Book of abstracts

18th Nordic Symposium on Catalysis
August 26-28, 2018
Copenhagen
The Organizing Committee
Anders Riisager (Chair) (DTU Chemistry)
Anker Degn Jensen (DTU Chemical Engineering)
Brian Brun Hansen (DTU Chemical Engineering)
Christian Damsgaard (DTU Physics/DTU CEN)
Jakob Munkholt Christensen (DTU Chemical Engineering)
Jan Rossmeisl (University of Copenhagen, Department of Chemistry)
Martin Høj (DTU Chemical Engineering)
Peter Vesborg (DTU Physics)
Susanne Mossin (DTU Chemistry)
Søren Kegnæs (DTU Chemistry)

The scientific program consists of
3 Plenary lectures including the 2018 Berzelius award lecture
4 Nordic Keynote talks
51 Oral contributions
49 Poster presentations

This booklet contains abstracts for each of these 107 scientific presentations.
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The programs on pages 5 to 11 have clickable links that will take you to the abstract. Clicking the presentation number (e.g. “Oral 4.3”) in the header section of each abstract will take you back to the program.
Overview program for the 18th Nordic Symposium on Catalysis (NSC), 2018 in Copenhagen

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Automotive and flue gas cleaning  
Biomass and biomolecules  
Synthesis and characterization  
Reduction/hydrotreating  
Syngas conversion  
Theory and modelling  
Photo and electro catalysis  
Oxidation
Program for the 18th Nordic Symposium on Catalysis (NSC), 2018 Copenhagen

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|              | **Emiel Hensen, Eindhoven University of Technology**  
|              | Valorization of lignocellulosic biomass: from catalytic chemistry to novel processes  
|              | Chairman: Anker Degn Jensen, Technical University of Denmark |
| 15.00-15.30  | Coffee                           |
|              | **Automotive and flue gas cleaning**  
|              | Room 101/102  
|              | Chairman: Brian Brun Hansen, Technical University of Denmark |
|              | **Biomass and biomolecules**  
|              | Room 104  
|              | Chairman: Anders Riisager, Technical University of Denmark |
|              | **Synthesis and characterization**  
|              | Room 105  
|              | Chairman: Christian Danvad Damsgaard, Technical University of Denmark |
| 15.30-15.50  | O1.1 Hanna Härelind  
|              | Chemistry and Chemical Engineering, Chalmers University of Technology  
|              | Detailed characterization of solid-state ion-exchanged Cu-CHA for ammonia SCR |
| 15.50-16.10  | O2.1 Peter S. Hammershøi  
|              | Umicore Denmark and DTU Chemical Engineering, Technical University of Denmark  
|              | Lifetime impact of SO₂-poisoning of a Cu-CHA catalyst for NH₃-SCR |
| 16.10-16.30  | O3.1 Anja Olafsen Sjåstad  
|              | Department of Chemistry, University of Oslo  
|              | Bimetallic Pt(Rh) catalysts for intermediate temperature ammonia oxidation – combining traditional catalysis with surface science |
| 16.30-16.50  | O4.1 Rui Wang  
|              | School of Environmental Science & Engineering, Shandong University  
<p>|              | Germanium-based polyoxometalates: preparation and application in adsorption-decomposition of NOₓ |
| 17.00-18.00  | Poster session with refreshments (All posters) |
| 18.00-19.00  | Welcome reception with standing dinner and poster session continued |</p>
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<td></td>
<td><strong>Riikka Puurunen</strong>, Aalto University</td>
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<td>Supported heterogeneous catalysts by atomic layer deposition</td>
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<td>Chairman: <strong>Christian Hulteberg</strong>, Lund University/Berzelius award committee</td>
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<td>9.55-10.15</td>
<td><strong>O5.1 Kirsten Leistner</strong> Chalmers University of Technology</td>
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<td>Volatilisation and Resulting Deposition of Platinum Oxides from Model DOC Catalysts</td>
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<td><strong>O5.2 Irene Tosi</strong> DTU Chemistry, Technical University of Denmark</td>
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<td>Kinetic insight into the production of methyl lactate from sugars with Sn-Beta catalyst</td>
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<td><strong>O5.3 M. Grazia Francesconi</strong> University of Hull</td>
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<td>Pd-based Catalysts for the Semi-Hydrogenation of 2-Methyl-3-Butyne-2-ol (MBY)</td>
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<td><strong>O6.1 Liqun Kang</strong> University College London</td>
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<td>Catalytic behaviors of Cu single site and clusters over ceria surface</td>
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<td><strong>O6.2 Aitor Arandia</strong> Department of Chemical and Metallurgical Engineering, Aalto University</td>
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<td>Aqueous phase reforming (APR) of bio-oil model compounds over different Ni-based catalysts</td>
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<td><strong>O6.3 Trine Marie Hartmann</strong> Dabros Haldor Topsøe A/S</td>
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<td>Heterogeneous catalysis-from research to industrial implementation</td>
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<td>11.35-11.55</td>
<td><strong>O7.1 Piotr Legutko</strong> Faculty of Chemistry, Jagiellonian University in Krakow</td>
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<td>Doping with cobalt as a potential method of boosting of catalytic activity of birnessite and cryptomelane in soot combustion</td>
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<td><strong>O7.2 Sebastian Meier</strong> DTU Chemistry, Technical University of Denmark</td>
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<td>Liquid State NMR Approaches to Catalyzed Reactions: Ultrahigh Resolution and Molecular Probes</td>
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<td><strong>O7.3 Abdulaziz Bagabas</strong> Materials Science Research Institute (MSRI), King Abdulaziz City for Science and Technology (KACST)</td>
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<td>Acetone Reaction with Hydrogen over Mesoporous Magnesium Oxide-Supported Rhodium Nanoparticles</td>
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<td><strong>Jia Yang, Norwegian University of Science and Technology</strong></td>
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<td>Isotopic labeling for kinetic and mechanistic investigation in Fischer-Tropsch synthesis</td>
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<td><strong>Zeolitic Imidazolate Frameworks as templates and self-sacrificing catalyst precursors</strong></td>
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<td><strong>Kinetic study of methanol and direct dimethyl ether synthesis from CO\textsubscript{2}-rich syngas</strong></td>
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<td><strong>DeNO\textsubscript{x} of flue gasses by end-of-pipe technologies</strong></td>
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<td><strong>Ulla Lassi, University of Oulu</strong></td>
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<td><strong>Chemical Engineering, KTH Royal Institute of Technology</strong></td>
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<td><strong>Department of Physics and Competence Centre for Catalysis, Chalmers University of Technology</strong></td>
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<td><strong>O14.1 Rainer Küngas</strong> <em>Haldor Topsoe A/S</em></td>
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<td><strong>O14.2 Andrea Lazzarini</strong> <em>Department of Chemistry, University of Oslo</em></td>
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<td>Operando FT-IR spectroscopy for the study of Pd-functionalized UiO-67 for CO2 hydrogenation reaction</td>
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<td>Calcined Al-Mg Hydrotalcite as Support in CuCl2 Based Oxychlorination Catalysts</td>
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<td><strong>O15.1 Manuel Saric</strong> <em>Department of Chemistry, University of Copenhagen</em></td>
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<td>Towards electrification of chemical syntheses by electrocatalytic synthesis of dimethyl carbonate</td>
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<td><strong>O15.2 Farnoosh Goodarzi</strong> <em>DTU Chemistry, Technical University of Denmark</em></td>
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<td>Direct CO2 hydrogenation to methane over zeolite encapsulated nickel nanoparticles</td>
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<td>Catalytic oxidation of NO to NO2 for nitric acid production over a supported Pt catalyst</td>
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<td><strong>O16.1 Sungeun Yang</strong> <em>DTU Physics, Technical University of Denmark</em></td>
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<td>Decentralized production of H2O2 using electrocatalysis</td>
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<td><strong>O16.2 Carlos Hernandez Mejia</strong> <em>Utrecht University</em></td>
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<td>Impact of Reduction-Oxidation-Reduction Treatments on Supported Cobalt Catalysts</td>
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<td><strong>O17.1 Ahmad Alshammari</strong> <em>Materials Science Research Institute, King Abdulaziz City for Science and Technology</em></td>
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<td><strong>O17.2 Edd A. Blekkan</strong> <em>Dept. of Chemical Engineering, Norwegian University of Science and Technology (NTNU)</em></td>
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<td>Mn-promotion of alumina-supported cobalt Fischer-Tropsch catalysts</td>
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<td><strong>O17.3 Kristian Raun</strong> <em>DTU Chemical Engineering, Technical University of Denmark</em></td>
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<td>Modeling of the Molybdenum Loss in Iron Molybdate Catalyst Pellets used for Selective Oxidation of Methanol to Formaldehyde</td>
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<td><strong>Peter Christian Kjærgaard Vesborg</strong>, <em>Technical University of Denmark (DTU)</em></td>
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<td>Ultrasensitive measurements of transient electrocatalytic phenomena</td>
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Plenary abstracts
The transition to a clean and sustainable economy is one of the great challenges of our time. There is plenty of renewable energy which however requires scalable storage solutions. On the materials side, there is an urgency to derive building blocks for the chemical industry from renewable resources. For instance, the demand for green aromatics is rapidly growing, while trends in fossil fuel pricing is expected to lead to lower aromatics supplies. Lignin is one of the major components of lignocellulosic biomass, constituting 15-30% of the weight and approximately 40% of the energy content depending on the source. It is the only large volume renewable feedstock that comprises aromatics. For this reason and also because of its richness in functional groups, lignin is a potential resource for the production of renewable chemicals and fuels.

In my lecture, I will provide an overview of various catalytic approaches to obtain aromatics from the lignin fraction of woody biomass. In many studies in this field, technical lignins are used as a feedstock. The recalcitrance of this type of lignin hinders effective depolymerization under mild conditions. Accordingly, we explored a catalytic approach in supercritical ethanol, which yields mainly alkylated mono-aromatics from soda, Organosolv and Kraft lignins. Oxygen-free BTX (benzene, toluene, xylenes) and other alkylated aromatics can replace reformate or serve as base aromatic chemicals. Oxygenated aromatics are promising fuel additives with low sooting properties and may also find application as building blocks for polymers. In this first part, I will focus on the underlying chemistry of this lignin ethanolysis process, which involves thermal cracking of lignin followed by alkylation reactions of monomers and fragments with ethanol. The use of ethanol is key as it is an effective scavenger of lignin-derived formaldehyde, which promotes repolymerization. 14C radiolabeling provides clues about the incorporation of the solvent in the products. Despite promising yields, solvent consumption is too high. Therefore, we now investigate a mild version of lignin ethanolysis in which solid lignin is converted into a crude lignin oil with diverse applications as a chemical feedstock and sustainable shipping fuel.

In the second part, I will discuss an alternative “lignin-first” process that yields a much better defined product slate. We combine a soluble Lewis or Brønsted acid with a noble metal hydrogenation catalyst to upgrade woody biomass into mono-aromatics, hemi-cellulose sugars and a solid cellulose-rich pulp. For instance, a combination of Pd/C and a metal triflate allows converting up to 55 wt% of the lignin contained in Eucalyptus wood chips into products such as 4-n-propylsyringol, 4-n-propanolsyringol and 4-n-methoxy propyl syringol and their corresponding guaiacyl counterparts. Using model compounds, we gained insight into the mechanism of this unusually effective chemistry involving cleavage of carbohydrate-lignin linkages followed by cleavage of ether bonds and hydrogenation of reactive intermediates.

Finally, I will show a catalytic approach designed to convert the alkylmethoxylphenols obtained from “lignin-first” processes into pure phenol. The chemistry involves a combination of demethoxylation catalyzed by a titania-supported gold nanoparticle catalyst and transalkylation of alkyl groups in alkylmethoxylphenols to low-value benzene promoted by HZSM-5 zeolite. We demonstrate that intimate contact between these two catalyst functions is crucial to transfer the methyl groups from the methoxy functionality to benzene rather than phenol. In a mixed-bed configuration, we achieved a yield of 60% phenol and 15% cresol from propylguaiacol in a one-step reaction at 350 °C at a liquid hourly space velocity of ~40 h⁻¹.

Supported heterogeneous catalysts by atomic layer deposition

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Atomic layer deposition (ALD) is a thin film growth method that allows the preparation of uniform inorganic material layers on arbitrarily complex three-dimensional structures. The three-dimensional uniformity, also termed “conformality,” is a consequence of the systematic use of repeated, self-terminating (saturating, irreversible), separated gas–solid reactions of at least two compatible compounds [1,2]. While the principles of ALD were formulated already in the 1960s and 1970s, independently twice [3-5], it has been during the 2000s that ALD has enabled the continuation of Moore’s law of transistor miniaturization and ALD has been recognized as a versatile multi-tool of nanotechnology. As of 2010, >700 two-reactant ALD processes had been developed [6]. In 2018, the Finnish inventor of ALD, Dr. Tuomo Suntola, received the prestigious Millennium Technology Prize [7].

ALD can coat conformally porous high-surface-area catalyst supports by catalytically active materials. The first reports of the use of ALD for preparing supported catalysts are from the Soviet Union in the early 1970s [4,5,8]. In 1990s, there was a strong industry-driven effort for ALD for catalysis in Finland [3,9]. Interest in ALD for the preparation of supported heterogeneous catalysts has again been increasing during the past decade [10,11]. The current interest in ALD is based for example in the ability of ALD to prepare (close to) monodisperse metal particles; to make overcoatings to temper the activity of highly active but non-selective sites; and to prepare single-atom catalysts. The solvent-free nature of ALD is generally regarded an environmental advantage and scaling up the catalyst preparation should be feasible. In the author’s perspective, interesting is also to bridge the worlds of planar model surfaces and real high-surface-area catalysts by creating the same kind of coating on both materials by ALD; recently developed lateral conformality test structures may help to bridge this gap [12,13].

This invited contribution will discuss historical achievements, challenges and opportunities in preparing supported heterogeneous catalysts by ALD. The discussion includes notations on the developing nomenclature and is supported by examples from the author’s own works as well as other works from the scientific literature.

References

Catalysts and reactors under dynamic reaction conditions in environmental catalysis and for energy storage and conversion

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1. Introduction
Supported noble metal catalysts can nowadays be designed from bottom-up by using dedicated preparation procedures for the support and the nanoparticles. However, the atomic structure and electronic state of metal nanoparticles often change, upon exposure to the reaction atmosphere [1]. Hence, new challenges in process control and catalyst design appear when reactions are operated under dynamic reaction conditions, such as occurring during the fluctuating availability of raw materials or for start/stop cycles in automotive applications. For example, in “power-to-chemicals”-processes using CO/CO2 and renewable H2 to produce chemical energy carriers for energy storage purposes [2], the dynamics originate from the fluctuating supply of wind and solar energies reflected in variations of the H2 feed (Fig. 1, ref. [3]). This is additionally critical in exhaust gas catalysts which are operated at tremendous gas and temperature changes [4]. Controlling these dynamics throughout the entire catalyst lifetime requires an in-depth understanding of the underlying structural processes and their kinetics [5].

2. Results and discussion
To follow the structural dynamics of a catalyst, in situ and operando characterization techniques are needed. In situ electron microscopy has provided insight into structural changes while varying the chemical potential [6]. X-ray based techniques even allow to perform spectroscopic studies under realistic reaction conditions. In this context, we have recently found that metal particles strongly change their structure during oxidation/reduction of a Pt/CeO2 catalyst. This effect even allows for tuning the particle size [7]. A prominent example for structural changes in the context of CO/CO2 hydrogenation is the Cu/ZnO methanol synthesis catalyst [8]. The catalyst strongly changes its nature when the redox potential of the gas atmosphere is varied, resulting in morphological changes of the copper particles. Further recent studies provide first insights into the dynamics during the methanation of CO2. Here, the focus is on the impact of fluctuating H2 supply on the structure and performance of Ni-based catalysts using operando XAS and Raman spectroscopy. It was shown that fast load changes influence the Ni-based catalysts, resulting in oxidation of the active sites and, thus, catalyst deactivation [9]. Moreover, the catalyst was exposed to various feed mixtures to investigate possible deactivation from deposited carbon via operando Raman spectroscopy. Improved catalytic performance was found using Ni-Fe alloy catalysts [10].

3. Conclusions
The results from these studies revealed important and first aspects concerning the structural changes of catalysts under dynamic reaction conditions using operando techniques. This plays an important role in exhaust gas catalysis, “power-to-X”-processes and selective oxidation. The dynamics may even allow rationally tuning the size and surface structure of noble metal particles in situ.

References
Keynote abstracts
Heterogeneous catalysis—from research to industrial implementation

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1. Introduction
There is a significant difference in developing products in the chemical engineering space compared to other areas, e.g. consumer goods. Despite this difference, product development is a process that more and more chemical engineers and chemists are involved in, as displayed in figure 1. There has been a large shift from actual working in plants to developing products. What is then product development? It is a procedure of translating consumer needs into commercial products and is central in developing heterogeneous catalysts that find their way into any application [1-4]. However, before getting to deep into the product development process, it is important to define what is not included in the process and that is the design of molecules.

2. Product development process
The product development process is divided into four stages or steps where the first stage is normally considered to be the identifying the needs a product should fulfil. This is normally done by communicating with potential customers, using the communication to interpret their expressed needs and translating the needs to product specifications. Using these specifications, the next step in the process is finding ideas of different products that could satisfy them. Thereafter, the next step in the process is to select the most promising idea. This is actually not that easy, but using a decision matrix to compare the different ideas, e.g. comparing factors such as:

1. Scientific maturity
2. Engineering ease
3. Minimum risk
4. Low cost
5. Safety
6. Low environmental impact

But also qualitative aspects such as, e.g. comfort and quite should be included in the assessment. Finally, the final stage in the process is manufacturing. But there is actually one very important question to answer before the product development process starts and that is to identify who is the customer? These may be identified in two ways by market pull or by technology push, depending on type of product.

This is a rather generic description of the actual process. For developing products for the chemical or chemical engineering market, it is important to understand the actors involved in technology development and commercialisation. There are several players in the chemical industry, starting with inventors (which may work in academia or industry). Their ideas normally end up with companies that owns the process and/or product concept. These companies normally license the technology to other companies that use the technology, therefore they are named licensors or specialised engineering firms. Aside from these actors, there are researchers/developers, consultants that help with specific questions in market and technology. When a process technology is developed to a point where it can be commercialised, the licensor provides a basic design of the process to an engineering, procurement, construction firm. This company uses the basic design for specifying the entire plant in all its details and parts needed may be procured from component suppliers or tailor made. When the plant is finished, it is handed over to the process user, where

4. Conclusions
In conclusion, it is important to ensure that some kind of product development process is followed such that the developed product is relevant to the intended group of users. There is, however, quite a span when it comes to products in the chemical and chemical engineering space, making it really important to clearly define the product to be developed.

References
Isotopic labeling for kinetic and mechanistic investigation in Fischer-Tropsch synthesis

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Isotopic studies are in situ/in operando non-invasive characterization method for various reaction systems. It has been show that isotopic labeling is a powerful tool to provide kinetic and mechanistic information of heterogeneous catalytic systems. Among that, isotope of H (D) and C (13C) are very useful for study of syngas and hydrocarbon formation chemistry. Kinetic isotopic effect (KIE) refers to the phenomenon that isotopically substituted molecules react at different rate. Strong KIE effect may be expected when substituting H with D if bond formation of rapture with H are involved in the rate limiting steps. Steady-State Isotopic Transient Kinetic Analysis (SSITKA) involves a switch between an isotopic unlabeled gas (e.g. 12CO) with an isotopic labeled gas (e.g. 13CO)in reactant and the relaxation of both reactants and products are detected by on-line MS. SSITKA is very useful to provide site coverage and reactivity of surface intermediates and probe the heterogeneity of the surface. A few examples will be given utilizing KIE and SSITKA to study reaction mechanism of Fischer-Tropsch synthesis.
Biomass-based carbon catalysts in catalytic conversion reactions

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1. Introduction
Chemical production from biomass is an interesting alternative for replacing the fossil resources. Typically biomass dehydration to chemicals is catalyzed by mineral acids or metal salts. In our earlier studies, we have applied mechanocatalysis for biomass (sawdust, barley straw, fiber sludge) conversion to reducing sugars [1-3] and further to added-value products. However, these homogeneous catalysts are difficult to recycle and are not always environmentally benign. In this abstract, heterogeneous biomass-based carbon-supported metal catalysts are considered and some recent research work of our group is presented.

2. Preparation and characterization of biomass-based carbon catalysts
Carbon catalyst supports were prepared from biomass (sawdust). Biomass carbonization and chemical/physical activation is performed in a single-step process, and significant properties (e.g. porosity) of carbons are adjusted during this process. Active metals are added by dry impregnation, and carbon support can also be modified by adding active groups to increase Brøns and/or Lewis acid sites on the catalyst surface. Further, carbon catalysts are characterized by well-known, sophisticated methods (i.e. BET and pore size distribution, TC, elemental analysis, ICP-OES, SEM-EDS, FTIR, XRD and XPS)

3. Results and discussion
Biomass-based carbon catalysts have several applications and these catalysts are studied in several model reactions. Carbonization and activation conditions are crucial for the end properties (e.g porosity) of carbon catalysts which cannot be further tailored. We also observed that the single-step process for carbonization and activation should be preferred [4].

In our studies, Co/C catalysts promoted with Re or Ru [5] showed a good activity in FT reaction with good selectivity to higher hydrocarbons. Carbon supported 1% AuPt catalysts were used in glycerol oxidation and levulinic acid hydrogenation reactions [6]. This study showed also the strong influence of support structure on the catalytic activity. Same effect was also observed in our recent study in which Ni/C, Ru/C and Pt/C catalysts were used in the hydrogenolysis of furfural into 2-methylfuran [7]. Recently, we have also prepared and studied carbon foams as active and selective catalysts (Varila et al. 2018, unpublished data).

Acknowledgements
Author acknowledges the Biomass value chains project (A71029, the EU/European Regional Development Fund) and the Bioraff Botnia project (20200327, Interreg Botnia-Atlantica) for financial support.

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Ultrasensitive measurements of transient electrocatalytic phenomena
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Introduction
Tracking electrochemistry as it happens using mass spectrometric detection offers a great way to discern which processes the electrochemical current corresponds to. Ideally, the measurement could provide calibrated, real-time rates for all reaction products. If such conditions were achieved, it would be a highly desirable alternative to batch methods which are slow and laborious.

The new approach and results
Electrochemical mass spectrometry based on Micro-ElectroMechanical Systems (MEMS)-fabricated inlet chips is a very advantageous alternative to conventional Differential Electrochemical Mass Spectrometry (DEMS).[1] Particularly, in the case of highly volatile species such as H₂, O₂, CH₄, etc. the sensitivity advantage over DEMS is greater than 100x. Augmenting the great sensitivity, the inlet-chip approach also allows quantitative product detection (often not possible with DEMS) which allows for faradaic efficiency determination in real time. [1]

The new inlet-chip approach is particularly appealing for transient phenomena such as isotope-label titration techniques. We give a few recent examples of this emerging technique to illustrate the power of the approach for analytical electrochemistry.

References
Oral abstracts
**Detailed characterization of solid-state ion-exchanged Cu-CHA for ammonia SCR**

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1. Introduction

The metal-exchanged small-pore zeolite Cu-SSZ-13 is a promising catalyst for selective catalytic reduction of nitrogen oxides (NOx) in diesel exhausts using ammonia as reductant (NH3-SCR) [1]. Conventionally, copper ions are introduced into the zeolite by aqueous ion-exchange (AIE) [2]. To avoid the use of water, copper is in the present study instead introduced to the micropores of the zeolite by solid-state ion-exchange (SSIE). The catalytic activity for NH3-SCR of Cu-SSZ-13 samples with a range of Cu loadings, is investigated, and the samples are characterized before and after the activity experiments in order to study the nature of the Cu species present in the micropores of the zeolite [3].

2. Experimental

The Cu-SSZ-13 samples were prepared by physically mixing different amounts of a Cu salt with the zeolite followed by heat treatment at 800°C. The activity for the standard NH3-SCR reaction was investigated in a flow reactor using powder samples of the catalyst (GHSV of 205,000 h⁻¹). The samples were characterized both directly after the synthesis, i.e. before the activity tests for NH3-SCR, as well as after the activity experiments. The characterization methods used were X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-Vis, X-ray photoelectron (XPS) and diffuse reflection infrared Fourier transform (DRIFT) spectroscopy, ammonia temperature programmed desorption (NH3-TPD) and hydrogen temperature programmed reduction (H2-TPR).

3. Results and discussion

The samples prepared by SSIE show high activity for NH3-SCR with maximum NOx conversions comparable to those reported for Cu-SSZ-13 synthesized by AIE [4] (Figure 1). Interestingly, significantly lower activities are observed for the first compared to the second and third consequent flow reactor experiment. In contrast to the results for Cu-SSZ-13 prepared by AIE reported in literature, the NOx conversions increased with increasing Cu loadings for the samples prepared by SSIE. Furthermore, UV-Vis spectroscopic, XPS and H2-TPR measurements suggest the existence of isolated Cu²⁺ species in the samples likely representing precursors for the active sites in the NH3-SCR reaction. Finally, DRIFT results show both Cu⁺ and Cu²⁺ species present in the zeolite structure (Figure 1). However, the presence of CuO outside the zeolite framework was observed for all samples.

4. Conclusions

In conclusion, we present a novel route for ion-exchange of Cu into the small-pore zeolite SSZ-13 utilizing solid-state ion-exchange. The results from the different characterization techniques suggest the existence of isolated Cu²⁺ species and, in addition, the DRIFT results indicate that Cu⁺ species are also present in the micropores of the zeolite. In contrast to findings for the corresponding samples ion-exchanged by AIE, however, also extra framework CuO species are observed to be present. This may explain the influence of the Cu loading on the NOx conversion in the NH3-SCR reaction.

References

Hydrogen assisted catalytic biomass pyrolysis for green fuels. Effect of catalyst in the fluid bed

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1. Introduction

Fast pyrolysis of biomass is a well-known technology for producing bio-oil. However, in order to use the oil as transportation fuel the oxygen content must be decreased from approximately 40 wt.% to below 1 wt.% [1]. This can be achieved by catalytic hydrodeoxygenation (HDO). Unfortunately, deactivation due to coking of the catalyst is a severe problem for this technology [1]. The objective of the present work is to produce oxygen free gasoline and diesel from biomass by hydrogen assisted catalytic fast pyrolysis.

2. Experimental

Fast pyrolysis of beech wood (feeding rate: 270 g/h) has been performed in 26 bar hydrogen (flow: 55-90 NL/min) in a fluid bed reactor operated at 450 °C with several different catalysts as bed material followed by an additional vapor phase, fixed bed HDO reactor (operated at 370-400 °C) using a sulfided commercial Ni-Mo/Al2O3 catalyst. The time on stream varied between 0.75 and 3.5 h. The tested catalysts in the fluid bed include olivine sand (OS), MgAl2O4 (MgAl), CoMo/MgAl2O4 (CoMo), zeolite HZSM5 mixed with alumina (ZA), NiMo impregnated on zeolite mixed with alumina (NiMoZA), and a cheap and non-toxic catalyst (HYCP). The HYCP catalyst was tested both in reduced (HYCP-R) and sulfided forms (HYCP-S), while the other catalysts, with the exception of OS, were sulfided prior to the experiment.

3. Results and discussion

The product distribution for the experiments where the HDO reactor was used is shown in Figure 1. The obtained bio-oil from these experiments was essentially oxygen free and was in the diesel and gasoline boiling point range. Using MgAl and ZA gave a high char yield and a lower yield of condensable organics compared to the supported active catalysts (CoMo and NiMoZA). Using the HYCP-R catalyst gave a condensable organic yield of 25 wt. %daf corresponding to the highest obtained energy recovery of 58 %. Using the HYCP-R catalyst in the fluid bed reactor and by-passing the HDO reactor decreased the C1-3 yield from 12 to 3 wt. %daf and increased the condensable organic yield from 25 to 34 wt. %daf. However, the oxygen concentration in the produced oil increased to 14 wt. %db. GC×GC-MS/FID showed that the oxygenates were mainly phenols (22 % FID-area) and oxygenated aliphatics (21 % FID area).

The carbon content on the spent catalysts was investigated using scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDS). This showed that there was up to 3 times as much carbon on the surface of the spent support materials (MgAl and ZA) compared to the supported catalysts (CoMo and NiMoZA) and the HYCP catalysts. Thus, having a more active catalyst in the fluid bed decreases the coking of the catalyst.

4. Conclusions

Our work indicates that hydrogen assisted catalytic pyrolysis is a feasible path for production of liquid renewable fuels. The presence of an active catalyst in the fluid bed is essential and has a significant impact on the product distribution. It is possible to obtain a high yield of condensable organics with the cheap HYCP catalyst, thus showing that it is not necessary to use expensive formulated catalysts. In our ongoing research the differences between CoMo, NiMo and Mo catalysts in the fluid bed is further investigated. Furthermore the effect of the metal loading and the effect of using different supports are also studied and the spent catalysts characterized by use of SEM and transmission electron microscopy (TEM).

References

Application of industrial wastes from iron and steel production in creation of zeolite type materials: Synthesis, characterization and evaluation of catalytic properties

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1. Introduction

Transformation of industrial wastes into value added products is important from scientific and industrial viewpoint. Ferrous slag, which is a by-product from steel manufacturing or iron recovery from ores, is usually used for cement production and road construction [1-4]. However, elemental composition makes it possible to use this type of wastes for synthesis of catalytic materials, namely zeolites [5, 6].

2. Experimental

Transformation of industrial slag was carried out by alkaline pretreatment and hydrothermal synthesis methods. Evaluation of physico-chemical properties of zeolitic materials by analytical methods such as nitrogen physisorption for surface area and pore volume determination, SEM and XRD for structural analysis, EDX for the quantitative analysis of elemental composition, TEM for the metal particle size measurement, TPD of CO2 and NH3 for determination basic and acidic sites was performed. Application of the catalysts in fast pyrolysis of sawdust was carried out with a filament pulse pyrolyzer.

3. Results and discussion

Elemental composition of the ferrous industrial slags allows also their utilization in the synthesis of zeolitic materials. Structural analysis of treated samples showed formation of crystals of a clearly defined shape (Fig.1). The crystal structure varied depending on the synthesis conditions. XRD analysis showed that the synthesized catalysts exhibit highly crystalline phases containing CaCO3, Ca(OH)2, SiO2, Al2O3, Fe2O3 and TiO2. Pretreatment of the industrial slag allows an increase of the specific surface area values, what accompanied with formation of a porous structure including pores on the external surface and internal channels as determined by TEM. Formation of metal/metal oxides nanoparticles was also observed (Fig.2). TPD showed that the original and treated materials exhibited strong basicity due to presence of large amounts of basic oxides. Fast catalytic pyrolysis of softwood sawdust demonstrated that the industrial slag base catalysts changed the product distribution and the yield of the degradation products in comparison with thermal pyrolysis or application of an unmodified industrial slag.

4. Conclusions

Application of industrial wastes from iron and steel industry in synthesis of catalytic materials is a promising field of research. As framework of this work utilization of ferrous industrial slag for synthesis of porous zeolite type materials has been successfully applied. It was found that variation of the synthesis parameters significantly influenced the physico-chemical and catalytic properties of synthesized materials.

References

Lifetime impact of SO2-poisoning of a Cu-CHA catalyst for NH3-SCR

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1. Introduction
NOx (NO+NO2) emissions from diesel vehicles are reduced by selective catalytic reduction with NH3 (NH3-SCR) over V2O5- or metal-zeolite-based catalysts. Due to their superior low-temperature activity, Cu-CHA zeolites are highly relevant for automotive SCR applications [1]. However, the inevitable presence of SO2 in diesel exhaust leads to deactivation of Cu-CHA catalysts [1-3], which is partially reversible at 550 °C [3]. With a lifetime of approx. 10000 h, it is crucial to assess the deactivation development over long-term SO2 exposures. In this work, the reversible and irreversible deactivation are measured after SO2 exposures comparable to that in the lifetime of a heavy-duty vehicle, and are related to the accompanying S uptake.

2. Experimental
24 samples of a Cu-CHA catalyst powder (Si/Al = 14.6 and 2.4 wt% Cu) of 150-300 μm sieve fraction, was aged in 50 ppmv SO2, 10 % O2, 5 % H2O and N2 at a total flow rate of 1.67 NL/min. The SO2 exposures were carried out at 200, 300, 400, or 500 °C, and for 1-120 h. Regeneration was 6 h at 550 °C with the same flow conditions, but in the absence of SO2. All SO2 exposed and regenerated samples were analysed for Cu and S with ICP-OES. Steady state NO conversions were measured over a 5 mg catalyst bed in a flow of 500 ppmv NO, 533 ppmv NH3, 10 % O2, 5 % H2O, and N2 at a rate of 225 NmL/min at temperatures between 160-550 °C.

3. Results and discussion
Upon exposure to SO2, the low-temperature (200-300 °C) NO conversion drops significantly, but most of it is restored by regeneration at 550 °C. Fig. 1 shows that the deactivation of the catalyst is fast, and reaches the saturation level already after a total SO2 exposure of 750 ppm-h, which is in the range 85-95 % for the SO2 exposed catalysts, and 20 % for the regenerated ones. Full deactivation is not observed, indicating that some Cu sites remain active. The data in Fig. 1 implies that regeneration at 550 °C in SO2-free gas restores the activity of the catalyst to 80 % of its original level even after 6000 ppm-h of SO2 exposure, at which point the S/Cu exposure is equivalent to that of an SCR catalyst in a heavy-duty diesel after treatment system. This demonstrates that the major part of the deactivation can be reversed by active regeneration. The irreversible part of the deactivation can be dealt with by proper dimensioning of the catalyst. The S/Cu ratios of the SO2 exposed and regenerated catalyst samples exhibit a fast initial increase analogous to that of the deactivation, showing the deactivating effect of SO2 on Cu-CHA catalysts. Furthermore, the S/Cu ratios are never significantly above 1, which indicates that the S compounds are associated with the Cu ions. The S/Cu ratios after regeneration are restricted to 0.2 regardless of the exposure temperature, which is consistent with a situation where the irreversible Cu,S species only are able to form at certain Cu sites. The S uptake of the SO2 exposed catalysts depends on the exposure temperature, which is seen by the different S/Cu levels for each exposure temperature. The highest S/Cu ratios occur at 300 °C, which means that the S uptake is actually highest at typical SCR operating temperatures.

4. Conclusions
The deactivation of Cu-CHA catalysts occurs fast, but the activity can be restored to 80 % of its original level by heating to 550 °C, even after an SO2 exposure equivalent to the lifetime of an SCR catalyst. The S uptake also increases fast initially, reaching saturation levels between 0.5-1, dependent on the exposure temperature. Furthermore, the deactivation of Cu-CHA catalysts by SO2 appears to be somewhat Cu site dependent since a 100 % deactivation is never reached, and since S/Cu ratios of irreversible Cu,S species are restricted to 0.2.

References
Hydrodeoxygenation of Levulinic Acid Dimers on a 3 % Ru/ZrO$_2$ Catalyst

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1. Introduction

In biorefining, the production of hydrocarbons for transportation fuels requires the chain extension of platform molecules such as levulinic acid (LA), a C$_6$ ketoacid. In the most studied strategy for LA, chain growth is attained after a series of hydrodeoxygenation (HDO) steps [1]. However, in a scarcely studied strategy, chain extension is attained by aldol condensation of LA into C$_{10}$ dimers [2, 3]. These dimers contain carboxyl, carbonyl, and lactone groups, so they are unsuitable for fuel applications. Therefore, HDO is necessary in order to remove these oxygen functionalities. The HDO of LA dimers has been reported in a patent [4] without elaboration on the conversion attained or on the nature or amounts of the products. This work addresses the knowledge gap on HDO of LA dimers, by reporting the results obtained with Ru, a well-known hydrogenation catalyst.

2. Experimental

Levulinic acid dimers were produced in a trickle bed reactor with a strong cation exchange resin catalyst containing 0.7 wt. % Pd. The dimerization was performed at 120 °C, 2 MPa, 0.5 h$^{-1}$ (WHSV) and with 3 L/h H$_2$ flow. Afterwards, HDO of the dimers proceeded in a 50 mL batch reactor in presence of a 3 wt % Ru/ZrO$_2$ catalyst, at 5 MPa and $\tau = 0.2 h$ g$_{metal}$ g$_{feed}^{-1}$. HDO was tested at 250, 275, and 300 °C. The volatile HDO products were identified by GCMS and the gases were analyzed in a refinery gas GC. The conversion of the dimers was approximated by LC-QTOF-MS. Finally, the presence of heavy products was assessed by GPC.

3. Results and discussion

The HDO experiments provided a wide array of products, which can be classified by their nature into cyclic hydrocarbons, cyclic ketones, lactones, and carboxylic acids (C$_2$-C$_7$). The yields of representative compounds obtained at different temperatures are reported in Table 1. The main gaseous product was CO$_2$. Methane formed to a lesser extent, its yield being inversely proportional to reaction temperature. In a non-catalyzed experiment, it was found that auto-thermal reactions start at 250 °C, producing high amounts of CO$_2$. On the other hand, heavy oligomers formed both in catalyzed and auto-thermal reactions. The mass range of the fresh dimers was 181-233 g mol$^{-1}$, while the masses of the oligomers formed in the experiments are reported in Table 1. Higher conversions of dimers were achieved by increasing the reaction temperature.

4. Conclusions

The dimerization of levulinic acid and subsequent HDO of its dimers is a potential alternative upgrading strategy to hydrocarbon-rich biofuels. The ruthenium catalyst was effective at removing oxygen moieties, but it also spent high amounts of hydrogen converting carbon oxides to methane. It is advisable to perform HDO at 250 °C in order to avoid oligomerization and in order to maximize the production of simple oxygenates, which can be valorized further to linear hydrocarbons. Additionally, the relatively low amount of cycloalkanes obtained at this temperature might prove acceptable in fuel blends.

References

Catalytic effects of nickel in activated sugar based carbon foams

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1. Introduction
Activated carbons (AC) are used for purification applications in industrial and municipal processes including wastewater treatment, gas cleaning processes and metal removal from waste streams [1-3]. The consumption of AC is continuously rising in the worldwide perspective. Traditionally ACs have been prepared from a number of carbon-rich biomasses like coconut shells and sawdust or fossil-based coals [2, 4, 5].

Sugar foams can be prepared from different sources such as disaccharides, starch and carboxylic acids (citric acid or oxalic acid) by direct polymerization caused by metal catalyst. In this study, the aim is to investigate the effects of different catalyst concentration on the formation of carbon foaming and the relative properties such as specific surface area and pore size distribution.

