

Faggruppe for katalyse



Norsk Kjemisk Selskap

NORWEGIAN CATALYSIS SYMPOSIUM 2017

Annual meeting of the Catalysis division of the Norwegian Chemical Society

Hurdalsjøen Hotel – November 6th and 7th 2017

Monday the 6th

16:00	NKS registration
16:50	NKS welcome
17:00	Plenary Lecture: Prof. Enrique Iglesia (University of California, Berkeley) “Towards More Accurate Descriptions of Reactivity in Acid and Oxidation Catalysis on Metal Oxides”
18:00	Poster session (Common for iCSI and NKS)
19:30	Dinner

NKS posters

1. Ole Håvik Bjørkedal - NTNU	Acid-modified mesoporous alumina as catalytic support for NH ₃ -SCR
2. Jia Yang - NTNU	Co-Ni mixed oxide catalysts for low temperature methane total oxidation
3. Karoline Kvande – UiO	Direct conversion of methane to methanol
4. Rune Lødeng - SINTEF	Global models for predicting Methanol To Formaldehyde (MTF) performance
5. Asbjørn Slagtern Fjellvåg - UiO	Reconstruction of Pd-Ni Catchment Gauze during High Temperature Ammonia Oxidation
6. Yalan Wang - NTNU	Microkinetic analysis of light olefins production from synthesis gas: Combined UBI-QEP method and BEP relationship
7. Xiaoyang Guo - NTNU	Suppressed carbon formation on Fe-Ni based high temperature alloys by combined near surface severe plastic deformation and thermal treatment
8. Eirik Østbye Pedersen - NTNU	Mn promotion effects in Co-based Fischer-Tropsch production of light olefins
9. Emil Sebastian Gutterød - UiO	CO ₂ Hydrogenation over UiO-67-Pt Zr-MOFs

Tuesday the 7th

8:30	Plenary Lecture: Prof. Graham Hutchings (Cardiff Catalysis Institute) <i>“Catalysis using gold”</i>
9:50 room B	NKS 1 - Carlos A. Grande – SINTEF Additive manufacturing as a tool to reshape catalytic reactors
10:10 room B	NKS 2 - Kun Guo – UiS Unravelling the Size Effect of Monodispersed Nickel Nanoparticles in the Hydrolysis of Ammonia Borane
10:30 room B	NKS 3 - Isaac Yeboah – NTNU Insight into catalytic in-situ co/pyrolysis of biomass powder and heavy fraction of bio-oil using Py-GC/MS
10:50 room B	NKS 4 - Sondre Eliasson – UiB The Mechanism of Rh-catalyzed Transformation of Fatty Acids to Linear Alpha-Olefins; a DFT-Study
11:10 room B	NKS 5 - Ingeborg-Helene Svenum – SINTEF Co(11-20) as a model system for investigating adsorption, surface restructuring and poisoning effects in Fischer-Tropsch chemistry
11:30 room B	NKS 6 - Mari Helene Farstad – NTNU CO oxidation over Pd-based alloys
11:50 room B	NKS 7 - Irene Pinilla-Herrero – UiO Dehydrogenation vs hydrogen transfer activity of Zn-ZSM-5 catalytic systems in methanol conversion to aromatics
12:00	Lunch
13:00	Plenary Lecture: Prof. Alessandra Beretta (Polytecnico di Milano) <i>“New challenges in the SCR technology for stationary applications: a focus on Hg oxidation”</i>
14:00	Coffee break
14:20	NKS 8 - Sigurd Øien-Ødegaard – UiO - NKS award lecture for best PhD thesis Preparation, structure, and reactivity of functionalized zirconium metal-organic frameworks
15:00	NKS 9 - Ljubiša Gavrilović – NTNU Deactivation of Co-based Fischer-Tropsch catalyst by aerosol deposition of potassium salts
15:20	NKS 10 - Marco Foscato – UiB Loss and Reformation of Ruthenium Alkylidene: Connecting Olefin Metathesis, Catalyst Deactivation, Regeneration, and Isomerization
15:40	NKS 11 - Dimitrios K. Pappas – UiO Searching for the Active Sites Responsible for the CH ₄ to CH ₃ OH Conversion over Cu-Chabazite Materials
16:00	NKS 12 - Shirley E. Liland – NTNU Rational Design of Ni-Co/Hydrotalcite Catalyst for Methane Total Combustion using operando UV-Vis spectroscopy
16:20-16:30	NKS closing

Additive manufacturing as a tool to reshape catalytic reactors

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Abstract

Additive manufacturing is one of the novel techniques for smart manufacturing of items. Two of its main advantages are (i) a relatively high freedom of design and (ii) economy of resources to make complicated shapes. In terms of reactors and catalysts, having freedom of design allow us to improve mass, heat and momentum transfer properties. In this context, we are exploring the utilization of 3D printing as a novel toolbox for process intensification of reactors and separation units.

