of the Pd-CeO2 interface in HOR opens new ways to reduce the amount of noble metals in alkaline fuel cells.

KEYNOTE LECTURE - DENMARK

Advancements in the Electroreduction of Carbon Dioxide using Manganese Bipyridine Complexes and Single-Atom Catalysts

Kim Daasbjerg

Novo Nordisk Foundations (NNF) CO_2 Research Center, Aarhus University, Gustav Wieds Vej 10, 8000 Aarhus C, Denmark

The electroreduction of carbon dioxide (CO_2) via electrocatalysis presents a promising strategy for harnessing CO_2 as a feedstock in the chemical industry. However, effectively controlling the selectivity for different CO_2 reduction products remains a challenge. In this study, we disclose a series of manganese complexes featuring bipyridine ligands, showcasing the ability to selectively reduce CO_2 to either formic acid (HCOOH) when strategically positioned tertiary amines are incorporated into the ligand structure, or carbon monoxide (CO) when amine groups are absent or positioned distantly from the metal center.[1-6] The amine-modified complexes emerge as highly active catalysts, demonstrating exceptional efficiency even at overpotentials as low as 300 mV. Mechanistically, the formation of a Mn-hydride species facilitated by in-situ protonated amine groups is identified as a crucial intermediate, elucidated through cyclic voltammetry, infrared spectroelectrochemistry, and theoretical calculations.

Another compelling material for CO_2 reduction is the single-atom catalyst (SAC). Our investigation focuses on nitrogen-stabilized SACs containing low-valence zinc or indium atoms within a carbonaceous network (M-NC; M = Zn or In). These catalysts feature saturated four-coordinate ($M\text{-}N_4$) and unsaturated three-coordinate ($M\text{-}N_3$) sites, with the latter metal center adopting a low-valence state.[7,8] Both metal-based materials exhibit remarkable electrocatalytic activity in reducing CO_2 to CO with near-unity selectivity in water, achieving an impressively low overpotential of 310 mV. When employed in a flow-cell setup, the SACs enable the attainment of a current density of up to $1\ \mathrm{A\ cm^{-2}}$ with a CO selectivity exceeding 95 %. Computational analyses suggest that the unsaturated $M\text{-}N_3$ sites play a pivotal role in lowering the energy barrier by stabilizing the COOH* intermediate. This study not only provides insights into the intricate relationship among coordination number, valence state, and catalytic performance but also demonstrates the potential for achieving high current densities relevant to industrial applications.

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Design, Integration and Catalytic Performance of Functional Single Cu-Sites in Metal-Organic Frameworks for Ambient C-H Activation.

Barbara Centrella, Valeria Finelli, Erlend Aunan, Rafael Cortez Sgroi Pupo, Beatrice Garetto, Mouhammad Abu Rasheed, Ning Cao, Alessandro Damin, Ainara Nova Flores, Matteo Signorile, Matteo Bonomo, Elisa Borfecchia, Silvia Bordiga, Unni Olsbye, Claudia Barolo, Petra Ágota Szilágyi

This presentation will showcase some of our latest results within the ERC Synergy CuBE project. (1) Informed by the class of lytic polysaccharide monooxygenases (otherwise known as LPMO) enzymes (2), capable of activating C-H bonds under ambient conditions, we have designed copper complexes displaying controllable redox bistability with demonstrated catalytic activity. Through adequate functionalisation, the complexes were integrated into the UiO topology, specifically both into the Zr (3) and Ce (4) varieties, and the heterogenised Cu-moieties have been tested in different conditions in order to optimise both conversion and selectivity. Importantly, they were found to be catalytically active in the liquid-phase C-H activation under ambient conditions (as were their homogeneous counterparts).

I will present the multi-technique advanced chemical and structural characterisation of the above-described functional MOFs and rationalise their catalytic performance in terms of the local structure. Importantly, the effect of the MOF framework, defective sites, and node chemistry will also be discussed.

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Abstracts: Oral Presentations

ORAL A-1

The dissolution and catalytic solvolysis of enzymatic hydrolysis lignin in alcohols

Yongdan Li , Yushuai Sang
Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Finland

Lignocellulose, the natural composite of cellulose, hemicellulose and lignin, is the most abundant form of biomass. Different from cellulose and hemicellulose, lignin is composed of aromatic units. Nowadays, cellulose and hemicellulose are fully utilized in pulping and the second-generation (2G) bioethanol industries. The 2G biofuel industry produces enzymatic hydrolysis lignin (EHL) as a low-value and large volume byproduct. As a renewable resource of aromatic molecules, EHL is an ideal feedstock for the sustainable production of industrial aromatic chemicals and fuels. Catalytic solvolysis of EHL is a promising method for EHL utilization, which achieves complete EHL liquefaction and high monomer yield. In our previous work, EHL was depolymerized with various catalysts, including unsupported Ni, Ni-Mo alloy, WO_3/Al_2O_3 and MoS_2 catalysts in ethanol, and all these catalysts achieve complete EHL liquefaction and high yield of alkylphenols[1].

Herein, EHL dissolution and catalytic solvolysis in alcohols were investigated. Ethylene glycol shows high EHL solubility and achieves complete EHL dissolution at room temperature, while methanol only dissolves part of EHL with high content of hydroxyls and β-O-4 linkages. The Gaussian simulation results indicate that ethylene glycol forms strong Van Der Waals interactions with EHL, including C-H··· O and lone pair··· π interactions, and these interactions break original π-π stacking in EHL, achieving complete EHL dissolution. The dissolution and solvolysis of EHL in monohydric alcohols, including methanol, ethanol, and isopropanol were enhanced with addition of water. In isopropanol-H_2O (3:2), 2 g of EHL was completely liquefied in 50 mL solvent at 250 ^{o}C without char formation. The roles of isopropanol and H_2O in EHL liquefaction involving their interactions with EHL at a molecular level were investigated. In isopropanol-H_2O (3:2), H_2O disrupts the intra- and inter-molecular hydrogen bonds in EHL, and isopropanol breaks π-π stacking interactions between benzene rings in EHL. Additionally, H_2O enhances EHL depolymerization, and isopropanol acts as a hydrogen donor solvent, leading to the stabilization of active intermediates. The resulting liquid phase product was further upgraded in the presence of Raney Ni at 320 ^{o}C, with isopropanol-H_2O reforming providing active hydrogens.

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ORAL A-2

Influence of Metal Support Interaction on Product Selectivity during Anisole Hydrogenation

Albert Miró i Rovira[1], Jørgen Skjæveland[1], Kishore Rajendran[1], Rune Myrstad[2],
De Chen[1]
[1]Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway
[2]Kinetics and Catalysis Group, SINTEF Industry, NO-7465 Trondheim, Norway

Fast catalytic hydropyrolysis (FCHP) of biomass shows potential for renewable liquid fuel production in transportation. However, pyrolysis oil's oxygen-rich compounds, mainly phenyls and ketones[1], require removal to enhance fuel quality. This involves an upgrading process where hydrogen is added to pyrolysis oil under pressure to break C-O bonds, producing hydrocarbons and water[2]. This study focuses on how metal-metal oxide interactions affect activity and product selectivity.

To understand the interaction between metal and support several metal-based catalysts on titania and silica supports were prepared and tested for catalytic performance in the anisole hydrogenation reaction. Various metals (Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, and Ag) were incorporated in the two supports by incipient wetness impregnation. Catalytic testing was conducted in a fixed-bed reactor at 350°C and 5 bar hydrogen partial pressure. Product analysis was done using GC-MS and GC-FID techniques.

The primary reaction pathways for anisole hydrogenation were identified as demethoxylation to benzene, demethylation to phenol, and methyl transfer to methyl-cresol as shown in Figure 1. Table 1 shows the selectivity of TiO_2-based catalysts for this system, further testing with SiO_2-based catalysts will be carried out to assess the effect of metal-support interactions on product selectivity.

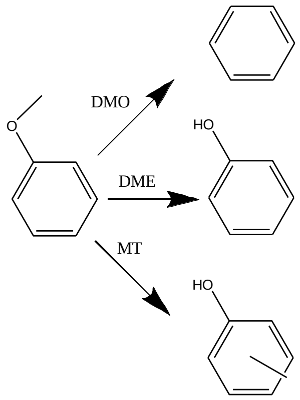
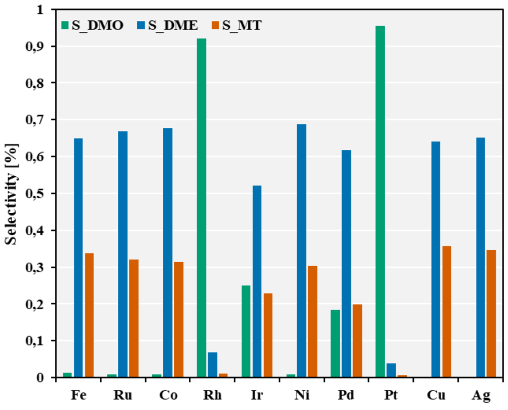


Figure 1. Schematic of the mechanism for the conversion of anisole

Table 1. The selectivity of the different TiO_2-based catalysts tested normalized.



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ORAL A-3

Tuning Performance of Ni–Mo Catalysts for the HDO of Lignin Oils to Fuels

Tove Kristensen[1,2,*], Christian Hulteberg[1,2], Filip Hallböök[1], Jonas Elmroth Nordlander[1], Jon Selimi[1,2], Omar Abdelaziz[3], Sara Blomberg[1]

[1]Division of Chemical Engineering, Department of Process and Life Science Engineering, Lund University, SE-221 00 Lund, Sweden
[2]Hulteberg Chemistry & Engineering AB, SE-212 25 Malmö, Sweden
[3]Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

The addition of La and Ce to Al_2O_3 has been demonstrated to be a beneficial tailoring approach to optimize textural properties, surface characteristics, and to further enhance the performance of Ni–Mo catalyst in the HDO of lignin oils to fuels. The development of catalysts with prolonged and enhanced activity is a crucial aspect of improving the performance and adding environmental value to the industrial hydrotreatment upgrading of lignin-based oils.[1,2]

In the present study, tuning possibilities of surface properties of the support are investigated, by impregnating La and Ce either simultaneously or in separate, subsequent steps. The La and Ce loadings were varied between 0–5 wt%, whereas the Ni and Mo loadings were 3.5 wt% and 8 wt%, respectively, for all catalysts. Several characterization techniques (physisorption, X–ray diffraction, chemisorption, temperature programmed desorption and reduction, and elemental analysis) are used to correlate the support and/or catalyst properties with activity experiments.

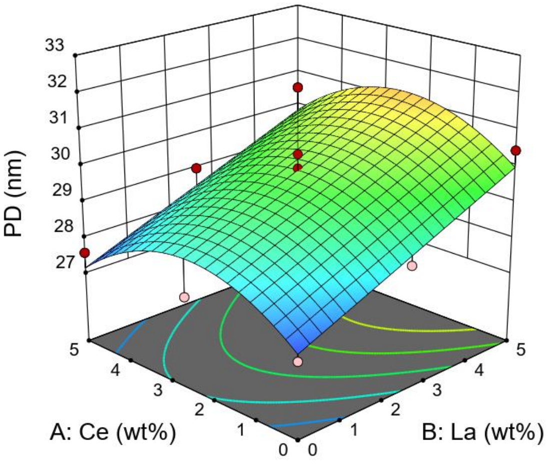

***Figure 1**. Three-dimensional response surface plot for pore diameter (PD) as a function of the Ce and La loadings.*

Our results demonstrate that depending on the impregnation approach, surface area and pore diameter of such support can be tailored differently. The La loading is found to be the dominant factor affecting the resulting pore diameter, whereas the Ce loading affects the surface characteristics. This approach enables minimizing diffusion limitations, carbon polymerization, and prevent short-term deactivation.

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ORAL A-4

Preparation of bimetallic nickel-palladium catalysts on various supports for an efficient hydrotreatment of waste plastic pyrolysis oil

Aitor Arandia, Farah Siddiq, Taina Ohra-aho, Juha Lehtonen
VTT Technical Research Centre of Finland Ltd. P.O. Box 1000, FI-02044 Espoo, Finland

The catalytic hydrotreatment (HT) is a primary alternative for the upgrading of plastic waste pyrolysis oils (PPOs).[1,2] Significant amounts of chlorine (Cl), bromine (Br), heteroatoms (O, N), and olefinic/aromatic compounds are typically present in the oil and must be reduced to comply with e.g. steam cracker feed specifications: aromatics < 3-10 wt%, olefins < 2wt%, O, N < 100 ppm, Cl < 3 ppm.[2] Heterogeneous catalysts with metals such as, Ni, Co, Fe, and noble metals (Pd, Pt, Ru) supported on medium/low acidic supports (carbon, SiO_2 or Al_2O_3) are expected to adequate the composition.[3] We have synthesized Ni-Pd bimetallic catalysts on various supports, and tested them in the HT of PPOs in a continuous trickle-bed reactor. These results are part of the integration of the chemical recycling of plastic waste in the existing infrastructure and value chains.

Nickel (10 wt%) and palladium (1wt%) were co-impregnated on Al_2O_3, TiO_2, SiO_2, SiO_2-Al_2O_3, and activated carbon (AC) via the vacuum incipient wetness impregnation method. A commercial Pd/AC catalyst (5 wt% Pd, supplied by Ranido) was used as a benchmark catalyst. The catalysts were tested in a continuous system at 350 °C, 50 bar H_2, H_2(l/h)/feed(g/h) ratio = 0,5, WHSV = 3 h^{-1} and 6 h time-on-stream (TOS). The PPO used in this study was supplied by Valmet Technologies Oy and was made from waste LDPE/LLDPE plastic.

The composition (left-axis) and O content (right-axis) of the liquid phase are shown in Fig 1. The composition of the oil is included for reference. The results after 6 h TOS revealed a complete saturation of olefins and n-dienes to n-alkanes and a significant HDO activity, especially the commercial Ru/AC. The content of aromatics remained practically unchanged. Cl was reduced under 5 ppm (analyzer detection limit) with all catalysts and the Br number was reduced by 10 times with all self-made catalysts. No evidence of deactivation was observed after 6 h TOS. Therefore, stability runs with the best catalyst(s) and the characterization of the spent samples is also part of this research.

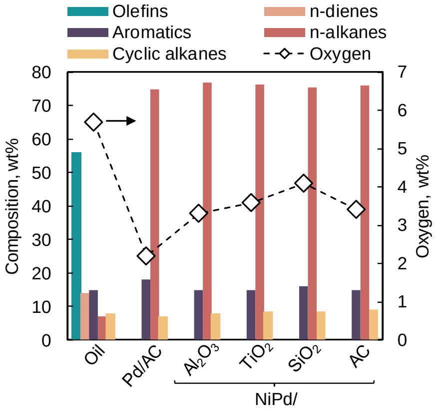

Fig 1. Liquid phase composition and O content of the oil and after the hydrotreatment of PPO with various catalysts. The experimental conditions are described along the text.

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Influence of TiO_2 Oxygen Vacancies on Hydrodeoxygenation and Carbon-Carbon Coupling during Beech Wood Pyrolysis Gas Upgrading

Kishore Rajendran[1], Ajaikumar Samikannu[2], Dipika Kanchan[3], Albert Miró i Rovira[1], Zhihui Li[1], Petter Tingelstad[1], Jyri-Pekka Mikkola[2], Arghya Banerjee[3], De Chen[1*]

[1]*Dep. of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway*

[2]*Technical Chemistry, Department of Chemistry, Chemical-Biological Centre, Umeå University, SE-901 87, Umeå, Sweden*

[3]*Department of Chemical Engineering, Indian Institute of Technology, Ropar, Punjab 140001, India*

Biomass pyrolysis vapors are composed of approximately 30-50% short-chain oxygenates (C_1-C_5 aldehydes, ketones, and acids), 30-40% phenolic derivatives, and 10-40% other oxygenated species like furanics and dehydrated sugars [1][2]. In this context, reducible TiO_2 has been utilized as a catalyst support for biomass upgrading processes such as hydrodeoxygenation (HDO) and Carbon-Carbon (C-C) coupling reactions (including ketonization and aldol condensation), where the metal cations and oxygen anions serve as active sites [3][4]. Altering the metal oxide's reduction state can modify its acid-base properties, yet the effects of oxygen vacancy coverage on TiO_2 during actual biomass vapor upgrading remain unclear. This study investigates the dynamics between C-C coupling and HDO reactions in the ex-situ upgrading of beech wood pyrolysis vapors at 600°C and 1 bar using TiO_2. It was found that varying degrees of oxygen vacancy coverage influenced the strength of TiO2's active sites. The modified TiO_2 were analysed using a range of techniques including BET, XRD, NH_3-TPD, CO_2-TPD, H_2-TPR, Raman, UV-vis, SEM, EDX, and FTIR. A reaction network was developed from these experimental observations, examining how the reaction pathways depend on the oxygen vacancies. The study revealed that oxygen vacancies generally enhance both C-C coupling and HDO reactions, but there is an optimal concentration of oxygen vacancies for maximum efficiency. Density Functional Theory (DFT) studies on the 101 plane of TiO_2 corroborated the experimental findings.

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ORAL A-6

Co-pyrolysis of biomass and plastic to produce high-quality liquid

Zhihui Li[1], Kishore Rajendran[1], Kjell Moljord[1,2], Geir Remo Fredriksen[2], De Chen[1]*
[1]Norwegian University of Science and Technology (NTNU), Trondheim, Norway
[2]Equinor, Arkitekt Ebbells veg 10, Ranheim, Norway

Biooil is a kind of renewable fuel instead of conventional fossil fuels. However, the high oxygen content (~50wt%) of bio-oil which comes from the oxygen-rich species in lignocellulose biomass inhibits its wide application. In this project, instead of the traditional hydrodeoxygenation method which is by feeding external H_2 during the pyrolysis of biomass, plastic was chosen as the hydrogen donor to achieve in-situ oxygen removal. In addition, modified natural clay, a relatively cheap material was applied as an in-situ catalyst during pyrolysis. The modified clay has shown weak to medium acidity strength and rich amount of acid sites.

The experiment was carried out in a semi-batch reactor, the catalyst and feedstocks were pre-mixed, to achieve in-situ catalytic co-pyrolysis. The mixture was injected into the preheated reactor as the reaction started, N_2 was performed as the carrier gas of 40 ml/min during the pyrolysis. In the co-pyrolysis of beechwood and LDPE (1:1), within 25 minutes, high liquid yield (85wt%) and oil with low oxygen content (7wt%) were achieved, oxygen was effectively removed. In the obtained oil, components with the carbon number of gasoline range (C4-C12) take over 80wt%.

Real plastic waste was attempted, while the study of co-pyrolysis of biomass with model species PE, PS, PP are also interesting. Among them, PE has shown the highest selectivity towards hydrocarbons (70%), while PS has shown the highest aromatic selectivity over 90% and the highest oxygen removal ability, with only 3wt% oxygen in the obtained oil.

The synergic effect between plastic and biomass can be observed by analyzing the oil content, while the detailed reaction mechanism, especially on clay catalyst surface mechanism, will be further studied by applying model compounds of plastic and biomass, together with operando technologies. Further attempts at full removal of oxygen and oil component regulation will also be carried out.

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ORAL A-7

Plastic waste valorization to clean H_2 and decarbonized chemicals through its catalytic deconstruction by novel ionic liquid-based catalytic systems (WASTE2H2)

Jonatan Pérez-Arce[1], Eduardo J. Garcia-Suarez[1,2]
[1]*Center for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Alava Technology Park, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain.*
[2]*IKERBASQUE, Basque Foundation for Science, Maria Diaz de Haro 3, 48013 Bilbao, Spain.*

Daily basis used plastics cause a huge amount of waste having an enormous impact on the environment and living species at the end-of-life of plastics disposal. In fact, around 300 million tons of plastic are produced annually in the world and only small percentage, less than 9 % according to UNEP, of this plastic is recycled, 12 % is incinerated and the 79% left generates big contamination problems.[1] There are already different ways, not all of them economically viable, to valorize plastic waste (PW) e.g., chemical recycling to feedstocks and energy.[2] The smart management and valorization of PW generated is a major challenge to be addressed by the scientific community. Furthermore, the decarbonization of all sectors of activity becomes of paramount importance and hydrogen is set to play a key role in decarbonizing hard-to-electrify sectors, as well as represent a zero-carbon feedstock for chemicals and fuel production but for H_2 to play the desired role in the energy transition, the scientific community must face the big challenge of decarbonizing H_2 production at a competitive cost. Consequently, the IEC-funded project WASTE2H2 is proposing a novel method where innovative Ionic Liquid-based catalytic systems are combined with microwave (MW) irradiation to selectively produce highly pure clean H_2 and valuable decarbonized chemicals (solid carbon) from PW, addressing simultaneously PW remediation and global climate change.

The ERC-funded WASTE2H2 project brings together a strong interdisciplinary consortium of five partners (CIC energiGUNE, Friedrich-Alexander-Universität, Institute of Chemistry for Life and Health Sciences, Iolitec and Sener Ingeniería) and adds novelty significant advances compared to other routes for PW mitigation and H2 production: i) plastic waste deconstruction by single-step method powered by renewable electricity and working under mild conditions; ii) fast production of highly pure H_2; iii) valuable solid carbon production as sole decarbonized co-product, with easy recovery for its commercialization; iv) expected long lifespan of catalytic system, easy recovery and reuse; v) reducing significantly the energy consumption due to MWs; and vi) high potential to reduce H_2 production cost.

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ORAL A-8

The reaction pathways of catalytic solvolysis of enzymatic hydrolysis lignin with Ni catalyst

Yushuai Sang, Yongdan Li
Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Finland

Lignocellulose, mainly composed of cellulose, hemicellulose and lignin, is a sustainable feedstock for the production of the commodity chemicals and fuels. For hundreds of years, cellulose has been utilized in paper production. Recently, cellulose and hemicellulose are converted into bio-ethanol in 2G biorefineries, while enzymatic hydrolysis lignin (EHL) from 2G biorefineries is poorly utilized, and is regarded as a volume solid waste. Our recent works focus on catalytic solvolysis of EHL into value-added chemicals and fuels.

In our previous work, EHL was depolymerized with various catalysts, including unsupported Ni, Ni-Mo alloy, WO_3/Al_2O_3 and MoS_2 catalysts in ethanol, and all these catalysts achieve complete EHL liquefaction and high yield of alkylphenols[1]. Herein, the reaction pathways of catalytic solvolysis of enzymatic hydrolysis lignin with Ni catalyst was investigated. Ni catalysts on different supports, i.e., SiO_2, Al_2O_3, MgO, and ZrO_2, were prepared with the aim of manipulating the relative importance of metal and acid-base functionalities to investigate the role of different active sites in the enzymatic hydrolysis of lignin (EHL) ethanolysis. Based on the heteronuclear single quantum coherence-nuclear magnetic resonance (HSQC-NMR) analysis of products as well as the phenol conversion and adsorption results, the two-step mechanism for lignin depolymerization is further clarified. The main ether linkage, i.e., β-O-4, in EHL is cleaved without the participation of a catalyst. The metal sites play a key role in suppressing repolymerization steps through the hydrogenation of active intermediates. The acid and base sites convert phenolic monomers into complex alkylated and etherified products through demethylation or/and demethoxylation, alkylation, and etherification, and also promote repolymerization steps. Among the catalysts examined, the Ni/SiO_2 sample with the highest hydrogenation activity and lowest amounts of acid and base sites achieves the highest yield of monomers of 24.7 wt% at 280 ^{o}C for 6 h under 2 MPa H_2 in ethanol.

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ORAL A-9

Sugarcane residues for bio-fuel production: catalytic hydrodeoxygenation of sugarcane bagasse and sugarcane straw fast-pyrolysis oils

Mariana M. Campos Fraga [a], Danilo Hirayama [b], Renata Moreira [b], Naiara da Costa Telis [a], Caroline C. Schmitt [a], Axel Funke [a], Klaus Raffelt [a], Nicolaus Dahmen [a]
[a] *Karlsruhe Institute of Technology (KIT), Karlsruhe/Germany*
[b] *Instituto de Pesquisas Tecnológicas (IPT), São Paulo/Brazil*

Renewable fuels are a promising alternative to fossil fuels, because they improve the security of energy supply and reduce climate impact issues, especially if they are produced from residual biomass. Brazil has a huge potential in the production of fuels from residual biomass such as sugarcane bagasse and straw. These residues can be converted through fast pyrolysis into a liquid fuel precursor, the bio-oil. Nonetheless, due to the high acidity, high oxygen, and water content of bio-oil, it requires further upgrading, such as via catalytic hydrodeoxygenation (HDO)[1]. Considering the harsh environment of bio-oil HDO, several catalyst compositions have been tested, including Nb_2O_5 catalysts, which have shown high solid acidity, enhanced water resistance, and adjustable morphology[1]. In this study, the HDO of bio-oils from sugarcane bagasse and straw with Pd/Nb_2O_5 was investigated.

Four different bio-oil were upgraded, two from bagasse only and two from bagasse and straw. The impact on the HDO of the pyrolysis quenching media (ethylene glycol or ethanol) was also investigated. The biomass was collected in Brazil and shipped to Germany, where the fast pyrolysis and the HDO were conducted. The hydrotreatment was conducted in a batch reactor, pressurized at 80 bar H_2 (RT), and then heated up to 250 °C at 3.33 °C/min, for 2 hours in total. The products (gas phase, upgraded oil, and aqueous phase) were extensively characterized.

The initial bio-oils had 46-54 wt.% carbon, 36-43 wt.% oxygen (wet basis), and 7-25 wt. % water. While the bio-oil from bagasse and straw quenched with ethanol (BSEt) led to a single-phase product, all the others had phase separation during the upgrading. This BSEt bio-oil had also the lowest H_2 uptake and the lowest gas generation (CO_2 and CO) during the HDO. However, despite the low H_2 consumption, the upgraded oil from BSEt had the highest H/C ratio due to the absence of phase separation. Since no oxygen was removed through the aqueous phase, this oil had the highest O/C ratio. In terms of chemical composition, ethanol and acetic acid were the main detected compounds in the initial bio-oils, independent of the quenching media. These compounds were preferentially accumulated on the aqueous phase after the HDO, although still present on the upgraded oil. Ethylene glycol was detected in significant concentration on the aqueous phase product, as well as on the bio-oil quenched with ethanol, possibly from levoglucosan. Hydroxypropanone, hydroxybutanone, furfural, and 2(5H)-furanone present on the initial bio-oils, were drastically or completely consumed.

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ORAL A-10

Catalytic conversion of lower olefins to BTX range of aromatics using zeolite-based catalysts

Paresh S. Butolia[1], Xiaoying Xi[1], Jozef G. M. Winkelman[1], Marc C. A. Stuart[2,3], Matthijs van Akker[4], André Heeres[5], Hero Jan Heeres[1], Jingxiu Xie[1,*]

1. Green Chemical Reaction Engineering, Engineering & Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands.
2. Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 7, 9747AG, Groningen, The Netherlands.
3. Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747AG, Groningen, The Netherlands.
4. BioBTX, Zernikelaan 17, 9747 AA Groningen, The Netherlands.
5. Research Centre Bio-based Economy, Hanze University of Applied Sciences, Zernikeplein 11, 9747AS, Groningen, The Netherlands

Aromatics, especially benzene, toluene, and xylenes (BTX), are an important class of platform chemicals that are used extensively for the production of specialty chemicals, paints, polymers etc. Considering the need to transit towards more circular alternative carbon feedstocks, production of BTX from lower olefins offers a viable solution as these olefins can be derived easily from biomass and waste plastics.[1, 2] Aromatization of olefins is typically carried out at ambient pressure and temperatures between 673 and 773 K using a zeolite-based catalyst. The selectivity towards BTX aromatics can be improved by incorporating promoters such as Ga, Zn, Ag etc. into the zeolite.[3, 4]

In this work, we first identified the preferred olefin feed, ethene or propene, for BTX production in a fixed-bed reactor using commercial H-ZSM-5 (Si/Al = 23) and Ga-modified ZSM-5 catalysts. At 773 K, 1 bar, 45 %v. olefin, 6.75 h^{-1}, aromatization of propene over Ga-ZSM-5 catalyst exhibited higher BTX selectivity of 55% and resulted in slower catalyst deactivation compared to ethene aromatization. These results suggest that the overall BTX yields can be improved if propene can be selectively produced during pyrolysis and additionally be converted in the recycle gas stream of biomass/ plastics pyrolysis. Considering the commercial importance of p-xylene, we aimed at improving its selectivity using propene as feed by further modifying the Ga-ZSM-5 catalyst. Two different surface-modification techniques were employed on the catalyst and upon modification, p-xylene selectivity was improved. Further structure-performance relations of the aromatization of propylene towards p-xylene will be discussed in this contribution.

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ORAL A-11

Conversion of acetic acid over metal deposited TiO_2 catalysts.

Petter Tingelstad, Robert L. Peters, De Chen.
Department of chemical engineering, NTNU, Trondheim, Norway.

Acetic acid (AA) is the major water soluble oxygenate formed during biomass pyrolysis, accounting for ~6 wt% of the formed products. Acetic acid is corrosive and water soluble and is regarded as an unwanted byproduct in the pyrolysis process. It is however an excellent carbon building block for oil-soluble hydrocarbons and aromatics through the ketonization and aldol condensation pathways. Ketonization reactions takes place on metal oxide surfaces[1]. Herein we unravel the bifunctional role of deposited metal clusters on TiO_2 catalysts for acetic acid ketonization.

Activity tests were conducted in a PID Microactivity Reference unit. Experimental conditions in figure text. Operando DRIFTS were conducted using a Bruker FT-IR with downstream GC-FID/MS. Mass balances were kept above 97 %. Catalysts were characterized by TPD, TPO, XRD, and BET.

Deposited metal clusters increased the ketonization rate more than four-fold. IR and descriptor studies revealed that deposited metal facilitates α-C-H bond breaking at H_2 rich conditions, while promoting O-H bond breaking at H_2 lean conditions. Deactivation can be described as two separate events: metal function deactivation and metal oxide deactivation. Carboxylates are MASI on metal oxide, with negligible coverage on deposited metal clusters. Initial site time yield is listed in the table.

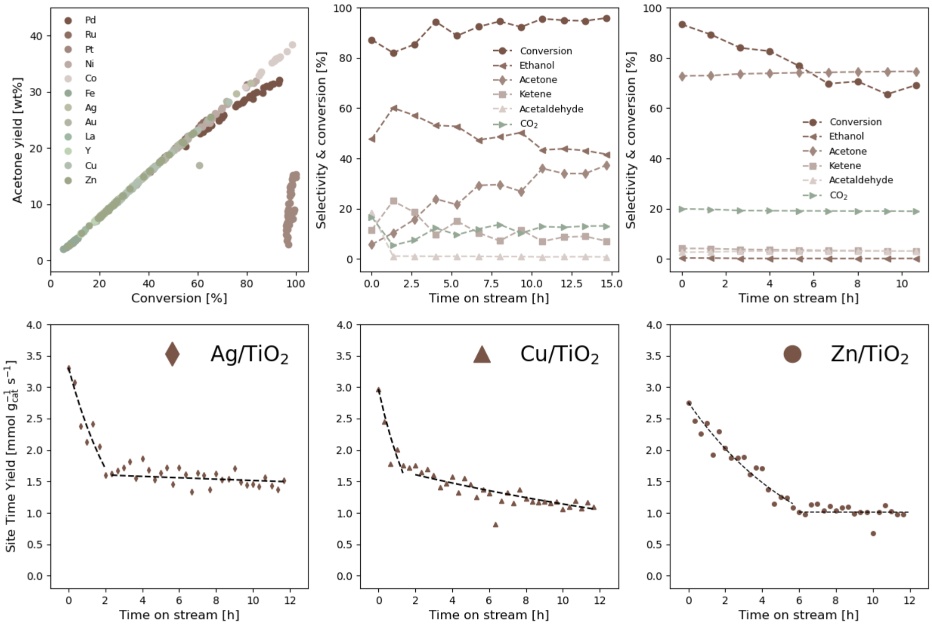

Figure 1: All experiments were conducted at 350 °C, 15 mg catalyst, WHSV = 15 g_{acid} g_{cat}^{-1} h^{-1}, 1 kPa AA, 20 kPa H_2, 79 kPa N_2. Time on stream 12 h. a) activity tests b) Pt/TiO2, c) Pd/TiO2,

Catalyst [M/TiO2]	Site Time Yield [mmol g_{cat}^{-1} s^{-1}]
Co	3.92
Pt	3.59
Pd	3.73
Ni	4.09
Ru	3.07
Au	2.9
Ag	2.88
Cu	2.66
Zn	2.75
Er	2.11
Y	1.67
La	1.43
---	1.2
Fe	0.2

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ORAL A-12

UiO-67 (Zr)/Pd (Zn) composite catalysts for CO_2 hydrogenation to methanol

Elif Tezel[a], Dag K. Sannes[a], Stian Svelle[a], Unni Olsbye[a] and Petra Ágota Szilágyi[a]

[a]*Department of Chemistry, Center for Materials Science and Nanotechnology,*
University of Oslo

Metal-organic frameworks (MOFs) are an ideal platform for designing selective novel catalysts for CO_2 hydrogenation under mild reaction conditions. The abundant porous structure and high surface area of MOFs play a crucial role in enhancing the dispersion of catalytic sites and facilitating the adsorption and activation of CO_2, enabling catalysis at lower temperatures. Additionally, MOFs offer the flexibility to incorporate various catalytic sites and adjust coordination environments, providing control over the CO_2 hydrogenation process to value-added and useful products.[1] These properties highlighted the importance of the MOF-based composite catalysts as alternative catalysts for CO_2 hydrogenation.[2]

I will present the design of composite thermal catalysts based on hexanuclear zirconium metal–organic framework matrices, primarily UiO-67, for the hydrogenation of CO_2. This promising framework was modified by incorporating Pd (/Zn) nanoparticles as catalytically active sites. We synthesized several composite catalysts as a function of the linker, active metal sites, etc. We also characterized as-synthesized and spent catalysts using different techniques, including X-ray diffraction (XRD), X-ray spectroscopy, thermal analysis, and Brunauer–Emmett–Teller (BET) surface area measurements. Also, we coupled the characterization techniques with catalytic testing experiments via varying pretreatment conditions to understand which properties of these catalysts, e.g., Pd particle size, dispersion, thermal and chemical stability, and oxidation state of the active metal, make them more active and selective for CO_2 to methanol.

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ORAL A-13

Influence of pre-treatment on the support effect in catalytic methanol synthesis

Jonas A. Boysen[1], Anker D. Jensen[1] and Jakob M. Christensen[1]*
[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, Søltofts Plads 228A, 2800 Kgs. Lyngby (Denmark)*

The reaction rate in Cu-catalyzed hydrogenation of CO_2 to methanol and the Cu surface area have a linear relationship for different support materials[1], which indicates a reaction occurring on the Cu surface. However, the industrially applied ZnO-support raises the turnover frequency per Cu surface atom by an order of magnitude and this essential metal-support synergy is not fully understood. Kuld et al.[2] found that H_2 pre-treatment of a $Cu/ZnO/Al_2O_3$ catalyst accelerated the reaction rate and suggested Zn-Cu surface alloy formation as the cause of this effect. However, this proposal seems to be at odds with the observation that metallic Zn is found to be oxidized in CO_2-containing reaction gas[3-4]. The aim of this work is to further enhance the understanding of the active site and the synergy of the industrial $Cu/ZnO/Al_2O_3$ catalyst by investigating how the catalyst is affected by pre-treatments with CO or H_2.

An industrially relevant $Cu/ZnO/Al_2O_3$ (60/30/10 wt%) catalyst was subjected to pre-reduction (with either 5 % H_2/N_2 or 10% CO/Ar) followed by a pre-treatment in different H_2 partial pressures. Raney Cu (referred to as pure Cu) was tested similarly to study the effect without support interactions. The pre-treated catalyst was tested in methanol synthesis using a synthesis gas flowrate of 200 NmL/min with a composition of H_2/CO_2 = 80/20% at T = 135 °C and P = 1 atm. Additionally, temperature programmed desorption (TPD), N_2O-Reactive frontal chromatography (RFC) and infrared spectroscopy (IR) experiments have been conducted on pre-treated catalysts to understand how catalyst surface and adsorbates are affected.

The pre-reduction atmosphere has a major impact on the catalytic activity. Pre-treatment of the reduced catalyst with varying H_2 pressures prior to catalytic tests show a beneficial effect upon the methanol reaction rate. However, this effect is not primarily due to a reduction of the support, since pre-reduction in a more reducing gas (CO vs H_2) leads to an inferior catalytic performance (see Figure 1).

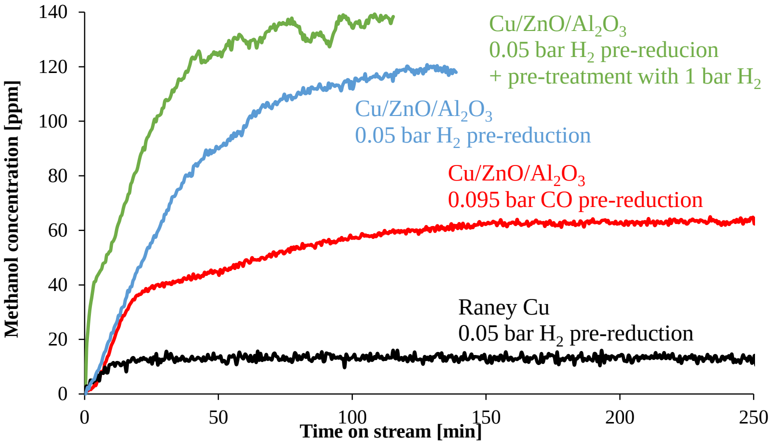

Figure 1: The methanol effluent concentration as a function of time on stream at H_2/CO_2 = 4/1, 135 °C, 1 atm for differently pre-treated catalysts.

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ORAL A-14

Catalytic CO_2 methanation over modified carbon– supported Ruthenium: The influence of the support type on the properties and activity of the catalyst

Elżbieta Truszkiewicz[1,*], Katarzyna Klimaszewska[1], Eliza Gauze[1], Zuzanna Gronkiewicz[1],
Dominik Wierzbicki[2,3,4], Ivo Alxneit[2], Andrzej Ostrowski[1]
[1] *Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland; * corresponding author: elzbieta.truszkiewicz@pw.edu.pl*
[2] *Paul Scherrer Institute, CH-5232 Villigen, Switzerland*
[3] *AGH University of Science and Technology, Faculty of Energy and Fuels, Al. A. Mickiewicza 30, 30-059 Cracow, Poland*
[4] *National Synchrotron Light Source II, Brookhaven National Laboratory, Upton, NY 11973, USA*

Ruthenium catalysts are known for their high activity and selectivity in the hydrogenation of carbon oxides to methane[1]. The reaction is commonly used to purify hydrogen streams from trace amounts of CO_x, for further H_2 use in the synthesis of ammonia, or in fuel cells. Among the carriers described in the literature, an interesting group are carbon materials, such as activated carbons, carbon nanotubes and nanofibers, and fullerenes[2]. However, there are very few reports involving the use of modified activated carbons as carriers for Ru in CO_2 methanation[3]. There is also lack of information concerning the effect of Ru crystallite sizes on the activity of such systems.