2. Experimental
In summary, known amounts of sucrose were dissolved in small volumes of distilled water. Different amounts of the metallic Ni catalyst was added in each 250 ml beaker using Ni(NO3)2 * 6 H2O as a precursor for the metal. The solutions were mixed at room temperature for 1 hour in order to obtain a homogeneous mixture. All samples were then placed in an oven at 120 °C for 48 hours using natural convection. The carbon foams were carbonized and steam-activated in a one-step process in a stainless-steel fixed-bed reactor placed in a tubular oven. The temperature was elevated from room temperature to 800 °C using a 2 hours’ temperature ramp corresponding to a temperature change of 7 °C/minute and finally kept for one hour at 800 °C. During this final step, the carbon foams were steam activated by feeding liquid water into the reactor at a velocity of 30 cm3/hour.

3. Results and discussion
According to the results, the rise of the foams is highly dependent on the mass of the catalyst added. As presented in Figure 1, there is a strong dependency between the catalyst added and the foaming properties of the samples. According to the data presented in Table 1, an increased amount of catalyst leads to the lower specific surface areas, except sample PS4.0 800AW. Higher initial concentrations of nickel in the samples will produce more micropores in the final carbons. On the other hand, lower macroporosity was obtained when increasing the concentrations of nickel catalyst in the sample.

4. Conclusions
According to the results obtained, highly porous carbons can be prepared by catalytic conversion of sugars followed by thermal carbonization and steam activation. In order to achieve higher yields the catalytic metal must be removed by acid wash before the carbonization step. The activated carbons produced from carbon foams have, with a few exceptions, a high degree of mesopores in all samples produced and mesoporosity close to 50%. Foam rising is highly dependent on catalyst amount added to the samples.

Table 1. Specific surface area (SSA) pore volume (PV) and pore size distribution according to BJH-model.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m²/g)</th>
<th>PV (cm³/g)</th>
<th>Micro- (%)</th>
<th>Meso (%)</th>
<th>Macro (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS0.1 800AW</td>
<td>580</td>
<td>0.38</td>
<td>11.1</td>
<td>64.9</td>
<td>24.0</td>
</tr>
<tr>
<td>PS1.0 800AW</td>
<td>467</td>
<td>0.26</td>
<td>16.0</td>
<td>58.0</td>
<td>26.0</td>
</tr>
<tr>
<td>PS2.0 800AW</td>
<td>470</td>
<td>0.25</td>
<td>28.5</td>
<td>59.6</td>
<td>11.9</td>
</tr>
<tr>
<td>PS4.0 800AW</td>
<td>735</td>
<td>0.35</td>
<td>45.0</td>
<td>52.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Aknowledgements
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References
Bimetallic Pt(Rh) catalysts for intermediate temperature ammonia oxidation – combining traditional catalysis with surface science

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1. Introduction
Motivated to develop next-generation selective-catalytic-reduction (SCR) catalysts for NOx abatement of exhaust from combustion engines, we look into the process where we add NH3 in excess. Unconsumed NH3 is subsequently oxidized to nitrogen by a second catalyst downstream; an NH3 slip catalyst operating at intermediate temperatures (< 450 °C). We aim at developing such a catalyst based on a bimetallic Pt(Rh) alloy, as they perform well in the Ostwald process. In this contribution, we will present our recent results on the synthesis of well-defined supported Pt(Rh) nanoparticles and Pt(Rh)/Pt(111) surfaces together with findings from fixed-bed reactor experiments, NAP-XPS studies, and ReactorSTM investigations. Our aim is to understand the optimal Pt(Rh) alloy composition and to explain the underlying reasons for the superior performance of the alloyed catalysts.

2. Experimental
Pt(Rh) NPs are synthesized by the polyl route, deposited onto Al2O3, and transformed to metal-on-support catalysts, following our previously reported approach [1], and tested for intermediate temperature (200–450 °C) NH3-oxidation (450 ppm NH3, 5 % O2 in inert). Model surfaces of Pt(Rh)/Pt(111) are prepared by traditional UHV preparation techniques, and investigated at UHV, and in O2- and NH3-containing atmosphere by means of NAP-XPS and ReactorSTM.

3. Results and discussion
Fixed-bed catalytic testing of Pt1−xRhx/Al2O3 documents that the Rh-enriched compositions possess a superior performance with respect to TOF and S/N2 [2]. Based on this finding we developed recipes giving stable nanostructured Pt(Rh)/Pt(111) surfaces suited for operando methods [3] to disclose the underlying reasons for a superior performance of the Rh-enriched catalysts. Prolonged thermal stability of the as-prepared surfaces in UHV is documented (Figures 1a, b), which is a prerequisite for NAP-XPS and ReactorSTM studies. NAP-XPS indeed reveals that Rh-enriched surfaces become oxidized (Rh2O3) whereas Pt(111) only loosely binds oxygen (Figures 1c, d). Furthermore, our results show that Rh-enriched surfaces produce atomic nitrogen more than Pt(111). With respect to surface morphology, ReactorSTM clearly documents morphological differences between reactive conditions relative to UHV, including between Rh promoted Pt(111) and un-promoted Pt(111).

4. Conclusions
Methodologically we report on the importance of combing traditional catalytic testing experiments with surface science for catalyst optimization. Furthermore, our NAP-XPS and ReactorSTM investigations give clear indication on reasons why the two systems perform differently for intermediate-temperature NH3 oxidation.

References
Upgrading biomass pyrolysis vapors over hierarchical Co/HZSM5: Activity and coking characteristics

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1. Introduction
Hierarchical zeolites have been identified as an important class of catalytic materials with improved catalytic properties. In this study, preparation of catalysts was carried out by post-synthetic methods i.e. desilication for controlled mesoporosity development [1] - and incipient wetness impregnation-for metal deposition. The development of intra-particle mesoporosity due to the desilication decreases the diffusion path length of the molecules, minimizing the secondary reactions that lead to coke formation [2, 3]. The present work evaluates the catalytic activity and coke formation tendency of Co modified desilicated HZSM5 (Co/Ds-HZSM5) during upgrading of biomass pyrolysis vapors, where coke formation is one of the showstoppers for industrial implementation.

2. Experimental
Commercial ZSM5 zeolite (TZP-302), in ammonium form, was calcined with air in order to obtain the HZSM5 and desilicated. Co modified catalysts were prepared by dry impregnation. Catalytic activity was evaluated using a bench-scale fixed bed reactor, equipped with a specially designed piston system to introduce the biomass feedstock into the reactor (Figure 1).

3. Results and discussion
All the catalysts exhibit the characteristic MFI diffraction pattern, while the relative to parent HZSM5 crystallinity of the desilicated counter parts was greater than 85%. The desilication resulted in increase of the pores in the range of 5-20 nm and decrease in Brønsted acidity, while Co incorporation increased the Lewis acidity considerably. The deoxygenation activity of the catalysts tested decreases with the following order: Ds-Co/HZSM5>Ds-HZSM5>Co-HZSM5>HZSM5 achieving 22.58%, 13.13%, 12.11%, and 10.83% reduction in O content compared to the thermal run respectively. Carbon deposition on the catalysts after pyrolysis test shows that the coking tendency is reduced for the desilicated catalysts due to less diffusion limitations within or from the porous network. The coking tendency of the investigated catalysts increases with the following order: Co/Ds-HZSM5<Ds-HZSM5<Co/HZSM5<HZSM5.

4. Conclusions
Altered Brønsted and Lewis acidities as well as pore size are responsible for differences in catalytic activity as well as coke deposition on the zeolites. Coke deposition is strongly affected by the pore size while the deoxygenation activity is increased due to the increased Lewis acidity of the resultant catalysts. Concluding, desilication and cobalt modification seems promising for developing more efficient catalysts biomass for pyrolysis vapors upgrading.

References
Sulfuric Acid Catalysts studied in situ by Transmission Electron Microscopy and Raman Spectroscopy

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1. Introduction

Commercial sulfuric acid catalysts are based on V₂O₅ dissolved in alkali-metal pyrosulfates on an inactive porous silica support [1]. In the active state, the vanadia-containing pyrosulfates transform into a liquid state which is well-known to exhibit a dynamic behavior and which sensitively depends on the local reaction environment. In situ studies at relevant temperatures, pressure and gas composition are therefore necessary to obtain relevant information about the structure, composition, and distribution of the catalytically active species. However, such studies have been hampered by the corrosive nature of the reaction environment.

2. Experimental

We employed a custom-designed transmission electron microscope [2] and Raman spectroscopy setup [3] enabling sulfuric acid catalysts to be studied in situ and operando under exposure to SO₂ oxidation reaction conditions. The experiments focused on model catalysts containing V₂O₅ and sulfates of either K or K+Cs on 100 nm SiO₂ spheres. Specifically, the in situ transmission electron microscopy (TEM) monitored the dynamic evolution of the catalyst at nanometer resolution under exposure to SO₂ and O₂. Complementary information about chemical transformations in the catalyst and their influence on the SO₂ oxidation catalysis was obtained by operando Raman spectroscopy.

3. Results and discussion

The Cs-containing and Cs-free catalysts exhibit similar dynamic behavior. At 450°C, the vanadia phase transforms into extended and faceted structures in convex regions of the silica, indicating precipitation of crystalline materials, cf. Fig. 1. In contrast, the molten vanadia phase seems to accumulate in concave regions by filling the interstitial space between neighboring silica particles, which eventually lower the surface energy. The observations reveal that a molten phase emerges in the Cs-containing catalyst at lower temperatures than in the Cs-free. Activity measurements show an abrupt slope change at a well-defined break temperature in the Arrhenius plot, which is attributed to the onset of precipitation of inactive VIV species. The break temperature is around 30 K lower for the Cs-containing samples and it corresponds well to the temperature at which precipitated VIV compounds are detected in the Raman spectrum.

4. Conclusions

The correlation of TEM and Raman data reveals that molten phases contain the dimeric (VIVO)₂O(SO₂)₄⁺ which is believed to be the catalytic important species. The molten phase dynamically disperses on the support with a strong dependency on the support morphology and at lower temperatures, the melt coexists with crystalline phases containing VIV species. The crystalline materials separate out during the activation onto convex support surfaces. The observations show a higher abundance of linked VV complexes in the Cs-containing samples, which we believe hinders the formation of VIV compounds and therefore the depletion of the melt from active VV species at low temperature.

References

Germanium-based polyoxometalates: preparation and application in adsorption-decomposition of NOx

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Nitrogen oxides (NOx) are considered as the primary air pollutants, which could be majorly attributed to the combustion exhaust of fossil fuels from both stationary factory chimneys and mobile vehicles. They contribute to a series of severe environmental issues such as acid rain, photochemical smog, ozone hole, and even exert detrimental effects on human health. In the last decades extensive efforts have been devoted to control the NOx emission. In this paper, a series of germanium-based Keggin-type polyoxometalates (POMs), including H₄GeW₁₄O₄₀ (abbr to HGeW), H₅GeW₁₁VO₄₀ (HGeWV), H₅GeMo₁₁VO₄₀ (HGeMoV) and H₅GeW₉Mo₂VO₄₀ (HGeWMoV), were first synthesized and utilized as catalysts for removal of NOx in lean-burning exhaust. The adsorption experiments revealed that HGeW had the highest NOx adsorption capacity up to 16.2 mg NOx per gram catalyst. Two infrared characteristic bands appeared at 2210 and 1851 cm⁻¹ after NOx adsorption, while the latter firstly discovered over NOx-absorbed POMs could be assigned to nitrosyl radical (NO·). The regeneration of HGeW could be realized via lowering the temperature in moist atmosphere to desorb NOx. Temperature-programmed desorption combined with mass spectroscopy (TPD-MS) was conducted to investigate the decomposition behavior of NOx over HGeW and tungstophosphoric acid (HPW). O₂ was firstly detected among the decomposition products, besides N₂ and N₂O. According to nitrogen element mass balance calculation, NOx removal rate of 81.5% and N₂ selectivity of 68.3% could be achieved for HGeW, while the NOx conversion rate and N₂ selectivity for HPW reached 54.1% and 53.4%, respectively. As a whole, HGeW has a significant potential for NOx removal under mild conditions.

References
Performance of mesoporous ZSM-5 for the upgrading of straw derived pyrolysis vapors

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1. Introduction

Fast pyrolysis of biomass produces a high yield of bio-oil through well-established technologies at optimized temperature, pressure, and residence time of the liberated pyrolysis vapors [1], [2]. In order to allow processing in oil refineries, further conversion that reduces the oil’s oxygen content and acid number deserve prioritized attention [3]. Deoxygenation can be obtained by catalytic upgrading over solid acid catalysts. A close coupled process operating at temperature and pressure conditions close to those for optimum liquid yields in pyrolysis units offers potential economic advantages for zeolite deoxygenation over high pressure hydrotreating [4]. To date, the medium pore size ZSM-5 zeolite provides a high aromatic yield and the least amount of coke [5] in upgrading of pyrolysis vapors. The coke caused by reactive pyrolysis vapors may form an envelope covering the zeolite crystals and block the pore mouth entries. The rapid decay in site accessibility requires frequent regeneration to recover activity. In addition, irreversible dealumination can be caused by steam from the pyrolysis process, the dehydration reactions during upgrading and the steam produced during oxidative regeneration.

We address the reversible deactivation due to coke by introducing an auxiliary mesopores network to improve the accessibility and prolong the zeolite’s active time on stream. In order to minimize the irreversible deactivation, the zeolites acid site strength and density have to be carefully balanced with additional metal promoters or modification by phosphorous.

2. Experimental

The screening of the modified ZSM-5 zeolites was performed with 20 -150g of catalyst in a fixed bed reactor downstream an ablative type pyrolysis unit. Crushed wheat straw pellets (Denmark) were used as feedstock at a feeding rate of ~2g/min. By varying the runtime and amount of catalyst, a wide range of biomass feed to catalyst (B:C) ratios is covered and real upgraded product is collected at an optimized condensation train, followed by detailed analysis of the liquid in terms of moisture, elemental analysis, size exclusion chromatography (SEC) and quantification of ~200 components by GC-MS/FID. The micro and mesoporous versions of ZSM-5 tested in this investigation cover the molar Si/Al range of 12.5 to 29.5. Catalyst characterization was performed with ICP, NH3-TPD, N2 and Ar-physisorption, TEM and XRD.

3. Results and discussion

Mass and energy-balances in the range 90-100% were obtained. At higher amounts of biomass converted, the obtained oil is the cumulative result of fully upgraded products when the catalyst was fresh and products from periods with partial breakthrough of primary pyrolysis vapors. In order to unravel the change in oil-quality with increased B:C ratio, a series of successive conversion steps was performed, as illustrated in Fig. 1a) for ZSM-5 with Si/Al=29.5. A clear reduction in the oxygen content of the oil fractions is observed at low B:C ratio over the steamed ZSM-5 with Si/Al=29.5 in comparison to oil obtained from passing the vapors over a silicon carbide bed at the same temperature (500°C), see e.g. Fig. 1b for CBV30, B:C = 0.6. After the conversion up to B:C=1.1, the additional conversion to reach B:C=2.5 reduces the selectivity for monoaromatics, especially the BTX fraction. When comparing the molar H/C and O/C ratio of the oils obtained from micro and mesoporous ZSM-5 at an operating temperature of 500°C (Fig. 1b), the benefit of the auxiliary mesopore network becomes apparent: while the microporous counterpart rapidly loses its deoxygenation ability, the mesoporous ZSM-5 maintains a similar degree of deoxygenation for almost four times higher B:C ratio.

Figure 1: (a) Change of deoxygenated liquid products with increasing catalyst deactivation by coke, here shown for steamed ZSM-5 (Si/Al=29.5); (b) Performance of micro and mesoporous ZSM-5 at operating temperature of 500°C based on molar H/C and O/C ratio

References

Coking of zeolite ZSM-5 during the conversion of methanol to hydrocarbons monitored by X-ray diffraction tomography

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1. Introduction
The microporous zeolite catalyst H-ZSM-5 is employed commercially for the conversion of methanol to propene (MTP) and gasoline (MTG). Catalyst deactivation by coking is a major challenge for these processes, leading to frequent catalyst replacement, the need for an extra reactor for regeneration, or fluidized bed reactors.

2. Experimental
We have employed X-ray diffraction tomography to monitor the deactivation of shaped ZSM-5 catalyst extrudates in the conversion of methanol to gasoline. The experiments were carried out at the ID15A beamline at the European Synchrotron Radiation Facility.

3. Results and discussion
Using a variety of ex situ methods, we have been able to demonstrate that the unit cell of the crystalline catalyst changes upon deactivation. The difference between the lengths of the a- and b-axes of the unit cell serve as a descriptor for deactivation, and we were able to establish a correlation between this descriptor and classical deactivation parameters, such as the total amount of coke, the remaining acidity, and the remaining surface area [1,2]. We have found that this descriptor lends itself well to operando experimentation, and Figure 1 below shows how it is possible to determine the radial deactivation gradients within a single extrudate by combing this descriptor with advanced X-ray imaging.

4. Conclusions
Using X-ray diffraction based tomography, it has been possible to monitor gradients in the coke deposition within a single zeolite catalyst during the conversion of methanol to hydrocarbons in an operando set-up.

Fig. 1. a) Photos of fresh (white) and deactivated (black) H-ZSM-5 extrudates. b) Slice showing the total integrated XRD intensity for a fresh (top) and deactivated extrudate. c) Line scans (following the diameter of the extrudate) showing the a minus b descriptor. d) Line scans showing the coke occupancies based on residual electron density in the channels. From b) – d), it is clear that there is a strong radial gradient in the deactivation. Treaction = 440 °C, WHSV = 12 gMeOH gcat-1 h-1.

References
Volatilisation and Resulting Deposition of Platinum Oxides from Model DOC Catalysts

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1. Introduction

One of the concerns in real exhaust aftertreatment systems is the deactivation of SCR components by noble metal poisoning [1-3]. Noble metal-containing DOCs and DPFs are often placed upstream of an SCR catalyst. Small amounts of noble metals can thus volatilise and deposit on the downstream SCR component. Since noble metals are highly active for ammonia oxidation, even these very small amounts severely compromise the function of the SCR catalyst. Ammonia oxidation by the noble metals consumes ammonia needed for the SCR reaction, thus reducing the SCR efficiency. While there exist some studies on the effect of noble metal poisoning on SCR efficiency [4, 5], there are to our knowledge no detailed studies on the way noble metals volatilise from a DOC.

2. Experimental

In this study, we have reproduced the DOC-upstream-of-SCR configuration in the laboratory, with model Pt/Al₂O₃, Pd-Pt/Al₂O₃ and Pd/Al₂O₃ catalysts upstream of an alumina-coated core, as in Fig 1. Amounts of volatilised noble metal were determined by ICP-SFMS analysis of the “capturing monoliths”. Presence of noble metal on these monoliths was further investigated by testing their NH₃ and CO oxidation ability. No other characterisation of the volatilised noble metals was possible, because of the very small amounts (<35 nmol). “Parent monoliths” were analysed for effects of sintering by determining relative particle size via TEM and XRD. Volatilisation experiments were performed in presence and absence of O₂, at different temperatures and durations.

3. Results and discussion

We found that only insignificant amounts of noble metal volatilised in an inert atmosphere, and that no palladium was detectable, thus confirming that poisoning occurs via volatile Pt oxides. Fig 2 shows that volatilisation from model DOCs increases with temperature, and the trend is exponential. We observe no difference in volatilisation upon addition of Pd, even though Pd stabilises against sintering. The deposited Pt is initially prone to extensive sintering upon characterisation by oxidation tests, with oxidation ability increasing after each cycle due to particle size increase [6].

4. Conclusions

We tested and confirmed the hypothesis that poisoning occurs mainly in form of volatile platinum oxides, even downstream of multi-component DOCs. In addition, we verified that this process also occurred over a commercial DOC. Further, we have investigated the dependence of volatilization on temperature, and, as predicted, found it to be exponential. Adding Pd to the DOC formulation had no significant effect on volatilised amounts, but sintering was thought in certain cases to be linked with decreased volatilisation. Deposited platinum was highly active for NH₃ oxidation, but the activity was not stable, and our results show that Pt is likely finely dispersed to begin with, and then particle size increases with exposure to reaction conditions, which further increases NH₃ oxidation ability.

References

Kinetic insight into the production of methyl lactate from sugars with Sn-Beta catalyst

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1. Introduction
A current challenge for catalysis research is the identification of new technologies for the development of a society independent of fossil feedstock. In this context, transformations of sugars are a central topic since they can lead to the production of several bio-based fuels and chemicals using heterogeneous catalysts. Among the different products, methyl lactate can be formed in high yields from hexoses using Lewis acidic materials, such as Sn-Beta zeolites, and used as green solvent or monomer for PLA (Polylactic acid) biodegradable plastics. The process is carried out at 160 ºC in methanol due to the increased stability of the catalyst in methanol as compared to water. However, under these conditions many forms of the substrate as well as intermediates are formed in the mixtures, making understanding of the reaction pathways difficult.

2. Experimental
Advanced 2D-NMR techniques have been used for identifying all the reaction products, distinguishing the forms of sugars and their glycosides and for an absolute quantification. In the spectral region of the primary alcohol in the ¹H-¹³C HSQC it is possible to resolve the α/β and pyrano/furano forms of the carbohydrates and their methyl glycosides present in the reaction mixtures. In particular, methyl fructosides were shown to play a central role in the conversion of sugars using zeolites [1] and in this way, it was possible to study their reactivity and to follow the influx of the various forms into the methyl lactate process.

3. Results and discussion
A kinetic model for the formation of methyl lactate from hexoses by Sn-Beta zeolites was established by performing a series of time-resolved experiments. The process follows two kinetic regimes: in a first fast regime, some starting substrate is converted into methyl lactate, but the majority is converted to methyl fructoside as a masked form of C6 sugar. The majority of methyl lactate is formed during the second slow regime by the conversion of methyl fructoside (Figure 1). The proposed model explains the drastic effect of water on the kinetic of methyl lactate formation, preventing the accumulation of methyl fructosides and accelerating their unmasking [2].

4. Conclusions
Kinetic and mechanistic insight into the process for the production of methyl lactate starting from simple carbohydrates is presented in this work, elucidating the role of methyl fructosides and water in the reaction mechanism.

Acknowledgement
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References
Pd-based Catalysts for the Semi-Hydrogenation of 2-Methyl-3-Butyne-2-ol (MBY)

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1. Introduction

Our work focuses on the design of catalysts for semi-hydrogenation of acetylene bonds, with emphasis on the phase purity and crystal structure of the catalytically active compounds. Here, we present the preparation and characterisation of Pd-M (M = Sn, In) nanocatalysts, which show improved activity and selectivity compared to pure Pd catalysts, towards the liquid phase semi-hydrogenation of 2-methyl-3-butyne-2-ol (MBY) to 2-methyl-3-buten-2-ol (MBE). Semi-hydrogenation refers specifically to the partial hydrogenation of a C≡C triple bond (alkyne) to a C=C double bond (alkene), and avoiding full hydrogenation to a C-C single bond (alkane). Semi-hydrogenation reactions constitute crucial steps in the synthesis of many fine chemicals including pharmaceuticals, and nutritional substances such as vitamins. [1]

2. Experimental

Stoichiometric amounts of palladium acetylacetonate and Sn/In acetate, each in 100 mL glycol, were combined into the reaction vessel with either ZnO or TiO$_2$ support (2 wt% Pd loading) and PVP as capping agent (10 monomer mol% of total Pd and Sn). The mixture was stirred under nitrogen gas at room temperature for at least 30 min to displace air before heating at reflux (176 °C) for 1 h, then cooled and centrifuged at 3500 rpm. The brown/grey solid obtained was washed alternately with acetone and deionised water (3 × 30 mL each) and dried into the reaction vessel with either ZnO or TiO$_2$ support (2 wt% Pd loading) and PVP as capping agent (10 monomer mol% of total Pd and Sn). The mixture was stirred under nitrogen gas at room temperature for at least 30 min to displace air before heating at reflux (176 °C) for 1 h, then cooled and centrifuged at 3500 rpm. The brown/grey solid obtained was washed alternately with acetone and deionised water (3 × 30 mL each) and dried at 60 °C in air for 1 h to yield a grey powder. The catalysts were stored in a vacuum desiccator until use. Unsupported Pd$_3$M compounds were prepared using the same method with exclusion of the support and PVP. The catalysts were tested in a batch, liquid phase semi-hydrogenation of MBY to MBE.

3. Results and discussion

Pd-Sn and Pd-In nanoalloys were prepared via a polyol-based method, using ethylene glycol (boiling point = 197 °C) and tetraethylene glycol (boiling point = 314 °C) to achieve different synthesis temperatures. In this way, we were able not only to prepare Pd-Sn and Pd-In catalytically active nanomaterials as pure compounds, but also to stabilise a new cubic polymorph with variable Pd:In ratio (referred to as “Pd:In”, Figure 1).

Pd$_3$Sn/TiO$_2$ and Pd$_3$Sn/ZnO showed selectivity to alkene higher than that of the Pd-only catalysts, specifically, the 96.4% compared to 97.4% on TiO$_2$ support, and 96.2% compared to 97.6% on ZnO support, at 90% MBY conversion. [2] Furthermore, the catalyst “Pd$_3$In”/TiO$_2$, prepared in ethylene glycol, shows a notable increase in the selectivity towards MBE (more than 1% at as low as 90% conversion) (Table 1). [3]

4. Conclusions

We prepared Pd$_3$Sn/ZnO, Pd$_3$Sn/TiO$_2$ with improved catalytic performance compared to Pd-only catalysts and we stabilized a cubic (CCP) form of the nanoalloy “Pd$_3$In” as well as varied the In content via the use of different temperatures in the synthetic process. “Pd$_3$In”/TiO$_2$ also show improved performance compared to Pd-only catalysts.

References

Table 1. Activities per mole of Pd and selectivities of catalysts in a batch, liquid-phase semi-hydrogenation of MBY at 35 °C. “Pd$_3$In”/TiO$_2$ was prepared in ethylene glycol. Selectivities are measured at 90% MBY conversion.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activity (s$^{-1}$)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_3$Sn/ZnO</td>
<td>0.06</td>
<td>97.6</td>
</tr>
<tr>
<td>Pd$_3$Sn/TiO$_2$</td>
<td>0.22</td>
<td>97.4</td>
</tr>
<tr>
<td>“Pd$_3$In”/TiO$_2$</td>
<td>0.30</td>
<td>97.7</td>
</tr>
<tr>
<td>Pd/TiO$_2$</td>
<td>0.37</td>
<td>96.4</td>
</tr>
</tbody>
</table>

Figure 1. PXRD pattern and Rietveld refinement of one of the “Pd$_3$In” polymorphs, with cubic unit cell; Inset: Large area image of “Pd$_3$In” nanoparticles on TiO$_2$ support by HAADF-STEM imaging mode.
Catalytic behaviors of Cu single site and clusters over ceria surface

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1. Introduction
Identifying surface active species is a major motivation in catalysis research. Due to the complex nature of metal oxide surface, a range of distinct active species are always presented. They can be the true active sites, spectators or sites that lead to side reactions. Here we successfully identify Cu$^{2+}$ single site and clusters over ceria surface for CO chemistry using operando EPR, EXAFS, XRD and ex situ Cs-TEM toolbox. On one hand, Cu$^{2+}$ single site is the most active species for CO oxidation, giving a TOF of 0.07 s$^{-1}$ at 373 K. On the other hand, Cu cluster is the only active species for water-gas-shift.

2. Experimental
CuO/CeO$_2$ composites at different Cu loading were prepared via flame spray methods. The catalytic activity for CO oxidation and water gas shift were measured in a conventional fixed bed reactor in a reactive gas mixture. The catalysts were initially activated in situ at 573 K in a sequence of synthetic air (20 vol.% O$_2$ / 80 vol.% N$_2$, Air Liquide) for 60 min, 20 vol.% H$_2$ in N$_2$ for 40 min, and again synthetic air for 60 min.

3. Results and discussion
The Cu/CeO$_2$ catalyst has high specific surface area, evenly distributed Cu sites and high thermal stability. When the loading of Cu is below 1wt%, only monomeric Cu site present on the CeO$_2$ surface. As showed in Figure 1a, the catalytic activity presents an upward trend with the increase of Cu content. The activation energies $E_a$ at the same Cu weight hour space velocity are uniformly around 66 kJ/mol. The catalytic activities at each loading are very similar to each other. This suggests the presence of only one type of active site. HAADF-STEM images of the catalysts show clear CeO$_2$ lattice fringes with small particle sizes (Figure 1c,d).

Figure 1. a) Conversion of CO as a function of temperature and Cu content (1% CO + 10% O$_2$). All the catalysts were tested with same WHSV of 150,000 mL h$^{-1}$ g$^{-1}$. b) Arrhenius plots of the Cu/CeO$_2$ catalyst. The kinetics results were obtained with same Cu WHSV (75,000,000 mL h$^{-1}$ g$^{-1}$ Cu). c, d) HAADF-STEM images of 0.80% CuO-CeO$_2$.

EPR identifies the presence of Cu monomer (Figure 2a, 2b) and the peak intensity is in nearly linear relationship with Cu loading (Figure 2c, 2d). When the Cu loading exceeding 1wt%, the single site intensity starts to decrease, indicating the formation of dimers and CuO clusters. This also verified by XRD measurement. The activation energy starts to increase from 68 kJ/mol to 100 kJ/mol, indicating a change of reaction active site.

The Cu single site is not active for water gas shift reaction. The active of WGS starts at 5wt% Cu loading, suggesting that either CuO clusters or metallic Cu is the active species.

4. Conclusions
We have shown that Cu single site and CuO clusters are presented on the surface of ceria upon different Cu loadings. They are quantified by operando EPR, XRD and EXAFS. Cu$^{2+}$ single site dominates at the loading below 1wt% and is the most active species for CO oxidation. CuO clusters are formed above 5wt% and will transform in to Cu nanoparticles, which are the only active site for water-gas-shift.

References
Aqueous phase reforming (APR) of bio-oil model compounds over different Ni-based catalysts

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1. Introduction

Aqueous-phase reforming (APR) is a quite novel technology for the production of hydrogen and light hydrocarbons (as products of interest) from aqueous-organic mixtures in a single stage [1,2]. Its simplicity, versatility and relative low cost makes the APR process an interesting way of valorizing biorefinery streams (i.e. Fischer-Tropsch and pyrolysis waters) due to its proper composition [1,3,4]. This way, one of the greatest challenges of this process is the transition from the conversion of oxygenated model compounds (mainly alcohols) to the valorization of real biorefinery wastewater fractions. Therefore, the APR of four representative model compounds of bio-oil aqueous fraction (ethanol, acetic acid, hydroxyacetone and catechol), as well as the possible synergistic effects of the mixture of all of them (simulating a pyrolysis wastewater) has been studied with three different Ni-based catalysts (NiAl2O4, Ni/γCeAl2O3, Ni/La2O3–αAl2O3).

2. Experimental

The experimental runs were conducted in a laboratory-scale system with continuous feeding of the organic solution. The operating conditions were: 230 °C; 3.2 MPa; 10 wt% of oxygenated compound diluted in water for ethanol, acetic acid and hydroxyacetone, 5 wt% for catechol and 2.5 wt% of each reactant for the mixture. Accordingly, the WHSV has shifted depending on the feed in the 2-8 h⁻¹ range. The solution was fed downward with a constant flow rate of 2 mL/min. The catalysts NiAl2O4, Ni/γCeAl2O3, Ni/La2O3–αAl2O3 were prepared by coprecipitation (first one) and incipient wetness impregnation with different Ni contents, that is, 33, 15 and 10 wt%, respectively. The fresh and used samples were characterized by the following techniques: N2 adsorption-desorption isotherms, X-ray diffraction, atomic absorption spectroscopy and X-ray florescence.

3. Results and discussion

The difference in reactivity of the studied model compounds is large as shown in Figure 1 for the conversion (columns) and H2 yield (black lines). In the selected conditions, hydroxyacetone is the most converted molecule with a conversion in the range of 18-28 %, although the yield of H2 is very low, with CO2 (not shown) as the main product, formed from C-C-bond breaking. The highest yield of H2 is obtained with ethanol with values close to 10% for all the catalysts, despite the low stability of Al2O3 phase with this molecule since in all the runs the boehmite phase has been formed. The reactivity of acetic acid is low in comparison with the other model compounds and its acid character has led to a significant decrease in Ni content by leaching (obtained by AAS analysis). The results with the mixture do not show a remarkable synergy.

4. Conclusions

The reforming by means of APR process of different bio-oil model compounds has been assessed. The Ni/γCeAl2O3 catalyst shows the highest activity in the conversion of all the solutions with the exception of catechol, which conversion seems to be more promoted with the presence of La in the support (with Ni/La2O3–αAl2O3 catalyst). The highest Ni content of the NiAl2O4 catalyst does not show an improvement in terms of activity and H2 selectivity with respect to the other catalysts. These results, especially those corresponding to the mixture, can be taken as an approach to the real valorization of the aqueous phase of bio-oil.

References

Influence of active phase loading in hydrodeoxygenation (HDO) of ethylene glycol over promoted MoS$_2$/MgAl$_2$O$_4$ catalysts

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1. Introduction
Catalytic fast hydropyrolysis can be used to convert solid lignocellulosic biomass into liquid fuels by combined fast pyrolysis and catalytic hydrodeoxygenation (HDO) [1]. The advantage of this technique is that the pyrolysis vapors can be deoxygenated and stabilized against polymerization immediately when formed, since fast pyrolysis occurs in the presence of an HDO catalyst and hydrogen. Promoted MoS$_2$ catalysts are active and selective for HDO [2]. Since the cellulosic part of biomass contributes to polymerization and coking [3], a key focus of the catalyst and process development is to investigate HDO of cellulose and hemicellulose derived compounds. Ethylene glycol (EG) represents these compounds and was used as model compound in this work.

2. Experimental
Catalysts (Ni- and Co-promoted MoS$_2$/MgAl$_2$O$_4$) where prepared at different active phase loading by incipient wetness impregnation followed by in-situ sulfidation in a fixed bed reactor setup, which was also used for activity testing. In activity tests, 0.5-4.0 g catalyst was loaded into the reactor, and ethylene glycol was fed at $\approx 0.15$ mL/min giving a weight hourly space velocity (WHSV) of 2-19 gEG/(gcat·h). Activity tests were run for up to 172 h at 400 °C, a total pressure of 40 barg, 27 bar H$_2$, and a co-feed of H$_2$S typically around 550 ppm. Gaseous products were quantified with GC-TCD, while liquid products and unconverted EG were quantified with GC-MS/FID. Fresh and spent catalysts were analyzed with BET, TEM, ICP-OES, XRD, and Raman spectroscopy.

3. Results and discussion
The conversion of EG over the pure MgAl$_2$O$_4$ support (WHHSV = 9 h$^{-1}$) showed that it catalyzed coupling reactions such as alcohol condensation, dehydration, and acetalization. The conversion of EG over low (L, 0.8-0.9 wt% Mo) and moderate (M, 2.8-3.4 wt% Mo) loading catalysts showed that Ni- and Co-MoS$_2$ catalyzed both HDO (giving ethane and ethylene (C$_2$H$_6$ and C$_2$H$_4$)) and cracking (giving CO, CO$_2$, and CH$_4$ (C$_4$)). There was a higher selectivity towards HDO as seen from the C$_2$/C$_1$ yield ratio of 1.1-1.5, independent of catalyst loading (see Table 1). The moderate loading catalysts showed superior hydrogenation activity (ethane formed rather than ethylene), whereas the low loading catalysts formed a mixture of ethylene and ethane during activity tests (see Table 1). The EG conversion was $> 90\%$ for all catalysts at an EG WHSV of 2 h$^{-1}$, whereas the low loading catalysts formed a mixture of ethylene and ethane during activity tests (see Table 1). Catalyst deactivation was observed for the low loading catalysts (WHHSV = 2 h$^{-1}$), and by increasing the WHSV, deactivation could also be observed for the moderate loading catalysts (see Figure 1). Carbon deposition was the main reason for catalyst deactivation, determined by TEM, elemental analysis and Raman spectroscopy.

4. Conclusions
Ni-MoS$_2$ and Co-MoS$_2$ supported on MgAl$_2$O$_4$ is active and selective for HDO. The MoS$_2$ based active phase catalyzes HDO, but also cracking, with a C$_2$/C$_1$ yield ratio $>1$. The active phase loading and WHSV influences the hydrogenation activity and the level of deactivation.

References

<table>
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<tr>
<th>Catalyst</th>
<th>Loading</th>
<th>X [%]</th>
<th>Y$_{\text{ETA}}$ [%]</th>
<th>Y$_{\text{ETY}}$ [%]</th>
<th>Y$_{\text{C}<em>2}$/Y$</em>{\text{C}_1}$</th>
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</thead>
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<tr>
<td>(L) Ni-MoS$_2$</td>
<td>Mo:0.83 Ni:0.17</td>
<td>99</td>
<td>3.4</td>
<td>7.5</td>
<td>1.2</td>
</tr>
<tr>
<td>(L) Co-MoS$_2$</td>
<td>Mo:0.88 Co:0.16</td>
<td>96</td>
<td>2.5</td>
<td>8.2</td>
<td>1.3</td>
</tr>
<tr>
<td>(M) Ni-MoS$_2$</td>
<td>Mo:2.83 Ni:0.58</td>
<td>100</td>
<td>43</td>
<td>0</td>
<td>1.4</td>
</tr>
<tr>
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<td>100</td>
<td>44</td>
<td>0</td>
<td>1.4</td>
</tr>
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<td>MgAl$_2$O$_4$</td>
<td>-</td>
<td>25</td>
<td>0.2</td>
<td>0.9</td>
<td>1.6</td>
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</table>
Doping with cobalt as a potential method of boosting of catalytic activity of birnessite and cryptomelane in soot combustion

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1. Introduction

Pollution of the environment with solid particles (called usually as PM - Particulate Matter) emitted from mobile sources, and in particular with soot as their main component, has been an extremely challenging problem for large agglomerations, routes with intense road transit and poorly ventilated urban areas. It is generally accepted, that Diesel Particle Filters (DPFs) are the most efficient way to reduce emissions from car exhaust pipes. Their main disadvantage is the accumulation of particle matter on a filter material. That usually leads to filter clogging. The most convenient way of DPF regeneration is the use of a catalyst that enables the combustion of soot during routine engine operations. Currently used catalytic systems for soot combustion are based on noble and rare earth metals, which are relatively expensive and hard to access. For this reason, advanced studies have been launched to propose a reasonable alternative to the noble metal-based catalysts mentioned above. The catalytic systems based on transition metal oxides promoted with alkali metals belong to the most promising from the viewpoint of soot combustion. Birnessite (KMnO4) and cryptomelane (K MnO3) – the complex manganese-alkali metal oxides, exhibiting layered and tunnel structures, respectively, have been investigated in the framework of the current project. Our aim was to elucidate the effect of doping with cobalt on the structural and functional properties of both birnessite and cryptomelane, in terms of their stability and activity in the oxidation of soot. In particular cobalt speciation, stabilization and distribution have been studied.