A brief presentation of the initiatives that are under development in SINTEF will be presented with special highlight to the European project PRINTCR3DIT (Process Intensification through Adaptable Catalytic Reactors made by 3D Printing). In this project, three industrial sectors of different scales are targeted aiming to understand the impact that this novel way of thinking reactors can affect the industrial network. In this project, we are also aiming to demonstrate the technology with two pilot units: one of them will be hosted by Yara. Moreover, examples of introducing 3D printing to education are being developed.

Unravelling the Size Effect of Monodispersed Nickel Nanoparticles in the Hydrolysis of Ammonia Borane

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Abstract: Monodispersed nickel (Ni) nanoparticles (NPs) with different average particle sizes in the range of 4.9–27.4 nm are controllably synthesized by tuning the ratio of nickel acetylacetonate precursor and trioctylphosphine in the presence of oleylamine. These unsupported Ni NPs are found to be effective catalysts for the hydrolysis of ammonia borane (AB), and their catalytic activities are size dependent. A volcano-type activity trend is observed with 8.9 nm Ni NPs presenting the highest catalytic activity. Characterization of the spent NP catalysts indicates that smaller sized NPs face severe agglomeration, resulting in poor stability and activity. To address this issue, the Ni NPs are further immobilized onto Ketjenblack (KB) carbon support. Results show that the catalytic activity of KB supported Ni NPs increases monotonically with decreasing Ni NP size with 4.9 nm Ni/KB presenting the highest turnover frequency of $447.9 \text{ mol}_{\text{H}_2} \cdot \text{g}_{\text{Ni}}^{-1} \cdot \text{h}^{-1}$ as well as excellent reusability in the dehydrogenation of AB after five cycles. The high catalytic performance can be attributed to the intrinsic activity of Ni NPs and the improved activity and stability due to the Ni–KB metal–support interactions.

Insight into catalytic in-situ co/pyrolysis of biomass powder and heavy fraction of bio-oil using Py-GC/MS

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Abstract

The production of renewable fuel and green chemicals from biomass is a promising path to global eco-friendliness due to negative climate issues with fossil fuel. Biomass utilization via fast pyrolysis pathway is the most economically and only sustainable way to transport fuel production when compared with gasification, liquefaction and biological route. The product from fast pyrolysis is known as bio-oil, which is a potential feedstock to existing refinery configuration, most especially the fluid catalytic cracking (FCC) unit. In order to enhance the transition from fossil to bio-refinery requires comprehensive understanding of the biomass to bio-oil chemistry to aid catalyst screening and upgrading. Bio-oil has higher oxygen functional groups (aqueous layer) such as acids, ketones, aldehydes, alcohols, esters, furan, phenols and non-oxygenated (organic layer) includes aromatics, indene and polyaromatics (anthracene, naphthalene etc.). These mostly originate from cellulose, hemicellulose and lignin fraction and thus biomass dependent. To fully comprehend several biomass chemistry, Py (EGA/PY-3030D) coupled with GC, Agilent 6890, using Ultra ALLOY, (Agilent HP-5, 40 m, 320 μ m ID, 0.25 μ m film) connected to mass spectrometer (MSD 5977 E) was used to study the catalytic pyrolysis of the biomass powders as a function of temperature. Several biomass powder (<1 mm) such as pine, poplar, chestnut, spruce, sweet sorghum and sludge, from waste treatment plant were studied with respect to temperature. The optimum temperature for tested biomass powders is 500 °C in terms of hydrocarbon pool-product selectivity and conversion where the phenolics products are dominant. Although, similar oxygenated product trend is observed for all tested biomass powder, but at 600 °C, thermal cracking of pine gave some aliphatic products (12 %). Vapor phase in situ catalytic pyrolysis of pine was further studied at 500 °C. Herein, HZSM-5 (Si/Al = 30) was selected as a model catalyst. The effects of HZSM-5/pine weight ratio on flash pyrolysis of pine were probed. In that, the product selectivity shifted to aromatics and aliphatic hydrocarbons at catalyst: biomass ratio of 3. A one-step in situ catalytic co-pyrolysis of Higher Molecular Weight (HMW) fraction of bio-oil and pine were further explored. Catalytic co/pyrolysis of pine and heavy fraction of bio-oil gave significant aromatics and cycloalkanes selectivity of 52 %. However, both mono and polycyclic hydrocarbons were formed in copyrolysis while only monocyclic aromatics were produced in pine pyrolysis. These products C₆-C₁₆, cyclic hydrocarbons form significant fraction of the aviation fuel pool.