Our work includes ruthenium systems (1 wt.% of Ru) deposited on four different carbon supports. Their activity in CO_2 methanation in a model mixture of CO_2(1 vol.%)/H_2 was investigated. The catalysts were characterized with various techniques including TEM, XRD, chemisorption, CO_2–TPD and TPR among others. We observed an interesting dependence between the catalytic activity and Ru particle size in a range of 1 – 4.5 nm.

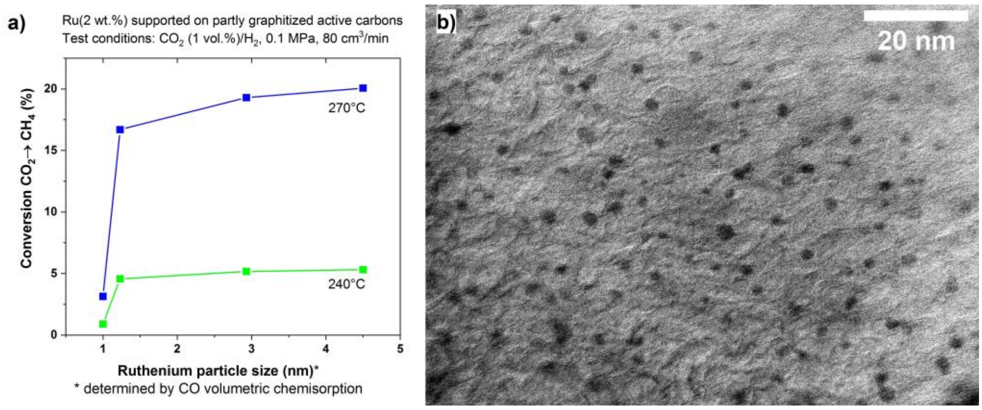

Figure 1. a) CO_2 conversion over Ru/Carbon catalysts; b) TEM image of the most active Ru/C catalyst (fresh sample).

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ORAL A-15

Identifying the Active Species in Ga-promoted Cu Catalysts for CO_2-Hydrogenation

Lorena Baumgarten[1,2], Patrik Hauberg[3], Sebastian Mangelsen[3], Mariam L. Schulte[1,2], Claude Coppex[2], Jelena Jelic[2], Malte Behrens[3], Felix Studt[2], Erisa Saraçi[1,2,] Jan-Dierk Grunwaldt[1,2]
[1]*Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[2]*Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany*
[3] *Institute of Inorganic Chemistry, Kiel University, Germany*

The emerging field of renewable energy storage has in its core the concept of “Power-to-Liquid”[1]: green H_2 and CO_2 are transformed into liquid chemicals and fuels, such as methanol. However, the shift from using the standard CO to utilizing CO_2 brings new challenges. CO_2-hydrogenation is thermodynamically less favored compared to CO-based feed and is leading to higher water formation as couple product. Both CO_2 and water deactivate the classical $Cu/ZnO/Al_2O_3$ catalyst (CZA). Addressing these limitations, modification with Ga-oxide have shown significant promise for advancing methanol catalysts.[2,3] The combination of *operando* X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) is a powerful tool to unravel the structural dynamics of catalysts under reaction conditions.[1,3]

Activity tests of a Cu/Ga_2O_3 (CG) systems showed 100% selectivity towards methanol with relatively high methanol formation rates in a lab reactor setup. To better understand the performance of this catalyst, *operando* XAS- and XRD studies were performed at MAX IV Synchrotron Light Source in Lund. During activation of the catalyst in H_2/N_2 atmosphere, transformation of the Ga-species occurred, visualized by the changes in the X-ray absorption near-edge structure at the Ga K-edge (XANES, Figure 1). This state persisted during reaction conditions (230 °C, H_2/CO_2=3:1, 20 bar), where methanol was selectively formed. Elevated temperatures induced another structural transformation, as evidenced by *operando* XAS and XRD, with the catalyst now producing methane as main product instead of methanol. This study provides valuable and novel insights into the structure-activity relationship of Ga-promoted Cu catalyst for CO_2 hydrogenation, elucidating the role played by the oxidation state and structure of the Ga-species.

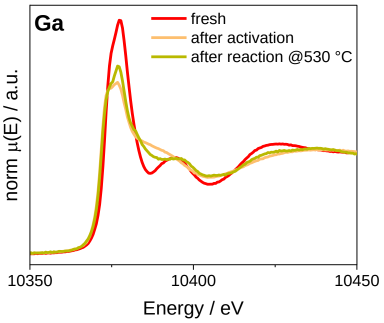

Figure 1: XANES at Ga K-edge of fresh CG, after activation and after reaction atmosphere up to 530 °C

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ORAL A-16

Electrocatalytic conversion of glucose and xylose into value-added chemicals

Jay Pee Oña[1,2], Rose-Marie Latonen[2], Narendra Kumar[1,2], Laura Laverdure[3],
Karoliina Honkala[3], Henrik Grénman[1,2]
[1]Laboratory of Industrial Chemistry and Reaction Engineering, Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, FI-20500 Turku/Åbo, Finland
[2]Laboratory of Molecular Science and Engineering, Faculty of Science and Engineering, Åbo Akademi University, Henriksgatan 2, FI-20500 Turku/Åbo, Finland
[3]Department of Chemistry Nanoscience Center, University of Jyväskylä, P.O.Box 35, FI-40014, University of Jyväskylä, Finland

Catalytic conversion of biomass into fuels and value-added chemicals presents a sustainable and environmentally friendly alternative to fossil-based processes. Electrochemical routes for biomass valorization allow for the aqueous processing of biomass feedstocks under milder reaction conditions than conventional catalytic processes without the need for costly and possibly toxic reductive and oxidative reagents. The energy required for electrochemical conversions can be supplied by renewable electricity (e.g. solar, wind). In this work, the electrocatalytic valorization of glucose and xylose, the main components of wood hemicellulose, was studied. In the electrocatalytic hydrogenation (ECH) of the sugars over different roughened metal surfaces (Ag, Au, Cu, Pt, and Zn), the Cu catalyst showed the highest glucose and xylose conversion with selectivity towards sorbitol of 21.1 % and towards xylitol of 67.1 %.[1] ECH of sugars over carbon-supported Au nanocatalysts revealed the influence of the cluster size of the metal catalyst on the ECH rates.[2,3] On the other hand, the electrocatalytic oxidation (ECO) of glucose and xylose over mesoporous Sibunit carbon supported Au nanocatalyst showed high turnover frequencies for glucose (4300 h^{-1}) and xylose (1897 h^{-1}) at 25 ^{o}C and 0.1 M NaOH supporting electrolyte (pH~12.5), with gluconic and xylonic acid selectivity of 81.5 % and 87.8 %, respectively. From DFT calculations, the presence of co-adsorbed OH^- on the Au surface facilitates the formation of sugar acid products. Furthermore, xylonate desorption was determined to be slightly more endothermic than gluconate desorption.[4] This work provides the bases for catalyst development and ideal reaction conditions for the electrocatalytic hydrogenation and oxidation of sugars, with insights into the reaction mechanisms and reactivity of substrates from DFT calculations.

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ORAL A-17

Electrochemical characterization of NiFe nanoparticles on colloidal CeO_2 for Anion Exchange Membrane Electrolysers

Neethu Kochukunnel Varghese[a], Massimiliano Boccia[b], Vincenza Marzocchi[b], Antonio Comite[a]
[a]Department of Chemistry and Industrial Chemistry, University of Genoa, Genoa, Italy
[b]H2 Energy SRL, Pizzighettone, Cremona, Italy

Hydrogen is gaining momentum as a fuel of the future because it significantly reduces CO_2 emissions, has high energy density and versatility, and can be integrated easily with renewable energy[1]. Anion exchange membrane (AEM) electrolysis is an emerging technology which can produce hydrogen using non-expensive transition metal catalysts at high energy efficiency. NiFe class of catalysts have garnered significant attention due to their promising catalytic performances, cost-effectiveness, and relative abundance. These bimetallic catalysts, leveraging the synergistic properties of nickel and iron, have showcased their prowess, particularly in the oxygen evolution reaction (OER) segment of water splitting. In this study we evaluate Nickel and Iron nanoparticles dispersed on colloidal CeO_2 for their catalytic activity and performance for applications in AEM water electrolysis for water splitting reactions.

We synthesize catalysts with multiple Ni:Fe ratios on 30 weight percent commercial colloidal CeO_2 through chemical reduction method using $NaBH_4$. Morphological and structural properties of the catalysts are studied by using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and XRD. N_2 Physisorption studies show a BET surface area in the range of 20-80 m^2/g. For electrochemical characterization, we conduct Cyclic Voltammetry (CV) for Oxygen Evolution Reaction (OER) in a rotating disc electrode setup using 1 M KOH electrolyte.

Our results indicate that $Ni_{90}Fe_{10}/CeO_2$ has the highest catalytic activity among the catalysts with an overpotential of 344 mV at 10 mA/cm^2 current density. Tafel slope analysis shows lowest Tafel slope for $Ni_{90}Fe_{10}/CeO_2$ catalyst which suggests faster reaction kinetics and lower overpotentials higher current densities. Chronopotentiometry studies were conducted for 2 hours and all the catalysts were found to be stable. Nyquist plots and equivalent circuits show $Ni_{90}Fe_{10}/CeO_2$ catalyst has the lowest charge transfer resistance and higher efficiency compared to other compositions. These findings highlight the importance of Fe addition to improve the catalytic activity of Ni catalysts as well as the stability improvement provided by a catalyst support like colloidal CeO_2.

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ORAL A-18

Photocatalytic degradation of Diuron in water – impact of Rh impregnation on P25 visible light activity

Jennyffer Stefania Martinez Quimbayo[ab], Manoj Kumar Ghosalya[a], Assa Aravindh Sasikala Devi[a], Marko Huttula[a], Matti Alatalo[a], Samuli Urpelainen[a], Satu Ojala[b]
[a]*Nano and Molecular Systems Research Unit (NANOMO), Faculty of Science, University of Oulu. Oulu, Finland P.O. Box 8000, FI-90014.*
[b]*Environmental and Chemical Engineering, Faculty of Technology, University of Oulu. Oulu, Finland P.O. Box 8000, FI-90014.*

Water pollution caused by emerging contaminants concerns the society. As the global population continues to grow ensuring food security becomes essential, leading to the widespread use of herbicides and pesticides in crop cultivation. Among these chemicals, Diuron, a prevalent herbicide, has been detected in water sources and demands effective degradation strategies[1]. Photocatalyst such as titanium dioxide (TiO_2), utilize light energy to initiate chemical reactions for contaminant degradation. Significant efforts have been lately put on the development of visible light activated photocatalysts for degradation of emerging pollutants in water. The addition of transition metal in semiconductors is one of the techniques applied in research to obtain activity under visible range[2]. This work shows how impregnation of Rh impacts on TiO_2 photocatalytic performance in Diuron degradation using several experimental approaches and DFT modelling. Three samples with different Rh loading (0.5%, 1%, and 2%) were synthesized, characterized and their activities were evaluated under different light conditions. It was found that the activity of RhP25 under white light irradiation was improved when increasing the amount of Rh. At low Rh loadings the Rh atoms interact with Ti and may be stabilized in the TiO_2 lattice. At higher loadings Rh interacts with the O atoms forming two different clusters Rh_3O_4 and Rh_4O_6 on the TiO_2 surface. This was evidenced by DFT, XPS and XRD results. Addition of Rh leads to narrower bandgap that improves visible light absorption. The results showed three times higher removal of Diuron under white light irradiation for 2%RhP25 compared with P25. Repeated experiments did not show significant deterioration of the activity.

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ORAL A-19

Operando AP-XPS investigations of Ta_3N_5-based electrodes during photoelectrochemical water splitting

Ingeborg-Helene Svenum[1], Øystein Dahl[1], Martin Fleissner Sunding[2], Veronica Killi[3], Mathieu Grandcolas[2], Magnus Andreassen[4], Ola Nilsen[3], Annett Thøgersen[2], Ingvild Julie Thue Jensen[2], Athanasios Chatzitakis[3]

[1]*SINTEF Industry, P.O. Box 4760 Torgarden, NO-7465 Trondheim, Norway*
[2]*SINTEF Industry, Forskningsveien 1, NO-0373 Oslo, Norway*
[3]*Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Gaustadalléen 21, NO-0349 Oslo, Norway*
[4]*Centre for Materials Science and Nanotechnology, Semiconductor Physics, Department of Physics, University of Oslo, NO-0349 Oslo, Norway*

Photoelectrochemical (PEC) water splitting can be a viable route for production of hydrogen. In such systems sunlight is used to split water into hydrogen and oxygen at two different electrodes with no or limited applied potential. Ta_3N_5 is a promising candidate as photoanode material and has been shown to produce high photocurrent densities for certain morphologies.[1,2] However, deactivation due to photo corrosion is a major problem.[3] The stability and resistance to photo corrosion can be improved by modifying the surface, for example through coatings.

In this study ambient pressure x-ray photoelectron spectroscopy (AP-XPS) together with the "dip & pull" method[4] at the HIPPIE beamline at MAX IV is used to investigate the solid/liquid interface of Ta_3N_5-based systems under operando conditions (solar illumination and applied potential). The Ta_3N_5 films (~500 nm) were prepared on fused silica substrates.[5] The films were made by sputtering of metallic Ta films followed by nitridization at 950 ºC in NH_3 for 8 hours. NiO_x protective coatings were subsequently deposited using atomic layer deposition. 1 M KOH is used as electrolyte.

The PEC performance of a pure Ta_3N_5 is compared to a NiO_x-coated Ta_3N_5 photoanode, as well as the chemical changes and band alignment at the liquid solid interface. For Ta_3N_5, the system PEC performance is rather rapidly reduced which can be ascribed to Ta-N-O and Ta-O formation at solid/liquid interface. For the Ta_3N_5/NiO_x system the PEC performance is sustained, and the stability is greatly improved.[5] The operando XPS results show that the difference in PEC performance is related to changes in Fermi-level pinning for the two systems.

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ORAL A-20

Depolymerization of nylon-6 over supported ruthenium catalyst to ε-caprolactam

Prabin DHAKAL, Abdenour ACHOUR, Phuoc HOANG HO, Derek CREASER, and Louise OLSSON *

Chalmers university of Technology, Chemical engineering Division, 41296, Gothenburg, Sweden

*Corresponding author: louise.olsson@chalmers.se

Recycling plastic waste into monomers and value-added chemicals could contribute to the circular economy of the plastics industry while minimizing its carbon footprint and impact on the environment. Catalytic depolymerization is one such technique that could lead to high-quality monomers that serve as building blocks for new polymers. Over 32% of the plastics produced worldwide are made from heteroatom-containing polymers, which are often polar, such as polyamide, polycarbonates, polyethylene terephthalate, and polyurethane. In addition, around 50% of the plastics produced consist of non-polar polyolefins. Thus, the depolymerization of polar plastic waste in the presence of a non-polar solvent opens the door to economically viable recycling of plastics, which, to our knowledge has never been presented before. Therefore, we investigate hydro-depolymerization of nylon-6 in nonpolar hexadecane using Ru on a zirconia support.

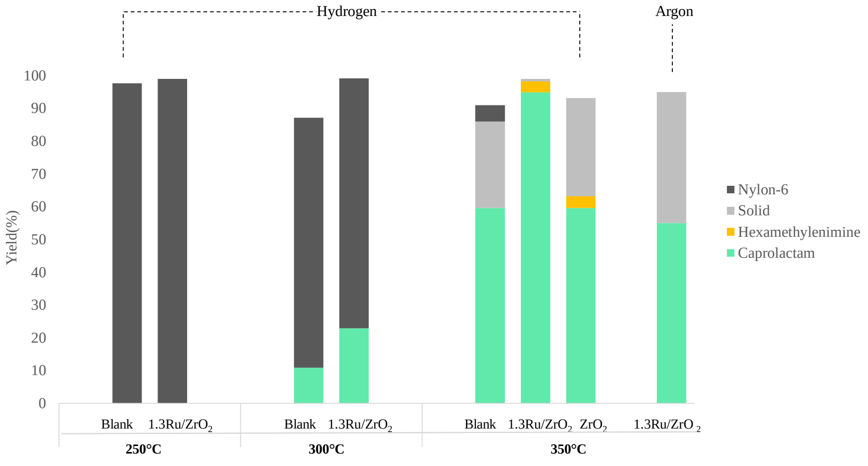

Figure 1:nylon-6 hydrodepolymerisation at different temperatures.Reaction Condition: nylon-6 (mw-10,000)-3g, Catalyst: 0.15g, Hexadecane : 57g, 30 bar hydrogen or Argon, Reaction time : 5 h.

H_2-reduced Ru nanoparticles supported on zirconia were used to study depolymerization in a batch reactor at different temperatures and pressures. In contrast to depolymerization in the polar solvent shown by Milstein and co-workers[1], and Zhou and co-workers[2], the depolymerization of nylon-6 in hexadecane proceeds at temperature >300 °C and leads to a yield of 95% by weight of ε-caprolactam at 350°C, 30 bar H_2 and 5 h reaction time, Figure 1. Increasing hydrogen pressure resulted in 3-5 wt% de-oxygenated caprolactam (hexamethyleneimine), however still a near quantitative ε-caprolactam yield. The yield of ε-caprolactam decreased to 55 wt% at 350 °C in 30 bar Argon and 5-hour reaction time. With twice the catalyst-to-polymer ratio caprolactam yield was 91 wt% with shortened reaction time of 2 hour. However, if the reaction time was longer than 5 hours, the product decomposed. The process robustness was further investigated using common plasticizers such as water and 2-ethylhexyl 4-hydroxybenzoate. The efficiency of the catalyst was investigated by varying the metal-to-support ratios and reusing the spent catalyst.

The result suggests that ruthenium metal sites accelerate the depolymerization of nylon-6 into the desired monomers. The study lays the foundation for further research into recycling mixed plastic waste before separating it.

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ORAL A-21

Catalytic upgrading of fast pyrolysis oils of biomass and residual waste with calcium-based catalysts towards alternative fuels for marine engines

Moritz Böhme[1], Peter A. Jensen[1], Magnus Z. Stummann[2], Martin Høj[1], Anker D. Jensen[1]*
[1]*Technical University of Denmark (DTU),*
Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark
[2]*TOPSOE A/S, Kgs. Lyngby, Denmark*
** aj@kt.dtu.dk*

The marine industry contributes around 3% to the worldwide CO_2 emissions today and is expected to grow over the next decades due to increasing need for logistics and transportation. To reduce this sector's greenhouse gas emissions significantly together with other hard-to-abate sectors like land and air-based transportation, innovative sustainable technologies and fuels will be needed in the near future. Direct electrification or battery-based technologies face challenges for these applications, particularly the low energy density compared to many liquid fuels [1].

Biomass and residual solid waste utilization with fast pyrolysis to produce oils has seen strongly increased interest over the last decade both in fundamental research and industrial application. The crude pyrolysis oil often has a high water and oxygen content leading to a high acidity, low storage stability and energy density. Wax formation from the plastic parts in waste results in poor fuel properties [2]. Removing oxygen-containing groups through catalytic upgrading and cracking long chain hydrocarbons can improve the properties and lead to a high value fuel. This can be mixed with conventional fossils as drop-in fuels or can prospectively replace them totally [3].

This contribution focuses on the application of low cost calcium-based catalysts for in-line ex-situ upgrading of pyrolysis vapours. A fixed bed upgrading unit was developed following a flash catalytic pyrolysis unit and different solid catalysts were tested regarding activity, yield and coking propensity.

The upgraded pyrolysis oils were analysed by gas-chromatography mass-spectroscopy (GC-MS), Karl-Fischer titration and elemental analysis (EA). The exhaust gas was analysed by on-line gas chromatography (GC) with a thermal conductivity detector (TCD-FID).

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ORAL A-22

Catalytic Reductive Liquefaction of Bark into Biofuel using Ni-based Catalysts: Char Formation Prevention Strategies

Quoc Khanh Tran[a], Huy Xuan Le[a], Hoang Phuoc Ho[a], Christian Kugge[b], Derek Creaser[a], Louise Olsson[a]
[a]*Chemistry and Chemical Engineering Department, Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden*
[b]*SCA R&D Centre, Sundsvall, Sweden*

Bark is a valuable feedstock for biorefineries since it is a significantly under-utilized stream from wood processing industries. However, its structure and chemical composition is complex, which causes high char formation and low monomeric product yields from a catalytic liquefaction process to produce biofuels. Here in, we report various routes to suppress the char formation from catalytic liquefaction of bark, including acid washing, extractives removal, and co-solvent addition to the liquefaction process. The extractive compounds (18.3 wt%) were removed using a Soxhlet method. They mainly consisted of rosin acids, abietic acids, and benzanthracene. Extractive compounds contributed strongly to char formation due to coupling reactions involving them during the liquefaction of the bark. Among the mentioned routes used to reduce the char yield, the use of a co-solvent achieved the largest reduction in char formation (see Table 1). The use of 5 g ɤ-Terpinene as a co-solvent additive (60 g in total) could reduce the char yield to 8.2 wt% from 20.4 wt% with only hexadecane as solvent. ɤ-Terpinene plays a vital role in stabilization of reactive intermediates, to prevent self-coupling reactions of the reactive extractive components which increases the monomeric yield and reduces char formation as well as formation of heavy liquid fraction compounds. In this study, 5 wt% Ni loaded onto Al_2O_3 ($5Ni/Al_2O_3$ catalyst) gave the highest catalytic activity compared to other higher loadings, and use of bimetallic catalysts; NiX/Al_2O_3 (X = 2.5 wt% Mn, Co, Zn, Mg, and Mo). Bark could be converted into monomeric compounds such as cycloalkanes (C4-C7), aromatics, phenolic compounds, as well as liquified heavy compounds.

Table 1. Product distribution from one-step bark liquefaction at 400 °C, 30 bar H_2 (@ 25°C), 4 h residence time with 0 or 30 wt% catalyst loaded.

Experiment Conditions	Product distribution (wt%)				
	Solid yield	Monomeric yield	Heavy fraction	Gas yield	Moisture content
Without catalyst, Bark	44.1	26.3	23.7	3.8	2.1
$5Ni/Al_2O_3$ - Bark	20.4	42.8	25.8	4.2	6.8
$5Ni/Al_2O_3$ - Acid washed bark	23.2	49.1	18.1	4.1	5.5
$5Ni/Al_2O_3$ - Bark, extractive removal	12.2	61.1	15.2	4.5	7.0
$5Ni/Al_2O_3$ - 5 g ɤ-Terpinene added	8.2	67.1	13.2	4.3	7.2

ORAL B-1

Upscaling production of tandem catalyst for single-step CO_2-to-hydrocarbons conversion

Rasmus Y. Brogaard,[a] Tomás Cordero-Lanzac,[b] Andrea Jouve,[c] Ørnulv Vistad,[d] Ayşegül Bayat,[e] Kübra Ç. Aytekin,[e] Silvia Bordiga,[c] Unni Olsbye[b]
[a]*Topsoe A/S, Haldor Topsoes Allé 1, 2800 Kgs. Lyngby, Denmark*
[b]*SMN Centre for Material Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway*
[c]*Department of Chemistry, NIS Center and INSTM Reference Center, University of Turin, Turin 10125, Italy*
[d]*SINTEF, Forskningsveien 1, 0373 Oslo, Norway*
[e]*TÜPRAŞ-Turkish Petroleum Refineries Co., R&D Center, Guney Mah. Petrol Cad., 41790, Kocaeli, Turkey*

Recent academic research has devoted substantial efforts to tandem catalysts for hydrogenation of CO_2 via methanol (and other oxygenates) to hydrocarbons in a single reactor.[1] These catalysts contain a methanol synthesis component and a zeolite for further conversion to hydrocarbons. To realize single-step CO_2-to-hydrocarbons conversion on an industrial scale it is preferred to bring the two functions together in a single catalyst pellet. Maintaining synergy between the catalytic functions is a fundamental challenge in upscaling production of such tandem catalysts. Our work reported on the difficulties of upscaling a PdZn/SAPO-34 tandem catalyst, as Zn migration in the pellet harmed both the methanol synthesis and zeolite functions.[2] Conversely, in this work we report on successful upscaling of a $GaZrO_x$/MgAlPO-18 tandem catalyst in a single pellet that maintains synergy between the catalytic functions in single-step CO_2-to-hydrocarbons conversion.

The GaZrOx exists as a solid solution[3] limiting metal migration to the MgAlPO-18 zeotype. $GaZrO_x$ and Mg-AlPO-18 raw materials were synthesized in kg scale and mixed with a binder. The resulting paste was extruded and calcined to produce single pellets of the GaZrOx/MgAlPO-18 tandem catalyst. We found that depositing GaZrOx on alumina prior to mixing achieves the highest dispersion of the metal oxide in the catalyst pellet. However, the intrinsic methanol synthesis activity of GaZrOx is lowered when interacting with the alumina binder. Adsorption of CO and reduction with H_2 followed by FTIR spectroscopy shed light on the origin of the lower activity; the Ga(III) sites observed on GaZrOx are not detected when the metal oxide is deposited on alumina. Further improvement of catalytic performance should thus focus on the binder.

The GaZrOx/MgAlPO-18 tandem catalyst was produced in kg scale and tested in hydrogenation of CO_2 to hydrocarbons in a pilot unit. The performance matched that of small-scale trial batches tested in lab, illustrating a successful production procedure.

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ORAL B-2

LOHC dehydrogenation catalyst synthesis by ball milling

Krista Kuutti[1], Manoj Ghosalya[2], Jacopo De Bellis[3], Ferdi Schüth[3], Mika Huuhtanen[2], Samuli Urpelainen[2], Sari Rautiainen[1]
[1]*VTT Technical Research Centre of Finland Ltd, 02044 Espoo, Finland*
[2]*University of Oulu, 90014 Oulu, Finland*
[3]*Max-Planck-Institut für Kohlenforschung, 45470 Mülheim an der Ruhr, Germany*

Liquid organic hydrogen carriers (LOHCs) provide a promising form of hydrogen storage to enable green hydrogen usage as a carbon neutral energy carrier.[1] The hydrogenation/dehydrogenation reactions of LOHCs are reversible and effective when suitable catalysts are used. However, the dehydrogenation reaction is industrially a new process, and the catalysts are still under development.[2] Supported platinum catalysts are highly active in the dehydrogenation reaction, but they suffer from deactivation.[3] Ball milling (BM) is an emerging solvent-free one-pot synthesis method for supported metal catalysts: High kinetic energies deposit metal particles on catalyst support particles, and in some cases also phase transformations may be facilitated.[4] In this work we synthetized LOHC dehydrogenation catalysts by ball milling and studied the effect of catalyst synthesis method to its properties and performance.

Catalyst BM Pt/TiO_2 was synthetised by ball milling. The jars were filled with platinum and TiO_2 (anatase) powders, sealed, and milled for 3 h at 600 rpm. Catalyst IWI Pt/TiO_2 was synthetised by impregnating Pt to TiO_2 support material via incipient wetness technique. Both catalysts had 1 wt.% Pt loading. Continuous LOHC dehydrogenation experiments were operated in atmospheric pressure in a packed bed quarts glass reactor. The catalyst was activated by reduction. Methylcyclohexane was co-fed with nitrogen, and the reaction took place in vapor state (reactor bed 345−365 °C).

BM synthetized Pt/TiO_2 catalyst had a stable methylcyclohexane (MCH) conversion and 100% selectivity to toluene at 365 °C reactor temperature, whereas its IWI synthetized counterpart deactivated during the 15-hour-experiment. In lower temperature (345 °C) the two catalysts had nearly the same conversion at the end of the experiment.

As a result, a solvent-free, well reproducible, and scalable ball milling method for Pt-based LOHC dehydrogenation catalyst synthesis can be introduced.

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ORAL B-3

Selective Catalysis using Metal Nanoparticles Confined in Porous Materials

Jerrik Mielby[1], Dimitra Iltsiou[1], Emil Kowalewski[1], Søren Kegnæs[1]
[1]Department of Chemistry - Technical University of Denmark
Kemitorvet Building 207, 2800 Kgs. Lyngby, Denmark

Despite the great technological, environmental, and economic interests, general methods for the stabilization of metal nanoparticles against sintering are missing. However, for some specific systems, it has been achieved by optimizing the interaction of nanoparticles with a support material or by encapsulating the metal particles [1-3]. However, these known catalytic systems are generally rather expensive and difficult to synthesize, and they cannot be produced on an industrial scale.

Recently, we have developed several different catalytic systems where metal nanoparticles are confined in different porous materials, including zeolites [3,4,5], porous polymers (POP) [6], and carbon materials [7]. Here, we give an overview of the progress made in synthesizing metal nanoparticles confined in different porous materials and their application in catalysis. The encapsulation of metal nanoparticles in porous materials prevents the metal nanoparticle from sintering during a high-temperature catalytic reaction. Furthermore, the porous materials can also contribute actively to the catalytic reaction by improving the catalyst's activity or selectivity, for instance, by controlling the accessible or type of activity sites [3,5].

We have tested the produced materials as catalysts in different selective oxidation and hydrogenation reactions. As an example, nickel-encapsulated nanoparticles in zeolites are highly active in the methanation of carbon dioxide to methane [5,8]. Furthermore, the location of the metal particles has a significant influence on the catalyst activity. Additionally, the encapsulated other metal nanoparticles, like Cu, Ru, Pd, and Pt, were demonstrated to be highly active and selective in various gas-phase reactions, including catalytic oxidation of ethanol to acetaldehyde and hydrogenation of alkenes [9,10].

Furthermore, we have characterized the materials with various techniques, including SEM, in situ TEM, STEM, TEM tomography, XPS, XRF, BET, and XRD.

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ORAL B-4

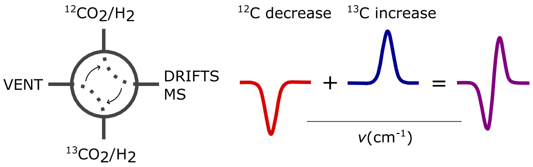
Unravelling a solid Mn-based catalyst for Reverse Water-Gas Shift reaction by modulation excitation

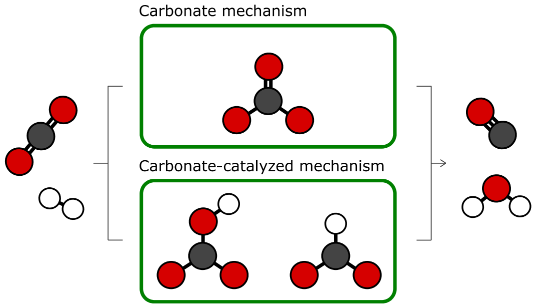
Mikkel Kock, Emil Kowalewski, Jerrik J. Mielby, Søren Kegnæs
Technical University of Denmark, 2800, Kgs. Lyngby, Denmark

Catalytic reduction of CO_2 to CO via the Reverse Water-gas Shift reaction is attracting renewed interest in producing more sustainable syngas. Many catalysts have been researched but often suffer from price and selectivity.[1]

In this work, we present a novel, active, and selective catalyst consisting of supported Mn, and we have shown that it can be improved significantly by doping it with a simple alkali promoter and can compete with top-of-the-shelf catalysts.

To understand this unique and dynamic catalyst, the reaction mechanism was studied with different operando infrared spectroscopy techniques.[2,3]





The steady-state spectroscopy under reaction conditions ($H_2/CO_2/He$ at 450 °C), showed that the surface was abundant with surface carbonate species on the catalyst's surfaces. But are they responsible for the great catalytic activity and selectivity?

To answer this question, the gas stream was periodically perturbated by excluding CO_2 and filtering the data by a modulation excitation algorithm. It did reveal that the short-lived and active species on the surface of the promoted catalyst were only bicarbonates and formates.[3] This signified that the reaction undergoes two different mechanisms dependent on whether the sample is promoted or not.

Experimental/methodology. The catalysts have been tested in a flow reactor equipped with a water condenser and an NDIR detector, which is tuned for CH_4, CO, and CO_2.

The operando IR studies were performed in a Nicolet iS50 FTIR spectrometer equipped with a Harrick Praying Mantis Cell with an Pfieffer Vacuum OmniStar MS.

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ORAL B-5

Characterization of Unmodified and Zn-modified ZSM-5 Zeolites with Temperature-programmed Desorption of Ammonia and Isopropylamine – An Initial Study

Ellen Järvinen, Jorge A. Velasco, Reetta Karinen, Riikka L. Puurunen
Department of Chemical and Metallurgical Engineering, Aalto University, Kemistintie 1, 02150 Espoo, Finland
e-mail: ellen.jarvinen@aalto.fi

Effective methods for analyzing the acidity of solid materials are advantageous in research related to zeolite catalysts, as they allow for a way to study the relationship between catalytic activity and material properties. Temperature-programmed desorption (TPD) of basic probe molecules, such as ammonia (NH_3-TPD) and isopropylamine (IPAm-TPD), is a group of acidity characterization methods commonly used for zeolites.[1] Automated TPD instruments requiring little operator input are available commercially, which makes TPD methods particularly accessible for routine acidity measurements.

NH_3-TPD is suitable for determining the combined Lewis and Brønsted acidity of a sample, while IPAm-TPD selectively yields the Brønsted acidity. The aim of this work was to study the acidity of zeolite samples with NH_3-TPD and IPAm-TPD and examine changes in the acidity after metal modification. NH_3-TPD and IPAm-TPD were performed with H-ZSM-5 samples with varying SiO_2/Al_2O_3 ratios and γ-Al_2O_3 using the Micromeritics AutoChem III 2930 instrument coupled to a MKS Cirrus 3 mass spectrometer.[2] Change in the acidity of a zeolitic sample due to Zn-modification was examined by comparing the NH_3-TPD and IPAm-TPD results of an unmodified H-ZSM-5-50 sample and a Zn-modified Zn/H-ZSM-5-50 sample prepared by atomic layer deposition (ALD).[3]

The NH_3-TPD and IPAm-TPD results showed logical trends with respect to the theoretical acidity of the tested H-ZSM-5 and γ-Al_2O_3 samples. The NH_3-TPD results of the Zn/H-ZSM-5-50 sample indicated changes in the Brønsted acidity of the material caused by the Zn-modification, as demonstrated in Figure 1a. The Zn/H-ZSM-5 sample also produced an unusual IPAm-TPD profile visible in Figure 1b, which was not explained by other results obtained in this work nor existing reports in literature.

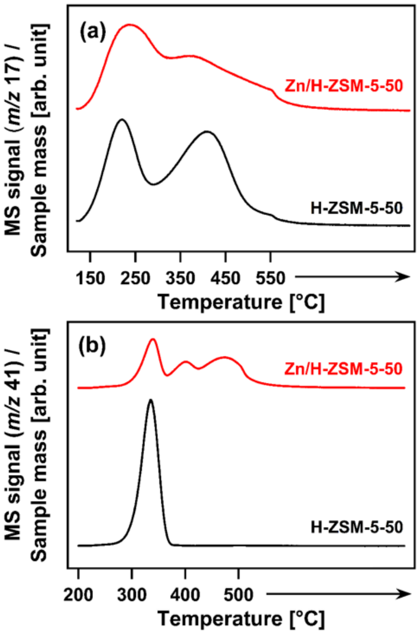

Figure 1. The mass spectrometer (MS) signal measured from unmodified and Zn-modified H-ZSM-5-50 during (a) NH_3-TPD (samples saturated at 120 °C, *m/z* 17 followed for NH_3) and (b) IPAm-TPD (samples saturated at 200 °C, *m/z* 41 followed for propylene).

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ORAL B-6

Investigating the mechanism of the iron-catalyzed ammonia synthesis

Simon I. Hansen[1], Anker D. Jensen[1], Jakob M. Christensen[1]*
[1]*Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark*
*jmc@kt.dtu.dk

The synthesis of NH_3 through the Haber-Bosch process is one of the most important and examined chemical reactions. However, the reaction pathway may not be fully understood despite the extensive research this reaction has undergone. It is widely accepted that the rate-limiting step of the process is the dissociative breakage of the N≡N triple bond[1]. However, early studies[2] has reported the presence of an H_2/D_2 isotope effect in NH_3 synthesis, which has been attributed to the hydrogen isotope affecting the number of free sites available for N_2 dissociation. This assumption has never been evaluated, but we here show that the N coverage on an industrial iron catalyst from Topsoe is very similar during steady-state conditions for both NH_3 and ND_3 synthesis (Figure 1A).

The isotope effect was studied in more detail at different H_2/D_2 ratios, which shows an increase in the overall rate with increasing D_2 content (Figure 1B). Although the presence of D_2 shifts the equilibrium, the isotope effect is a kinetic effect as the approach to equilibrium remains of similar magnitude at all the measured H_2/D_2-ratios albeit with a with a notable increase for moderate D_2 levels. The presence of the isotope effect therefore indicates that a rate-limiting step through an associative mechanism must exist. Such a pathway is also observed in nature, where the biological process, catalyzed by the enzyme nitrogenase, runs via an associative mechanism where the N_2 is protonated prior to internal bond breakage[3].

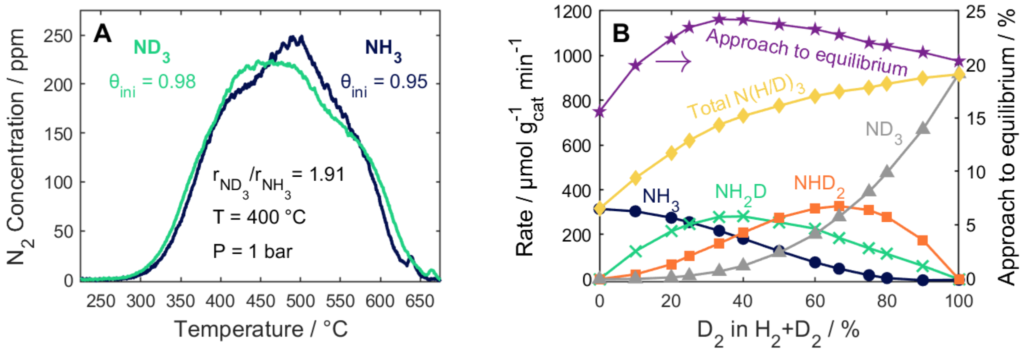

Figure 1 The H_2/D_2 isotope effect of NH_3 synthesis. **A:** TPD spectra obtained after steady-state NH_3 and ND_3 synthesis respectively at 400 °C, 200 NmL min^{-1} ($N_2/H_2 = 1/3$), 1 bar. Conditions: 2 °C min^{-1} ramp, 50 NmL min^{-1} Ar, 1 bar. **B:** Reaction rates for $N(H/D)_3$ synthesis performed with varying H_2/D_2-ratios at 400 °C, 1 bar and the corresponding approach to equilibrium (stars, secondary axis).