2. Experimental

The investigated samples were synthesized by hydrothermal method (at 170 °C and 36 bar for 20 min) from KMnO4 and KNO2 as the substrates, at pH equal to 3 (cryptomelane) and 9 (birnessite). The modification of synthetic pathway included increasing the concentration of the reacting substrates. Doping with 5 and 12% of Co has been accomplished by adding a corresponding amount of Co(NO3)2 directly to the reaction mixture or by impregnation of synthesized samples. The reference cryptomelane and birnessite samples were synthesized by a classic sol-gel method, while the reference manganese and cobalt oxides were obtained from the corresponding nitrates by precipitation with (NH4)2CO3 solution and subsequent calcination at 430 or 950°C for 8 h.

3. Results and discussion

Structural analysis of the obtained samples by XRD and RS showed that the main phases present in the obtained preparations are cryptomelane and birnessite, respectively. Analysis of the elemental composition by XRF showed that cobalt was present in the investigated samples. XPS, ATR-IR and UV/Vis-DR spectra of the investigated samples showed a lack or presence of cobalt species on the surface, dependently on synthesis route. TGA analysis suggested that thermal stability of birnessite was not sensitive to cobalt doping, whereas that of cryptomelane was quite sensitive. Exemplary results of the catalytic activity in NO-assisted soot oxidation on investigated samples was showed in Figure 1. These results showed that stabilizing of cobalt on the catalyst surface was crucial for soot combustion.

4. Conclusions

It can be concluded that synthesis dependent location of cobalt is a key factor for designing an active and stable catalyst based on birnessite and cryptomelane.
Liquid State NMR Approaches to Catalyzed Reactions:
Ultrahigh Resolution and Molecular Probes

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1. Introduction
Catalysis research can draw from a plethora of high-resolution analytical methods developed in metabolic research during the last two decades, but many of these techniques seem underemployed. Advanced methods should permit the detailed study of catalyst function and dysfunction in catalytic pathways. These pathways can be derived e.g. from the nuclear magnetic resonance (NMR) spectroscopic analysis of complex reaction mixtures [1-3], isotopic isomers [4,5] and directly observed reaction progress on timescales of 1 second and above [6,7].

2. Experimental
Recent developments in the NMR spectroscopic study of catalyzed reactions will be exemplified on bio- and chemocatalytic conversions of carbohydrates. Ultrahigh resolution 2D spectra using high-field (800 MHz) NMR instrumentation and tracer methods are employed to this end. Unexpected intermediates can be detected and structurally identified without a priori knowledge in complex reaction mixtures, even for compounds of identical mass, such as isomeric carbohydrate forms or isotopic isomers. Particular emphasis is placed on obtaining quantitative NMR data [8], obtained on a timescale comparable to commonly used chromatography methods but avoiding empirical response factors. Identifying new chemicals in situ makes intensive purification and characterization steps obsolete.

3. Results and discussion
Novel types of information become accessible through the use of the NMR methodologies described herein. This information includes the detailed mechanistic study of elusive reaction pathways in carbohydrate conversion by stannosilicates [3]; the first kinetic models of widely used pathways in carbohydrate conversion [1]; mechanistic changes on the seconds timescale in biocatalysis by living cells; the discovery of previously elusive rare molecular forms, including transient complexes of acyclic carbohydrates with catalysts or the distinction of the promoting or inhibiting effects of additives at catalyst active sites [9]; the unambiguous distinction of cyclic and acyclic reaction pathways of carbohydrate valorization.

4. Conclusions
An increased molecular understanding of the mechanism and kinetics of heterogeneous and homogeneous catalytic transformations can be attained by transferring NMR spectroscopic concepts of metabolic research to biocatalytic and chemocatalytic reaction systems.

References
Acetone Reaction with Hydrogen over Mesoporous Magnesium Oxide-Supported Rhodium Nanoparticles

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1. Introduction
Methyl isobutyl ketone (MIBK) is very useful extracting agent of heavy metal and antibiotics in liquid-liquid extraction process, and solvent for paints, varnishes, and resins. MIBK is produced from acetone (DMK) self-condensation in a tradition, environmentally detrimental process, consisted of separate three steps of DMK addition, condensation, followed by selective hydrogenation. This process is not economic due to its low conversion of DMK, low yield, etc. Thus, one-step, liquid-phase process has become interested over multifunctional heterogeneous catalyst systems (MHCS) [1]. However, synthesis of MIBK in one-step, gas-phase is a challenge due to the requirement of high temperature. Therefore, we attempted to prepare MHCS comprised of rhodium nanoparticles (RhNPs) supported on mesoporous magnesia (meso-MgO) for the conversion of DMK into MIBK.

2. Experimental
meso-MgO support was prepared by precipitation of magnesium hydroxide [Mg(OH)2] in ethanol medium using cyclohexylamine, followed by calcination of Mg(OH)2 at 550°C for 3h. RhNPs were supported on meso-MgO by wet impregnation using an appropriate amount of rhodium(III) acetylacetonate, which was reduced under H2 at 250°C for achieving 1 wt/wt% of Rh loading. Catalyst was characterized by ICP, PXRD, XPS, SEM and TEM, nitrogen physisorption, and TPD. The catalyst was tested in a vertical, tubular glass, fixed-bed micro reactor for the gas-phase DMK self-condensation under various reaction temperatures (75-150°C) and different H2:DMK mole ratios. The products were analyzed off-line using a Varian CP-3800 GC.

3. Results and Discussion
The Rh metal content was confirmed by ICP. XRD showed the presence of MgO pattern and no peaks related to Rh metal were detected, implying the fine dispersion of RhNPs. TEM images showed RhNPs with size ≤5 nm, which were in agreement with the XRD results. As shown in the Fig., increasing the H2:DMK mole ratio, at fixed temperature, led to increase the DMK conversion and IPA selectivity and to reduce the selectivity towards MIBK. In addition, increasing the reaction temperature, at fixed H2:DMK mole ratio, resulted in a volcano-shaped curve with a maximum at 100°C for acetone conversion, increase of selectivity towards MIBK and decrease of selectivity towards isopropyl alcohol (IPA) with increasing reaction temperature.

4. Conclusions
We succeeded in preparing a multifunctional catalyst, composed of Rh NPs supported on meso-MgO, for the one-step, gas-phase acetone self-condensation. At fixed H2:DMK mole ratio, increasing the temperature favored the formation of MIBK while reducing it favored the formation of IPA.

References
Generation of trace ammonia free hydrogen from ammonia for power generation via Proton Exchange Membrane Fuel Cell

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1. Introduction
Ammonia is an important zero carbon hydrogen carrier with volumetric H2 density of 121 kg-H2/m3. The challenge, however, is to generate the H2 from ammonia at the point of use. This is specially the case if the hydrogen generated from ammonia is fed to a PEM fuel cell, which is the typical type for automobile and other kW scale power generation. In order to extract hydrogen from ammonia, a high temperature catalytic reaction step, known as reforming is performed. This reaction is equilibrium controlled, and even at very high temperature leaves some trace ammonia in the product besides the main product H2 and N2. Trace ammonia, even in the rage of 1 ppm is detrimental to PEM fuel cells so need to be removed. The state of the art is to use Pd based membrane [1] which is not only expensive but also possesses significant technological challenge and durability issues. One of the major technical issues is that to have a significant H2 flux through the Pd membrane, at least 10 bars of pressure at the inlet side is needed. This means a compression step after the cracking process. Furthermore, pinholes are very common in the Pd-based membrane and this results in ammonia leaking into the separated hydrogen. The loss of H2 because of the H2 coming out of the filter exhaust makes the process inefficient also. We have invented a selective catalytic oxidation (SAO) process for removing trace ammonia from the product of ammonia cracking using inexpensive metal oxides [2]. The reaction works at atmospheric pressure and at a temperature range between 200-300°C. This is to our knowledge, the first reported process of selectively oxidizing ammonia from a mixture containing up to three orders of magnitude hydrogen compared to ammonia. A 1 kW fuel cell stack was fed with the hydrogen generated from ammonia in the process. In this work, we are going to present our result of the catalyst screen process as well as the operation of an ammonia fueled power generator using the technology.

2. Experimental
Several oxides of elements from group V to VII in the periodic table were synthesized. These oxides include the oxides of Cr, V, Mn, W, and Re. The catalysts were then tested in a glass plug flow reactor by flowing gas mixtures of varying composition containing H2, N2 and ppm level ammonia (e.g. 1000 ppm of ammonia) and O2 adjusted to the ammonia concentration. The outlet gas composition was measured either by a mass spectrometer, FTIR or Drager tubes. For power generation experiment, a prototype was developed by RenCat (RenGen™ Converter) containing an ammonia cracking reactor and a selective ammonia oxidation reactor capable of generating 20 nL/min H2.

3. Results and discussion
Figure 1 shows the effect of trace ammonia oxidation catalyst. In the first step (denoted by R1), ammonia was cracked at 600°C in a reactor containing FeNi/Al2O3 catalysts. The outlet gas contains 550 ppm ammonia (measured by FTIR) which is close to the equilibrium ammonia concentration at the temperature. When the cracker outlet was introduced to a reactor (R2) containing the selective ammonia oxidation catalyst, the trace ammonia concentration came down to 0.15 ppm. Figure 2 shows an example of power generation by feeding the PEMFC stack with H2 generated by RenGen™ Converter.

4. Conclusions
Catalysts and catalytic process have been invented and implemented for trace ammonia free hydrogen generation from ammonia. The catalysts are shown to be extremely effective in removing trace ammonia from hydrogen. A prototype ammonia to hydrogen generator, RenGen™ Converter, has been built and tested for power generation with a 1 kW level PEM fuel cell stack. RenCat is currently performing product development and maturation based on the catalytic technology.

References
NMR Spectroscopic Isotope Tracking Reveals Cascade Steps in Carbohydrate Conversion by Tin-Beta

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1. Introduction

Due to their low cost and high abundance carbohydrates have great interest as alternative resources to petro-chemicals. Industrially relevant Sn-zeolites have been studied for the conversion of carbohydrates to lactate precursors for poly(lactic acid) production since 2009.[1] Subsequent developments have increased reaction selectivity and discovered new polymer building blocks.[2-5] Here, we enhance mechanistic understanding of the reaction process through NMR spectroscopy on the complex reaction mixtures, starting from isotopically labelled substrates, to enable atomic tracking as shown in Figure 1.[6]

2. Experimental

Reactions were conducted with a Biotage microwave reactor in a 0.5 mL glass reaction vial with 18 mg Sn-Beta (Si/Sn = 200, hydrothermally synthesized), 36 mg substrate, 0.5 mL methanol and 5 mg dimethylsulfoxide (internal standard). D-[1-13C]-Xylose, D-[5,5'-2H2]-arabinose and D- [UL-2H6]-ribose, Figure 2, were employed as reaction substrates. Quantitative proton decoupled 1D 13C NMR spectra were acquired on a 800 MHz Bruker Avance III NMR spectrometer with recycle delays of 60 s using a pulse sequence that employs inverse-gated decoupling to avoid the nuclear Overhauser enhancement of protonated sites. 2D 1H-13C NMR HSQC spectra were used to validate the assignment of the integrated 1D 13C NMR spectra.

3. Results and discussion

Tracking of the C1 position of the carbohydrate substrate (Substrate 1) showed incorporation into the C3 position of methyl lactate (84%), a result of retro-aldol cleavage of the ketose substrate form and subsequent cascade steps that avoid the release of symmetric dihydroxyacetone. For C5 alpha hydroxy esters, labelling was largely retained at the C1 position (81%) with a small transfer to the C2 and C5 positions, consistent with Sn-Beta catalyzing a 1,2-carbon shift and a 5,1-hydride shift. Reactions from D-[5,5'-2H2]-arabinose (substrate 2) also confirmed the 1,5-hydride shift by the presence of 2,5-2H2 alpha hydroxy ester products in yields up to 29%. Finally, D-[UL-2H6]-ribose (substrate 3) was employed to show that the beta-gamma unsaturated alpha hydroxyl ester (2,5-dihydroxy-3-pentenoate, DPM) was not formed via the same intermediate as the 3-deoxy esters, 3-deoxy-γ-xylonolactone (3DL), and methyl 3-deoxy-xylonate (3DE) contrary to the previously proposed reaction pathways for such esters.[2]

4. Conclusions

We employed isotope-labeled substrates to track isotope redistribution and solvent exchange in different products formed during chemocatalytic carbohydrate conversion by a Sn-Beta zeolite. These findings lead to key elucidations concerning the reaction pathway and catalytic activities: 1) methyl lactate is primarily formed from ketoses and 2) remains bound throughout the reaction cascade. Sn-Beta may catalyze 3) a 1,2-carbon shift and 4) a 5,1-hydride shift of carbohydrates. 5) DPM is formed by a different pathway than 3DL and 3DE.

References

Shell protected mesoporous zeolites for selective catalysis

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1. Introduction
Zeolites are used extensively in the chemical industry as catalysts or as a support for metal nanoparticles to provide both size- and shape selectivity and to stabilize the metals. The microporous zeolites, however, suffers from limited diffusion, which may result in lower yield and deactivation by coking. Mesoporous zeolites can be used to enhance the diffusion in zeolites which results in improved yield and reduced deactivation.[1-3]

In here, we present our progress to obtain mesoporous zeolites with metal encapsulated in the mesoporous structure. Additionally, the effect of having a microporous protective shell around the mesoporous zeolite is studied.

2. Experimental
Mesoporous zeolites were prepared by a steam assisted method using carbon as hard template to provide the mesopores in the zeolite crystal. Metals were introduced in the mesoporous zeolite crystal by incipient wetness impregnation. A microporous zeolite shell was synthesized also around the mesoporous zeolite crystal using a steam assisted synthesis method.

The materials were tested in hydrogenation reactions to evaluate the effect of a shell. Additionally, we have characterized the different materials using techniques such as X-ray powder diffraction, SEM, TEM, XPS, N₂ physisorption, and chemisorption.

3. Results and discussion
From the transmission electron microscopy image (Figure 1) it is possible to see the microporous shell encapsulating the mesoporous zeolites. Additionally, the zeolites were also analyzed by N₂ physisorption which show a microporous shell around the mesoporous silicalite-1 (see Figure 2). The selectivity of the metals encapsulated in the mesoporous silicalite-1 and with the additional shell show promising results in e.g. hydrogenation reactions.

4. Conclusions
Several mesoporous materials with different metals have been made by steam assisted hard carbon templating. Additionally, a microporous shell was grown around these. The materials were tested in hydrogenation reactions which showed promising results for selectivity for these materials.

References
Science and industrial practice in methanol synthesis

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1. Introduction
Methanol was consumed in 70 million tons in 2016 and is considered to play an important role as transport fuel in realizing the vision of a new green economy [1]. Methanol can be manufactured from renewable resources such as organic waste or from CO2 waste streams after addition of hydrogen produced by electrolysis. In the latter case, methanol can make use of excess electricity from wind mills or solar panels. Today, methanol is made industrially from synthesis gas obtained mainly from steam reforming of natural gas but also to some extent from coal gasification. The optimal module (M) of the synthesis gas, $M = (H_2 - CO_2)/(CO + CO_2)$, used for preparation of methanol is close to 2.
The synthesis gas is converted in a single or a series of large cooled or adiabatic reactors over a Cu/ZnO/Al2O3 catalyst. This catalyst consists of Cu nanoparticles mixed with nanoparticles of ZnO and Al2O3. Although Cu can work alone as a methanol synthesis catalyst, its activity is substantially boosted by the interaction with ZnO, which on its own has only negligible catalytic activity at the conditions of the industrial synthesis [2]. The industrial practice and discussions of the basic science behind the methanol synthesis catalyst are the subjects of this abstract.

2. Results and discussion
In chemical processes, the reactor is the single most important piece of equipment. Formation of methanol is equilibrium limited and exothermic, thus reactors are constructed for effective control of the temperature. Industrial reactors may be divided into reactors with external cooling such as boiling water reactors and gas cooled reactors and adiabatic reactors with interstage cooling including quench reactors and heat exchange cooling between the adiabatic reactors. These reactor systems are designed to remove heat efficiently and obtain high conversion per pass to minimize cost of downstream separation and gas recycle.

Cu/ZnO/Al2O3 catalysts are applied industrially, but in spite of a significant scientific effort, a common understanding of the reaction mechanism, the active site for methanol synthesis and the promotional effect of ZnO (the Cu – ZnO synergy) are still debated. The origin of the Cu – ZnO synergy has been ascribed to gas-dependent morphological changes of Cu on ZnO, support-induced strain in Cu particles, ZnO species/layers covering part of the Cu nanoparticles, interface sites between Cu and ZnO nanoparticles or Zn atoms incorporated into active Cu step sites [3]. Recently, ZnO layers over Cu particles in Cu/ZnO catalysts [4] and highly active Cu/ZnO sites were reported [5,8], but increased activity has also been observed of reduced Zn atoms in Cu nanoparticles [3] and in Cu single crystals [3,6,9]. Theoretically, both Zn covered Cu steps and a Cu surface with a ZnO-H island have shown high methanol synthesis activity [5,7]. The apparently contradicting views will be discussed in this contribution.

3. Conclusions
Methanol production is highly interesting from both an economical and scientific point of view – now and for future purposes. This contribution covers an overview of the industrial practice and developments in methanol production and recent discussions of the basic understanding of the complexed catalyst used industrially for this process.

References
High Pressure Pre-turbine SCR reactor for NOx Reduction on Ships

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1. Introduction

The 1st of January 2016, a new IMO Tier III regulation was enforced for all new built ships, requiring 75% NOx reduction compared to the earlier Tier II regulation, when ships are sailing within NOx emission controlled area’s (NECA’s)[1]. One approach for Tier III NOx compliance on 2 stroke engines is to install a selective catalytic reduction (SCR) reactor. An SCR reactor installation upstream of the turbocharger will ensure temperatures above 300°C [2] and thereby a high SCR efficiency and no sulfate contamination of the catalyst despite the high sulfur maritime exhaust environment (up to 600 ppm [3]). The pre-turbocharger location also features pressures up to 4.5 bar [2], making additional knowledge on pressurized SCR important.

2. Experimental

A commercial vanadium based marine SCR catalyst from Umicore Denmark was used in this study. The catalyst was tested both as a crushed and sieved catalyst powder (150-300 μm) and in the form of a monolith (hydraulic diameter of 4.3 mm). The crushed catalyst was used to measure intrinsic kinetics using a packed bed reactor (PBR) system, in which 20 mg of catalyst was loaded. The pressure was regulated between 1-5 bar and gas concentrations were measured using an MKS multigas 2030 FTIR. Typical test conditions were: 8% O2, 8% H2O, 600 ppm of NO and an ammonia to NOx ratio (ANR) of 1.2 or 0.8. The monolith catalyst was tested at a test facility at Umicore Denmark at similar conditions. To clarify the effect of pressure on the reaction, the actual residence time in the catalysts was kept constant, by increasing the total flow rate proportional to the pressure increase.

3. Results and discussion

The measurement performed on the catalyst powder showed that the NOx reduction was independent of the pressure when the actual residence time was kept constant, at pressures of up to 5 bar and temperatures of 200-400°C using an ANR of 1.2 or 0.8 as shown in Figure 1. The full monolith experiments using an ANR of 1.2 were performed at 1 and 3 bar and showed a decrease in NOx reduction from 6.1 % to 5.6 % at 201°C and from 33.8 to 30.2 % at 353 °C at the high pressure of 3 bar compared to at 1 bar. The decrease in NOx reduction at increased pressure using a monolith catalyst is due to increased diffusion limitations, as also confirmed by calculations using a monolith model. Because of the inverse proportionality of the molecular diffusion coefficient and pressure, the diffusion becomes slower as the pressure increases. The relatively small decrease in conversion is because the Knudsen diffusion is unaffected by the pressure, and therefore, the effective diffusion coefficient does not scale proportionally to the pressure change. For instance, by changing the pressure from 1 bar to 3 bar, the effective diffusion coefficient is only halved. At an actual ship where the residence time is not kept constant, the total conversion at a fixed temperature will therefore also increase with pressure.

4. Conclusions

The pressurized pre-turbine configuration of a maritime SCR reactor looks like a promising solution for IMO Tier III compliance. The intrinsic kinetics and main SCR reaction were found to be unaffected by the total pressure. The total NOx reduction across a real size monolith is, however, affected by the change in residence time and component diffusion, both of which depends on the pressure. Overall the NOx reduction is expected to increase at increased pressure due to the higher residence time.

References

Zeolitic Imidazolate Frameworks as templates and self-sacrificing catalyst precursors

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1. Introduction

Conventional nanoparticle catalysts often suffer from deactivation by nanoparticles sintering at high temperatures [1]. However, highly sinter stable catalysts have recently been achieved by encapsulation of individual nanoparticles in porous materials [2-4]. Here we present the use of Zeolitic Imidazolate Frameworks (ZIFs) as templates and self-sacrificing precursors to obtain various high surface area catalysts with encapsulated metal nanoparticles. The ZIF precursors can be exploited for preparation of high surface area nitrogen doped carbon catalysts as well as “nanorattle” catalysts, see Figure 1. The final catalysts are obtained after a carbonization and/or calcination step in either Ar and/or air, which has a large effect on the metal dispersion. The resulting catalysts show promising activity and stability as catalysts for several reactions including hydrolytic dehydrogenation of ammonia borane and CO oxidation.

Figure 1. a) Illustration of catalyst synthesis pathway. b) TEM and c) tomographic reconstruction of Co nanoparticles inside a mesoporous SiO$_2$ nanorattle catalyst.

2. Experimental

All prepared materials were synthesized from commercially available chemicals. The ZIFs were prepared by mixing metal nitrates with 2-methylimidazole in methanol. The metal oxide shells were synthesized by adding a surfactant and a metal oxide precursor. All syntheses included a final carbonization and/or calcination step in either Ar and/or air to yield the final catalysts.

The catalysts were characterized with TEM, SEM, STEM, XRD, XPS, XRF and N$_2$ physisorption.

3. Results and discussion

We were able to synthesize nitrogen doped carbon catalysts with variations in size. Depending on the ZIF precursors, Co (ZIF-67) and/or Zn (ZIF-8) nanoparticles can be obtained with the possibility of impregnation with other metals as well. Here, a Co catalyst prepared from the bimetallic ZIF-67/8 precursor showed promising results in the hydrolytic dehydrogenation of ammonia borane. Additionally, we have synthesized “nanorattle” catalysts with different metal oxide shells from ZIFs. It was possible to control the 3D distribution and size of the encapsulated metal nanoparticles in the “nanorattles” by simple changes in the carbonization or calcination step. The synthesis route had a large effect in CO oxidation, where the best activity was achieved with Co nanoparticles in a mesoporous SiO$_2$ shell.

4. Conclusions

These results illustrates a simple way to prepare various catalysts from ZIFs, which can be used to develop efficient and more sinter stable catalysts.

References
Kinetic study of methanol and direct dimethyl ether synthesis from CO2-rich syngas
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1. Introduction
Dimethyl ether (DME) is a suitable chemical energy carrier that can be manufactured efficiently and directly from synthesis gas streams derived from a variety of feed-stock such as natural gas, crude oil, coal and bio-waste products [1]. DME can be used to directly produce gasoline (DME-to-Gasoline, DTG) [2] or to synthesize oxymethylene ethers (OMEs), which can be used as diesel additives to reduce soot formation during the combustion [3]. New possible applications of DME lead to an increase of the global production but also to the search for new ways to optimize the processes efficiency. The key to optimize a catalytic process in order to maximize its viability lies in a better understanding of the mechanism behind the reaction. Within this study, the kinetics of methanol and direct dimethyl ether synthesis are investigated in different reactor configurations following an approach for the development of a reliable mechanism.

2. Experimental and modeling approach
For the kinetic studies, the methanol and direct synthesis of DME are investigated on an industrial Cu/ZnO/Al2O3 (CZA) and an in house prepared Cu/ZnO/ZrO2 (CZZ) catalyst, which are commonly used in the methanol synthesis in the presence of CO/H2/CO2. Commercially available H-zeolites (abbreviated as HZ) serve as dehydrating acid. Catalyst systems (CZA-HZ and CZZ-HZ) for the single step DME synthesis are generated by suitable mixing procedure (100 – 500 µm sieve fraction). The kinetic experiments are carried out in a fixed-bed (up to 100 bar, 450 °C) and a Berty type reactor (up to 50 bar, 450 °C) at different experimental conditions: inlet H2/CO/CO2 concentrations, temperatures 220-260 °C, total volumetric flows 0.1-0.7 SLPM and catalysts mass weight ratio. Mass flow controllers dose the feed gases and the product analysis is performed by Fourier-transform infrared spectroscopy (FTIR) as well as gas chromatography (GC). A micro-kinetic mechanism developed for this study is used to model the experimental results for methanol synthesis from syngas, the numerical simulation is performed using the software package DETCHEM™. The experimental results for the DME synthesis are correlated with global kinetic models using equations implemented in MATLAB.

3. Results and discussion
The DME synthesis from CO/H2/CO2 can be described using three reactions: methanol formation (CO + 2H2 ↔ CH3OH), methanol dehydration (2 CH3OH ↔ CH3OCH3 + H2O) and reverse water-gas shift reaction (CO2 + H2 ↔ CO + H2O). Kinetic parameters were calculated for each of the above mentioned reactions using global kinetic models and the experimental results obtained for the single steps. The mean field micro-kinetic mechanism for methanol synthesis is based on a surface reaction mechanism from theoretical studies [4] consisting of 34 elementary-step like reactions with 12 surface and 5 gas-phase species, this mechanism will be extended to model the DME synthesis from H2:CO:CO2 inlet mixtures. An example of the kinetic measurements and simulations preformed in the fixed bed reactor for DME synthesis is shown in Figure 1.

4. Conclusions
The kinetic models used in this study make possible the prediction of the product distribution for DME and methanol synthesis as well as the impact of the co-feed of products. The kinetic data obtained in this work can be used to predict the reactor behavior by numerical methods, which becomes a useful diagnostic tool to enhance the process efficiency.

References

Table 1. Comparison of experimentally determined and numerically predicted DME-yield as function of the temperature at 50 bar, inlet feed H2/CO/CO2/Inert (44/15/3/38), total flow rate of 0.3 SLPM.
DeNO\textsubscript{x} of flue gasses by end-of-pipe technologies

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1. Introduction
Due to deactivation of the commercial deNO\textsubscript{x} SCR catalyst in the flue gas from biomass as fuel in power plants and the demand of a catalyst working at lower temperatures in waste incineration plants and onboard ships, research efforts have grown to develop alternative catalysts or new technologies for flue gas cleaning end-of-pipe. However, at present no low temperature, commercial deNO\textsubscript{x} catalyst or alternative technology is available on the market.

2. Experimental
The present study investigates the effects of different support materials (Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2}) and methods of preparation (wet impregnation, deposition precipitation) on the activity and water resistivity of promising MnFe containing low temperature SCR deNO\textsubscript{x} catalysts. Another approach for end-of-pipe deNO\textsubscript{x} technologies is absorption and catalytic conversion of NO by ionic liquids [1], e.g. [BMIM][NO\textsubscript{3}] (1-butyl-3-methylimidazolium nitrate, from Io-Li-Tec, GMBH, Germany). The SILP (Supported Ionic Liquid Phase) absorbers were prepared by impregnating hollow-sphere silica (HS) [2,3] or silica 100 (Fluka) with [BMIM][NO\textsubscript{3}] dissolved in methanol and successively dried by rotary evaporation at decreased pressure for 2 h at 60 °C. The materials were exposed to a gas stream containing NO (500-3000 ppm), O\textsubscript{2} (12-20%), H\textsubscript{2}O (2-20%) and balance N\textsubscript{2} at temperatures ranging from 125-300 °C with appropriate ammonia injection for the heterogeneous catalysts and 30-120 °C for the SILP samples occasionally with alcohol injection, respectively, in a continuous flow setup using mass flow controllers (GE50A, MKS instruments) with total gas flow rates of 100-200 NmL/min.

3. Results and discussion
For the heterogeneous MnFe catalysts deposition precipitation results in more active catalysts, regardless of the support material. No major difference in activity was seen between alumina and titania supported MnFe. In the temperature range around 150 °C, the MnFe catalysts showed much higher activity than the industrial VWT standard SCR catalyst. However, water at high levels as 20% has a strong inhibiting effect as does even low levels of SO\textsubscript{2} in the flue gas.

The [BMIM][NO\textsubscript{3}] SILP materials provides a novel method for oxidizing NO to NO\textsubscript{2}, HNO\textsubscript{2} and HNO\textsubscript{3} at low temperatures in a continuous flow process design. The oxidant is dioxygen and the reaction is promoted by water. It was further shown to be enhanced by injecting small amounts of methanol in the gas phase before the SILP absorber/converter achieving up to around 50% conversion to NO\textsubscript{2}.

4. Conclusions
The optimized MnFe heterogeneous SCR catalysts are very active at low temperatures, but suffers from severe deactivation by high levels of water and low concentrations of SO\textsubscript{2} and may thus only find application for deNO\textsubscript{x} in selected types of flue gases.

We have also presented a novel method for low temperature ionic liquid catalyzed oxidation of NO by using methanol as a promoter. To the best of our knowledge, this is the only reported low-temperature oxidation method utilizing methanol. When comparing results obtained under wet conditions, the presented method shows reaction rates several orders of magnitude higher than found in the recent literature [4]. The combination of the SILP converter with traditional SCR catalysts may pave the way for low temperature fast SCR performance of the deNO\textsubscript{x} catalyst.

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References
About the absence of stable hydroxyl nests in acid leached Y zeolites

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1. Introduction
Zeolites are important heterogeneous catalysts. Their Brønsted acidity (BA) plays pivotal role in numerous catalytic processes. Si/Al > 1, but the strength and number of BA sites varies with the Al contents. In the initial form of the still most used Y zeolites Si/Al ~ 2.5, but frequently even times higher ratio is desirable. A frequent way for modifying the Al content is to carefully leaching it out from the crystal lattice with an acid. Barrer and Makki [1] succeeded first to do this without crystal collapse. Based on their proposal, it is widely believed that a thermally stable (up to 400 oC!) hydroxyl nest, [OH]4, remains in the lattice on the place of the removed Al atoms. However a thorough literature review could not point at any solid proof for the existence of stable [OH]4 units and for example targeted thermogravimetric tests could not detect their presence in acid leached Y zeolites [2]. Here we present experimental and DFT modeled FTIR results as well as molecular dynamics based model calculations on such zeolites, which also prove the absence of [OH]4.

2. Experimental
Samples were prepared from a commercial CBV 100 NaY zeolite (Si/Al ~2.55), from which about 20% of Al was removed by the Rive procedure [3]. The acid leached NaY(-Al) sample was stoichiometrically (Na/Al =1) back-exchanged with Na+ to avoid interference with any acidic OH. FTIR spectra of both NaY and NaY(-Al) samples were measured in transmission (TR) mode on self-supported pellets at around 5 x 10⁻⁶ mbar at room temperature after stepwise (~50 °C/step) increased in situ calcination temperatures from 25 °C to 500 °C. The FTIR spectra of expected [OH]4 nests were modeled by DFT calculations implemented in the plane wave based program CASTEP [4]. To model the thermal stability of [OH]4 nests in DFT optimized structures we used the reactive force field approach implemented in the ReaxFF program [5].

3. Results and discussion
Comparative FTIR measurements in TR mode were carried out on NaY and NaY(-Al) samples to search for distinguishing signs of [OH]4 nests on the dealumminated material, which has never been exposed to higher than 25 °C during its synthesis. Once samples were placed into the FTIR sample holder and evacuated, they have never been exposed to higher pressures until finishing measurement on the 500 °C calcined pellet. Fig. 1 illustrated terminal Si-OH vibrations, near ~3740 cm⁻¹, are new on the NaY(-Al) zeolite. Fig. 2 shows that the computed [OH]4 FTIR bands are absent from the experimental spectrum of NaY(-Al). Fig. 3 points out that an initial [OH]4 nests, if it forms, would start to decompose within picoseconds even at 25 °C.

4. Conclusions
Contrary to the common belief, combined TG/DTG, FTIR and computer modeling results prove that even if [OH]4 nests form upon Al removal from a zeolite lattice with acids, their existence is ephemeral on a picosecond time scale at temperatures above >25 °C.

References
New Type of Catalysts on the Base of Intermetallides for carbon Dioxide Reforming of Methane

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1. Introduction
The process of carbon dioxide reforming of methane, or dry reforming of methane (DRM), has gained much attention as it reduces greenhouse gases, CO 2 and CH 4. Besides, the DRM process produces valuable chemicals (CO + H 2), provides one of the approaches to utilizing biogas and natural gas with a significant amount of carbon dioxide, has good capability as a chemical energy transmission system as compared to steam reforming, and yields the desired unity H 2/CO ratio for Fischer–Tropsch synthesis. The proposed work includes the application of a novel synthetic approach for catalyst materials, activity tests of these materials as well as different physicochemical methods of investigation [1-3]. This is of great interest and importance for many institutes and chemical industry [4]. The overall objective of this work is description of research within the field of innovative catalyst materials for high temperature upgrading processes for natural gas conversion, biomass and waste gasification systems.

2. Experimental
Self-propagating high-temperature synthesis (SHS) was used as a method of catalyst synthesis. Ion implantation was used to change the physical, chemical and catalytic properties of Ni 3Al as a matrix for this new type of catalysts for DRM. Ions of Mo, Pt were accelerated in an electrical field and impacted into a solid Ni 3Al. The catalytic performances were evaluated between 600 °C and 900 °C at atmospheric pressure. The feed was CH 4/CO 2/He = 20/20/60 vol.% mixture. Particle size and chemical evolution of catalysts were studied by XRD (in situ and ex situ), SEM, EDS, HRTEM + EDS and XPS.

3. Results and discussion
In general, the results indicated that the addition of a low amount (less than 0.1 wt %) of Pt to Ni 3Al leads to a decrease in carbon deposition and Pt-implanted catalysts were stable for a long period of time. The evidence suggests that the differences in the stabilities may be due to the following reasons: 1) Pt prevents Ni phase sintering by avoiding particle coalescence, which is the main sintering process under severe CH 4/CO 2 reforming conditions, 2) Pt hinders deactivating carbon formation by limiting bulk nickel carbide and therefore carbon filament formation, which may lead to reactor plugging and/or particle fragmentation, and by suppressing encapsulating carbon formation which limits access of reactant to the active nickel phase.
Modification of catalyst by ion implantation had several positive impacts: 1) high catalytic activity and stability in DRM, 2) reducing of carbon deposits, 3) Mo and Pt prevent Ni phase sintering by avoiding particle coalescence.

4. Conclusions
In order to obtain the matrix structure that ensures partial delivery of nickel as an active component, containing a large number of defects and irregularities, SHS method was chosen as a method of catalyst preparation since it has some great advantages, such as: simplicity, low power consumption, simple and small-sized equipment, high-performance, high purity of products and environmental safety. Modification of catalyst by ion implantation had several positive impacts: 1) high catalytic activity and stability in DRM, 2) reducing of carbon deposits, 3) Mo and Pt prevent Ni phase sintering by avoiding particle coalescence. Proposed bimetallic Ni-based catalysts show remarkable performances in the DRM process. But, carbonaceous deactivation of the catalysts is the major problem faced during this process [2]. Therefore, one part of this work will be devoted to description of carbonaceous deposition problems and some strategies to reduce the carbonaceous deactivation of catalysts for improved DRM efficiency by appropriate catalyst development and operating conditions. In general, description of this work has really significant importance for development of new catalysts for DRM.

References
Operando study: Oxidation of Ni-Co/HT Catalyst for Catalytic Combustion of Methane
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1. Introduction

The catalytic combustion of methane (CCM) is a significant process for energy production and reduction of direct emission from methane¹. Our study uses an operando setup to explore the synergy between Ni and Co catalysts to control the oxidation state of the transition metals. The idea is to develop a method were the retrieved in-situ knowledge on the oxidation state is used to improve the CCM activity.

2. Experimental

A series of well-controlled Ni-Co catalysts supported on a hydrotalcite-HT)-like structure have been synthesized using co-precipitation. The catalysts contain a total metal loading of 12wt% with various ratios of Ni and Co content. In addition, the pure Co catalyst was impregnated with 0.1wt% Pd. The catalysts activities were analyzed in a fixed-bed quartz reactor equipped with a fiber optic probe. The probe is pointing directly towards the catalyst bed and connected to a UV-vis-NIR spectrometer giving valuable information on the in-situ state of the catalyst. The compositional gas changes were analyzed using a gas chromatograph (GC) and a mass spectrometer (MS). The experiment consists of alternating between O₂ and CH₄ conditions in 3 cycles to compare the oxidation and reduction rates of the catalysts. In addition, complete combustion was performed over 4 h. All analyses were performed at 670 °C to keep it at isothermal conditions.

3. Results and discussion

Figure 1 shows the activity during complete combustion for catalyst with different Ni/Co ratios, it is evident that increasing the amount of Co increases the activity. This could be explained by the oxygen conversion rate shown in figure 2, which shows that cobalt is a much better metal for converting oxygen from the feed compared to nickel. When looking at the methane conversion rate the trend is opposite; cobalt has the lowest reduction rate. For all catalysts the oxidation rate is faster than the reduction rate which is also confirmed by the UV-vis spectra’s showing the Co⁹ goes to Co³⁺ and the Ni⁰ goes to Ni²⁺ during combustion. It is evident that the activity is related to the oxidation of the catalysts. Due to this the pure Co was impregnated with Pd, which is an oxidative metal. The results clearly show an increase in the methane conversion during combustion. Although the rate of the O₂ conversion is lower for the first 200 s during the O₂ conditions, it is evident that the oxidation time is more than doubled. A similar technique has also been done for oxychlorination on copper in our group²⁻⁴. Using these results, we believe that a method utilizing the in-situ data from UV-vis-NIR spectroscopy can be developed which relates the activity with the oxidation state of the catalysts.