Key words: Catalytic in situ co-pyrolysis, Biomass, Bio-oil, HZSM-5, Aromatics

The Mechanism of Rh-catalyzed Transformation of Fatty Acids to Linear Alpha-Olefins; a DFT-Study.

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Department of Chemistry, University of Bergen.

The important and versatile linear alpha-olefins (LAOs) are currently obtained from fossil resources. A renewable pathway to the LAOs is available by decarbonylative dehydration of fatty acids. However, the currently best catalysts for this transformation, based on palladium, are not active and stable enough for industrial use. To provide insight for design of better catalysts, we present the computationally derived mechanism for another attractive transition-metal for this reaction, rhodium. We compare the calculated mechanisms and free energy profiles for the two metals, Pd and Rh, and single out important factors for a facile, low-barrier reaction and for a stable catalyst. The olefin-forming β -hydrogen transfer is rate limiting for both metals, but the rate-determining intermediate for Rh is, in contrast to Pd, the starting complex, $(\text{PPh}_3)_2\text{Rh}(\text{CO})\text{Cl}$. This complex largely draws its stability from the strength of the Rh(I)-CO bond. CO is a much less suitable ligand for the high-oxidation state Rh(III). However, for steric reasons rhodium dissociates a bulkier triphenylphosphine (PPh_3) and keeps a carbonyl all the way through the reaction, which thus largely explains the higher overall barrier for rhodium. The stability of the Rh-catalyst also ensures that, unlike Pd, a large excess of PPh_3 in the reaction mixture is not favorable for the transformation.

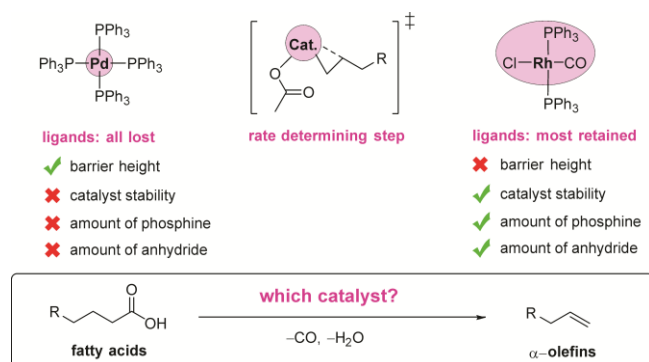


Figure 1. Comparison of Pd and Rh catalysts for decarbonylative dehydration.

Co(11-20) as a model system for investigating adsorption, surface restructuring and poisoning effects in Fischer-Tropsch chemistry

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In the hydrogenation of CO to Fischer-Tropsch products over Co based catalysts, the nature of the active surface and the effects of contaminants are under investigation. Co(11-20) is not the dominating surface termination under reactions conditions, but can be considered a model system for understanding adsorption induced restructuring involving the mobility of Co atoms and the importance of step edges and defects. We have investigated Co(11-20) with STM, HR-PES and DFT to elucidate the CO adsorption, the resulting Co restructuring, and the effect of small amounts of deposited K. CO exposure at room temperature induces anisotropic migration of Co from the step edges along and the [0001] direction and to eventually yield (3×1) periodicity in well-ordered areas. The HR-PES results suggest that this restructuring is kinetically inhibited at low temperatures (~77 K), rendering less CO accommodated on the surface. The theoretical investigations support our proposed missing row-added row structure resulting from the CO induced restructuring, showing an increased stability of CO on the reconstructed compared to the unreconstructed model surfaces. Co migration was investigated by displacing single Co atom or a CO+Co complex along the [0001] direction. The calculated barriers points towards CO-Co complex migration as responsible for the mobility, and the relative high energy cost involved in the process supports the inhibition of the restructuring observed experimentally. The adsorption of CO and associated restructuring is strongly affected by K adsorption, which predominately occurs at step edges to yield Co step edge atoms immobilized. This may have importance for the effects observed for supported Co catalysts.

CO oxidation over Pd-based alloys

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Pd is a well-known catalyst for complete oxidation of CO and hydrocarbons and has been extensively studied^{1,2}. In order to further improve the catalytic properties and potentially reduce costs, selected Pd-based alloys are investigated. The present study is part of a long-term effort to further the understanding of the surface behavior of Pd-based alloys and their catalytic properties.

