

2.3.9. Research Area “Formation of Nanoporous Silicates”

(W. Schmidt)

Involved: X. Gu, M. Castro, I. Lim

Objective

Nanoporous silicates possess pores with sizes equivalent to molecular dimensions and serve as molecular sieves and selective catalysts in various applications. Pore diameters as well as pore shapes and pore organization determine the interaction with molecules from fluid phases. Crucial factors that affect the properties of such materials are composition, pore sizes, particle sizes and morphologies. They determine adsorptive and diffusional properties as well as catalytic activity. Understanding the formation processes of nanoporous silicates is subject of this research area.

Results: Zeolites are well known adsorbents and highly efficient catalysts in petrochemistry. Nevertheless, their nucleation and crystallization processes remain still not well understood. The formation of early silicate species in the crystallization of zeolites has been investigated by a combination of liquid state ^{29}Si , ^{27}Al , and ^1H nuclear magnetic resonance (NMR) spectroscopy, small angle X-ray scattering (SAXS), dynamic light scattering (DLS) and electrospray ionization mass spectroscopy (ESI MS) in collaborations with colleagues from the Universities of Versailles, France, and Leuven, Belgium.

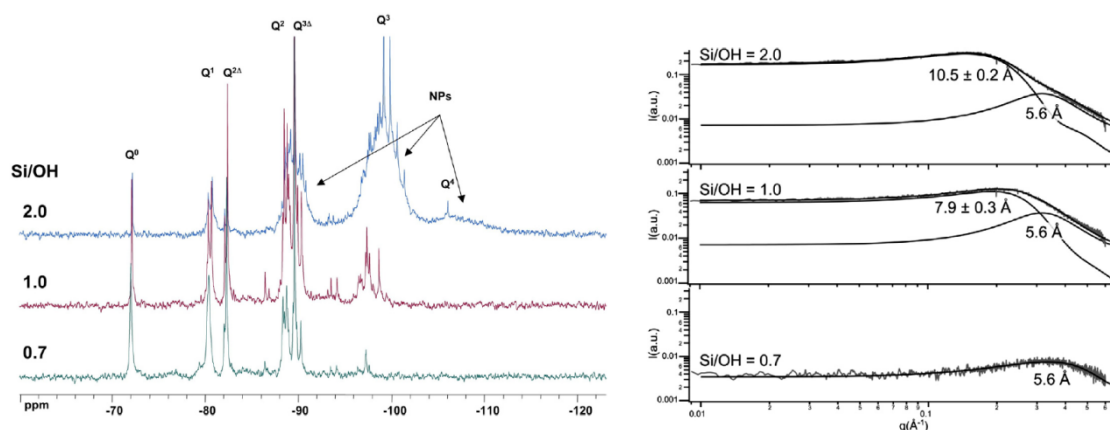


Fig.1. ^{29}Si NMR spectra (left) and SAXS data (right) measured on synthesis mixtures for zeolite beta with different Si/OH ratios prior to heating of the solutions (particle radii are given under the SAXS curves).^[83]

Starting from clear reaction solutions with tetraethylammonium hydroxide (TEAOH) as the structure directing template, the silicate speciation has been monitored^[83]. The appearance of nanoparticles, indicated by very broad NMR signals, depends strongly on the Si/OH ratio of the reaction mixture as illustrated in Fig. 1. At low Si/OH ratios, no nanoparticles are observed in reaction mixtures prior to hydrothermal reaction whereas at Si/OH > 1 nanoparticles are observed already at room temperature. The NMR line broadening is caused by restriction of the rotational freedom of the silicate species in the emerging solid particles. These observations are corroborated by ESI MS, DLS, and SAXS data. The SAXS curves, as shown in Fig. 1, can be modeled by populations of spherical nanoparticles. In addition, SAXS reveals individual silicate species with sizes of about 1 nm for solutions with Si/OH < 1. They can be either larger silicate oligomers or very small silicate nanoparticles that also condense into amorphous nanoparticles upon hydrothermal treatment. ¹H NMR and ²⁷Al NMR reveals that the amorphous nanoparticles contain a fraction of the structure directing agent tetraethylammonium hydroxide (TEAOH) and all aluminum present in the reaction mixture. Crystallization of zeolite beta upon hydrothermal heating proceeds then from the amorphous particles and nucleation of the zeolite appears to proceed on the silicate nanoparticles.

