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Electron Microscopy Studies of Structure and Dynamics in MoS_2-based Hydrodesulfurization Catalysts

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New environmental legislation for clean fuels demands an enhanced removal of sulfur and other impurities from mineral oil. Production of ultra-low sulfur transport fuels at oil refineries requires very efficient catalytic hydrodesulfurization processes, and attention is currently being devoted to understand the catalysts' structure-activity relationships. This requires a detailed characterization of the catalyst's nanostructure and in particular the nature of the atomic-scale active sites.

For industrial hydrodesulfurization at oil refineries, the catalysts are based on MoS_2 nanostructures [1]. Basically, the MoS_2 structure consists of two-dimensional S-Mo-S slabs which can be stacked to varying degrees by van der Waals interactions. In each layer, hexagonally arranged Mo atoms are trigonal-prismatically coordinated to S atoms. Such two-dimensional S-Mo-S structures have been found to form polymorphs including fullerene structures, nano-tubes/wires and platelets with physico-chemical properties significantly different from bulk MoS_2 [2]. It is well-known that the catalytic reactivity of the MoS_2 slabs is associated with their exposed edges and relies on the size, morphology and the degree of slab stacking [3]. Consequently, the ability to synthesize MoS_2 structures with controlled morphology and specific size is of particular interest. However, although MoS_2 nanostructures are synthesized at a very large scale in the refining industry, insight into the structure and dynamics of the MoS_2 nanostructures has remained a challenge to unveil.

Recent advancements have made transmission electron microscopy (TEM) a powerful technique for studying individual (supported) nanoparticles at the atomic-level [4,5]. In this presentation, we demonstrate the application of such advancements for single atom sensitivity and in situ electron microscopy of MoS_2-based hydrotreating catalysts. By means of time-resolved TEM imaging, the growth of MoS_2 nanocrystals is monitored in situ during the sulfidation reaction that transforms a molybdenum oxide precursor material into highly dispersed MoS_2 nanocrystals (Figure 1a-b). Specifically, the time-resolved image series provide new information about the evolution of MoS2 nanocrystals with different size, morphology and stacking and thus uncover the nucleation and growth of the MoS_2 nanocrystals. The in situ observations are beneficially combined with single-atom sensitive imaging by (S)TEM, because such microscopy techniques enable detection of the catalytic active edge structures at the levels of a single atom (Figure 1c-e). Thus the combined use of in situ and single-atom sensitive (S)TEM provides unprecedented new insight into the formation of MoS_2 nanocrystals with specific distribution of active sites. In combination with information about structure-sensitive catalytic functionality, obtained from scanning tunneling or density functional theory calculations, the electron microscopy observations provide information that can help establish new, improved structure-functionality relationships of the technological relevant hydrodesulfurization catalysts.

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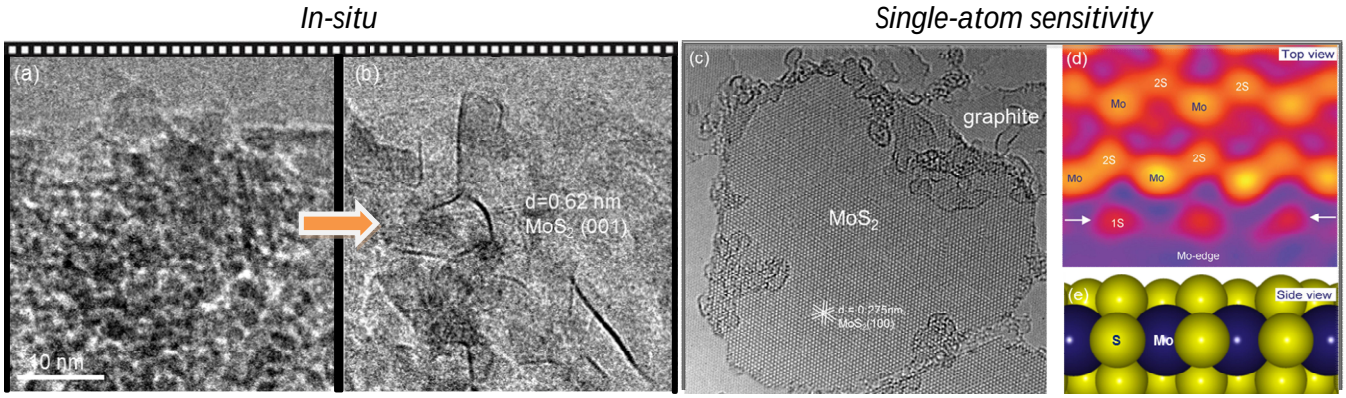

Figure 1. TEM images of (a) a molybdenum oxide precursor dispersed on a high surface area Mg-spinel support, and (b) the same area after in situ exposure to 1 mbar H_2S:H_2 1:9 at approx. 700 °C for 5 hours. (c) High resolution TEM image of a MoS_2 nanoparticle in (001) projection on a graphite support. (d) High resolution STEM image of region at the catalytically important edge of a MoS_2 particle showing the detailed atomic arrangement of single sulfur atoms (1S) terminating the so-called Mo-edge. (e) Ballmodel of the Mo-edge (side view) [4,5].

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