Single crystals of selected Pd-alloys have been used as model systems during investigations with Near Ambient Pressure Photoemission Spectroscopy (NAPXPS), Mass Spectroscopy (MS), Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM). CO oxidation experiments have been performed with large excess of oxygen as well as near-stoichiometric conditions. The most recent results of Pd₃Au(100)³ and Pd₅₇Cu₄₃(100) will be compared to the previously studied Pd(100)⁴ and Pd₇₄Ag₂₅(100)⁵ surfaces. The influence of surface oxides and segregation of the alloying element on the CO oxidation reaction will be in focus.

References

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DEHYDROGENATION VS HYDROGEN TRANSFER ACTIVITY OF Zn-ZSM-5 CATALYTIC SYSTEMS IN METHANOL CONVERSION TO AROMATICS

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The increasing demand of light aromatic hydrocarbons together with the gradual crude-oil reserves depletion has renewed the interest of the methanol to aromatics process (MTA) as a route to obtain these petrochemicals from sources alternative to petroleum. Transition metal containing zeolites are known to be active catalysts in the MTA process, favouring the dehydrogenation rather than the hydrogen transfer reactions, and thereby enhancing the selectivity to aromatic molecules while keeping the production of alkanes low.

In this work we study the effect of the Zn/Al ratio in the dehydrogenation *vs* hydrogen transfer activity of Zn-ZSM-5 catalysts. To this aim, we have produced eight catalysts by exchanging two parent ZSM-5 zeolites with different density of acid sites (Si/Al 40 and 15) with three increasing Zn loadings. Samples were tested in MTA and the nature of Zn sites was studied by spectroscopy using both laboratory and synchrotron techniques. XANES and EXAFS data suggest the presence of $[\text{Zn}(\text{H}_2\text{O})_n(\text{OH})]^+$ species located in the exchange positions of the materials, and the catalytic testing results reveal that the aromatization mechanism is governed by the Zn/Al ratio. For Zn-free samples, the presence of a high density of zeolite acid sites leads to higher yields of aromatics that seem to be the result of hydrogen transfer reactions. On the other hand, the incorporation of higher Zn contents in samples with similar Si/Al ratio causes an increase in the yield of aromatics together with a decrease in the production of alkenes, what indicates a higher dehydrogenation rate.

Deactivation of Co-based Fischer-Tropsch catalyst by aerosol deposition of potassium salts

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Present work investigated the effect of potassium salts (KNO_3 , K_2SO_4 , K_2CO_3 , KCl) on a Co-based Fischer-Tropsch catalyst using the aerosol deposition technique. Based on the characterization results there are no clear indications that catalyst is altered by the deposited poison (K). However, catalyst activity is severely hindered with increasing potassium loading. Selectivity data were only slightly affected with an observed tendency in increasing S_{C_5+} , S_{CO_2} and decreasing S_{CH_4} with increasing the potassium loading. These results are in agreement with hypothesis that potassium mobility plays a role during the catalyst deactivation. The experimental data of CO conversion with K content were nicely described by simple deactivation model which implies a strong non-selective poisoning by potassium species.

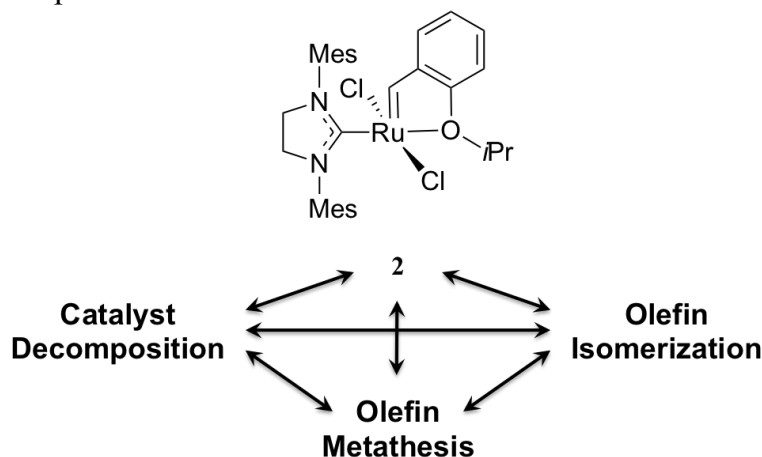
Loss and Reformation of Ruthenium Alkylidene: Connecting Olefin Metathesis, Catalyst Deactivation, Regeneration, and Isomerization.