Mixing of tetraalkylammonium molecules with an amphiphilic template results in mesoporous silicate with microporous pore walls. That has been investigated in collaboration with the colleagues from the Ruhr University in Bochum. Precursor solutions with tetrapropylammonium hydroxide (TPAOH) have been synthesized and mixed with solutions containing cetyltrimethylammonium bromide (CTAB). In contrast to conventional ordered mesoporous silicates such as MCM-41 and MCM-48, the resulting materials possess microporous walls as could be shown by a combination of analysis techniques, including wide and low angle XRD, adsorption studies, and ¹²⁹Xe NMR spectroscopy^[81]. Analysis of the pair distribution function (PDF) of high resolution XRD data showed that the structure of the silica in the pore walls resembles that of MFI zeolites even though no distinct XRD reflections are observed.

Using the same combination of CTAB and TPAOH in combination with NaF as mineralizing agent, ordered mesoporous aluminosilicate (OMA) with exceptional hydrothermal stability could be synthesized in our laboratory. Structural integrity is maintained in boiling water for at least 5 days as well as upon exposure to water vapor at 600°C for a couple of hours^[78]. The silica is formed as spherical particles within radial mesopores (Fig. 2 left) and a large fraction of the aluminium in the pore walls was found to be coordinated tetrahedrally (54 ppm signal in ²⁷Al MAS NMR spectrum, Fig. 2 right). Only a smaller fraction is found in octahedral coordination (signal at 0 ppm). The IR spectrum of pyridin adsorbed on that aluminosilicate showed signals

typical for both, Bronsted and Lewis acid sites, indicating that the obtained aluminosilicate probably also contained structural units similar to those in the MFI zeolite.

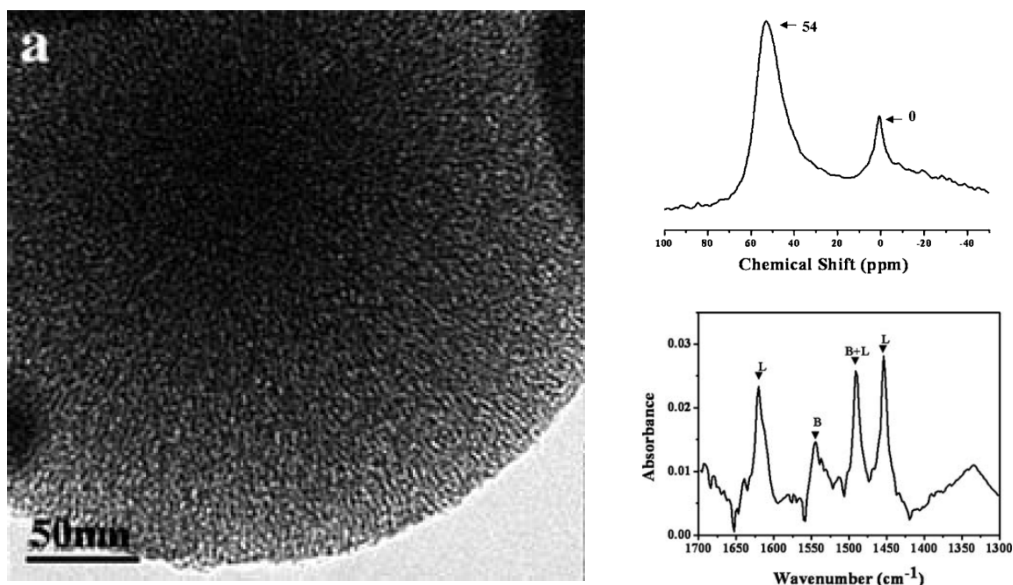


Fig. 2. TEM image of radial channels in ordered mesoporous aluminosilica from CTAB-TPAOH-NaF system (left) and ^{27}Al MAS NMR spectrum (top right) and IR spectrum of adsorbed pyridine (bottom right).^[78]

Benylation of toluene with benzyl alcohol is catalyzed by Bronsted acid sites and the OMA showed more or less quantitative conversion and high selectivity to benzyl toluene ($S_{\text{BT}} > 70\%$) whereas commercial ZSM-5 mainly produced benzyl ether ($S_{\text{BE}} >$

90%) at very moderate conversion ($C_{\text{BzOH}} < 5\%$). The large mesopores in OMA promote mass transfer and the acidity of the aluminosilicate facilitates the benzylation of toluene.

