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High-Resolution Electron Tomography Study of an Industrial Ni–Mo/ γ -Al₂O₃ Hydrotreating Catalyst

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The growing demand for high-quality transportation fuels requires their cost-effective production by hydrodesulfurization of crude oils using heterogeneous catalysts. To study the three-dimensional (3D) structure of such a commercial, sulfided Ni–Mo/ γ -Al₂O₃ catalyst, electron tomography was applied. The MoS₂ particles form an interconnected complex structure within the mesopores of the alumina support. Spatial organization, morphology, and orientation of the MoS₂ particles in the pores were resolved with sufficient accuracy to display the 6-Å-spaced MoS₂ crystal planes. The proximity of the MoS₂ edge planes and more loosely interacting MoS₂ basal planes to the alumina support showed the presence of pores smaller than 3 nm, which was confirmed by physisorption experiments. The actual shape of the MoS₂ particles cannot be described by simple models as derived from studies on model catalysts. Electron tomography is a unique tool to study the actual 3D structure of complex industrial catalysts with sub-nanometer resolution.

Introduction. Oil refining relies on the use of heterogeneous catalysts to deliver high-quality transportation fuels that comply with environmental legislation and address social concerns. In particular, the need for low-sulfur fuels calls for the continuous improvement of hydrotreating catalysts and a better understanding of their properties. Heterogeneous hydrotreating catalysts are composed of a mesoporous alumina support containing a catalytically active phase. The active phase in such catalysts consists of layered MoS₂ structures decorated with the promoter (Ni or Co), the so-called Ni–Mo–S or Co–Mo–S phase.¹ The active sites for hydrodesulfurization reactions are associated with sulfur vacancies or metallic character sites at the edges of the MoS₂ structures.²

Two types of active phases, Type-1 and Type-2, have been described in the literature.^{1,3} The active phase of a Type-2 catalyst, as the examined Ni–Mo/ γ -Al₂O₃, is characterized by a more complete sulfidation, a weaker interaction between metal sulfides and the alumina support, and a higher intrinsic activity.^{1,3a} The morphology of the active phase and its bonding to the alumina support define the extent of the surface area available for hydrodesulfurization reactions. For a detailed account on MoS₂ catalysts we refer to relevant reviews.⁴

Transmission electron microscopy (TEM) has become an indispensable technique to obtain detailed structural information on materials. Since the examined volume in TEM is very small

compared to the bulk material it is mandatory to complement TEM findings with results from bulk techniques such as nitrogen physisorption, extended X-ray absorption fine structure spectroscopy (EXAFS), or X-ray diffraction (XRD).^{4,5} One of the key problems in the characterization of complex porous catalysts by TEM is the projection of three-dimensional (3D) structural information into the image plane. Several authors have pointed out that the distinction between edge and basal bonding of MoS₂ stacks on γ -Al₂O₃ is hardly possible from conventional TEM images.² In contrast, electron tomography combines multiple images taken at different tilt angles to reconstruct the object's 3D morphology. This approach has been shown to be a versatile method to characterize the 3D structure of biological specimen,⁶ quantum dots,⁷ and catalysts.⁸ For more detailed accounts on the role of electron tomography in catalysis research we refer to the reviews by Anderson, Ziese, or Thomas.⁹

In this paper we report for the first time on the application of high-resolution electron tomography to a complex industrial Ni–Mo/ γ -Al₂O₃ catalyst. Key questions in this study are: the 3D spatial organization of the MoS₂ particles, the shape of individual MoS₂ particles, and the location and orientation of the MoS₂ particles with respect to the γ -Al₂O₃ support. In addition we used nitrogen physisorption experiments and XRD measurements to complement and verify our conclusions.