4. Conclusions

Based on catalysts with different Ni/Co ratios the Co has the highest activity, and that impregnating with Pd has a significant effect since it is an oxidative metal. From MS and UV-vis-NIR results this can be explained by the fast oxidation of the Co in combination with high amount of surface oxygen.

References
Advanced Nanorattle Catalysts Derived from Metal-Organic Frameworks

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1. Introduction

Beside their high porosity, high surface area and low density, hollow nanomaterials offer a number of key advantages with respect to loading and functionalization of the hollow interior. Hollow nanostructured materials therefore hold great promise for new and emerging technologies in energy conversion and catalysis [1]. Until now, several methods have been developed to prepare hollow nanomaterials. The most common methods are templating using either hard or a soft templates or template-free methods that rely on the Kirkendall effect [2], Ostwald ripening [3], selective dissolution [4] or recrystallization [5-6]. In general, these methods all have advantages and disadvantages, but usually suffer from complicated synthesis procedures, expensive additives, poor yield or non-uniform materials. Subsequent loading or functionalization often causes further challenges and limitations.

Here, we report a new approach to synthesize metal nanoparticles inside mesoporous nanorattle catalysts. In this method, metal-organic frameworks are exploited as structural template for the preparation of a mesoporous metal oxide shell as well as sacrificial precursor to form metal nanoparticles inside the shell. Depending on the metal and metal oxide composition, the nanorattle catalysts were tested for CO oxidation, CO2 methanation or CH3OH synthesis.

2. Experimental

In one example, small crystals of metal-organic framework ZIF-67 were synthesized from cobalt nitrate and 2-methylimidazole in methanol. The ZIF-67 were then used as structural template for the synthesis of a mesoporous ZrO2 shell using hexadecylamine as pore generating template. The ZIF-67@ZrO2 composite material were then dried and calcined to remove the organic templates. Alternatively, the materials were carbonized under inert atmosphere to leave the Co nanoparticles supported on a N-doped carbon matrix inside the shell.

The prepared catalysts were characterized using a variety of techniques, including XRD, XRF, XPS, N2 physiisorption, TPR, SEM, TEM, STEM and electron tomography. The catalytic tests were performed in a fixed bed reactor equipped with an online GC-FID/TCD, MS or NDIR detector.

3. Results and discussion

Figure 1 show a TEM image of a core-shell material comprised of ZIF-67 metal-organic framework core and a mesoporous ZrO2 metal oxide shell. Figure 2 show the same material after calcination for 2 hours at 400°C in air. By introducing an intermediate carbonization step, it was possible to decrease the final calcination temperature to 300 °C, which is well below the thermal decomposition temperature of ZIF-67. This resulted in a higher dispersion of Co3O4 and, consequently, a higher catalytic activity as exemplified by CO oxidation and CO2 methanation. Exchanging ZIF-67 with the Zn containing ZIF-8 modified with Cu resulted in a novel nanostructured Cu/ZnO/ZrO2 catalyst with promising activity for hydrogenation of CO2 into methanol.

4. Conclusions

Exploiting metal-organic frameworks as both structural template and sacrificial precursor offers extraordinary control of size, shape and structure and opens up new exicting opportunities for designing advanced nanorattle catalysts.

References
Oxidative Depolymerisation of Lignosulphonate Lignin into Low-Molecular-Weight Products: A Catalyst Screening Study

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1. Introduction

Lignin is recognised as the third most abundant biopolymer available on Earth after cellulose and chitin, presenting a potential source for production of renewable materials and high-value products [1]. Despite its potential, lignin remains the most underutilised biopolymer, in contrast to other lignocellulosic polymeric components [2], and its efficient valorisation presents an ongoing challenge. The challenges in using lignin as a raw material for low-molecular-weight (LMW) chemicals production [3] originate from the fact that the polymer is markedly heterogeneous, and the oxidative depolymerisation emerge as a promising route among other deconstruction strategies.

2. Experimental

The sodium lignosulphonate lignin (LS) was kindly provided by Domsjö Fabriker AB (Örnsköldsvik, Sweden) and used as the starting raw material. The oxidative depolymerisation experiments were carried out in a 100 mL mechanically stirred Parr reactor equipped with a 4843 PID temperature controller. Three heterogeneous catalysts and the support were screened and tested for their ability to depolymerise the LS substrate under O\textsubscript{2} pressure. The experimental runs were conducted at moderate operating conditions using appropriate amounts of lignin solids loadings and catalyst-to-lignin ratios. The product mixtures were characterised using size exclusion chromatography (SEC) and 2D \textsuperscript{1}H-\textsuperscript{13}C HSQC NMR spectroscopy.

3. Results and discussion

Figure 1 depicts the SEC curves of the initial LS substrate and the product mixtures generated from different experimental runs. As can be seen, Cat A showed a superior behaviour in the capability of converting the high-molecular-weight LS material into LMW products (M\textsubscript{p} \approx 1,400 Da). The product fractions also exhibited much narrower molecule-weight distributions in comparison to the starting material, which exhibited a rather broad peak. In addition, it was revealed from the NMR measurements that there are notable differences between LS sample and sample generated utilising Cat A, particularly in the inter-unit/oxygenated aliphatic region.

4. Conclusions

Different heterogeneous catalysts were synthesised and screened for their ability to depolymerise sodium lignosulphonates, a technical lignin stream generated from sulphite pulping. Under O\textsubscript{2} pressure, Cat A showed a surpassing performance for converting LS into LMW compounds. Such product streams can potentially be utilised in a diverse form of value-added applications in current fast-growing chemical and bio-based industries.

Acknowledgements

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References

Effects of soot, sulphur, sodium, calcium and phosphorus on diesel oxidation catalyst after operation in a FAME biodiesel-fueled heavy-duty vehicle

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1. Introduction
Fatty acid methyl ester (FAME) may contain relatively high levels of contaminants, including Na, K, P, Ca and Mg, due to its production process. The European standard for FAME, EN14214, specifies that B100 may contain up to 4 ppm of P, up to 5 ppm combined of Na and K, and up to 5 ppm combined of Ca and Mg [1]. Such fuel impurities may deposit on the aftertreatment equipment and act as catalyst poisons. The DOC is exposed to high concentrations of impurities in the exhaust gas, because of its position at the inlet of the aftertreatment system, and may therefore be susceptible to poisoning. We studied a DOC from a vehicle that had been operating an entire lifetime on B100 FAME biodiesel to assess the impact of biodiesel impurities on DOC activity. Selective step-by-step removal of catalyst poisons [2] was performed to isolate the effects of different deactivation routes.

2. Experimental
Cylindrical Pt/Pd on Al2O3 DOC samples (diameter: 20 mm, length 30 mm) were taken from the front of a DOC that had been in operation for over 700 000 km in a vehicle using B100 FAME biodiesel. Contaminants on the DOC samples were removed by successive selective contaminant removal procedures [2], the effects of which on catalyst composition were probed by XRF. Catalyst activity was tested before contaminant removal, and after each subsequent contaminant removal step, in a quartz flow reactor at a space velocity of 80 000 h⁻¹, at a heating rate of 3.5 °C/min. A fresh DOC of the same type was tested for comparison.

3. Results and discussion
The effects of the successive selective contaminant removal procedures are shown in Figure 1. Ocular inspection showed that the oxidative treatment at 400 °C removed soot, while XRF showed that S was not simultaneously removed. According to XRF, removal of S, Na and Ca, and P by each subsequent removal procedure was selective, as illustrated schematically in Figure 2. Contaminant removal had little effect on CO oxidation activity. NO oxidation activity recovered after removal of Na and Ca, and further after removal of P. C3H6 oxidation activity showed the greatest activity recovery after soot removal. Even after near-complete contaminant removal by acids, NO and C3H6 oxidation activities were not fully recovered to those of a fresh catalyst, indicating a considerable effect of thermal deactivation on catalyst activity. Reductive removal of S had little effect on activity. This could be explained by a previously observed phenomenon that long-term operation in oxidizing atmospheres and at moderate temperatures (such as in diesel exhaust) causes S freshly deposited on active metal sites to migrate to the sulphating Al2O3 support, where it does not much affect catalyst activity [3].

4. Conclusions
Activity testing of a DOC that had been used for a full lifetime in a FAME biodiesel truck revealed considerable deactivation compared to a fresh catalyst. Successive selective contaminant removal procedures revealed that thermal deactivation, as well as poisoning by soot, P, and water-soluble contaminants (Na and Ca) were the main causes of the activity loss. S seems to not have significantly affected DOC activity.

References
The Site-Assembly determines the Catalytic Activity of Nanoparticles
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1. Introduction
Extended surfaces with a single type of active sites are often used as model systems in heterogeneous catalysis. However, technical catalysts are often realized as nanoparticles supported on oxides. A nanoparticle is characterized by the presence of a multitude of different sites which may be coupled kinetically [1,2]. In this sense, extended surface model systems can fail to capture the possible complex kinetic couplings.

In the present work, we study the kinetics over nanoparticles explicitly. By studying representative particle-morphologies, we show that the catalytic activity of a site on a nanoparticle is strongly determined by its surroundings. Thus, the site-assembly determines the kinetics of reactions over nanoparticles.

2. Computational Method
We perform Scaling Relation Monte Carlo (SRMC) simulations [3], where kinetic Monte Carlo simulations are realized using scaling relations in generalized coordination numbers, established by Density Functional Theory (DFT) calculations. The generalized coordination number (CN) [4] is an extension of the coordination number that includes the first nearest neighbor coordination numbers. In SRMC the CN is used to describe all adsorption energies and reaction barriers, and rate-constants are calculated using transition state theory. CO oxidation over Pt nanoparticles is studied as an archetype reaction, where the following reaction scheme was considered:

\[
\begin{align*}
\text{CO(g)} + \star & \leftrightarrow \text{CO}^* \\
\text{O}_2(g) + 2\star & \leftrightarrow 2\text{O}^* \\
\text{CO}^* + \text{O}^* & \leftrightarrow \text{CO}_2(g) + 2\star \\
\text{A}^* + \star & \leftrightarrow \star + \text{A}^* \text{(Adsorbate diffusion)}
\end{align*}
\]

3. Results and Discussion
Figure 1 shows the light-off of the reaction for five particle geometries (Sphere, decahedron, octahedron, icosahedron, cube). The results indicate that a high activity is correlated with particle roughness. Figure 2 shows the activity of the sites for the different geometries. A particular site-type yields various TOFs with a maximal variation in the order of \(10^6\) /site/s. Thus, the site-type alone is insufficient to predict the TOF on a nanoparticle, and thus the site-assembly determines the catalyst performance. Given the relatively simple reaction scheme, this behavior is expected to be present for more complex reactions over nanoparticles.

4. Conclusions
First-principles based kinetic Monte Carlo simulations are used to elucidate catalytic activity of nanoparticles. The activity is governed by complex kinetic couplings, and thus modeling reactions using isolated sites is an approximation when nanoparticles are considered. The detailed geometric arrangement of sites has a large impact on catalyst performance, and the site-assembly is a key concept to understand active sites in nanoparticle catalysis.

References
Catalytic Upgrading of Ethanol using Pincer type Complexes

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1. Introduction
The catalytic conversion of (bio) ethanol into butanol is an attractive route to upgrade the modest fuel characteristics of this widely available bioderived substrate into a molecule that has properties much closer to conventional gasoline. [1] In this respect Guerbet reaction is an ideal choice to generate a longer-chain alcohol from ethanol via alcohol condensation with water as only byproduct. [2] Likewise, the transformation of ethanol ethyl acetate by acceptorless dehydrogenation is a key tool towards the sustainable production of valuable chemicals and advancement of green chemistry. [3-5] Simple nature of these reactions provides formidable challenges, especially in term achieving high selectivity. Toward this end, we have develop effective PNP-pincer metal-based catalysts.

2. Experimental
This project provides insights into rigorous synthetic and mechanistic studies for dehydrogenation reactions of ethanol, one of the simplest alcohols and model substrate for biomass derivatives with the following methodology development: 1) the isolation and structural characterization of intermediate complexes and/or in situ spectroscopic characterization to understand reaction steps. 2) the development of new and more useful catalytic system (i.e. higher rates, lower temperature, higher product selectivity, and functional group tolerance) for the application of AAD to organic methodology and fuel materials syntheses and H2 production.

3. Results and discussion
The starting point involves a setup using PNP pincer complexes such as [MH2(CO)(H-PNP)] and [MH(CO)(PNP)] for catalytic homogeneous upgrading of ethanol to butanol as well as ethanol conversion to ethyl acetate. A detailed account on the effect of the temperature, solvent, nature, and proportion of base used and the stereoelectronic effects of the ligand substituents was analyzed.

4. Conclusions
In summary acceptorless dehydrogenation of alcohols (AAD) for the production of biofuel from ethanol was carried out with metal-based catalysts supported by a cooperating PNP pincer ligand. Ongoing efforts are focused on mechanistic analyses as well as other sustainable energy applications derived from renewable biomass feedstock.

References
Deactivation study of DeNOx Catalysts from heavy-duty vehicles powered with biofuels
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1. Introduction
A common DeNOx catalyst used for emission control in heavy-duty vehicles is the vanadium-based SCR catalyst and in this project the impact from two different biofuels on the catalyst properties of this catalyst has been analysed after use in a vehicle.

2. Experimental
The two different fuels used to power the vehicles in this study are FAME (fatty acid methyl ester) and HVO (hydrotreated vegetable oil). The vehicles used meet Euro V standards. The vehicle powered by FAME was driven 10,000 hours and the vehicle powered by HVO was driven 4,400 hours. Samples were taken from the inlet and the outlet of the SCR catalyst and a fresh reference sample was also analysed. The surface area of the five samples (inlet and outlet of two catalysts and a reference) and the SCR activity were measured. Furthermore, ammonia oxidation and NH3-TPD experiments and XPS analysis were performed.

3. Results and discussion
From the activity tests, Figure 1, it could be seen that the samples taken from the HVO vehicle have slightly lower activity when compared to the fresh reference sample. Furthermore, it can be seen in the figure that the sample taken from the inlet of the SCR catalyst has slightly lower SCR activity than the sample taken from the outlet of the SCR catalyst. From the SCR activity test, it is also clear that the samples taken from the vehicle powered by FAME have considerably lower activity than the samples from the vehicle powered by HVO, in particular the sample taken from the inlet of the SCR catalyst. The results from the NH3-TPD experiments are shown in Figure 2. In accordance with the SCR activity test, the TPD experiments show that the samples taken from the vehicle powered by FAME have considerably lower NH3 storage capacity than the samples from the HVO powered vehicle. However, here the sample taken from the inlet of the SCR catalyst has slightly higher NH3 capacity than the sample taken from the outlet of the SCR catalyst. This is likely due to soot compounds on the inlet that store NH3. For both fuels, the specific surface area measurements show loss of specific surface area for the sample taken from the SCR catalyst. The loss of surface area is highest for the samples taken from the vehicle powered by FAME. The results from the XPS analysis indicate higher concentrations of some poisons like phosphorous, magnesium, potassium and sodium on the FAME samples.

4. Conclusions
From the analysis performed on these engine deactivated SCR catalyst samples it seems that FAME is more detrimental to the vanadium catalyst than HVO. This is of interest when designing catalytic systems for biofuel vehicles and when making fuel regulations and limits on poisons in the new biofuels.
Water–gas shift reaction over Rh/ZrO₂: A DFT based multiscale study

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1. Introduction
Zirconia supported rhodium catalyses the water–gas shift (WGS) reaction [1,2], but the exact mechanism, the nature of the intermediates and the active site are still under debate. One key step of the WGS, regardless of the reaction mechanism, is water activation; the catalyst has to be able to dissociate water. More unclear is how CO reacts to form CO₂. This can occur through a direct reaction with oxygen, which can come either from the oxide lattice (“Mars-van-Krevelen-like”) or from water (“surface redox”). CO can also react with an OH group to form an intermediate species (e.g. carboxyl) which then dissociates to form CO₂ and hydrogen, in the “associative” pathway. The aim of our study is to identify the most important reaction intermediates and rate controlling steps, and to understand the roles that the metal, support, and the interface have in the WGS reaction over Rh/ZrO₂.

2. Computational
DFT calculations using GPAW software were performed to determine the adsorption energies of surface species on Rh, ZrO₂, and the interface. CI-AutoNEB was used to locate the transition states for each elementary step. Rh (Fig.1a) and ZrO₂ (Fig.1b) surfaces were modeled with 2D slab models. The interface (Fig.1c) was modeled with a 40-atom Rh nanorod placed on top of a 2×2 m-ZrO₂ (111) slab. The edge of the nanorod mimics the perimeter of a large metal nanoparticle, with the Rh exposing a 111-facet towards the oxide. The continuous stirred-tank reactor microkinetic model was solved with an in-house Python based code to obtain surface coverages and partial pressures with respect to time at different experimental conditions.

3. Results and Discussion
The energetics of 13 elementary steps were determined on each surface. The three surfaces exhibit varying affinities for the adsorbates as well as differences in activation energies for the elementary steps. DFT results indicate that the Rh surface will have a high coverage of CO, but is not very good for water activation due to its low binding energy and high dissociation barrier. On ZrO₂ water dissociates without a kinetic barrier, but CO is bound quite weakly. The interface is able to easily dissociate water and binds CO strongly. The competing CO oxidation steps have similar enough energetics that DFT alone cannot be used to conclude which one is dominant under reaction conditions. The microkinetic analysis shows that under a range of reaction conditions, the Rh surface is indeed covered by CO, and produces a small amount of H₂ and CO₂, starting at 700 K. The ZrO₂ is covered by hydrogen and formate, but no product is formed at any of the conditions studied. The interface has a moderate coverage of CO, formate, and hydroxyl, and produces a significant amount of H₂ and CO₂, starting at 600 K. Degree of rate control analysis [3] shows that dissociation of carboxyl is the rate controlling step at the interface, which implies that the WGS proceeds via the associative route. On Rh the rate controlling steps are water dissociation and CO oxidation by oxygen from dissociated water, showing that surface redox is the main reaction pathway.

4. Conclusions
The DFT based microkinetic analysis highlights the metal-oxide interface as the most active “domain” of the Rh/ZrO₂ catalyst towards the WGS. Zirconia surface accumulates formate which acts as a spectator species, while the rhodium surface is essentially poisoned by CO. The dominant pathway for WGS at the interface under reaction conditions is the associative carboxyl route.

References
High temperature electrolysis activities at Haldor Topsoe: status and perspectives on electrification of the chemical industry

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1. Introduction
Haldor Topsoe considers high temperature electrolysis (SOEC) as an enabling technology for the electrification of the chemical industry. Compared to other electrolysis technologies, SOEC allows for the conversion of CO₂ into useful chemicals (such as CO) at very high efficiencies and at a faradaic yield of 100%. Haldor Topsoe is commercializing the CO₂ electrolysis technology as eCO₂: a platform for on-site CO₂ generation from CO₂ feedstock for customers requiring a reliable and safe feed of carbon monoxide at a scale of up to 1000 Nm³/h (see Figure 1 (top)). The use of solid oxide electrolysis for the production of H₂ is also interesting not merely due to the inherently high conversion efficiencies that can be achieved due to high-temperature operation, but also due to system-level synergies found in integrating the endothermal electrolysis process with an exothermal chemical synthesis process. An example of such integration is provided by the pilot plant for upgrading CO₂ in biogas into pipeline quality synthetic natural gas (SNG), located at Foulum, Denmark, and combining a 16 Nm³/h SOEC module with a methanation unit (see Figure 1 (bottom)). Common for both applications mentioned above is that the SOEC stacks must have high robustness to handle dynamic operation, as well as long lifetimes, to lower the overall cost of stacks and systems. At Topsoe we have a systematic lifetime testing approach for screening stack-level improvements. The technical features of the stack will be presented, along with lifetime test results in different electrolysis operations.

2. Experimental
A number of cell and stack-level improvements have been screened and evaluated using a systematic approach to lifetime testing. Several stack tests were carried out for 2000 hours at a reference operating point, including a robustness test with several thermal and load cycles, and then intentionally stopped in order to evaluate the extent of degradation in stacks by post-mortem analysis tools (microscopy and chemical analysis) and to qualify/disqualify different design modifications.

3. Results and discussion
The test protocol consists of a 500-hour initial degradation test, a robustness test including load ramping and repeated thermal cycles, and a 1500-hour extended degradation test. Initial degradation test of five stacks with different modifications suggested that 1) the implemented modifications do not necessarily affect the initial performance of the stack, but have a significant impact on stack degradation rate, 2) a stack optimized for fuel cell operation is not necessarily a good stack for CO₂ electrolysis, 3) modifications, however promising from the standpoint of internal resistance and degradation rate, may negatively affect stack robustness.

4. Conclusions
Degradation test of different stacks with various modifications suggested that 1) even after 1000+ h of operation in CO₂ electrolysis, thermal cycles do not seem to harm the stack, but indeed can lead to performance enhancements, 2) different cell- and stack-level modifications can significantly affect stack degradation rate, 3) 2000 hours may be too short a time to objectively evaluate the effect of some modifications due to the differences in degradation rate (stacks that perform better initially may degrade faster, leading to poorer performance at 2000+ hours). Based on these lifetime tests and results from various demonstration projects, Haldor Topsoe’s high temperature electrolysis technology opens up for a whole new segment of green and sustainable chemicals from renewable carbon sources. By combining the technology with electricity from a sustainable source such as wind or solar and a non-fossil CO₂ source, 100% renewable, carbon-neutral syngas (CO + H₂) can be obtained.

Figure 1. (top) A simplified schematic of the eCO₂ platform for on-site on-demand CO₂ generation from CO₂ feedstock. (bottom) A simplified schematic of the Foulum biogas upgrading demonstration unit.
Operando FT-IR spectroscopy for the study of Pd-functionalized UiO-67 for CO₂ hydrogenation reaction

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1. Introduction

Metal-functionalized MOFs are gaining importance in the field of heterogeneous catalysis [1]. In the recent years, our research group focused its efforts on the production of Zr-carboxylate based MOFs, among which, mixed linker UiO-67 materials, represent an interesting example. 10% of bipyridyl-based linker, substituting the classical bpdc linker, allowed the grafting of PtCl₂ moiety on the bipyridyl functionality (Figure 1a) [2a]; thermal reduction in H₂ results in the formation of metal nanoparticles encapsulated in the MOF pores [2b]. The obtained material was tested for the CO₂ reduction with H₂, showing a good selectivity towards CO and excellent stability at operating conditions [3]. Among all the metals investigated up to now, Pd is one of the less explored in the field of MOFs [4], despite its well-known high activity for hydrogenation and reduction reactions in general. In the present study, PdCl₂-functionalised UiO-67 was successfully tested in operando conditions for CO₂ reduction process.

2. Experimental

The sample (hereafter Pd-Uio-67-bpy) was obtained following the post-synthetic functionalization (PSF) method described in Ref. [3]. PXRD and surface area analysis were performed to check the structural stability of the material before and after the reaction. SEM microscopy was used to control the shape of the crystals after each step of the process. The material was then activated and tested in operando conditions by means of a combined DRIFT/GC-MS method, able to have a simultaneous control on both the status of the catalyst and the products developed during reaction.

3. Results and discussion

Figure 1b shows the PXRD pattern of the sample before and after Pd impregnation. From that, it is possible to confirm that the MOF maintained its crystallinity. As expected, the surface area slightly decreases after the PSF with PdCl₂, passing from 2618 m⁡²/g to 2398 m⁡²/g (Figure 1b - inset). The catalyst was placed inside a Praying Mantis DRIFT cell for IR measurements and activated in a 10% H₂ flow (10 ml/min) at 300°C for 15h, allowing the formation of Pd NPs inside the pores of the MOF. Maroon curve in Figure 1c shows the DRIFT spectrum of the sample after activation. All the typical features of UiO MOF family are present: i) ν(ZrOH) at 3660 cm⁻¹, ii) ν(CH) between 3100-3000 cm⁻¹, iii) ν(CO) between 1550-1300 cm⁻¹, iv) δ(CH) between 1200-700 cm⁻¹. The MOF is chemically stable in reaction conditions (240°C, 25% CO₂, 75% H₂): the only additional IR bands present are the one at 2350 cm⁻¹ (CO₂) and the one at 2900 cm⁻¹ (probably due to a slight degradation of the MOF). The latter however, doesn’t find any degradation fragment in the acquired chromatograms.

4. Conclusions

Pd-Uio-67-bpy, shows a slightly lower CO₂ conversion compared to the Pt system. However, the material shows a much higher selectivity towards CH₄ (Figure 1c - inset), making it a good candidate to convert CO₂ into CH₄.

References

Calcined Al-Mg Hydrotalcite as Support in CuCl₂ Based Oxychlorination Catalysts

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1. Introduction

Ethylene oxychlorination is an industrially important process where the CuCl₂/γ-Al₂O₃ based catalyst undergoes a reduction-oxidation process (Eq. 1).[1] It is generally agreed that alumina acid sites catalyze dehydrochlorination of the desired 1,2-dichloroethane. The acidity can be abated by e.g. K addition or a less acidic support. Unfortunately, previous attempts [2,3] (TiO₂, α-Al₂O₃ and SiO₂) have resulted in less active catalyst due to alterations in Cu-support interactions. The current contribution investigates calcined Al-Mg hydrotalcite (HT) as support and uses it as a model system to evaluate the step transient hydrochlorination rate by means of UV-Vis spectroscopy, a rate that is not easily obtained by gas analysis due to the corrosive nature of humid HCl.

$$2\text{CuCl}_2 - \text{C}_2\text{H}_4\text{Cl}_2 + 2\text{CuCl} \xrightarrow{\text{C}_2\text{H}_4\text{OCl}} \text{Cu}_2\text{OCl}_2 \xrightarrow{2\text{HCl}} 2\text{CuCl}_2 + \text{H}_2\text{O}$$  (1)

2. Experimental

The catalysts were prepared from the chloride salts with the incipient wetness method on hydrotalcite (Mg/Al=3) previously calcined at 500, 700, 900 and 1100 °C and contains 5wt% Cu. All experiments were performed at 230°C while step transient experiments were performed with a 0.1 respective partial pressure of C₂H₄, O₂ and HCl while steady-state experiments was performed with a stoichiometric composition (P₂H₄=0.009) in our setup combining in situ UV-Vis-NIR spectrometry and mass spectroscopy (MS).[4]

3. Results and discussion

Upon exposure to HCl, XRD patterns determined the formation of MgOCl₁ species in HT₅₀₀ and HT₇₀₀, resulting in a loss of surface area while no such species was detected in HT₇₀₀ or HT₁₁₀₀. However, a calcination temperature above 900°C resulted in decomposition of the mixed MgAl oxide and the formation of MgO crystals (SEM) with a similar loss in surface area. Figure 1a shows the steady state performance of 5Cu-HT₇₀₀ compared to a conventional 5Cu/γ-Al₂O₃ catalyst with stoichiometric feed composition. After an initial induction period, the HT₇₀₀ supported catalyst has twice as high activity as the conventional catalyst and a slightly lower content of volatile Cu⁺⁺ species as determined by quantitative UV-Vis spectroscopy (not shown).

Figure 1b shows the step transient reduction, oxidation and hydrochlorination rate. The two former obtained by MS while the latter was estimated by integrating the change in UV-Vis signal intensity at 350nm. This wavelength is in the ligand to metal charge transfer region, able to separate between CuCl₂ and Cu₂OCl₂ phases not possible on γ-Al₂O₃ due to signal overlap. In order to estimate a quantitative rate, two assumptions were made: 1) UV-Vis intensity increases linearly with the transformation of Cu₂OCl₂ to CuCl₂ and 2) the number of active sites as measured during the reduction and oxidation half cycles, remain unchanged. The fact that the UV-Vis intensity changes linearly during the reduction (CuCl₂ to CuCl) and oxidation (CuCl to Cu₂OCl₂) supports the first assumption

4. Conclusions

For the first time, a CuCl₂ based oxychlorination catalyst with and alternative support to γ-Al₂O₃ have been proposed where comparable or better activity have been found. In addition, a methodology for determining the step transient hydrochlorination rate have been proposed. The methodology will be used to evaluate the impact of K loading on the hydrochlorination step in particular and in combination with extended by product analysis (GC), calcined hydrotalcite supported catalysts will be thoroughly evaluated.

References

Towards electrification of chemical syntheses by electrocatalytic synthesis of dimethyl carbonate

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Dimethyl carbonate is an environmentally-friendly precursor in various chemical reactions and is currently synthesized by hazardous processes but an electrocatalytic approach could result in a process abiding to the principles of Green Chemistry[1]. We demonstrate how density functional calculations and experiment advance our understanding of electrocatalytic production of chemicals. Using density functional theory, we form design criteria[2] for dimethyl carbonate electrosynthesis on metallic surfaces. The criteria are based on adsorption energies of reactants and reaction energies of possible products. In the literature, gold is shown to be a suitable electrode material[3]. We predict copper to be more selective for dimethyl carbonate compared to the major co-product, namely dimethyl oxalate, and more energy efficient by operating at a significantly lower potential than gold. Electrosynthesis experiments support these predictions, confirming the activity of copper at 1 V lower applied potential than gold and increased dimethyl carbonate selectivity over dimethyl oxalate. However, the reaction on copper occurs through a more complex mechanism. Initially copper is oxidized to Cu(I) which, in the presence of carbon monoxide, turns to copper carbonyl, [CuCO]+ and dimethyl carbonate as final product.

Figure 1: Thermodynamic analysis
Figure 1 shows the thermodynamic analysis of dimethyl carbonate electro-synthesis. The catalysts found in green are selective towards dimethyl carbonate while the ones found in blue and orange are selective to dimethyl oxalate at lower potentials and require an overpotential for dimethyl carbonate production. The height of the datapoints determines the potential that needs to be applied in order to activate methanol as methoxy and to produce dimethyl carbonate on each of the catalysts.

References:


Direct CO\textsubscript{2} hydrogenation to methane over zeolite encapsulated nickel nanoparticles

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1. Introduction

Power-to-gas processes are promising strategies to store renewable energy. In particular, many studies have been devoted to the production of CH\textsubscript{4} by hydrogenation of CO\textsubscript{2}, which could be recovered from several industrial processes as well as from biogas facilities \cite{1,2}. While several noble metals, including Rh, Ru, Pt and Pd, are highly active for CO\textsubscript{2} hydrogenation to methane, supported Ni nanoparticles remain the most cost-efficient catalysts. For CO\textsubscript{2} methanation, which is a highly exothermic reaction operated at high temperatures, sintering of Ni nanoparticles has a large impact on the deactivation of the catalyst. Therefore, many researches have been devoted to obtain more active and stable Ni catalysts \cite{3}. Highly stable Ni catalysts have been obtained by optimising the three-dimensional distribution of nanoparticles in ordered mesoporous materials or by encapsulation of nanoparticles in porous inorganic frameworks. Based on our previous work \cite{4}, we present here a simple method for the preparation of encapsulated nickel nanoparticles in MFI zeolite materials. In this method, the synthesized zeolites are modified by a desilication process, which creates intraparticle voids and mesopores in order to facilitate the encapsulation of Ni nanoparticles upon simple impregnation and reduction.

2. Experimental

Conventional MFI zeolite is selective desilicated in an autoclave under hydrothermal conditions using a dilute aqueous solution of ammonium hydroxide and cetyl trimethylammonium bromide (CTAB). The desilicated zeolite is impregnated with an aqueous nickel solution. The prepared catalysts are characterized further by SEM, TEM, XRD, Nitrogen physisorption and XANES analysis. The catalytic activity for CO\textsubscript{2} methanation was tested in a standard fixed-bed reactor at 0.1 MPa using a ratio of H\textsubscript{2}/CO\textsubscript{2}=4 and a GHSV=60.000 ml/g catalyst h\textsuperscript{-1}.

3. Results and discussion

The TEM (figure 1) and XPS results confirm a significant part of the Ni nanoparticles are situated inside the desilicated zeolite while Ni particles agglomerate on the surface of conventional zeolite. Non-encapsulated Ni only resulted in 42% conversion and 40% selectivity at 450°C. The catalytic activity of encapsulated Ni was significantly higher and resulted in 57% conversion and 91% selectivity under the same conditions (figure 1).

![Figure 1](image.png)

**Figure 1.** Left: TEM image of Ni nanoparticles encapsulated in MFI zeolite. Right: Molar fraction of CH\textsubscript{4}, CO and CO\textsubscript{2} as function of the reaction temperature.

4. Conclusions

In conclusion, we have developed a simple and effective method to encapsulate Ni nanoparticles in MFI zeolite. The method is cost-effective, practical, and results in a narrow size distribution of small nanoparticles that are situated inside the zeolite crystals. Furthermore, we demonstrate that the encapsulated Ni nanoparticles are significantly more active for CO\textsubscript{2} hydrogenation to methane than the non-encapsulated Ni nanoparticles. The encapsulated Ni nanoparticles show no change in activity or selectivity after 50 h of operation.

References

Catalytic oxidation of NO to NO\(_2\) for nitric acid production over a supported Pt catalyst

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1. Introduction

Nitric acid is an important commodity chemical produced industrially via the Ostwald process. Oxidation of NO is an important chemical step in the process, carried out as a gas phase homogeneous reaction in a series of heat exchangers [1]. A catalyst can potentially speed up the process, enable significant heat recovery and reduce CAPEX. Despite the obvious advantages, several efforts have been made to find a suitable catalyst, but no catalyst effective under industrial conditions has been found. [1] On the other hand, catalytic oxidation of NO has been extensively studied with respect to treatment of diesel exhaust with concentrations typically varying from 100-1500 ppm NO and 0.1-30% O\(_2\). [2]

Herein we report the performance of supported platinum catalysts at industrial nitric acid plant conditions. A reaction mechanism was proposed based on observed kinetic parameters.

2. Experimental

1wt.% platinum catalysts supported on Al\(_2\)O\(_3\) and ZrO\(_2\) were prepared by incipient wetness impregnation. The catalysts were characterized by CO chemisorption, N\(_2\) adsorption, X-ray fluorescence and monitored in-situ using X-ray absorption spectroscopy (XAS) at the European Synchrotron Radiation Facility (ESRF, France).

Catalysts activity was investigated using a fixed-bed reactor (I.D 9mm) with an artificial feed (10% NO, 6% O\(_2\), 15% H\(_2\)O) at one bar partially simulating nitric acid plant conditions. Effect of temperature on the catalytic activity was investigated by ramping the temperature from 150 to 450 °C at a rate of 5 °C/min. For kinetic studies, the reactor was operated in differential mode by restricting NO conversion below 15%.

3. Results and discussion

Figure 1 shows the effect of temperature on the NO conversion over the Pt/Al\(_2\)O\(_3\) catalyst. The blank run shows the contribution from gas phase reactions decreasing with increasing temperatures, which is in accordance with the negative activation energy for NO oxidation.[3] At low temperatures, the conversion declines up to 250 °C with the same trend as for the gas phase reactions. Catalytic activity starts increasing at 250 °C and a maximum is achieved at 400 °C. The reaction becomes thermodynamically limited above 400 °C. Pt/ZrO\(_2\) had identical conversion curve as Pt/Al\(_2\)O\(_3\), but Pt/Al\(_2\)O\(_3\) has a higher TOF than ZrO\(_2\) which is in accordance with results reported for diesel exhaust conditions.[4]

The apparent activation energy was found to be 35kJ/mole for both catalysts. Forward reaction orders were extracted by varying feed concentration at 300 °C and found to be zero for NO and 0.5 for O\(_2\). Based on our finding of reaction orders a LHHW mechanism, shown in Scheme 1, is proposed explaining the experimental observations. Assuming desorption of NO\(_2\) as rate determining step and NO as most abundant reaction intermediate, the rate expression becomes \(r = k_1k_G (P_{O_2})^{0.5}\).

Using reference spectra, a linear combination fitting of EXAFS collected during in-situ NO oxidation on Pt/Al\(_2\)O\(_3\) and Pt/ZrO\(_2\) at 300 °C indicate that platinum is oxidized to a different degree depending on metal support interactions. On Al\(_2\)O\(_3\), Pt is present as 75% Pt(0) and 25% as PtO\(_2\) at steady-state.

4. Conclusions

Supported platinum catalysts possess significant activity capable of increasing NO oxidation rates in the nitric acid production above 250 °C.

References

Decentralized production of H₂O₂ using electrocatalysis

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1. Introduction

Hydrogen peroxide, H₂O₂, is a versatile and environmentally friendly oxidant with a wide range of applications, including pulp bleaching, chemical synthesis, and waste water treatment. At present, more than 95% of H₂O₂ is produced by large and centralized infrastructure using anthraquinone method. Electrochemical production of H₂O₂ using proton exchange membrane electrolyzer system is an attractive alternative. H₂O₂ can be produced in a decentralized facility only requiring O₂, water, and electricity.

2. Experimental

We discuss the influence of catalyst material, electrolyte pH, and mass transport at the mesoscopic scale on the electrochemical H₂O₂ production. A set of different catalysts was tested to demonstrate the effect of pH on the electrochemical H₂O₂ production using rotating ring disk electrode technique. Mass transport effect at the mesoscopic scale was studied using three different cell geometries: rotating ring disk electrode, catalyst coated electrode submerged in the electrolyte, and membrane electrode assembly.

3. Results and discussion

The efficiency of the electrochemical H₂O₂ production is largely controlled by the electrocatalysis at the cathode, where O₂ is reduced to H₂O₂ via 2 electron reduction. Electrode itself and electrolyte in vicinity are critical factors controlling the efficiency of H₂O₂ production. Electronic and geometric effects are two factors controlling electrocatalysis at the electrode surface. Electronic structure of the electrode tunes adsorption energies of reaction intermediates affecting the activity and the selectivity. Geometric arrangement of surface atoms also change the selectivity by providing isolated active sites. Three types of catalysts are discussed as promising candidates: Metal alloys, single-atom catalysts, and high surface area carbon materials. Electrolyte in vicinity also affects the activity and the selectivity via pH, and mesoscopic mass transport effect. Higher pH enables smaller overpotential, thus higher activity, but lowers selectivity in most cases. Mass transport effect at the mesoscopic scale is critical in determining the selectivity toward H₂O₂. Rotating ring disk electrode technique with faster mass transport condition provides an upper boundary for the selectivity towards H₂O₂, while more realistic conditions with slower mass transport tend to underperform, calling for more reliable model system to benchmark electrochemical H₂O₂ production.

4. Conclusions

Electrochemical production of useful chemicals will attract more attention as the renewable energies take over the conventional energy sources based on fossil fuels. H₂O₂ is an attractive commodity chemical, which will take advantage of decentralized production using electrochemical devices. Efficient catalysis at the surface is determined by electronic and geometric effects at the electrode. Often overlooked, the effect of electrolyte is also important where the activity and selectivity is largely dependent on the pH and the mass transport condition.