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Olefin metathesis is the most versatile reaction known for the formation of carbon-carbon bonds. The reaction is most commonly catalysed by ruthenium-based homogeneous catalysts such as the Hoveyda-Grubbs second-generation catalyst **2** (see illustration). Despite its robustness against functional groups, **2** and similar catalysts decompose via little-understood routes to species that promote alkene isomerization.¹ To gain the insight necessary to prevent this decomposition, we have investigated the reactivity of **2** using density functional theory (DFT).² The calculations have identified a new and facile decomposition pathway involving loss of alkylidene to give the 12-electron complex (SIMes)RuCl₂ (**R21**, SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene). **R21** can promote isomerization of olefins both via an η^3 -allylic and a hydride mechanism, and can also regenerate ruthenium alkylidenes and thereby restart olefin-metathesis. Experimental tests using a *p*-cymene-stabilized **R21** complex confirm the predictions and suggest that loss and reformation of alkylidene via **R21** may be frequent events in olefin metathesis using **2** and similar catalysts, and that this electron-deficient intermediate is an important contributor to metathesis-related olefin isomerization.



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Searching for the Active Sites Responsible for the CH₄ to CH₃OH Conversion over Cu-Chabazite Materials

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The stepwise conversion of CH₄ to CH₃OH over Cu-exchanged zeolites constitutes a extensively investigated topic due to the potential implications in the energy sector and chemical industry. The nature of the active Cu species in the different zeolite frameworks impacts the performance of the materials as it controls the yield and can lead to rationalized material synthesis. Currently in the literature Cu-MOR and Cu-MFI samples are reported to possess dinuclear and trinuclear Cu-oxo species. Cu-CHA is an established NH₃-SCR of NO_x catalyst¹ and also exhibits the potential of the CH₄ to CH₃OH transformation.^{2,3} Z[Cu^{II}OH] species in the 8mr have been reported to be the dominant Cu speciation at the activated state.¹ Herein we combine bench reactor testing with spectroscopic characterization (XAS, IR and Raman) in order investigate the influence of reaction parameters and material elemental composition on the methanol productivity and Cu-speciation. Our results propose the instability of Z[Cu^{II}OH] species at high temperature activation and their role as a precursor of the active species. We find that the Cu_xO_y species responsible for the conversion are formed at high temperature O₂ activation and their population and nature are influenced by the pretreatment conditions. Monomeric Z[Cu^{II}O₂] species with end-on and side-on configuration are proposed as the active sites while multimetric moieties are evidenced through Raman spectroscopy. In addition our results clearly demonstrate the impact of Si:Al and Cu:Al, at low values high populations of 2Al Z₂Cu^{II} sites in 6r are observed. Such species inhibit the material performance by being inactive for the conversion and affect the reducibility of Cu-CHA materials which is linearly correlated to their methanol productivity

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Rational Design of Ni-Co/Hydrotalcite Catalyst for Methane Total Combustion using operando UV-Vis spectroscopy

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A complete oxidation of methane has been a significant topic in the field of heterogeneous catalysis for decades since methane is the most abundant hydrocarbon source on earth. Very recently, Ni/Co mixed oxide is explored to study the catalytic performance on catalytic combustion of methane (CCM) knowing the synergism between Co₃O₄ and NiO¹. The active sites in the oxidation process are dynamic, and the oxidation state of the transition metals might changes with operation conditions. The oxidation state of the metal could be a crucial parameter for the catalyst design, which could govern the surface O concentration and barriers for methane activation¹⁻². Our operando setup combined with a novel, *in situ* UV-Vis-NIR and MS spectroscopy approach allows for detailed kinetic studies of the individual reduction and oxidation steps as well as for the overall reaction. A series of well-controlled Ni-Co catalysts supported on a hydrotalcite-like structure have been synthesized using co-precipitation and tested in the CCM set-up. It is found that the bimetallic Ni-Co catalyst possess higher activity (in the order of Ni/Co > Co > Ni) at low temperature (below 500 °C) compared to the pure Ni and Co catalysts. Whereas at higher temperatures (above 650 °C), Ni/Co and Co catalyst possess similar activities. Adding Co into the catalysts increased the oxidation state of the catalysts due to the oxophilicity of Co, which increase the O surface concentration and reduce the barrier of methane activation. What is interesting is the activity drop around 600-700 °C for all the Ni-Co catalysts, which is found to be due to reduction on the catalyst surface. This is confirmed by results showing the surface reduction rate becomes faster than the oxidation rate at 670 °C, while the UV-vis verifies the oxidation of bulk structure. Using this technique, we can develop Ni-Co bimetallic catalysts to have a high activity. We expect our approach to rational catalyst design to be general in nature, applicable to any catalysts partaking in redox reactions³⁻⁴. It is a cheap and time efficient screening tool which will pave the way for rational design of heterogeneous catalysts which undergoes oxidation state changes.