This work was supported by the Villum Foundation Center for Science of Sustainable Fuels and Chemicals, Villum Foundation V-SUSTAIN Grant 9455.

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ORAL B-7

Surface states governing activity and selectivity of Pt-based ammonia slip catalysts for selective ammonia oxidation

Vasyl Marchuk[1], Dmitry I. Sharapa[2], Jan-Dierk Grunwaldt[1,2],
and Dmitry E. Doronkin[1,2]*
*[1]Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstr. 20, 76131 Karlsruhe, Germany; [2]Institute of Catalysis Research and Technology (IKFT), KIT, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. *E-mail: dmitry.doronkin@kit.edu*

The use of ammonia as a carbon-free energy carrier alternative to hydrogen[1] would require efficient ammonia slip catalysts (ASCs) to prevent its potential release into the atmosphere. Typical Pt/Al_2O_3 ASCs were studied in selective oxidation of NH_3 to N_2 in order to determine Pt species responsible for activity and selectivity under conditions similar to those of realistic emission control applications.[2] For this purpose, the measurements of reaction rates and apparent activation energies at different reaction feed compositions were combined with *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and *operando* X-ray absorption spectroscopy (XAS). XAS results were interpreted based on density functional theory modelling, XAS spectra calculations and machine-learning-based techniques. This approach allowed to reveal three main chemically different states of Pt under reaction conditions corresponding to varying performance of the catalyst (see fig. 1). At low temperatures (below approx. 150 °C), oxygen covering Pt surface poisoned the catalysts. It needed to be at least partially reduced during heating in the reaction mixture for a light-off to begin. During a light-off, at 150–300 °C, Pt surface was more reduced and mostly covered with NH_x species. This state led to the highest N_2 selectivity. When ammonia was completely converted at elevated temperatures, its surface coverage dropped, and Pt was more available for re-oxidation. However, oxygen did not entirely cover the surface and was rather likely to diffuse into Pt subsurface. This state did not prevent ammonia activation but shifted the selectivity towards undesired N_2O and NO_x due to higher probability of surface NH_x species to interact with adsorbed O.

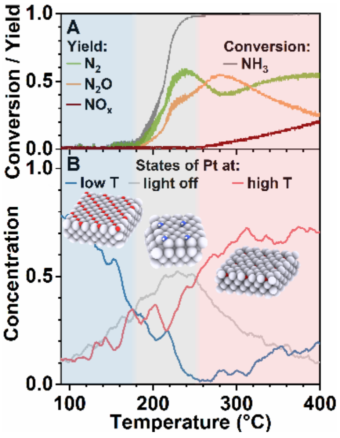

Figure 1. Species in top layers of Pt governing its catalytic performance. Adapted from ref. [2] licensed under CC-BY-NC-ND 4.0. Copyright 2024. https://creativecommons.org/licenses/by-nc-nd/4.0/.

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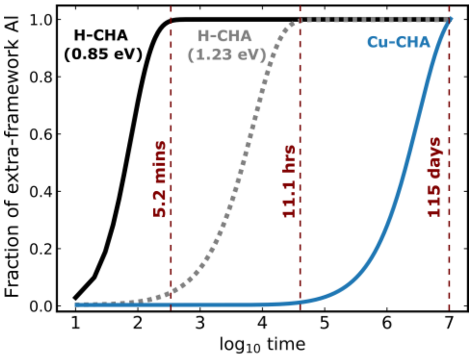
Effect of copper on the hydrothermal stability of Cu-CHA

Shivangi Singh[1,2*], Ton V. W. Janssens[2], and Henrik Grönbeck[1*]
[1]*Department of Physics, Competence Centre for Catalysis,*
Chalmers University of Technology, Sweden
[2] *Umicore Denmark ApS, DK-2970 Horsholm, Denmark*

NH_3-SCR is a leading technology for diesel emission control. Cu-CHA zeolites are preferred catalysts due to their activity and hydrothermal stability linked to dealumination at high temperatures in the presence of water vapor.[1] Cu-CHA has better stability than H-CHA. [2]



We used DFT calculations to investigate dealumination in H-CHA and Cu-CHA zeolites, involving four hydrolysis steps and extra-framework aluminum condensation. In H-CHA, a single product, $Al(OH)_3H_2O$, formed with hydrolysis barriers below 0.90 eV. In Cu-CHA, we observed two products: $Al(OH)_3H_2O$ removed from the framework and Cu-Al species bound to the framework. The 3rd and 4th hydrolysis step barriers were notably high (1.8 and 1.54 eV), which may explain the higher temperature required for dealumination in Cu-CHA. Additionally, Cu-CHA exhibits a preference for the formation of Cu-Al species over complete dealumination due to lower barrier associated with this step. To understand, the kinetics of the reaction we constructed microkinetic model. The microkinetic model revealed a clear temperature difference in the onset of dealumination for H-CHA and Cu-CHA. These finding suggests that dealumination begins at lower temperatures in H-CHA. Additionally, the time evolution of the $Al(OH)_3H_2O$ coverage at 923K reveals that the process of dealumination is significantly faster for H-CHA as compared to Cu-CHA. The first hydrolysis step significantly dictates the kinetics of H-CHA. We observed difference in the barrier for this step depending on the aluminum distribution. When we incorporated these barrier values into a Microkinetic model, we noted a noticeable delay in the reaction when the aluminum distribution associated with the highest barrier was used.

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ORAL B-9

Probing the reactive intermediates in catalytic CO_2 hydrogenation with Ni/Al_2O_3 catalysts by Modulation Excitation Spectroscopy

Emil Kowalewski, Mikkel Kock, Dimitra Iltsiou, Jerrik Mielby, Søren Kegnæs
Technical University of Denmark, Kgs. Lyngby, 2800, Denmark
e-mail: emiko@dtu.dk

Constant and uncontrolled development has led modern civilization to a breakthrough point in which further operating on the current principles may lead to a climate catastrophe. The CO_2 concentration in the atmosphere has reached an alarming level and the detrimental effects are already visible[1,2,3].

CO_2 hydrogenation via Reverse Water-Gas Shift reaction (RWGS) and methanation (the Sabatier reaction) is one of the most promising solutions to this problem. However, there is still a strong need to search for better and more cost-effective catalysts. The development of such catalysts requires a thorough investigation of the crucial structural parameters combined with a detailed understanding of the reactive surface intermediates.

In this study, we prepared three archetypical Ni/Al_2O_3 catalysts that showed significantly different catalytic activity and selectivity for CO_2 hydrogenation, depending on the calcination and reduction temperature. After thorough characterization (N_2 physisorption, chemisorption, XRD, XPS, SEM, TEM), we applied the combination of Modulation Excitation-Phase Sensitive Detection-Diffuse Reflectance Infrared Fourier Transform Spectroscopy (ME-PSD-DRIFTS) and Steady State Isotopic Kinetic Analysis (SSITKA) to identify key reactive intermediates and spectator species.

Our experiments showed that even minor changes in the pretreatment procedure will have a pronounced effect on the catalytic performance in CO_2 hydrogenation. Moreover, we demonstrated that bicarbonates and formates are key reactive intermediates, which undergo different transformations, depending on the metal active phase nanoparticles size. All of the obtained results proved that CO_2 hydrogenation occurs in an associative and consecutive reaction pathway that is highly structure-sensitive[4].

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ORAL B-10

Chemical imaging of Carbide formation and its effect on Alcohol selectivity in Fischer Tropsch Synthesis on Mn-doped Co/TiO_2 pellets

Danial Farooq[1,2], Andrew M. Beale[1,2, 3]

[1]*Department of Chemistry, University College London, 20 Gordon Street, WC1H 0AJ, UK*

[2]*Research Complex at Harwell, Rutherford Appleton Laboratories, Harwell Science and Innovation Campus, Harwell, Didcot, OX11 0FA, UK*

[3]*Finden, Building R71, Harwell Campus, Oxfordshire, OX11 0QX, United Kingdom*

X-ray diffraction/scattering computed tomography (XRS-CT) were used to create 2D images, with 20 µm resolution, of passivated Co/TiO_2/Mn Fischer Tropsch catalyst extrudates post-reaction after 300 h on stream under industrially relevant conditions. This combination of scattering techniques provided unprecedented insights into both the spatial variation of the different cobalt phases and the influence of increasing Mn loading has on this. It also demonstrated the presence of a wax coating throughout the extrudate and its capacity to preserve the Co/Mn species in their state in the reactor. Correlating these findings with catalytic performance, highlights the crucial phases and active sites within Fischer Tropsch catalysts required for understanding the tunability of the product distribution between saturated hydrocarbons or oxygenate and olefin products. In particular a Mn loading of 3 wt. % led to an optimum equilibrium between the amount of hexagonal close-packed Co and Co_2C phases resulting in maximum oxygenate selectivity. XRS-CT revealed Co_2C to be located on the extrudates' periphery, while metallic Co phases were more prevalent towards the centre, possibly due to a lower [CO] ratio there. Reduction at 450 °C of a 10 wt. % Mn sample resulted in $MnTiO_3$ formation which inhibited carbide formation and alcohol selectivity. It is suggested that small MnO particles promote Co carburisation by decreasing the CO dissociation barrier and the Co_2C phase promotes CO non-dissociative adsorption leading to increased oxygenate selectivity. This study highlights the influence of Mn on catalyst structure and function and the importance of studying catalysts under industrially relevant reaction times.

ORAL B-11

Avoiding reactions to quantify diffusion of alkenes in zeolites: a new benchmark set by Temporal Analysis of Products (TAP)

Vladyslav Shostak[1], Jenna Mancuso[2], Evgeniy Redekop[1],
Veronique Van Speybroeck[2], and Unni Olsbye[1, *]

[1] Department of Chemistry, Centre for Materials Science and Nanotechnology (SMN), University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway
[2] Center for Molecular Modeling (CMM), Ghent University, Technologiepark 46, 9052 Zwijnaarde, Belgium

Experimental studies of alkene adsorption and intracrystalline transport in zeolites under catalysis-relevant conditions are hampered by their oligomerization activity[1]. The Temporal Analysis of Products (TAP) technique[2,3] offers the advantage of high-vacuum conditions and nano-amounts of injected gas that minimize alkene oligomerization even at high temperatures. In this work, we applied TAP to study the transport of C_2-C_4 hydrocarbons in different zeolites with MFI topology within 100-400 ˚C temperature range. In acidic H-ZSM-5, the transport of alkenes is greatly hindered in comparison to alkanes due to the stronger adsorption and larger microporous diffusion delay. Measured enthalpies of adsorption in H-ZSM-5 indicate predominantly π-complex formation between alkenes and Brønsted Acid Sites (BAS) and strength of adsorption increases in series: $C_2H_4 < C_3H_6 \leq$ cis-$C_4H_8 <$ iC_4H_8. Also, it can be concluded that the presence of Brønsted acidity inside zeolite channels significantly impedes alkene transport since the diffusion energy barrier is consistently larger for alkenes in H-ZSM-5 ($\geq$ 48 kJ/mol) than in Silicalite-1 (< 20 kJ/mol). This is in contrast to the cage-window CHA structure, in which BAS accelerate alkene transport in comparison with alkanes[4]. Measured adsorption and diffusion data showed good consistency with computational studies (DFT, QTAIM, MD), however, intracrystalline diffusivity for alkenes in acidic ZSM-5 is several orders of magnitude lower than estimates provided by molecular dynamic simulations. These findings set a new benchmark in systematic studies of intracrystalline diffusion in microporous materials, especially when it comes to highly reactive alkene probe molecules relevant for catalysis.

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ORAL B-12

Understanding Water-Induced Deactivation of Palladium Based Methane Oxidation Catalysts

S. Mossin[1], R. L. Mortensen[1,2], K. H. Pedersen[2], H.-D. Noack[2], J. Mielby[1]
[1] *Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, Kemitorvet 207, 2800 Kgs. Lyngby, Denmark.*
[2]*Umicore Denmark, Kogle Allé 1, 2970 Hørsholm, Denmark*

Introduction: Catalysts for complete methane oxidation suffer from water-induced deactivation due to the high concentrations of steam in the exhaust from natural gas-fired large engines. It is commonly accepted that water deactivates the surface by covering the active sites with hydroxyl groups.[1] Here we show through a series of CH_4-TPR and activity measurements that the deactivation takes place by two distinguishable pathways. A reversible deactivation due to surface coverage (inhibition) and an irreversible deactivation due to a structural change in the palladium oxide.

Methods: Palladium oxide (3 wt% Pd) on a modified alumina support was tested in a dedicated catalytic setup fitted with water injection (0-20 vol% water) and methane detector (FID) and with temperature and pressure control (up to 5 bar) during methane oxidation. The catalyst can be completely regenerated using pulses of 1000 ppm methane.[2] CH_4-TPR data was obtained using the same setup as for catalyst testing.

Results: Irreversible deactivation is only taking place when the catalyst is converting methane. The CH_4-TPR performed both with and without water reveals a significant shift of the reduction temperature of palladium oxide after the irreversible deactivation and is shown to be the best method to follow the deactivation. Kinetic modelling shows that the rate of deactivation of the catalyst depends on both the water concentration and on the rate of methane conversion. Pd L_3-edge XAS show a significant decrease in the white line intensity upon deactivation of the catalyst.

Conclusions: We propose that the irreversible deactivation at wet oxidizing conditions is due to the palladium on the alumina surface dispersing into inactive surface structures and that the fast regeneration at reducing conditions is due to the palladium agglomerating/ripening again to catalytically active particles. This interpretation is in accordance with all the data.[3]

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ORAL B-13

Effect of hydrothermal aging on Cu-CHA catalysts for NH_3-SCR

Vasco A. C. Saltão[1,2 *], Valentina Crocellà[2], Silvia Bordiga[2], Gloria Berlier[2], Ton V.W. Janssens[3], Reza K. Abasabadi[2,3]
[1]*Umicore AG & Co KG, Autom. Catal. Div., Rodenbacher Chausee 4, Hanau, Germany*
[2]*University of Turin, Departm, of Chem. & NIS Centre, Via P. Giuria 7, Turin, Italy*
[3]*Umicore Denmark ApS, Res. & Tech. Autom. Catal., Kogle Alle 1, Hørsholm, Denmark*
**Presenter's e-mail address: vascoantnio.correiasalto@unito.it*

Combustion engines are usually followed by a catalytic converter of harmful NO_X into N_2 and H_2O via the selective catalytic reduction by NH_3 (NH_3-SCR). Cu-CHA has good catalytic performance for this reaction at low temperatures,[1] which is relevant given the increasing fuel efficiency which should lower combustion temperatures.[1] Cu-CHA is hydrothermally stable but can still dealuminate after prolonged exposure to the hot and humid exhaust conditions,[2] reducing its catalytic efficiency by removing the framework charges that stabilize the active Cu sites through dealumination. Therefore, the goal of this project is to study Al and Cu structures after hydrothermal aging, and how differently dealumination affects zeolites with different Cu and Al contents.

Fresh and hydrothermally aged (650 °C for 100 hours) CHA samples (Si/Al ratio 6.7 and 15, 0, 0.8 and 3.2 Cu wt%) were characterized by XRD, in situ IR spectroscopy, Ar volumetric measurements and tested in the NH_3-SCR reaction. Volumetric CO adsorption was used to titrate Cu^I ions after reduction in NH_3.[3] Aging did not affect crystallinity but did in turn increase surface area and micropore volume; most of the Brønsted sites were removed, while a sizable amount of reducible Cu ions was retained, which does not seem to correlate with the catalytic activity. Catalysts with Si/Al = 6.7 were more extensively deactivated with aging than those with Si/Al = 15 (Figure 1).

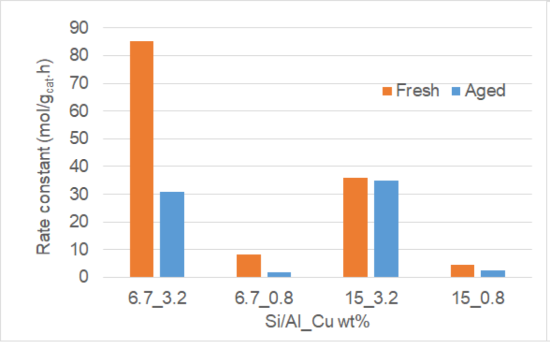

Figure 1 – Rate constants in NH_3-SCR at 200 °C of fresh and aged Cu-CHA samples

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ORAL B-14

Na-jarosite based catalysts for water treatment applications

Miia Kokkonen, Hanna Runtti, Tao Hu, Ulla Lassi, Anne Heponiemi
Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland

Jarosite is an iron containing sulfate mineral, which is formed in ore deposits by the oxidation of sulfides. Therefore, it is produced as a side stream in the purification and refining of zinc. In addition to Fe and S, jarosite can include As, Ni and Pb, which is the reason why it is treated as a hazardous waste[1]. However, due to its high iron content, jarosite is an interesting material for catalytic experiments.

In this research, Na-jarosite was used as a catalyst in the catalytic wet peroxide oxidation (CWPO). The powdered material was first heat treated at five different temperatures namely 105, 300, 500, 700 and 900°C under atmospheric air for 2h. The X-ray diffraction (XRD) analysis of heat-treated materials (Fig.1) reveals the existence of Fe_2O_3 at 700°C and 900°C treated samples. Moreover, according to X-ray fluorescence (XRF) analysis heat treatment decreased the concentration of S from 15 to 1.3 wt.% at temperature range 105 – 900°C and purified the material so, that the Fe concentration increased to 48 wt.% for sample heated to 700°C. All heat-treated Na-jarosite samples were active in the CWPO of aquatic solution of bisphenol A 60mg/l at 50°C for 3h with the catalyst concentration of 4g/l while the oxidant (H_2O_2) concentration was 0.075 wt.%.

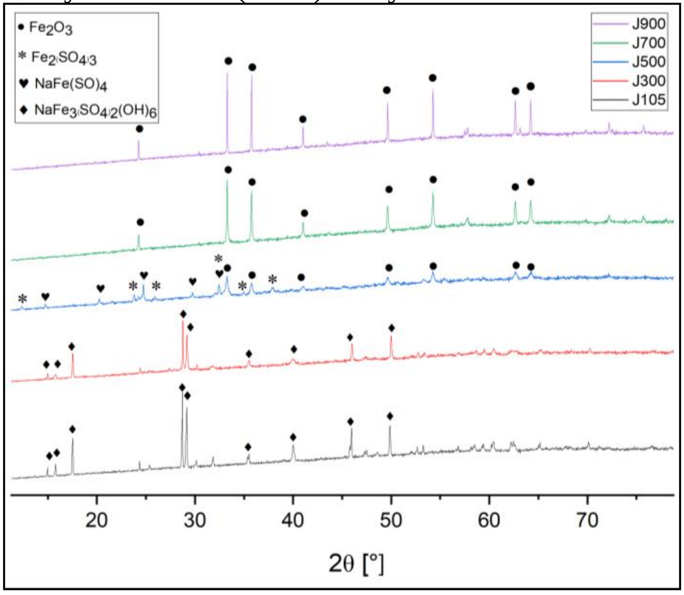

Fig.1. XRD patterns of heat-treated Na-jarosites.

The most promising material was the Na-jarosite heat-treated at 700°C which showed 100% removal of BPA also at reaction temperature of 20°C and with catalyst concentration of 2 g/l. The possible leaching of iron and sulfate was studied from oxidized water samples. It was observed that the heat treatment at 700 and 900°C prevented the leaching of iron and decreased the leaching of sulfate compared to samples heat-treated at lower temperatures. As a conclusion, Na-jarosite is a promising material for catalytic water treatment applications, but more research is needed to improve the stability of the material.

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ORAL B-15

Catalytic aftretretment systems for combustion exhaust gases from hydrogen, ammonia and e-HC engines

Teuvo Maunula, Kauko Kallinen and Thomas Wolff
Dinex A/S, Catalyst development, Middelfart, Denmark

International low or zero Green House Gas (GHG) emission targets create challenges for the industry developing combustion engines. In addition to electric vehicles and fuel cells, carbon-free fuels offer also an opportunity to decrease CO_2 emissions, particularly in heavy-duty applications. Hydrogen produced by green electricity is a key fuel resulting in carbon (CO_2) free emissions [1]. Currently, ammonia is receiving more interest among green fuels as an energy-intense hydrogen carrier (e.g. marine). Synthetic hydrocarbon fuels (methanol, e-diesel) produced from carbon capture and green hydrogen is a flexible route for future combustion and emission control. Renewable biofuels (natural gas, diesel, ethanol) is also applied in an interim period before carbon-free applications. Catalytic methods for these emission removal were reviewed in this presentation.

Even if particulate emissions will be low with carbon-free fuels, new fuels as large scale are causing new challenges for combustion but also for emission removal based on catalyzed aftertreatment systems (ATS). New emission legislations will include limits for NH_3, N_2O and aldehydes. A high water content (15-25%) in H_2 and NH_3 engine exhaust is challenging for zeolite-SCR catalysts efficient in diesel applications. Therefore, metal oxide based SCR catalysts (e.g. vanadium) have received more attention again. H_2 is planned both for heavy- and medium-duty applications, where lean combustion results often in lower exhaust gas temperatures than e.g. with diesel fuel. Twin-SCR and passive NO_x storage catalysts (NSC) by adsorption-desorption were resulted in higher NO_x conversions in simulated exhaust gases at low temperatures (100-200°C), before an efficient use of NH_3-SCR catalysts above 200°C. Even if limited efficiency and higher H_2/NO_x requirements (→ fuel economy), H_2-SCR on modified Pt and Pd catalysts was proven to create additional NO_x conversion below 150°C.

Higher ammonia emissions at low temperatures and higher N_2O emissions due to nitrogen containing fuel are the challenges in ammonia engines, which are planned for marine applications. At higher temperatures, ammonia emissions are low and thermally formed NO_x was removed with SCR (e.g. V-SCR) with additional NH_3 as a reductant and the assistance of selective ammonia oxidation catalyst. The formation of stable N_2O is best to prevent already in combustion, when N_2O decomposition catalysts require practically above 400°C. Hydrogen, HC and aldehyde emissions from e- and biofuels (H_2, methanol, ethanol, natural gas) are removed efficiently on PtPd based oxidation catalysts, except methane which removal above 400°C in lean required particular methane oxidation catalyst (MOC). Particular solutions with integrated properties in catalytic units were shown to cut both low and high temperature emissions (NH_3, NO_x, N_2O, HCs, H_2).

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Influence of Acidic and Structural Properties of Al-SBA-15 on the Kinetic Rates of Hexene Oligomerization

Moritz N. Link[1], Martin Høj[1], Pablo Beato[2], Martin D. P. Sørensen[2], Anker D. Jensen[1]
[1]*DTU Chemical Engineering, Technical University Denmark, 2800 Kgs. Lyngby, Denmark*
[2]*Topsoe A/S, 2800 Kgs. Lyngby, Denmark*

Oligomerization of olefins has gained significant importance in recent years regarding the decarbonization of the transport sector and especially in the production of sustainable aviation fuels[1]. Although the demand for jet fuel is high, strict regulations on its physical and chemical properties tailor its composition to a specific mix of linear, branched, and aromatic hydrocarbons[1,2]. Facilitating the oligomerization through acid catalysis is beneficial, as the underlying carbenium ion mechanism is reported to support branching and aromatization reactions, while still giving good control of selectivity[3]. Especially pentene and hexene are interesting reactants, as fewer oligomerization steps are necessary to achieve the targeted jet fuel range hydrocarbons, compared to shorter olefin reactants[2]. Regarding the catalyst, it has been found that acidity and pore properties are the governing characteristics. The microporous H-ZSM-5 zeolite is not optimal due to diffusion limitations, particularly for the larger hydrocarbons produced during oligomerization[3,4]. In contrast, mesoporous catalysts, such as Al-SBA-15 are not restricted by diffusion limitations, making them an attractive choice for olefin oligomerization towards jet fuel[4]. However, the understanding of the correlation and interplay between acidic and structural properties remains limited, highlighting the necessity for kinetic studies[3,4].

In this study, the influence of acidity and structural properties of mesoporous Al-SBA-15 has been evaluated based on the kinetic rates of 1-hexene dimerization. Samples with various Si/Al ratios have been synthesized and subjected to identical reaction conditions of a temperature of 473 K, pressure of 30 bar and low conversion by adjusting the weight hourly space velocities. Furthermore, Al-SBA-15 with similar Si/Al ratios, but different structural characteristics have been synthesized and studied under the same conditions. The findings of this study give insight into the initial step of oligomerization, assisting the development of a kinetic model for jet fuel production from olefins.

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ORAL B-17

Homogeneous catalytic peroxidation of cyclohexane over Cu-*N,N,N,N* complexes: Mechanistic insight by copper intermediates characterization

Mouhammad Abu Rasheed[1], Ning Cao[2], Isabelle Gerz[1,3], Gabriele Deplano[4], Matteo Signorile[4], Ainara Nova[2], Erlend Aunan[1], Raquel J. Rama[1], Matteo Bonomo[4], Sergio A. V. Jannuzzi[3], Mohamed Amedjkouh[1], Serena DeBeer[3], Silvia Bordiga[4], Unni Olsbye[1]
[1]*Centre for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0315 Oslo, Norway.*
[2]*Hylleraas Center for Quantum Molecular Sciences, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0315 Oslo, Norway.*
[3]*Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34–36, 45470 Mülheim an der Ruhr, Germany.*
[4]*Department of Chemistry and NIS Interdepartmental Center and INSTM reference center, University of Turin, via Pietro Giuria 7 and via Gioacchino Quarello 15/A, I-10125 and 10135 Turin, Italy.*

The ability of some copper-containing enzymes (e.g., pMMO and LPMO) to oxidize C–H bonds in methane and polysaccharides[1–4] has inspired the catalysis community to mimic these systems by introducing synthetic copper-based catalysts. Several copper complexes were developed by our group as potential catalysts for C–H activation,[5] using H_2O_2 as co-substrate.

The oxidation is believed to be driven by a Fenton-like mechanism, where H_2O_2 splits over the copper site forming $^{\bullet}OH$, $^{\bullet}OOH$ radicals.[6] However, the fate of the active site and the copper intermediates involved are still poorly understood. The versatile variation in the organic moieties attached to copper as well as the nuclearity of the metal site[7] have led to different catalytic cycles being reported. While some report a Cu(I)/Cu(II) cycle,[8] others suggest Cu(II)/Cu(III) is involved.[6]

In this study, two Cu-*N,N,N,N* complexes with identical structure but different initial oxidation state, Cu-(I) and Cu-(II), were investigated for the peroxidative oxidation of cyclohexane (CyH) to the corresponding alcohol and ketone (Fig. 1). Besides the Fenton-like mechanism that was observed in this work via selective testing and screening studies, the copper species involved were characterized *in situ* and *ex situ* using multiple techniques. A DFT-based catalytic cycle was proposed in line with experimental data supporting a Cu(I)/Cu(II) redox cycle as the main pathway.

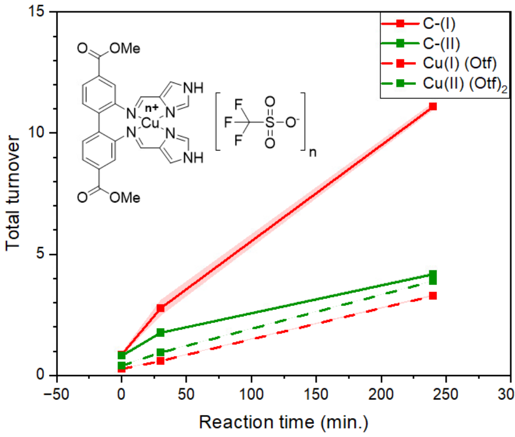

Fig-1. Reactivity of copper complexes C-(I) and C-(II) for cyclohexane peroxidation compared to the corresponding triflate salts (3 replicates). Solvent: acetonitrile, 25°C, 4h, Cu:CyH:H_2O_2 is 4:155:1370 mM.

Cu intermediate characterisation (UV-Vis, XAS, NMR, Cyclic voltametry) show that structural changes of the cooper site take place during the redox cycle. MS / CID-MS data suggest that oxidation of the Cu site by H_2O_2 leads to LCu(II)-OO(•/H) formation. H_2O oxidation, on the other hand, induces imine-to-carbinolamine conversion, slowly decomposing the complex through hydrolysis and explaining the experimental finding of a deactivating effect of H_2O. Both NMR and MS indicate imine hydrolysis as a first step leading to complex deactivation/precipitation.

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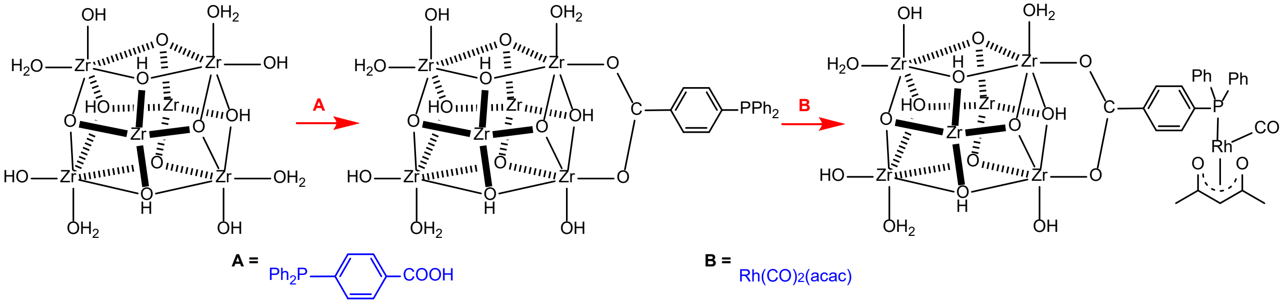
ORAL B-18

Gas phase hydroformylation with the post-modified Metal-Organic Framework NU-1000

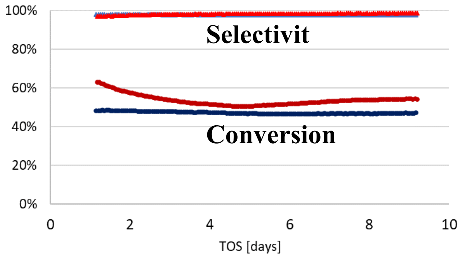
Morten Frøseth, Silje F. Håkonsen, Bjørnar Arstad, Terje Didriksen, Knut Thorshaug and Richard H. Heyn
SINTEF Industry, Department of Process Technology, P. O. Box 124 Blindern, 0314 Oslo, Norway

Hydroformylation (HF), the reaction of alkenes, CO and H_2 to aldehydes, is one of the largest applications of homogeneous catalysis in the chemical industry.[1] High (> 95 %) alkene conversions and aldehyde selectivities are achieved with these catalysts. Because of the industrial importance of this reaction, there has been effort over many years to find heterogeneous catalysts that match this activity, to eliminate the intrinsic process challenge of separation of catalyst from product.

Metal-organic frameworks (MOFs) are materials that provide stable, porous, uniform, isolated and atomically precise structures and are very well suited platforms for active metal catalysts[2] and for solid-gas catalysis.[3] The MOF NU-1000 was chosen as support because of its large pore sizes (30 Å)[4] and the availability of a large scale synthesis.[5] The homogeneous HF catalyst precursor $Rh(CO)_2(acac)$ was successfully impregnated into NU-1000 via reaction of $Ph_2P(4\text{-}C_6H_4COOH)$ with the Zr_6 units of NU-1000, followed by phosphine coordination (Figure below).



These Rh@NU-1000 materials have been tested as heterogeneous gas-phase catalysts for the HF of both ethene and propene. For ethene, conversions of 50 % and selectivity to propionaldehyde > 95 % have been observed, with catalyst stability of at least 9 d (Figure right). Details of the catalysis for the HF of both ethene and propene will be presented.



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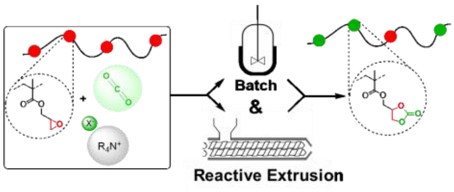
ORAL B-19

Carbonatation of ethylene - glycidyl methacrylate based polymers using carbon dioxide as reagent: from batch to reactive extrusion

Véronique Dufaud,[1] Bruno Guerdener,[1,2,3] Jean Raynaud,[1] Vincent Monteil,[1] Véronique Bounor-Legaré,[2] Yvan Chalamet[3]
[1]*Univ. Lyon, CNRS, UMR 5128, Catalysis, Polymerization, Processes and Materials, 43 Bd du 11 novembre 1918, F-69616 Villeurbanne, France.*
[2]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-69622 Villeurbanne, France.*
[3]*Univ Lyon, CNRS, UMR 5223, Ingénierie des Matériaux Polymères, Université Claude Bernard Lyon 1, INSA Lyon, Université Jean Monnet, F-42023 Saint-Etienne Cédex 2, France.*

The major socio-economic challenges for the plastics industry are to move from a linear economic model to a circular one to face resource depletion. One of the main ways to enable this economic transition is to introduce polarity onto ethylene unit-rich copolymers by post-modification targeting further recycling or even better upcycling.



Herein, we report on the carbonatation of semi-crystalline [ethylene–glycidyl methacrylate]-based polymers using CO_2 as a reagent and quaternary ammonium salts as organocatalysts to transform the polymers' epoxide pendant groups into cyclic carbonate moieties.[1] Studies in batch reactor were first undertaken to assess the kinetics, dependence on catalyst and optimal reaction parameters. For the first time, this reaction was successfully transposed to reactive extrusion under CO_2 using a dedicated co-rotating twin-screw extruder to allow for CO_2 containment within the polymer melt. This solvent-free reactive process is perfectly adapted to semi-crystalline and/or high-Tg polymers. After optimization, a yield of up to 78 % of cyclic carbonate could be obtained with tetrahexylammonium bromide (7.5 mol% vs. epoxy content, $\sim$30 g h^{-1} of catalyst) at 150 °C with an industry-compliant polymer flow rate of 2 kg h^{-1}. The reactivities of three Lotader® grades were compared in batch and in extruder and their modifications were also successful. These modified [cyclic carbonate + epoxide]-featuring polymers may have several direct applications e.g. as intermediates for the synthesis of polyhydroxyurethanes, as reactive compatibilizers for blends of polyolefins with polyamides, polyesters, polyacids and polycarbonates, and could also display good permeability properties for membranes. The enhanced sustainability of our reactive extrusion process (kg-scale production of functionalized polymers in a continuous fashion under solvent-free conditions using CO_2 as a direct C1 source) could pave the way for the post-functionalization of other industrially-relevant (co)polymers.

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ORAL B-20

Direct syngas to light olefins using supported ZnO and acidic CHA catalysts

Michael T. Nikolajsen[a,b], Niels Christian Schjødt[b], Uffe V. Mentzel[b], Jens Sehested[b], Rasmus Y. Brogaard[b], Jacob M. Christensen[a] and Martin Høj[a]
[1] Department of Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, 2800 (Denmark). [2]Topsoe A/S, Kgs. Lyngby, 2800 (Denmark). e-mail: mitni@kt.dtu.dk

In 2019, the production of ethylene- and propylene-based plastic products reached 200 million tons. Substituting fossil-derived with CO_2-derived monomers, could potentially store around 600 million tons of CO_2[1]. Bi-functional oxide-zeotype catalysts have demonstrated potential for selectively generating light olefins from CO_2, although current CO_2 to hydrocarbon conversion remain low[2-3]. Several ZnO-based catalysts, including ZnO/ZrO_2, $ZnAl_2O_4$, and $ZnGa_2O_4$, were synthesized and evaluated for methanol synthesis activity. Characterization techniques such as ICP, XRD, BET, XAS, XPS, and TEM were employed to understand the structure-activity relationship, aiming to enhance the low CO_2-to-hydrocarbon conversion when combined with zeotype/zeolite catalysts. The study revealed that the methanol synthesis activity of ZnO-based catalysts depended on Zn-loading. Optimized activity was achieved at loadings allowing the creation of a surface-supported ZnO phase (Fig 1 (a)). These sites exhibited high selectivity to methanol, and their concentration controlled CO_2 conversion. At high Zn-loadings, less active crystalline ZnO phases were formed removing the highly active surface ZnO phase. In-situ MES-EXAFS studies indicated that the electron-deficient surface ZnO phase on ZrO_2 could partially reduce under changing reductive and oxidative atmospheres, potentially contributing to the high activity of the ZnO/ZrO_2 catalyst. In-situ DRIFTS analysis revealed that methanol production followed a formate pathway, where CO_2 adsorbed as carbonate, hydrogenated into formate, and further transformed into methoxy, and finally desorbing as methanol (Fig. 1 (b)). Combining ZnO-based catalysts with H-SAPO-34 resulted in a light olefin selectivity > 70 carbon mol%, however, at a low CO_2-to-hydrocarbon conversion (Fig. 1 (c)). Operating at different temperatures and pressures showed a trade-off between selectivity and activity. Co-feeding CO limited the reverse-water-gas-shift reaction rate, improving activity by removing water. The bi-functional catalysts exhibited a longer lifetime than the methanol-to-olefin process. However, solid-state titration of Zn onto the solid acid, observed through TEM, and metal oxide sintering, identified via XRD, reduced the CO_2 conversion and the light olefin selectivity with time on stream.

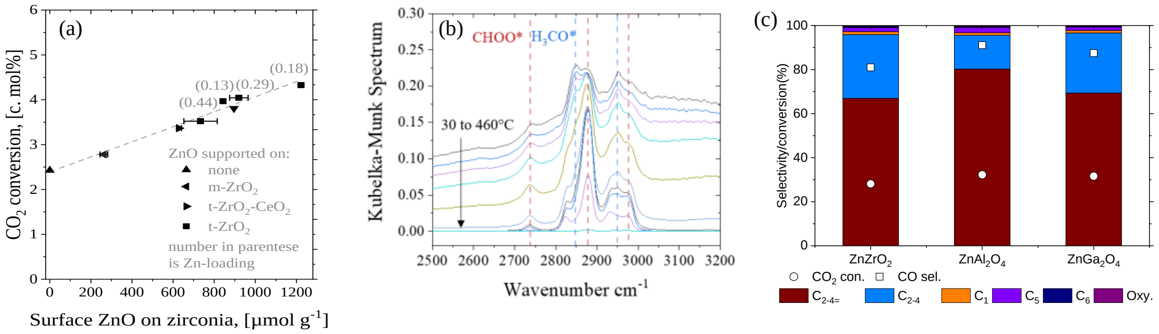

Fig. 1. (a) The CO_2 conversion with the concentration of surface ZnO on Zirconia at P = 50 bar, $CO_2/H_2/Ar$ = 20/60/20, GHSV = 50000 Nml g^{-1} h^{-1}. (b) DRIFTS He-TPD after catalyst treatment in syngas (c) CO2 conversion, CO selectivity and hydrocarbon distribution at T = 400 °C, P = 10 bar, $CO_2/H_2/Ar$ = 23/69/8, GHSV = 4980 Nml g-1 h-1, catalyst/SAPO-34 = 4/1 wt. ratio.