Experimental Methods. The commercial Type-2 Ni–Mo/ γ -Al₂O₃ (Albemarle Catalysts Company BV) had a metal loading of 2.5 atoms/nm² for Ni and 8.1 atoms/nm² for Mo.¹⁰ The catalyst contains also phosphorus, which is a common additive in the preparation of commercial Ni–Mo hydrotreating catalysts. For additional details on catalyst preparation, composition, and MoS₂ particles (average length 5.8 nm, average stacking 2.6 layers) we refer to ref 10 (sample ID “NiMo3-T2-G-H”). The

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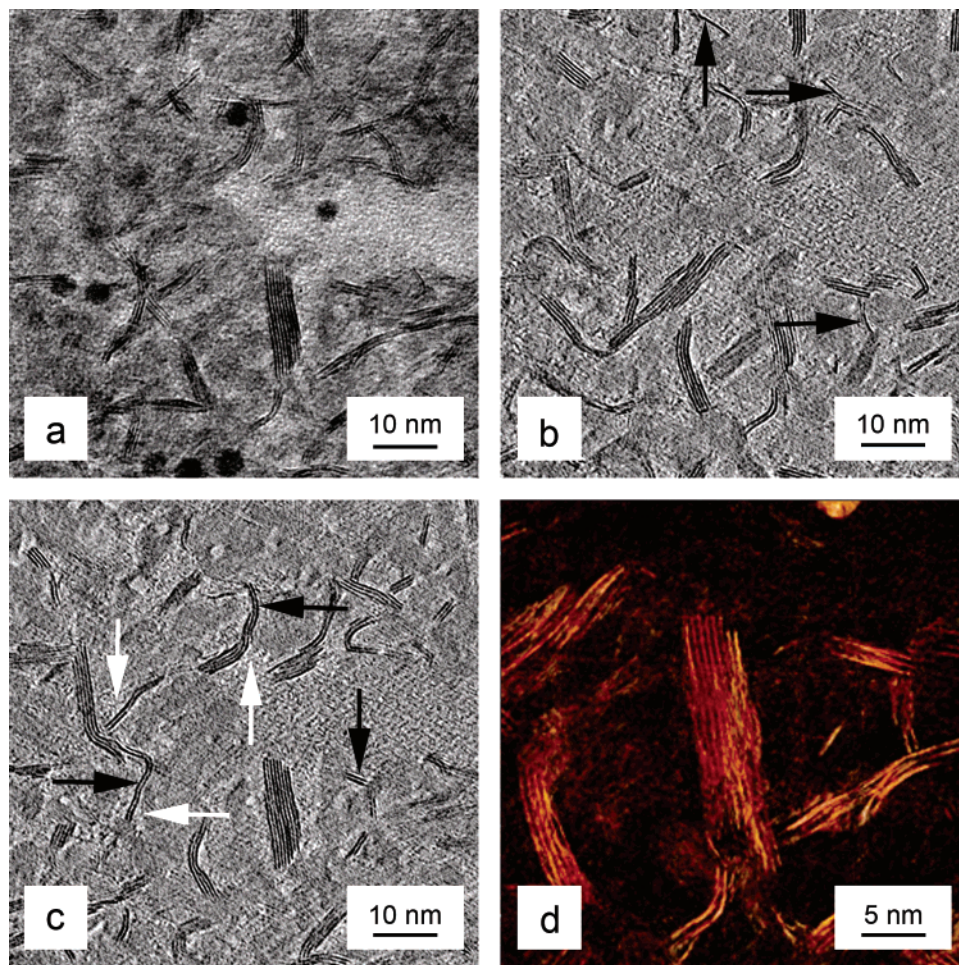


Figure 1. TEM image and reconstruction of an epoxy-embedded ultrathin section of the catalyst: (a) image from the tomographic tilt series; (b and c) 5-Å-thick cross-sections through the reconstruction, 6 nm apart. Black arrows indicate MoS₂ particles, and white arrows indicate small pores between MoS₂ and alumina support. (d) MoS₂ particles within a 44 × 44 × 32 nm³ volume visualized without alumina support by volume rendering.

