

Characterization of Nanoporous Catalysts for Heterogeneously Catalysed Transesterification of Oils into Biodiesel

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Topic

Compared to catalysts used in homogeneous solution, nanoporous solid catalysts are advantageous because of their easier separation from the reaction products and the possibility for the subsequent regeneration and re-use. However, one of the issues when using nanoporous catalysts with bulky molecules are limitations of the reaction rate by diffusion of the reactants and products due to imposed confinement within the catalyst pores. One example for such limitations is the heterogeneously catalyzed conversion of oils and fats, such as, e.g., biodiesel production. Biodiesel, a renewable alternative to fossil fuels, is produced by converting the bio-based raw materials, such as vegetable oil or animal fat, into transportation fuel by transesterification of the triglycerides comprising the fats and oil with methanol in the presence of basic catalyst.

The goal of this case study will include characterization of basic catalysts supported on mesoporous silica, such as SBA-15, silica gel, for transesterification of oleic and linoleic triglycerides with methanol into biodiesel. It will also include determination of their textural properties using nitrogen sorption and X-ray diffraction, as well as estimation of the presence and distribution of the catalytically active component by means of inductively coupled plasma optical emission spectroscopy and temperature-programmed desorption of carbon dioxide. These catalysts will be further utilized for quantification of diffusion properties of sunflower oil and fatty acid methyl esters with different chain lengths.

keywords: biodiesel, transesterification, characterization, diffusion limitations

Chemical Aging of NH₃-SCR Catalysts by Lab-Scale Poisoning Methods

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The exhaust gas of diesel vehicles is a major source of nitrogen oxides (NO_x), which are produced at high temperatures during the combustion process in the engine. NO_x are harmful pollutants and can cause acid rain, smog and ground-level ozone. Thus, an aftertreatment of the diesel exhaust gas is required. Current and future NO_x emission standards can be met by using the NH₃-Selective Catalytic Reduction (SCR) process for NO_x reduction in the exhaust gas. During the lifetime of a vehicle, the SCR catalyst undergoes an aging process. This leads to deactivation and lower NO_x reduction performance.

Within a current project, a deeper understanding of the deactivation of NH₃-SCR catalysts due to their operation using modern liquid biofuels such as biodiesel, is aimed at. In particular, a rapid test for the quantitative evaluation or estimation of the long-term stability of those catalysts is to be developed. By using a lab scale based rapid-test, the time-to-market could be shortened significantly and time-consuming experiments with vehicles running with the catalyst for years on the road can ultimately be avoided. For this purpose, poisoning experiments with commercial monolithic catalysts will be conducted. In particular, different poisoning methods (gas phase/liquid phase poisoning) will be used on V₂O₅-WO₃/TiO₂ (VWT) or on zeolite catalysts.

In this Case Study, poisoning experiments will be conducted using gas- and liquid-phase poisoning methods. Thus, the fresh catalyst will be loaded with poisons in different amounts and distributions over the catalyst monolith. In addition, a novel burner system will be used for more realistic poisoning conditions. Thus, the poisons are deposited on the catalyst through a flame imitating the burning process in the vehicle engine. The poisoned catalysts will be characterized by several physico-chemical techniques (elemental analysis (ICP-OES, XRF), XRD, SEM/TEM, TPR) and the catalytic properties will be studied on catalyst test bench in the lab scale with a model gas similar to the diesel engine off-gas.

keywords: NH₃-SCR, catalyst deactivation, exhaust aftertreatment, VWT-catalyst, zeolite

Hydrophobization of Zeolites with Multimodal Porosity for the Aqueous-Phase Valorization of Biomass

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Topic

Heterogeneously catalyzed processing in the aqueous phase is an attractive route for biomass valorization, since it can be conducted at mild reaction conditions, i.e., $T < 500\text{ K}$ and $p < 5\text{ MPa}$. However, these route poses new challenges on the hydrothermal stability of the catalysts, since most of them are designed for high-temperature gas-phase reactions.

In view of this challenge, the hydrothermal stability of zeolite catalysts with a multimodal pore system will be systematically modified by hydrophobization through silylation. Therefore, silylation will be conducted with different organosilanes (linear or branched, different carbon chain length) and different silylation degrees are aimed at. The stability of the silylated zeolites will be investigated in the aqueous-phase processing of a biomass-based model mixture in the batch mode and compared to the stability of the unmodified parent zeolite. The fresh and spent zeolite catalysts will be thoroughly characterized by elemental analysis, XRD, N_2 sorption, NH_3 -TPD, UV-Vis- and DRIFT-spectroscopy as well as thermogravimetric analysis. These studies will provide leads to a rational design of catalysts with enhanced hydrothermal stability as desired for biomass valorization.

keywords: biomass valorization, zeolites, hydrothermally stable catalysts, aqueous-phase processing

Pseudomorphic Transformation of Hexagonal Mesoporous Silicas into Hierarchical Mesoporous Silicas with Bimodal Pore Size Distribution

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Topic

The pseudomorphic transformation of porous matrix materials is a useful way to produce monoliths with a hierarchical pore system. In this regard, "pseudomorphic transformation" is defined as the transformation of the matrix material into other structures with maintenance of the original matrix body shape. The pseudomorphic transformation of a disordered pore system into an ordered micellar templated silica (MTS) material was first introduced by Galarneau *et al.* in 2002. An advantage of this dissolution-reconstruction method is that the macroscopic shape of the original material will not be changed, so that shaped bodies (monoliths) of MTS can be produced without applying binder materials or mechanical forces. The relevant publications show a wide range of amorphous silica materials that could be transformed into MTS. The method offers the possibility to synthesize substances with a high surface area and a highly ordered pore system that could be used for HPLC columns, for the entrapment of drugs, or as catalyst support. Further applications include enzyme binding and sensors.