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ORAL B-21

Highly selective production of isobutene from syngas – Isosynthesis over zirconia

Laura Keskiväli[1], Niko Heikkinen[1], Rasmus Ikonen[2], Bhumi A. Baraiya[2], Ville Korpelin[2], Toni Kiljunen[2], Karoliina Honkala[2], Juha Lehtonen[1], Matti Reinikainen[1]
[1] VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Finland
[2] Department of Chemistry, Nanoscience Center, University of Jyväskylä, P.O. Box 35, 40014, Finland

Introduction. There is an ever-increasing need for sustainable fuels and chemicals. Many of the technologies for the manufacturing of these products such as the Fischer–Tropsch synthesis suffer from poor selectivity. Isosynthesis is a highly selective process for the manufacture of isobutene and -butane, discovered already in the 1940s [1]; however, interest towards the isosynthesis process has been fluctuating. Over the decades, the extreme reaction conditions (about 300 bar) and harmful ThO_2 catalysts have been replaced by more feasible and practical alternatives, while also increasing the catalytic performance [2]. Due to these positive developments and recent demand for selective renewable feedstock conversion routes, isosynthesis has again become an interesting topic. Isobutane can be utilized, e.g., as an intermediate for the selective production of jet fuel range hydrocarbons. This paper reports both experimental and computational results of the isosynthesis reaction over a range of zirconia-based catalysts.

Experimental/methodology. Monoclinic and tetragonal ZrO_2, as well as Ce-, La- and Y-doped ZrO_2, were tested for the isosynthesis reaction in a tubular fixed bed reactor. Reaction conditions varied between 400–450 °C, 20–45 bar and GHSV 2000–3000 h^{-1}. To better understand the reaction mechanism and catalyst properties affecting catalyst activity, the isosynthesis reaction network was also explored computationally using vdW-corrected DFT calculations. Monoclinic $ZrO_2(-212)$ was chosen as the model surface to account for the possible role of edge sites.

Results and discussion. Monoclinic ZrO_2 (450 °C, 45 bar, GHSV = 2000 h^{-1}) performed best out of the tested catalysts, producing iso-C4-hydrocarbons with a high selectivity of 33–40 mol-% and up to 75% CO conversion, while tetragonal ZrO_2 was much less active and selective. The computational results for the monoclinic ZrO_2 mechanistic pathway agree with the experimental findings. In the computational work, the modeled surface was found active for both H_2 dissociation and CO activation. Hydrogen was found to preferentially dissociate on the step edge, indicating that the conversion may be enhanced by the presence of such undercoordinated reaction sites. We currently investigate the cause of the selectivity decrease related to monoclinic ZrO_2, as well as a reason for the different catalytic performances between tetragonal and monoclinic ZrO_2 samples.

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ORAL B-22

Effect of the support and active phase loading in the production of H_2 and high-quality carbon in the thermocatalytic decomposition (TCD) of methane

Zouhair El Assal, Lasse Yli-Varo, Prem K. Seelam, and Ulla Lassi

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

Recently, hydrogen is considered a good alternative to the fossil fuels in reducing the CO_2 emissions from process and chemical industries such as ironmaking. Naturally, hydrogen doesn't exist in free form and there are challenges in how to produce H_2 with low or zero carbon emitted processes.[2] Several techniques are used for H_2 production but the thermocatalytic decomposition (TCD) of methane offers few advantages compared to other techniques such operated at low temperatures and producing valuable carbon materials. In TCD, hydrogen and carbon are produced without CO/CO_2 emissions. TCD is based on the following reaction: $CH_4 \rightarrow 2H_2 + C$ and studied over different heterogeneous Ni and Fe catalysts. In this study, we prepared and characterised Fe-based reference catalysts with different loadings (from 20 to 60 wt.% Fe_2O_3) over α, θ and γ alumina supports (Saint-Gobain).

The prepared catalysts are characterised by different physico-chemical techniques to determine the key properties. The catalysts are tested in TCD of methane reaction and the performance was evaluated in terms of H_2 concentration, carbon yield and CH_4 conversion at 750°C. Before the test, the catalytic material is reduced under H_2. The XRD analysis shows the presence of Fe_2O_3 on the catalysts. After wet impregnation with Fe precursor, the BET surface area reduced compared to bare alumina supports.

The ICP analysis shows a small difference between the nominal and final loadings of the Fe content. Fe supported on γ- and θ-Al_2O_3 catalysts showed good activity and stability in CH_4 decomposition regardless of the amount of loading Fe. However, Fe supported on α-Al_2O_3 showed good results only with the catalysts containing a high loading of Fe. The XRD results after the TCD test showed the presence of graphitic carbon at 26^o (2θ), and the iron carbide (Fe_3C) as the main phases in the used catalyst. Overall, the preliminary results with maximum carbon and H_2 yield were achieved over Fe/ γ-Al_2O_3. The potential application of graphitic carbon is explored in energy storage devices e.g., batteries.

Keywords: Catalytic pyrolysis of CH_4, CH_4 splitting, hydrogen production, thermocatalytic decomposition, TCD, Fe catalysts, graphitic carbon.

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ORAL B-23

Catalytic methane splitting from lab to pilot scale: key challenges & opportunities

Prem Kumar Seelam[1,2], Riikka Kupila[1,2], Lasse Yli-Varo[1,2], Samuli Räsänen[2],
Ulla Lassi[1]

[1]Sustainable Chemistry Research Unit, Faculty of Technology, P.O. Box 4300,
University of Oulu, Oulu-90014, Finland.
[2]Hycamite TCD Technologies Oy, Kemirantie 15,
Kokkola-67900, Finland.

Methane splitting technology is one of the key decarbonisation strategies for the fossil-driven industries. At industrial scale, hydrogen traditionally produced *via* methane steam reforming and coal gasification. However, both technologies are CO_2 and energy intensive processes. There is a need for a sustainable technology for the hydrogen economy and other potential industries. The thermocatalytic methane decomposition (TCD) is a well-known process for decades and it is a potential methane splitting technology for H_2 and valuable solid carbon production[1]. Moreover, TCD offers many benefits in terms of cost, energy consumption, clean tech. and scalability compared to other technolgies *i.e.*, thermal, plasma, and molten catalyst[1]. Successful commercialisation of TCD is a big challenge in terms of catalyst and reactor technology upscaling. Separation of carbon from metal particles, catalyst stability, and efficient reactor design are some of the key issues must be considered in TCD scale-up. The Ni, Cu, Co, and Fe-based catalysts are found to be the most active and selective transition metal catalysts in TCD[1,2]. In TCD, relatively low amount of CO_2 emitted per kg of H_2 produced and the carbon sink in the form of carbon nanomaterials (e.g., carbon nanofibers, graphitic carbon, carbon nanotubes, carbon nano onions, etc.) which can be used for e.g., in battery and conductive polymer applications[2]. The form of carbon nanomaterials is formed was solely depends on the metal type and the catalyst composition[2]. A case study of Hycamite TCD process is successfully demonstrated at pilot scale (TRL 6) with low-cost and zero carbon H_2-production[3]. The most common reactor technologies operated in TCD are fluidized bed and rotary kiln reactors. Thus, the TCD is a promising cost and environmentally efficient technology in H_2 production. Innovation in sustainable catalysts and novel reactor design are key in successful implementation at commercial scale. Overview on current status of TCD technology in comparison with Hycamite process will be presented in this symposium.

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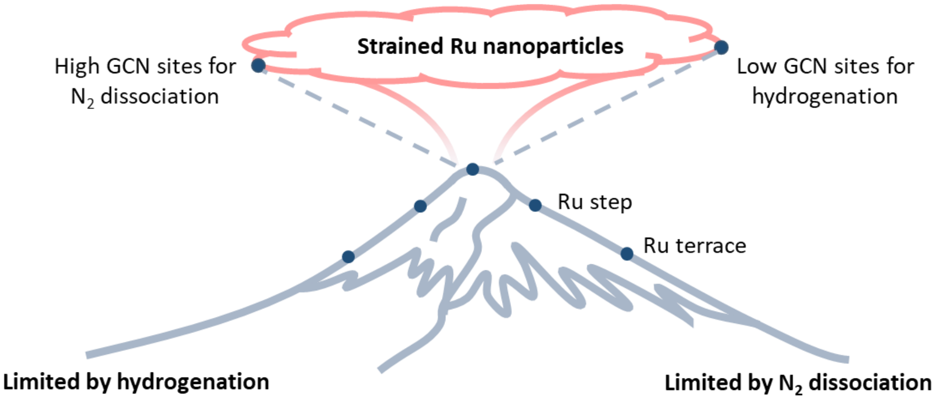
ORAL C-1

The Effect of Strained Ru Nanoparticles in Ammonia Synthesis Reaction

Yuqi Yang, Anders Hellman*, Henrik Grönbeck*
Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, 41296 Göteborg, Sweden.

Large-scale ammonia synthesis using the Haber-Bosch process is considered one of the most important scientific inventions of the 20th century. Over Ru nanoparticles (NP), it is established that the rate limiting step for ammonia synthesis is N_2 dissociation, which is facilitated by the presence of step sites. However, lowering the barrier for N_2 dissociation will eventually make NH_x ($x = 0$ to 2) hydrogenation rate limiting.[1] Thus, the reaction can be regarded as limited by the competing scaling relationships for N_2 dissociation and NH_x hydrogenation, yielding the volcano curve, Scheme 1. However, the current atomistic understanding of ammonia synthesis over Ru NP is based on ideal surfaces or nanoparticles, neglecting inherent strain effects. Experimentally, NPs are strained due to surface defects, grain boundaries, and interaction with the support materials.[2] Moreover, the surface sites in NPs can be artificially strained by alloying and the formation of core-shell structures.

Here, first-principle-based kinetic Monte Carlo (kMC) simulations[3] are utilized to explore the effects of strain on Ru nanoparticles for the ammonia synthesis reaction. We find that applying a +5% strain on Ru NP (which has been measured[4]) results in a considerable enhancement in the activity compared to unstrained NPs. Analysis shows that the enhanced activity is related to kinetic couplings where the N_2 dissociation and NH_x hydrogenation reactions occur on different sites on the NPs. We propose that kinetic couplings on strained-designed Ru nanoparticles offer a possibility to break the limitation of the scaling relationships in Scheme 1.



Scheme 1: Strained Ru nanoparticles break the limitation of the scaling relationship.

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ORAL C-2

Coupling kinetics and transport in a fixed-bed reactor from first-principles modelling

Torstein Fjermestad[1]*, Riccardo Uglietti[2], Daniele Micale[2], Mauro Bracconi[2], Anh Phan[3], Izar Capel Berdiell[1], Alberto Striolo[4,6], Francesco Iacoviello[5], Stian Svelle[1], Matteo Maestri[2]

[1]Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Sem Sælands vei 26, 0371 Oslo, Norway
[2]Dipartimento di Energia, Politecnico di Milano, Via Lambruschini 4, 20156, Milano, Italy
[3] Department of Chemical and Process Engineering, University of Surrey, Guildford, Surrey, GU2 7XH, UK
[4] School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, USA
[5] Electrochemical Innovation Lab, Department of Chemical Engineering, University College London, London WC1E 7JE, U.K
[6]Department of Chemical Engineering, University College London, London WC1E 7JE, UK

To optimize the performance of a catalytic reactor, it is essential to understand all physical processes contributing to its observed behavior. Two important processes in a catalytic reactor are the transport of species and their reactions. These two processes are strongly coupled. The rate of the various elementary reactions depends on the presence of reactants, which again is determined by their transport in the reactor and their consumption and formation by other elementary reactions. This interdependency often leads to strong concentration gradients throughout the reactor. Obtaining this detailed description of the catalytic process by experimental methods is very challenging. We therefore opted for a detailed first-principle modelling to obtain the desired insight.

The first step of the modelling is to construct a 3D model of the reactor and the catalyst pellets. The process occurring outside the catalyst pellets are transport of gas phase species by diffusion and convection. This process is modelled by computational fluid dynamics. Inside the catalyst pellets, the species are transported through diffusion and can react at the catalytic sites that are evenly distributed throughout the pellets. At each location in the pellets, the reactions are described by a DFT based microkinetic model. Through a multiscale methodology,[1] all processes can be coupled together, and we apply this methodology on the methanol to dimethyl ether reaction. We do the modelling at temperatures varying from 423 to 523 K, and we compare the simulated methanol conversion with the experimentally determined values (Figure 1). In the simulations, we have used the species diffusivities in the pellets computed at 423 K for all temperatures. This could explain the discrepancy between simulations and experiments at higher temperatures. Despite the discrepancy, we believe that the methodology shows a great potential to be used as a tool for obtaining insight into catalytic processes that could not be achieved experimentally.

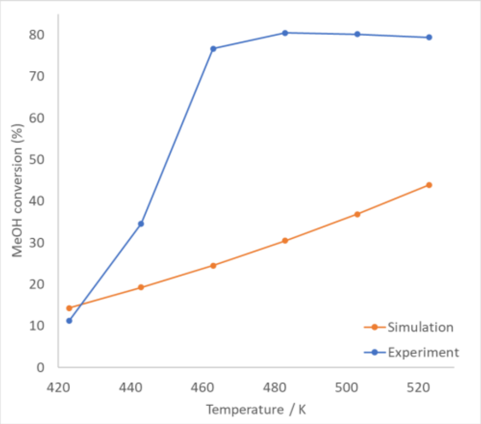

Figure 1. Simulated and experimentally measured methanol conversion as a function of temperature.

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ORAL C-3

Machine Learning Assisted Discovery of Electroactive Catalysts

Paulina Pršlja, and Miguel Caro
Aalto University, Otakaari 24, 02150

Electrochemical CO_2 conversion towards valuable chemicals using renewable electricity as an input is a useful strategy for closing the carbon cycle. To make the process efficient, it is necessary to design catalysts with high selectivity for a certain product at an economically viable current density and low overpotential. Tuning the structural features and elemental composition can facilitate selective production. However, the search space for new catalysts is large. Therefore, in this study, we developed a new technique for efficient screening. Machine learning was used to fit the interatomic Gaussian approximation potential (GAP)[1-4], which is an inexpensive and accurate alternative to density functional theory. We generated Cu- and SnO_x-based nanoparticles using the GAP method to investigate the thermodynamic stability of various composition ratios and size effects under high-temperature annealing. The selectivity was tested using selectivity descriptors for the identified active sites at different coverage levels.

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ORAL C-4

How first-principles simulations helped explain ethylene epoxidation on silver

Matej Huš[a,b], Miha Grilc[a], Janvit Teržan[a], Sašo Gyergyek[c],
Andraž Pavlišič[a], Blaž Likozar[a], Anders Hellman[b]
[a]*Kemijski inštitut, Hajdrihova 19, SI-1000 Ljubljana, Slovenia*
[b]*Chalmers tekniska högskola, Fysikgränd 3, SE-412 96 Gothenburg, Sweden*
[c]*Inštitut Jožef Stefan, Jamova 39, SI-1000 Ljubljana, Slovenia*

Ethylene epoxidation is an important reaction, which is carried out on a megaton scale. Being industrially and commercially an important selective oxidation, it is performed with silver under oxygen. The efficiency of silver catalysts has been steadily improving with empirical discoveries of dopants and co-catalysts. The reaction has been extensively described using experimental and theoretical methods. We first briefly review what is known about this reaction from experiments and macroscopic modelling. [1, 2, 3]

Recently, first principles modelling has harnessed the newly available computational power and increased tremendously in scope. We will overview different first principles models of this reaction and their predictions. We will show how well they match with experimental data. The differences that set apart ethylene epoxidation from other epoxidation reactions will be rationalized using quantum modelling. [4]

Finally, we report on a computational screening of the metals in the periodic table, which identified prospective superior catalysts and experimentally demonstrated that Ag/CuPb, Ag/CuCd and Ag/CuTl outperform the pure-Ag catalysts, while they still confer an easily scalable synthesis protocol. [5] We include relevant in-situ conditions e.g., surface oxidation, parasitic side reactions and ethylene epoxide decomposition, as neglecting such effects leads to erroneous predictions. We combine ab initio calculations, scaling relations, and rigorous reactor microkinetic modelling, which goes beyond conventional simplified steady-state or rate-determining modelling on immutable catalyst surfaces. Feasibility was confirmed by experimental agreement.

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ORAL C-5

Operando X-ray absorption spectroscopy on $Cu/ZnO/ZrO_2$ during methanol synthesis by CO_2 hydrogenation in a reactor made by additive manufacturing

Mariam L. Schulte[1,2], Vera Truttmann[1], Dmitry E. Doronkin[1,2], Lorena Baumgarten[1,2], Alexander Nicolai[3], Diego A. Montalvo B.[3], Florian Summ[3], Christoph Kiener[3], Erisa Saraçi[1,2], Jan-Dierk Grunwaldt[1,2]

[1]Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

[2]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany

[3]Siemens AG, Technology, Advanced Manufacturing & Circularity, 13629 Berlin /81739 Munich

The Power-to-Liquid (PtL) concept offers a promising approach to store surplus electrical energy derived from renewable sources, converting green H_2 in combination with (atmospheric) CO_2 to liquid fuels/chemicals, such as methanol (MeOH). Compared to conventional MeOH synthesis from syngas ($CO+H_2$), hydrogenation of CO_2 to MeOH in PtL rises new challenges: i) higher water content in the product stream accelerates the deactivation of the standard $Cu/ZnO/Al_2O_3$ (CZA) catalyst, and ii) the thermodynamic equilibrium significantly limits methanol yield. To circumvent these limitations, *in situ* condensation and separation of MeOH (and H_2O) can be induced by a temperature gradient, effectively shifting the equilibrium to the product side. However, condensation inside the catalyst bed presents a strong risk for catalyst deactivation. Given the high sensitivity of the methanol synthesis reaction to the catalyst structure, which undergoes strong changes during activation, reaction and deactivation, it is imperative to investigate the catalyst under industrially-relevant conditions.

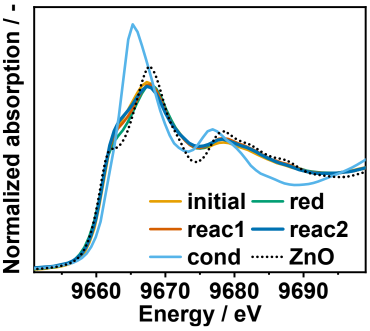

Figure 1: XANES at Zn-K edge of a Cu-Zn-based catalyst in 5 states: initial, reduced (red), after CO_2 methanol synthesis (reac1), after induced temperature gradient (reac2), forced condensation in catalyst bed (cond), ZnO as reference.

To address this need, we have developed a spectroscopic reactor through additive manufacturing, enabling high-pressure (up to 90 bar) *operando* X-ray absorption spectroscopy (XAS) studies equipped with a specifically-introduced temperature gradient zone. Temperature measured at multiple positions inside the reactor and the 10x10 mm X-ray window facilitate spatially-resolved measurements of the catalyst for monitoring the induced temperature gradients. A larger catalyst reservoir above the X-ray window section ensures the production of sufficient liquid products for condensation in the temperature gradient zone. We investigated the structure of a Cu-Zn based catalyst closely resembling commercial CZA composition. *Operando* XAS during methanol synthesis from CO_2 and H_2 at 40 – 90 bar, and during induced condensation of the reaction products revealed remarkable dynamics in the catalyst behavior. While the state of Cu remained mostly unchanged, Zn exhibited highly dynamic changes (Figure 1). We observed possible formation of oxygen vacancies in ZnO including geometrical changes of Zn during reduction which were subsequently refilled during reaction. Upon forcing condensation inside the catalyst bed, the Zn spectra changed significantly and irreversibly indicating a phase transition. These changes were accompanied by a decrease in CO_2 conversion. This study provides valuable insights into the active state of a close-to-industrial MeOH catalyst under realistic conditions, offering the potential to unravel deactivation phenomena caused by condensation of the reaction products, namely methanol and water.

ORAL C-6

In situ ATR-IR spectroscopy and fast high-energy X-ray diffraction uncover the mechanism of aqueous, room-temperature synthesis of MOF-74 catalysts

Ilia Kochetygov[1], Luca Maggiulli[1], Marco Ranocchiari[1], Davide Ferri[1]
[1]*Paul Scherrer Institut, 5232 Villigen, Switzerland*

Metal-organic frameworks (MOFs) show great promise among porous materials due to their intrinsic tunability and structural versatility, leading to their use in numerous applications in catalysis,[1] in particular selective catalytic reduction of ammonia[2] and electrocatalytic oxygen reduction reaction.[3] While the MOF field currently offers a great choice of materials, one of the remaining challenges for their real-world implementation is the development of reliable synthetic procedures with speed, scale, and quality matching the industry requirements. Recently, green, high-yielding aqueous-based room temperature synthesis methods of MOF-74/CPO-27 were developed, allowing outstanding space-time yields of up to 18 720 kg m^{-3} day^{-1}.[4] There is, however, a lack of understanding of the underlying synthesis mechanisms, which is crucial for further extension and optimization of such facile aqueous syntheses to other MOF families and the fundamental understanding of MOF formation pathways.

In this work, we studied the mechanism of the MOF-74 family formation in aqueous solutions on a preparative scale (> 0.5 g), employing *in situ* Attenuated Total Reflection IR spectroscopy (ATR-IR) in a custom-made stainless steel batch reactor cell equipped with a ZnSe crystal (30°, 50x44x2 mm, 1.5 s time resolution), and an external loop for XRD data collection at the ID15A beamline of the ESRF (50 ms time resolution).

The ATR-IR spectra revealed that MOF synthesis proceeded via the formation of an intermediate, which contains a twofold deprotonated ligand molecule. The kinetics of the MOF formation were found to depend upon synthesis temperature and type of zinc precursor. The excellent quality of produced MOFs was confirmed by their conformity to the expected crystal structure and high BET surface area values over 1350 m^2g^{-1}.

The analysis of the evolution of FWHM of several characteristic XRD peaks and the lattice parameters indicated that growth of the MOF crystals occurred along the *c* axis in the R-3 hexagonal cell. Gualtieri model fitting of the XRD data revealed the kinetic parameters of MOF nucleation and growth, as well as the nucleation probability in time, which correlated with the evolution of the peak width of the ν(C=C) vibrational mode of the material. Coupled with electron microscopy, these observations allowed us to propose a zinc precursor-dependent MOF synthesis mechanism, as well as to establish optimized synthetic protocols for MOF-74 materials.

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Seeing the active site for N_2O activation and decomposition in Fe-exchanged zeolites

Filippo Buttignol,[1,2] Daniel C. Cano Blanco,[1,2] Jörg Fischer,[3] Gunnar Jeschke,[3] Oliver Kröcher,[1,2] Davide Ferri[1]
Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
EPFL, CH-1015 Lausanne, Switzerland
ETH Zurich, CH-8093 Zurich, Switzerland

N_2O can be found in the exhaust gases of industrial plants. Its high environmental impact asks for the development of technologies to remove it efficiently especially in complex feeds such as those containing NO and NH_3. Fe-exchanged zeolite catalysts are active towards the decomposition of N_2O and the selective catalytic reduction of NO.[1] In the case of N_2O decomposition, Fe^{2+} ions are oxidized to Fe^{3+} upon N_2O coordination and N_2-O bond cleavage. Complete N_2O conversion further occurs via release of molecular oxygen coupled with a rate limiting Fe^{3+}/Fe^{2+} autoreduction process and is achieved at high temperature. The nature and the chemical environment of the active Fe sites remain debated particularly because of the difficulty to obtain homogeneously dispersed Fe centers in zeolite frameworks. Thus, disentangling the contribution of the active sites from complex signals of species likely not involved in the reaction is challenging even using in situ/operando spectroscopic methods.

We have analyzed Fe-zeolite catalysts comprising a number of Fe species of different degrees of agglomeration (monomers in different environments and clusters) using XAS, DRIFTS, DRUV and EPR combined with the modulated excitation approach[2] and mass spectrometry (MS). The operando spectroscopic methods used under pulsing conditions of N_2O in Ar at 400 °C provided insights beyond what has been obtained so far under reaction conditions. The four spectroscopic methods demonstrate that while most monomers and clusters can be oxidized by N_2O (DRUV/EPR), only square-planar Fe^{2+} sites (XAS) in β-cationic position of the framework (EPR) provide complete red-ox dynamics by transitioning to square-pyramidal (XAS/EPR) Fe^{3+} hydroxyls (DRIFTS) and returning to the Fe^{2+} state upon autoreduction and $O_2 + H_2O$ release (MS). In further support of the involvement of these Fe species, their concentration correlates with the reaction rate. It emerges that we can identify Fe ions in specific positions of the framework that are responsible for N_2O activation and decomposition.

The transient nature of the experiments allowed extraction of key mechanistic details that remain otherwise hidden. Thus, we were able to observe the formation of specific alpha-O sites that are responsible for N_2O activation and decomposition among a multitude of Fe species and to define their chemical environment.

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ORAL C-8

Silver Catalysed Partial Oxidation of Methanol to Formaldehyde and its Sub-reactions.

Youri van Valen[1], Tina Bergh[1], Rune Lødeng[2], Ole H. Bjørkedal[3], Ann Kristin Lagmannsveen[4], Jia Yang[1] and Hilde J. Venvik[1*]
[1)]Dept. Chem. Eng., NTNU, 7491 Trondheim, Norway
[2)]SINTEF Industry, 7465 Trondheim, Norway
[3)]Dynea AS. P.O. box 160, 2001 Lillestrøm, Norway
[4)]K.A. Rasmussen, Birkebeinervegen 24, 2316 Hamar, Norway
[*]hilde.j.venvik@ntnu.no

Half of the global formaldehyde production is realised by the silver (Ag) catalysed partial oxidation of methanol to formaldehyde (MTF). CO, CO_2, H_2 and H_2O are relevant intermediates and side products in the suggested reaction system [1, 2]. Dissolution dynamics of O_2 and H_2 play a significant role in the restructuring of the Ag (sub-)surface [3], affecting the resulting activity and selectivity. Herein we present investigations into the oxidation reactions of CH_3OH, CO, and H_2, with and without H_2O as co-feed.

Use of an annular reactor concept to reach isothermal conditions and suppress gas phase reactions allows investigations into the kinetics of the MTF reaction [2, 4]. Fresh Ag catalysts were exposed to a range of distinct atmospheres for subsequently 12, 36, and 84 hours in a temperature range of 620-650 °C. On-line gas chromatography was used to quantify all reactant and product species except H_2O. After each exposure, surface characterisation was performed using scanning electron microscopy (SEM). Sub-surface characterisation was performed using focused ion beam (FIB) – SEM tomography.

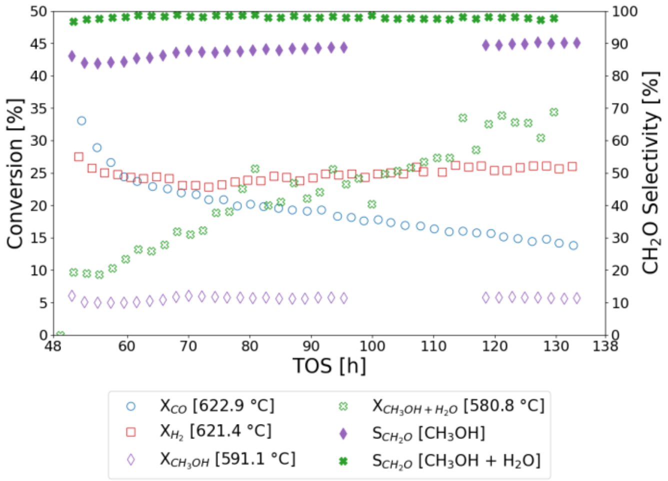

Figure 1: Conversion (Left axis) and selectivity towards CH_2O (Right axis) for CO, H_2, and methanol oxidation. Temperatures in brackets are average measured bed temperatures at T_{max}.

Results of the CO, H_2, and CH_3OH oxidations with and without water present are visualised in Figure 1 for the 48 – 132h period. During both MTF experiments CO_2 was the only carbon containing side-product. CO oxidation shows a gradual activity decrease, likely being negatively affected by the oxygen dynamics. H_2 and MTF do not show a similar trend. Addition of H_2O to the MTF reaction results in a significant increase in selectivity towards CH_2O, as well as a gradual increase in activity over the 84h. The restructuring of the polycrystalline Ag is highly dependent on the atmosphere it is exposed to, with the resulting morphology of our annular catalyst bearing a strong resemblance to the industrial particle Ag catalyst. Different faceting and pinhole formation is observed in all oxygen containing atmospheres. Pores of varying sizes are observed beyond 10 μm into the sub-surface of the silver. H_2 containing atmospheres show distinct differences from those without.

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ORAL C-9

Enhanced activity of ceria nanoparticles doped with lanthanum and zinc for the synthesis of dimethyl carbonate from methanol and carbon dioxide

Aitor Arandia, Florian Rathmann, Jessica Ekholm, Yukho Sok-Sar, Juha Lehtonen
VTT Technical Research Centre of Finland Ltd. P.O. Box 1000, FI-02044 Espoo, Finland.

Dimethyl carbonate (DMC) is a versatile chemical with several industrial applications such as, polycarbonate synthesis, production of electrolytes, solvent for paints and coatings, chemical intermediate (e.g. in methyl isocyanate synthesis) or fuel additive.[1] The traditional synthesis of DMC through phosgenation of methanol with $COCl_2$ has evolved towards more environmentally friendly routes like the carboxylation of methanol with carbon dioxide: $2CH_3OH + CO_2 \leftrightarrow OC(OCH_3)_2 + H_2O$.[2] This reaction is thermodynamically limited and shifting the equilibrium to the product side by e.g., removing water, is needed for the commercialization of the process.[2] Regarding the catalysts, ceria (CeO_2) has been reported as a material with unique acid-base and redox properties.[1,3] The ability of CeO_2 and dopants to create oxygen vacancies is a crucial parameter for an enhanced activity.[1,3] In this work we have synthesized Ce-La and Ce-Zn mixed oxides with various La and Zn content as interesting materials to improve the surface/chemical properties of ceria to drive the catalytic activity towards DMC.

The $La_xCe_{1-x}O_\delta$ and $Zn_xCe_{1-x}O_\delta$ with different La and Zn loadings (x=0.01, 0.05 and 0.1, mol base) were synthesized via hydrothermal synthesis method with urea and Ce, La and Zn nitrates as precursors. The urea to nitrates molar ratio was set to 2.66 and the total molar concentration to 0.1 M. The synthesis was performed in a 500 ml Teflon-lined autoclave reactor in a static oven at 120 ºC for 8 h. The solution was filtrated, washed several times with deionized water and ethanol, and dried at 80 ºC for 24 h. The dried powders were last calcined at 600 ºC for 5 h to obtain the final catalysts.

The physio-chemical properties of the catalysts are studied by physisorption, X-ray diffraction and scanning-electron microscopy (SEM). The activity of the catalysts is measured in batch conditions at different temperatures from 120 to 160 ºC and pressures from 1 to 5 MPa with a stoichiometric MeOH to CO_2 molar ratio of 2. The composition of the products is analyzed by GC-FID. The correlation between the properties of the catalysts and the activity results will be discussed in detail. The best performing catalyst(s) identified through the runs in batch reactor will be later tested in a continuous flow reactor with special emphasis in the stability with time on stream. Ionic liquids will be also explored as potential dehydrating agents in order to boost the DMC production.

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ORAL C-10

Preventing Deactivation during Dry-Reforming of Methane

Gordon Zhuo, Mikkel Kock, Emil Kowalewski, Søren Kegnæs, Jerrik Mielby*
DTU Chemistry, Technical University of Denmark, Kemitorvet 206, DK-2800 Kgs. Lyngby, Denmark, jjmie@kemi.dtu.dk

Dry reforming of methane (DRM) offers an attractive opportunity for upgrading biogas produced by anaerobic digestion of biomass, wastewater sludge, or even municipal landfills.[1] Such biogas often contains high amounts of CO_2, which makes it uneconomic for other reforming processes, such as steam reforming. The direct conversion of CO_2 and CH_4 into synthesis gas also results in a higher CO/H_2 ratio, which is an advantage for several downstream processes, such as the synthesis of methanol, dimethyl ether, or liquid hydrocarbons.[2] Therefore, DRM could provide essential building blocks for the chemical industry, hydrogen gas for fuel cells, and liquid fuels for transportation. In this way, DRM can potentially convert large amounts of greenhouse gases and renewable off-peak energy into valuable fuels and chemicals without disrupting the current infrastructure. The main technical challenge, however, is the lack of cost-effective and durable heterogeneous catalysts. DRM is a highly endothermic reaction that requires high temperatures and an effective catalyst to proceed. Under these conditions, the catalyst typically suffers from fast deactivation due to coking. The formation of coke is particularly severe between 550-700°C due to the Boudouard reaction and above 900°C due to methane pyrolysis. Consequently, the catalyst needs periodic decoking by combustion, which produces CO_2, increases costs, and prevents commercial applications.

In this work, we prepared a series of supported Ni-based catalysts by simple impregnation, drying, and calcination. Then, we tested the catalysts for DRM in a fixed-bed reactor equipped with an online GC. For example, we show that Ni nanoparticles supported on Y-stabilized zirconia (5% Ni/YSZ) result in 89% CO_2 conversion and an H_2/CO ratio of 0.95 at 700°C. Under the given reaction conditions (1 bar, $H_2/CO_2=1$, and GHSV=54.000 ml/g/h), this conversion decreased to 73% after 50 h on stream. After the test, post-catalysis characterization by temperature-programmed oxidation showed that the catalyst formed up to 5% carbon by mass. However, by optimizing the metal-support interaction and modifying the surface chemistry, we also show how this coke formation and deactivation may be prevented. Ultimately, a better understanding of the coking mechanism will result in the development of more active, selective, and durable DRM catalysts that will eliminate the need for expensive regeneration procedures.

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ORAL C-11

Tuning the amount of Aluminum pairs in the Mordenite Zeolite to improve Oxidation of Methane to Methanol.

Peter Njoroge[1], Sebastian Prodinger[1*]
[1]*Center for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, 1033 Blindern, 0315 Oslo, Norway*
*Corresponding author: Sebastian.prodinger@smn.uio.no

Methane to methanol conversion has gained a lot of interest with the overall approach being an attempt to replicate the active sites found in nature responsible for the same reaction which is the methane monooxygenase enzyme (MMO). Despite the copper speciation involved in the active sites for methane to methanol conversion being elusive, the critical role of aluminum paired sites in methane oxidation to methanol on Cu-exchanged mordenite zeolites has been explored[1] with the conclusion that the Cu-oxo clusters derived from the Al pair sites were more reactive than the CuOH species grafted at the isolated Al sites. Our hypothesis is as a consequence of increasing the aluminum paired sites we inherently increase the number active of Copper-oxo species, thus the activity of the catalysts.

In our work we explore the possibility of increasing the aluminum pairs in the K-MOR[2] by introducing strontium as a cation structure directing agent and varying its amount with respect to potassium. It should be noted that no organic structure directing agents are used in this synthesis highlighting the important role of in-organic structure directing agents. The following work follows the differences observed in crystallization curves obtained from the zeolites synthesized as well as the difference of the number of aluminum pairs formed compared to a pure MOR and will also discuss future experiments.

We successfully synthesized a range of mordenite zeolites containing increasing parts of Sr^{2+} in the gel. The materials exhibit different rates of crystallization but as the amount of Sr^{2+} increased it took a longer time to achieve full crystallinity. The morphology of the crystals also appears to change with introduction of Sr^{2+} as seen from the images acquired from the scanning electron microscope with the mordenite with pure potassium forming cubes while the introduction of Sr^{2+} changes the shape to rectangular prisms. When probing the H+ forms the surface area and pore volume was as expected for mordenite whereas the isotherms of the as-made alkali containing zeolites exhibited low-surface area characteristics without any systematic trend as a function of the Sr^{2+} loading.

An increase in cobalt intake into the different mordenite was established which represents an increase in paired Al as we introduce strontium into the mordenite as well as increase its content. Further tests planned include ^{27}Al MAS NMR to check the state of the Al, NH_3 and alkylamine temperature programmed desorption to check the acidity and then Cu introduction and testing for the methane to methanol reaction.

By introducing strontium in the synthesis of K-MOR we influence the crystallinity rate of the zeolite formed as well as increase the number of Al pairs in the final mordenite formed. By further adjusting the ratios of the amount of strontium in the K-MOR and studying the catalytic activity we will eventually form the maximum amount of Al pairs that are allowed in K/Sr-MOR increasing the overall catalytic activity towards methane to methanol conversion.

The authors acknowledge the Norwegian Research Council for funding the project grant no. 334997.

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ORAL C-12

Evaluating hydrotreating catalysts for dynamic operations

Jacob Venuti Björkman[1,2*], Tallal Belkheiri[2], Lilla Lukovicsová[1], Lars J. Pettersson[1], Efthymios Kantarelis[1]
1 - KTH Royal Institute of Technology, Department of Chemical Engineering, Stockholm, SE-100 44 (Sweden), 2 - Process Technology, Nynas AB, Nynäshamn, SE-14 982 (Sweden)

Introduction

Hydrotreatment of mineral oil distillates over sulfided NiMo/Al_2O_3 catalysts enable the production of lubricant base oils free of undesired organonitrogen compounds and polyaromatic hydrocarbons. While the continuous operating period for hydrotreaters can extend over many years, there are variations in the products and as well as the feedstocks processed over time. This results in transitional periods with varying catalyst activity due to the preceding operating mode[1]. Due to the broad variation of feedstock and product compositions, catalyst selection is crucial for maximizing the feedstock utilization. In this regard, the catalyst activity for hydrodenitrogenation (HDN) and hydrogenation reactions can be related to the interaction between the active phase and the support; typically, hydrotreating catalysts are categorized as Type I, modified Type I, and Type II catalysts. In this study, different types of NiMo catalysts were prepared and assessed under dynamic reactor operation, enabling the evaluation of their activity towards HDN and hydrogenation reactions while also investigating the inhibition affecting mode switches.

Experimental

Four different catalysts were prepared using dry impregnation of Al_2O_3 with solutions of $(NH_4)_6Mo_7O_{24}$ and $Ni(NO_3)_2 \cdot 6\,H_2O$ as the Mo and Ni precursors, respectively. Citric acid (CA) was used as chelating agent in two of them, while two of the catalysts had their support modified with phosphoric acid (P). To elucidate the differences, the step response upon introduction of carbazole and acridine in the feedstock during phenanthrene hydrogenation was chosen as the model system.

Results and Discussion

The table below summarizes the catalyst compositions and their relevant kinetic parameters. It is worth noting that the increased hydrogenation activity due to P-modification is positively corelated with the sensitivity to organonitrogen compounds.