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Poster presentations

Acid-modified mesoporous alumina as catalytic support for NH_3 -SCR

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Trondheim

As availability of LNG and the likelihood of stricter emission-regulation in the maritime sector increases, LNG propulsion could become a viable option for ships. With this follows a need for efficient NO_x -reduction at these operating conditions. Mesoporous alumina with regular pore structure have been synthesized as a potentially stable and efficient support material for Ammonia-Selective Catalytic Reduction (NH_3 -SCR).

High surface area and available acidic sites are important factors for efficient SCR-catalysts. The surface area can be regulated by controlling the porosity of the alumina during synthesis. This has been done by synthesizing alumina by the sol-gel method, and simultaneously introducing a structure-guiding polymer. The acidity of the support can be improved by introducing a Keggin-type acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$, abbrev. HPW) to the structure. Fe and Cu was introduced as active metal components by incipient wetness impregnation. In Situ XAS analysis of the catalysts have recently been performed at the Swiss-Norwegian Beamline at ESRF to determine the active state of the metal under relevant conditions.

The surface area and porosity of the catalysts were measured by the BET method. The supports show specific surface area of $\sim 300 \text{ m}^2/\text{g}$ and pore size of 4-6 nm. XRD has shown that the materials have low crystallinity.

Co-Ni mixed oxide catalysts for low temperature methane total oxidation

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Natural gas as fuel represents an attractive alternative for power trucks, ships or stationary applications, due to low emission of SO₂ and particulates. Removing any unburned methane is, however, necessary because of its high greenhouse gas potential. A recent study claimed superior performance of spinel catalysts compared to Pd¹. In the current work, cobalt and nickel spinel oxides with different Co/Ni ratios and the effect of water on the activity are investigated for methane total oxidation under diluted, excess oxygen conditions. The performance is compared against Pd reference catalysts.

The Co-Ni mixed oxide catalysts show only slightly lower activity compared to a 2 wt% Pd/Al₂O₃ catalyst for low temperature methane oxidation. Small differences in activity were observed for catalysts with different Co/Ni ratio, except for pure NiO catalysts showing lower activity. Since all catalyst except NiO contain a spinel phase, this suggests that the spinel phase is critical with respect to the oxidation reaction. By co-feeding 10% H₂O, we found a negative effect on the activity for both Ni_{0.5}Co_{2.5}O₄ and Pd/Al₂O₃. However, this effect is completely reversible, i.e. the initial activity is completely restored upon removing H₂O from the feed. Notably, the water inhibition effect appears weaker for the Co-Ni catalyst compared with the Pd based catalyst, and the catalyst shows good stability for 700 h TOS.

The Co-Ni spinel based catalysts hence show promising activity and stability under reaction conditions relevant to control of methane slip in natural gas-fueled engines.

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Direct conversion of methane to methanol

Karoline Kvande

Abstract

In the recent years methane has become increasingly abundant. However, transportation costs are high and methane recovered as side product is often flared rather than valorized. The chemical utilization of methane is highly challenging and currently mainly based on the cost intensive production of synthesis gas and its conversion into methanol and hydrocarbons.

Alternative routes have been discovered in academia, though high temperatures are mostly required.

This study will look into the selective oxidation of methane to methanol over Cu-loaded SAPO-34 catalysts. This route can be carried out over relatively low temperatures, and from published data, it has been showing promising results for other zeolite/zeotype structures.

Global models for predicting Methanol To Formaldehyde (MTF) performance

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Formaldehyde is a base chemical widely used for adhesives and resins. Production proceeds by catalytic oxidation of methanol, either in excess air over a mixed base metal oxide or excess methanol over an electrolytic silver based catalyst [iCSI partner K.A. Rasmussen]. The Ag based process has an improvement potential. A key is higher formaldehyde yields and the iCSI project goal is going beyond 90 - 92%.

State-of-the art literature on oxygen species and reaction kinetics has been addressed [1, 2, 3, 4]. Many O-species have been identified and it is known that they transform and diversify along the temperature dimension (α -O, β -O, γ -O, O₂-, OH, i.e. including surface and sub-surface by nature). The role and individual contribution to performance (activity, selectivity) is still unclear and a topic of controversy. Microkinetic descriptions have been proposed [4], but these are based on a hypothesis of one working O species only. Such detailed models contain a huge set of reactions and parameters, which are to some degree based on an in-complete knowledge of reaction intermediates and sites. There is also a need to decrease model complexity for reactor simulations.

