

2.3.13 Research Area “Advanced X-ray Diffraction Techniques” (C. Weidenthaler)

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Objective: Advanced laboratory X-ray diffraction techniques are crucial for the understanding of complex systems and for the establishment of structure-property relationships in catalysis. In-situ techniques and sophisticated data analysis methods are applied in close cooperation with the catalysis groups in order to elucidate the structural details of catalytic materials and to correlate them with the performance of the solids in the catalytic reactions. Moreover, also the limits of the methods are being extended, with a focus on laboratory techniques.

Results: As a continuation of detailed crystallographic investigations of complex aluminum hydrides (see report 2008-2010), powder diffraction studies were extended to aluminum hydrides with cations of higher atomic numbers (EuAlH_4)₂, $\text{Sr}(\text{AlH}_4)_2$.^[19] The crystal structures of new members of the family of aluminum hydrides could be solved from heavily overlapping and less resolved XRD patterns by simulated annealing. A major focus of the studies was on the understanding of phase and structure changes during the decomposition of complex aluminum hydrides by means of in situ high temperature X-ray diffraction. The studies reveal also the appearance of new intermediate hydride structures which could be studied in detail. Knowledge about the crystal structures and their structural relationships contributes to the fundamental understanding of the crystal chemistry and the chemical properties of complex aluminum hydrides.

Many of the studies of hydrides have to be carried out in a controlled sample environment. This is even more important in heterogeneously catalyzed reactions. Such in-situ experiments are mostly performed at large facility synchrotron radiation sources providing high intensity radiation and a very flexible experimental setup. However, the experimental time at such facilities is very restricted. Over the last year, a reaction chamber has been adapted on a conventional laboratory powder diffractometer. The catalysis chamber is linked to a gas distribution station which allows the adjustment of the reaction gas flows accordingly to conventional catalysis experiments. This setup enables in situ investigations of catalysts during a catalytic reaction on laboratory instruments also over a long and flexible time period and with high quality data.

Nanostructured hematite (Fe_2O_3), encapsulated in a porous silica shell, was studied in detail with respect to structural changes during the decomposition of ammonia.^[11] The sample was prepared on a sieve plate into a ceramic sample holder and heated up from room temperature to 800 °C in a dry NH_3 atmosphere. The reaction gas flowed through the sample with a flow rate set to 15000 $\text{cm}^3/\text{g h}$. The analysis reveals a complex sequence of crystalline iron oxide, iron nitride, and metallic iron phases. Additionally, the chemical composition and the crystal structures of the iron nitrides formed between 450 and 700 °C change with temperature and time exposed to ammonia. In comparison to the in situ studies, ex situ diffraction experiments performed in parallel emphasize, that phase changes can occur after removing samples from the reaction environment.