Sample	MoO_3 [wt.%]	Ni/Mo [mol/mol]	P_2O_5 [wt%]	Rel.Hyd.activity [-]	Rel. Inhibition Intensity [-]
NiMo	7.9	0.62	-	1.0	1
NiMoCA	7.8	0.54	-	1.2	1.33
NiMoP	7.3	0.66	4.1	2.4	3.5
NiMoPCA	7.3	0.53	3.2	2.0	2.6

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ORAL C-13

Activity of vanadia based catalysts in methanol and methanethiol dehydrogenation

Tiina Laitinen[1], Satu Ojala[1], Tamara Chidiac[2,3], Samer Aouad[2], Jane Estephane[2], Riitta L. Keiski[1]
[1]Environmental and Chemical Engineering (ECE), P.O. Box 4300, FI-900014 University of Oulu, Finland; [2]University of Balamand, El-Koura, Lebanon; [3]Technical University of Darmstadt, Institute of Construction and Building Materials, 64287 Darmstadt, Germany

In the chemical pulp mill, significant amounts of methanol-rich emissions are formed[1]. This side stream is currently used for power production due to its contamination with reduced sulphur compounds (e.g. methanethiol, MT). The aim of this research is to use sulphur contaminated methanol (MeOH) emission for formaldehyde production.

The activity of the vanadia catalysts was studied by using gadolinia, hafnia or silica promoted alumina supports. Alumina was prepared using sol-gel method[2]. Vanadia (~1.5 wt-%) and the promoter (~20 wt-%) were impregnated on alumina. The VOx surface density of the catalysts was ~0.6 V nm^{-2}. Raman analysis showed that mainly polymeric vanadia species were formed on the catalysts[3]. In addition, monomeric vanadia species were formed on the 1.5V-GdAl catalyst[3]. The results of dehydrogenation and desulphurization of MeOH and MT show that the highest formaldehyde concentration (~755 ppm) at the lowest temperature (~410 °C) was achieved over the V-HfAl catalyst (Fig. 1). The sulfur poisoning treatment was performed for the SiAl-based samples. The samples showed the high resistance to Sulphur poisoning deactivation since the support and catalyst retained only a small amount of Sulphur upon their surfaces by 0.05 wt-% for V-SiAl and 0.03 wt-% for SiAl. In formaldehyde production, poisoning slightly improved the activity of the SiAl and slightly decreased the activity of the 1V-SiAl.

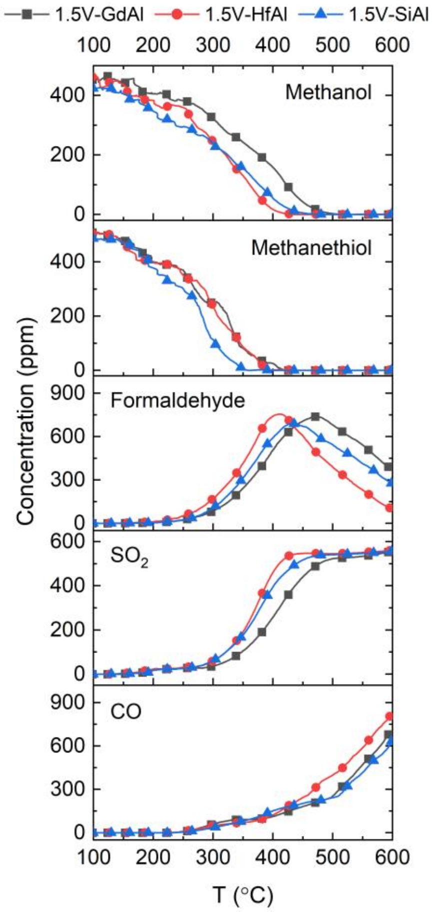

Fig 1. MeOH and MT dehydrogenation and desulphurisation over catalysts

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ORAL C-14

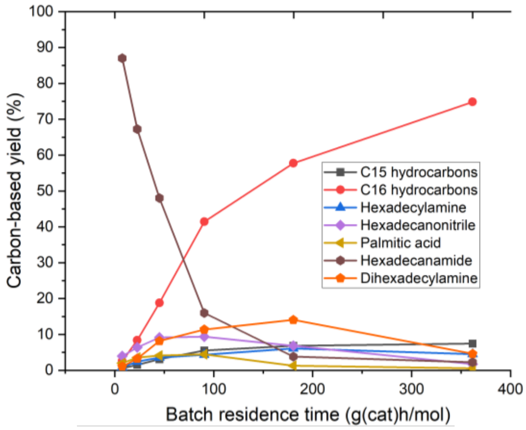
Hydrodeoxygenation and hydrodenitrogenation of n-hexadecanamide with NiMo sulfide catalysts

Joakim Kattelus[1], Jorge Velasco[1], Paavo Auvinen[1], Aitor Arandia[1], Emma Verkama[1]
Hua Jiang[1], Kristoffer Meinander[1], Reetta Karinen[1], Riikka L.Puurunen[1]
*[1]Aalto University, Department of Chemical and Metallurgical Engineering, Espoo, Finland. *joakim.kattelus@aalto.fi*

Renewable fuels offer a promising alternative to fossil fuels [1,2]. However, many potential feedstocks contain significant amounts of oxygen and nitrogen, which must be removed to obtain high-quality fuel [1,2]. Amides are present in renewable feedstocks [3,4] and thus there is a need to study their hydrodeoxygenation (HDO) and hydrodenitrogenation (HDN). In this work, the hydrotreating of hexadecanamide using $NiMo/Al_2O_3$ and $NiMo/TiO_2$ sulfide catalysts was studied.

Catalysts were prepared with incipient wetness impregnation, followed by calcination and sulfidation at 400 °C in 10 vol% H_2S/H_2. Hydrotreating experiments were performed at 300 °C and 70 bar H_2 in a batch reactor. Products were analyzed by GC-FID and the N-content quantified with a total nitrogen content analyzer. Catalysts were characterized with a variety of methods, such as ICP-OES, XPS and TEM.

Figure 1 shows the major reaction products at different batch residence times for $NiMo/Al_2O_3$. Hexadecanamide was found to either undergo dehydration into hexadecanenitrile or deammonization into palmitic acid. HDN of the nitrile and HDO of the acid gave hexadecane as the major product. The secondary amine dihexadecylamine was a significant N-containing intermediate.



On both catalysts, the dehydration pathway dominated, HDN of the amide was thus slower than HDO. $NiMo/TiO_2$ had significantly higher HDO activity and slightly higher HDN activity than $NiMo/Al_2O_3$. This was attributed to TiO_2 catalyzing HDO through dehydration as well as to more complete sulfidation of Mo and better incorporation of Ni at the active MoS_2 edge sites.

Figure 1. Yields of the major products with the $NiMo/Al_2O_3$ catalyst as a function of batch residence time.

This work was funded by Neste Corporation.

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ORAL C-15

Scalability and Performance of Niobium Pellet Catalysts in HDO Reactions

Naiara C. Telis[1*], Mariana C. Fraga[1], Klaus Raffelt[1], Nicolaus Dahmen[1]
[1]Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT),
Hermann-von-Helmholtz-Platz 1. Eggenstein-Leopoldshafen
**naiara.telis@kit.edu*

Catalytic performance, encompassing catalyst conversion, activity, selectivity, and stability, is critical for industrial applications. This study examines scalability of niobium pellets as supports in hydrodeoxygenation (HDO) reactions, addressing the gap between laboratory research and industrial application. It assesses how pelletization and the addition of a carbon binder affect structural integrity, metal impregnation, dispersion of the active metal and the influencing in the catalytic performance. Our approach combined XRD, SEM, XPS, NH_3-TPD, BET analyses to compare the performance of the Nb_2O_5 in pelletized form against its powdered counterpart from the same source. XRD and CHN analysis detected carbon in pellets calcined below 800°C. However, XPS and H_2-TPR profiles comparing the pellet and powder impregnated with 5%Ru, the results suggested a more complete reduction of ruthenium in the pellet form, implying the carbon binder does not adversely affect this aspect. The composition analyses revealed discrepancies in metal loading in the surface and bulking profile. ICP analysis reveals that the powder catalyst has approximately 2.4 times higher Ru content compared to the pellet catalyst; while REM/EDS surface composition, analysis shows a slightly higher amount of Ruthenium (8.14) on the powder catalyst compared to the pellet catalyst (7.44). However, the catalyst test performed in batch reactor showed that both catalysts have similar conversions and selectivities. Investigating the influence of calcination temperatures on Nb_2O_5 polymorphism, we found that similar structures could be achieved, the surface area significantly reduced, as shown by BET measurements. The findings suggest that with refined preparation techniques, niobium pellets can preserve the essential characteristics for effective catalysis, thus representing a feasible option for industrial applications.

ORAL C-16

Self-induced Surface Strain Enhances Oxygen Reduction Reaction Kinetics

Mailde S. Ozório,[1] Marcus F. Nygaard,[1] Amanda S. Petersen,[1] Jürgen Behm,[2]
Jan Rossmeisl[1]

[1] Center for High Entropy Alloy Catalysis (CHEAC), Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark, E-mail: mdso@chem.ku.dk, jan.rossmeisl@chem.ku.dk

[2] Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany

Alloying Pt with other metals has been a viable strategy to improve the ORR kinetics.[1] Here, we combined previously published experimental data with theory to investigate the effect of Ag on the activity of binary Ag_xPt_{1-x}/Pt(111) surfaces. We constructed a model to generate Ag_xPt_{1-x}/Pt(111) surfaces based on the experimental behavior shown by STM analysis,[2] i.e., the phase-separation Ag_xPt_{1-x}/Pt(111) surfaces with x values between 7% and 50%, where only the topmost layer of Pt(111) is alloyed with Ag. In linking catalytic activity to the structures, our model predicts similar Ag_xPt_{1-x}/Pt(111) ORR activity trends that are in accordance with the experiments. Our analysis reveals that Ag atoms in the surface leads to surface compression of the Pt atoms, i.e. a self-induced surface strain phenomenon. This differs from a conventional strain that are induced by the bulk of material. Additionally, our results give the insight that rationally introducing larger elements into the Pt surface might prove an excellent strategy to design of more active catalysts, thanks to the self-induced surface strain effect.

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Effect of Aluminum Distribution on the Diffusion and Pairing of $[Cu(NH_3)_2]^+$ Complexes in Cu-CHA

Joachim D. Bjerregaard[1,2], Martin Votsmeier[2], Henrik Grönbeck[1]
[1] *Department of Physics, Chalmers University of Technology, Gothenburg, Sweden*
[2] *Umicore AG & Co. KG, Hanau, Germany*

Copper exchanged chabazite (Cu-CHA) is currently state of the art for ammonia assisted selective catalytic reduction (NH_3-SCR) in aftertreatment systems for $deNO_x$. During NH_3-SCR conditions, the Cu ions are solvated by NH_3, forming $[Cu(NH_3)_2]^+$ complexes, which are mobile and can diffuse in the zeolite[1]. If two $[Cu(NH_3)_2]^+$ complexes are in the same cage, they can adsorb O_2 forming a peroxo complex $[Cu_2(NH_3)_4O_2]^{2+}$, a critical step in the NH_3-SCR mechanism[2]. Since O_2 adsorption requires two $[Cu(NH_3)_2]^+$ complexes in the same cage, the diffusion and subsequent pairing are paramount for the NH_3-SCR activity. The current understanding of the mobility and pairing of $[Cu(NH_3)_2]^+$ complexes is mainly based on DFT calculations which are restricted to smaller unit cells and short simulation times.

Here we have constructed a machine learning force field (ML-FF) augmented with long-range interactions. The ML-FF has been trained using DFT calculations of Cu-CHA with the counter ions $[Cu(NH_3)_2]^+$ and NH_4^+ using the deePMD-kit package. The DFT calculations are performed using Vienna Ab initio Simulation Package (VASP) with the PBE functional. Molecular dynamic (MD) simulations are performed using LAMMPS at 200 °C in the NVT ensemble. The ML-FF is trained on 50000 single point calculations based on 160 different structures.

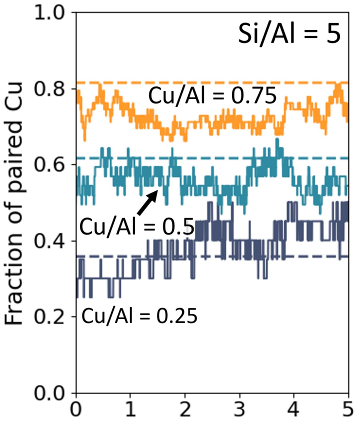

Figure 1: Fraction of paired Cu-complexes

We have performed MD simulations on 3X3X3 supercells with different zeolite compositions (Si/Al and Cu/Al). The fraction of paired $[Cu(NH_3)_2]^+$ complexes as a function of simulation time is computed for Si/Al ratio of 5 and Cu/Al ratio of 0.25, 0.5, and 0.75, shown in Figure 1 (solid lines). This is compared to the estimated fraction of paired $[Cu(NH_3)_2]^+$ complexes that are randomly distributed (dashed lines). For a Cu/Al ratio of 0.5 and 0.75, the simulated fraction is below the dashed line, indicating a repulsion between the $[Cu(NH_3)_2]^+$ complexes. For a Cu/Al ratio of 0.25, the simulated fraction is below the dashed line. Thus the higher fraction of Al and NH_4^+ ions can possibly enhance the stability of paired $[Cu(NH_3)_2]^+$ complexes. The study demonstrates the ability of ML-FF's augmented with long-range interactions, to study the dynamic behavior of counter ions in zeolites.

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ORAL C-18

Spontaneous Charge Separation at the Metal-Water Interface

Rasmus Svensson, Henrik Grönbeck

Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE41296, Göteborg, Sweden

Many important catalytic reactions take place at the metal-water interface. It is well known that the presence of water may alter both the turn-over frequency and selectivity towards desired products, by stabilization of certain reaction intermediates[1]. The presence of a solvent may, however, affect the reaction in a more direct way by acting as a cocatalyst, offering alternative reaction mechanisms. Due to the complicated potential energy landscape of highly dynamic water molecules over a metal surface, reaction mechanisms at the metal water interface are not as developed as at the metal-gas interface.

In this work, we have investigated the effects of the metal-water interface on H and O_2 adsorption over the (111) surfaces of Cu, Ag, Au, Pd and Pt. The potential energy landscapes in the presence and absence of water are explored using Density Functional Theory calculations. *Ab Initio* Molecular Dynamics simulations, in combination with the blue moon ensemble method, are employed to describe both the electronic and free energy profiles at the metal-water interfaces.

We find that, in the presence of water, adsorbed H may undergo a spontaneous redox reaction, where the proton desorbs into the water solution, whereas the electron is donated to the metal surface. The process is exothermic over Ag, Au, and Pt, and accompanied by low barriers. The free energy profile for the charge separation event from adsorbed H over Pt(111) is shown in Figure 1. Water is also found to affect the O_2 adsorption properties, by promoting a metal-to-O_2 charge transfer, increasing the O-O bond length and the adsorption strength. The possibility for facile charge separation and altered adsorption strengths at the metal-water interface have important consequences for the understanding of reaction mechanisms, as it enables mechanisms that drastically differ from those at the metal-gas interface. One example is direct H_2O_2 formation over dilute PdAu alloy nanoparticles, where the selectivity of the reaction is dependent on the facile charge separation of H[2].

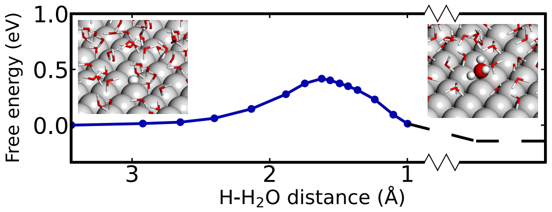

Figure 1. The free energy profile for the complete charge separation over Pt(111) at 293 K.

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ORAL C-19

Unveiling closed and open site stability of Sn-, Ti-, Hf-, and Zr-Beta zeolites: A DFT investigation for biomass sugar conversion

Nawras Abidi [1], Yacine Boudjema [1], Céline Chizallet [1], Kim Larmier [1]
[1]*IFP Energies nouvelles, Rond-point de l'échangeur de Solaize – BP 3 69360 Solaize, France*

Zeolites, with their unique nano-porous structures, are highly efficient catalysts. By substituting Al in zeolites with Sn, Ti, Zr, or Hf, we impart distinct Lewis acidic properties, crucial for converting carbohydrates like glucose, fructose, and xylose into furan compounds and organic acids.[1] Our research utilizes DFT and VASP, incorporating the PBE-D2 density functional with dispersion correction, to study stability, Lewis acidity, and sugar adsorption in Sn-, Ti-, Hf-, and Zr-Beta zeolites.

We applied first-principles thermodynamics to construct phase diagrams (Fig. 1), demonstrating stable closed sites predominating at low pressure (P) and high temperature (T). Our findings reveal a preference for undissociated H_2O in water adsorption, contradicting earlier theories.

Lewis acidity, assessed by pyridine adsorption, varies across different T sites, with T6 being the most acidic and T9 the least. Titanium (Ti) shows the lowest Lewis acidity among the studied dopants. Our analysis of glucose, fructose, and xylose adsorption consistently favors cyclic tautomers, regardless of the T site or metal type. Hafnium (Hf) emerges as the most potent adsorbent. Dispersion forces play a significant role in adsorption energy, highlighting their importance in sugar-zeolite interactions.

This study sets the stage of a further kinetic study of the mechanisms involved in the conversion of different sugars by the studied sites in the zeolite. By delving into these complex reactions, we aim to enhance our understanding and provide critical insights, contributing significantly to the development of advanced catalysts for sustainable chemical processes.

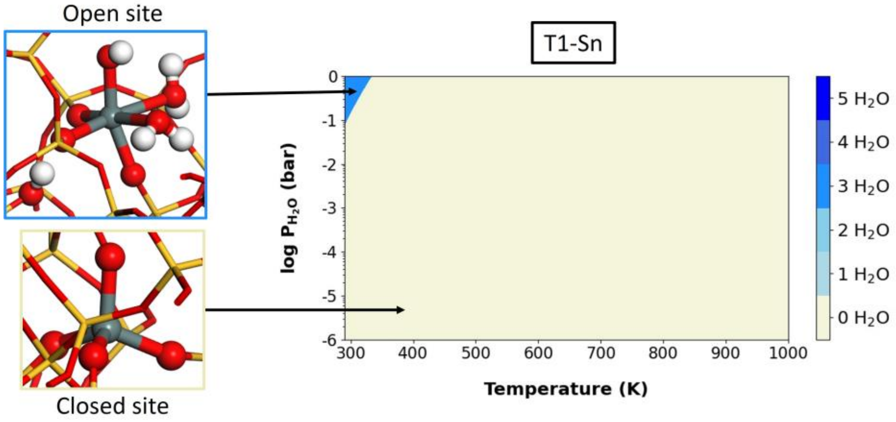

Fig. 1. Stability diagram of T1-Sn as function of T and P

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ORAL C-20

In situ AP-XPS in a Plasma Environment

Sam Taylor[1], Filip Hallböök[1], Jinguo Sun[2], Robert Temperton[3], Johan Zetterberg[2],
Andreas Ehn[2], Sara Blomberg[1]

[1]*Division of Chemical Engineering, Lund University*

[2]*Division of Combustion Physics, Lund University*

[3]*MAX IV Laboratory, Lund university, Sweden*

Plasma catalysis is a rapidly emerging as a new approach for gas processing applications such as the production of ammonia. Yet, the application is limited by the lack of understanding of the plasma interaction with the surface chemistry due to its high underlying complexity and non-equilibrium conditions [1]. Ambient Pressure X-ray Photoelectric Spectroscopy (APXPS) is a powerful surface sensitive technique, often used for detailed chemical analysis with gas pressure on the order of a mbar.

In this study, we have demonstrated the possibility of performing in situ AP-XPS in a non-thermal plasma environment. The experiment, conducted at MAX IV's HIPPIE, simultaneously examines various plasma conditions using an optical spectrometer as well as the plasma's interaction with potential catalytic materials Ni, Co and Au [2] as shown in Figure 1. This data is expected to provide valuable insight into plasma-surface chemistry, which is greatly needed to further utilize and understand plasma catalytic processes.

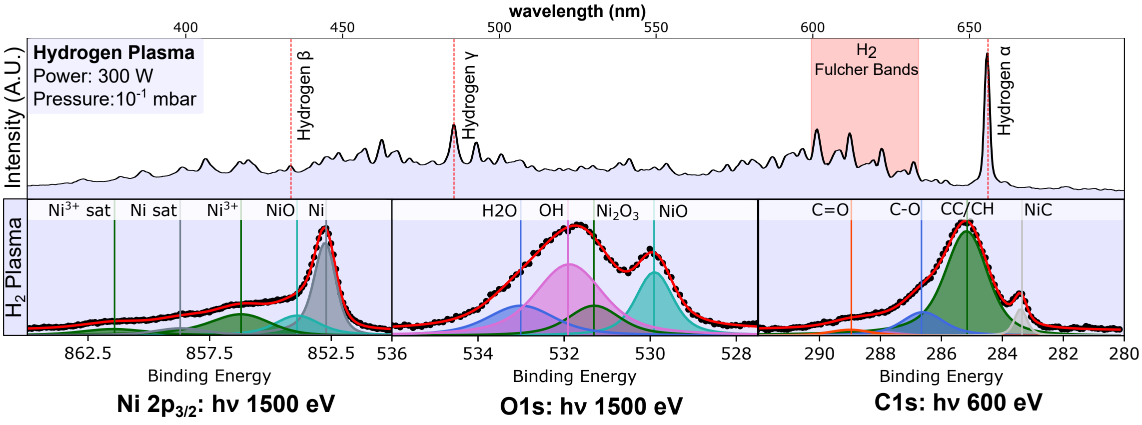

Figure 1: Room temperature nickel foil during H_2 plasma environment. Top) Plasma's optical emission. Bottom) AP-XPS at Ni $2p_{3/2}$, O1s (1500 eV) and C1s (600 eV) region.

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ORAL C-21

Exploring ZSM-5/alumina Shaped Objects with X-ray Diffraction Computed Tomography after Methanol-to-Hydrocarbons reaction

Izar Capel Berdiell[1*], David Wragg[2], Pablo Beato[3], Lars F. Lundegaard[3] and Stian Svelle[1]
[1] Center for Materials Science and Nanotechnology (SMN), University of Oslo, Oslo, Norway
[2] Institute for Energy Technology, Kjeller, Norway
[3] Haldor Topsøe A/S, Lyngby, Denmark
**izarc@uio.no*

Most frequently the academic sector studies pure catalyst powders, while in industry catalysts are usually formulated into objects whose composition, size and shape are optimized for a given process and reactor. Extrudates in cylindrical (Fig 1a) or other shapes are common, but spray-dried particles [1] (Fig 2) can also be used. We are pioneers in using XRD for tracking catalyst deactivation by coke. We recently used operando X-ray diffraction computed tomography (XRDCT) to image cylindrical extrudates using crystal structure parameters [2-3], showing how radial coking gradients develop in such objects during MTH [4]. In this work, we use operando XRDCT to follow the coke burning process during temperature-programmed oxidation (TPO) of the coked cylindrical extrudates.

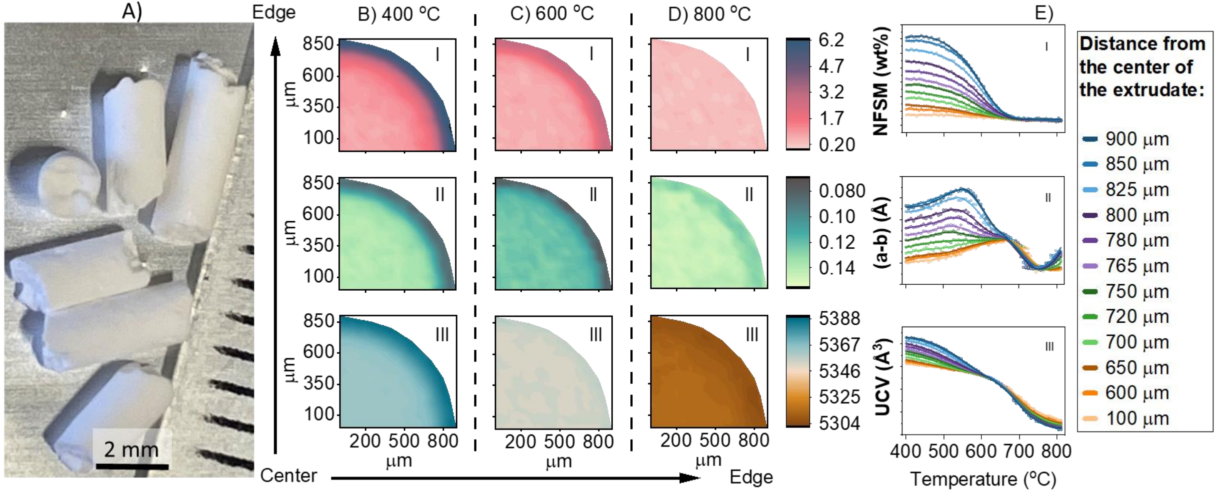

Figure 1: a) Photo of cylindrical extrudates. b) XRDCT slices of a cylindrical extrudate at 3 temperatures during TPO and c) XRD descriptors evolution at integrated radial distances.

Fig 1b-d shows radial coke gradients with temperature during TPO and Fig 1e the coke evolution at different radial distances which suggests that coke is removed from inside out and different coke species. XRDCT on coked spray dried spheres (Fig 2), show an even spread of coke through the whole object, suggesting that there are no diffusion limitations typical of cylinder extrudates.

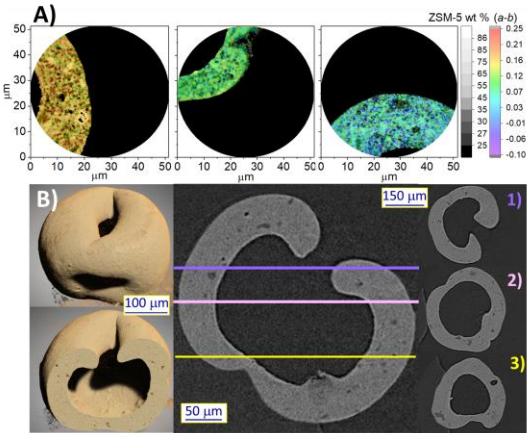

Figure 2: a) Coke distribution in the sphere walls for fresh, partially and fully deactivated spheres. b) Nano-CT 3D reconstruction of the sphere showing voids and density variations in the walls.

Acknowledgments:

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ORAL C-22

Low-pressure, isomer-selective kinetic characterization using PEPICO

Morsal Babayan[1,*], Esko Kokkonen[2], Tomas Cordero Lanzac[3], Satya Joshi[1], Juan Ignacio Mirena[3], Evgeniy A. Redekop[3], Samuli Urpelainen[1], Unni Olsbye[3], and Marko Huttula[1]
[1] *Nano and Molecular Systems Research Unit, University of Oulu, Oulu, Finland*
[2] *MAX-IV Laboratory, Lund University, Lund, Sweden*
[3] *Centre for Materials Science and Nanotechnology (SMN), University of Oslo, Oslo, Norway*
e-mail: morsal.babayan@oulu.fi

Keywords: PEPICO, methanol-to-hydrocarbons (MTH), zeolite

The Methanol-To-Hydrocarbons (MTH) process, converting methanol into hydrocarbons using acid zeolite or zeotype catalysts, represents a novel approach in industry aimed at shifting from fossil fuels towards sustainable resources [1]. The reaction yields a complex mixture of intermediates and products, many of them present as multiple isomers, which poses challenges for effluent analysis. The conventional gas-phase chromatography (GC), commonly employed for effluent analysis [2], is typically limited to ambient pressure flow and is not suitable to detect highly reactive molecules. Mass spectrometry (MS) offers advantages for kinetic experiments under well-defined low-pressure transport conditions but is usually not isomer-selective when coupled with the electron-impact ionization. A potential solution to enhance the isomer selectivity and analytical power of MS is to employ photoionization and detect ions in coincidence with the emitted photoelectron through the Photoelectron-Photoion Coincidence (PEPICO) method [3].

Here, the reaction of dimethylether (DME) on a ZSM-5 is investigated using *in situ/operando* PEPICO at low pressure conducted at the FinEstBeAMS beamline in MAX IV. The reaction of DME over freshly activated zeolite sites is performed at 1×10^{-6} mbar and 375 °C, while PEPICO was performed with 40 eV photon energy in coincidence with electrons in a binding energy range of approximately 7-17 eV. Ions are identified using Time of Flight (TOF) mass spectrometry, and parent molecules are distinguished from fragments by analyzing the coincidence ion yield photoelectron spectra (CIY-PES) for each cation. To show the isomer selectivity of this study, isomers of xylene are studied in detail. While the overall PES for different isomers of xylene are similar, they differ in their first peak related to the ionization channel of $C_8H_{10}+h\nu \rightarrow C_8H_{10}^+ + e^-$. Comparison between the CIY-PES for $C_8H_{10}^+$ with reference spectra of xylene isomers reveals that m-xylene is the dominant one in the effluent. Consequently, PEPICO-based effluent analytics is well-suited for systematic, quantitative, isomer-selective kinetic studies of MTH-relevant reactions under well-defined, low-pressure conditions, with minimized interference from secondary and deactivating reactions. These methodological advances expand the toolkit for detailed kinetic studies of important catalytic reactions.

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Abstracts: Poster Presentations

Strategies for preventing deactivation of hydrodeoxygenation catalysts caused by inorganic impurities in feed

Emma Olsson Månsson[a], Olov Öhrman[b], Derek Creaser[a], Louise Olsson[a]
[a] *Chalmers University of Technology, Gothenburg Sweden*
[b]*Preem AB, Gothenburg Sweden*

Hydrodeoxygenation (HDO) is a catalytic process which uses hydrogen to reduce the oxygen content in liquids (such as fast pyrolysis bio-oil, FPBO) and remove it as water. The process is vital for increasing the stability and processability in converting to a high-quality biofuel. If done in optimum conditions, it can even eliminate coke and char precursors caused by e.g. sugars and furans.[1] One of the most common catalysts is sulphided NiMo supported on e.g. aluminium oxide support. However, the HDO catalysts has been found to deactivate when using bio-oils due to the presence of inorganic elements, mainly traces of plant nutrients like Ca, K, Mg, Fe and P.[2] Using a less sensitive material as a guard bed could therefore be used as a trap before the HDO catalysts, and thus prolong its lifetime.

Based on a published method for reducing the inorganic material in FPBO from <10 ppm down to <0.1 ppm using ion-exchange resins, zeolite and aluminium oxide,[3] we also found that re-using a strongly acidic ion-exchange resin (with no wash in between) resulted in similar removal efficiency when exposing it to fresh FPBO up to three times. This indicates the resin remained unsaturated and have capacity for additional removal.

As the ion-exchange resins and zeolite successfully targeted the cationic species, and the aluminium oxide targeted the anionic species, the combination of these materials was further studied. Additional results showed that both the cationic species Ca, Fe, K, and Mg and the anionic P was removed when combining the resin with the aluminium oxide in a 50/50 mix. Interestingly, the removal of Ca, Fe, and Mg from the oil when combining the two materials was higher compared to using the sorbent materials separately. The boosting effect when combining the sorbents increased the removal of Fe by more than 25 %, and Ca and Mg 1-5 %.

By removing the inorganic species in the feed, the HDO process becomes more economically viable as the frequency for shutdowns for replacing the spent catalysts are decreased. Enabling a wider sustainable feedstock to be used for biofuels, which is not limited by its inorganic content, is an important path towards reducing fossil dependency and reducing the carbon footprint in an economically competitive way.

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A new mesoporous carbon carrier for fixed bed applications

Markus M. Schubert[1]*, **Michelle K. Lynch**[2], **Matteo Baraldi**[1]
[1]*Exacer SRL, via Puglia 2/4, 41049 Sassuolo, IT*
[2]*Enabled Future Limited, Solihull, West Midlands, UK*
**Corresponding author:markus.schubert@exacer.com*

Abstract

In the realm of chemical engineering, particularly for pharmaceutical and aroma chemical processes, there is a significant shift towards more efficient and sustainable methods driven by two trends: the transition from slurry beds to flow chemistry for enhanced efficiency and reduced metal loss, and the advent of new sustainable processes like waste recycling, biomass-based chemical production, and hydrogen production and transport. These processes often involve hydrothermal conditions and extreme pH levels, challenging the viability of standard carriers such as alumina, silica, or zirconia.

Addressing these challenges, Exacer has introduced a new class of shaped carbon carriers designed for fixed bed applications. These carriers are characterized by their predominantly mesoporous structure, crucial for the efficient transport and conversion of larger molecules. They also exhibit mechanical stability comparable to gamma-alumina extrudates, commonly used in fixed bed applications. Significantly, they maintain stability under varying hydrothermal conditions and across all pH ranges. Furthermore, as the support is provided as an extrudate or other shaped solid, they offer the potential for easier and more efficient recovery of expensive precious metals compared with powdered catalyst materials.

When tested for the catalytic oxidation of glucose to glucaric acid, a 0.8% Au, 1.2% Pt catalyst supported on the new carbon carrier demonstrated superior performance, with 52% yield and 87% selectivity. This was notably higher than the yields and selectivity of other commercial activated carbon extrudates such as Donau Supersorbon K4-35 (22% yield, 66% selectivity), Donau Supersorbon SX30 (18% yield, 68% selectivity), and Norit RX3 Extra (20% yield, 70% selectivity).

This development marks a significant advancement in material science, offering a viable and efficient alternative for various chemical processes, especially those requiring stability under challenging conditions.

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Bimetallic catalysts for catalytic upgrading of biomass pyrolysis vapors

Nora N. Corneliussen, Petter Tingelstad, De Chen.
NTNU Department of chemical engineering, Trondheim, Norway

Introduction.

In 2020, fossil fuels comprised 80% of global energy supply and contributed significantly to greenhouse gas emissions[1]. With depleting reserves and environmental concerns, the focus shifts to renewable alternatives, with biomass emerging as a promising source for liquid fuel. Despite its advantages, bio-oil from biomass presents challenges like high oxygen content and limited compatibility with other fuels. This study aims to enhance the presence of non-acidic carbon compounds in biomass pyrolysis oil, optimizing the transfer of carbon-containing compounds from the aqueous phase to the organic phase.

Experimental/methodology.

In this study, bimetallic catalysts on TiO_2 support were tested in a fluidized bed reactor for upgrading of pyrolysis vapors to aviation fuels. $NiPt/TiO_2$, $CoPt/TiO_2$, $CuPt/TiO_2$, $CrPt/TiO_2$, $FePt/TiO_2$ were synthesized with 0.5 wt% loading (1:1) using incipient wetness impregnation. The catalysts were characterized with TPX, XRD and BET, and analyzed by GC-FID/MS. Karl fischer titration was also done.

Results and discussion.

A previous study conducted this fall using monometallic catalysts showed that Pt/TiO_2 and ZSM-5 gave the highest transfer of carbon-containing compounds from the aqueous to the organic phase. Consequently, it was decided to conduct a study on bimetallic catalysts to combine Pt with transition- and non-noble metals to look for a good and cheaper catalyst. Figure 1 illustrates the yield of functional groups in the oil phase.

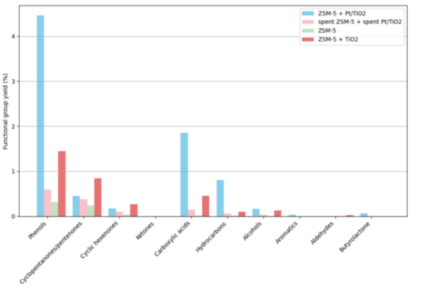

Figure 1. Yield of functional groups using four different catalysts; ZSM-5 + 0.2wt% Pt/TiO_2, spent ZSM-5 + spent 0.2wt% Pt/TiO_2, ZSM-5 and ZSM-5 + TiO_2. 500°C bed, p = 1 atm, 20g/h biomass, 0.4L/min N_2, 0.6L/min H_2.

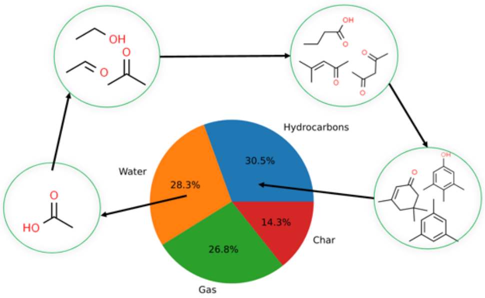

Figure 2. Illustration of the carbon transfer from the aqueous to the organic phase.

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Acetylation of Cellulose Nanomaterials: Ab Initio Mechanisms, Reaction Microkinetics, and Experimental Structural Insights

Ana Oberlintner[1], Matej Huš[1], Blaž Likozar[1], Uroš Novak[1]
[1]*Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, 1000 Ljubljana, Slovenia*

Nanocellulose, readily accessible, biocompatible and biodegradable, holds significant potential as a material of the future. Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) contain reactive hydroxyl (-OH) groups that facilitate surface modifications. Through controlled functionalization, wetting properties can be tailored. Hydrophobic nanocellulose exhibits promising applications in polymer reinforcement, surgical scaffolds, hydrophobic drug delivery, biosensing, bioimaging, and food packaging. Chemical covalent modification methods for nanocellulose include esterification, carbamation, silylation, nucleophilic substitution, and etherification. Additionally, non-covalent adsorption of molecules like surfactants onto the nanocellulose surface and plasma treatment are employed to achieve hydrophobic properties[1,2]. However, literature lacks comprehensive descriptions of hydrophobic nanocellulose functionalization mechanisms and the kinetics of these catalytic transformations[3].

Therefore, to address this deficiency, the present study first focuses on understanding the mechanism of pyridine-catalyzed esterification reactions of CNCs and CNFs through *ab initio* calculations, which serves as a skeleton for a development of a kinetic model. The data on kinetics was collected experimentally through analysis of FT-IR spectra, coupled with advanced characterization methods such as ^{31}P NMR to determine accessibility of surface hydroxyl groups, CP-MAS solid-state NMR to confirm successful modification, XRD to follow possible change in crystallinity that would point to alteration of the bulk of the material, TEM and SEM for morphology.

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Poster-5

Pentaerythritol synthesis through a heterogeneous catalysis route

Aqsa Noreen[1], Derek Creaser[1], Oleg Pajalic[2], Louise Olsson*[1]
[1]Competence Center for Catalysis, Chemical Engineering, Chalmers University of Technology, SE-422096 Gothenburg, Sweden
[2]Perstorp AB, Industriparken, 284 80 Perstorp, Sweden

Pentaerythritol (Penta) is a common platform chemical used in the production of resins, plastics, paints, and various other commercial products. Industrially, penta is produced with high over-all yields and a good product grade through a homogeneous catalysis system in which formaldehyde and acetaldehyde undergo three sequential cross condensation reactions followed by the cannizzaro reaction in the presence of a liquid alkaline solution. In this existing liquid alkaline homogeneous catalysis system, an excess of formaldehyde and alkaline solution is needed due to the sodium formate salt formation during the reaction [1]. As an alternative, a heterogeneous catalytic system would have several benefits, such as replacing the alkaline solution. For the first time, according to our knowledge, we present a heterogeneous catalyst which can be used for Penta production.