References
Impact of Reduction-Oxidation-Reduction Treatments on Supported Cobalt Catalysts

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1. Introduction

Production of chemicals and fuels from synthesis gas (a mixture of H₂ and CO) has received great interest as an alternative route to traditional oil-based processes [1]. Cobalt- or iron-based catalysts are applied in industry for the production of hydrocarbons from synthesis gas using the Fischer-Tropsch (FT) synthesis process. Cobalt-based catalysts show a high selectivity for long chain hydrocarbons, mainly diesel and waxes, particularly when supported on reducible oxides (e.g. TiO₂, Nb₂O₅) [2]. These oxides display strong metal-support interactions (SMSI) with various metals [3], occurring during activation treatments when the support is partially reduced and forms suboxides. Partial surface coverage with these suboxides is known to promote the intrinsic catalytic activity and selectivity towards C₅+ products [4]. On the other hand, a dense SMSI overlayer can block active sites. Therefore, careful tuning of the metal-support interaction offers the possibility of designing improved FT catalysts. To this end, we have investigated the effect of reduction-oxidation-reduction (ROR) treatments in cobalt FT catalysts supported on reducible and non-reducible metal oxides.

2. Experimental

Cobalt-based catalysts were prepared by incipient wetness impregnation method on reducible (TiO₂, Nb₂O₅) and non-reducible (α-Al₂O₃) supports. The samples were submitted to an ROR treatment (figure 1): first, reduction of supported-CoOₓ took place at 350 °C to obtain metallic cobalt, followed by oxidation at different temperatures: 50, 100, 200, 300 and 400 °C (RO-samples). Finally, prior to reaction or H₂-chemisorption measurements the samples were reduced again at 220 °C (ROR-samples). Catalysts were tested at industrially relevant FT conditions.

3. Results and discussion

Upon ROR, cobalt supported on reducible oxides showed an increase in H₂-uptake, reaching a maximum when oxidation was performed at 200 °C and subsequent reduction took place at 220 °C. STEM images and EDX mapping (figure 2) of RO-samples showed cobalt oxide hollow nanoparticles, which are explained by the Kirkendall effect. The hollow nanoparticles formation depended in this case on the temperature in which oxidation took place. The increase in H₂-uptake corresponded with a proportional increase in catalytic activity up to a factor of two. Therefore, more active sites of the same nature became available maintaining the promotional effect of the reducible supports. On the other hand, catalysts supported on non-reducible α-Al₂O₃ showed a decrease in metallic surface area for any ROR treatment, coinciding with somewhat lower catalytic activity. Hence, the increase in H₂-uptake and FT activity upon ROR was specific to catalysts supported on reducible oxides only. Selectivities towards C₅+ hydrocarbons were similar in all cases (85-89 wt.%). The formation of hollow cobalt oxide nanoparticles on reducible oxides is proposed to be instrumental in tuning the metal-support interaction in the related catalysts. Interestingly, the surface-specific activity remained constant upon ROR, indicating that the promoting effect of the reducible oxides was preserved with turnover frequencies of 0.10 and 0.06 s⁻¹ for Co/TiO₂ and Co/Nb₂O₅ respectively, and 0.02 s⁻¹ for Co/α-Al₂O₃.

4. Conclusions

Activity enhancement was achieved in cobalt-based catalysts by tuning the metal-support interaction via ROR treatments. Selecting the proper ROR treatment led to 100% increase of both H₂-uptake and FT activity for cobalt supported on reducible supports. This effect was not observed for the non-reducible support. The formation of hollow cobalt oxide nanoparticles seemed instrumental in tailoring the SMSI displayed by the reducible oxide supports. Overall, ROR provides a versatile tool to tune the interaction between these supports and metallic nanoparticles, increasing the accessible metal surface area and the catalytic activity.

References
Methane to Methanol over Cu-Zeolites: Establishing Structure-Activity Relationships

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1. Introduction

The conversion of CH4 to oxygenates bypassing the syngas route would constitute a feasible small-scale solution for CH4 utilization. Cu-zeolites have exhibited the ability to convert CH4 to CH3OH through a chemical looping process. Oxygen activated Cu-zeolites contain species capable to activate the C-H bond and stabilize the resulting intermediates, which are finally hydrolyzed to CH3OH. Different frameworks including CHA1, MOR2,3 and MFI3 have been reported to be active in the conversion. However, differences in the performance as well as in the Cu speciation are observed. Herein by employing activity measurements and operando/in situ characterization techniques we try to establish structure-activity relationships aiming to rationalize the Cu-zeolites performance.

2. Experimental

The performance of Cu-zeolites in conversion of CH4 to CH3OH was measured in a fixed bed reactor following a stepwise protocol.1 X-Ray Absorption Spectroscopy (XAS) measurements were conducted at BM23 and BM26 beamlines of the ESRF.

3. Results and discussion

Cu-CHA zeolites with different compositional characteristics in terms of Cu/Al and Si/Al ratio have been evaluated for the stepwise CH4 to CH3OH conversion under identical conditions. Intermediate Si/Al ratio appears to be beneficial for the productivity (Figure 1a). In order to access the properties of Cu ions in the zeolite we employed in situ XAS. Figure 2b shows the XANES spectra obtained after He-activation at 500 °C. High temperature along with inert atmosphere drives the so-called self-reduction of CuII to CuI probing the reducibility potential of the samples. Indeed from the spectra we observe the differences in the 1s→4p transition peak of CuI ions at 8982.5 eV. Utilizing linear combination fitting with theoretical XANES spectra of pure Cu-species from our previous study1 as references, we obtain the relative fraction of ZCuI which have been identified as the precursors of O2 activated species.1 Plotting this relative fraction of ZCuI after He-activation at 500 °C against the productivity in molCH3OH/molCu we observe a linear trend among the samples. This particular trend links the reducibility of the Cu-CHA to the performance of the materials.

4. Conclusions

In this contribution we establish structure-activity relationships that assist in the performance rationalization of Cu-zeolites for the CH4 to CH3OH conversion. We show that for frameworks possessing multiple Cu locations like CHA the reducibility is a key aspect since it provides the precursor species to the active sites. Such work can provide a framework for rational design of Cu-zeolites for the CH4 conversion as well as additional applications.

References
Effect of the Nature of Metal Nanoparticles on the Photocatalytic Degradation of Rhodamine B

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1. Introduction
Toxic waste triggered by different types of dyes (e.g. Rhodamine B) is considered to be one of the most crucial problems that facing our environment. Dyes are generally used in numerous industrial areas such as paper, drugs, electronics, cosmetics and textile. For instance, the wastewaters released from textile industries contains highly concentrated organic compounds is a major concern because are hazardous chemical, non-biodegradable, showing high resistance against chemical and physical reactions [1]. Thus, there is a need to remove such organic compounds from wastewater before discharging them to receiving water. Removal of such colored organic compounds can be obtained using various physical and chemical methods such as coagulation, adsorption, and chemical oxidation. However, these treatment methods are found to have several disadvantages as they are non-destructive, expensive and unfriendly route process since transferring the organic compounds in wastewater to sludge leads to another type of waste. Interestingly, supported metal nanoparticles (MNP) photocatalysis is provided active sites that are more efficient in order to improve the photocatalytic degradation of dyes [2]. Therefore, the present work is to investigate the effect of the nature of MNP on the photocatalytic degradation of Rhodamine B using TiO$_2$ as carrier.

2. Experimental
Catalysts were prepared using wet impregnation method. Acetone solution of metal acetylacetonate (Macac = Pt, Pd and Ru) in an appropriate amount to get 1wt% of metal content was used to impregnate to TiO$_2$ (DTS). The suspension mixture was then evaporated overnight at RT. The resulting solid was treated in a stream of 10 vol. % H$_2$ in Ar at 200 °C for 2h to yield 1.0 wt%M@DTS. Catalysts were characterized ICP, $N_2$ physisorption, XRD, HR-TEM, Solid-state UV-Vis. The photocatalytic experiments were performed in a glass beaker containing 100 ml, 20 mgL$^{-1}$ of RB solution and 100 mg of photocatalyst sample, using Luzchem Photoreactor. The reaction mixture was irradiated by 365-nm UV light at a power of 54.3 W/m$^2$. Absorbance was recorded at $\lambda_{max}$ of 554 nm using the UV/Vis/NIR spectrophotometer.

3. Results and discussion
ICP analysis confirmed the loading of M@DTS and found their values comparable to the nominal values. BET surface areas of M@DTS catalysts are varied in the range from 100 to 110 m$^2$/g. XRD results showed the presence of anatase phase of TiO$_2$ but no crystalline metal was observed in these solids, probably they are finely dispersed on the surface of the supports. TEM images of catalysts showed a homogenous metal dispersion with average particle size ranging from 1 to 5 nm. In term of photocatalytic activity, the degradation of RB in aqueous medium using different type of metal photocatalysts supported on DTS were found to be depended on the nature of metal, as evidenced by the degradation plot in Figure 1. As we can observe from the Fig. 1 that the reaction showed somehow limited photocatalytic activity using the titanium alone, whereas the photodegradation process was significantly enhanced by the presence of metal nanoparticles on the surface of DTS. The RB degradation of ~98% efficiency was obtained using Pt nanoparticles over DTS at less than 20 minutes of reaction and the degradation efficiency was constant afterwards with increasing reaction time. However, the RB photodegradation reactions over Pd/DTS showed less activity with degrading ~98% of RB dye in 40 minutes.

4. Conclusions
Supported different metal particles were successfully and their photocatalytic performance toward RB degradation was reported. The photodegradation activity were ordered as Pt/DTS > Pd/DTS > Ru/DTS > DTS. Such discovery obviously show the key role of the nature of metal particles in the photocatalytic degradation of RB dye under UV A light irradiation.

References
Mn-promotion of alumina-supported cobalt Fischer-Tropsch catalysts

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1. Introduction

The Fischer-Tropsch synthesis (FTS) is an important tool for converting syngas to hydrocarbons. Cobalt is the chosen active metal for hydrogen-rich systems (e.g. syngas produced from natural gas), and when middle distillates (fuels) are the desired products. FTS is also a source to chemical intermediates such as light olefins [1-3]. Promotion by manganese is reported to enhance the selectivity to light olefins, both for cobalt and iron-based catalysts [2], but the reported effects of Mn promotion on cobalt-based catalysts varies a lot [4]. In this contribution we present a study of the effect of Mn on an alumina-supported cobalt FTS catalyst, using both experimental and theoretical tools to investigate the role of the promoter.

2. Experimental

Catalysts were prepared using incipient wetness impregnation, either sequential or co-impregnation of the components. The catalyst activity and selectivity were investigated at industrially relevant conditions, and the catalysts were characterized using a range of techniques, including TPR, XRD, XPS, XANES and hydrogen chemisorption. Steady State Isotopic Transient Kinetic (SSITKA) experiments were performed in order to explore surface coverages and intrinsic activities. DFT calculations were done using the Vienna ab initio simulation package (VASP) code [5,6]. For details of the procedures see [4,7].

3. Results and discussion

Figure 1 shows the specific activity and olefin selectivity of the samples. Mn promotion enhances the specific activity, here reported as site-time yields, and as expected also influences the selectivity. As expected, the selectivity to light olefins is clearly enhanced, and this is accompanied by an increase in the C5+-selectivity and a reduction in the selectivity to methane. The promotion effect of Mn is independent of preparation route. The catalysts undergo a restructuring during the reduction treatment, following which the catalytically relevant part of the surface is saturated with Mn. Mn inhibits Co reduction, and the observed differences in the Co-specific activity is probably due to a varying degree Co reduction, caused by a varying degree of Mn incorporation in the Co-oxide particles. A range of Co-Mn mixed oxides are possible, and the XRD pattern show a broad contribution from Mn compounds during reduction, but the concentrations were not high enough to allow differentiation between these with XANES. The catalyst also contains larger Mn particles, not associated with Co, indicating that Mn is in excess in these samples. DFT calculations were used to investigate the effect of a MnO overlayer on a Co(111) surface on the adsorption properties. A clear effect of Mn was only found on sites close to the MnO-covered atoms (interface sites), demonstrating a short-range effect of Mn. The adsorption energies of CO, C and O were found to increase significantly (0.1 - 0.3 eV), while the adsorption energies of H and hydrogenated carbons were decreased by the same amount. Initial studies of the influence of MnO on the FT reactions indicate that MnO favours CO dissociation, both through reducing the activation barrier for CO dissociation, and through increasing the stability of the dissociated state.

References

Modeling of the Molybdenum Loss in Iron Molybdate Catalyst Pellets used for Selective Oxidation of Methanol to Formaldehyde

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1. Introduction
Formaldehyde (CH₂O) may be synthesized industrially by selective oxidation of methanol over an iron-molybdate (Fe-Mo) oxide catalyst, known as the Formox process [1]. The fresh catalyst consists of a mixture of Fe₂(MoO₄)₃ and MoO₃. Fe₂(MoO₄)₃ is the active phase and excess MoO₃ must be present to form a surface layer of MoOₓ and make the pellets mechanically stronger. However, under the reaction conditions molybdenum oxide forms volatile species with methanol in the feed gas and migrates through the catalyst bed. The volatile molybdenum species decompose and accumulate downstream in the reactor bed leading to pressure drop build-up and finally plant shutdown. The volatility of the Mo in the catalyst and pressure drop build-up in the industrial reactor is the main reason for the short lifetime of only 1–2 years [2]. In this work the rate of volatilization of Mo from industrial catalyst pellets has been studied as a function of operating conditions and a single pellet model that take the relevant phenomena into account has been developed.

2. Experimental
The molybdenum loss of industrial iron molybdate catalyst pellets (atomic Mo/Fe ≈ 2.6, OD = 4.5 mm, hole diameter 1.7 mm) was investigated using a multitube reactor (ID = 6.5 mm) each exposing a single catalyst pellet. Each cylindrical pellet was placed on the tip of a thermocouple and centered in the middle of the reactor. The feed gas consisted of 4.4 vol.% MeOH and 10 vol.% O₂ in N₂ with a flow of 3 NL/min. Pellets were tested at varying temperatures (250, 300 and 350 °C) and varying time on stream (up to 240 hours). The pellets were recovered after each experiment and cut through the middle. The cross-sections of the pellets were characterized by SEM-EDX for concentration profiles and area analyses, and Mo/Fe elemental ratios were determined.

3. Results and discussion
Figure 1 (Left) shows a SEM image of the cross-section of a catalyst pellet after 70 hours on stream. The bulk of the pellet is light gray indicating a composition similar to the fresh catalyst with excess MoO₃ present. However, a dark gray layer 120 µm thick at the pellet surface indicates a depletion of the excess MoO₃, leaving only the Fe₂(MoO₄)₃ phase present (Mo/Fe = 1.5) at the outer layer of the pellet. To model the influence of operating conditions on the rate of Mo loss, a dynamic 1D model for a single pellet in which methanol oxidation to formaldehyde and simultaneous Mo volatilization takes place was developed and validated. The model considers the diffusion and oxidation of methanol, the reversible volatilization reaction between molybdenum and methanol, and the diffusion of the volatile molybdenum species through the pellet. The model calculates the loss of Mo as a function of radial position as a function of time on stream and reaction conditions. Figure 1 (Right) shows the model prediction of the Mo/Fe ratio in the pellet after 70 hours on stream. At the surface of the pellet a decreasing Mo/Fe ratio is predicted corresponding to the experimentally measured depletion layer thickness.

4. Conclusions
The influence of temperature and time on stream on the molybdenum loss in iron molybdate pellets under reaction conditions was investigated experimentally. The volatilization and diffusion of molybdenum leads to a depletion layer evolving from the surface of the catalyst pellet. A dynamic single particle model was developed which calculates the Mo concentration as a function of radial position in the cylindrical catalyst pellets as function of time. The model is in good agreement with the experimental data.

References
Poster abstracts
Selective hydrodeoxygenation of alkyl lactates to alkyl propionates with Fe-based bimetallic supported catalysts

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1. Introduction
Lactic acid is a bio-platform chemical derived from glucose, which can be produced by fermentative or alternative chemo-catalytic processes [1]. Lactic acid/alkyl lactates are important feedstocks to make biodegradable polylactide (PLA) plastics, but can also serve as feedstocks for producing precursors (e.g., methyl propionate, MP) for existing large-volume acrylic plastics such as the thermoplastic poly(methyl methacrylate) (PMMA, Plexiglas). Preferentially, MP is made for PMMA production by methoxycarbonylation of ethylene with CO gas in methanol using a Pd-based homogeneous catalyst in a batch process [2]. Drawbacks of this process are cautious handling of reactant (e.g., poisonous CO gas, expensive metal complex, reactive ligands) as well as tedious catalyst recovery and recycling. Here, a new and highly selective route to make alkyl propionates by efficient hydrodeoxygenation (HDO) of alkyl lactates with cheap and reusable heterogeneous base metal catalysts are reported (Scheme 1) [3].

2. Experimental
Catalysts were prepared by wetness impregnation using aq. solutions of various metal precursors and metal oxide supports followed by drying (110 °C, 4 h) and calcination in air (450 °C, ramp 3 °C/min, 4 h). All catalysts were characterization by standard H₂-TPR, XRPD, TEM and XPS methods. HDO of alkyl lactates was performed in SS Parr reactors (50 ml) using, typically: Alkyl lactate (2 mmol), catalyst (100 mg; pre-reduced at 300 °C for 3 h with 10 % H₂/N₂, 50 ml/min), alcohol (8 g), 50 bar H₂, 220 °C, 12 h. Products were quantified by GC-FID/GC-MS analysis using naphthalene as internal standard.

3. Results and discussion
HDO of methyl lactate provided unprecedented high yield of 77% MP with Fe-Ni/ZrO₂ in methanol with both Ni and the support behaving as activity promoters, while comparable MP yields using precious metal/ZrO₂ catalyst was only 20-55%. The Fe-Ni/ZrO₂ catalyst proved highly durable for MP formation in five consecutive HDO reactions loosing no activity. Moreover, the catalyst also efficiently catalyzed HDO of other short chain alkyl lactates to the corresponding alkyl propionates in high yields (~70%), and demonstrated to be generally applicable for HDO of other compounds with α-hydroxyl groups, thereby making the system highly interesting for biomass valorization.

4. Conclusions
The supported base metal catalyst Fe-Ni/ZrO₂ is a versatile, selective and efficient catalyst for HDO and transfer hydrogenation of alkyl lactates to the corresponding alkyl propionates in the respective alcohols. The HDO route provides a new, attractive approach to make bio-methacrylate ester precursors from lignocellulosic sugars.

Acknowledgements
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References
Promotors in the restructuring of Ethylene Epoxidation catalysts

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1. Introduction

The epoxidation of ethylene towards ethylene oxide (EO) is a major industrial chemical process with an annual production of ca. 34.5 million tons per year. [1] Industrially, EO is being produced with a selectivity of 90% using an Ag/α-Al₂O₃ catalyst with added solid promotors such as Cs and Re, additionally a gaseous organochloride promoter is added on-stream. As CO₂ is one of the side products, the EO process is also one of the biggest producers of CO₂ in the chemical industry. Additionally, as the catalysts deactivates, often the operating temperature is increased to maintain a sufficient conversion, which decreases the selectivity leading to an additional production of CO₂. Therefore, improving the process in terms of selectivity and catalyst life time are of great societal and commercial interest. In general, a better insight in the deactivation mechanism of heterogeneous catalysts is of utmost importance. Here, we systematically investigate the influence of Cl and Cs promotors on the catalyst structure and catalytic performance. Additionally we investigate the underlying deactivation mechanisms in the ethylene epoxidation.

2. Experimental

A 10wt% Ag/α-Al₂O₃ and a series of Ag-Cs/α-Al₂O₃ catalyst were synthesized by impregnating the support with a silver oxalate - ethylene diamine solution. After drying, the catalysts precursor was heated to 275 °C in a O₂ and He flow for 4 h. The synthesized catalysts were evaluated in a plug-flow reactor heated to 225 °C in 5% C₂H₄ and 10% O₂ balanced by Helium at 20 bar, optionally 1 ppm of vinyl chloride was added on-stream. Samples where characterized using HAADF-STEM, STEM-Tomography, XRD, XPS and O₂-desorption.

3. Results and discussion

Three different systems where reviewed; Ag/α-Al₂O₃ (without any promotors, Figure 1a), Ag/α-Al₂O₃+Cl (vinyl chloride added on-stream) and Ag-Cs/α-Al₂O₃+Cl. In the Ag-only system, during the epoxidation, the 100 nm sized Ag particles increased their size towards 170 nm after 60 h of reaction. Additionally, the silver particles developed pores with an average diameter of ~20 nm (Figure 1b). Using STEM-Tomography, the location of the pores in the particles was determined, showing that the pores not only appear on the surface but also are present within the bulk of the particle. The formation of the pores appear to be linked to the grain boundaries present in the silver particle. We propose a crucial role of the grain-boundsaries within the particles, facilitating oxygen diffusion into the sub-surface, one of the most selective oxygen species. [2] Moreover, it was found that upon addition of vinyl chloride on-stream to increase EO selectivity, the porosity of the silver particles decreased. Remarkably, also the size of the particles decreased and the size distribution was narrowed (Figure 1c). Highlighting the dynamic behavior of the silver particles during catalysis. With Cs added to the catalyst, it seems that particle size growth was faster and more severe. Analyzing the size distribution showed that within the first few hours of the reaction a substantial fraction of smaller particles appeared and simultaneously larger particles where observed. This proves that Cs promotes Ostwald ripening as underlying deactivation mechanism.

4. Conclusions

We show that silver catalysts dynamically restructure during the ethylene epoxidation and that the structure changes as function of reaction environment. Additionally, using different catalysts and analysis of particle size as function of time-on-stream we reveal the Ostwald ripening is the dominating particle growth mechanism for industrial epoxidation catalyst.

References

Synthesis and reuse of nickel-based catalysts for upgrading of pyrolysis oil
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1. Introduction
The fast pyrolysis of residual biomass is a renewable alternative for fuels and chemicals production [1]. The resulting bio-oil generally has high acidity, high water concentration and high oxygen concentration. These properties need to be improved for the substitution of fossil-based materials [2]. In this context, the hydrotreatment performed at high temperatures and hydrogen pressure in the presence of metallic catalysts can be applied mainly for oxygen reduction [3]. A variety of catalysts have already been tested; however, problems related to stability, poisoning, and selectivity have not yet been completely solved [4]. In this way, the synthesis and evaluation of new catalysts becomes necessary in addition to the evaluation in cycles of hydrotreatment-regeneration.

2. Experimental
Four nickel catalysts (Ni/SiO2, Ni/ZrO2, NiCu/SiO2 and NiCu/ZrO2) were synthesized by the wet impregnation technique. The nickel concentration in the monometallic catalysts was 8.6 wt.% [5] whereas in the bimetallic catalysts was 28 wt.% Ni and 3.5 wt.% Cu [6]. The reactions were conducted in a 200 mL autoclave (325 °C, 80 bar of H2, 2 h reaction). 50 g of beech wood bio-oil (BWBO) and 2.5 g of catalysts were used. The final products (gas, aqueous phase, upgraded oil and spent catalyst + solids) were deeply characterized in terms elemental analysis, pH and water content. The catalyst with the best performance was selected and used in cycles of hydrotreatment-regeneration (calcination at 450 °C, 4 h and reduction at 3 L/min at 25% H2/N2).

3. Results and discussion
More than half of the products obtained is composed by upgraded oil, especially to the Ni/SiO2 catalyst (49.3 wt.%) (Fig.1). The carbon concentration increased in the upgraded oils as well as a significant reduction in the oxygen concentration is observed, especially for the Ni/SiO2 catalyst (Table 1). For that reason this catalyst was selected for further cycles of hydrotreatment-regeneration. Along the regeneration cycles, the carbon content is slightly reduced and the oxygen concentration is slightly decreased.

4. Conclusions
In this work four catalysts were synthesized and evaluated in the bio-oil hydrotreatment reactions. Among all the catalysts, Ni/SiO2 showed the best performance, resulting in higher yields of upgraded oil, lower concentration of oxygen, higher carbon content and lower water concentration. The reuse showed that even after the third cycle the catalyst was able to significant reduce the oxygen content of the upgraded oil.

Table 1. Upgraded oils physicochemical properties (dry basis)

| Table 1. Upgraded oils physicochemical properties (dry basis) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | C (wt.%)        | H (wt.%)        | O (wt.%)        | pH              |
| BWBO            | 57.31           | 6.82            | 35.84           | 26.77           |
| Ni/SiO2         | 73.1            | 8.4             | 17.8            | 3.5             |
| Ni/ZrO2         | 72.2            | 8.25            | 19.4            | 3.0             |
| NiCu/SiO2       | 72.3            | 8.5             | 19.0            | 3.3             |
| NiCu/ZrO2       | 72.1            | 8.5             | 20.3            | 3.2             |

Figure 1. Mass Balance

Cycles of hydrotreatment-regeneration of Ni/SiO2:

<table>
<thead>
<tr>
<th>Cycle</th>
<th>C (wt.%)</th>
<th>H (wt.%)</th>
<th>O (wt.%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>73.5</td>
<td>8.2</td>
<td>17.7</td>
<td>2.8</td>
</tr>
<tr>
<td>2nd</td>
<td>72.3</td>
<td>8.5</td>
<td>19.0</td>
<td>3.5</td>
</tr>
<tr>
<td>3rd</td>
<td>72.1</td>
<td>8.5</td>
<td>20.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

References
In situ microscopy of formation of nickel-based bimetallic nanoparticles

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1. Introduction
Nickel based catalysts are well-known heterogeneous catalysts for hydrogenation and reforming reactions. Furthermore, nickel is a good and less expensive alternative to much less abundant materials such as palladium and platinum active for similar reactions. As nickel based catalysts may change their morphology and catalytic performance with respect to the environment, it is essential for the fundamental understanding to investigate the materials under conditions similar to conditions applied during the catalyst lifecycle e.g. calcination, nanoparticle (NP) formation, and catalytic reaction conditions. This study will focus on the NP formation process of Ni-M (M=Cu[1], Ga[2], and Fe[3]) alloys. The important NP characteristics e.g. crystal structure, morphology, uniformity, and size are investigated for Ni-M (M=Cu, Ga, and Fe) alloys. The characteristics are monitored on the single NP scale as well as over an ensemble of NPs in the same sample. Furthermore, the NP formation process in an intermetallic Ni-M system (M=Ga and Fe) is compared to a substitutional alloy (M=Cu) regarding especially crystal phase composition and purity.

2. Experimental
The studied material systems were synthesized by incipient wetness impregnation method using aqueous solutions of metal nitrate salts as precursor. In the case of NiFe system the impregnation was further developed by using glycerol as solvent. Dedicated complementary techniques were applied to investigate the material systems. In situ X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) were used to follow the average catalyst’s structural and electronic changes during formation and reaction conditions[1]. High resolution environmental TEM (ETEM) was used to follow the dynamics of the catalysts on the nanoscale (sintering, crystallinity)[1]. Spatially resolved information on the meso scale (50 nm–1 µm) was obtained by X-ray microscopy[4].

3. Results and discussion
At high Ni contents, Cu-Ni samples predominantly form a homogeneous solid solution of Cu and Ni. At lower Ni contents Cu and Ni are partly segregated and form metallic Cu and Cu-Ni alloy phases. For the Ni-Ga system, highly dispersed Ni(II) nanocrystallites serve as centres for further reduction of the nickel and gallium oxides and metallic gallium is incorporated into the nickel crystal lattice to form an intermetallic phase (Fig. 1). SEM-EDX and X-ray micro tomography confirmed even distribution of the active Fe-Ni phase throughout the entire volume of the catalyst (Fig. 2). By use of TEM Fe and Ni alloyed nanoparticles with approximately 5 nm were measured.

4. Conclusions
This study illustrates how the formation of NP in Ni-based catalyst have been investigated by in situ diffraction, imaging and spectroscopic methods. The phase purity of the Ni-based NPs in an entire ensemble depends highly on the Ni-M ratio and the complexity of the phase diagram. The results clearly underlined the need for complementary techniques and highlight the potential of these for application in catalysis.

References
Probing the coordination of metal centers in zeolites by in-situ EPR-spectroscopy

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1. Introduction
Copper exchanged zeolites are active for the selective catalytic reduction (SCR) of nitrogen oxides with ammonia [1]. Recently small-pore zeolites and zeotypes with the CHA framework topology has attracted much attention and has been commercialized for use in the abatement of NOx in diesel exhaust due to favorable properties such as high stability towards hydrothermal ageing and high resistance towards the presence of hydrocarbons[2].

2. Experimental
Cu²⁺ ion-exchanged zeolites were placed inside a quartz tube and positioned in the resonance cavity. Gas lines were connected allowing for a variety of gas mixtures to flow through the sample. A heater was connected facilitating EPR measurements at different reaction conditions with different gas flows. Thus, it was possible to probe the change in coordination environment of the Cu-species under varying reaction conditions.

3. Results and discussion
Electron paramagnetic resonance spectroscopy (EPR) is very sensitive towards paramagnetic Cu²⁺ and offers the possibility for both quantification and speciation of Cu²⁺ sites with unrivalled sensitivity [3]. Recent results obtained on Cu-CHA show that the elucidation of the different copper species is possible using EPR by exposing the Cu-CHA to different gas mixtures [3,4]. In this way, the Cu exchange sites can be used as a probe to investigate the local microenvironment of the zeolite framework and to distinguish between different local configurations of aluminium.

In this work, the primary focus was zeolites with the CHA structure and the samples were exposed to varying concentrations of gaseous NH₃, NO and O₂ or mixtures thereof in balance He. In these materials, Cu²⁺ is located in at least to distinct sites, giving rise to the blue spectrum illustrated in Figure 1. Two sets of quadruple lines are visible in the parallel region of the spectrum and are assigned to Cu²⁺ in 6-membered rings coordinating to oxygen in the zeolite framework. The difference observed in the parallel spin Hamiltonian parameters are caused by the difference of local aluminium configuration, i.e. two Al-sites (site A and site B) located in para- and meta-positions in the 6-membered ring. The samples were investigated in NH₃-TPD like conditions to investigate the role of NH₃ in the SCR reaction and to probe the interaction between ammonia and copper in the zeolite framework. The exposure to ammonia at low temperatures gives rise to a significant change in the EPR spectrum as seen in the red spectrum in Figure 1. The parameters of the red spectrum is most likely caused by a Cu[NH₃]₄²⁺ species, which is loosely contained within the CHA cage, possibly restricted by electrostatic attraction to the negative Al tetrahedral sites of the framework.

4. Conclusions
The use of EPR to probe the Cu-sites in small pore zeolites open the possibility for a deeper understanding of the catalytic mechanism of the SCR reaction at low temperature. This in-turn, may give rise to the possibility of designing catalyst with specific metal sites that are highly active for catalytic processes.

References

Figure 1. EPR-spectra obtained in He flow after exposure to oxidizing mixture of NO and O₂ (blue) and after exposure to NH₃ (red).
Effect of support acidity on the hydrodeoxygenation (HDO) activity of lignin derived bio-oil model compounds

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1. Introduction
Substantial research focus has been devoted to lignin and lignin derived feedstocks (e.g. black liquor from the pulp and paper industry) to make useful chemicals and fuels [1]. Raw oils from such feedstocks are usually a mixture of mono/di/tri-lignols having large molecular weight compounds with residual C-C and C-O linkages from the original lignin structure including β-O-4, α-O-4, 4-O-5, β-5, β-β etc. in the higher lignols [1]. Hence an efficient upgrading process must achieve simultaneous breakdown of these linkages (depolymerization) and subsequent deoxygenation with a robust catalyst to produce stable and quality bio-fuels by HDO. In this study, we aimed to understand the influence of support acidity of NiMo based catalysts on the HDO activity of typical lignin linkages present in bio-oil.

2. Experimental
A set of Ni and Mo containing catalysts have been prepared by a wet impregnation process using pre-calcined γ-alumina and ultra-stable-Y as the support materials. Ammonium molybdate tetrahydrate and nickel (II) nitrate hexahydrate were used for the impregnation of Mo and Ni respectively. The resulting catalysts, after drying, were calcined at 450 °C for 2 hours. About 500 mg of the catalyst was sulfided using DMDS at 340 °C and 25 bar of hydrogen. The liquid feed consisting of 5 mol % benzyl phenyl ether, BPE (representative of α-O-4 lignin linkage) in dodecane was used for the investigation. The reaction conditions were maintained at 320 °C, and 50 bar of H2 with a stirring rate of 1000 rpm.

3. Results and discussion
Textural properties (Table 1) indicate that surface area of the mixed support (alumina-USY) catalysts increases notably. Ethyl amine (C2H5NH2) temperature programmed desorption data (Table 1) shows the increasing trend of the Bronsted acidity of the zeolite containing catalysts with the varying amount of USY zeolite. During TPD, ethylamine adsors on a Bronsted acid site of the catalyst where proton (H+) transfer occurs which then undergoes the Hoffman elimination reaction to give ethylene and ammonia at higher temperatures [2].

Table 1. Composition and textural properties of the synthesized catalyst.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition, (%)</th>
<th>Surface area (m2/g)</th>
<th>Bronsted acidity, μmol/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/γ-Al2O3</td>
<td>15Mo, 5Ni, 80γ-Al2O3</td>
<td>142.9</td>
<td>264.1</td>
</tr>
<tr>
<td>NiMo/γ-Al2O3-USY</td>
<td>15Mo, 5Ni, 55γ-Al2O3, 25USY</td>
<td>185</td>
<td>312.2</td>
</tr>
<tr>
<td>NiMo-USY</td>
<td>15Mo, 5Ni, 80USY</td>
<td>762.6</td>
<td>401.4</td>
</tr>
</tbody>
</table>

Figure 1 presents the progress of the reaction. BPE becomes completely converted after about 4 h of reaction. With the Y-zeolite based catalysts, cleavage of the ether linkage (aliphatic C-O) in BPE is faster in yielding phenol and toluene. Phenol undergoes direct deoxygenation on the sulfided catalyst to produce benzene which is further hydrogenated to yield cyclohexane. Interestingly, sulfided NiMo/USY selectively yields benzene and monoaromatics (including cresols). The eventual phenolic conversion occurs quite slowly for all the catalysts. However, these preliminary results suggest possibilities for tuning of the catalyst.

4. Conclusions
Activity tests with the catalysts show that BPE, can predominantly be converted to fuel additives toluene and cyclohexane after 6h of reaction in the batch reactor. The intermediate phenol conversion occurred quite slowly. Further measures are being investigated to substantially improve the conversion of phenolics.

References
Effect of rosin acid on hydrodeoxygenation of fatty acid

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1. Introduction

Tall oil is derived from renewable non-edible woody biomass and has been recognized as a suitable feedstock to produce renewable diesel via hydrodeoxygenation (HDO) process. The commercial types of tall oil feedstocks such as crude tall oil (CTO), tall oil fatty acid (TOFA), tall oil rosin acid (TOR) and distilled tall oil (DTO) mainly contain long chain mono carboxylic fatty acid and tri-ring abietic type rosin acids [1]. During HDO, the oxygen atoms are removed and paraffinic diesel like hydrocarbons are produced. The HDO of fatty acids has broadly been studied in literature. However, only very few studies address HDO of rosin acids, and also to our knowledge, there are no studies in literature investigating the effect of rosin acids on HDO of fatty acids. In this study, we show the possible inhibiting effect of abietic acid on HDO of oleic acid.

2. Experimental

An alumina supported bimetallic NiMo catalyst was synthesized via an impregnation method and sulfided in a sulfur and hydrogen atmosphere which is described elsewhere [2]. The HDO experiments were performed in a batch reactor starting with 10 wt.% reactant (with different concentrations of abietic and oleic acid) mixed with 90 wt.% dodecane (solvent). The HDO experiments were started at 320°C under 54-56 bar H₂ pressure. After completion of each HDO experiment, the catalyst was recovered from the reactant mixture and further analyzed by temperature programmed oxidation (TPO) and elemental microanalysis.

3. Results and discussion

Figure 1 presents the effect of abietic acid (AA) concentration on the rate of fatty acid (FA) oxygenate conversion. The rate of the FA oxygenate conversion for the feed containing only oleic acid (OA) was the highest compared to other feeds. Moreover, the increase in the start concentration of abietic acid in the feed decreased the rate of FA oxygenate conversion. The inhibiting effect of abietic acid on HDO of oleic acid was also confirmed from the experiments done with a higher catalyst/feed ratio. However, it was observed that the rate of oxygenate conversion of rosin acid was not affected by the concentration of fatty acids. The carbon content and textural property of the recovered catalysts were measured (Table 1). The results in Table 1 shows that the carbon content of the recovered catalysts increased with an increase in the concentration of abietic acid in feed. Further investigation of the TPO results (not shown here) also revealed that compared to oleic acid, abietic acid produced greater quantities of deposited carbon with a higher temperature stability.

4. Conclusions

The observed inhibiting effect of abietic acid on HDO of oleic acid is possibly due to the strong adsorption of bulkier abietic acid molecules that may have sterically hindered the adsorption of fatty acid molecules. Furthermore, abietic acid produced higher amounts of deposited carbon with higher temperature stability that contribute to catalyst deactivation.

Table 1. Carbon content and textural property of recovered catalysts.

<table>
<thead>
<tr>
<th>Feed from which catalyst recovered</th>
<th>C (wt.%)</th>
<th>BET (m²/g)</th>
<th>Average pore size (Å)</th>
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<tbody>
<tr>
<td>10% OA</td>
<td>0.98</td>
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<td>65.2</td>
</tr>
<tr>
<td>9.5% OA+0.5% AA</td>
<td>1.32</td>
<td>125.6</td>
<td>64.9</td>
</tr>
<tr>
<td>9% OA+1% AA</td>
<td>1.56</td>
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<tr>
<td>8.5% OA+1.5% AA</td>
<td>1.94</td>
<td>118.1</td>
<td>61.5</td>
</tr>
</tbody>
</table>

References

Amorphous silica-alumina Catalyst Support Materials with Tailored Density of Acidic Sites

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Amorphous silica-aluminas (ASA) are the support material of choice for a number of heterogeneously catalyzed reactions in refining [1], fine chemicals production [2] and biomass conversion [3]. The purpose of this work was to develop tailored silica alumina supports in order to address the specific need of any of the catalytic applications named above. The preparation procedures were always based on the SASOL alkoxide-based sol-gel process, depicted in the figure below and fully described in the literature [4]).