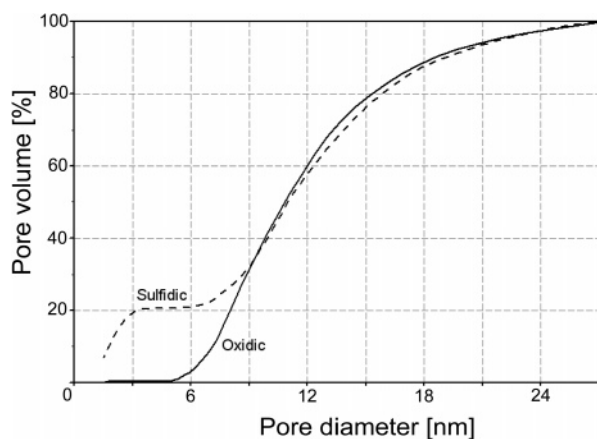


Figure 2. Pore-size distributions calculated from the adsorption branches of nitrogen physisorption experiments of the sulfidic catalyst and its corresponding oxidic precursor.

catalyst was sulfided in the gas phase using a mixture of 60 vol % H₂S in H₂ at 300 °C for 4 h, cooled to room temperature, and passivated in air. The high H₂S concentration was used to stimulate the formation of MoS₂ stacks on catalyst sulfidation. Nitrogen physisorption measurements were performed with Micromeritics (ASAP 2400, Tristar 3000, ASAP 2010) on the sulfidic catalyst and the oxidic precursor. From the adsorption branches of the isotherms pore-size distributions were deduced using the Broekhoff–de Boer formalism.

Extrudates were used in a hydrocracker pretreatment activity test carried out in a trickle flow reactor unit. The feed was coker gas oil, and the reaction conditions were $T = 380$ °C, $p = 100$ bar, liquid hourly space velocity = 2.0/h, H₂/oil = 1000 NL/L. These reaction conditions were maintained for a total of 8 days. The extrudates were rinsed in toluene to remove residual oil and powdered in a mortar. After some of the powdered material was embedded in epoxy resin, ultrathin sections (nominally 15-nm-thick) were cut using an ultramicrotome. The sections were then transferred onto a Cu TEM grid. In the last step 5-nm-sized gold colloid particles (Sigma-Aldrich) were applied to the surface of the thin sections to aid in image processing.

Electron microscopy was performed with a Tecnai20 (FEI Company). Bright-field TEM tilt series were recorded at 200 kV using Xplore3D software (FEI) in combination with a bottom-mounted 1k × 1k CCD camera (Gatan GmbH, model 694). The pixel size was 1.7 Å corresponding to a nominal microscope magnification of 100 000×. The tilt series were typically acquired from −70° to +70° with 1° increments. For imaging of the 6 Å features we used an underfocus of a few tens of nanometers. However, when the sample was tilted, areas to the right and left of the rotation axis change their height relative to the focal plane. This change is proportional to the sine of the tilt angle times the distance from the tilt axis, and thus, large focus variations exist between the two extreme sides of the sample. In the presented high-resolution transmission electron microscopy (HRTEM) tilt series the focusing of the area of interest throughout the tilt series was sufficiently accurate