Na/support (prepared by conventional inciptness wetness co-impregnation), where TiO_2, SnO_2 and Al_2O_3 were used as solid support to prepare the catalysts. All the catalyst activity tests were performed in a glass-flask setup. Formaldehyde and acetaldehyde were mixed with the solid catalysts and the reaction mixture was heated under continuous stirring. Prior to the catalyst tests, blank reaction was performed under the same reaction conditions. After cooling down the reaction mixture, the solid catalysts were separated out from liquid reaction mixtures. Products were then analysed and quantified by GC/MS.

In the Na/TiO_2 catalyst activity test reaction, some diols were produced with 14% yield along with 0.2% yield of penta was observed. Na/Al_2O_3 exhibited slightly higher activity towards penta formation with 7 mol% yield, along with other products i.e. 4% formals, and 24% other oxygenates. Interestingly, with Na on SnO_2 support Na/SnO_2 showed comparatively higher activity towards penta formation with 23% yield as shown in Figure 1. Additionally, this catalyst was also selective towards penta-based derivative compounds (simply named as -ols in figure) with 23% yield that are likely formed due to penta reaction with formaldehyde.

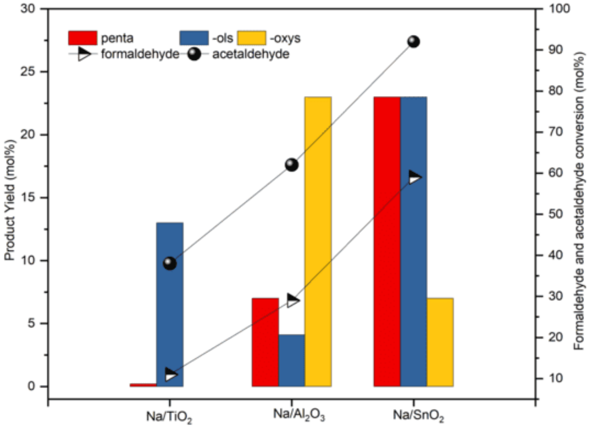

Fig. Penta synthesis over different catalysts.

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Poster-6

Flexibility of MFI zeolite upon adsorption of guest species: DFT study

Agnieszka Seremak, Torstein Fjermestad, Stian Svelle
Center for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo, Norway

MFI type zeolite is a widely studied and applied catalyst, used in the methanol-to-hydrocarbons reaction. Its main limitation is the formation of nonreactive species *i.e.*, coke, which ultimately causes the loss of catalytic performance.[1] Additionally, it has been experimentally observed that the presence of organic (coke) compounds distort the architecture of the zeolite framework.[2,3] In the present work we apply periodic density functional theory to explore the flexibility of the MFI type zeolite upon adsorption of various organic molecules. Particular attention is given to the effect of Brønsted acid site (BAS) position, and the type and number of adsorbed molecules on the changes of the pore shape and unit cell dimensions. The investigated MFI zeolite model has Si/Al ratio of 31. The calculations are executed with PBE exchange correlation functional, Grimme D3 dispersion interactions correction and a plane-wave auxiliary basis set cutoff at 660 Ry.[4] The guest species are placed in the zeolite pores in a stepwise manner – up to 4 molecules per unit cell (uc.).

The geometry optimization procedure revealed that all examined hydrocarbons preferred the easily available channel intersection, along the straight channel. The orientation of guest molecule is driven by a strong interaction between BAS and molecule's electron cloud (Fig.1.). We identified two most stable structures – first with BAS in the intersection, and second with BAS in the straight channel. At a maximum loading upon adsorption of smaller molecules the most energetically favorable structure is with the BAS in the straight channel, whereas for larger organic species the most stable active site location is in the intersection. Regardless of proton siting the most pronounced flexibility is observed for naphthalene and large methylated benzenes, due to their size effects and proximity of the molecule to the zeolite framework. No flexibility is discovered as a response to benzene and toluene adsorption. This study presents a non-identical structural behavior of MFI zeolite catalyst depending on the active site location and type of guest compound. It reveals high complexity of catalysts material interactions with guest molecules, where depending on BAS position and type of molecule we can expect various responses of the framework. These responses can provide a better understanding of catalyst deactivation and navigate us towards modifying the catalysts to hinder its deactivation.

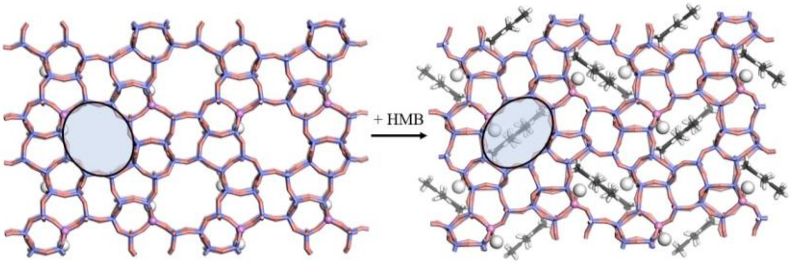

Fig.1. Flexibility of MFI upon adsorption of one hexamethylbenzene molecule/uc. The orientation of organic molecule causing noticeable deformation of straight channel.

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Poster-7

Production of C3 hydrocarbon from GaInOx with addition of SAPO -34

Bjørnar Arstad, Silje F. Håkonsen, Joanna Pierchala, Ørnulv Vistad,
SINTEF Industry, Department of Process Technology, P. O. Box 124 Blindern, 0314 Oslo, Norway

The presented work is the result of SINTEF's activities within EU project COZMOS where the main goal was to validate an efficient and selective transformation of CO_2 to propane and propene, two key products for energy storage and displacement of fossil fuels in commodity chemicals production, respectively (1).

The biggest challenge of COZMOS project was to combine the sequential reactions of CO_2 hydrogenation to methanol (preferred conditions 200 °C – 300 °C, 50 bar – 100 bar) and methanol to C3 hydrocarbons (preferred conditions 450 °C – 515 °C, 2 bar – 4 bar), exploiting Le Chatelier's principle to overcome low equilibrium product yields of methanol.

For this purpose, a set of CO_2 activation catalyst was made: $Ga_{1-x}In_xO_3$ (x=0, 0.1, 0.25 and 0.5). The element composition was selected as a follow up of results obtained on the sample set made at SINTEF within earlier project work and based on literature data (2) suggesting expected performance of these catalysts at higher temperature and pressure than typical for methanol synthesis.

The catalysts were physically mixed with SAPO-34 powder to increase hydrocarbon production by varying weight ratios of CO_2 hydrogenation catalyst and SAPO-34 (1:2, 1:1, 2:1). Catalyst candidates were tested in a high throughput system within conditions selected as an intermediate value between the optimal conditions for methanol synthesis and conversion to olefins – 30 bars pressure and temperature up to 400 °C, where the gas feed molar ratio was 3:1 H_2/CO_2.

Figure below shows the catalyst performance for methanol production and for the of C3 hydrocarbons after SAPO-34 was added.

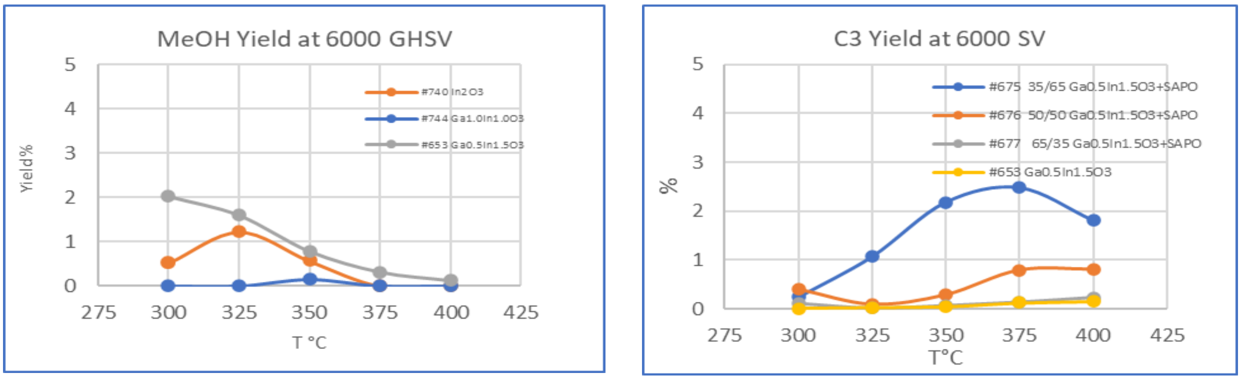

Fig.1 Yield of methanol (left) and C3 production (right).

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Modified Zeolites for Catalytic Valorisation of Furans to Aromatics

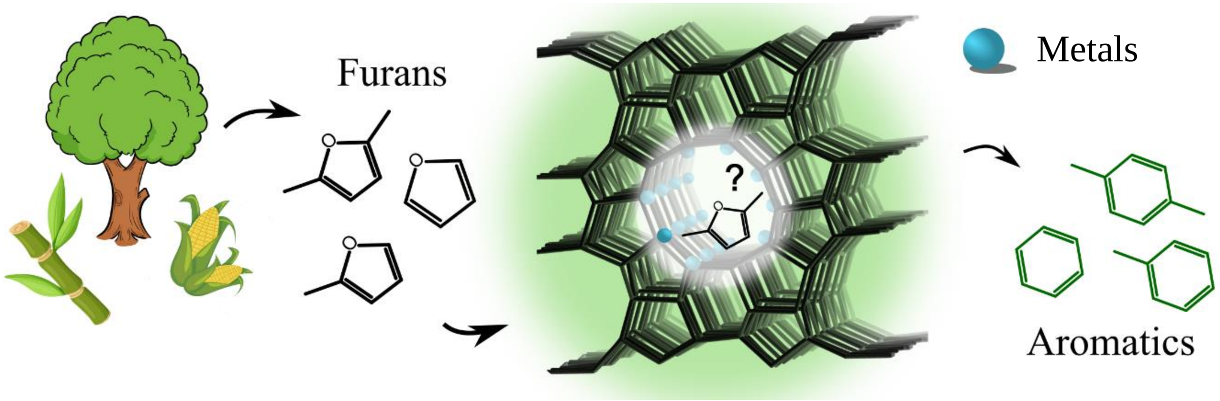
Guido de Reijer, Andreas Schaefer, and Per-Anders Carlsson
Department of Chemistry and Chemical Engineering, Chalmers University of Technology,
Gothenburg, 412 96, Sweden

The growing demand for a sustainable chemical industry can be satisfied by utilising renewable carbon sources like lignocellulosic biomass. One interesting model reaction is the conversion of biomass-derived furans into valuable aromatic building blocks such as benzene, toluene, and xylenes (BTX). Microporous solid acid catalysts, such as zeolites and zeotypes, are employed for their readily tuneable acidity and porosity.

Here, 2,5-dimethylfuran is converted into aromatics in a continuous fixed-bed reactor coupled to an online Fourier Transform Infrared (FTIR) spectrometer and Mass Spectrometer (MS). Catalysts are prepared through hydrothermal synthesis and analysed using techniques such as XRD, XRF, TGA/DSC, N_2/Ar-physisorption, SEM, EDX, and NH_3-TPD. Properties of the catalysts that were investigated are the framework of the catalysts, MFI and beta, the incorporated metal, Al or Ga, the metal loading, synthesis conditions, and the reaction conditions.

In a previous work, Ga-MFI exhibited a production of aromatics which was superior to Al-MFI, due to a decreased coking of the catalyst and thus an increased catalyst lifetime.[1] Here, it was found that the selectivity can be tuned from BTX towards other valuable products, such as the isomerisation product 2,4-dimethylfuran, by lowering reaction temperatures,. Moreover, the production of BTX can be increased by increasing the gallium loading, which increased the acidity of the catalyst. However, there is a limit to the amount of gallium that can successfully incorporated into MFI framework zeolites at which different (amorphous) phases are formed.

Furthermore, a post-synthesis modification of the catalysts was performed to introduce mesopores that enhance the accessibility of the catalytic acid sites, at the cost of losing some acid sites. Further one-step synthesis of mesoporous is explored to prevent loss of acidity. In short, this work identifies and investigates catalytic descriptors that are important for the valorisation of 2,5-dimethylfuran, aiding future catalyst design.



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Poster-9

Investigating Stabilization – A Model Compound Study of Catalytic Stabilization of Pyrolysis Bio-Oil

Amalie Paarup Krebs[1], Ida Schiødte Overgaard[1], Rui Pedro da Cruz[1], Martin Høj[1], Alexander Søgaard[1], Magnus Zingler Stummann[2], Michael Brorson[2], Lived Y. Lemus-Olsen[2], Anker Degn Jensen[1]*
[1]DTU Chemical Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark,
[2]Topsoe A/S, 2800 Kgs. Lyngby, Denmark

Biomass pyrolysis oil must be hydrotreated to produce a fuel that can be used in the present infrastructure[1]. Due to their poor stability a two-step is required to avoid operational problems[2]. In this contribution, we will present our research into the activity and sulfur tolerance of hydrotreating catalysts for stabilization of pyrolysis oils using model compounds.

Experiments were carried out using a 500 mL batch autoclave (Parr) with different catalysts (4 wt% to feed). The model compounds (furfural (FU), guaiacol, and octanoic acid) were treated individually and in a mixture to investigate their interactions during stabilization. The autoclave was pressurized at 90 bar H_2, heated to 180 °C, and kept there for one hour. The catalysts were tested without and with an organic sulfur component (dodecane-1-thiol) added to the feed. The study revealed the catalysts activities towards converting the model compounds to more stable molecules, along with insight into the interactions between the compounds in the tests. The sulfur tolerance of the tested catalysts was investigated along with its impact on the model compound conversion. The FU conversion for the catalysts with/without added sulfur is seen in Figure 1, along with the furfuryl alcohol selectivity. The sulfur addition had a negative impact (15 to 69 % reduction) on the FU conversion in most cases, apart from a few catalysts. The increase in FU conversion for the Ni-Mo-S/Al_2O_3 catalyst was to be expected, but for the Pt/C catalyst, it remains to be understood and could warrant further investigation. For several of the catalysts, the sulfur had a positive influence on the furfuryl alcohol selectivity. Whether this is because the sulfur impacts the selectivity of the catalyst, or it is due to deactivation of the catalyst after the initial conversion of FU to furfuryl alcohol remains to be determined.

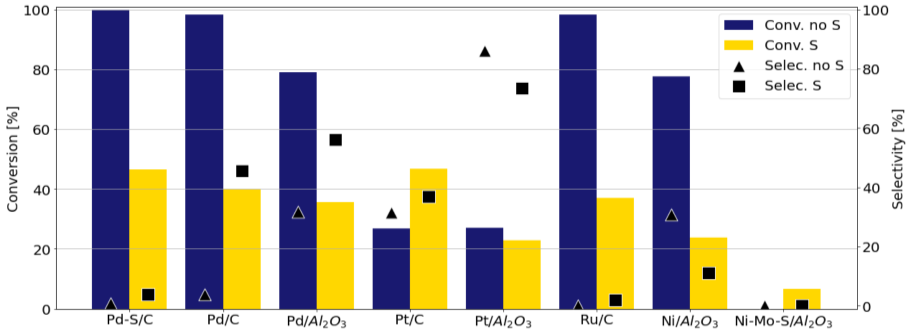

Figure 1. Conversion of furfural (calculated from GC-MS/FID) at 180 °C, 90 bar H2, 60 min for different catalysts, both with sulfur added (yellow) and without (blue). Selectivity for furfuryl alcohol is displayed on the second axis.

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Poster-10

Characterization of noble metal catalysts for plasma-oxidation of methane

Abhinash Kumar Singh[1], Irzam Javed[1], Jasmiina Palo[1], Johanna Kihlman[1], Pekka Simell[1].
[1]*VTT Technical Research Centre of Finland, Espoo, Finland.*

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, cold 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]

The primary objective of this study was to explore the catalytic properties of various noble metals, namely Pt, Pd, and Cu, supported on γ-Al_2O_3 and NH_4-ZSM-5, synthesised by the impregnation method. The study evaluated the oxidation efficiency of 1% CH_4 in air and the selectivity of different catalysts under similar conditions in a Dielectric Barrier Discharge (DBD) plasma reactor. To assess the impact of plasma on the investigated catalysts, several characterization techniques were employed, including N_2 physisorption, H_2 chemisorption, XRD, and SEM. The main objective was to understand if any structural or other changes on the catalysts could be observed and whether these were typical changes for oxidation catalysts or unique for plasma system.

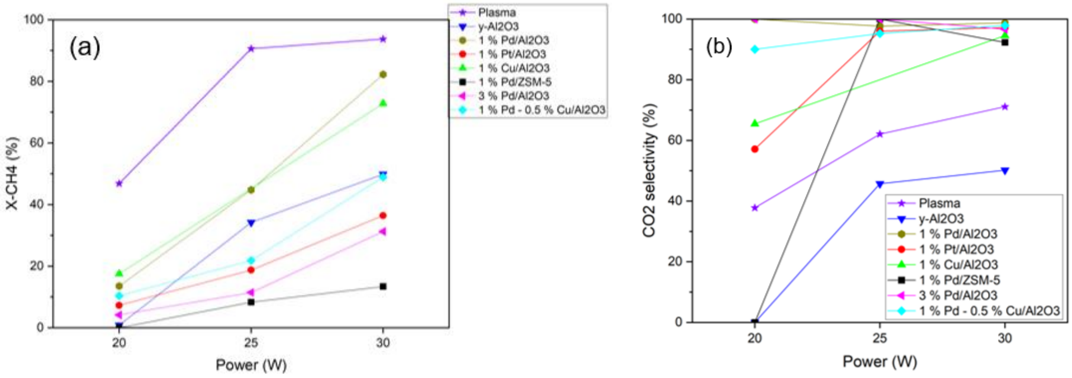

Fig 1. Effect of catalysts at different plasma power on (a). Oxidation of methane (b). CO_2 selectivity.

Funded by
the European Union

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Dynamically responsive ammonia cracking for H_2 release utilizing magnetically-heated catalyst

Žiga Ponikvar[a,b], Anja Sedminek[a,b], Janvit Teržan[c], Luka Skubic[a,b], Žan Lavrič[c,d], Matej Huš[c,d,e,f], Miha Grilc[c,d], Blaž Likozar[c], Andraž Kocjan[a], Darko Makovec[a], Sašo Gyergyek[a]
[a] Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia
[b] Faculty of Chemistry and Chemical Technology, Smetanova ulica 17, 2000 Maribor, Slovenia
[c] National Institute of Chemistry, Hajdrihova ulica 19, 1000 Ljubljana, Slovenia
[d] University of Nova Gorica, Vipavska 13, SI-5000 Nova Gorica, Slovenia
[e] Association for Technical Culture of Slovenia (ZOTKS), Zaloška 65, SI-1000 Ljubljana, Slovenia
[f] Institute for the Protection of Cultural Heritage of Slovenia (ZVKDS), Poljanska 40, SI-1000 Ljubljana, Slovenia

Green hydrogen is becoming an important energy vector however, storing and transporting pressurized or liquid hydrogen is expensive and hazardous[1]. Safer methods of containment and transport, such as storage in molecules than can reversibly bond hydrogen on demand, are becoming increasingly important. One such molecule is ammonia; however, due to issues related to heat transfer, the instantaneous start of a conventionally heated decomposition reactor is challenging[2]. Here we report on the electrified and dynamically responsive decomposition of ammonia as a means of releasing on-demand chemically bonded hydrogen based on the rapid magnetic heating of a hierarchical nanocomposite catalyst. The developed catalyst is composed of ferromagnetic CoNi alloy nanoparticles embedded in a high-surface-area alumina decorated with catalytic Ru nanoparticles. CoNi precursor nanoparticles were synthesized by a simple aqueous co-precipitation of Co^{2+} and Ni^{2+} cations by addition of base. Those were incorporated within alumina by hydrolysis of AlN in colloidal suspension. The produced nanocomposite was reduced to transform CoNi precursor nanoparticles to metallic alloy. Ru nanoparticles were deposited on the surface of alumina by precipitation followed by reduction. Experimental observations of activity coupled with modelling at the level of density functional theory and micro-kinetic modeling confirmed the minute-scale response of the H_2 release. The fast response of our catalytic system would, at least in principle, enable the utilization of intermittent renewable electricity and a tunable H_2/NH_3 ratio in the reactor's effluent.

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Design of Cu-zeolites for the selective hydrogenation of CO_2

Dimitra Iltsiou[1], Jerrik Mielby[1], Søren Kegnæs[1]Authors
[1]*Department of Chemistry - Technical University of Denmark*
Kemitorvet Building 207, 2800 Kgs. Lyngby, Denmark

The carbon circular economy provides solution, to address the high levels of CO_2 in the atmosphere, by researching ways to store, use and remove it. As an inexpensive, abundant and non-toxic, renewable carbon source, the use of CO_2 has received a great interest in many areas. Lately, the focus of researchers is the production of fuels and high-value-added chemicals such as alcohols, throughout the hydrogenation of CO_2. Among alcohol products, ethanol attracts great attention due to its notable energy density and current engine knowledge. However, the conversion of CO_2 to ethanol has been difficult, due to the presence on the catalyst of various functional groups and the high energy barrier of the C-C coupling [1]. Therefore, the development of novel stable heterogeneous nanoparticle catalysts, for the selective production of ethanol directly from CO_2, is of great importance.

Zeolites are the most widely used industrial heterogeneous catalysts. They are classified as aluminosilicate materials with intracrystalline pores and cavities of molecular dimensions. The catalytically active sites in zeolite micropores can be acid sites that result from the charge compensation of the framework with protons, which is necessary when e.g. Al^{3+} substitutes Si^{4+} in the framework. Alternatively, it can also be redox active sites resulting when the charge compensation is done with redox active ions such as Cu(II), rather than with protons [2-3].

Here we report the synthesis and encapsulation of different zeolite frameworks, with Cu metal nanoparticles. The different zeolite-based catalysts were tested under high pressure continues flow conditions in order to optimize the selectivity for ethanol. We have shown that, the structure of the zeolite framework has great influence on the catalytic activity. All the obtained materials were characterized using IR, XRD, BET, TEM and FTIR [3].

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Catalytic Reduction of N_2O by NH_3+NO over Fe-CHA, -BEA and -FER catalysts

Rishav Chand[1], Libby Brungardt[3], Brian B. Hansen[1], Jakob M. Christensen[1], Michael Brorson[2], Siddarth H. Krishna[3], Anker D. Jensen[1*]

[1]Technical University of Denmark (DTU),
Department of Chemical and Biochemical Engineering, Kgs. Lyngby, Denmark
[2]TOPSOE A/S, Kgs. Lyngby, Denmark
[3]University of Wisconsin-Madison,
Department of Chemical and Biological Engineering, Madison, WI, USA
** aj@kt.dtu.dk*

Abstract

N_2O (nitrous oxide) is known to be ~300 times more potent to cause global warming than CO_2 on a per-unit-mass basis[1]. Anthropogenic sources are responsible for ~35% of N_2O emissions and the N_2O concentration in the atmosphere has increased at an alarming rate of ~0.2–0.3%/year in the last century[2]. N_2O emissions can be countered by either direct catalytic decomposition into N_2 and O_2 or selective catalytic reduction (SCR) into N_2 and H_2O/CO_2 depending on type of reductant[3]. Fe-zeolite catalysts have been predominantly studied in the literature and used in practice to catalyze the reduction of N_2O using NH_3. However, the nature of active sites and the effects of zeolite topologies in such catalysts are still debated to this day.

To further explore these questions, we synthesized three Fe-zeolite catalysts – Fe-CHA, Fe-BEA, and Fe-FER – via ion-exchange method and tested their catalytic activity for N_2O reduction in the temperature range of 150-450 °C. Light-off curves were obtained in the presence of 5% O_2, 2.5% H_2O and either NH_3 ($[N_2O]:[NH_3] = 1:1$) or NH_3+NO ($[N_2O]:[NH_3]:[NO] = 1:2:2$) as the reductant. Both in the presence and absence of NO, the Fe-BEA catalyst resulted in the highest N_2O conversion, followed by Fe-CHA and Fe-FER catalysts. Unsurprisingly, Fe-BEA catalysts are also the preferred choice in the industry at present. Then, steady-state kinetic data ($[N_2O]:[NH_3]:[NO] = 2:1:1$, 1% H_2O, 10% O_2) were also collected for all the catalysts at 350 °C. The reactions carried out in the absence of O_2 yielded conversions for all the nitrogenous species in the differential regime, and hence the data obtained thereof were used for comparing the rate of N_2O reduction over the three catalysts. Fe-CHA and Fe-BEA catalysts yielded very similar reaction rates, suggesting similar Fe ion active sites in these materials. In contrast, the rate over Fe-FER catalyst was about 4 times lower, suggesting that there are either fewer active Fe ionic species, or that the Fe ions have lower intrinsic reactivity.

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Exploration of Liquid Organic Hydrogen Carriers using First-Principles Calculations: Dehydrogenation of methylcyclohexane on Pt(111) and Pd(111)

Alvaro Posada-Borbón[1], Tobias Möslinger[1], and Henrik Grönbeck[1]
[1]*Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*

Hydrogen production from water splitting is one way to produce fuel that is free of greenhouse gas emissions. However, storage of H_2 is challenging due to its gaseous state, requiring either high pressures (~700 bar) or low temperatures (~20K) for its liquification and storage. An alternative is to load H_2 onto organic molecules that are liquid at room temperature, so-called Liquid Organic Hydrogen Carriers (LOHC), such as methylcyclohexane (C_7H_{14}) / toluene (C_7H_8).[1]

Here, we use density functional theory calculations with dispersion corrections to investigate the dehydrogenation of methylcyclohexane to toluene on Pt(111) and Pd(111). The reaction mechanism considers the direct dehydrogenation route of methylcyclohexane [R1: $C_7H_{14} \rightarrow C_7H_8 + 3H_2$]. On both surfaces, R1 is found to be exothermic (Fig.1), with a calculated reaction energy for the absorbed carbon-based product of -0.70 and of -0.27 on Pt(111) and Pd(111), respectively. In general, the adsorption energies of the reaction intermediates are ~0.5 eV lower on Pd(111) as compared to Pt(111). The barriers for the dehydrogenation steps are calculated to be about 0.9 eV.

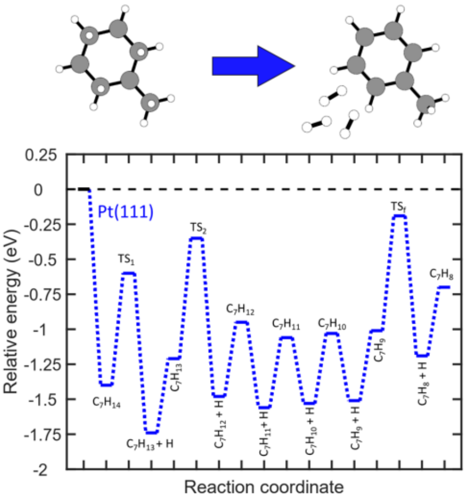

Fig.1 Potential energy diagram for C_7H_{14} dehydrogenation to C_7H_8+$3H_2$ on Pt(111).

In addition to the potential energy diagram for the dehydrogenation/hydrogenation reactions, we consider the unwanted competing reaction of hydrodemethylation of toluene into benzene [R2: $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$]. R2 is exothermic by -0.92 (-0.54) eV, with respect to the initial state for Pt(111) [Pd(111)], which is slightly higher than for the wanted product C_7H_8. However, the barrier for the hydrodemethylation to benzene appears to be slightly higher than for the wanted dehydrogenation reaction. The kinetic behavior of the reaction is explored with the use of mean field microkinetic modeling.

Our results predict in summary that the dehydrogenation of methylcyclohexane to toluene is more favorable on Pt(111) than on Pd(111), while the hydrodemethylation of toluene to benzene is relatively more favorable on Pd(111) than on Pt(111).

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Alkali-Promoted Zeolite Catalysts for One-Step Conversion of Glycerol Waste into High-Added-Value Chemicals

Andrii Kostyniuk, Blaž Likozar

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, 1000 Ljubljana, Slovenia

Glycerol, a predominant byproduct in the biodiesel industry, comprises around 10% of the total biodiesel mass production. The surplus of glycerol has led to a decrease in its commercial price, given its widespread availability in the global market. Effective valorization of glycerol can be achieved through gas-phase processes utilizing heterogeneous catalysts. In this regard, various value-added products, such as ethanol, allyl alcohol, and glycidol, exhibit significant promise due to their versatility and attractive market profitability[1-3].

Alkali-promoted zeolite catalysts were synthesized using the wet impregnation method, with SiO_2/Al_2O_3 ratios of both 30 and 1500. Catalytic experiments were carried out in a Microactivity-Reference unit (PID Eng&Tech). The standard procedure involved loading 0.5 g of the catalyst into a tubular reactor, introducing a 10 wt% aqueous glycerol solution into the reactor, and operating at a temperature of 350 °C under ambient pressure in a N_2 atmosphere. The structural, morphological, acidic, and basic properties of alkali-treated zeolite catalysts were systematically investigated using various analytical techniques.

The impact of incorporating alkali into ZSM-5 zeolite on acidity, basicity, and catalytic performance was explored. This catalyst exhibited relatively high stability and selectivity, attributed to the presence of an appropriate amount of basic sites and a strong Metal/H-ZSM-5 support synergetic interaction. Therefore, by depositing varying amounts of $CsNO_3$ onto the H-ZSM-5(1500) parent zeolite, we can effectively adjust both the strength and abundance of basic sites within the catalysts. This adjustment plays a crucial role in determining catalytic activity and, more importantly, selectivity in the gas-phase conversion of glycerol into glycidol and/or allyl alcohol.

Upon introducing alkali metal, it was observed that some Si components partially dissolved from the H-ZSM-5 framework. The highest glycidol yield achieved was 40.4 mol%, obtained with a feed containing 10 wt.% glycerol, a reaction temperature of 350 °C, and a total GHSV of 1250 h^{-1}. The most stable allyl alcohol selectivity achieved was 46.1 mol.% at 98.1 mol.% glycerol conversion over the 5wt.%Cs–2.5wt.%Fe–2.5wt.%Mo/H-ZSM-5. A relationship between catalytic activity and overall basicity was established, and a reaction scheme was proposed for the production of glycidol and allyl alcohol.

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Bismuth-rich photocatalysts for the removal of paracetamol

Sajad Ahmadi[1*], Satu Ojala[1], Velma Kimbi Yaah[1], Sergio Botelho de Oliveira[2]
[1]Environmental and Chemical Engineering (ECE), Faculty of Technology, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland [2]Department of Chemistry, Federal Institute of Goiás, Goiania 72910-733 Brazil

Bi-rich bismuth oxyhalides ($Bi_aO_bX_c$) bear similarities to BiOX in that they possess layered structures with high density [1]. Due to the band structure, Bi-rich oxyhalides have enhanced light-harvesting ability, overcoming the issue of limited photo-absorption of BiOBr [2]. For instance, Bi_3O_4Br and $Bi_{24}O_{31}Br_{10}$ exhibit a narrower band gap than BiOBr. However, these photocatalysts require further investigation, and more efforts need to be made to enhance their activity.

In this study, bismuth-based photocatalysts were prepared by solvothermal method. For the preparation of BiOBr, 0.971 g of $Bi(NO_3)_3.5H_2O$ was dissolved in 50 mL of 10 % ethylene glycol and stirred for 10 min. Then, 0.238 g of KBr was added to the above mixture and stirred at room temperature for 15 min. The solution pH was around 1.5 and did not need further adjustment because, at this pH, pure-phase BiOBr can be obtained. Then, the solution was transferred into a 100 ml autoclave and heated at different temperatures for 18 hours. Bi_3O_4Br and $Bi_{24}O_{31}Br_{10}$ were synthesized using the solvothermal method by dissolving 0.971 g $Bi(NO_3)_3.5H_2O$ in 10 mL of ethylene glycol followed by adding 10 ml KBr solution with continuous stirring. Then, 2 mL and 5 mL of $NH_3{\cdot}H_2O$ were dropped into the mixed solution to adjust the pH to get the $Bi_{24}O_{31}Br_{10}$ and Bi_3O_4Br, respectively. All the samples were synthesized at different temperatures for 18 hours. The prepared samples were characterized thoroughly.

The photoluminescence (PL) spectra of BiOBr, Bi_3O_4Br, and $Bi_{24}O_{31}Br_{10}$ were measured to assess their carrier separation efficiency. Low PL peak intensity indicates a higher electron-hole separation efficiency. The fluorescence emission intensity of Bi_3O_4Br was the lowest in comparison with BiOBr and Bi24O31Br10. The charge transfer efficiency of BiOBr, Bi_3O_4Br, and $Bi_{24}O_{31}Br_{10}$ was studied using electrochemical impedance spectroscopy (EIS). The arc radius is related to the value of electron transfer resistance. The smaller the radius, the less hindrance to charge transfer and the more efficient electron-hole separation. The smallest arc radius was found in Bi_3O_4Br, indicating that its charge transfer ability is the best. The EIS results were consistent with PL results. Enhanced carrier separation rate and reduced transfer resistance were responsible for the superior photocatalytic activity of Bi_3O_4Br. Around 80 % of the paracetamol was removed with Bi_3O_4Br, while 55 % and 35 % were removed with $Bi_{24}O_{31}Br_{10}$ and BiOBr.

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One-pot hydrothermal synthesis of tungsten-based photocatalysts for the photocatalytic degradation of 5-Fluoruoacil under solar-LED.

Velma Beri Kimbi Yaah[1,2]*, L.M. Pastrana-Martínez, F.J. Maldonado-Hódar, S. Morales-Torres[1]

[1]Nanomaterials and Sustainable chemical technologies-Nanotech, Dept. Inorganic chemistry, Faculty of Science, University of Granada, Avda. Fuentenueva s/n, 18071, Granada Spain
[2]Environmental and Chemical Engineering (ECE), Faculty of Technology, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland
**velma.kimbiyaah@oulu.fi*

Tungsten-based photocatalysts have gained popularity in sunlight-driven photocatalysis due to their relatively lower band gaps and good light absorption under visible light. However, the limited porosity and high electron-hole recombination rate with slow charge transfer is still a problem[1]. Carbon materials can enhance porosity, delocalize charge carriers of semiconductors hence, reducing the electron hole recombination rate and extending the photoactivity to longer wavelengths. So, incorporating carbon in photocatalysts can be beneficial in increasing their efficiencies in the degradation of contaminants[2]. In our work, several tungsten-based metal oxides and composites were synthesized hydrothermally and used as photocatalysts in the solar-light driven degradation of 5-FU in water. The effect of doping the metal oxides with carbon was equally studied. The $B_{i2}WO_6$ (BW) sample was prepared hydrothermally, and the tungsten (WO) were further calcined at 450 °C for 5 h. To prepare the composites, the metal oxides were doped with 2 % (BW-C) and 3 % (WO-C) of a physically activated carbon prepared from spruce wood. The prepared materials were characterized by different techniques and their activity was evaluated in the photodegradation of 5-FU aqueous solution under solar-LED irradiation. The XRD patterns of the prepared materials corroborate the formation of orthorhombic phase of Bi_2WO_6 (JCPDS 39-0256) and monoclinic phase of WO_3 (JCPDS 71-2141). No peak of carbon was observed in the composites possibly due to the little amount added. Band gap values estimated from the tauc plots were about 2.3 and 2.5 for BW-C and BW, respectively, and 2.6 and 2.9 for WO-C and WO, respectively. The specific surface areas (S_{BET}) of BW and WO are ~45 and ~4 m^2g^{-1}, while that of BW-C and WO-C are 68 and 13 m^2g^{-1}, respectively. So, the addition of any amount of activated carbon enhanced the metal oxide properties. The composites performance was assessed in the photocatalytic degradation of 5-FU, those performing better at a given time than the metal oxides under solar-LED irradiation (BW-C 98 %, WO-C 75 %, BW 94 %, and WO 30 %). Therefore, doping with C played a role in improving the performance of the photocatalysts. No degradation was observed during photolysis.

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Ni/Al_2O_3 catalyst for efficient debromination of brominated flame retardants from water phase

Paavo Auvinen*, Eerika Olkkonen, Ville Nissinen, Krista Grönlund, Mika Suvanto,
Janne Jänis, Jarkko J. Saarinen
University of Eastern Finland, Department of Chemistry, Joensuu, Finland
**paavo.auvinen@uef.fi*

The escalating generation of plastic waste is a mounting issue for our society and lifestyle. Instead of resorting to landfills or energy production, repurposing waste as a feedstock for new products aligns with the principles of sustainability and improving circular economy. The problem, however, is that the mixed waste contains several unwanted additives, including brominated flame retardants (BFR) that pose both environmental and health related challenges. Despite recently established regulations, the concentrations of BFRs in already accumulated waste can surpass tens of thousands of ppm.[1] Therefore, it is imperative to remove the BFRs from plastics before further recycling. One approach is to employ catalytic debromination.

We studied catalytic debromination of the tetrabromobisphenol A (TBBPA) containing high-impact polystyrene (HIPS) in a batch reactor, employing a combined extraction–catalytic debromination approach. Two model HIPS batches, with bromine concentrations of 2500 ppm and 25000 ppm Br, were employed in the experiments. Extraction-debromination was done in a mixed water-isopropanol solvent, under N_2 atmosphere, utilizing Ni/Al_2O_3 catalysts. The extraction solution was qualitatively analyzed with high-resolution timsTOF ion mobility mass-spectrometer (Bruker, DE), while quantification was carried out with a gas chromatograph equipped with a flame ionization detector (GC-FID). The additive composition of the extracted HIPS was analyzed using timsTOF equipped with direct-inlet-probe (DIP) technology, along with X-ray fluorescence (XRF).

The efficient extraction and conversion of TBBPA into completely debrominated bisphenol A was successfully achieved at a temperature of 150 °C. The findings from this study hold the potential to further advance the mechanical recycling of BFR containing plastics waste and contribute to the principles of a circular economy.

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Exploring the reaction network in the catalytic debromination of tetrabromobisphenol A

Eerika Olkkonen*, Paavo Auvinen, Ville Nissinen, Krista Grönlund, Mika Suvanto, Janne Jänis,
Jarkko J. Saarinen
University of Eastern Finland, Department of Chemistry, Joensuu, Finland
**eerika.olkkonen@uef.fi*

Brominated flame retardants, and more precisely tetrabromobisphenol A (TBBPA), has been widely used as a plastic additive in electronic devices to enhance the fire resistance.[1] Waste electrical and electronic equipment (WEEE) contains plastic that has previously been treated with landfilling and incineration, but the formation of highly toxic compounds during thermal treatment has emerged a need for more environmentally viable recycling methods.[2] In this study we conducted a catalytic debromination reaction for TBBPA and analyzed the formed products. Since the debromination of TBBPA is a complex reaction, detailed analysis of reaction products is needed to better understand the mechanism of debromination.

