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Transmission electron microscopy on live catalysts

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Summary

This thesis describes our efforts to understand how catalysts work under reaction conditions, using (quasi) *in situ* transmission electron microscopy (TEM).

Chapters 2 and 3 focus on (Ni/Co)MoS₂ supported on γ -Al₂O₃, a catalyst used for the hydrodesulfurization (HDS) of fossil fuel.

Chapter 2 describes how we investigated the effect of exposing (Ni/Co)MoS₂-samples to ambient air using a combination of quasi *in situ* TEM and XPS. By imaging the exact same regions of the sample before and after air exposure, we concluded that the (Ni/Co)MoS₂-slabs were shrinking from the edges towards the center. Quantitative analysis of TEM image series revealed that the average slab length decreased as a function of air exposure time. Larger slabs shrunk, while short slabs disappeared completely. Complementary quasi *in situ* XPS experiments on the same samples showed that Ni-, Co-, Mo-, and S-oxides were formed. Initially, the slabs shrink relatively fast, while prolonged exposure to air only causes moderate further slab length decrease. Since oxides are formed at the edges of the slabs first, we propose that these oxide species form a protective, ring-like barrier around the inner MoS₂-species which shields them from further oxidation.

In chapter 3 the work on these HDS catalysts continues. The effect of a sequential oxidation and resulfidation treatment of (Ni/Co)MoS₂ was investigated using quasi *in situ* TEM and XPS, and the activity of the catalysts was determined for gas-phase thiophene HDS experiments. After the resulfidation treatment, the average slab length, the slab length distribution and chemical composition of the samples were determined and compared with the freshly sulfided samples. The average slab length increased, while the slab length distribution was more narrow compared to the freshly sulfided sample. XPS showed a slight increase in oxidic species after the oxidation-resulfidation step. Remarkably, the catalytic activity of the samples exhibited a significant increase of up to 39% after resulfidation. We attribute these changes to a size effect of the (Ni/Co)MoS₂ slabs: the smaller slabs (< ~1.6 nm) might be less catalytically active.

Chapters 4 and 5 discuss the preparation and characterization of Co-Re nanoparticles, and the application of Co nanoparticles in *in situ* TEM experiments.

In chapter 4, β -Mn-type Co_{1-x}Re_x nanoparticles were prepared via colloidal chemistry. For $x \leq 0.15$, the Re-content could be controlled readily, as (S)TEM-(EDX) analysis showed homogeneous Re distribution through the uniformly sized nanoparticles. Synchrotron powder X-ray diffraction, in combination with Rietveld refinement, showed that the Re atoms occupy the 12-fold site preferably. Preparation of nanoparticles with Re concentrations of $x > 0.15$ yielded inhomogeneous particles, showing segregation of Re atoms into separate clusters, indicating that a maximum of 15 atom % Re can be incorporated in the Co lattice. Heating the Co-Re nanoparticles under reducing atmosphere in an *in situ* synchrotron powder X-ray diffraction cell

showed that the nanoparticles were stable up to 300 °C.

Chapter 5 shows how Co nanoparticles were studied using *in situ* TEM experiments. The nanoparticles were imaged under 1 bar of CO:N₂ (1:1) at 500 °C, when the deposition of multiple layers of carbon was captured live. Due to the high temperature and presence of CO, the nanoparticle surface facilitated the Boudouard reaction, which is the dissociation of CO and the deposition of solid carbon. Over the course of about 40 minutes, more and more layers of carbon were formed up to a maximum of around 10 layers, after which no more deposition was observed. New layers of carbon were formed in between the surface of the nanoparticle and the already existing carbon layers. During imaging, the formed carbon layers induced mechanical stress in the nanoparticle, proven by the appearance of twin boundaries. Eventually the nanoparticle got permanently deformed by the capping carbon layers.