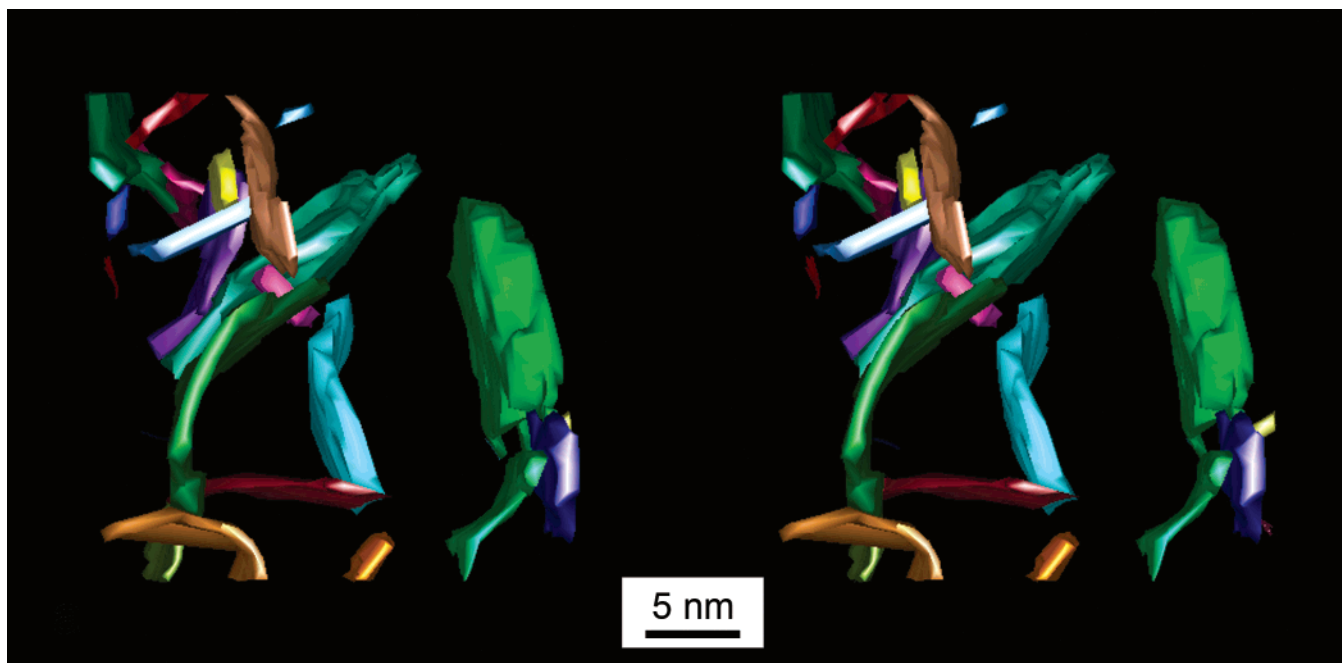


Figure 3. Stereoview of interconnected MoS₂ particles within a $44 \times 44 \times 44 \text{ nm}^3$ volume of the 3D reconstruction.

to include 126 of the original 141 images for reconstruction of the 3D volume. Images of the tilt series were aligned with respect to a common origin by fiducial markers (colloidal gold particles), and the tomograms then were reconstructed via weighted backprojection in the IMOD program.¹¹

Results and Discussion. Figure 1a shows an $87 \text{ nm} \times 87 \text{ nm}$ HRTEM image of the ultrathin-sectioned epoxy-embedded sulfidic Ni–Mo catalyst. It is a detail from one image of the tomographic tilt series (original size $174 \text{ nm} \times 174 \text{ nm} \times 141$ images). Epoxy (bright, granular), alumina support (darker, smooth), and MoS₂ crystal planes (dark lines) can be differentiated. The dark circular spots in Figure 1a are 5-nm-sized colloidal gold particles on the surface of the epoxy section that aid in alignment and reconstruction of the tilt series.

Figures 1b and 1c display two 5 \AA thin cross-sections through the reconstruction. Again we discern epoxy (granular), alumina support (smooth), and MoS₂ crystal planes (dark lines). Even though the spacing between the cross-sections is only 6 nm , Figures 1b and 1c show completely different MoS₂ particles. The resolution in the individual cross-sections is sufficient to resolve MoS₂ particles (black arrows) consisting of as few as one (Figure 1b) or two crystal planes (Figure 1c). It is immediately apparent that most crystal planes are bent. This bending is displayed in Figure 1d over a $44 \times 44 \times 32 \text{ nm}^3$ volume. Resolving the 6-\AA -spaced crystal planes of MoS₂ is to the best of our knowledge unprecedented in bright-field (BF) TEM tomography of porous materials.