The debromination of TBBPA was studied with supported nickel catalysts in a batch-type autoclave reactor under reductive atmosphere (210°C, 80 bar H_2). TBBPA was first dissolved in toluene yielding a bromine content of 2500 ppm, and the mixture was inserted into autoclave. Samples were withdrawn regularly during the catalytic reaction. The qualitative analysis of reaction products was conducted with high-resolution timsTOF mass-spectrometer (Bruker, DE) and the quantification of reaction products was carried out with gas chromatography together with a flame ionization detector (GC-FID). Observed results were compared to a literature survey of DFT calculations.

In this study we conducted a catalytic debromination of TBBPA with supported nickel catalysts and the attention was paid to reaction products, which were analyzed by GC-MS and GC-FID. Different catalysts seemed to direct the debromination reaction into different paths, depending on the catalyst's support material. The product distribution varied accordingly. The scheme of the reaction was suggested based on the GC-MS data. Besides the step-by-step debromination, a ring breaking reaction followed by debromination was observed. Understanding the mechanism of TBBPA debromination and identifying the reaction products can help in improving the catalytic upcycling of WEEE derived plastics.

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CO_2 Hydrogenation using Mn-based Catalysts

Jie Wang, Mikkel Kock, Søren Kegnæs and Jerrik Mielby*
DTU Chemistry, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark, jjmie@kemi.dtu.dk

Hydrogenation of CO_2 by reverse water-gas shift (RWGS) produces CO and H_2O. CO is a versatile chemical building block that is found in syngas (CO and H_2), which is an essential industrial feedstock for producing fuels and chemicals such as methanol or synthetic hydrocarbons. Therefore, RWGS is a key technology for future CO_2 utilization. Although RWGS is considered an individual process, it is also an intermediate step in several other processes involving CO_2 hydrogenation. For example, CO_2 methanation can occur in a consecutive reaction pathway that involves RWGS in the first step.[1] Compared to CO_2 methanation (ΔH=-164.7 kJ/mol), RWGS is a mildly endothermic reaction (ΔH=41.3 kJ/mol). Therefore, the process requires a relatively high reaction temperature and a highly selective and durable heterogeneous catalyst.

Over the last decades, researchers have developed many different supported transition metal catalysts for the RWGS reaction. In general, it appears that the catalytic activity is highly dependent on the metal properties. For example, a recent literature review [2] suggests that Pd- and Pt-based catalysts are highly selective for producing CO, while metals with a higher oxophilicity, such as Ni, Cu, Rh, and Ru, typically form more CH_4. In this work, we have investigated a series of Mn-based catalysts that do not follow this trend and result in almost 100% selectivity towards CO.

Although Mn is a cheap and abundant first-row transition metal, the literature on Mn-catalyzed CO_2 hydrogenation is very limited. Therefore, we prepared a series of supported Mn catalysts by simple impregnation, drying, and calcination. Then, we tested the catalysts for RWGS in a fixed-bed reactor equipped with an online GC. For example, we tested a 10% Mn/ZrO_2. At 650°C, the catalysts resulted in 44% conversion and 100% selectivity towards CO. Under the given reaction conditions (1 bar, H_2/CO_2=3, and GHSV=40.000 ml/g/h), this corresponds to a site time yield of STY=64 mol CO/mol Mn/h. These results demonstrate that Mn easily competes with the other first-row transition metals.

To study the reaction mechanism in more detail, we developed a new method that relies on operando Modulation Excitation Phase-Sensitive Detection Diffuse Reflectance Infrared Fourier Transform Spectroscopy (ME-PSD-DRIFTS) using isotopic CO_2 labeling. By switching between $^{12}CO_2$ and $^{13}CO_2$, we identified the reactive surface species and related their exchange rate to the transient kinetics under steady-state conditions. The results indicated that the Mn-catalyzed RWGS followed a dissociative reaction pathway with a single pool of carbonate intermediates.

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Towards a MOF-based Single-Atom Catalyst: Investigating the Effects of the Immobilization of Pd Single Atoms in UiO-66

Sahra Ahmed[1], Stian Svelle[1], Petra Ágota Szilágyi[1]
Center for Materials Science and Nanotechnology, Department of Chemistry, University of Oslo, Norway

Single-atom heterogeneous catalysts (SACs) are a class of supported catalysts that are able to synergize the advantages of solid and molecular catalysts, owing to their unique geometric and electronic properties. Herein, metal-organic frameworks (MOFs) are utilized as a support material enabling the immobilization of catalytically active and otherwise unstable single atoms in a way that is not possible on conventional supports. In this manner, overall catalytic performance is enhanced as the atomically dispersed catalyst is stabilized, while still preserving the well-defined active site of single-site catalysts.[1] Although MOFs have been shown to be desirable supports for catalytically active species, [2] examples in which SACs have been successfully anchored on them, particularly those of neutral charge and no ligands, are few and far between,[3] and they typically contain a mixture of SAs and nanoclusters (NCs) or nanoparticles (NPs). In this work, single atoms of Pd have been anchored on a functionalized UiO-66-type MOF. A combined experimental and theoretical approach has been undertaken to ascertain the nature and speciation of the well-defined Pd moieties.

Functionalized terephthalic acid-based linkers have first been synthesized and integrated into the UiO-66 topology. The *in-situ* reduction of Pd-salts in the pores of the functionalized UiO-66(Zr) framework results in the incorporation of neutral single Pd atoms, confirmed using a combination of advanced characterization methods, including *in-situ* and operando X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS), Inelastic Neutron Scattering (INS) spectroscopy, Transition Electron Microscopy (TEM), and X-ray Photoelectron Spectroscopy (XPS). DFT calculations suggest that the preferred site for the Pd single atoms would be bridging between the linkers, and it was found that the Lewis base nature of the linker functionalities aided in the anchoring of the atomically dispersed Pd single atom, stabilized by strong host-guest interactions of the functionalized MOF framework with the Pd guest catalysts. As such, a new class of catalysts supported on the UiO-66 framework have been investigated.

Previous work carried out within the group of Szilágyi has already demonstrated the catalytic activity of the Pd-laden UiO-66 MOFs towards butadiene hydrogenation, selective acetylene hydrogenation and deNO$_x$ reactions.[4] The catalytic activity of the Pd decorated MOF-based SACs was subsequently assessed for some industrially relevant reactions.

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Poster-22

Preparation of bimetallic nickel-palladium catalysts on various supports for an efficient hydrotreatment of waste plastic pyrolysis oil

Aitor Arandia, Farah Siddiq, Taina Ohra-aho, Juha Lehtonen
VTT Technical Research Centre of Finland Ltd. P.O. Box 1000, FI-02044 Espoo, Finland

The catalytic hydrotreatment (HT) is a primary alternative for the upgrading of plastic waste pyrolysis oils (PPOs).[1,2] Significant amounts of chlorine (Cl), bromine (Br), heteroatoms (O, N), and olefinic/aromatic compounds are typically present in the oil and must be reduced to comply with e.g. steam cracker feed specifications: aromatics < 3-10 wt%, olefins < 2wt%, O, N < 100 ppm, Cl < 3 ppm.[2] Heterogeneous catalysts with metals such as, Ni, Co, Fe, and noble metals (Pd, Pt, Ru) supported on medium/low acidic supports (carbon, SiO_2 or Al_2O_3) are expected to adequate the composition.[3] We have synthesized Ni-Pd bimetallic catalysts on various supports, and tested them in the HT of PPOs in a continuous trickle-bed reactor. These results are part of the integration of the chemical recycling of plastic waste in the existing infrastructure and value chains.

Nickel (10 wt%) and palladium (1wt%) were co-impregnated on Al_2O_3, TiO_2, SiO_2, SiO_2-Al_2O_3, and activated carbon (AC) via the vacuum incipient wetness impregnation method. A commercial Pd/AC catalyst (5 wt% Pd, supplied by Ranido) was used as a benchmark catalyst. The catalysts were tested in a continuous system at 350 °C, 50 bar H_2, H_2(l/h)/feed(g/h) ratio = 0,5, WHSV = 3 h^{-1} and 6 h time-on-stream (TOS). The PPO used in this study was supplied by Valmet Technologies Oy and was made from waste LDPE/LLDPE plastic.

The composition (left-axis) and O content (right-axis) of the liquid phase are shown in Fig 1. The composition of the oil is included for reference. The results after 6 h TOS revealed a complete saturation of olefins and n-dienes to n-alkanes and a significant HDO activity, especially the commercial Ru/AC. The content of aromatics remained practically unchanged. Cl was reduced under 5 ppm (analyzer detection limit) with all catalysts and the Br number was reduced by 10 times with all self-made catalysts. No evidence of deactivation was observed after 6 h TOS. Therefore, stability runs with the best catalyst(s) and the characterization of the spent samples is also part of this research.

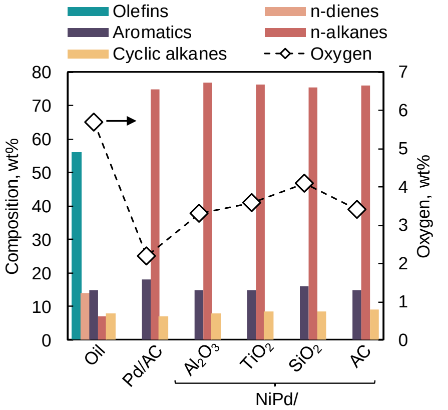

Fig 1. Liquid phase composition and O content of the oil and after the hydrotreatment of PPO with various catalysts. The experimental conditions are described along the text.

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Poster-23

Modification of zeolite Y for the upcycling of polypropylene waste: A systematic study

Claudia Fabris[1], Sebastian Prodinger[1], Valentina G. Brunella[2], Elena Groppo[2], Silvia Bordiga[2], Stian Svelle[1]
[1]*Center for Materials Science and Nanotechnology (SMN), Department of Chemistry, University of Oslo, 1033 Blindern, 0315 Oslo, Norway;*
[2]*Department of Chemistry, NIS Centre and INSTM Reference Centre, University of Turin, via P. Giuria 7, 10125 Turin, Italy*

Some key aspects to obtain a better catalyst for the catalytic pyrolysis of plastic waste, are improving the diffusion of products and reactants to reduce the fast deactivation of the catalyst [1], and mitigating the negative effects of impurities, like PET and chlorine. Said impurities can lead to higher char formation, acidic products and catalyst poisoning. To tackle the first problem, zeolite Y with four different Si/Al ratios was successfully modified by introducing mesoporosity, based on a modified approach by García-Martínez et. al. [2] and Imbachi-Gamba et. al. [3]. To address the second issue, the samples were impregnated with two different CaO or MgO loadings based on a modified approach by Ballieul et. al. [4].

N_2 adsorption-desorption isotherms of the mesoporous samples showed a shift from microporous to mesoporous solids. As the Si/Al ratio increased, a reduction in the overall microporosity was observed in favour of the mesoporosity. The crystallinity was preserved for most samples, with only one composition showing lower crystallinity than the parent material.

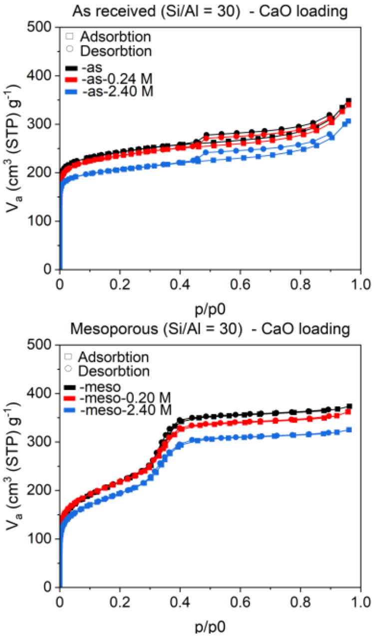

Figure 1: N_2 isotherms for the highest Si/Al ratio sample (Si/Al = 30) in the as received (top) and mesoporous state (bottom) both loaded with CaO (0.24 M and 2.40 M solutions).

The starting materials and the hierarchical ones were both loaded with the same CaO and MgO loadings (0.24 M and 2.40 M solutions). Figure 1 shows the N_2 adsorption-desorption isotherms for the sample with the highest Si/Al ratio (30) and, as expected, the higher loading led to a decrease in the surface area. The presence of mesopores allowed higher amounts of oxide to be loaded compared to the as received samples. The samples retained their crystallinity. Further studies will be performed to better understand the influence of the Si/Al ratio and the mesoporosity on the loading of the alkaline-earth metal oxides, and the position of the oxides in the pores. The catalysts will then be tested in the catalytic pyrolysis of polypropylene to determine their catalytic activity.

The samples were effectively modified as both the mesopores and the alkaline-earth oxides were introduced in the starting material. The results obtained so far are promising to allow the identification of a better catalyst for the catalytic pyrolysis of polypropylene.

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Advanced reactor designs for continuous pyrolysis oil conversion into renewable hydrocarbon fuels through hydrodeoxygenation catalysis

Alexander Søgaard,[1] Amalie P. Krebs,[1] Rui P. da Cruz,[1] Magnus Z. Stummann,[2]
Martin Høj,[1] Anker D. Jensen[1*]
[1]DTU Chemical Engineering, Technical University of Denmark (DTU), Kgs. Lyngby, Denmark
[2]TOPSOE A/S, Kgs. Lyngby, Denmark
**corresponding author. E-mail: aj@kt.dtu.dk*

Renewable hydrocarbon fuels derived from biomass have recently drawn much attention as more sustainable alternative fuels. They can be easily blended with fossil fuels as drop-in fuels or fully replace them. This is especially attractive in the aviation and heavy transportation sectors, where other alternatives such as electric and hydrogen mobility have been deemed impractical and cost-ineffecetive.[1]

Fast pyrolysis and catalytic fast pyrolysis are two widely applicable and low-cost processes used to convert solid biomass into a condensed bio-oil.[2,3] However, the produced pyrolysis oils are complex chemical mixtures with high water and oxygen contents, which limits their stability and applicability in internal combustion engines. By further upgrading by catalytic hydrodeoxygenation (HDO), the properties of pyrolysis oils can be improved significantly, where oxygen is removed through the formation of water with limited negative effect on the carbon yield.[2,4]

In this contribution, we present possible reactor designs for the catalytic HDO of pyrolysis oils derived from biomass. Two intrinsically different reactor systems were developed and compared to identify the optimal process design and parameters for an efficient, continuous HDO of pyrolysis oils, and thus the production of sustainable biofuels. The dual trickle bed reactor design allowed for treating the pyrolysis oil under a temperature gradient. By introducing an initial stabilisation step at moderate temperatures (180-250 °C) before the HDO at high temperature (350-450 °C) in the trickle bed reactor, catalyst stability was found to be improved significantly as reactor blockages due to coking was suppressed. Initial results from the slurry-type reactor also show great prospects for efficient HDO. Research is ongoing to establish the most efficient design for the process which allows for stable continuous upgrading of pyrolysis oils to sustainable biofuels.

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Aldol Condensation of Cyclopentanone and Furfural on Different Metal Organic Frameworks for Synthesis of Jet-Fuels from Renewable Biomass

Olha Yevdokimova[1*], Mark Martínez-Klimov[1], Natalia Shcherban[2], Irina L. Simakova[1], Kari Eränen[1], Päivi Mäki-Arvela[1], Dmitry Yu. Murzin[1]
[1]*Åbo Akademi University, Turku/Åbo, Finland*
[2]*L.V. Pisarzhevsky Institute of Physical Chemistry, NAS of Ukraine, Kyiv, Ukraine*
[*]*olha.yevdokimova@abo.fi*

The aviation industry's pursuit of cleaner energies has intensified the need for fuel synthesis methods complying with emission standards and producing fuels compatible with the current engines. The aldol condensation reaction, capable of producing higher carbon-number products, remains relevant for optimizing the use of biomass-derived compounds. Metal organic frameworks (MOFs) were successfully used for aldol condensation reaction[1]. This research introduces MOFs catalysts for the first time for the aldol condensation reaction between furfural (FF) and cyclopentanone (CP), yielding valuable products (Fig.1). Several parameters during preparation of MOFs were explored. For example, one of these parameters was the use of formic acid to create defects in MOFs which enhanced catalytic performance. The study focuses on achieving high reactant conversion and desired product yield, as well as correlating catalyst performance with structural attributes through various physico-chemical analyses.

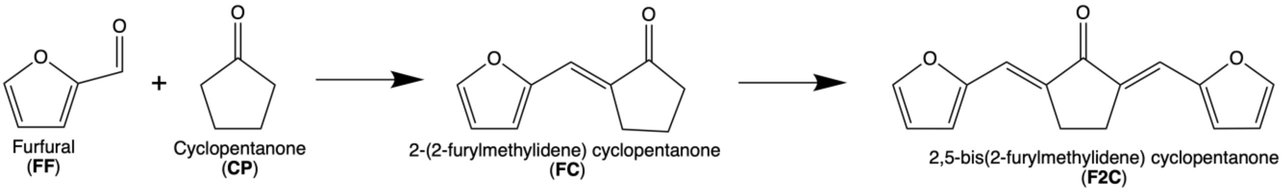

Fig. 1. A simplified reaction scheme for the aldol condensation of furfural and cyclopentanone.

A series of MOFs (UiO-66) catalysts were prepared, characterized with several physico-chemical methods and tested in aldol condensation reaction. Screening of the catalysts in aldol condensation between FF and CP was performed in the temperature range of 60 to 150 °C using various CP:FF ratios in a batch reactor. The samples were analyzed by gas chromatography (GC) and the products were identified by gas chromatography coupled to mass-spectrometry (GC-MS).

As an example, when the reaction was performed at 130 °C during 6 h with the molar ratio of CP:FF 10:1 and the mass ratio FF:cat 10:1 using formic acid modulated Uio-66 as a catalyst resulting in 34% FF conversion, 15% and 13% FC and F2C product yields respectively were obtained with 83% overall selectivity. For the same reaction but with CaO as the catalyst despite high conversion (80%) selectivity to the main products reached only 50%.

In the final work the catalyst property-performance relationship will be presented.

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Dynamic Modeling of CO_2 Mass Transfer in Ionic Exchange Resins for Enhanced Direct Air Capture Processes

Dana Marinič, Janvit Teržan, Blaž Likozar

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

The rise in atmospheric CO_2 concentration from 250 ppm in the pre-industrial era to over 400 ppm today is primarily attributed to anthropogenic emissions. The challenge of global climate change, has prompted the exploration of various strategies. Notably, direct air capture (DAC) has emerged as a significant solution not only for carbon removal but also for generating valuable feedstock for industrial applications, such as generating methanol from CO_2 and renewable H_2, especially in areas with surplus renewable electricity but lacking specific CO_2 point sources [1].

Presently existing DAC systems operate by directing air through the air contactor, where sorbents capture CO_2 through physisorption or chemisorption. Subsequently, the captured CO_2 is typically released as a concentrated stream through temperature, pressure, or moisture adjustments.

Kinetic studies play a crucial role in reducing the costs of prohibitive processes by providing insights into optimal operating conditions. This is particularly significant for DAC as it is considered an energy-intensive process that requires improvement. The adsorption rate is influenced by various phenomena.

Initially, the adsorbate molecule needs to transfer from the bulk fluid to the adsorbent exterior, then pass through the external film surrounding the sorbent before diffusing through and along the porous structure, where it's captured by the amine groups of the sorbent [2]. Our model encompasses the mass transfer phenomena involved in this description for an ion exchange resin which has a primary benzylamine group that reacts with CO_2.

Activation energies and pre-exponential factors were determined by fitting the mathematical model to experimental data using the least squares approximation method. The rate equation based on the Toth isotherm was identified to effectively predict the experimental results. The results also indicated that the impact of internal mass transfer is negligible.

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New strategies to develop low-temperature Mn-based NH_3-SCR catalysts with improved water and SO_2 tolerance

Huirong Li, Leonhard Schill, Qi Gao, Susanne Mossin, Rasmus Fehrmann, Anders Riisager

Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Nitrogen oxides (NO_x) emitted from combustion processes endanger human health by contributing to acid deposition, photochemical smog, and ozone depletion. Selective catalytic reduction of NO_x with ammonia (NH_3-SCR) is the most effective and widely used technology to mitigate NO_x emissions in stationary installations. Industrially applied NH_3-SCR catalysts based on vanadium (VWT catalysts) exhibit high N_2 selectivity and good thermal stability, but they require a relatively high operating temperature (> 250 °C). To avoid a costly reheating of the flue gas, it is thus necessary to locate the VWT catalyst upstream of dust removal and/or desulfurization to avoid significant lowering of the flue gas temperature. This position makes VWT catalysts prone to deactivation or inhibition by flue gas impurities such as SO_2, alkali or heavy metals.

Manganese oxide (MnO_x) catalysts exhibit superior NH_3-SCR activity at low-temperature (≤ 200 °C) and are thus low cost and environmentally benign catalysts that can be utilized in a preferred “tail-end” SCR system without the need for flue gas reheating. Various strategies have previously been attempted for developing industrially viable MnO_x catalysts, however, challenges such as too narrow temperature operating range, limited resistance to water, and susceptibility to SO_2 poisoning have hampered their practical application.[1]

In this work, new strategies have been explored for NH_3-SCR MnO_x catalysts to expand their operational temperature window, improve N_2 selectivity, and increase resistance to water and SO_2. The strategies include the rational constructing of novel Mn-Ti-Ce oxide core-shell catalysts,[2,3] doping MnOx catalysts with Fe and Al,[4] and optimizing the synthesis approaches of Mn-Fe oxide catalysts.[5] The obtained results demonstrate how rational catalyst design can lead to both high low-temperature performance and enhanced durability for Mn-based NH_3-SCR catalysts. This insight may inspire future catalyst design with enhanced applicability for removing NO_x from flue gases.

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Poster-28

Surface analysis of LSCF perovskite anodes for solid oxide ammonia-fuel cells

Alicia San Martin Rueda[1], Ingeborg-Helene Svenum[2], David Waller[3], Faranak Foroughi[3], Magnus Rønning[1]*
*[1]Department of chemical engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway. *Corresponding author: magnusrønning@ntnu.no*
[2]SINTEF Industry, 7465 Trondheim, Norway
[3]Yara Technology Center, Ammonia & Nitric acid Technology Department, Herøya Forskningspark, 3936 Porsgrunn, Norway

Introduction. Due to the current instability of energy markets, the search for reliable and sustainable energy sources is crucial. Solid oxide ammonia-fuel cells (SOFC) have been claimed as an efficient and carbon-free alternative for direct conversion of chemical energy into electricity[1]. Ammonia is an excellent option as a hydrogen carrier, overcoming the limitations of hydrogen as fuel. Moreover, SOFCs are the most efficient fuel cells (65-85%) operating at high temperatures (600-1000 °C), facilitating high ionic conductivity and giving fuel flexibility. One of the key features of SOFC performance is the material selection of the cell components. Perovskites are proposed as promising catalysts for both anode and cathode owing to their compositional and structural tunability and their excellent ionic and electrical conductivity[2]. A symmetrical cell where both anode and cathode have the perovskite structure has some attractions. However, the performance of ammonia oxidation in the anode has been little studied. Gaining an in-depth understanding of perovskite-based anode materials for SOFC by studying the catalyst surface under operating conditions using advanced characterization methods can give a better comprehension of this emerging technology.

Experimental/methodology. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD instrument using a monochromated Al-Kα X-ray source on LSCF perovskites. Core level spectra was recorded at a pass energy of 40 eV. Ex-situ X-ray diffraction (XRD) was carried out on a Bruker D8 Advance at 40 kV and 40 mA, using a Cu-Kα X-ray source.

Results and discussion. Figure 1a shows the acquired XPS spectra of $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskites, where La 3d, Co 2p, Fe 2p, C 1s, O 1s and Sr 3d regions are collected. Figure 1b displays the XRD diffraction pattern. The XPS spectra will provide a reference for subsequent experiments where high density LSCF pellets will be tested at temperatures in the range 25-600 °C. The XRD diffractogram will be used a reference for in-situ XRD experiments (25-700 °C in reductive atmosphere) and grazing incidence XRD analyses on high density LSCF pellets. Raman and FTIR spectroscopy will complement these studies, providing a first insight into the surface composition and structure of LSCF perovskites.

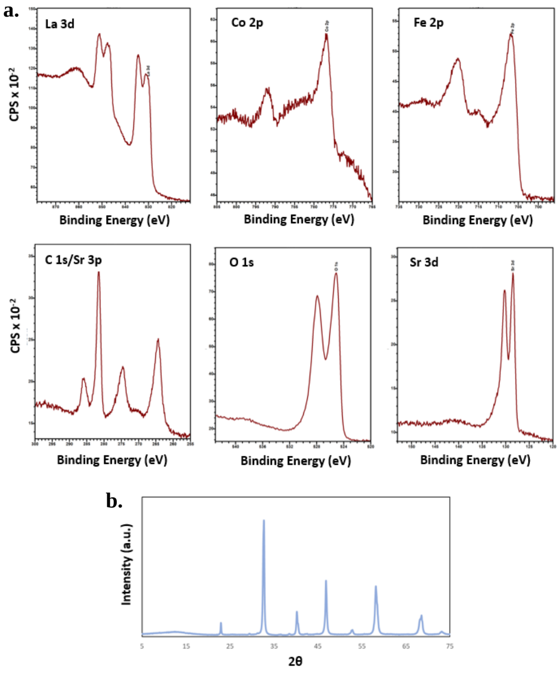

Figure 1. $(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$ spectra obtained by (a) XPS and (b) XRD

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Poster-29

Co-pyrolysis of biomass and plastic to produce high-quality liquid

Zhihui Li[1], Kishore Rajendran[1], Kjell Moljord[1,2], Geir Remo Fredriksen[2], De Chen[1]*
[1]*Norwegian University of Science and Technology (NTNU), Trondheim, Norway*
[2]*Equinor, Arkitekt Ebbells veg 10, Ranheim, Norway*

Biooil is a kind of renewable fuel instead of conventional fossil fuels. However, the high oxygen content (~50wt%) of bio-oil which comes from the oxygen-rich species in lignocellulose biomass inhibits its wide application. In this project, instead of the traditional hydrodeoxygenation method which is by feeding external H_2 during the pyrolysis of biomass, plastic was chosen as the hydrogen donor to achieve in-situ oxygen removal. In addition, modified natural clay, a relatively cheap material was applied as an in-situ catalyst during pyrolysis. The modified clay has shown weak to medium acidity strength and rich amount of acid sites.

The experiment was carried out in a semi-batch reactor, the catalyst and feedstocks were pre-mixed, to achieve in-situ catalytic co-pyrolysis. The mixture was injected into the preheated reactor as the reaction started, N_2 was performed as the carrier gas of 40 ml/min during the pyrolysis. In the co-pyrolysis of beechwood and LDPE (1:1), within 25 minutes, high liquid yield (85wt%) and oil with low oxygen content (7wt%) were achieved, oxygen was effectively removed. In the obtained oil, components with the carbon number of gasoline range (C4-C12) take over 80wt%.

Real plastic waste was attempted, while the study of co-pyrolysis of biomass with model species PE, PS, PP are also interesting. Among them, PE has shown the highest selectivity towards hydrocarbons (70%), while PS has shown the highest aromatic selectivity over 90% and the highest oxygen removal ability, with only 3wt% oxygen in the obtained oil.

The synergic effect between plastic and biomass can be observed by analyzing the oil content, while the detailed reaction mechanism, especially on clay catalyst surface mechanism, will be further studied by applying model compounds of plastic and biomass, together with operando technologies. Further attempts at full removal of oxygen and oil component regulation will also be carried out.

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Poster-30

The impact of Cu addition on Ni-catalysts for the dehydrogenation of Liquid Organic Hydrogen Carriers

Pol Fernandez *, Efthymios Kantarelis
*KTH Royal Institute of Technology, Department of Chemical Engineering,10044, Stockholm, Sweden, *polfir@kth.se*

Liquid organic hydrogen carriers (LOHC) have the potential to address the challenge of storing and delivering hydrogen on a global scale by chemical fixation of hydrogen in their molecular structure (hydrogenation) and release by the reverse chemical reaction (dehydrogenation) respectively.[1] This can allow for the accelerated adoption of hydrogen technologies in the industry and facilitate the transition to a sustainable society. In addition, LOHC can meet the H_2-purity requirements for PEM fuel cells (ISO 14687:2019) and synthesis processes applications with minimal purification making them ideal for on-demand applications in remote areas creating financially competitive infrastructure in the Nordic countries.

Conventional Pt-based dehydrogenation catalysts are not fully optimized for this specific application giving rise to undesired cracking reactons.[2] Ni-based alternatives have been previously studied (Figure 1) on supports of varying acidity with promising results. In this work, the effects of Cu addition on Ni-based catalysts on activity and selectivity are investigated. The results from this study aiming at optimizing the Ni-based metal catalysts and facilitate the adoption of the technology.

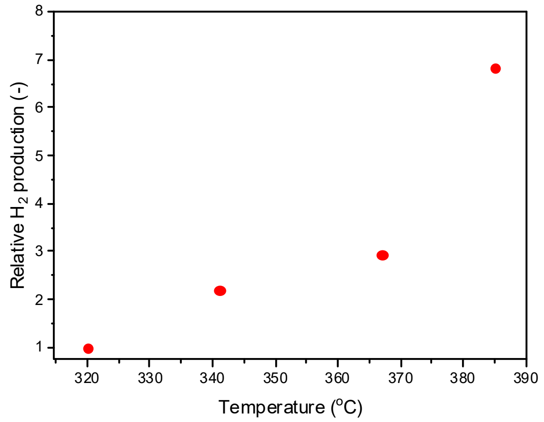

Figure 1 Effect of temperature on H_2 production during dehydrogenation of MCH over Ni/Al_2O_3; LHSV= 1.5 dm^3MCH/ (kg_{cat} h)

Acknowledgments

The work is a part of the research centre for Production Use and Storage of Hydrogen (PUSH) funded by the Swedish Foundation for Strategic Research (SSF).

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Poster-31

Application of Box-Behnken Design for Enhanced HCl Electrolysis

Alen Rupnik[a,b], Blaž Likozar[a] , Miha Grilc[a,b]
[a] *Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana, Slovenia*
[b] *Materials graduate study program, University of Nova Gorica, Nova Gorica, Slovenia*

Meeting the future demand for effective hydrogen production is crucial for achieving a carbon-free energy source and realizing the net-zero future envisioned by the European Union[1]. There is a growing interest in exploring alternative electrolytes, such as HCl, a by-product of polycarbonate or polyurethane production[2]. This study focuses on the onsite conversion of HCl into hydrogen and chlorine, presenting economic and safety benefits. However, due to the corrosive nature of HCl, designing a stable-operating cell for its electrocatalytic decomposition requires careful selection of construction materials. Although electrolyzers can be constructed from HCl-resistant materials like PTFE, and various electrodes and membranes are functional in such systems, the mechanism still needs to be optimized and well understood, so optimization of key variable parameters is crucial.

This study introduces the utilization of the Box-Behnken Design (BBD) in optimizing Hydrochloric Acid (HCl) electrolysis—a pivotal step towards eco-friendly hydrogen generation. The BBD, known for its efficiency in experimental design, is employed to systematically investigate the influence of key variables on the electrochemical process. We tested three most important variables in HCl electrolysis, that being potential, temperature and HCl concentration in anolyte in order to define the magnitude of impact of bespoke conditions. The BBD not only allows for a comprehensive exploration of the optimal conditions but also facilitates the minimization of experimental runs, offering a cost-effective and resource-efficient approach. Testing campaign was conducted using a non-modified commercial cell from Electrocell as well as using our 'in-house' modified zero-gap version of such commercial cell. We varied potential conditions from 1,6 V to 2,0 V, temperature conditions from 20 °C to 80 °C and HCl concentration from 10 wt.% to 20 wt.% in anolyte.

Electrolysis of HCl holds promise for sustainable utilization of oversaturated by-products. In summary, the application of Box-Behnken Design for HCl electrolysis not only contributes to optimizing the electrochemical process but also opens doors to a future where artificial networking could furthermore enhance operational efficiency and process control. This research lays the foundation for sustainable hydrogen production while embracing the transformative potential of intelligent connectivity in the realm of electrochemical engineering.

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CO_2 Conversion over Zeolite-Encapsulated Ni Nanoparticles

Jerrik Mielby,* Emil Kowalewski and Søren Kegnæs
DTU Chemistry, Technical University of Denmark, Kemitorvet 207, DK-2800 Kgs. Lyngby, Denmark, jjmie@kemi.dtu.dk

With the worldwide efforts to keep the global temperature increase well below 2°C, there is a critical need for new and efficient processes to utilize CO_2. For example, CO_2 and H_2 may be converted into CO and H_2O by the reverse water-gas shift reaction (RWGS). CO finds extensive use in syngas ($CO+H_2$), which is an essential industrial feedstock for producing a range of chemicals and liquid transportation fuels. Although the RWGS reaction is considered an individual process, it is also an intermediate step in several other processes that involve CO_2 hydrogenation, including CO_2 methanation (the Sabatier reaction). From a green and sustainable perspective, CO_2 methanation offers an attractive opportunity for upgrading biogas produced by anaerobic digestion of biomass or wastewater sludge, which often contains high amounts of CO_2. However, because of the thermodynamics and the complicated reaction pathways of CO_2 conversion, achieving a high selectivity towards the desired product (CO, CH_4, or CH_3OH) still poses a significant challenge.[1]

Another significant challenge is that the catalytic activity of supported metal nanoparticles is often related to their small size and high fraction of surface exposed atoms. Unfortunately, such nanoparticles are often prone to sintering, a thermal deactivation caused by Ostwald ripening or particle migration and coalescence. A promising strategy to overcome this challenge is to encapsulate the active metal nanoparticles inside the microporous framework of a zeolite.

In this work, we compare two new methods to encapsulate Ni nanoparticles inside MFI-type zeolites. In the first method, the zeolite is first modified by a selective recrystallization process that creates intra-particle voids and mesopores, which facilitate the formation of small and dispersed Ni nanoparticles upon simple impregnation.[2] In the second method, a stable Ni ethylenediamine complex is added directly to the zeolite gel before the hydrothermal crystallization. Although both methods result in catalysts that have the same chemical composition, the exact location and size distribution of the metal nanoparticles have a remarkable effect on the catalytic activity and selectivity for CO_2 hydrogenation. Therefore, our results demonstrate the importance of considering not only the size of the Ni nanoparticles and the nature of the support material but also the three-dimensional distribution and the structure of the Ni–support interfacial sites.

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Poster-33

In situ AP-XPS reduction study of engineered NiMoO$_4$ nanoparticles

Jonas Elmroth Nordlander[1,2], Sabrina Gericke[3], Marie Bermeo Vargas[2,3], Pau Ternero[2,3], David Wahlqvist[2,4], Filip Hallböök[1,2], Mattia Scardamaglia[4], Johan Zetterberg[3], Martin Ek Rosén[2,4], Maria E Messing[2,3] and Sara Blomberg[1,2]

[1] *Department of Process and Life Science Engineering, Lund University*
[2] *NanoLund, Lund University*
[3] *Physics Department, Lund University*
[4] *Chemistry Department, Lund University*
[5] *MAXIV Laboratory, Lund University*

Ni-Mo catalysts are important in many different catalytic applications[1-3], such as hydrodesulfurization (HDS)[1,3] and hydrodeoxygenation (HDO) reactions[1]. To develop these catalysts further detailed knowledge about the properties of the material is needed. However, fundamental studies of industrial catalysts are challenging due to the low concentration and limited accessibility of the active phase. As such, model systems with a high concentration of the active phase are useful for studying basic catalyst properties.

Here, we design a model system of well-defined nanoparticles generated by a previously published spark discharge method[4]. This offers the possibility of creating and depositing catalytically active nanoparticles of well-defined size and composition, allowing for the construction of high-concentration model systems where the active phase can be studied in isolation.

Through following the reduction as a function of temperature for $Ni_{45}Mo_{55}$ oxide nanoparticles as well as the concomitant phase changes using AP-XPS and *ex situ* TEM (Figure 1), we obtain results indicating that the reduction of NiMoO$_4$ proceeds via separation into separate Ni and Mo phases. Upon reaching the metallic state, the separate phases then mix to form intermetallic δ-NiMo. This has possible consequences for H$_2$-based catalyst activation processes, as over-hydrogenation might separate Ni from Mo, eliminating the cooperative effects of the bimetallic catalyst.

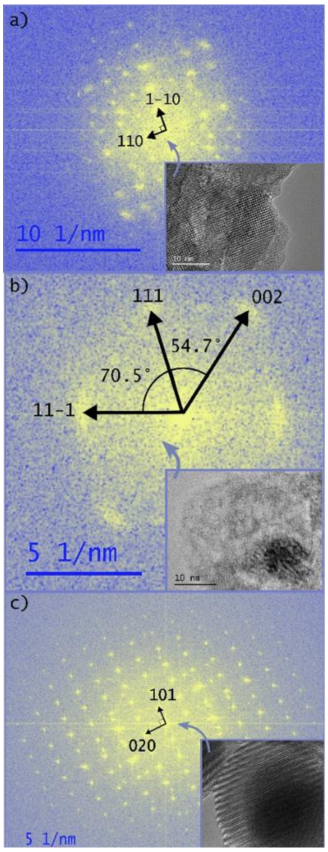

Figure 1: a) Oxidised nanoparticle (inset) and FT with distances corresponding to NiMoO$_4$. b) Partially reduced nanoparticle (inset) and FT with distances corresponding to NiO. c) Reduced nanoparticle (inset) and FT showing distances corresponding to δ-NiMo.