The goal of this case study is to synthesize Hexagonal Mesoporous Silica monoliths with pore diameters larger than 8 nm and conduct the pseudomorphic transformation with different n-alkyltrimethylammonium hydroxides to generate a second hexagonal pore system (MCM-41). For larger pore sizes of the MCM-41 system, a swelling agent for the hexagonal micelles of n-hexyltrimethylammonium hydroxide is to be used. In the current project, linear Amines are selected as the micelle expanders. Additionally, OH⁻/Br⁻-ratio in the transformation solution is to be altered in order to synthesize different bimodal pore materials. The systems are characterized by nitrogen sorption at 77 K and by mercury intrusion.

keywords: Pseudomorphic Transformation, Hexagonal Mesoporous Silicas (HMS), MCM-41-Material, Nitrogen Sorption, Mercury Intrusion

Salt/Zeolite Composites with Increased Heat Storage Density at Low Humidity Conditions

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Topic

Technologies for an efficient energy storage become increasingly important for a stable renewables-based energy supply. For the purpose of long-term heat storage, thermochemical systems based on the sorption of water are of highest scientific interest. In our group, we investigate composites of hygroscopic salts and porous desiccant materials as thermochemical heat storage materials. These composites provide superior heat storage densities of up to 260 kWh m^{-3} as compared to hot water tank storage with about 90 kWh m^{-3} , which is the current state of the art in commercial heat storage devices. The composite materials prepared in our group feature an increased heat storage density as compared to the salt-free porous desiccant material at high humidity. For application of these composites under low humidity conditions as they are typical for the winter season, where the heat is typically required, the composites have to be tuned adequately.

In this project case study, a modified preparation route for the composites based on the incipient wetness impregnation of nanoporous supports will be investigated. One objective will be the preferred deposition of hygroscopic salt within the secondary pore system of commercial zeolite-based granulates. Furthermore, the identification and deposition of an ideal amount of salt will be determined. Therefore, the composites will be thoroughly characterized by physico-chemical methods to elucidate the microscopic phenomena involved. Also, the thermochemical storage properties will be studied on the lab scale.

keywords: thermochemical heat storage, zeolites, sorption, physico-chemical characterization

Title: Carbaboranes as Versatile Inorganic Building Blocks in Biologically Active Molecules

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Topic

Carbaboranes are highly hydrophobic and extremely stable icosahedral carbon-containing boron clusters. The cage framework of these clusters can easily be modified with a variety of substituents both at the carbon and at the boron atoms. We are interested in substituted carbaboranes which can be used in medicine as suitable boron neutron capture therapy (BNCT) agents or as pharmacophores in which the carbaborane replaces the phenyl rings in drug candidates.

This topic involves the synthesis of respective compounds, their full characterization by NMR, MS, IR and X-ray crystallography, and for selected examples, test of their biological activity in collaboration with biochemists.

keywords: Boron clusters, cancer therapy, biomimetic compounds

Title: Hybrid Materials: Inorganic Polymers

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Topic

Strained inorganic phosphorus-based rings will be employed in ring-opening polymerisation or copolymerisation reactions, or catalytic dehydrogenation of suitable precursors will be employed as an innovative route to novel inorganic/organometallic polymers that are more than just carbon-based polymer mimics. These polymers can function as scaffolds, e.g., for transition metals (homo- or heterometallic) with applications in catalysis or as novel materials with interesting magnetic (molecular magnets) and optical (non-linear optics) properties.

This topic involves the synthesis of respective building blocks, their full characterization by NMR, MS, IR and X-ray crystallography, the preparation of the respective polymers and for selected examples, test of their physical properties in collaboration with physicists and physical chemists.

keywords: Inorganic polymers, hybrid materials, applications in catalysis, molecular magnets, non-linear optics

Title: Tailored Phosphines and their Application in Catalysis

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Topic

Phosphine-based ligands are designed in which the phosphanyl group is located inside a basket-, bucket- or tub-like cavity. Transition metal complexes thereof should allow selective transformation of molecules (regio-, stereo-, enantioselectivity) depending on the size and shape of the cavity, similar to the function of enzymes (bioinspired synthesis) or zeolites (heterogeneous catalysis). Furthermore, suitable phosphorus-based ligands such as (chiral) ferrocenylphosphines and related bimetallic catalysts (for tandem catalysis) will be immobilised on surfaces (e.g., graphite, gold, silica, etc.) or incorporated in polymers (via copolymerisation). A major target will be to manipulate or vary the properties by external stimuli (electrochemically, UV-vis, pH, etc.). The application of these immobilised molecular switches will be scrutinised with respect to changing the catalytic activity at will and shutting down or activating catalysts to trigger catalytic events.

keywords: Catalysis, immobilised catalysts, catalyst design, selectivity, chirality