Modifications of this process have led to a new series of materials named SIRAL/SIRALOX MPV, which differs from the state of the art versions (SIRAL, SIRALOX /SIRAL HPV, SIRALOX HPV) by a significantly higher concentration of Brønsted and Lewis acidic sites. This originates from a high level of phase homogeneity along with increased loose bulk density. The optimized volume based concentration of acidic sites make this series a promising candidate for applications in which the catalytic performance is limited by the reactor volume.

Properties of materials with 20% SiO$_2$ and 40% SiO$_2$ are listed in Table 1 and 2 below.
### Variations of Siral 20

<table>
<thead>
<tr>
<th>Typical Properties</th>
<th>SIRAL 20</th>
<th>SIRAL 20</th>
<th>SIRAL 20</th>
<th>SIRAL 20</th>
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<tbody>
<tr>
<td>Al₂O₃ : SiO₂</td>
<td>Std.</td>
<td>MPV-1</td>
<td>MPV-2</td>
<td>HPV</td>
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<td>%</td>
<td>80:20</td>
<td>80:20</td>
<td>80:20</td>
<td>80:20</td>
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<tr>
<td>Loose bulk density</td>
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<td></td>
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<td>560</td>
<td>330</td>
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<td>524</td>
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<tr>
<td>Pore Volume*</td>
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</tr>
<tr>
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<td>0.9</td>
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<tr>
<td>Acidity</td>
<td>ml NH₃/g</td>
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<td>18</td>
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<td>13.4</td>
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### Variations of Siral 40

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<td>Std.</td>
<td>MPV-1</td>
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<tr>
<td>%</td>
<td>60:40</td>
<td>60:40</td>
<td>60:40</td>
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<tr>
<td>Loose bulk density</td>
<td>g/l</td>
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<tr>
<td></td>
<td>320</td>
<td>450</td>
<td>360</td>
<td>160</td>
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<td>Surface Area*</td>
<td>m²/g</td>
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<td>480</td>
<td>539</td>
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<td>Pore Volume*</td>
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<tr>
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<td>0.90</td>
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<td>1.4</td>
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<tr>
<td>Acidity</td>
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<td>9.1</td>
<td>7.4</td>
<td>2.5</td>
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</table>

4. US 5 045 519: Process for the Preparation of a Catalyst Carrier based on Aluminosilicate
Development of catalytically active high temperature particulate filter for simultaneous reforming of biomass derived tars and particle separation.

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1. Introduction

During biomass gasification undesirable compounds such as tar represent a major limitation to the use of the produced gas, and for the process unit. Tar presence in the gas is responsible for clogging of pipes and filters, deposits on surfaces reducing heat transfer rates, as well as reduced carbon efficiencies. Moreover, small amounts of tar in the gas phase challenge the downstream high temperature gas upgrading systems. Among the existing methods for tar elimination, downstream conversion using a catalytic reformer is particularly advantageous [1].

Integrating catalytically active material with high temperature (T>800°C) low-density particulate filters with cut points <1μm will result in an improved gasification efficiency and economics by cleaning the producer gas, decreasing heat losses and lowering the investment costs due to reduced downstream gas cleaning and conditioning.

In this work an inosilicate mineral based filter with cut point of 500 nm is used as a substrate of the catalytic filter containing Ni and/or Fe and the long term (>20h) catalytic activity and stability of the filter is assessed at different operating conditions.

2. Experimental

Filter material was provided by Tenmat Ltd. in form of filter pads. The filter pads consisted mainly of wollastonite (CaSiO3); disks of 35mm in diameter and 10mm thick were used. The reactor tube a placed inside a 3-zone furnace (Figure 1). A tar containing model gas, with a composition corresponding to mean values of air-gasification in an atmospheric fluidized bed gasifiers [2] was used for the experiments with toluene and naphthalene being used as model tar compounds. Prior to use the catalytic filter pads were aged according to [3] for 15h. The adhesion of different support material on the filter pad substrate was also evaluated. Gas composition was measured using a Thermo C2V microGC while tar was measured using solid phase adsorption with sampling at frequent intervals. Dispersion of active metals and resistance towards sintering was also evaluated.

3. Results and discussion

Experimental work is still ongoing. Experiments focus on long term activity and carbon deposition.

4. Conclusions

This work aims at integrating high temperature filters with catalytic material for tar reforming in biomass gasification derived gas. Long term catalytic activity, carbon deposition and overall process stability was assessed over a test period of >20h on stream.

References

Influence of Catalysts on Isocyanic Acid Hydrolysis Reaction in a Urea-SCR System

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1. Introduction
As an effective exhaust aftertreatment measure, selective catalytic reduction (SCR) is currently the most widely used in marine diesel engines. The Urea-SCR has become the main method for marine diesel engines to meet the IMO Tier III emission regulations. Isocyanic Acid (HNCO) is the main intermediate in a urea-SCR system, which affecting the efficiencies of urea and NOx removal. The study on HNCO hydrolysis process has been carried out in this paper.

2. Experimental
A research is given on the action of HNCO catalytic hydrolysis process by tests with the selected four catalysts, i.e. loaded TiO2 catalyst, loaded V2O5-WO3/TiO2 catalyst, extruded V2O5-WO3/TiO2 catalyst and loaded CuO/TiO2 catalyst, meanwhile the influence of excess NH3 on HNCO hydrolysis is also studied.

3. Results and discusses
3.1 The effect of loaded TiO2 catalyst on HNCO hydrolysis
By placing the loaded TiO2 catalyst samples in SCR reactor, and operating under the test procedure, the test results of HNCO hydrolysis are gained. The amount of HNCO hydrolyzed and its ratio with unreacted HNCO are displayed in Figure 1. TiO2 catalyst has a promote effect on HNCO hydrolysis, which increased with the temperature. Compared with the tests without catalyst, and with experimental temperature between 50°C and 150°C, the promote effect of TiO2 on HNCO hydrolysis is limited and has a hydrolysis rate less than 10%. During 150~300°C, TiO2 catalyst exerts on HNCO hydrolysis, and the amount of HNCO hydrolyzed, with a maximum value of 28%, depends linearly on the increased temperature. Thus, above 150°C, the promote effect of loaded TiO2 catalyst on HNCO hydrolysis increases gradually. During 300~400°C, the rate of HNCO hydrolyzed remains at around 31%. It means the promote effect of loaded TiO2 catalyst on HNCO hydrolysis reaches its upper limitation.

3.2 The effect of loaded V2O5-WO3/TiO2 catalyst on HNCO hydrolysis
3.3 The effect of extruded V2O5-WO3/TiO2 catalyst on HNCO hydrolysis
3.4 The effect of loaded CuO/TiO2 catalyst on HNCO hydrolysis

4. Conclusions
(1) The loaded TiO2 catalyst has the best effect on HNCO hydrolysis. (2) For the tested four catalysts, the most effective test temperature range is 350~400°C. (3) With the increased V2O5 load, the effect of catalyst on HNCO hydrolysis reduces gradually. (4) Excess NH3 has an inhibition effect on HNCO catalytic hydrolysis, however when test temperature above 350°C, the action becomes decrease and disappear gradually.

References
The effect of the mecanocatalytic pretreatment of birch on the production of reducing sugars

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1. Introduction

Production of chemicals from biomass is an interesting alternative to replacing the fossil resources. Biomass can be converted into reducing sugars, like xylose and glucose, for further processing into value-added products. A lignocellulosic biomass is widely available and does not compete with food production resources.[1,2] Birch is the most common broadleaf tree in Finland [3] and thus interesting woody residue resource for local production of chemicals. However, the structure of lignocellulosic biomass protects hemicellulose and cellulose so pretreatment is needed. Pretreatment can minimize the amount of catalyst needed for the conversion reactions and decrease the processing costs, the corrosive effects of acidic catalyst and further reactions.[1,4] Dong et al.[5] showed that direct acid catalyzed mechanical depolymerization can be used for pretreatment of fiber sludge without separate impregnation step. In this study the focus is on the mecanocatalytic pretreatment of birch without impregnation step. The effect of different parameters were studied in order to find the optimal pretreatment parameters for the production of xylose and total reducing sugars. In addition, the effect of the pretreatment on the glucose yield and sawdust was observed.

2. Experimental

Birch sawdust was converted into reducing sugars by mecanocatalytic pretreatment combined with subsequent acid hydrolysis. The pretreatment was performed in ball mill with 96% H2SO4 as catalyst. Different milling times (0-90 min, cycles comprising of 5 min milling and 10 min pausing) and catalyst to sample ratios (C/S ratio, 0, 0.5, 1.0, and 1.5 mmol/g) were studied. The hydrolysis of the pretreated sample (0.5 g) was done at 100 °C for 1 h. A part of pretreated sawdust (0.5 g) was mixed in distilled water for 20 min at room temperature. The total reducing sugars (TRS) before and after the hydrolysis was determined by dinitrosalicylic acid (DNS) method. The amount of monosaccharides in hydrolysate was analysed by HPLC. The effect of the pretreatment on the structure of sawdust was studied by FTIR, XRD and FESEM.

3. Results and discussion

The effect of mechanical treatment was first studied by varying the milling duration of birch sawdust while other parameters were kept constant. The amount of TRS increased with increasing milling time. TRS reached its maximum value (24.4%) after 30 min milling before it started to decrease (Fig 1). Also the xylose yield reached its maximum value (3.7g/100g(birch)) after 30 min milling. The glucose yield still increased after 90 min milling. The yield of sugars depended significantly on the C/S ratio i.e. acid was needed to produce glucose and xylose. The maximum xylose yield was reached already with C/S ratio of 1.0 mmol/g in 30 min milling and increase of the C/S ratio or milling time decreased the yield. Observing the relationship between monosaccharide yield, milling time, and C/S ratios revealed that xylose started to release from birch much before glucose and mechanical treatment increased both glucose and xylose yields.

4. Conclusions

The mecanocatalytic pretreatment is an effective way to fractionate monosaccharides from birch since it disturbs the protective structure and reveals hemicellulose and cellulose for further processing. Thus it decreases the amount of catalyst needed for the conversion reactions and minimizes the unwanted reactions and corrosion. The product fractions of the process can be changed by adjusting the pretreatment process parameters.

Acknowledgements

Authors acknowledge the Biomass value chains project (A71029, the EU/European Regional Development Fund, Leverage from the EU program) and the Bioraff Botnia project (20200327, Interreg Botnia-Atlantica) for financial support.

References

Mg and K effects on the CuCl$_2$/$\gamma$-Al$_2$O$_3$ catalyst in ethylene oxychlorination

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3. INOVYN Norway, Porsgrunn, 3936, Norway
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1. Introduction

Ethylene oxychlorination is an industrially important process where the CuCl$_2$/$\gamma$-Al$_2$O$_3$ based catalyst undergoes a reduction-oxidation process (Eq.1). [1] Mg and K are usually present in an industrial catalyst, but the exact nature of the promoter effect and interaction between the two promoters remain uncertain.

$$2\text{CuCl}_2 \rightarrow \text{C}_2\text{H}_4 \rightarrow \text{Cu}_{2}\text{OCl}_2 \rightarrow 2\text{CuCl}_2 + \text{H}_2\text{O}$$

2. Experimental

The catalysts, prepared from the chloride salts with the incipient wetness method, contain 5wt% Cu and e.g. 0.4K have a K : Cu molar ratio of 0.4 and 5wt%Cu. TPR was performed with $P_\text{C}_2\text{H}_4=0.3$, a total flow of 2 ml/s and a 2°C/min heating rate. Step transient and steady-state (ss) activity tests ($F_{\text{tot}}=3$ ml/s, $P_\text{C}_2\text{H}_4=0.08$, $P_{\text{O}_2}=0.04$, 230°C) was performed in our operando setup combining in situ UV-Vis-NIR spectrometry and mass spectrometry. [2]

3. Results and discussion

It has been reported that addition of MgCl$_2$ does not affect the reducibility of the active phase of CuCl$_2$ while KCl and CsCl addition decrease the reducibility because of the formation of the mixed salts of CuKCl$_{2+x}$ and CuCsCl$_{2+y}$. [3] Revealed by the TPR profiles, all samples display a sharp peak around 180°C. The temperature at the peak position increase with K addition, indicating stronger Cl bonding with Cu or decreased the adsorption of ethylene. On the contrary, Mg addition to both Cu and promoted by K catalysts shifts the temperature peak position. The relation of reduction temperature peak versus Mg (or K) percentage (molar ratio of K or Mg in total molar of K and Mg) is shown in Figure 1. The higher the Mg content, the lower is the temperature peak position, while K behaves the opposite. In the impregnated catalysts, only Al$_2$O$_3$ was visible in XRD patterns. Hence, dried (120°C) precipitates from equimolar, aqueous solutions of CuCl$_2$·2H$_2$O and the respective KCl and MgCl$_2$·6H$_2$O salt determined the presence of CuKCl$_3$ and indicated Cu$_3$Mg(OH)$_6$Cl$_2$. A likely OH source in the latter is moisture adsorbed during analysis. While XRD analysis in a heated, dry atmosphere is planned at the ESRF beamline in April, it seems evident that K can be incorporated into the Cu lattice much more easily than Mg.

Based on our group’s previous research, step transient and steady-state operando kinetic studies can provide the exact information of the transformation of Cu (II) and Cu (I). Also by using in situ UV-Vis-NIR spectrometry, reaction rate and band gap information will obtain. Last, temperature programmed oxidation experiments are also under running; more information about the effect of promoter to the oxidation step will be added.

4. Conclusions

As proved by previous studies, alkali metals, like K are used as promoters to improve the catalysts stability, while Mg has been used to titrate Cu in alumina surface vacancies. Until now, it has been thought that Mg does not affect the Cu reducibility. However, from our TPR results, we can directly see both Mg and K can influence the reducibility of active phase CuCl$_2$. Mg enhanced while K suppressed the reduction of CuCl$_2$ and the effect of Mg and K on the reduction is proportional to the content of the promoters. More experiment must be undergo to investigate how the dopants contribute in increasing the fraction of active copper phase and are currently in progress.

References

The Effect of Vacancies of Fe/Co-Nx Doped Graphene for ORR: DFT Analysis
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1. Introduction:
Fuel cells have attracted much attention as a clean and sustainable power source. One of the bottle necks of fuel cells lies in the sluggish oxygen reduction reaction (ORR) on the cathode site [1]. To date, large amount of research is performed to develop nonplatinum group metal catalysts to replace platinum due to its scarcity and high price. Recently Fe and Co in combination with N doped graphene was shown as promising electrocatalysts in ORR [2,3].

In this work we analyze using Density Functional Theory (DFT) the effect of vacancies formation in the lattice of Fe/Co-Nx doped graphene on the activity of Fe/Co active sites towards ORR.

2. Experimental
Spin polarized DFT calculations were performed at the GGA level within PAW-RPBE [4] formalism using real space uniform grids GPAW code [5]. A 0.2 gridspacing was used. The defects (Fe/Co-Nx) and vacancies were modeled in an orthorhombic graphene supercell (29.8x18.015 Å) with an armchair structure and with 15Å vacuum along Z direction. The Brillouin zone was restricted to Γ point. The Kohn-Sham states were populated using Fermi-Dirac distribution with an electronic temperature of \( k_B T = 0.1 \text{ eV} \) and the total energies were extrapolated to \( k_B T = 0 \text{ eV} \). The ORR intermediates (HOO*, HO*, O*) were adsorbed on the top of transition metal atom and the geometries were optimized using a force convergence criterion of 0.05 eV/Å.

3. Results and discussion
From the vacancy formation energies calculated as:

\[
E_v = E_{G-Fe/Co-Nx} + \Delta n_C \mu_C + \Delta n_N \mu_N - E_{G-Fe/Co-N4} - \Delta n_H/2 \mu_H, \text{ (where } E_{G-Fe/Co-Nx} \text{ – total energy of Fe/Co-Nx doped graphene with vacancies, } E_{G-Fe/Co-N4} \text{ total energy of Fe/Co-N} \text{ doped graphene, } \mu_C, \mu_N, \mu_H \text{ chemical potentials of } C, H, N \text{ referred to the energy of } C \text{ atom in graphene, the energy of } H \text{ atom in } H_2 \text{ molecule and of } N \text{ in } N_2 \text{ molecule) indicate that the structures with vacancies situated nearby Fe/Co-Nx sites are the most stable ones (see in Figure 1a the structure without vacancies and in Figure 1b,c,d the most stable structures with one unsaturated, one saturated and two unsaturated vacancies). Concerning the vacancy effect on the activity of Fe/Co-Nx sites it depends on the type of vacancy: it can improve or can decrease the activity of the Fe/Co sites. In Table 1 we show the theoretical overpotentials calculated for the structures from Figure 1 for Fe-Nx doped graphene. Therefore compared to doped graphene without vacancy the structures with 1 vacancy (unsaturated and saturated) increase substantially the overpotential, while the structure with two vacancies decrease slightly the overpotential. Similar behavior is registered for Co-Nx doped graphene structures (data not shown).

4. Conclusions
We have shown that the presence of vacancies in the lattice of Fe/Co-Nx doped graphene tend to localize in the vicinity of Fe/Co-Nx sites and depending on the type of vacancy the overpotential of active Fe/Co site could be significantly increased when compared to the structure without vacancies or could be further decreased.

References

Table 1. Theoretical overpotentials of Fe-Nx doped graphene without vacancies and with vacancies (1 vacancy, 1 vacancy saturated with 1H, 2 vacancies)

<table>
<thead>
<tr>
<th>Fe-Nx-G structures</th>
<th>Overpotential/eV</th>
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<tr>
<td>Fe-N4-G</td>
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<tr>
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</tr>
<tr>
<td>Fe-N3-G-1v-1H</td>
<td>1.48</td>
</tr>
<tr>
<td>Fe-N4-2v</td>
<td>0.68</td>
</tr>
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</table>

Figure 1. Structure of a) Fe/Co-N4-G doped graphene active center b) Fe/Co-N4-G with 1C vacancy c) Fe/Co-N4-G with 1N vacancy saturated with 1H d) Fe/Co-N4-G with 2 vacancies
Investigation of the effect of organic nitrogen on the hydrogenation of phenanthrene

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1. Introduction
Many consumer products are produced from materials which contains mineral oils. For example, the rubber handle of a toothbrush typically uses a plasticizer derived from mineral oil. The crude oil from which the plasticizer is produced from contains polyaromatic hydrocarbons (PAHs). PAHs are known carcinogens and must be removed to have a non-carcinogenic product. The mineral oil fraction is typically treated catalytically with hydrogen at elevated pressure and temperature, so called hydrotreating, to saturate the PAHs. For the transport fuel producers, the sulfur removal via the hydrosulfurization reaction is traditionally the most important reaction as it is critical to meet the legislated 10 ppm sulfur content of the fuel. However, due to the stricter legislative requirements concerning carcinogenic PAHs in consumer goods, it has become increasingly important to lower the PAH content substantially in the mineral oil components used in the consumer products.

The PAH content is lowered via catalytic hydrogenation reactions called hydrodearomatization. The hydrodearomatization reaction is inhibited by organic nitrogen compounds present in the mineral oil. Furthermore, partially hydrogenated PAH could still be carcinogenic, this means that the selectivity of the hydrogenation is crucial. Therefore, it is of interest to study how the selectivity of the hydrogenation reactions are affected by the presence of organic nitrogen at different process conditions.

Using a model compound system is a practical way to gain insight on more complex systems by simplifying the experimental and analytical procedure. Phenanthrene is a model compound typically utilized to study the catalytic hydrogenation of PAHs. The inhibition of hydrogenation reactions of phenanthrene by nitrogen compounds has been demonstrated in other studies [1,2]. However, only limited studies have been performed how the inhibition changes with different process conditions.

2. Experimental
The inhibition effect of organic nitrogen compounds on hydrogenation of phenanthrene was studied at industrially relevant process conditions. A commercial hydrotreating catalyst of the NiMo type was used, crushed and sieved to minimize mass transfer limitations. In the present study, the nitrogen compounds carbazole and acridine were blended into the reactant mixture to study the effect on the product distribution. To get a statistical optimized experimental matrix a design of experiments approach has been utilized. A microflow system was used, which can operate up to 380 °C and a system pressure of 170 bar and is shown schematically in Figure 1.

The products were analyzed offline using a GC-FID system for quantitative analysis and a GC-MS system for qualitative analysis.

3. Results and discussion
The experimental results indicate that the inhibition effect by organic nitrogen on the hydrogenation of phenanthrene is affected by the process conditions.

4. Conclusions
The introduction of organic nitrogen into the reactant feed had an impact on the conversion of phenanthrene.

References

Figure 1. Schematic diagram of the experimental setup. TIC (Temperature indicator controller), PIC (Pressure indicator controller), PI (Pressure indicator), PRV (Pressure relief valve).
Integrated Catalytic-Membrane Separation Reaction System

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Catalysis with supported homogeneous catalyst systems has successfully been established over the last decades as an industrially attractive approach.[1] Hydroformylation of olefins by syngas to produce aldehydes is an important industrial reaction.[2] However, the long-term catalytic performance of such systems is often negatively influenced due to the formation of “heavies” by undesired condensation reactions hampering activity and selectivity.

In the HORIZON2020 project Reactor Optimisation by Membrane Enhanced Operation (ROMEO)¹²³ a new “two-in-one” reactor concept is being developed. The unique ROMEO reactor will overcome present challenges in the hydroformylation technology and its industrial application by combining two process steps in one module as depicted in Figure 1.

The ROMEO reactor is based on a catalytically active membrane, which is combined with a homogeneous catalyst to generate the “two-in-one” reactor module. Depending on the properties of the membrane, either the product or byproduct passes through the membrane once the reaction has taken place at the catalytic surface.

Preliminary investigations of olefin hydroformylation have demonstrated that the system is catalytically active affording high activity and selectivity. The results indicate that the ROMEO “two-in-one” reactor concept has a great potential to be applied in the chemical industry. Furthermore, a reduction in emissions, energy consumption, space needs and costs in the chemical industry are expected with this novel reactor type.

Fig. 1. Reactor Optimisation by Membrane Enhanced Operation (ROMEO) technology combines two standard process steps.

Acknowledgments
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References
Deactivation of a Vanadia on Titania Diesel SCR Catalyst in an Engine Rig.

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1. Introduction
The Selective Catalytic Reduction (SCR) technique, for reduction of NOx with ammonia, is today a compulsory method for mobile applications like marine and automotive diesel engines. When the catalysts are used compounds in the exhaust gas like P, Zn, Ca, Na, S and Fe deactivate them. The source for the deactivating compounds can be the lubricant oil, FAME (bio diesel) and urea solution used as reducing agent [1-6].

2. Experimental
A cordierite monolith (300 cpsi) was wash-coated, with a slurry of pre-prepared V2O5/TiO2 (5.6 wt% V2O5) powder suspended in water until 18.2 wt% (dry) was reached. Two cores, 100 mm long and 25 mm in diameter, were drilled from the coated monolith and used in the deactivation test in the engine rig. The accelerated test was supposed to simulate the normal running of a truck for a distance of 500 000 km. One of the cores was collected after 890 h online and the other after 2299 h. The core was cut into 10 mm pieces before analysis. The samples were analyzed by BET, BJH, XPS and SCR activity tests.

3. Results and discussion
There is a large decrease in the BET surface as a function of time. The decrease is, however, more or less constant through the length of the monolith. The fresh catalyst has a distinct maximum in pore diameter at 130 Å. When aged, for 890 and 2299 h, this fraction vanishes and is replaced by a broad pore distribution centered around 350 Å. Those morphological changes are due to thermal sintering caused by the highest temperatures in the deactivation cycle. The XPS analysis shows that carbon (soot) and catalyst poisons (P, Ca, Zn, S) are accumulated in the very first part of the monolith (Fig 2). Ca and P can also be found in much lower concentrations in the entire used monolith. The loss of activity is severe in the inlet part of the monolith. The rate constant (cm³/(s m²)) at 350 °C decreases by 94 % after 2299 h compared to fresh catalyst (Fig. 1). The rear part (pieces 3-10) of the monolith has a more moderate decrease. The rate constant (cm³/(s m²)) at 350 °C decreases by ~50 % after 2299 h compared to fresh one in this part.

4. Conclusions
The entire monolith deactivates rather uniformly due to sintering caused by the high peek temperatures during the repeated deactivation cycles in the engine rig. Superimposed, the activity loss due to sintering, there is a deposition of catalytic poisons (P, Zn, Ca and S) primarily in the inlet, but for P and Ca in the entire length of the monolith. The presence of these poisons causes further activity loss and in the inlet the loss at 350 °C is 95 % of the fresh activity after 2299 h.

References
Catalytic Roles of Histidine and Arginine in Pyruvate Class II Aldolase

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1. Introduction
The retro-aldol reaction catalyzed by pyruvate class II aldolase is investigated with QM/MM metadynamics; this enzyme transforms the substrate of 4-hydroxy-2-ketoacid into pyruvate and aldehyde through the aldol cleavage. The hydroxyl group of the substrate is deprotonated by H45 with the aid of the metal-bound water, while the metal-bound hydroxide is observed as a transient species. Computational results [1] suggest that the deprotonation could enhance substrate binding between the deprotonated substrate and the active site. The reactive alkoxide is further stabilized by the salt bridge of R70 −D42, which promotes aldol cleavage in the next stage. The C−C bond cleavage is the rate-determining step, and the calculated barrier of approximately 14 kcal mol −1 agrees reasonably with experimental data [2].

2. Experimental
Mg2+ and (R)-4-hydroxy-2-oxopentanoate (HPA) are chosen as the divalent metal cofactor and the substrate in the simulations. Initial structures of the reactant, product, and mutant Hpal enzyme are taken from PDB codes of 4B5V (Figure 1), 4B5U and 4B5W, respectively. The QM region composed of 104 atoms (Mg2+, HPA, three waters, and nine residues of D42, H45, R70, E44, Q147, E149, D175, D84’ and V118’) is computed by the density functional theory at ωB97X-D level. Amino acids and waters in the non-QM region are treated by MM with force fields of AMBER99SB and TIP3P. The well-tempered QM/MM metadynamics is run using Gromacs combined with PLUMED.

3. Results and discussion
Free energy landscape of the deprotonation step shows two main wells corresponding to the pre-reactant and the deprotonated reactant states which exist at equilibrium, while the metal-bound hydroxide is a transient species during the deprotonation. Proton abstraction by H45 followed by the deprotonation of the hydroxyl group is also confirmed by the metadynamics, and the low barrier of 5.7 kcal mol −1 indicates that the formation of the alkoxide is facile in the assistance of H45. In the product state forming pyruvate enolate, calculations exhibit that acetaldehyde leaves from the metal-bound pyruvate if constraint to the C−C bond is absent; this poor binding between aldehyde and the active site pocket is also reflected by the experiments [3]. Amide NH bonds can act as an oxyanion hole to stabilize an alkoxide [4], and in the case of the Hpal enzyme the oxyanion hole composed of the salt bridge and the metal-bound water tends to stabilize alkoxide for the subsequent aldol cleavage. Figure 2 displays the free energy surface of the aldol cleavage with a ΔG‡ value of 13.7 kcal mol−1.

4. Conclusions
We used metadynamics to demonstrate the catalytic roles of H45 and R70 in the retro-aldol reaction. H45 is involved in the deprotonation and substrate binding, and the metal-bound hydroxide is a transient species during the deprotonation. R70 forms a salt bridge with D42, which facilitates the formation of the reactive alkoxide. Barrier of the deprotonation is lower than that of the aldol cleavage, which indicates that the latter step is rate-determining. Estimated free energy of activation of ~14 kcal mol −1 agrees with the experimental rate constant [2]. The observed solvent isotope effect might be the result of a secondary isotope effect caused by the H/D exchange in the metal-bound water and R70.

References

Figure 1. 4B5V in hexamer assembly. Each chain is colored, and backbone atoms around the active site (D42, E44, H45, R70, V118’, Q147, E149, D175) are depicted in balls.

Figure 2. Free energy (in kcal mol−1) landscape of C−C bond cleavage. The energies are given in parentheses, and the snapshot structure of the transition state is denoted as TS*. Selected bond lengths are given in Å.
Catalytic Oxidation of VOCs in Indoor Air Using Ozone Based Advanced Oxidation Technology

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Abstract

Since people spend most of their time at indoors, concentrations and characteristics of indoor pollutants could cause a potential risk to inversely affect human health. Up to now, there is no single pollution prevention system with satisfaction for odor removal from indoor air due to the difficult degradation with diversity and variability of odorous compounds. The traditional treatment technologies, such as filtration and activated carbon adsorption, may not efficiently decompose the recalcitrant airborne pollutants including smoke, cooking oil fume, and formaldehyde within a short retention. Therefore, this research focuses on the removal of odorants by using ozone/catalyst/UV based catalytic oxidation technology, which has been designed and developed for the improvement of pollutant removal by our research group for many years. The synthetic approaches include ultrasound irradiation method and microwave irradiation method. Meanwhile, the novel photocatalysts were modified to substantially enhance the photocatalytic activity and improve the long-term stability. Subsequently, we have established fundamental operational parameters by using ozone/catalyst/UV catalytic oxidation technology to simulate the pollution prevention and control system in our laboratory. In addition, we also designed a full-scaled system setup, including ozone, catalyst, and UV, as a controlling equipment. At the same time, we combine the ozone, VOCs, and PM$_{2.5}$ sensors within the equipment to facilitate the smart operation. The implementation of this study can solve the odorous problems and optimize the quality of indoor air.
Screening of Novel Catalyst for the Selective Oxidation of Methanol to Formaldehyde

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1. Introduction
Formaldehyde (CH₂O) is produced industrially by the Formox process (CH₃OH + ½O₂ → CH₂O + H₂O) over a ferric molybdate catalyst with a yield of up to 95% [1]. During the last couple of decades, the methanol feed concentration has steadily increased [1], which has resulted in a catalyst lifetime of only 1-2 years due to volatilization and migration of the active component (molybdenum) leading to an increasing pressure drop over the reactor and loss of selectivity [2,3]. Due to these difficulties, it is of interest to investigate alternative catalyst systems for the oxidation of methanol to formaldehyde.

2. Experimental
Various catalyst systems have been prepared by methods such as impregnation, co-precipitation, citric acid-based sol-gel method and a reflux procedure. The samples were characterized by XRD and BET. The catalysts were tested in a fixed bed reactor with catalyst loadings of 10-50 mg. The feed flow consists of 15 SmL of O₂, 127.5 SmL of N₂ and methanol added through a bubble flask at 6 °C leading to a methanol feed concentration of 3.5-5%. Measurements were performed at app. 250 °C, 300 °C, 350 °C and 400 °C. Experiments with longer time on stream was done for some samples to investigate their instability. The effluent gas was analyzed using a gas chromatograph.

3. Results and discussion
Figure 1 shows the DME corrected selectivity (DME is considered as two methanol when calculating selectivity) for the catalysts containing molybdenum together with results for an industrial iron-molybdate catalyst. In Figure 2 it is shown for vanadium containing systems. It can be seen from both Figure 1 and Figure 2 that catalysts with high selectivities at low conversions have been found. Especially the 25.8 wt% MoO₃ supported on hydroxyapatite (HAP) is interesting, since it performs better than the industrial catalyst at conversions below 80% (temperatures below 350 °C). It can also be seen that some of the vanadium containing catalysts have better DME corrected selectivity than the industrial catalyst at low conversion (low temperature). However, the selectivities at higher conversions for the vanadium based catalyst are generally not as high as for the molybdenum based catalysts. In most cases the vanadium catalysts have higher activity than the molybdenum based catalysts. This is also the case for the vanadium oxide (3 or 5 wt%) on hydroxyapatite catalysts. However, the main problem for the ferric molybdate catalyst is not selectivity and activity, but stability. This will be further investigated for the catalyst with activity and selectivity similar to the industrial catalyst.

4. Conclusions
A range of different Mo and V-based catalysts have been synthesized and tested for selective oxidation of methanol to formaldehyde. In general, the Mo-based catalysts are more selective than the V-based catalysts. A catalyst with high loading of molybdenum oxide on hydroxyapatite seems the most promising with activity and selectivity similar to an industrial iron molybdate catalyst.

References
Brønsted and Lewis acid catalyzed conversion of pulp industry waste biomass into levulinic acid with microwave irradiation

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1. Introduction
Fiber sludge is a cellulose-rich by-product generated ca. 750000 tons per year in Finland by pulp and paper industry [1]. At the moment fiber sludge is mainly incinerated or placed in the landfills. However, new applications are actively sought for its utilization. In this work fiber sludge was converted into levulinic acid (LA), which is one of the most important platform chemicals. LA can be further converted into various other important chemicals and hence be used as a raw material for e.g. resins, plasticizers, textiles, coatings and fuel additives. [2,3] In order to accelerate the conversion reactions in this study, microwave irradiation was used as the heating method and various Lewis acid catalysts were used in combination with the commonly used Brønsted acid, H2SO4.

2. Experimental
Conversion reactions were performed in glass reactor vessels (Figure 1) in a microwave reactor (Biotage Initiator). First the reaction conditions i.e. reaction time (15-60 min), temperature (140-180 °C), H2SO4 concentration (0.1-0.5 M) as well as the concentration of the Lewis acid catalyst (CrCl3, 0.0019-0.0075 M) were studied with a full 24-factorial design and then the reaction time (48-132 min) and the concentration of the Lewis acid catalyst (CrCl3, 0-0.022 M) in more detail. In the second part of the work the effect of various Lewis acid catalysts (FeCl3, ZnCl2, CuCl2 and NiCl2) on the LA yield was studied. Previously determined optimal reaction conditions, i.e. 180 °C for reaction temperature and 0.3 M for H2SO4 concentration, were used in the reactions. The concentration of the Lewis acid catalyst was 0.0075 M or 0.019 M and the reaction time 60 or 120 min.

3. Results and discussion
According to the results from the first part of the study, the reaction temperature and the H2SO4 concentration had the most significant effect on the LA yield. The highest yield, 34%, was achieved at 180 °C in 60 min with H2SO4 concentration of 0.3 M and CrCl3 concentration of 0.019 M. The CrCl3 catalyst clearly enhanced the conversion of biomass into LA since without the catalyst it took 120 min to achieve similar LA yield (Table 1).

The results from the second part of the study indicated that the other studied Lewis acid catalysts had a similar effect on the LA yield as CrCl3 (Table 1). The highest LA yield (34%) was achieved with ZnCl2 (0.0075 M) in 60 min. It has been found in studies with glucose that the Lewis acid catalyst improves the conversion of biomass into LA, since it catalyses the glucose to fructose isomerization step, which is necessary for the conversion reaction to occur. [4,5] However, many of the studies have been performed only with CrCl3 catalysts. [4]

4. Conclusions
To conclude, the results achieved in this study indicate that fiber sludge can be used as the raw material for LA production. The combination of Bronsted acid and Lewis acid catalyst slightly improves the LA yield and decreases the reaction time considerably. The studies regarding the further optimization of the reaction conditions in order to improve the LA yield are on going.

References
Mesoporous manganese-cobalt hybrid oxide catalyst for CO₂ hydrogenation to methanol
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1. Introduction
The efficient utilization of CO₂ to produce valuable fuels and chemicals is attracting research interest from both academia and industry. Methanol is an important chemical that can be utilized as fuel or in the chemical industry. The catalysts currently employed for hydrogenation of CO₂ to methanol is mainly Cu-based catalysts, which suffers from limited conversion even at elevated pressures. Developing new-class catalysts for this reaction is therefore of great interest. Recent experimental and theoretical works have indicated cobalt-based materials as a promising candidate for CO₂ hydrogenation reactions [1] [2].

2. Experimental
A series of mesoporous catalysts consisting of different manganese/cobalt ratios have been prepared by a modified sol-gel inverse micelle method [3]. In addition, a monometallic mesoporous cobalt catalyst was synthesized for comparison. The catalysts were characterized by N₂ adsorption-desorption, XRD, H₂-TPR, CO₂-TPD, H₂-chemisorption, SEM, and TEM. Catalytic performance is to be evaluated in a continuous flow reactor at different operating conditions.

3. Results and discussion
BET and XRD characterization confirmed the successful synthesis of mesoporous spinal cobalt oxide (m-Co₃O₄) and mesoporous manganese-cobalt oxides (m-MnOₓ·Co₃O₄). Smaller Co₃O₄ particle size was observed with increasing Mn loading, which was confirmed by both TEM (Figure 1) and XRD (Figure 2). H₂-TPR revealed enhanced Co₃O₄ stability upon Mn addition, where the main reduction peak occurred at 340, 385, and 420 for m-Co₃O₄, m₀.₁MnOₓ·Co₃O₄, and m₀.₂MnOₓ·Co₃O₄, respectively. The CoO phase has been proposed to correlate with the methanol synthesis activity [2]. Thus, we expect that the higher stability of the oxidized state of Co due to the incorporation of Mn in the support structure will improve their catalytic performance. Furthermore, the surface basicity increased with Mn loading. The existence of a MnO/CoO interface was identified as key for high methanol synthesis activity [2]. The high Mn dispersion (XRD) combined with the CO₂ desorption data indicate that a fraction of Mn is present at the catalyst’s surface. Further characterization will be conducted to obtain more information on the surface architecture and interfacial domains.

Table 1. Characterization results of mesoporous cobalt oxide and mesoporous manganese-cobalt oxides.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Crystallite size (nm)*</th>
<th>H₂ chemisorbed (μmol/g-Co)</th>
<th>H₂ consumption (mmol/g-Co)²</th>
<th>CO₂ desorption (mmol/g-cat)²</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Co₃O₄</td>
<td>56</td>
<td>17.8</td>
<td>9.5</td>
<td>17.5</td>
<td>0.09</td>
</tr>
<tr>
<td>m₀.₁MnOₓ·Co₃O₄</td>
<td>54</td>
<td>13.9</td>
<td>8.6</td>
<td>15.1</td>
<td>0.15</td>
</tr>
<tr>
<td>m₀.₂MnOₓ·Co₃O₄</td>
<td>59</td>
<td>10.5</td>
<td>8.0</td>
<td>14.8</td>
<td>0.18</td>
</tr>
</tbody>
</table>

* calculated from XRD; ² calculated from H₂-TPR; ³ calculated from CO₂-TPD

4. Conclusions
We have successfully prepared a series of different mesoporous manganese-cobalt catalysts. The catalyst characterization revealed promising catalytic features when Mn is incorporated into the support structure, such as enhanced cobalt oxide stability and the existence of a manganese/cobalt interface. Catalytic testing and further characterization will yield valuable insight into a new catalytic system for CO₂ hydrogenation to methanol.