In this work, global kinetic models have been built and calibrated to experimental data produced in iCSI [5], in both an electrolytic Ag particle bed and annular reactor with tubular Ag for addressing kinetics. In addition, data from relevant literature [1,2,3] is included in the preliminary calibration data base, thus merging available state-of-the-art knowledge and providing a widest possible basis for calibration. Sets of pathways have been gradually extended and rate parameters (Frequency factor - A, Activation energy - E_{act}) tuned to improve the general model calibration and fit. As wide variations of parameters as possible has been implemented, including temperatures of ca. 300 – 700 °C, CH₃OH/O₂ ratios from 1.15 to zero O₂, catalyst particle sizes ranging from 0.25 – 2 mm, and different linear gas velocities (LGVs) and contact times. Model pathways are selected based on a hypothesis that they represent specific individual oxygen types (γ -O, α -O, O₂-), thus decoupling and potentially shedding insight to condition dependent contributions. Criteria of relevance for the degree of fit include the contact time, conversions of CH₃OH and O₂, as well as the distribution of products CH₂O, CO₂, CO, H₂ and H₂O. Low temperature products like HCOOH and CH₃OOCH are not included.

In summary, global pathway models have been built and coarsely fitted to experimental calibration data. Reasonable predicting properties are established for main parameters, i.e. the temperature and CH₃OH/O₂ ratio. All major products are accounted for. Future models will be refined to provide an improved potential for interpolative predictions (also including other parameter-performance correlations), phenomenological understanding and a guide for selection of experimental conditions to improve precision and general applicability.

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Reconstruction of Pd-Ni Catchment Gauze during High Temperature Ammonia Oxidation

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One of the key reactions in production of artificial fertilizer is high temperature (900 °C) oxidation of ammonia, performed over a metallic Pt-Rh catalytic gauze. Due to the exothermic nature of the reaction, combined with a high process temperature, large quantities of platinum are lost in form of PtO₂ vapor. Evaporated PtO₂ is transported downstream before it is captured by a Pd-Ni catchment gauze. During the lifetime of the catchment gauze (~6-12 months), the wires reconstruct completely, is depleted of Ni, and 0.3-0.4 grams of Pd is lost per gram Pt captured.

In the current ex-situ lab scale experiments we are recreating plant conditions, with the aim to understand the underlying mechanisms for the reconstruction of the Pd-Ni catchment gauze. In Figure 1 we report selected SEM- and EDS analyses of Pd-Ni wires exposed to various feed gas mixtures. Results indicate a fast oxidation of Ni to NiO (Figure 1b), mainly along grain boundaries. Furthermore, in the presence of steam, the wire is depleted in NiO (Figure 1c), probably leaving the wire as volatile Ni(OH)₂. Reconstruction of grains and pore formation is observed only when there is a Pt-piece upstream, so that PtO₂ is present in the gas stream (Figure 1d and 1e). The present results show that these lab scale ex-situ experiments are able to reproduce the reconstruction of the industrial Pd-Ni catchment gauze. We are thus able to search for mechanistic insight through further investigations.

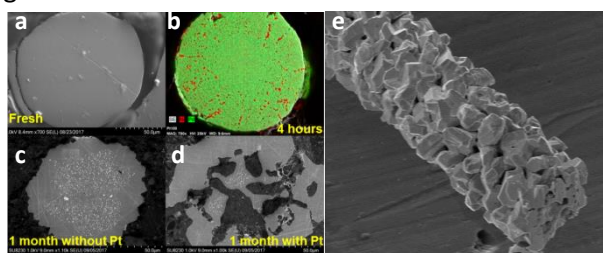


Figure 1. SEM and EDS analysis of fresh Pd-Ni wire (a), Pd-Ni wire exposed to wet oxygen for 4h (b) and 1 month (c), and Pd-Ni wire exposed to wet oxygen for 1 month with Pt upstream (d) and (e).

Microkinetic analysis of light olefins production from synthesis gas: Combined UBI-QEP method and BEP relationship