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Poster-34

In-situ reduction study of Pd-NiMo and Ru-NiMo catalysts using AP-XPS

Filip Hallböök[1], Sabrina M. Gericke[3], Tove Kristensen[1,2], Jonas Elmroth Nordlander[1], Burcu Karagoz[4], Matthijs Van Spronsen[4], Christian Hulteberg[1,2], Sara Blomberg[1]

[1]*Division of Chemical Engineering, Department of Process and Life Science, Lund University, 221 00 Lund, Sweden*

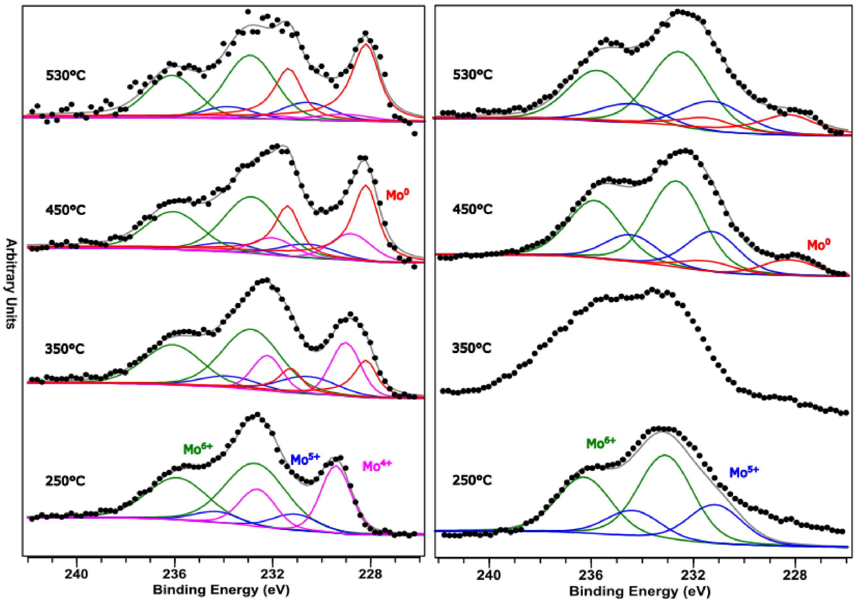
[2]*Hulteberg Chemistry & Engineering AB, 212 25 Malmö, Sweden*

[3]*Division of Combustion Physics, Lunds University, P.O. Box 118, 221 00 Lund, Sweden*

[4]*Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0DE, UK*

Many oxide-based hydrodeoxygenation catalysts utilize a bi- or trimetallic composition to incorporate several different functionalities such as redox centra and hydrogen activation ability.[1] Noble metals are often used as promotors, but the nature of the interaction effect is not fully understood. In this study we thoroughly investigate the reduction process in situ in 1 mbar H_2 of two trimetallic; Pd-NiMo and Ru-NiMo catalysts supported on Al_2O_3, utilizing AP-XPS which provides detailed chemical information about the catalyst.

The noble metal-NiMo/Al_2O_3 catalysts were synthesized using incipient wetness impregnation and were studied using Temperature programmed reduction, Powder X-ray Diffraction and Transmission Electron Microscopy, to characterize the distribution and structure of the impregnated metals. The reduction process of each metal in the trimetallic catalysts was followed in situ by measuring, Mo3d, Ni2p, Pd3d/Ru3d and Al2p while the catalysts were heated stepwise in 1 mbar of H_2. Our results show that the addition of Pd induced a higher reducibility of the Mo compared to the addition of Ru, shown in figure 1.



1. AP-XPS spectra of the Mo3d core-level measured at 1400eV. ***Left:*** *Pd-NiMo* ***Right:*** *Ru-NiMo. Measured under 1mbar of H_2 and stepwise increasing temperature.*

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Poster-35

Bioinspired Cu(I) MOFs for C-H activation

Rafael Cortez Sgroi Pupo,[1,2]* Mouhammad A. Rasheed,[1,2] Erlend S. Aunan,[1,2] Sebastian Prodinger,[2] Unni Olsbye,[1,2] Petra Á. Szilágyi[1,2]
[1]Department of Chemistry, University of Oslo, P. O. Box 1033 Blindern, N-0315 Oslo, Norway
[2]Centre for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1126 Blindern, N-0316 Oslo, Norway
**Email address: r.c.s.pupo@kjemi.uio.no*

Enzymatic oxidants, more specifically, oxygenases are desirable models for the development of high-performance catalysts.[1] Several monooxygenases, such as the *Lytic polysaccharide monooxygenases* (LPMOs) and the *particulate methane monooxygenase* (pMMO) include a copper center coordinated to histidines.[2,3] In addition to the histidine brace (1st coordination sphere), these enzymes feature an additional oxygenated group in their second coordination sphere, such as tyrosine (LPMO) and asparagine (pMMO). These oxygenated groups have been shown to influence the kinetics of the catalytic oxidation cycle.[4,5] To reproduce these enzymatic coordination environments, inorganic materials such as metal organic frameworks (MOFs) may be used to immobilize/heterogenize said coordination moieties.[6]

The heterogenization of a copper bearing histidine-like complex into the UiO-67 MOF was carried out post-synthetically. Factors such as activation conditions of the framework, excess of the copper source relative to the ligand and the nature of the solvent were investigated. In order to provide the oxygenated groups, present in the 2nd coordination sphere of the enzymes, we selected phenol (OH) and propionamide (C=O) to be infused into the MOF. Lastly, cyclohexene oxidation using t-BuOOH as the oxidant allowed us to assess the catalytic activity of the copper-bearing MOF was tested. The MOFs synthesized here, demonstrated catalytic activity, exhibiting a preference for the allylic oxidation of the substrate.

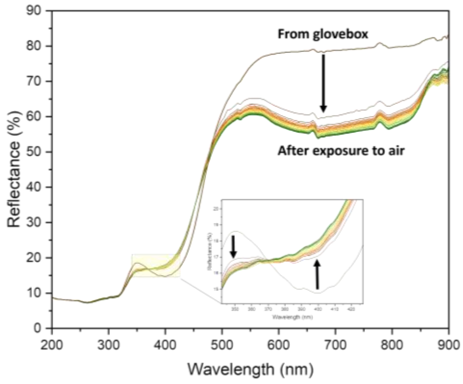

Figure 1. DR/UV-Vis spectra of copper-bearing MOF showing the emergent* d-d *transition band on exposure to air

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Poster-36

Metallosalen tethered Polyoxometalates: Potential candidates for CO_2/epoxide copolymerization

Tuba Iftikhar[1] *and Mali Husby Rosnes*[1]
[1]*Department of Chemistry, UiB, Allégaten 41, Realfagbygget; 5007 Bergen, Norway.*

Abstract: Metallosalen (M–salen) complexes are considered some of the most active catalysts for CO_2 / epoxide copolymerization to form polycarbonates.[1] There are, however, still several attractive bio-based epoxides that are proving challenging to introduce into polymers of high quality.[2] Interestingly, related metallosalen-type ligands can be tethered to a class of materials known as polyoxometalates (POMs).[3] This functionalization introduced a strong electronic effect between the catalytic M–salen complexes and the POM unit, yielding charge-transfer complexes, which are reported to result in higher catalytic activity than the units alone and yielding charge transfer complexes.[4]

POMs are polyanionic metal-oxo clusters with remarkable physicochemical properties. Their structural versatility, unique modularity, electronic properties, and ionic nature, make them interesting for applications in diverse areas ranging from catalysis to energy storage. POMs can be functionalized with catalytic units such as metallosalen complexes, which allows for tuning of their chemical properties for advanced applications in materials science and catalysis.[5] This kind of structural modifications to synthesize hybrid POMs represent a challenging venture in the field of novel material chemistry.[6]

In 2003, Neuman et al. reported the tethering of M–salen complexes to the monolacunary Keggin, $(\alpha\text{-SiW}_{11}O_{39})^{8-}$ ($\{SiW_{11}\}$), via silicon-based alkylene bridging groups.[3] These hybrid derivatives were reported to have high catalytic activity for alkene oxidation than M–salen units alone.[2] To the best of our knowledge, there are no reports available using these catalytic systems for CO_2 / epoxide copolymerization.

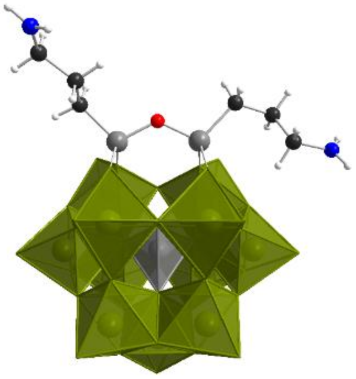

Figure. 1 Structure of $\{SiW_{11}\}$–Amine. Color code: $\{WO_6\}$ olive-green octahedra, $\{SiO_4\}$ pink tetrahedra, {Si} grey, {C} black, {H} white, {N} blue and {O} red

In our quest to develop catalysts for CO_2 / epoxide copolymerization, we are expanding the metallosalen-POM system. Here, we present a library of amine, salen, and metallosalen-type functionalized $\{SiW_{11}\}$ POMs, with three different cations, incorporating metals such as Ni and Zn. We also present novel single crystal data of the silicon functionalized $\{SiW_{11}\}$ with the amine group present (see **Figure 1**), highlighting the parent building unit for further functionalization of such systems.

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Oxidative Depolymerization of Hardwood Lignin into Valuable Aromatics

Lucy I. Ajakaiye Jensen[1], Lina El Manira[1], Selda Bekirovska[1], Christian P. Hulteberg[1], Omar Y. Abdelaziz[2,3]

[1]*Division of Chemical Engineering, Department of Process and Life Science Engineering, Lund University, SE-221 00 Lund, Sweden*
[2]*Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*
[3]*Interdisciplinary Research Center for Refining & Advanced Chemicals, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia*

Abstract

Lignin, a complex and abundant biopolymer found in lignocellulosic biomass, poses challenges and opportunities in the quest for sustainable resource utilization.[1] In this study, the oxidative depolymerization of hardwood lignin (HWL), derived from beechwood through aldehyde-assisted fractionation,[2] is investigated. The objective is to develop an environmentally benign and economically viable reaction conditions for breaking down the lignin into valuable low-molecular-weight products.

The experimental investigation involved subjecting HWL to controlled oxidative conditions, with oxygen serving as the principal oxidizing agent. Systematic optimization of critical reaction parameters such as temperature, pressure, and reaction time using design of experiments (DOE) is performed to enhance depolymerization efficiency and selectively yield valuable products. Preliminary results show a diverse array of low-molecular-weight aromatic compounds with syringaldehyde and vanillin having the highest yields.

The results highlight the effectiveness of oxygen as an oxidant in the oxidative depolymerization process, leading to the generation of a diverse spectrum of valuable compounds from HWL. These depolymerized products exhibit promising applications in the development of bio-based chemicals, materials, and renewable energy sources. The proposed reaction conditions offer advantages in terms of sustainability, as it utilizes a readily available and environmentally benign oxidant, paving the way for an eco-friendly utilization of HWL as a sustainable feedstock. The insights derived from this study contribute to the advancement of scalable and industrially relevant lignin valorization strategies.

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Poster-38

Atomically dispersed Fe-Cu dual-sites on carbon black for efficient electroreduction of CO_2 to CO

Song Lu[1,2*], Zhixin Yu[2]

[1]*Institute of New Energy, School of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing 312000, China*

[2]*Department of Energy and Petroleum Engineering, University of Stavanger, 4036 Stavanger, Norway*

Introduction

Electrochemical carbon dioxide reduction (ECR) presents a promising technology to attain carbon neutrality. However, the current ECR process still has challenges of CO_2 activation and the complicated product distribution, which limits practical CO_2 reduction. Therefore, it is necessary to develop electrocatalysts with good activity and high selectivity for ECR. There has been widespread research on single-atom catalysts (SACs) for electrocatalysis, owing to their high atom-utilization efficiency, unique electronic properties, and well-defined active sites. However, the single active center makes it difficult to break the constraint of scaling relationship between the adsorption energies of intermediates due to the complicated multiple proton-coupled electron transfer[1]. Constructing heteronuclear dimer sites to form dual-atom catalysts (DACs) is an efficient way to modify the coordination environment and the electronic properties of the SAC active centers.

Experimental/methodology

Fe-NC, Cu-NC and Fe-Cu-NC supported on N-doped carbon black were synthesized via a facile ion adsorption and calcination process.

Results and discussion

The catalysts were charactered by XRD, Raman, HRTEM, HAADF-STEM, XANES, EXAFS, XPS, etc. XRD results indicated that there are no Fe and Cu metallic clusters or compounds in the Fe-Cu-NC catalyst. XPS results suggest that the Fe and Cu species are likely to be in a partially oxidized state. Fe-Cu-NC catalyst exhibits the highest ECR activity, yielding a current density of 22.5 mA/cm² under −0.80 V (vs. RHE) and maximum FE_{CO} of 96.4% (Fig. 1a and b). Theoretical calculations demonstrate that constructing Fe-Cu dual site could decrease the free energy barrier of *COOH formation (Fig. 1c).

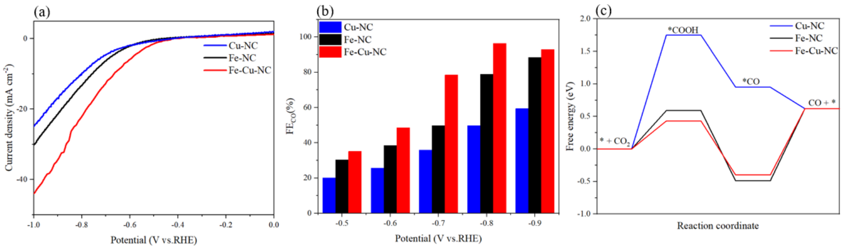

Fig. 1 (a) LSV curves of catalysts; (b) The Faradic efficiencies of CO generation; (c) Free energy change for CO generation.

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Effect of impurities on catalytic dehydrogenation of ethanol to acetaldehyde

Maria S. Chino[1,2], Lars J. Pettersson[1], Jorge Velasco[3], Efthymios Kantarelis[1,*]
[1] *KTH Royal Institute of Technology, Department of Chemical Engineering, SE-10044, Stockholm, Sweden*
[2]*Major the San Andres University, Engineering faculty, La Paz, Bolivia*
[3]*Aalto University, Department of Chemical and Metallurgical Engineering, FI-00076, Aalto, Finland*

Bioethanol-derived acetaldehyde is an important intermediate, that can be used to produce a variety of important chemicals and has the potential to become a primary intermediate in the biobased chemicals industry[1].

Cu-based catalysts have shown promising results in the direct dehydrogenation of ethanol; however, secondary condensation reactions make it challenging to maximize acetaldehyde's selectivity[2]. Moreover, Cu proneness to sintering and the overall stability on the support are added challenges[3]. Metal-support interactions become important for stabilizing particles and controlling the Cu crystalline size, which together with the acidic properties of the support affect the selectivity of the conversion[4]. In addition, bio-ethanol impurities and water content can affect the long-term stability and reliability of the process since water plays a key role in controlling the reaction pathway[5].

The aim of this study is to evaluate the effect of the impurities on selectivity and long-term stability of different Cu-based catalysts for acetaldehyde production. Cu supported on carriers of varying acidity (e.g. γ-Al_2O_3, $MgAl_2O_4$ etc.) have been prepared by dry impregnation and used for evaluation using simulated ethanol grades (different water content and added impurities). All catalysts have been characterized by means of XRD, NH_3-TPD, H_2-TPR, N_2 physisorption and N_2O chemisorption to evaluate crystalline phase and size, acidity reducibility, textural properties, and metal dispersion, respectively. All the tests were conducted at a temperature range of 200-350°C at atmospheric pressure using a fixed bed reactor system.

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Acknowledgments

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Poster-40

Further enhancement of hydrodeoxygenated lipid oil by isomerization

Jon Selimi[1,2,*], Per Tunå[2], Christian P. Hulteberg[1,2] and Omar Y. Abdelaziz[3]

[1]Division of Chemical Engineering, Department of Process and Life Science Engineering, Lund University, Naturvetarvägen 14, SE-221 00 Lund, Sweden
[2]Hulteberg Chemistry & Engineering AB, Krusegatan 32, SE-212 25 Malmö, Sweden
[3]Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
**Corresponding author: jon.selimi@chemeng.lth.se (J.S.)*

Intermediate oils intended for conversion into aviation fuels must comply with stringent standards, which are affected by its hydrocarbon composition. The composition requirements are crucial, as a higher isomer concentration would enhance the cold flow properties of the final fuel[1]. Moreover, minimizing the olefin levels is essential due to the inherent risk of gum formation[2].

In this experimental work, lipid oil, which had undergone a hydrotreatment process beforehand for oxygen removal, has been further treated by an isomerization process to enhance its properties for aviation fuel applications. The experiments were conducted using a fixed bed reactor system. Parameters such as temperature (300 and 350 °C), pressure (20 and 30 bar(abs)) and catalyst type (Pt on ZSM-5 and Pt on Y-zeolite) were varied. Gas analysis was conducted utilizing a refinery gas analyzer, whereas oil samples were analyzed using a GC-VUV and simulated distillation methods.

The screening series revealed the optimal parameters within the selected pressure and temperature ranges. Subsequently, a prolonged testing was conducted using Pt on Y-zeolite at 30 bar(abs) and 350 °C. The isomer levels increased from 12.11 wt-% in the feed to 29.15 wt-% after a 6-hour run, while the olefin levels lowered from 5.03 wt-% to 0.19 wt-%. The results obtained demonstrate the potential to significantly enhance the intermediate oil properties for aviation fuel production.

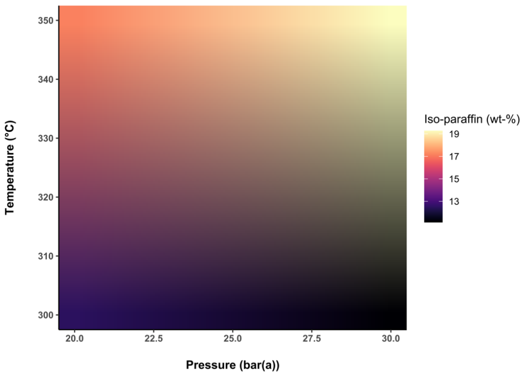

Figure 1. A heatmap presenting the isomer concentration over pressure and temperature using Pt on Y-zeolite

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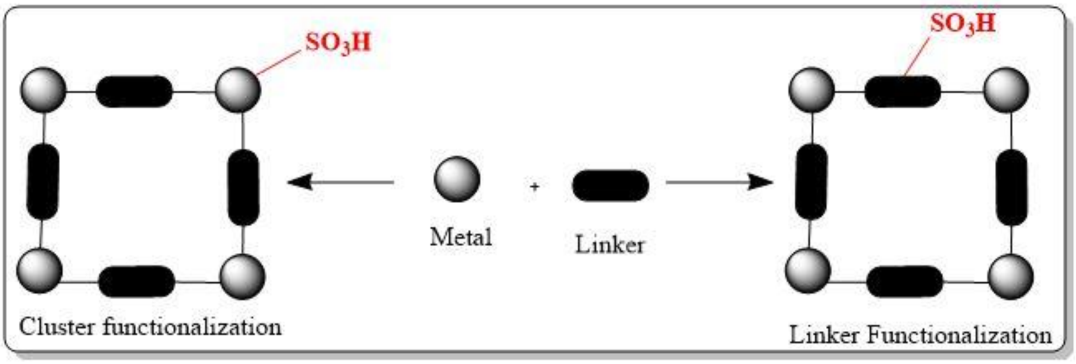
Introducing Brønsted Acidity via Sulfonic Acid Functionalization in Zr Metal-Organic Framework

Simmy Rathod[1], Ananya Chari[1] and Sachin M. Chavan[1]
Department of Chemistry, Bioscience and Environmental Engineering, University of Stavanger, Norway

Sulfonated Metal-Organic Frameworks (MOFs) exhibit promising potential as acid catalysts across various applications. The introduction of SO_3H functionality into MOFs can occur at multiple sites, including the metal cluster, within the pore structure, or at the linker. In this study, we present the synthesis of two distinct sulfonated MOFs: UiS-1, featuring functionalization at the linker, and MOF-808-SO_3H, highlighting functionalization at the metal cluster. These tailored MOFs can serve as catalysts for a range of reactions, including isobutene dimerization, Friedel-Crafts alkylation, quinoxaline synthesis, and several others. Our findings highlight potential utility of sulfonated MOFs as efficient acid catalysts, offering opportunities for enhanced catalytic performance in diverse chemical transformations.



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Poster-42

Hydrodeoxygenation of Pyrolysis Oils A Catalytic Approach for Rural Areas Sustainability

Ronald M. Lara Prado[1,2], *Luis Lopez*[2], *Henrik Kusar*[1]
1.KTH Royal Institute of Technology
2.Universidad Mayor de San Andrés (UMSA)
Corresponding author: ronaldlp@kth.se

Nowadays, different research groups, industrial actors, and decision-makers are gathering their efforts to find alternatives to produce clean energy from sustainable and renewable sources. One alternative is the use of lignocellulosic biomass, a cheap and abundant resource that is constantly produced from agriculture, foresting, and other human activities[1]. These resources become even more important since in underdevelopment countries most of the agricultural activities are performed in rural areas, where electricity access sometimes is a problem. The distance to the main cities and electricity plants might represent a limitation causing high distribution and high electricity costs[2].

Biomass can be thermally treated, to recover added-value products such as biochar, biogases, and bio-oil. The biochar can be directly applied as a soil amendment, and the biogases are commonly used to reduce the overall energy requirement during the thermal process. However, the bio-oil obtained is highly reactive due to its high oxygen content. In general, bio-oils are upgraded through a hydrodeoxygenation process (HDO). This process involves the removal of oxygenated functional groups from the bio-oil leading to the production of water and is conducted under high hydrogen pressures[3]. During the HDO reaction, the catalyst is usually deactivated mainly due to sintering and coking. Sintering occurs due to the high temperature applied and the high water content. Depending on the catalyst composition, some metals and high acidity can lead to breaking the C-C bond, producing active species ideal for carbon deposition, and thus promoting coking[3].

Considering all the challenges mentioned in the previous paragraphs, this study aims to compare the catalytic performance of different iron-based catalysts as a low-cost alternative for the hydrodeoxygenation of bio-oils obtained from pyrolysis of lignocellulosic biomass. The experiments were based on the hydrodeoxygenation of model compounds as a first stage. The model compounds were selected according to their functional groups, to compare the hydrodeoxygenation capacity of the synthetized catalysts.

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Insights into the Hydrodeoxygenation (HDO) Reaction Mechanism of Guaiacol on Ni_2P Catalyst Surface: A Combined Study of Density Functional Theory (DFT) Simulation and Experimental Investigations

Gen Li, Yushuai Sang, Yongdan Li
Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, Kemistintie 1, Espoo, P.O. Box 16100, FI-00076, Finland

Lignin depolymerization has the potential to produce lignin oil rich in aromatic compounds. However, the complexity of these aromatic compounds in lignin oil precludes direct utilization as chemical raw materials. Furthermore, lignin oil exhibits a substantial oxygen content, resulting in a diminished calorific value and rendering it unsuitable for direct use as a fuel source. Consequently, further treatment is essential to mitigate both the oxygen content and compound complexity within lignin oil. Among various methods, hydrodeoxygenation (HDO) emerges as the most efficient approach.

In this work, the HDO reaction of lignin monomers on the Ni_2P catalyst surface was explored. Notably, HDO products exhibited significant variations under different atmospheric conditions. Under an N_2 atmosphere (300°C, 5 hours), the product yield was a mere 15%, with no completely deoxygenated product observed. Guaiacol demonstrated partial deoxygenation and benzene ring hydrogenation under low hydrogen pressure (0 MPa H_2) (300°C, 5 hours), while at medium hydrogen pressure (1 MPa H_2) (300°C, 5 hours), complete hydrodeoxygenation occurred, yielding 86.5% cyclohexane. Conversely, the cyclohexane yield decreases under high hydrogen pressure (3 MPa) (300°C, 5 hours). Density functional theory (DFT) calculations were employed to simulate the adsorption configurations of guaiacol at different hydrogen pressures and determine the reaction pathway for HDO. The varying number of hydrogen atoms adsorbed on the Ni_2P surface results in different adsorption configurations of guaiacol on the catalyst surface, subsequently influencing the hydrodeoxygenation reaction process.

Poster-44

First-principles investigation of CO adsorption on a PdAg surface

Tor S. Haugland, Ingeborg-Helene Svenum
SINTEF Industry, Trondheim N-7465, Norway

Palladium-based alloys are used in various hydrogen technologies. One application of palladium is in hydrogen separation technologies, where palladium-based thin films are membranes. The surface composition and properties of the membrane may play an important role in the overall hydrogen permeation, especially if the thickness is lower than ~5 µm[1]. One known problem is surface poisoning, often caused by CO and other adsorbates[2,3]. The surface composition of PdAg alloys, commonly used as membranes, is known to be sensitive to the surrounding environment[4,5]. In this study, the composition of PdAg alloy surfaces with and without adsorbed CO is explored using density functional theory and the Alloy Catalysis Automated Toolkit (ACAT)[6]. ACAT allows for a systematic sampling of the surface composition under different environmental conditions, including adsorbate coverage on the surface. This is done in ACAT using an evolutionary algorithm to maximize/minimize some chosen value, for instance the chemical potential. With a properly document workflow it becomes easier to extend and tune workflows to investigate new alloy systems and environments, and it also streamlines the setup of high-throughput calculations making it easier to test more variations of the same system. The surface composition for a PdAg surface with 25% Ag model particle and a surface with (111) facet depending on CO coverage will be presented.

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Catalytic low temperature ammonia decomposition for COx free hydrogen production

Sahra Louise Guldahl-Ibouder,[1] Monica Pazos Urrea,[1] Jithin Gopakumar,[1] Ingeborg-Helene Svenum,[2] Magnus Rønning[1]*
[1]*Norwegian University of Science and Technology (NTNU),* 7491 *Trondheim, Norway*
[2]*SINTEF Industry, Kinetic and Catalysis group, 7465 Trondheim, Norway*
**Corresponding author: magnus.ronning@ntnu.no*

Introduction: Ammonia has been suggested as a promising hydrogen vector, as it has a high gravimetric hydrogen content (17.8%)[1]. In addition, ammonia has a much lower liquefaction pressure than pure hydrogen, and there is already extensive infrastructure in place for storage, transport, and handling[2]. Ammonia can subsequently be decomposed by a thermocatalytic process to produce hydrogen and nitrogen.

Experimental/methodology: A 4wt% Ru catalyst on a cordierite monolith was prepared as a benchmark catalyst. Bimetallic transition metal (TM) nitride catalysts are being synthesized, and their activity will be compared to the Ru-based catalyst. The catalytic activity of the Ru-based catalyst was assessed at temperatures between 100-500°C and ambient pressure with a feed composition of 0.5% NH_3 in He. The ammonia conversion is shown in Figure 1. In-situ XAS-XRD was performed at the European Synchrotron Radiation Facility (ESRF).

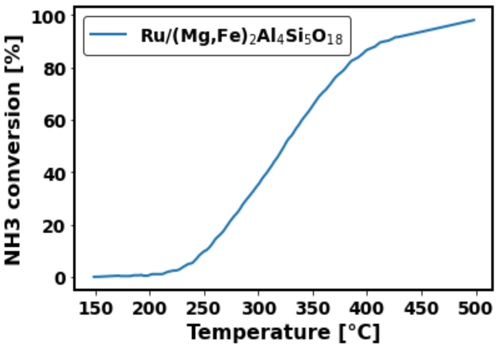

Figure 2 Decomposition of ammonia over a 4wt% Ru catalyst on

Results and discussion: Activity testing revealed high activity for the Ru-based catalyst, achieving 60% NH_3 conversion at 340°C as can be seen in Figure 1. Figure 2 shows the XAS measurements revealing that the state of Ru does not change at the reaction conditions. Bimetallic TM catalysts will be compared to the Ru-based catalyst. Detailed characterization of the electronic and structural properties of the catalysts will be discussed in light of their catalytic performance at different reaction conditions.

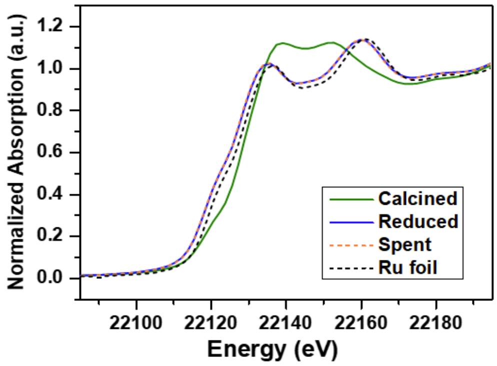

Figure 1 XAS spectra showing the oxidation state of ruthenium.

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New strategies to develop low-temperature Mn-based NH_3-SCR catalysts with improved water and SO_2 tolerance

Huirong Li, Leonhard Schill, Qi Gao, Susanne Mossin, Rasmus Fehrmann, Anders Riisager

Centre for Catalysis and Sustainable Chemistry, Department of Chemistry, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Nitrogen oxides (NO_x) emitted from combustion processes endanger human health by contributing to acid deposition, photochemical smog, and ozone depletion. Selective catalytic reduction of NO_x with ammonia (NH_3-SCR) is the most effective and widely used technology to mitigate NO_x emissions in stationary installations. Industrially applied NH_3-SCR catalysts based on vanadium (VWT catalysts) exhibit high N_2 selectivity and good thermal stability, but they require a relatively high operating temperature (> 250 °C). To avoid a costly reheating of the flue gas, it is thus necessary to locate the VWT catalyst upstream of dust removal and/or desulfurization to avoid significant lowering of the flue gas temperature. This position makes VWT catalysts prone to deactivation or inhibition by flue gas impurities such as SO_2, alkali or heavy metals.

Manganese oxide (MnO_x) catalysts exhibit superior NH_3-SCR activity at low-temperature (≤ 200 °C) and are thus low cost and environmentally benign catalysts that can be utilized in a preferred "tail-end" SCR system without the need for flue gas reheating. Various strategies have previously been attempted for developing industrially viable MnO_x catalysts, however, challenges such as too narrow temperature operating range, limited resistance to water, and susceptibility to SO_2 poisoning have hampered their practical application.[1]

In this work, new strategies have been explored for NH_3-SCR MnO_x catalysts to expand their operational temperature window, improve N_2 selectivity, and increase resistance to water and SO_2. The strategies include the rational constructing of novel Mn-Ti-Ce oxide core-shell catalysts,[2,3] doping MnOx catalysts with Fe and Al,[4] and optimizing the synthesis approaches of Mn-Fe oxide catalysts.[5] The obtained results demonstrate how rational catalyst design can lead to both high low-temperature performance and enhanced durability for Mn-based NH_3-SCR catalysts. This insight may inspire future catalyst design with enhanced applicability for removing NO_x from flue gases.

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Further insights on the effect of potassium on cobalt-based Fischer-Tropsch catalysts

Lj. Gavrilović[1, *], I.H. Svenum[1], L. Xu[2], A. O. Elnabawy[2], E. Ø. Pedersen[1], J. Tafjord[1], Q. Chen[1], J. Yang[1], A. Holmen[1], Hilde J. Venvik[1], M. Mavrikakis[2], Edd A. Blekkan[1]

[1]*Norwegian University of Science and Technology, Norway*

[2]*University of Wisconsin-Madison, USA*

[*]*ljubisa.gavrilovic@ife.no*

The effect of potassium (K) on cobalt- (Co) based Fischer-Tropsch catalysts was investigated experimentally, using Steady-State Isotopic Transient Kinetic Analysis (SSITKA) and X-Ray Photoelectron Spectroscopy (XPS), and theoretically with Density Functional Theory (DFT) calculations. Two catalysts, a clean reference catalyst (20%Co/0.5%Re/γ-Al_2O_3) and the same catalyst poisoned with 3500 ppm potassium added as KNO_3 aerosol particles, were investigated experimentally. SSITKA-experiments showed that K has a negative effect on catalyst activity for CO hydrogenation. However, it was also found that the selectivity to methane decreased, while the selectivity to higher hydrocarbons increased following potassium deposition. SSITKA experiments showed that the surface residence time of intermediates leading to methane formation increased for the catalyst poisoned with K. XPS measurements showed that cobalt is not fully reduced after hydrogen treatment, as also observed for Ru-promoted catalysts[1]. Following syngas exposure, the K-poisoned sample showed some cobalt re-oxidation, whereas no significant difference was found in the oxidation state of cobalt for the catalyst without added potassium.

DFT calculations were performed on two relevant Co crystallographic structures (fcc (111) and hcp (0001)) to understand the effect of K species (K, KOH, OHKOH) on the Co catalyst. Hydroxyl groups (OH) enhance K adsorption on both Co structures such that stability of the adsorbed K species is increased. The influence of K species on the energy barriers for the most important steps in the previously proposed hydrogen-assisted mechanism was investigated[2]. The effect of CO coverage, with K species present on the surface, on the activation energy barriers was also studied and discussed.

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Nickel alumina-based catalyst for sorption enhanced reforming - Effect of calcination temperature

Lj. Gavrilović[1*], S. S. Kazi[1], A. Nelson[1,2], A. Oliveira[1], J. Meyer[1]

[1]*Institute for Energy Technology, Kjeller, Norway*

[2]*ZEG POWER AS, Kjeller, Norway*

*ljubisa.gavrilovic@ife.no

Effect of calcination temperature (350 °C – 850 °C) on the physicochemical properties as well as catalytic performance of Ni-based catalyst for the hydrogen production via steam methane reforming (SMR) and sorption enhanced reforming (SER) has been investigated. Catalyst calcined at highest temperature (850 °C) shows formation of $NiAl_2O_4$ confirmed by XRD. Consequently, a much higher reduction temperature (875 °C) is required to reduce this Ni aluminate spinel to an active Ni catalyst. Catalyst calcined at highest temperature (850 °C) showed much higher CH_4 conversion and H_2 production in SMR compared to the catalysts calcined at lower temperatures. In addition, higher CH_4 conversion and H_2 production was observed for the 15%Ni/alumina_850 catalyst after aging (long exposure to steam and high temperature) compared to commercial reforming catalyst. Finally, a much better stability is observed for the 15%Ni/alumina_850 catalyst compared to the commercial reforming catalyst after 100 SER/regeneration cycles under relevant reaction conditions, Figure 1. The formation of $NiAl_2O_4$ [1] [2] during high temperature calcination plays a vital role in the robustness and stability of the Ni-based catalysts and can be useful synthesis procedure for increasing the catalyst lifetime.

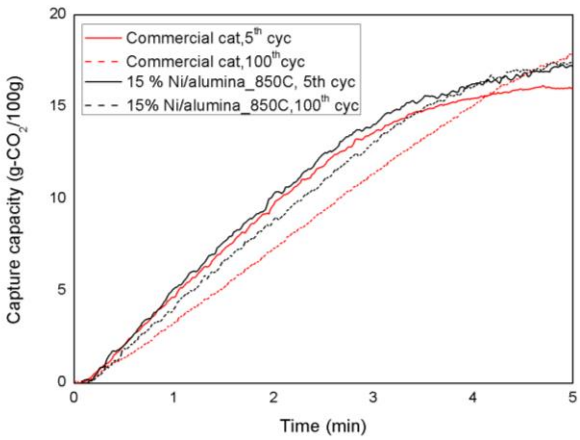

Figure 1. *Comparison of catalytic activity of the commercial and 15%Ni/Puralox catalyst in SER TGA. multi-cycles*

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In-situ EPR study of the effect of sulfur poisoning and regeneration on Cu-CHA catalysts

Thomas K. Rønne-Nielsen[1], Qi Gao[1], Ton V. W. Janssens[2], Fei Wen[3], Peter N. R. Vennestrøm[2], Susanne Mossin[1]
[1]Technical University of Denmark, Kemitorvet 207,2800 Kgs. Lyngby, Denmark
[2]Umicore Denmark Aps, Kogle Allé 1, 2970 Hørsholm, Denmark.
[3]Umicore AG & Co. KG – Hanau, Rodenbacher Ch 4, 63457 Hanau, Germany.

Zeolite-supported copper catalysts (Cu-CHA) exhibit great potential and activity in catalyzing NO_x removal from vehicle exhaust via Selective Catalytic Reduction using NH_3. NO_x emissions are potent pollutants and international legislation keeps pushing the transport sector to reduce their emissions. In particular, diesel-powered vehicles used for long-range transportation emit considerable amounts of NO_x, which is proving the need for novel and enhanced catalysts. However, an unresolved issue regarding the Cu-CHA as exhaust cleaning catalysts is the trace amounts of sulfur present in the exhaust gas, which deactivates the catalysts necessitating the need for catalyst regeneration[1,2,3,4].

In this collaboration, sulfur deactivation and regeneration of a series of Cu-CHA catalysts (Si/Al = 7, wt% of copper between 0.8 and 4) were investigated. The investigation was carried out by ex-situ and in-situ Electron Paramagnetic Resonance (EPR) spectroscopy. The oxidation state of copper is clearly followed by EPR because of the alternating para- and diamagnetic configuration[1]. The focus of the investigation was to quantify the impact of deactivation and regeneration on the copper species, along with the quantification of the copper distribution between different possible copper species.

The investigation proved that sulfur strongly influences the amount of redox active copper[2,3,4] while also influencing rates of both reduction and oxidation. The sulfated copper species were proved to be caught in the oxidized (+2) state and thus could not enter into the reduction half cycle of the SCR reaction. It is only partly reclaimed during the regeneration procedure[1,3].

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Poster-50

Atomically dispersed Fe-Cu dual-sites on carbon black for efficient electroreduction of CO_2 to CO

Song Lu[1,2*], Zhixin Yu[2]
[1]Institute of New Energy, School of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing 312000, China
[2]Department of Energy and Petroleum Engineering, University of Stavanger, 4036 Stavanger, Norway

Introduction

Electrochemical carbon dioxide reduction (ECR) presents a promising technology to attain carbon neutrality. However, the current ECR process still has challenges of CO_2 activation and the complicated product distribution, which limits practical CO_2 reduction. Therefore, it is necessary to develop electrocatalysts with good activity and high selectivity for ECR. There has been widespread research on single-atom catalysts (SACs) for electrocatalysis, owing to their high atom-utilization efficiency, unique electronic properties, and well-defined active sites. However, the single active center makes it difficult to break the constraint of scaling relationship between the adsorption energies of intermediates due to the complicated multiple proton-coupled electron transfer[1]. Constructing heteronuclear dimer sites to form dual-atom catalysts (DACs) is an efficient way to modify the coordination environment and the electronic properties of the SAC active centers.

Experimental/methodology

Fe-NC, Cu-NC and Fe-Cu-NC supported on N-doped carbon black were synthesized via a facile ion adsorption and calcination process.

Results and discussion

The catalysts were charactered by XRD, Raman, HRTEM, HAADF-STEM, XANES, EXAFS, XPS, etc. XRD results indicated that there are no Fe and Cu metallic clusters or compounds in the Fe-Cu-NC catalyst. XPS results suggest that the Fe and Cu species are likely to be in a partially oxidized state. Fe-Cu-NC catalyst exhibits the highest ECR activity, yielding a current density of 22.5 mA/cm² under −0.80 V (vs. RHE) and maximum FE_{CO} of 96.4% (Fig. 1a and b). Theoretical calculations demonstrate that constructing Fe-Cu dual site could decrease the free energy barrier of *COOH formation (Fig. 1c).

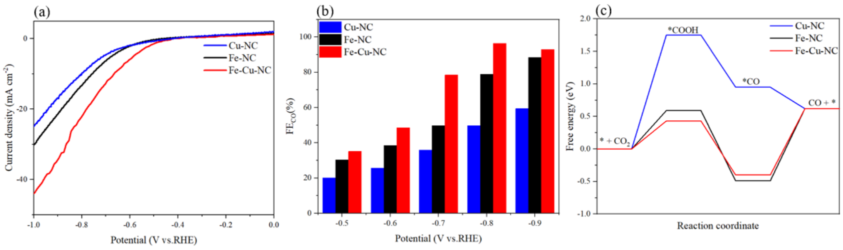

Fig. 1 (a) LSV curves of catalysts; (b) The Faradic efficiencies of CO generation; (c) Free energy change for CO generation.

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