It must be noted that MoS₂ crystal planes oriented parallel to the image plane are not resolved due to limitations in the angular tilt range of the microscope tilt stage. However, most MoS₂ crystal planes are viewed in at least some images of the tilt series, and thus the number of resolved crystal planes in a reconstruction is close to the actual number. When looking at Figure 1c it appears as if the bent MoS₂ particles are “peeled off” the alumina support, therefore creating small pores (white arrows) and suggesting a loose interaction between both phases. This effect might become more apparent when consulting the movies in the Supporting Information. The contrast between epoxy, alumina support, and MoS₂ particles is not sufficient

yet to resolve and quantify the pore volume directly from the reconstruction for comparison with physisorption data.

The nitrogen physisorption data in Figure 2 show that pores smaller than 3 nm are created upon sulfidation of the oxidic precursor. The MoS₂ particles have grown to occupy a substantial fraction of the available mesopore volume within the alumina support. We found that the Brunauer–Emmett–Teller (BET) surface area increased from $131 \text{ m}^2/\text{g}$ (oxidic precursor) to $196 \text{ m}^2/\text{g}$ for the sulfided catalyst. The decrease of the total pore volume from 0.344 mL/g (oxidic) to 0.300 mL/g (sulfidic) nicely coincides with the substantial occupancy of the mesopores by MoS₂.

Taking full advantage of the 3D information in the reconstruction as displayed in Figure 1d, we found that most of the MoS₂ particles in the investigated area were interconnected in space. In Figure 3 a stereoview of the MoS₂ phase within a $44 \times 44 \times 44 \text{ nm}^3$ volume of the 3D reconstruction is displayed. This visualization was created by manually tracing the contours of MoS₂ particles in all cross-sections throughout the volume. Separate MoS₂ particles consisting of one or more crystal planes are indicated by different colors. It is immediately apparent that the MoS₂ particles form a complex structure within the mesoporous alumina support. When looking at the shape of single MoS₂ particles it becomes clear that the particles cannot be described by simple models, e.g., triangles or (truncated) hexagons, as derived from studies on model catalysts.^{2d,e} X-ray diffraction measurements confirmed deviations from ideal crystalline geometry of MoS₂ in the sample.¹⁰ Bending of the crystal planes, as seen in Figures 1 and 3, and the resulting relaxation of the crystal lattice did cause a shift in the position of the (002) diffraction peak from $2\theta = 14.4^\circ$ to 14.0° .¹⁰ This result points to an expansion of the average crystal plane spacing from 6.15 \AA to approximately 6.45 \AA as bending of the MoS₂ crystal planes causes a lattice mismatch in a fashion similar to the one observed for turbostratic graphite.

Conclusions. On the basis of the presented data we conclude that the MoS₂ particles in the sulfided catalyst are loosely connected to the alumina support, which is in agreement with earlier models for the Type-2 active phase. Due to this loose

interaction of the MoS₂ with the alumina support a network of pores smaller than 3 nm is created upon sulfidation, which was confirmed by nitrogen physisorption. The MoS₂ particles form a complex interconnected structure within the alumina support and occupy a substantial fraction of the mesopore volume. At the resolution obtained in this work the individual crystal planes of MoS₂ particles have been imaged, and the shapes of the resolved particles deviate largely from studies on model catalysts. A generalization of the presented results is not possible from our data and beyond the scope of this letter. The significance of the observation is limited to the described catalyst and provides a "proof of principle" for this new methodology. The presented results can be seen as a first measurement in a multivariant space relating preparation, activation, and test conditions with the actual 3D structure of the active catalyst. High-resolution electron tomography has delivered new fundamental insights into the structure of a complex catalyst and is expected to play a major role in the understanding and development of this important class of materials.

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Supporting Information Available: Movies of the aligned HRTEM tilt series with an angular increment of 4° (Projections.qt), consecutive cross-sections through the reconstruction with 1 nm spacing between sections (Reconstruction.qt), and interconnected MoS₂ particles viewed at different rotations with an angular increment of 5° (Surface.qt). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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