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Fischer-Tropsch synthesis (FTS) is a process for producing hydrocarbons and oxygenates by converting synthesis gas generated from coal, natural gas and biomass. Light olefins (C₂ - C₄ olefins) production directly from FTS has drawing increasing attention, because of extensively used of light olefins in the chemical industry as key building blocks. Although the F-T synthesis has been applied in industry for decades since discovered in the 1920s, the exact reaction mechanism is still under debate. In this work, a descriptor-based microkinetic analysis was preformed to investigate the mechanisms of FTS. Adsorption energies were estimated by modified UBI-QEP (unity bond index-quadratic exponential potential) method, which could satisfactorily fit the DFT calculated values. Brønsted-Evans-Polanyi (BEP) relationships were applied to obtain activation energies based on DFT computations. The modified UBI-QEP method combined with BEP relationship reduces radically the computational expenses, but keeps the accuracy compared to DFT calculation, therefore could be used to rapidly generate input parameters of microkinetic model. The predicted relatively high activity catalysts for light olefins production in FTS are Co, Ru and Iron carbide, among 8 transition metals (Co, Ru, Fe, Ni, Rh, Pt, Pd and Cu), under conditions: T= 483 K, P = 1.85 bar, H₂/CO=2, consistent with experiments. CO activation mainly occurs via hydrogen-assisted CO dissociation. The major chain growth takes place through the coupling of CH+CH, CH+CO and CH₃+CO pathways.

Suppressed carbon formation on Fe-Ni based high temperature alloys by combined near surface severe plastic deformation and thermal treatment

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Fe and Ni are excellent catalysts for producing carbon nanotubes and carbon nanofibers due to their ability to activate gaseous carbon-containing molecules to form carbon-carbon bonds. However, when Ni- and Fe-based alloys are exposed to highly carburizing atmospheres ($a_c > 1$), metal dusting corrosion - a catastrophic phenomenon - may take place. The initial stages of carbon formation and metal dusting corrosion of Fe-based Incoloy 800 alloy were studied by Raman spectroscopy, SEM/EDS and FIB/TEM coupled with EDX/EELS. The results show that Incoloy 800 samples treated by near surface severe plastic deformation (NS-SPD) after consecutive oxidization under synthesis gas at elevated temperature exhibit no carbon formation, compared with the untreated sample exposed to the same conditions. The good corrosion resistance performance is a result from the NS-SPD process producing an ultrafine-grained structure with higher fraction of grain boundaries together with crystal twinning near the surface. This microstructure increases the effective diffusion coefficient for Cr in the alloy by introducing a higher density of rapid diffusion paths, hence promoting formation of a thin, protective Cr-rich oxide scale, which prevents contact between the carburizing atmosphere and the Ni and Fe contained in the alloy. The results imply that the metal dusting resistance performance of Incoloy 800 in industrial applications can be significantly improved by NS-SPD followed by thermal oxidative treatment.

Mn promotion effects in Co-based Fischer-Tropsch production of light olefins

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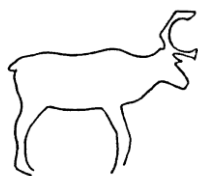
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The Fischer-Tropsch synthesis (FTS) process is considered an attractive alternative to promising, as it has been shown that high yields of light (C₂-C₄) olefins are obtainable through the right combination of catalyst properties and operating conditions. Manganese is in both Co- and Fe based FTS a frequently reported promoter for increasing olefin selectivity. The nature of the promotion effect is however debated, and is reportedly dependent on the catalyst preparation method [1]. In the present work, Mn-promoted Co catalysts were experimentally investigated for the purpose of FTS production of light olefins.

4 different 15%Co/ γ -Al₂O₃ catalysts were prepared, with and without Mn-promotion, by the IWI route using metal nitrates in aq. solution as precursors. They were characterized by i.a. XPS with various pretreatment, TPR, XRD and tested at 240 °C, 5 bara and H₂/CO = 2.1 as well under SSITKA conditions. Independent on preparation method, Mn was found to positively affect intrinsic activity and selectivity towards C₂₋₄ olefins and C₅₊ species as well to inhibit CH₄ formation.

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Faggruppe for katalyse



Norsk Kjemisk Selskap

NORWEGIAN CATALYSIS SYMPOSIUM 2017

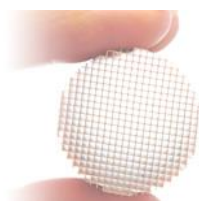
This year's symposium is organized in conjunction with an iCSI seminar (<https://www.ntnu.edu/icsi>). As a consequence, we will enjoy world class plenary speakers!

Plenary Lecture: **Prof. Enrique Iglesia** (University of California, Berkeley)
“Towards More Accurate Descriptions of Reactivity in Acid and Oxidation Catalysis on Metal Oxides”

Plenary Lecture: **Prof. Graham Hutchings** (Cardiff Catalysis Institute)
“Catalysis using gold”

Plenary Lecture: **Prof. Alessandra Beretta** (Polytecnico di Milano)
“New challenges in the SCR technology for stationary applications: a focus on Hg oxidation”

Sigurd Øien-Ødegaard (University of Oslo) - NKS award lecture for best PhD thesis
“Preparation, structure, and reactivity of functionalized zirconium metal-organic frameworks”



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