Replacing TPAOH by NaOH in the same reaction mixture as used for the synthesis of the OMA, hollow aluminosilica polyhedra with very thin walls are formed as

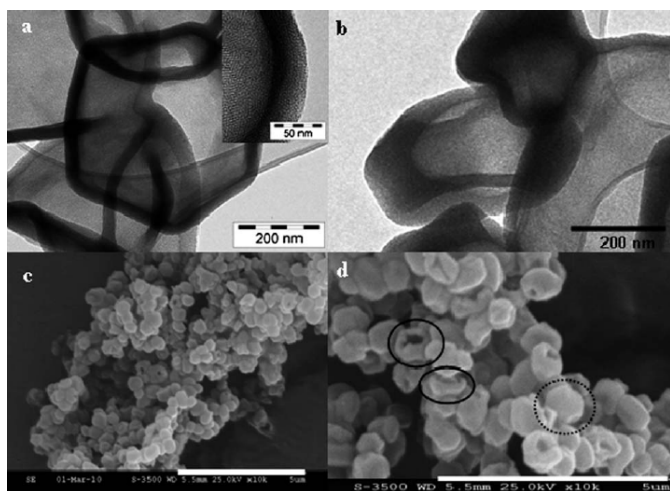


Fig. 3. TEM and SEM images of hollow mesoporous aluminosilicates.^[79]

he hollow polyhedra depends on the thermal reaction at 140°C, the solid

phase is MCM-41 and consists of particles with similar shapes as the final products. The hollow cores are formed during hydrothermal treatment of the aluminosilicate particles. The aluminum-rich outer rims of the MCM-41 particles withstand dissolution whereas the siliceous centers are dissolved. The presence of regular wormhole-type pores with 2-3 nm in diameter indicates a rearrangement of the aluminosilicate in the remaining part of the particles.

The studies on the different silicates allow for a better understanding of formation processes of porous silicates involving particle formation and nucleation. In addition the effect of different mineralizing agents has been evaluated. Dissolution and re-crystallization processes play a crucial role in the later stages of silicate formation. Nanoscopic zeolite particles grow into larger particles via such processes and partial dissolution of larger particles results in largely extended pores as exemplified on the hollow shell materials that could be obtained in a one pot reaction.

2.3.10. Research Area “Photocatalysis on Transition Metal containing Microporous Silicates”

(W. Schmidt)

Involved: U. Wilczok, X. Gao, H. Tüysüz

Objective

Quantum chains in microporous titanasilicate materials absorb light and create hole and electron pairs allowing photocatalytic conversion of substrate molecules on terminal sites of the quantum chains. Then investigation of photocatalytic conversions on such titanasilicates is subject of this research area.

Results: Titanium incorporation into the MFI structure results in a zeolite in which the titanium is present in tetrahedral coordination. Octahedral coordination of titanium is observed the microporous titanasilicate ETS-10 as illustrated in Fig. 4.

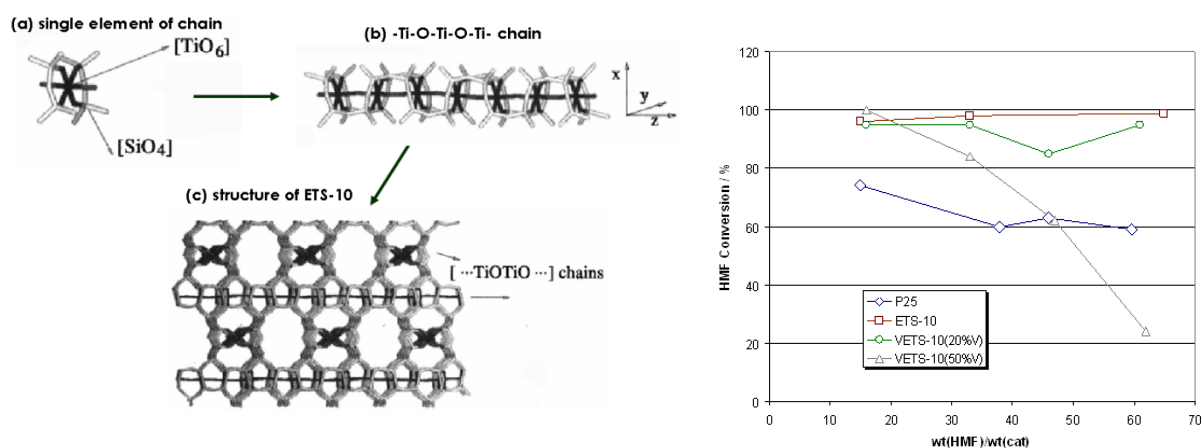


Fig. 4. ETS-10 structure (left) and photocatalytic conversion after 8h reaction time of HMF over different photocatalysts (right).

