

Atomic-scale Dynamics in Catalysts for Sulfur Chemistry.

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In recent years, new opportunities for catalysis research have opened up due to a remarkable progress in transmission electron microscopy (TEM). Advances of differentially pumped vacuum systems and of closed gas cells, in combination with heating devices, enable observations of catalysts during the exposure to gasses at elevated pressure and temperature. Such *in situ* observations are of vital importance because catalysis is a surface phenomenon and because surfaces tend to restructure to adapt to the surrounding gas environment; strictly speaking, the catalytic active state is only present during catalysis. Information about surface structures and dynamics under conditions mimicking those encountered during catalysis is therefore very important to further improve the understanding of structure sensitive functionality and properties of catalysts.

The different types of instrumentation provide complementary possibilities for *in situ* TEM experiments. In particular, the differentially pumped vacuum system is advantageous to exploit *in situ* TEM at the ultimate atomic resolution and sensitivity [1-2]. The differentially pumped vacuum system contains the gas phase as an integrated part of the microscope vacuum system. Thus, experiments involving gasses that strongly interact with the exposed surfaces are challenging, as cross-contamination of experiments and corrosion of electron optical elements, such as the objective lens or electron source, may occur. For those reasons, high-resolution TEM of catalysts in a sulfur-containing gas environment has not previously been emphasized despite their pivotal role in reduction of sulfur emissions that are harmful to environment and human health. To remedy this situation, we have dedicated a differentially pumped TEM to experiments with sulfur-containing gasses and the first *in situ* observations of catalysts involved in sulfur emission abatement will be presented.

Specifically, the first *in situ* TEM experiments with sulfur-containing gasses focused on hydrotreating catalysts used for, e.g., the removal of S impurities in oil distillates [3]. The hydrotreating catalysts are activated by sulfidation of a supported MoO₃ precursor into MoS₂ nanocrystals that serve as the catalytic active phase. In the microscope, the gaseous sulfidation of a MoO₃ precursor, atomically dispersed on a MgAl₂O₄ support, was monitored by means of time-resolved high-resolution TEM (Figure 1). The TEM images show that single-layer MoS₂ nanocrystals form preferentially and that multi-layer MoS₂ nanocrystals form later in the sulfidation process. Moreover, the single-layer MoS₂ nanocrystals are observed to grow from steps and along the support surface, and the multi-layer MoS₂ nanocrystals form layer-by-layer by the growth of additional MoS₂ layers onto already formed single-layer MoS₂ nanocrystals. As the catalytic active sites for S removal are associated with the MoS₂ edges, the mechanistic insight explains how edge sites with better accessibility for more refractory S-containing compounds in the oil distillates can be obtained. This improved understanding of the formation of MoS₂ edges helps tuning the catalyst activity.

The second example concerns SO₂ emission reduction from, e.g., steel industries. The industrial catalyst oxidizes SO₂ to SO₃ over vanadium oxides mixed with alkali metal pyrosulfates dispersed on a porous

silica carrier. The oxidation is followed by hydration of SO_3 and condensation into sulfuric acid. In operation, the vanadia is dissolved in the molten pyrosulfate and forms a liquid film that is only present during the harsh reaction conditions. Detailed information about the catalytic active liquid species and their dynamic behavior in the pore system during SO_2 oxidation has remained inaccessible. However, *in situ* TEM and Raman spectroscopy allows us to retrieve unprecedented new insight into the dynamic behavior and chemical functionality of SO_2 oxidation catalysts in the active state [4].

References:

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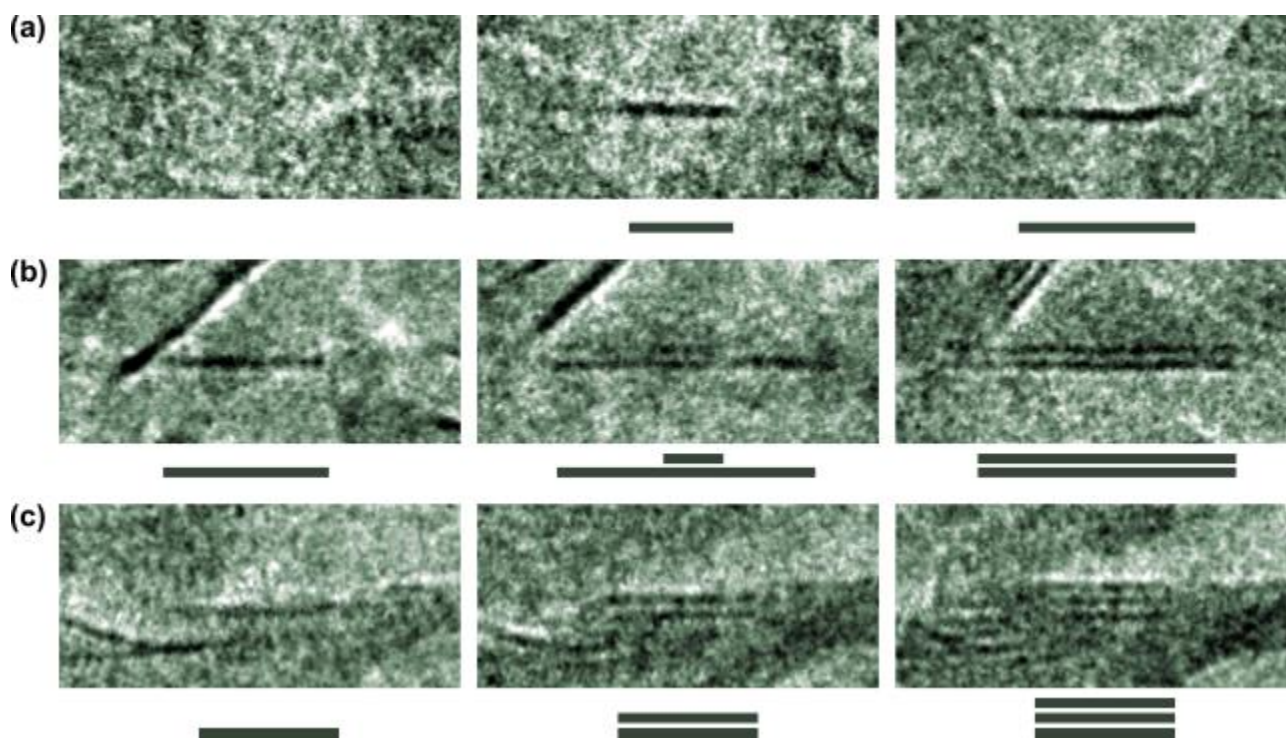


Figure 1. Time-resolved *in situ* high-resolution TEM image series of the growth of MoS_2 nanocrystals consisting of (a) 1-layer (b) 2-layer, and (c) 3-layer MoS_2 slabs. Growth conditions: 0.8 mbar of $\text{H}_2\text{S}:\text{H}_2 = 1:9$ at 690°C . The images represent times of (a) 122 min, 138 min, 152 min (b) 225 min, 243 min, 257 min, and (c) 178 min, 192 min, 208 min, relative to the time $t=0$ min of reaching the temperature 690°C . Sketches are included to guide the eye in identifying the MoS_2 slabs. The frame sizes are $17.3 \text{ nm} \times 7.9 \text{ nm}$. Adapted from [3].