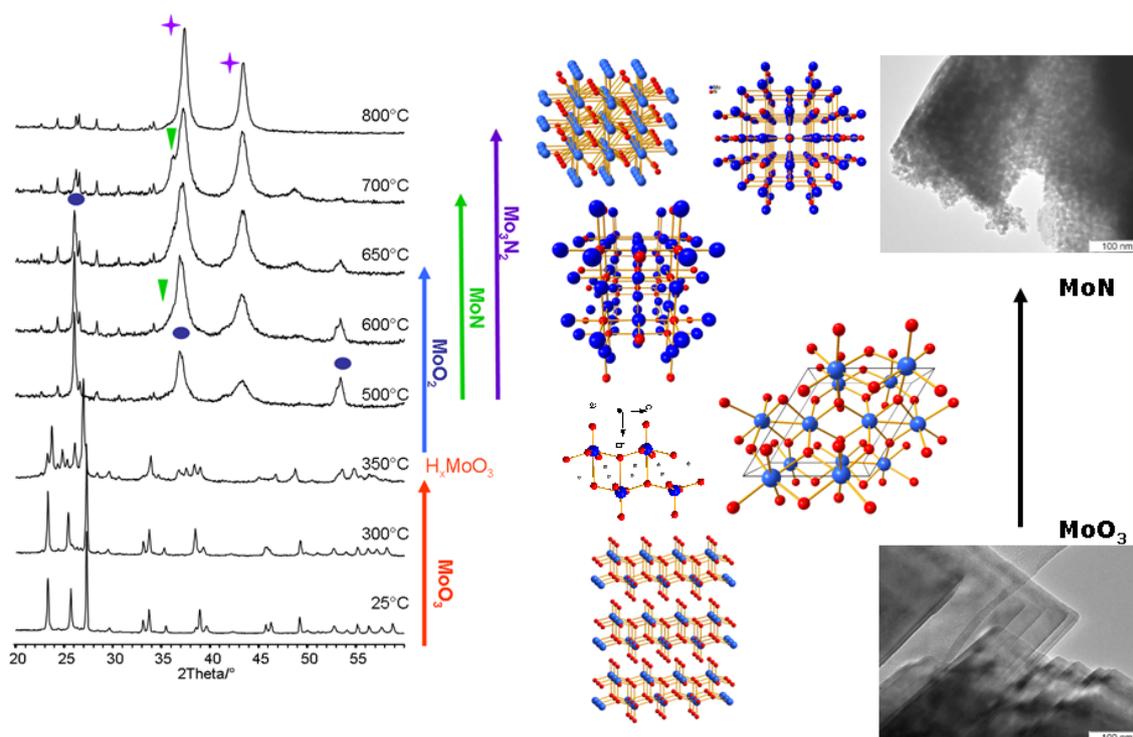


Fig. 1: In situ investigations of the formation of nanosized Mo_xN_y catalysts during the ammonolysis of large MoO_3 crystals

Another type of material investigated as potential catalysts for ammonia decomposition were nanostructured molybdenum nitrides. The entire formation pathway of the nitrides by ammonolyses of oxides was studied qualitatively and quantitatively by in situ XRD and the data were correlated with the catalytic performance (Fig. 1).^[40]

These in-house experiments do not only provide a qualitative information on the crystalline catalyst phases involved, but also a quantitative analysis of the sample composition over the entire temperature range. The variation of the chemical composition of the individual phases can be analyzed in detail, and microstructure properties, such as size and defect concentrations, can be evaluated in parallel. The

comprehensive dataset of structural properties can be directly related to the catalytic properties of a distinct catalyst (Fig. 2).

However, it is not only the chemical and the phase composition which influence catalytic performance, it is widely accepted that the microstructure of solid catalysts (defined as domain size and different types of defects) also significantly influence the catalytic properties.

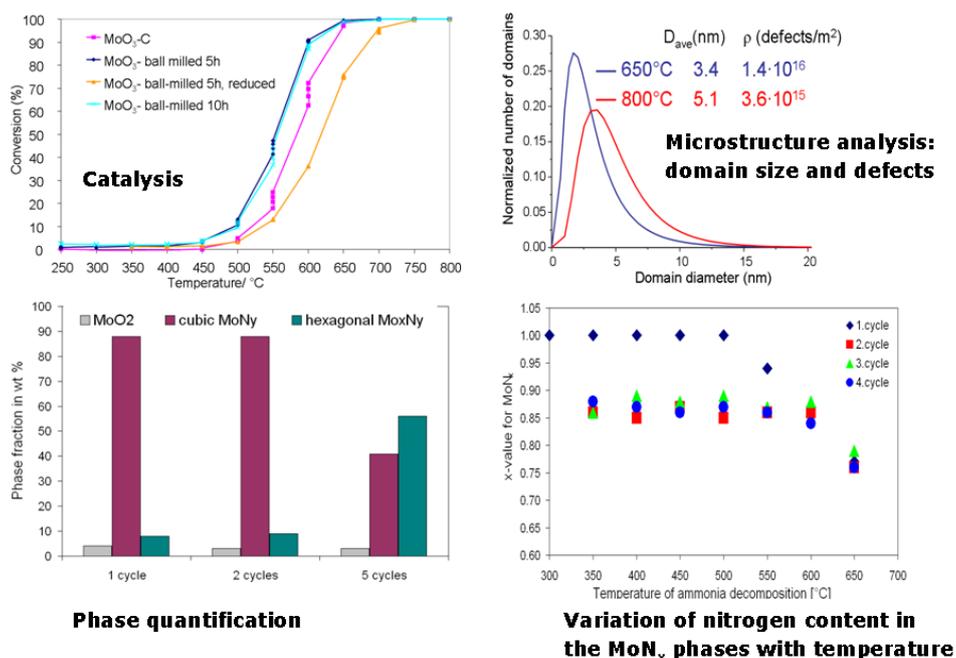


Fig. 2: Results obtained from diffraction experiments and catalytic testing.