References
**In-situ ATR IR Spectroscopy Study on Zeolite Cu/SSZ-13 Catalyst for Low Temperature NH3-SCR of NO**

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1. Introduction

Cu2+ ion-exchanged SSZ-13 has superior activity and selectivity in the selective catalytic reduction of nitric oxide from mobile source with ammonia (NH3-SCR) [1]. Compared with iron-based zeolite catalysts, copper-based zeolite catalysts are more active at low temperature (<350 °C) [2]. To gain deep understanding of the reaction process over Cu/SSZ-13 catalyst at low temperature, in-situ attenuated total reflectance infrared (ATR IR) spectroscopy was used to investigate the changes of surface species and possible intermediates under the different gas conditions.

2. Experimental

For in-situ ATR IR spectroscopy measurements, spectra were recorded on a NICOLET iS50 FT-IR spectrometer equipped with a (DTGS) detector by accumulating 64 scans at a resolution of 4 cm⁻¹. The sample was synthesized by ion exchange of a commercial SSZ-13 zeolite (Si/Al = 20, Cu/Al = 0.04) pre-treated with 200 mL/min He flow at ambient temperature and activated under 5 vol. % O2/He flow at 250 °C. The sample was cooled to 150 °C and, in succession, subjected to a flow of 200 mL/min of 1200 ppm NH3/He, 1200 ppm NO/5 vol. % O2/He and 1200 ppm NO/5 vol. % O2/1200 ppm NH3/He for 40 min.

3. Results and discussion

In order to find out the intrinsic changes of reacting surface species on catalysts under working conditions, it is efficient by pretreating and activating to remove physisorbed species, water, etc. before recording the in-situ ATR IR spectra [3]. Figure 1 shows the in-situ ATR IR spectrum (after pretreating and activation) of Cu/SSZ-13 under a flow of 200 mL/min of 5 vol. % O2/He at 150 °C (pink spectrum), and a series of differences (orange, green and blue) obtained at other gas conditions and given relative to the pink spectrum. The peaks in the difference spectra represent the creation and consumption of existing surface species.

Differences in intensity reveal the creation of three new bands at 1446, 1198 and 1007 cm⁻¹; whereas five bands disappear: 2358, 2153, 1079, 898 and 807 cm⁻¹. The intensity of peaks in difference spectrum under NH3/He condition is the weakest and increases gradually after co-adsorption of NO/O2 and NO/O2/NH3. Generally, the positive peak at 1446 cm⁻¹ originate from the N-H bending vibrations in adsorbed ammonia [4]. It is worthwhile to mention that the peak at 989 cm⁻¹ could be assigned to the 𝜃(O-H) mode of [Cu(OH)]⁻. The similar species in this region have been assigned to M-OH species on the surface of other metal containing zeolites [5-7]. The peak at 1057 cm⁻¹ in the spectra under oxygen conditions should belong to the overlapping multiplets of different species. Another interesting finding is in the region of 2500–2100 cm⁻¹: there is a fairly weak peak at 2358 cm⁻¹ under NH3/He condition, but it disappears under NO/O2 condition then appears obviously again under NO/O2/NH3. At the same time, a weak negative peak appears at 2153 cm⁻¹, which probably accounts for some original surface species are consumed during SCR reaction process.

4. Conclusions

The differences between in-situ ATR IR spectra are discussed to further verify subtle changes of surface species over zeolite Cu/SSZ-13 catalyst under different gas condition at 150 °C. Based on consumed and generated species, the possible reaction path could be described for low temperature NH3-SCR of NO.

References


Figure 1. Differences in intensity between in-situ ATR IR spectra obtained under different gas conditions and under oxygen at 150°C.
Homogeneous Catalysis for Sustainable Chemistry

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1. Introduction
The transformation of biofeedstock into higher value bulk and fine chemicals is of paramount importance to become fully independent of fossil fuels.

2. Experimental
Using homogeneous catalysis for such valorization processes allows for highly selective transformation to be carried out under mild conditions.

3. Results and discussion
Here, we demonstrate the use of homogeneous PNP transition metal complexes for catalyzing a range of biofeedstock valorization processes. In addition, we show how this catalyst type may be used for hydrogen storage in organic compounds.

For example (bio)ethanol may be transformed to sodium acetate, ethyl acetate, or butanol. Likewise, potassium lactate is produced from glycerol and gamma-valerolactone is made from levulinates. Furthermore, we show how methanol, (bio)ethanol, isopropanol, glycerol, sugar alcohols, and carbohydrates all are well tolerated substrates for extruding hydrogen molecules.

4. Conclusions
In conclusion, I aim to demonstrate the use homogeneous catalysis as a powerful tool for performing sustainable chemistry.

References
ALD for catalysis – new approaches for support materials, catalysts and overcoatings

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Atomic Layer Deposition (ALD) has been showing its versatility for preparing thin films for multitude of applications where conformal films with tailored properties are needed, including microelectronics, optics and many others. One of the early applications for ALD materials were preparation of heterogeneous catalysts [1]. More recently several different catalytically active materials have been deposited by ALD including the protection of catalysts by ALD oxide layers [2]. The wide applicability of ALD makes it intriguing method to make evenly dispersed catalyst on high surface area supports. In this presentation, we give insight of our efforts how to utilize ALD for various catalytically active materials and structures.

As an example, ALD preparation of Ni, Co and Pt catalyst on various support materials, such as microchannel plates, powders and electrospun fibers is discussed which materials can be used in various applications such as:

- Ni catalyst for gas cleaning
- Co catalyst for Fischer-Tropsch synthesis
- Pt catalyst for liquid organic hydrogen carriers (LOHCs)

In addition, the effect of protective Al₂O₃, TiO₂ or SiO₂ overlayers on commercial Ni and noble metal catalysts on steam reforming is examined. ALD coated commercial Ni and Rh catalysts had increased catalytic activity, showing trend on the performance as a function of overlayer thickness.

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Sustainable Production of Higher Alcohols from CO and H\textsubscript{2} via Rhodium based Catalysts – A Mechanistic Study

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**Introduction**  
Conversion of H\textsubscript{2} with CO is an interesting reaction, as it provides access to higher alcohols which can be used as chemical energy carriers. Supported single-metal Rh catalysts are known for their ability to produce C\textsubscript{2}-oxygenate (C\textsubscript{2}-O) compounds (mainly AcH and EtOH) from CO/H\textsubscript{2}\textsuperscript{[1]}. However, Rh based catalysts suffer from a low CO conversion range (ca. 5-10 %) within which C\textsubscript{2}-O are formed in considerable yield.

**Experimental**  
ZrO\textsubscript{2} and SiO\textsubscript{2} supported Rh catalysts were prepared via wet impregnation of Rh(NO\textsubscript{3})\textsubscript{3}. In a first type of experiment, 1% Rh/SiO\textsubscript{2} catalyst was populated with different adsorbates by directing a flow of 1) He loaded with CH\textsubscript{2}Cl\textsubscript{2} (DCM) and subsequently 9.5% CO, 2) He loaded with HCOOH and DCM as well as 3) only 9.5% CO over the catalyst. Subsequent subjection of the catalyst to a temperature programmed hydrogenation (TPH) was used to verify, whether C\textsubscript{2}-O production is a feasible reaction from the different created surface adsorbates. The TPH pattern from a catalyst that was treated in CO/H\textsubscript{2} (1:2) (250 °C, 0.25 bar) serves as reference. Secondly, on a 1% Rh/ZrO\textsubscript{2} catalyst via CO-H\textsubscript{2} reaction treatment formed C\textsubscript{2}-O precursor adsorbates were liberated via a TPH whereby pure and MeOH-enriched H\textsubscript{2} was used.

**Results and discussion**  
The similarity between the TPH patterns from a catalyst that was subsequently populated with CO and DCM respectively HCOOH/DCM and a catalyst that was exposed to reaction conditions (Figure 1a), provides strong evidence, that the C\textsubscript{2}-O production involves the reaction of CO and alkyl species, whereby molecularly adsorbed CO react as formate. Further, it is hypothesized that alkyl moieties migrate into bidentate binding formates that than form acetate-like intermediates. Hydrogenating these species into favorable products (AcH, EtOH) may be a crucial sequence in the reaction that has to compete with their decomposition into hydrocarbons. Figure 1b shows that a larger amount of C\textsubscript{2}-O adsorbate species can be liberated as C\textsubscript{2}-O compounds when they are subjected to a TPH in MeOH-enriched H\textsubscript{2} (blue line) compared to pure H\textsubscript{2} (red line). Presumably, co-feeding MeOH results in the formation of methyl acetate (green line, shift in \(T_{\text{max}}\) from 192 to 263 °C). The MeOH may provide a free OH-group that assists in cleaving a tight bond between the Rh and an oxygen atom from the C\textsubscript{2}-O adsorbate. Thus, the C\textsubscript{2}-O skeleton leaves the Rh without decomposing into hydrocarbons.

**Conclusion**  
C\textsubscript{2}-O production from CO/H\textsubscript{2} is likely to occur via the reaction of C and formate adsorbate species into an acetate like intermediate. Liberation as AcH may be a crucial reaction sequence. Co-feeding MeOH and releasing formed C\textsubscript{2}-O precursors as methyl acetate can circumvent their decomposition.

**References**  
Deactivation of PtPd/Al₂O₃ gas oxidation catalyst by sulphur and phosphorus in laboratory and vehicle aging

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1. Introduction
The combustion of fossil fuels in motor vehicles is one of the most significant causes of air emissions. Using natural gas or biogas reduces significantly the amount of particulates and nitrogen oxides compared to conventional fuels (gasoline and diesel). However, from gas vehicles, relatively high levels of unburned methane (CH₄) may be emitted and, therefore oxidation catalysts are needed to oxidize the unburned hydrocarbons to less harmful emissions. The effect of sulphur and phosphorus on catalyst activity/functionality was studied by using fresh, vehicle aged (160 000 km), and laboratory scale treated metallic monolith PdPt/Al₂O₃ natural gas oxidation catalysts. Separate sulphur and phosphorus treatments were carried out at 400 °C for 5h in a gas phase using a laboratory scale flow reactor. Characterizations of fresh and treated catalysts were done using physiosorption analyses (BET-BJH), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) together with elemental analysis (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Activity measurements were done for the fresh and laboratory treated catalysts: the inlet gas composition was 600 ppm CH₄, 500 ppm CO, 10 vol-% CO₂ 12 vol-% O₂ and 10 vol-% H₂O, and N₂ was used as balance gas.

2. Experimental
The effect of sulphur and phosphorus on catalyst activity/functionality was studied by using fresh, vehicle aged (160 000 km), and laboratory scale treated metallic monolith PdPt/Al₂O₃ natural gas oxidation catalysts. Separate sulphur and phosphorus treatments were carried out at 400 °C for 5h in a gas phase using a laboratory scale flow reactor. Characterizations of fresh and treated catalysts were done using physiosorption analyses (BET-BJH), transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM) together with elemental analysis (EDS), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). Activity measurements were done for the fresh and laboratory treated catalysts: the inlet gas composition was 600 ppm CH₄, 500 ppm CO, 10 vol-% CO₂ 12 vol-% O₂ and 10 vol-% H₂O, and N₂ was used as balance gas.

3. Results and discussion
Characterization of vehicle aged catalyst done by FESEM and XPS shows that sulphur and phosphorus accumulate mainly on the inlet part of the catalyst. Concentration of sulphur and phosphorus in the inlet part of the catalyst was detected to be 12 wt% and 8 %wt and in the outlet part 1.3 wt% and 0.2 wt%, respectively. FESEM-EDS analysis show that sulphur accumulated throughout the support (from the surface to the bottom), but phosphorus was located mainly in the region of 10 μm from the surface. The XPS results indicate sulphur to be sulphate (SO₄²⁻) and phosphorus in phosphate (PO₄³⁻) form. These compounds are adsorbed onto alumina. More detailed analysis by TEM for the laboratory treated catalysts shows that both sulphur and phosphorus slightly increased the average size of the precious metal particles. In addition, a partial transformation from PdO to Pd and a change in the shape of the precious metal particles due to phosphorus were detected by XRD and TEM, respectively. Due to the structural and chemical changes of the catalysts in sulphur and phosphorus treatments reduced the catalytic activity moderately causing shifting of the light-off temperatures (T₅₀) to higher temperatures (~30 °C). [4]

4. Conclusions
The stability of the natural gas oxidation catalyst during its entire lifetime is essential to meet the continuously tightening emission limits set by authorities. The understanding of deactivation phenomena gives tools for the development of catalysts with better resistance to poisons. Sulphur and phosphorus were found to cause morphological and chemical changes on the studied catalysts reducing the catalytic activity. The most significant difference between sulphur and phosphorus was found to be that sulphur adsorbed vertically throughout the entire catalyst support from the catalyst surface to the metallic monolith, while phosphorus accumulated on the surface region of the precious metal containing catalysts.

References
Pt and Pd decorated TiO₂ catalysts for CO₂ activation – surface plasmon studies

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1. Introduction
The continuously increasing concentration of carbon dioxide (CO₂) in the atmosphere caused by the intensive use of fossil fuels is one of the major reasons behind the greenhouse effect and currently ongoing global warming. [1,2] Recycling and valorizing CO₂ from industrial effluents and from the atmosphere by the means of thermal, electrochemical, and photochemical reactions using renewable energy and feedstock would inevitably alleviate such a burden of our globe [1,3]. However, the high thermodynamic stability of CO₂ and the associated high activation energies of all chemical reactions that could yield higher energy products make the conversion very challenging. Although the principle of energy conservation cannot be circumvented, the activation energy may be decreased by applying engineered catalytic materials thus enabling feasible and fast routes towards valorized products. In our work, thus we explore a number of TiO₂ derivatives to study CO₂ activation by H₂ and H₂O in photocatalytic and surface-plasmon assisted routes.

2. Experimental
The studied catalysts were Pd and Pt nanoparticles supported on pristine as well as N-doped TiO₂ nanowires (NWs, derived from hydrothermally grown titanate NWs by calcination) and on nanoparticles (NPs, commercial anatase). N-doping of TiO₂ was achieved by high temperature annealing in NH₃, whereas decoration of the surface by Pd and Pt nanoparticles (loading of 1 wt.%) was done by wet impregnation and subsequent thermal decomposition of the corresponding acetylacetonate precursor. [4] The structure as well as chemical composition and optical properties of the catalytic materials were studied by the means transmission electron microscopy, X-ray diffraction, Raman spectroscopy, surface adsorption, X-ray photoelectron spectroscopy and UV/Vis/near-IR spectroscopy techniques. The photocatalytic activity of the materials, in the 400-500 nm spectral range, was assessed by diffuse reflectance infrared Fourier transform spectroscopy analysis. [5]

3. Results and discussion
The Pt decorated TiO₂ NPs (anatase) show good activation of CO₂ with CO, CO₃²⁻ and CHₓ products. N-doping seems to have only minor effect on the catalytic activity. The NW based catalyst have only very moderate activity, which might be do to the alkaline character and/or the presence of β-TiO₂ phase beside anatase in the crystal. Optical measurements and simulations of the absorption cross-section indicate a significant increase of the optical absorption in the 400-500 nm spectral window for the metal decorated TiO₂ as compared to their non-decorated counterparts. Despite the surface plasmon absorption in both Pd and Pt NPs, the catalysts with Pd nanoparticles show poor activity, which can be caused by the presence of surface oxide layer on the metal as observed by X-ray photoelectron spectroscopy. [5]

References

Acknowledgements
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Urea Synthesis with Pd-complexes in Supported Ionic Liquid Catalysts

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Ureas are indispensable building blocks commonly found in the structures of a large number of biologically active compounds, and are widely used as agrochemicals, dyes, antioxidants and HIV inhibitors. Furthermore, ureas are key intermediates in organic synthesis.[1] Ureas are, among other procedures, prepared via the oxidative carbonylation of amines in the presence of a palladium-complex catalyst, usually at high pressure and temperature and, at times, under an explosive CO/O2 gas mixture[2] making the overall system unsafe. Accordingly, it is desirable to develop an active catalytic system applicable for the oxidative carbonylation of amines under milder reaction conditions.

In the past decade, IL’s have frequently been applied as solid supported ionic liquid phase (SILP) catalysts, where the IL serve either as organocatalyst[3] or as solvent for a homogeneous catalyst.[4] SILP technology combines the benefits of both homogeneous and heterogeneous catalysts allowing high activity and selectivity due to the large interfacial reaction areas, good product separation and catalyst recovery. This can be achieved because the resulting IL film is only a few nanometer thick shortening the diffusion path and the mass transport resistance is minimized compared with biphasic systems.[5] SILP catalysts have been shown to very applicable for gas phase or gas/liquid phase reactions, whereas SILP catalysts in liquid phase reactions have displayed IL phase leaching. In this sense, covalently anchored supported ionic liquid catalysts have been proven to overcome these challenges via covalent anchoring of the IL.[6,7]

In this work, we present a new palladium-complex/SILP catalytic system for continues liquid-phase flow synthesis of diphenyl urea (figure 1), as well as the optimization of catalytic reaction parameters e.g. reaction temperature, space velocity and pressure.

References
Gold- and silver-catalyzed oxidation of 5-(hydroxymethyl)furfural
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1. Introduction
Using biomass and the corresponding platform molecules, highly functionalized chemical intermediates can be produced in a sustainable way [1-3]. This is particularly important for future chemical processes as most of them still heavily rely mostly on fossil resources [2,3]. Hydrolysis and subsequent dehydration of cellulosic biomass leads to for example 5-(hydroxymethyl)furfural (HMF), a promising platform molecule [4,5]. Its selective oxidation results in the interesting intermediates 2,5-furandicarboxylic acid (FDCA) and 5-hydroxymethyl-2-furanca rboxylic acid (HFCA). FDCA is considered to be an important monomer that might replace terephthalic acid in sustainable polymers; similar applications are also possible for HFCA [6]. However, the selective catalytic oxidation of HMF to either FDCA or HFCA under environmentally benign conditions is still challenging. In this study, gold- and silver-based catalysts have been used for the selective oxidation of HMF to FDCA and HFCA in aqueous solution with air as oxidant.

2. Experimental
Au and Ag catalysts on different support materials were prepared by different methods including deposition-precipitation, co-precipitation or flame-spray pyrolysis. The catalysts were characterized by nitrogen physisorption, X-ray powder diffraction, X-ray fluorescence and transmission electron microscopy. Reactions were performed in batch autoclaves using air as oxidant in aqueous solution.

3. Results and discussion
Gold- and silver-based catalysts on different support materials were tested in the oxidation of HMF. For both metals, ZrO$_2$ supported catalysts showed superior product yields compared to other support materials. The reaction conditions including temperature (Figure 1), pressure and amount of base were optimized for 1.6 wt% Au/ZrO$_2$ and 1.0 wt% Ag/ZrO$_2$ catalyst prepared by deposition-precipitation. By variation of the reaction conditions using the Au/ZrO$_2$ catalyst, a switch in the selectivity from HFCA to FDCA was observed, indicating that the alcohol oxidation was the rate-limiting step. On the contrary, HFCA was produced exclusively in the presence of silver catalysts. In general, the synthesis of HFCA was possible under milder conditions compared to FDCA synthesis. Under optimized conditions, HFCA and FDCA could be obtained in high yields (≥ 90 %) and afterwards separated from the reaction solutions.

4. Conclusions
The oxidation of HMF in water with air as oxidant has been performed over gold- and silver-based catalysts. While Au catalysts were active in FDCA synthesis, Ag catalysts produced HFCA exclusively by selective oxidation of the aldehyde moiety. Both products could, after optimization of the respective reaction conditions, be produced in high yields and selectivities. With both catalysts the synthesis of two monomers from HMF for the production of sustainable plastics is possible.

References
Influence of the nature of nickel precursor and its concentration on both functional properties and activity of Ni/ CeO₂-ZrO₂ catalyst in dry reforming of methane

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1. Introduction

A simultaneous reduction of emission of two CO₂ and CH₄ greenhouse gases, the practical use of carbon dioxide and a possibility of replacing carbon-based fuels with hydrogen, are the essential prerequisites for undertaking advanced studies of a reaction known as catalytic dry methane reforming (DMR). In this reaction, the mixture of methane and carbon dioxide undergoes a catalytic conversion to synthesis gas (i.e. hydrogen and carbon monoxide) at temperatures above 700 °C. The mixture being a final product of the DMR is crucial for chemical technology and can be further used for synthesis of a number of key products, including: methanol, ethanol or synthetic hydrocarbon fuels. Moreover, DMR can also be regarded as a valuable source of hydrogen. The main practical drawback, accompanying the DMR reaction, is related with carbon deposition on catalytic surfaces, that results in dramatic decrease in catalytic activity. From this reason various active phases and supports have been intensively investigated. Ni/CeO₂-ZrO₂ systems seems to be one of the most promising. However, further optimization of the parameters decisive for catalytic activity of this system is absolutely necessary. It can be assumed that both the nature of nickel precursor and its dispersion may be important for preventing the system from deactivation. The aim of this study was thus to investigate an influence of nickel precursor and its concentration on functional properties of Ni/CeO₂-ZrO₂ systems, their stability and catalytic activity in DMR.

2. Experimental

Ni/CeO₂-ZrO₂ catalysts were prepared by impregnation of ceria-zirconia supports (of whole concentration range) with such nickel precursors as: Ni-EDTA, Ni-citrate, Ni(CH₃CH(OH)COO), Ni(CH₃COO), Ni(HCOO), Ni(C₂H₃COO) and NiSO₄ as well as with the classic Ni(NO₃)₂. After impregnation all samples were dried overnight at 120 °C and then calcined at 400 °C for 3 h to decompose the precursors. Catalysts of nickel concentrations ranging from 0.5 % to 15 % have been investigated in depth. All samples were characterized by X-Ray Diffraction (XRD), Raman Spectroscopy (RS), X-Ray Photoelectron Spectroscopy (XPS), Infrared Spectroscopy in the diffuse reflectance mode (DRIFT) and electronic spectroscopy (UV/Vis range) in the diffuse reflectance mode (DR). Catalytic activity has been investigated in the temperature range 600-800 °C with initial composition of gaseous reactants: 5% CH₄ in He and 5% CO₂ in He.

3. Results and discussion

Considering a series of Ni/CeO₂-ZrO₂ samples as a reference, it can be stated, that the presence of massive oxide-like forms of NiO were confirmed by both XRD (Figure 1A) and RS (Figure 1B) at 10 mol. % of Ni. Contrary to this, a better dispersion can be observed for samples synthesized from organometallic precursors, investigated by a plethora of spectroscopic methods (XPS, UV/Vis-DR, DRIFT). It was found that nickel dispersion can have a pronounced influence on catalytic activity of Ni/CeO₂-ZrO₂ systems in DMR regarding also the formation of carbon deposits.

4. Conclusions

Concentration of nickel on the surface and its dispersion determined by type of precursor have great influence on properties of Ni/CeO₂-ZrO₂ catalyst.

Acknowledgements

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Preparation and characterization of granulated biomass-based carbon for the catalytic water purification applications

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1. Introduction

Commercial granular activated carbon (GAC) has been acknowledged to be an excellent, but expensive material for removing low-solubility contaminants, such as bisphenol A (BPA), from wastewater [1-3]. Usage of the granules is more favorable than powders as the granules e.g. prevent the dust problem and thus the material processing is easier [4]. After use granules are easier to separate from the liquid phase. Biomass-based carbon offers an environmental friendly and cost-effective alternative for GAC to catalytic processes. The aim of the present work was to examine the optimized conditions for the granulation process of the biomass-based carbon to produce novel, porous, and stable catalytic materials for catalytic wet peroxide oxidation (CWPO) of BPA.

2. Experimental

Granulation of biomass-based wastes, carbonized willow (CW) and carbon residue from the biomass gasification (CRG) process, were investigated. The granulation process was conducted using a rotary drum granulator. The influence of agitation rate and time, solvent and its amount, and the use of binder (e.g. sodium silicate, potassium water glass, methyl cellulose) were evaluated. The stable granules were calcined under nitrogen gas flow (2 L/min) for 5 h at 280 °C. Physical properties of the prepared granules were measured e.g. by BET surface area method. Furthermore, the mechanical strength, stability and surface chemistry (e.g. X-ray diffraction, X-ray photoelectron spectroscopy) were examined. The catalytic activity was studied in the CWPO of BPA.

3. Results and discussion

The results indicate that stable granules can be produced from biomass-based wastes. The receipt for most stable granules as well as mechanical strength are presented in Table 1. For all prepared granules the optimized binding agent-carbon ratio was 1.5:5, metakaolin combined with cement or CaO and the agitation rate 1200 rpm. The mechanical strength values indicate stable and durable structure of the studied granulated carbon materials. In addition, the porous structure on the surface of the granule CRG 3 can be clearly seen in the FESEM image (Fig. 1). Preliminary results from oxidation experiments indicate that catalysts, even without impregnation of an active metal on catalysts surface, were active in the removal of BPA from aqueous solution and approximately 50% abatement was achieved after 3 h CWPO reaction.

![FESEM image of granulated CRG 3 carbon surface.](image)

Figure 1. FESEM image of granulated CRG 3 carbon surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Binding agent (1:1)</th>
<th>Solvent (5 M)</th>
<th>Solvent to carbon ratio</th>
<th>Mixing time (s)</th>
<th>Mechanical strength (N)</th>
</tr>
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<td>KOH</td>
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<td>700</td>
<td>19</td>
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<tr>
<td>CRG 2</td>
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<td>NaOH</td>
<td>1.2</td>
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<td>21</td>
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<td>KOH</td>
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</table>

4. Conclusions

In this research, biomass-based carbon was granulated in order to produce porous and stable materials for catalytic water phase applications. The prepared carbons were mechanically strength and indicated porous structure. Furthermore, the prepared granules were effective in the CWPO of BPA. Therefore, these new granulated biomass-based carbon materials could be further applied as catalysts in catalytic water treatment processes.

References

Conversion of acetone to methyl isobutyl ketone using a bifunctional zeolite catalyst

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1. Introduction
With more focus towards energy and environment, future chemical industry production of bulk and fine chemicals is gradually relying on renewable resources. On-going developments in biomass processing and alternative method of producing bio-acetone by fermentation [1] makes bio-acetone an important platform molecule for the production of chemicals from renewable resources. One particular chemical that can be produced from acetone is methyl isobutyl ketone (MIBK) [2], which has applications in surface-coatings materials and in a variety of non-surface-coating applications as a solvent [3]. Here, we present a novel bi-functional catalyst comprised of Pd nanoparticles encapsulated in ZSM-5 zeolite to produce MIBK from acetone.

2. Experimental
Methyl isobutyl ketone is synthesized via direct conversion of acetone using palladium nanoparticles supported over conventional HZSM-5 and Mesoporous HZSM-5. The encapsulation of Pd nanoparticles in zeolite ZSM-5 for this reaction is done according to a modified literature procedure [4]. Additionally, effect of morphology and the close proximity between the acid and metal active sites is studied by supporting Pd nanoparticles on the external surface of a conventional ZSM-5 zeolite and on a mesoporous ZSM-5 prepared by carbon templating. The prepared materials were characterized with various techniques including SEM, TEM/STEM, TPD, XRF, nitrogen physisorption and XRD among others.

3. Results and discussion
A TEM image of as-synthesized Pd@ZSM-5 zeolite is shown on the Figure 1. As seen from the figure, Pd clusters encapsulated within zeolite crystals are uniformly distributed throughout the crystals with average size of encapsulated nanoparticles in the range of 1-2 nm. Further studies on pore size distribution, porosity, pore volume, area of adsorption etc. of the synthesized material were carried out using N₂ physisorption. Figure 2 illustrates stability of synthesized catalyst with different encapsulation strategies during the conversion process. The result shows that in-situ encapsulation of nanoparticles on ZSM-5 zeolite (Pd@ZSM-5) gives better conversion result as compared to other catalysts.

4. Conclusions
Pd nanoparticles were encapsulated in ZSM-5 and used as bifunctional catalyst for the one-step synthesis of methyl isobutyl ketone from acetone. Of different methods employed to encapsulate Pd nanoparticles in ZSM-5, in-situ encapsulation of (ethylendiamine) -palladium (II) chloride during hydrothermal synthesis was found to be simple and effective method. The encapsulated nanoparticles have improved thermal stability and higher catalytic activity compared to the corresponding catalysts prepared by simple impregnation.

References

![Figure 1. TEM image of Pd nanoparticles encapsulated in HZSM-5.](image_url)

![Figure 2. Stability of synthesized catalyst with different encapsulation strategies.](image_url)
The effect of biofuel and lube oil-derived contaminants on the durability of Cu-SSZ-13 and V$_2$O$_5$-WO$_3$/TiO$_2$ SCR catalysts for heavy-duty vehicles

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1. Introduction

To comply with upcoming more stringent emission legislations, highly active, selective and durable exhaust aftertreatment catalysts are needed. A challenge for these catalysts is catalyst deactivation due to contaminants in the fuel or lube oil, e.g. sulfur and phosphorus, or high temperatures. In Europe, the concentration of sulfur in diesel and biodiesel is limited to maximum 10 ppm; the highest allowable concentration of phosphorus in biodiesel is 4 ppm. For the total life of a heavy-duty vehicle this corresponds to around 2.4 and 0.8 kg S and P, respectively. The lube oil further contributes with additional S and P. [1] Most part of the sulfur in the exhaust is in the form of SO$_2$. However, when a diesel oxidation catalyst (DOC) is present in front of the SCR catalyst, a significant amount of this SO$_2$ can be converted to SO$_3$/H$_2$SO$_4$. [2] SO$_3$ has been shown to cause a more severe deactivation than SO$_2$ for Cu-zeolite SCR catalysts. [2-4] In this study, we investigate the effect of phosphorus and sulfur (SO$_2$, SO$_3$) on the performance of V$_2$O$_5$-WO$_3$/TiO$_2$ and Cu-SSZ-13 selective catalytic reduction (SCR) catalysts. The aging is performed using a diesel burner operated on contaminant-doped biodiesel. The results presented in this study will lead to an increased understanding of fuel- and lubricant-related deactivation of exhaust aftertreatment catalysts, thus providing knowledge for producing more durable aftertreatment systems.

2. Experimental

Fresh DOCs (Pt-Pd/Al$_2$O$_3$) and SCR catalysts (Cu-SSZ-13, V$_2$O$_5$-WO$_3$/TiO$_2$) are aged using a diesel burner that is operated on biodiesel (RME). Three different aging experiments are performed: one using only biodiesel while the other two use doped (P or P+S) biodiesel. In each aging experiment, four SCR catalysts and two DOCs are aged. The DOCs are positioned in front of two of the SCR catalysts, thus these SCR catalysts are exposed to a mix of SO$_2$ and SO$_3$, with a significant part being SO$_3$, for the aging with S-doped biodiesel. Prior to, and after the aging, the performance of all catalysts are evaluated. In the performance tests for the SCR catalysts, a gas composition of 0/500/1000 ppm NO and NH$_3$, 2/5/10 vol% O$_2$, 5 vol% H$_2$O, and a GHSV of 120,000 h$^{-1}$ is used.

3. Results and discussion

In Figure 1, the performance (NO conversion and N$_2$O production) of fresh Cu-SSZ-13 and V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts samples are shown. The Cu-SSZ-13 catalyst is considerably more active than the V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst, especially at low temperature. The durability of the two different SCR catalysts towards phosphorus and sulfur (SO$_2$, SO$_3$) will be presented. Elemental analysis of the aged catalyst will provide information about the capture efficiency of S and P in the different aftertreatment catalysts.

Figure 1: NO conversion (left) and N$_2$O selectivity (right) of fresh Cu-SSZ-13 and V$_2$O$_5$-WO$_3$/TiO$_2$ SCR catalysts during standard SCR reaction. GHSV 120,000 h$^{-1}$, 1000 ppm NO and NH$_3$, 10% O$_2$, 5% H$_2$O

References
**REALCAT: An Integrated and Advanced High-Throughput Platform for Catalysts Synthesis, Characterisation and Testing**

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Catalysis is of utmost interest in crucial domains such as, for instance, Environment, Food, Health and Energy. The development of new catalysts with improved performances is therefore a highly strategic issue [1]. Innovation in catalysis is based, on the one hand, on forefront fundamental research to develop new catalytic concepts and, on the other hand, on an experimental phase devoted to the synthesis, characterization of the catalytic formulations and on the measurement of their properties/performances. The experimental part of the development of a new catalyst is time- and money-consuming, as traditional “trial and error” methods for synthesizing and testing catalysts are still needed. A priori theoretical prediction of optimal catalyst composition, structure and conditions of preparation for a given reaction is actually not yet possible. Therefore, there is a strong need for rapid preparation, characterization and screening of catalytic systems.

The main objective of the REALCAT project (French acronym standing for ‘Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design’) is to set up a highly integrated platform devoted to the acceleration of innovation in all fields of industrial catalysis with an emphasis on catalytic processes for biorefinery. In this extremely competitive field, REALCAT consists in a versatile High-Throughput Technologies (HTT) platform devoted to innovation in heterogeneous, homogeneous or biocatalysts AND their combinations under the ultra-efficient very novel concept of hybrid catalysis. The REALCAT platform is a complete, unique, and top-level HTT workflow including (i) robots for the automated synthesis of catalysts and novel biocatalysts, (ii) rapid characterization tools and (iii) a series of versatile parallel continuous and batch reactors - for gas phase, liquid phase or three phases reactions - combined with ultra-fast analytical tools at the top of the state-of-the-art for the analysis of the products in the reactors effluents [2].

Three laboratories, all located in Lille University (North of France) have gathered their forces to design such a challenging project: UCCS, specialized in homogeneous and heterogeneous catalysis; Institute Charles Viollette, specialized in biocatalysis; and CRISStAL, specialized in data treatment, bio-informatics, modelling and analysis of biologic systems. This unique integrated combination of skills is of outstanding importance for the optimization of the different operations of the platform. This makes REALCAT a major actor of high-level R&D catalysis programs on hot topics such as energy, environment, food and health applications.

In this communication, the REALCAT project will be presented in details together with some examples of recent discoveries made using our high-throughput equipment and methodologies.

**Acknowledgement**

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**References**

Synthesis of Metal-containing Silicalite Zeotypes for the Direct Conversion of Methane to Methanol

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1. Introduction
The direct conversion of methane to methanol, DCMM, represents the “Holy Grail” for catalysis of the last two decades [1]. The oxidation of CH₄ to value added products, e.g. CH₃OH, via non-syngas based techniques is desirable to obtain higher energy storage capacity and more sustainable fuels. Metal-containing zeolites used as catalysts have shown the most appreciable results in the DCMM [2] in a four steps procedure: addition of metals to the zeolite, formation of the active site by oxidation at high temperature, reaction with methane at low temperature and extraction of methanol by solvents, e.g. water [3]. It has been shown that most of the products remain adsorbed on adsorption sites, making the extraction of methanol the limiting step [4]. In 2012, Hammond et al. obtained remarkable CH₄ conversion and selectivity towards CH₃OH using a mixture of Al-free zeotypes as catalysts. In particular, the catalysts consisted of Fe and Cu containing silicalite, the Al-free parent of the commercial ZSM-5 zeolite with MFI type of framework structure. Fe and Cu were added prior to and post crystallization, respectively, resulting in framework and extra-framework metal species [5]. The lower acidity of the Al-free zeotypes Fe- and Cu-silicalite zeotype compared to Fe-exchanged ZSM-5 zeolite is believed to facilitate CH₃OH desorption due to the higher hydrophobicity of the Al-free zeotype.

2. Experimental
Pure and Fe-, Cu- and Al-containing silicalite zeotypes (S, Fe-S, Cu-S and Al-S) are hydrothermally synthesized, characterized with diffraction and spectroscopy techniques and tested for the DCMM. The silica precursor is mixed with the structure directing agent, SDA, and the metal precursor in aqueous medium. The so obtained gel is crystallized in autoclave and the products are washed, filtered and dried. The SDA is then removed by calcination. The MFI type of framework structure is confirmed by PXRD and more insights about the incorporation of metals in the framework are given by spectroscopy techniques, e.g. DRIFTS, Raman spectroscopy and XPS. The tendency of CH₃OH to desorb from the internal surfaces of the catalyst is detected by CH₃OH-TPD, and the evolution of surface species is followed using DRIFTS. Furthermore, the catalytic activity is tested using a continuous gas-flow powder reactor where the outlet gas is analyzed by mass spectrometry, MS, and Fourier transform infrared, FTIR, spectroscopy.

3. Results and discussion
The as synthesized and the calcined powder samples of S, Fe-S and Al-S were white indicating high crystallinity and no or minor formation of metal clusters. On the other hand, the as synthesized and calcined powder samples of Cu-S were light-brown, indicating that some metal oxides and/or hydroxide formed homogeneously through the sample. The MFI type of framework structure was confirmed by XRD. Furthermore, the XRD patterns of the as synthesized samples and their respective calcined samples did not show any peak shifts, confirming the stability of the framework structure. The elimination of the SDA by calcination leads to the disappearance of the peaks associated to the organic molecule and the variation of some peak intensities, but does not influence the position of the peaks in the pattern. The XRD patterns of Fe-S, Cu-S and Al-S confirm the MFI structure but do not show any extra peaks associated to metal particles, neither any peak shifts compared to the XRD pattern of S. This means that the amount of metals is likely too low to be detected by XRD both if some particles formed and if Fe, Cu and Al were incorporated in the framework structure.

4. Conclusions
Pure, Fe-, Cu- and Al-silicalite were hydrothermally synthesized and subsequently calcined to remove the SDA. The MFI type of framework structure was confirmed by XRD and the removal of the SDA by calcination could be seen by the disappearance of the XRD peaks associated to the organic molecule. Nevertheless, no peak shifts associated to the metals incorporation in the framework or extra-peaks associated to metal particles could be observed. This might be due to the fact that the metal contents were too low to be detected by XRD.

References
The Research on Reduction of HNCO in a Urea-SCR System

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1. Introduction
As an effective exhaust aftertreatment measure, selective catalytic reduction (SCR) is currently the most widely used in marine diesel engines. The Urea-SCR has become the main method for marine diesel engines to meet the IMO Tier III emission regulations. Isocyanic Acid (HNCO) is the main intermediate in urea-SCR, which affecting the efficiencies of urea and NOx removal. The study on HNCO reduction process has been carried out in this paper.

2. Experimental
Based on the previous tests of NH3-SCR, with different catalysts, a research is given on the action of HNCO reduction process by varying the selected parameters, i.e. reaction temperature, space velocity and HNCO/NOx ratios. Meanwhile by adding water, SCR experiments are carried out with HNCO+NH3 as reductant.