Extended titanate chains are separated by a silicate framework and thus act as quantum chains with semiconductor properties. Illumination with UV light causes charge separation and as the consequence ETS-10 is a microporous photocatalyst. In an ongoing research project the capability of ETS-10 based photocatalysts is explored. The aim is conversion of molecules that are formed in the product chain of biomass derived molecules into platform molecules for further processing. Selective oxidation of 5-hydroxymethyl furfural, a product of the conversion of sugar, to 2,5-furandicarboxylic acid is under investigation. Different ETS-10 materials have been synthesized including

materials in which titanium was replaced partially by vanadium (20% and 50% replacement of Ti by V). In comparison with the standard TiO₂ reference catalyst P25, ETS-10 based catalysts performed well and showed high conversion under UV radiation. Vanadium containing V-ETS-10 with 20% replacement of Ti by V showed conversion similar to that of the normal ETS-10 whereas V-ETS-10 with 50% replacement of Ti by V showed lower conversion at higher concentrations of HMF. Analysis of the reaction products revealed that the major reaction products were organic acids with low molecular weight. Formic acid is one of the main products whereas little conversion to carbon dioxide is observed. Thus, HMF can be efficiently converted under UV radiation but the aimed product, namely 2,5-furandicarboxylic acid, is formed only in small amounts. It seems that the primary oxidation products get fragmented and formic acid is then found as the major product.

2.3.11 Research Area “Supported Transition Metal Oxide Catalysts for Low Temperature Application”

(W. Schmidt)

Involved: J. Tseng, C. Weidenthaler, A. Pommerin, C. Gawlik

Objective

Certain transition metal oxides, such as cobalt oxide, have been shown to be efficient catalysts for the conversion of CO at ambient conditions. The investigation of supported transition metal based catalysts as low temperature catalyst for alternative conversions is subject of this research area.

Results: Transition metal catalysts that are supported on activated carbons have been synthesized and tested for the conversion of NO₂ under ambient conditions. The research focuses on potential catalysts that can catalyze reactions at ambient conditions. The working principal comprises two steps, i.e. adsorption of noxious gases on an activated carbon followed by catalytic decomposition of the molecules on the catalyst

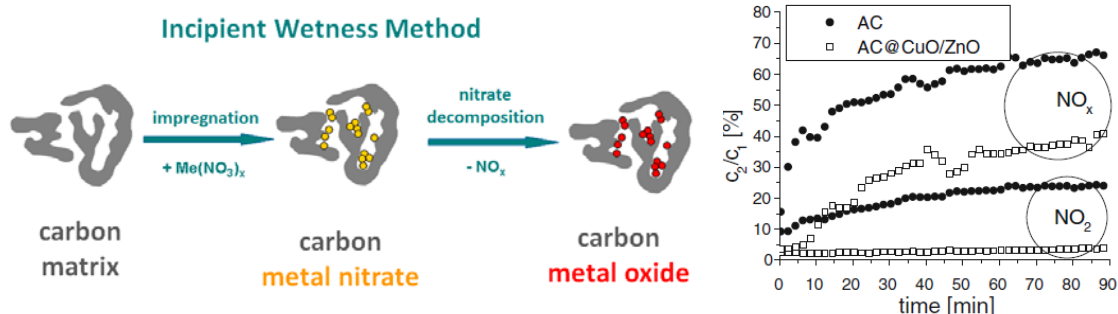


Fig. 1. Preparation of activated carbon (AC) supported transition metal catalyst via wet impregnation (left) and breakthrough curves of NO_x and NO₂ through AC@CuO/ZnO and AC after 6 cycles (right, 23 °C, 50 % r. H., c₁ NO₂ = 4 ppmV, v = 0.2 m/s).^[81]

deposited within the pores of the carbon. Different methods for the deposition of pure transition metal oxides (see Fig. 1, left) as well as mixtures thereof have been investigated, i.e. liquid phase impregnation with aqueous transition metal salts or alternatively deposition of oxide precursors via chemical vapor phase deposition^[76,82]. The investigations have been performed in collaboration with the Institut für Energie- und Umwelttechnik (IUTA, Duisburg) and the University of Duisburg-Essen.

Hopcalite and mixed CuO/ZnO catalysts showed best performance, especially after successive adsorption cycles as shown in Fig. 1 for CuO/ZnO on activated carbon^[82].

In comparison to the pure activated carbon, the NO_x concentration could be reduced significantly. NO₂ is reduced to NO at the carbon surface, a reaction that is also

observed for pure activated carbon. However, the breakthrough curve showing NO_x as the sum of NO_2 and NO for AC@CuO/ZnO proves that the amount of total NO_x is reduced in the presence of the transition metal oxide catalysts.

Transition metal catalysts that are deposited within activated carbons via chemical vapour phase deposition have also been tested for the conversion of NO_2 at a somewhat higher temperature of 150°C . Under these conditions also iron oxide nanoparticles in activated carbon showed conversion of NO_2 to NO that was followed by decomposition of NO to N_2 and CO_2 .