Usually, the different types of defects are analyzed by electron microscopy techniques. However, electron microscopy images are often not representative for the entire catalyst sample. To overcome this problem, modern approaches for the evaluation of microstructure properties from powder diffraction data (line profile analyses) have been implemented in the group. The method was used to study the influence of the microstructure of Co₃O₄ on the catalytic performance for CO oxidation. It has been shown, that the addition of small amounts of silica during synthesis enables the size-control of Co₃O₄ catalysts. The domain size and the size distribution were calculated from the diffraction data.^[26] The most preferable size distribution with respect to the catalytic performance was obtained for Si:Co of 0.5. Without addition of silica the mean domain size is large (40 nm) and the distribution is very broad. The activity is rather low compared to the samples with narrow size distribution and small mean domains (2-4nm) (Fig. 3). Additionally, microstructure changes taking place under non ambient conditions are more than difficult to monitor by electron microscopy methods. One big advantage of line profile analyses methods is that in addition to the atomic structures

also changes of defect concentrations and/or domain size changes under reaction conditions can be investigated.^[43]

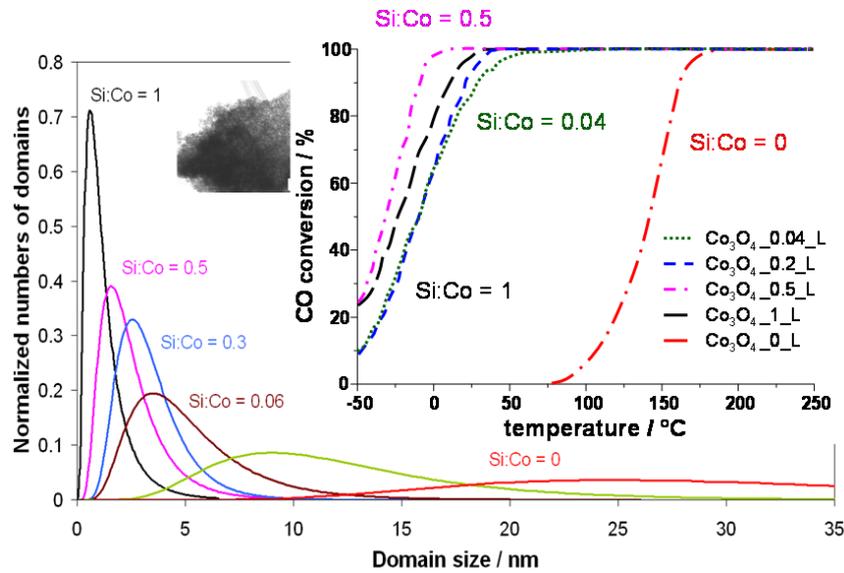


Fig. 3: Variation of size distribution in dependence of Si:Co ratio and influence on low temperature CO oxidation properties.

Microstructure changes of Cr₂O₃ due to ball milling or different temperature treatments have been intensively studied by diffraction methods. In situ studies of mesostructured Cr₂O₃ with interesting magnetic properties performed at lower temperatures (between 220 and 360 K) trace structural changes depending on the synthesis temperatures.^[28] In addition to differences on the atomic level, also temperature dependent changes of the crystallite shape are detected (Fig.4).

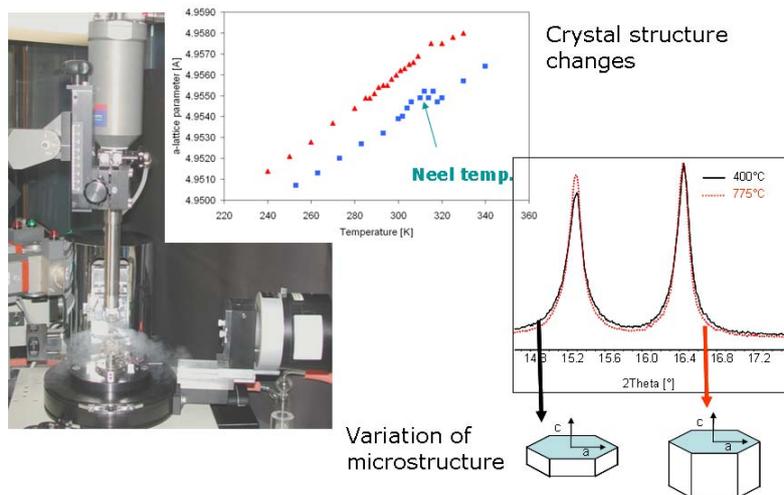


Fig. 4: Diffraction experiments performed in-house at low temperatures, dependence of microstructure properties (morphology changes) on the change of the synthesis temperatures.