3. Results and discusses
3.1 The effect of reaction temperature on HNCO reduction
With a space velocity of 12000h⁻¹ and a HNCO/NOx ratio of 1, the NOx removal efficiencies under different temperatures can be obtained. The trends of NOx removal performance on temperatures with different catalysts are shown in Figure 1. The NOx removal efficiencies of HNCO with temperatures under different catalysts are similar to but lower than those of NH3. In addition, by using HNCO reductant, the extruded V2O5-WO3/TiO2 catalyst has the best NOx removal efficiency in the tested catalysts.

3.2 The effect of space velocity on HNCO reduction
3.3 The effect of HNCO/NOx ratio on HNCO reduction
3.4 The effect of water on HNCO reduction

4. Conclusions
(1) For NH3 reductant, when test temperature is 350°C, SCR system has the best NOx removal efficiency; and the test system reaches its best NOx removal efficiency with a space velocity of 6000h⁻¹ and a NH3/NOx ratio of 1.3 respectively. (2) For reductant HNCO, when test temperature is 350°C, SCR system has the best NOx removal efficiency; also for space velocity, the best NOx removal efficiency is occupied by a space velocity of 6000h⁻¹; while the HNCO/NOx ratio does nothing to NOx removal efficiency. However, from an overall perspective, the efficiencies of NOx removal are less than those of NH3. (3) When using the composition of HNCO and NH3 as reductant, the NOx removal efficiency is with the same direction of temperature, and the actual NOx removal efficiency is between those of HNCO and NH3.

References
The Study on de-NOx activity of Mn catalysts based on TiO₂–MCNTs composite carrier

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1. Introduction
Low temperature selective catalytic reduction (SCR) with NH₃ as reducing agents has become one of the most promising technologies to meet the emission regulation of NOₓ from two stroke marine diesel engine. And the catalyst is one of the key issues at low temperature SCR. By sol-gel method the catalysts were prepared by MnOₓ as active components doped on carbon nanotubes and TiO₂ composite carrier, and the low temperature catalytic activity is investigated in this paper.

2. Experimental
In the paper, there are two kinds of experiments, catalyst preparation experiments and de-NOx performance tests of catalyst. Catalyst de-NOx performance experiments were carried out on the catalyst activity experiment device (SCR), mainly including the following experiments: (1) effects of mass ratio of carbon nanotubes and TiO₂ in catalysts on de-NOx catalytic activity; (2) effects of molar ratio of MnOₓ and TiO₂ in catalysts on de-NOx catalytic activity; (3) effects of calcination temperatures on catalytic activity; (4) effects of metals loaded in dual-metal catalysts on de-NOx catalytic activity.

3. Results and discusses
3.1 Effect of mass fraction of MCNTs and TiO₂ on the catalytic activity
The de-NOx efficiencies of Mn/TiO₂–MCNTs catalysts with different mass fractions of MCNTs and TiO₂, i.e. 0, 5%, 10% and 15%, were shown in Figure 1, with a molar ratio of 0.4 between MnOₓ and TiO₂. It can be found that, with the increasing of mass fraction of MCNTs, the catalytic activity of Mn/TiO₂–MCNTs catalysts displays a law of increasing at first and then decreasing. It also can be found that, compared with test results from Mn/TiO₂ catalysts with no MCNTs added, the de-NOx efficiency is raised from 34% to 60% on 150°C and 10% mass fraction of MCNTs.

4. Conclusions
(1) The increased MCNTs can significantly improve low temperature activity of the Mn/TiO₂–MCNTs catalysts. With the increasing MCNTs, MnOₓ and calcination temperature, the activity of Mn/TiO₂–MCNTs catalysts has the trends of increasing at first and then decreasing. (2) Metal elements can increase the specific surface area and dispersion of active components in Mn/TiO₂–MCNTs catalysts, also have obvious effect on de-NOx catalyst activity of dual-metal catalysts. Metal elements Ce can make a more even metal oxide coated on the surface of carbon nanotubes, increasing catalysts specific surface area and improving de-NOx efficiency of dual-metal catalysts. (3) Catalyst characterization shows that, the more even distribution of active components in catalyst surface and more amorphous MnO₂ can obtain a better low temperature catalytic activity in Mn-Ce/TiO₂–MCNTs when Ce added.

References
Metal nanoparticles in zeolites for selective catalysis

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1. Introduction

In spite of the great technological, environmental and economic interests, general methods for the stabilization of metal nanoparticles against sintering are missing. Although for some specific systems it has been achieved by optimizing the interaction of nanoparticles with a support material or by encapsulation of the metal particles [1-3]. However, these known catalytic systems are in general rather expensive and difficult to synthesize and they cannot be produced in industrial scale. Therefore, the development of novel sintering stable heterogeneous nanoparticle catalysts, which find use in the chemical industry, is of great importance.

Recently, we have developed several different catalytic systems where metal nanoparticles are con-fined in different porous materials. As an example, gold nanoparticles were encapsulated inside silicalite-1 zeolite [4]. The aim with encapsulation metal nanoparticles in zeolites, is first of all to prevent the metal nanoparticle from sintering during a high temperature catalytic reaction. Furthermore, the zeolite can also contribute active to the catalytic reaction. We have for instance shown that the encapsulated metal nanoparticles only are accessible through the pores which give highly size-selective reactions [3].

Here, we present the progress, which we have made, on the synthesis of different types metal nanoparticles confined in different zeolite materials and their application in catalysis.

2. Experimental

All the reported materials were synthesized from commercially available chemicals. Zeolite silicate-1 (above) was prepared using traditional synthesis method. Preparation of gold recrystallized silicate-1 was based on impregnation of recrystallized silicate-1 prepared by an alkaline dissolution-reassembly process in the presence of the surfactant [4].

We have tested the materials as catalysts in different selective oxidation and hydrogenation reactions. Furthermore, we have characterized the materials with various techniques including SEM, in situ TEM, STEM, TEM tomography, XPS, XRF, BET and XRD among others.

3. Results and discussion

Here, the progress which we have made on the synthesis of metal nanoparticles confined in different zeolite materials is presented. As an example, in figure 1, is shown gold nanoparticles trapped inside a silicalite-1 zeolite. The gold nanoparticles are 2–3 nm in diameter and the particles are only situated inside the zeolites [4]. The materials were characterized by X-ray photoelectron spectroscopy (XPS). The XPS also confirms that the metal particles only are trapped inside the zeolite. Addition-ally, the encapsulated nanoparticles were demonstrated to be highly active and selective for the catalytic gas-phase oxidation of ethanol to acetaldehyde. Other, metals produced and tested in various reactions. For instance, have we shown that nickel encapsulated nanoparticles in zeolites are highly active in methanisation of carbon dioxide to methane.

Moreover, all the obtained materials were tested as selective catalysts in different reactions and characterized with various techniques including SEM, TEM tomography, XRF, BET and XRD among others.

4. Conclusions

In conclusion, we have developed several simple and effective methods to encapsulate metal nanoparticles in different porous materials. The methods are cost-effective, practical, and results in a narrow size distribution of small nanoparticles that are situated inside the zeolite materials. Furthermore, the materials showed to be active selective catalysts.

References

Morphology study of electrolytic silver catalyst for partial oxidation of methanol to formaldehyde (MTF)

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1. Introduction
Formaldehyde is a highly versatile precursor/chemical applied in more than 50 branches of industry. The reactive aldehyde is produced from methanol by catalytic partial oxidation over either metal oxides, e.g. ferric molybdate, or pure silver. The silver morphology affects the methanol reactivity and selectivity towards formaldehyde [1-5], as well as stability. To further understand the role of the silver morphology in the MTF reaction, a study focusing on different atmospheres’ effect on the restructuring and catalytic activity was performed.

2. Experimental
Electrolytic Ag particles were supplied by K.A. Rasmussen AS (Figure 1), with a standard fraction of 0.25-0.5 mm applied in all analyses. Induction of morphological changes and measurements of catalytic activity were performed in a laboratory-scale fixed-bed reactor. Industrially relevant temperatures were applied, while atmosphere composition and experimental duration were varied (Table 1). When assessing catalytic activity for CO and H₂ oxidation experiments, an on-line GC was applied. All samples were analyzed by Scanning Electron Microscopy (SEM) post-reaction/treatment.

3. Results and discussion
Treating the silver with different atmospheres at elevated temperature results in evident changes of the silver surface and morphology. The most significant changes were caused by oxygen exposure and hydrogen oxidation, as well as the MTF reaction, creating holes, sintering and facet formation. Sintering and facet formation are in accordance with the increase in inter and surface diffusion occurring in the presence of oxygen and temperatures above Tamman temperature (477°C). The observed pinhole formation may be linked to increased diffusivity of oxygen and possibly hydrogen in the near surface region at industrial conditions. Silver enables oxidation of both hydrogen and carbon monoxide, causing formation of water and carbon dioxide. These are well-known byproducts in the MTF synthesis, and could be important in the assessment of the full reaction mechanism.

4. Conclusions
The silver catalyst undergoes structural changes during different atmospheres and temperature, resulting in a complex dependency upon which both variables play an important part. These morphological changes are relevant for both the catalytic performance and stability. Aiming at investigating the correlation between structural characteristics and activity, a systematic approach to expose the granular silver to different environments, changing one factor at a time could be a rewarding methodology.

References

Figure 1: SEM image of fresh electrolytic Ag particles.
In-situ Probing of the Oxidation/Reduction Dynamics of Pure and Na, P, K-contaminated Pt/Pd/Al₂O₃ DOC Catalysts by XAFS and flow reactor measurements

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1. Introduction

Emission level goals for heavy duty vehicles are typically achieved by a combination of diesel oxidation catalysts (DOC), diesel particulate filters, selective catalytic reduction catalysts and ammonia slip catalysts. The DOC is often a Pt/Pd/Al₂O₃ catalyst placed first in the exhaust after-treatment system, and is of key importance for the overall effectiveness. This oxidation catalyst is heavily exposed to untreated exhaust, and thus particularly susceptible to chemical aging. In this work, we probe the effects of P, Na and K contaminations on the oxidation/reduction dynamics of the DOC catalyst using in-situ XAFS and supporting flow reactor studies.

2. Experimental

Catalysts were prepared by wet impregnation of Al₂O₃ with Pt and Pd salts, with a mass ratio of Pt/Pd of 9/1. Uncontaminated samples and samples chemically aged by soaking in Na, P, or K salts were prepared. Dried samples were calcined and placed in the flow reactor for CO oxidation light-off studies to monitor catalyst activity. Catalysts were then examined using XAFS spectroscopy [1], with oxidation/reduction cycles and exposure to reaction conditions in situ. Following XAFS characterization, samples were examined using STEM to determine composition and morphology.

3. Results and Discussion

Flow reactor and EXAFS data show a difference in reduction and oxidation dynamics for contaminated vs fresh samples. P, K and Na contaminated samples all show a faster and more complete reduction of the Pt-O bond (the Na case is illustrated in fig. 1), an effect that persists to some extent during reoxidation by CO in H₂O and O₂. Correlating this observation with the light-off curves for fresh and Na contaminated samples (fig 2) we can conclude that these dynamics can be used to explain the lower light-off temperature seen for the Na contaminated samples in our flow reactor measurements. We further show using STEM studies that there is a preference for Na and P contaminants to associate with the Pt particles as opposed to the alumina support which suggest a chemical or strong physical interaction between the two.

4. Conclusions

A correlation between the reduction/oxidation dynamics as probed by XAFS and the light-off temperature has been found, indicating that Na, P and K-contaminated Pt/Pd/Al₂O₃ DOC catalysts are more susceptible to reduction of the Pt-O bond and that this effect can result in lower light-off temperatures. These trends hold true for P and K as well, to lesser degrees, and further synchrotron and flow reactor studies are currently underway to probe this effect.

References


Figure 1 illustrates the reduction B) and reoxidation C) of the fresh vs Na-contaminated samples. Panel A) shows the as prepared samples to be similar in structure showing only the Pt-O bond. During reduction the Pt-Pt bond quickly starts to dominate in the Na sample and this effect persists throughout reoxidation as the Pt-Pt bond is more pronounced even during CO oxidation in the Na case.

Figure 2. Light-off curves for CO-oxidation showing higher conversion for the Na-contaminated sample as a function of temperature.
Optimising the Composition of High Entropy Alloys for a Desired Adsorption Energy for Catalysis: Exemplified for the Oxygen Reduction Reaction

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1. Introduction
In this work we present our work on developing a theoretical model for predicting the adsorption energy on a recently developed type of highly disordered “high entropy” alloy (HEA) [1], consisting of approximately equal proportions of at least 5 different component elements. This work represents the first theoretical investigation into heterogeneous catalysis on an HEA surface, in this case focusing on the oxygen reduction reaction (ORR). The method directly relates the composition of an HEA to its catalytic activity, granting the ability to re-engineer the composition resulting in activity enhancements.

2. Experimental
DFT was used to calculate the adsorption energies of OH and O on the HEA Pt-PdIrRhRu. The calculations were performed using a plane-wave basis using GPAW in ASE. HEAs exist as a solid solution with the constituent elements randomly distributed throughout the lattice, leading to a very large number of possible binding sites. In order to fully investigate such a surface a simple linear model was developed to predict the adsorption energies of the available binding sites, considering only the binding-site nearest neighbour atoms in 1000 4 atom thick 2x2 slabs. Predictions were made using linear regression to learn from the DFT data. Further to this we optimise the fractional contributions of the constituent elements with the intention of increasing catalytic activity by maximising the “likelihood” of finding binding sites on the surface with corresponding adsorption energies close to an optimum predicted by the ORR volcano curve for OH binding [2].

3. Results and discussion
The 1000 DFT calculations on the HEA surface showed a near-continuous distribution of adsorption energies for both O and OH. We found our linear model to be very good at predicting the adsorption energies of O and OH on fcc and on-top binding sites, respectively, which can be seen for OH in fig.1. Our model is simple in that it only includes information about the number of each element constituting the nearest-neighbours to the binding site atom(s) (seen in fig.2), demonstrating that the effect of the next-nearest neighbour configuration around a binding site tends to a mean-field. Optimisation of the HEA composition resulted in new HEA compositions with upper-bound activity enhancements of up to a factor of 28 compared to a pure Pt(111) surface. The predicted adsorption energy distribution is seen in fig.3 with the OH volcano plot overlaid, indicating an exponential enhancement in catalytic activity

4. Conclusions
The model outlined in this work demonstrates the potential held by HEAs as a surface for the ORR reaction in electr ocatalysis. DFT calculations of the adsorption energies of OH and O on a randomly generated subset of available binding sites on HEA PtPdIrRhRu were used to train a simple model. The model was then applied to the remaining binding sites, showing a near-continuous distribution of adsorption energies available on the HEA surface. Activity calculations demonstrate enhancements compared to Pt(111), indicating that the existence of a small number of adsorption energies lying on or very close to the predicted optimum overcomes the reduction in activity due to the wide distribution.

References
Insight into the activity of Au/TiO2 catalyst coatings for gas-phase partial oxidation of 1-butanol in a microreactor: The effect of catalyst synthesis pH

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1. Introduction
Microreactors coated with catalytically active porous layers have emerged advantageous in the past decades over conventional reactors because of their inherently safe operation in nearly isothermal conditions and within the kinetic regime [1]. Bio-based 1-butanol produced by the acetone-butanol-ethanol (ABE) fermentation is considered an important platform chemical to increase the share of value-added chemicals through the development of new catalytic processes [2]. In our previous work, Au and Pd nanoparticles supported on TiO2 were coated on microreactors and tested for gas-phase partial oxidation of 1-butanol [3]. The Au/TiO2 (0.6 wt.%) coated catalyst showed the best yield of n-butyraldehyde (20% at 300 °C), as well as outstanding durability and reusability [3]. The aim of the present study was to improve the yield of this Au/TiO2 (0.6 wt.%) coated catalyst.

2. Experimental
Catalyst powders (0.6 wt.% Au/TiO2) were prepared with sol-immobilization method (recipe modified from [4]) adjusting the catalyst synthesis pH to either 1 or 3 [3]. The coating procedure of the microreactor plates was as in [3]. The catalyst powders and the coated plates were characterized by various techniques.

Partial oxidation of 1-butanol was studied at atmospheric pressure in a catalyst testing microreactor (CTMR) by IMM (Institut für Mikrotechnik Mainz GmbH, Mainz, Germany). 1-Butanol was evaporated and mixed with synthetic air. Reaction was studied at 130-400 °C. FTIR was used to analyze the product gas.

3. Results and discussion
The coating of 0.6 wt.% Au/TiO2 (pH 3) on microreactor plates yielded narrow particle size distribution of Au and small average particle size (ca. 3.6 nm), shown in Fig. 1. In the gas phase oxidation of 1-butanol, the conversion of 1-butanol was nearly the same for both Au catalyst coated plates (around 63% at 350 °C), i.e. independent of the pH applied in the synthesis. However, the yield of n-butyraldehyde was significantly improved at temperatures above 250 °C for the Au catalyst with synthesis pH of 1 compared to that of Au catalyst with synthesis pH of 3 (Fig. 2). The adsorption of Au nanoparticles can be modified by tuning the catalyst synthesis pH [5]. Moreover, it has been reported that in CO oxidation, gold is present in both cationic (Auδ+) and in metallic (Au0) form in active Au/TiO2 catalyst [6]. The characterization results in this work will be correlated to the activity of the 0.6 wt.% Au/TiO2 catalysts prepared with different catalyst synthesis pH.

4. Conclusions
Catalyst synthesis pH did not affect the conversion of 1-butanol. However, lowering catalyst synthesis pH from 3 to 1 increased the yield of n-butyraldehyde from 24% to 55% at 400 °C over 0.6 wt.% Au/TiO2 catalysts.

Figure 1. Gold particle size distribution of the 0.6 wt.% Au/TiO2 prepared with synthesis pH of 3 (modified from [3]).

Figure 2. Yield of n-butyraldehyde over 0.6 wt.% Au/TiO2 coated catalysts with different synthesis pH (1 or 3).

References
Efficient removal of bisphenol A from wastewaters: Catalytic wet air oxidation with Pt catalysts supported on Ce and Ce-Ti mixed oxides

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1. Introduction
Bisphenol A (BPA), 2,2-((4,4-dihydroxydiphenyl) propane, is used as an intermediate in the production of polycarbonate and epoxy resins [1]. It is classified as an endocrine disrupting chemical (EDC) which has been reported to affect sexual development and is associated with abnormal feminizing responses in animals and possibly in humans [2-4]. According to several studies related to the toxicity of BPA to animals and humans, the need for an effective treatment method for the destruction of BPA in contaminated waters is essential. One of the most interesting wastewater treatment techniques is catalytic wet air oxidation (CWAO) which is capable of mineralizing organic compounds of wastewater at elevated temperatures (130-200 °C) and pressures (0.5-5.0 MPa) in the presence of a catalyst to intermediates, CO2 and water [5]. In this research, platinum catalysts supported on cerium oxide and cerium-titanium mixed oxides have been studied in the CWAO of an aqueous solution of BPA.

2. Experimental
CeO2, Ce0.8Ti0.2O2 and Ce0.2Ti0.8O2 oxides were prepared via the sol-gel method and Pt was impregnated onto supports by the wet impregnation technique. Prepared catalysts were characterized by using BET, XRD, FESEM, XPS and elemental analysis techniques. CWAO of aqueous solution of BPA (60 mg L-1) was carried out in a batch reactor at a reaction temperature of 160 °C and pressure of air 2.0 MPa by using catalyst concentration of 4 g L-1. Water samples were analysed by UV-Vis, TOC and UPLC analytical techniques, in order to study the efficiencies of the used catalysts for the removal of BPA from water.

3. Results and discussion
According to characterization results, CeO2 and Ce0.8Ti0.2O2 have moderate surface area (Table 1). The addition of titanium into CeO2 turned Ce0.2Ti0.8O2 amorphous (see Fig. 1) and doubled the surface area.

However, CWAO of BPA is not a surface area specific reaction. The highest abatement of BPA was achieved with Pt/Ce0.2Ti0.8O2 and Pt/Ce0.8Ti0.2O2 catalysts, 97 and 95% respectively (Table 1). The activity of these catalysts is to do with the high concentration of chemisorbed oxygen (Table 1) and Ce4+ on the surface of the catalysts.

4. Conclusions
CWAO of BPA was carried out with sol-gel prepared Ce-Ti supports by using Pt as active metal. All catalysts were active in the removal of BPA from aqueous phase and Pt/Ce0.2Ti0.8O2 and Pt/Ce0.8Ti0.2O2 were the most active in the oxidation reaction. With those catalysts, no phase changes and carbonaceous deposits existed after oxidation reaction. Therefore, Pt/Ce0.2Ti0.8O2 and Pt/Ce0.8Ti0.2O2 show high potential in the removal of endocrine disrupting chemicals from wastewaters by catalytic wet air oxidation.

References
The Study on de-NOx activity of Mn catalysts based on P25-MCNTs composite carrier

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1. Introduction
Low temperature selective catalytic reduction with NH3 as reducing agents has become one of the most promising technologies to meet the IMO emission regulation of NOx from low speed marine diesel engine. And the catalyst is one of the key items at low temperature SCR system. However there are some defects in SCR catalysts, such as small specific surface area, low catalytic activity and weak dispersion of active components. By impregnation method the catalysts were prepared by MnOx as active components doped on carbon nanotubes and TiO2 composite carrier, and the low temperature catalytic activity is investigated in this paper.

2. Experimental
In the paper, there are two kinds of experiments, catalyst preparation experiments and de-NOx performance tests of catalyst. Catalyst de-NOx performance experiments were carried out on the catalyst activity experiment device, mainly including the following experiments: (1) effects of molar ratio of MnOx and TiO2, mass ratio of carbon nanotubes and TiO2 in catalysts and calcination temperatures of catalysts on de-NOx catalytic activity; (2) effects of metals loaded in dual-metal catalysts on de-NOx catalytic activity; (3) effects of the third metal loaded in ternary-metal Mn catalysts on de-NOx activity based on P25-MCNTs composite carrier.

3. Results and discuss
3.1 Effect of Mn on the catalytic activity
The catalytic activity of Mn/P25-MCNTs(10%) catalysts with different Mn content is shown in Figure 1. It can be found that, with the increasing MCNTs content, the activity of Mn/P25-MCNTs catalysts has the trends of increasing at first and then decreasing. The catalyst has the best activity when the molar ration of MnOx and TiO2 equals to 0.4.

3.2 Effect of mass fraction of MCNTs and TiO2 on the catalytic activity

4. Conclusions
(1) The increased MCNTs content can significantly improve low temperature activity of Mn/P25-MCNTs catalysts. With the increasing contents of MCNTs, MnOx in catalysts and calcination temperature of catalyst, the activity of Mn/P25-MCNTs catalysts has the trends of increasing at first and then decreasing. (2) The addition of metal elements on impregnated preparation catalysts almost has no effect on the de-NOx activity of the dual-metal catalysts, but to a great extent has a certain effect on that of ternary-metal Mn catalysts. The Mn-Ce-Ni/P25-MCNTs(10%) catalyst has the highest de-NOx efficiency in all tested temperatures. (3) In-situ infrared pyridine experiments show that, there are both Lewis acid site and Brönsted acid site exist in Mn-Ce-Ni/P25-MCNTs catalysts. The addition of Ce oxides will result in the increasing of acid site of weak acid, and this maybe the cause of increased catalyst activity.

References
**Catalytic Oxidation of Methane over Rhodium Catalysts**

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1. **Introduction**

Natural gas is an interesting engine fuel for ships in coastal zones, where high sulfur marine fuels cannot be used. However, unburnt methane poses another severe emission problem. A catalytic CH₄ oxidation unit, which can fully convert the unburnt CH₄ to CO₂ and H₂O under the real exhausts gas condition, is needed to solve the problem. Among the catalysts studied for CH₄ oxidation, Pd based catalysts are the most active in the absence of H₂O and SO₂[1], while they suffer from deactivation caused by H₂O and more detrimentally, SO₂. It was studied as a promoter for the Pd based catalyst to enhance the H₂O and SO₂ resistance, but the activity of Pd-Pt/Al₂O₃ catalyst still declines in the presence of 10 vol.% H₂O and 2.5 ppm SO₂ (from 55 % to 0% at 400 °C and from 100 % to 20 % at 450 °C after running for 25 h) [2]. A catalyst that remains sufficiently active under real exhaust gas conditions (350-550 °C, 5-10 vol.% H₂O and 1-2 ppm SO₂) is still being sought. In this contribution, a comparison between a commercial (Rh-Al-Cr) catalyst from Haldor Topsoe and a home made Rh based catalyst in the absence and presence of SO₂ is presented. The influence of operating temperature is studied for the home made Rh catalyst.

2. **Experimental**

A fixed-bed quartz reactor was used to study the activity in the presence of H₂O and SO₂ resistance of the catalysts at 450 °C and 500 °C. In each experiment, 0.24 g or 0.12 g catalyst was used and diluted with 0.96 g or 1.08 g sand (catalyst + sand = 1.2 g). The total gas flowrate was 300 Nml/min which gave a gas hourly space-velocity (GHSV) of 75,000 or 150,000 ml/(g cat·h). The feed gas contained 2500 ppm CH₄, 10 vol.% O₂, 5 vol.% H₂O, and 20 ppm SO₂, balanced by N₂. A higher SO₂ concentration than used in practice was adopt to accelerate the deactivation process and save experimental time. The exit gas was measured by an online IR gas analyzer and a Micro GC. The online gas analyzer was used to measure the concentration of O₂ and CO₂. The concentration of CH₄ was measured by a Micro GC for the calculation of CH₄ conversion.

3. **Results and discussion**

As shown in Figure 1, the conversion of CH₄ over the commercial Rh-Al-Cr catalyst starts at 55 % and then declines after the addition of 20 ppm SO₂, while it stays above 22 % after 240 h on stream. The conversion can be restored to 45 % after removing SO₂ from the reaction stream. The home made 1 wt.% Rh catalyst was more active than the commercial catalyst in the presence of 5 vol.% H₂O, as shown in Figure 2. The 1 wt.% Rh catalyst could fully catalyze CH₄ oxidation to final products (CO₂ and H₂O) at 550 °C while 750 °C was still not enough for the commercial catalyst to reach 100 % conversion. The SO₂ resistance of the home made 1 wt.% Rh catalyst was further tested at 450 and 500 °C for 14 h. As shown in Figure 3, the conversion of CH₄ decreases with time on stream, while the conversions finally stabilized at 15% and 50% after running for 14 h at 450 °C and 500 °C, respectively.

![Figure 1](image1.png) **Figure 1.** Conversion of CH₄ in time on stream with 20 ppm SO₂ present and after removal of SO₂ at 450 °C. 5 vol.% H₂O is always present. GHSV=75,000 ml/(g cat·h)  

![Figure 2](image2.png) **Figure 2.** Comparison between commercial Rh-Al-Cr catalyst and 1 wt.% Rh catalyst in the presence of 5 vol.% H₂O. GHSV=150,000 ml/(g cat·h)  

![Figure 3](image3.png) **Figure 3.** Conversion of CH₄ in time on stream with 5 vol.% H₂O and 20 ppm SO₂ present at 450 and 500 °C. GHSV=150,000 ml/(g cat·h)

4. **Conclusions**

Commercial Rh-Al-Cr shows stable activity for CH₄ oxidation in the presence of both H₂O and SO₂, indicating that Rh can be a promising active metal for the desired catalyst that can be used in the real engine exhaust condition to mitigate CH₄ emission from natural gas fired engines. The home made 1 wt.% Rh catalyst shows higher activity than the commercial catalyst in the SO₂-free stream and stable activity in the presence of 20 ppm SO₂ after running for 14 h.

**References**

Performance experiment and analysis of low temperature catalyst for marine urea SCR system

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1. Introduction
The engine exhaust gas temperature ranges from 150 to 250 degree Celsius for light duty and from 200 to 350 degree Celsius for heavy duty, so the low temperature activity of the catalyst is extremely important to the urea SCR system[1-4]. This paper mainly studies the influence of the active component and the molding method on the activity of the catalyst at low temperature.

2. Experimental
Catalyst A, catalyst B and catalyst C are taken as research objects. catalyst A and B are moulded by the honeycomb coating, and the catalyst C is moulded by the honeycomb extrusion. The main active ingredients of catalyst A and C is V2O5/WO3, but the main active ingredients of catalyst B is V2O5. Cummins diesel engine is used to test the catalytic performance of three kinds of catalysts, the exhaust gas temperature range is from 180 to 270 degree Celsius. MAN marine diesel engine was selected to test the SCR system performance within catalyst A. The performance of the SCR system is tested under the E3 cycle, the test equipment is CAI600 (made in USA).

3. Results and discussion
The maximum denitrification efficiency of the catalyst A reaches 89.36% under the range of test temperature. When the temperature is higher than 200 degrees Celsius, the denitrification efficiency of catalyst A is kept above 80% steadily. Catalyst C showed poor denitrification efficiency in the test temperature range, however, the pressure drop of catalyst C is very small compared with other catalysts. Another experiment is carried out under the condition that the mixing section of the SCR reactor is extended. The denitrification efficiency has a great increase with the increase of temperature when the temperature is below 210 degrees Celsius, when the temperature is over 210 degrees Celsius, the denitrification efficiency increases with the temperature, but the growth rate becomes smaller. Urea injection, which affect the denitrification performance of the catalyst, is an important parameter for SCR system. the denitrification efficiency of the catalyst A is up to 95.14%, when the temperature is 230 degrees Celsius and the urea injection flow rate is 0.529l/h. The catalyst A is tested by the marine diesel engine, Figure 1 shows that When the diesel power is 2437kw, the NOx emissions from the SCR system of the marine diesel engine is 6.3 kg/h, and the NOx emission characteristic value is 2.58 g/ (kw-h).

4. Conclusions
1) The additional additives in the honeycomb extruded catalyst will greatly influence the denitrification performance of the catalyst, and the pressure drop of the honeycomb extrusion catalyst is obviously lower than that of the honeycomb coating catalyst. 2) The length of the mixing section in the SCR system has a significant influence on the denitrification efficiency of the catalyst. At low temperature (below 200 degrees Celsius), the temperature has great influence on the catalytic activity of the catalyst. Besides, extending the length of the mixing section of the SCR system will not have an important impact on the pressure drop of the system. 3) the effect of temperature on the denitrification efficiency of the catalyst is greater than that of the urea injection flow rate. 4) The honeycomb coating catalyst with V2O5/WO3 as the main active ingredients has high denitrification efficiency in the low temperature range of 210–250 degrees Celsius, and its pressure drop is reasonable. This catalyst can make the diesel engine exhaust meet the Tier III emission standard of IMO.

References
Reaction Mechanism and Chemical Kinetics of NH₃-NO/NO₂-SCR System with Vanadium-based Catalyst under Marine Diesel Exhaust Conditions

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Abstract: As one of most effective NOx emission removing technologies to meet the Tier III limitation by International Maritime Organization, Urea-SCR technology is starting to be used in the two-stroke marine diesel. Comparing with power plants and four-stroke diesel, Urea-SCR system in the two-stroke marine diesel works under the exhaust conditions of high flow, low temperature and complex composition, and different elementary reaction pathways are appeared in the catalytic process. Basing on the two-cycle catalytic mechanism proposed by Topsoe, combining with the exhaust characteristics of marine diesel, expansion studies on detailed SCR reaction model were carried out in the paper. According to the temperature dependence of reaction pathway, SCR reaction model was divided into three parts: low temperature reaction pathway, standard SCR reaction path-way and high temperature oxidation pathways, and an expanded NH₃-NO/NO₂-SCR reaction model for V₂O₅ catalyst was proposed in the paper. In order to verify accuracy of the expanded SCR reaction model, simulating and testing studies of SCR reaction under marine diesel conditions were carried out with a commercial extruded V₂O₅/TiO₂ catalyst. It is found that simulation values are agree well with experimental values at 150°C ~500°C, and kinetics characteristics of SCR reaction process under V₂O₅/TiO₂ catalyst can be predicted accurately with the expanded NH₃-NO/NO₂-SCR reaction model in the paper.

Keywords: NH₃-NO/NO₂-SCR; Vanadium-based Catalyst; Diesel Engine; Elementary Reaction Pathway; Numerical Simulation.
Bimetallic Ni-Fe hydrotalcite-derived catalysts for dry reforming of methane

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1. Introduction
Dry reforming of methane (DRM) has been intensively studied in the past decades due to its advantage of converting two major greenhouse gases into valuable syngas. Ni-based catalysts are the most attractive catalysts for DRM since Ni has good activity and low cost compared to noble metals. However, Ni catalysts are prone to deactivation by carbon deposition. The addition of bimetallic Fe has been demonstrated to suppress this problem, showing a beneficial effect on the catalytic activity [1]. In this work, a series of Ni-Fe catalysts with different Fe/Ni molar ratios were prepared via hydrotalcite (HT) precursors to study their performance during DRM.

2. Experimental
HT precursors were prepared by co-precipitation method [2]. The precursors are denoted as HT-NiFe-x where x represents Fe/Ni molar ratio (x = 0, 0.1, 0.2, 0.5, 1). Subsequently, the as-prepared catalysts were calcined in flowing air at 600 °C for 6 h, resulting five catalysts denoted as HTC-NiFe-x. Ni loading in all samples was maintained at 20 wt.% The catalysts were characterized by N2 adsorption-desorption, X-ray diffraction (XRD) and temperature programmed reduction of H2 (H2-TPR).

3. Results and discussion
XRD results of as-prepared samples (Fig. 1) with different Fe/Ni ratios show characteristic diffraction peaks of pure HT-like structure (PDF 22-0700) without impurities [3]. The decomposition of the HT precursors after calcination is complete since only the diffraction peaks of the mixed oxide were obtained (Fig. 2). The peaks of calcined samples are attributed to diffraction peaks of NiO (PDF 01-089-5881) but also possibly overlapped with NiAl2O4, MgAl2O4, NiFe2O4, and MgFe2O4 as well as Fe2O3. The oxide crystallite sizes calculated by Scherrer equation show small particles for all catalysts, demonstrating the advantage of preparing catalysts through HT precursors (Table 1). In addition, the BET surface area and the pore volume of all catalysts are very high. H2-TPR profile (Fig. 3) of HTC-NiFe-0 exhibits a single peak at 797 °C, while the peak shifted to lower temperature as the Fe/Ni molar ratio increases from 0.1 to 0.5. Therefore, the addition of Fe apparently promoted the reducibility of the catalysts, showing the successful incorporation of Fe into the HT lattice. The sequential reduction of Fe2+ species to metallic Fe via Fe3O4 is clearly demonstrated in sample HTC-NiFe-1 by two peaks at 388 °C and 590 °C. The last peak of this sample at 798 °C was ascribed to the reduction of NiFe2O4 spinel [3].

4. Conclusions
Promising Ni-Fe bimetallic catalysts were prepared through the HT precursors with good physiochemical properties. The addition of iron eases the reduction of active Ni species. Further characterization measurement and catalytic activity test will be investigated to study the intimate interaction between Ni and Fe with optimal Fe/Ni molar ratio to suppress carbon formation in DRM reaction.

Table 1. Physiochemical properties of calcined catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface area (m²/g)</th>
<th>BJH pore volume (cm³/g)</th>
<th>Oxide crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTC-NiFe-0</td>
<td>205</td>
<td>0.59</td>
<td>4.07</td>
</tr>
<tr>
<td>HTC-NiFe-0.1</td>
<td>216</td>
<td>0.59</td>
<td>3.80</td>
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<tr>
<td>HTC-NiFe-0.2</td>
<td>247</td>
<td>0.62</td>
<td>3.72</td>
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<tr>
<td>HTC-NiFe-0.5</td>
<td>208</td>
<td>0.58</td>
<td>4.06</td>
</tr>
<tr>
<td>HTC-NiFe-1</td>
<td>141</td>
<td>0.65</td>
<td>5.25</td>
</tr>
</tbody>
</table>

References
Study on de-NOx activity of Mn catalysts based on MCNTs, TNTs and its composite carriers

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1. Introduction
Forced by the increasing demands of reducing marine engine emission, low temperature selective catalytic reduction (SCR) has been one of the most promising technologies to meet IMO NOx emission regulation. And the catalyst is one of the key issues in a marine SCR system. There are some defects in SCR catalysts, such as small specific surface area, low catalytic activity and weak dispersion of active components. In this paper, MCNTs, TNTs and their complexes MCNTs-TNTs were used as carriers to prepare SCR catalyst by doping the active component MnOx. Furthermore the catalytic activity of above catalysts was studied.

2. Experimental
In the paper, there are two kinds of experiments, catalyst preparation experiments and de-NOx performance tests of catalyst. The catalysts were prepared on catalyst preparation bed, including the following steps: (1) pre-treatment of MCNTs; (2) preparation of TNTs; (3) preparation of MCNTs-TNTs; (4) preparation of Mn/MCNTs-TNTs catalysts and Mn-Ce/MCNTs-TNTs catalysts. Catalyst de-NOx performance tests were carried out on the catalyst activity experiment device, including the following experiments: (1) effects of calcination temperatures on catalytic activity; (2) effects of MCNTs content in MCNTs-TNTs composite carrier on de-NOx catalytic activity; (3) effects of different catalysts on catalytic activity.

3. Results and discussions
3.1 Effects of calcination temperature on catalytic activity of Mn/MCNTs-TNTs catalyst
With a constant molar ratio of MnOx and TiO₂ in 0.4, and with the optimum content of MCNTs 10%, calcination temperatures of catalysts are set to 350°C, 450°C and 450°C respectively for preparing MCNTs-TNTs catalysts, the tested de-NOx activity performance with reaction temperature is shown in Figure 1. It can be found that, when the calcination temperature is 450°C, the catalyst has the maximum catalytic activity.

4. Conclusions
(1) With the increasing of MCNTs content and calcination temperature, the activity of Mn/MCNTs-TNTs catalysts has the trends of increasing at first and then decreasing. (2) For the Mn-Ce catalysts with different kinds of carriers, when using MCNTs carrier, the whole catalytic activity is lower than those of using MCNTs-TNTs and TNTs carries respectively. Especially for Mn-Ce/MCNTs-TNTs catalyst, when reaction temperature is 100°C, it has a de-NOx efficiency of above 70%, while reaction temperature reaches 150°C, the de-NOx efficiency raise to over 90%. (3) TEM results show that, the added element Ce will reduce coacervate in the surface of Mn-Ce/MCNTs-TNTs catalysts, and helps to put more even oxides loaded on MCNTs. And H₂-TPR shows the added Ce can improve the ability of reduction in low temperature, the low temperature activity of Mn-Ce/MCNTs-TNTs is some stronger than that of Mn/MCNTs-TNTs catalyst.

References