

HREM and HAADF Study of Nanostructured MoS₂ Bulk Catalysts

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Molybdenum and tungsten sulfides are probably the most widely used catalysts for hydroprocessing of fossil fuels. This includes hydrogenation (HYD) of aromatic compounds and removal of sulfur from organic molecules. Both, sulfur rich and highly aromatic compounds, contribute to the production of harmful emissions and decrease the fuel quality [1]. These two processes and HYD more particularly, have to proceed in a very selective way so as to avoid olefin hydrogenation what would decrease the octane number in gasoline. Furthermore, recent regulations have decreased the limit to sulfur and aromatics contents to very stringent limits; for example, the regulation for 2006-2010 limits the sulfur content to 15 ppm in diesel and 30 ppm to gasoline.

Even though non-supported molybdenum sulfide and alumina supported catalysts have been extensively studied, the catalytic mechanisms and structure of the active sites is still to be fully understood. We have previously studied commercial spent catalysts [2] and in this paper we present a structural study of a model non-supported nanostructured molybdenum sulfide catalyst. The catalyst was prepared by sulfidation of α -MoO₃ nanoribbons that were prepared by hydrothermal synthesis. The sulfidation process was carried out at 723 K in order to avoid fullerene-like structures to form.

The resulting sulfides were placed on carbon tape and coated with Au-Pd. Their morphology was studied by scanning electron microscopy (SEM) in a Hitachi S-4500 field emission SEM operating at 5 KV and a Jeol JSM 7700F (Cs corrected, 0.6 nm resolution) microscope operating at 2KV and at 30KV for scanning transmission (STEM) imaging. Transmission Electron microscopy (TEM) and associated techniques such as energy dispersive X-ray spectroscopy (EDS), nanobeam diffraction (NBD), selected area diffraction (SAD), high-resolution electron microscopy (HREM) and high angle annular dark field (HAADF) were applied to determine the subnanometer structure, chemical composition and homogeneity of the sulphides.

TEM analysis was carried out in a JEOL 2010 F microscope equipped with Schottky-type field emission gun, ultra-high resolution pole piece (Cs= 0.5 mm), and a STEM unit with a high angle annular dark field detector (HAADF), operating at 200 KV. An Oxford spectrometer, attached to the 2010F was used for EDS analysis. The resulting powders presented rod-like particles with sets of platelets growing perpendicularly to the long axis, as it is observed in figure 1. The elemental analysis showed only the presence of Mo, S and O. This is in well agreement with the two phases identified by electron diffraction, which were MoO₂ and MoS₂.

Dark field imaging was used to determine the distribution of the two crystalline phases, the oxide was found to be the core and the sulfide phase to grow from it. The samples were analyzed by HAADF, the MoS₂ wires showed a very strong contrast in this mode even though they were measured to be one to two unit cells across Fig. 2.

The HREM images of the resulting sulfides showed two kinds of terminations, one corresponds to regular hexagonal MoS₂ and the other consists of bundles of nanowires of a MoS₂ phase (Fig. 3). We have also performed EELS and nanodiffraction studies of the sample. We show the plasmon image in Fig 4 Catalytic results show that these materials that have a selectivity for hydrogenation.

References

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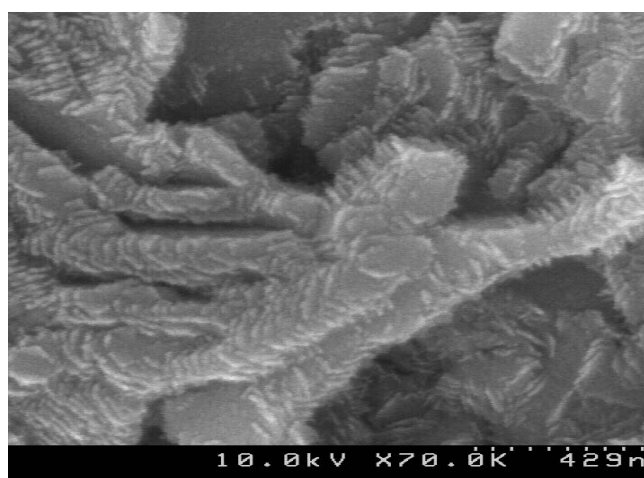


Fig. 1. SEM image of the nanostructured sulfides the rod-like particles are visible.

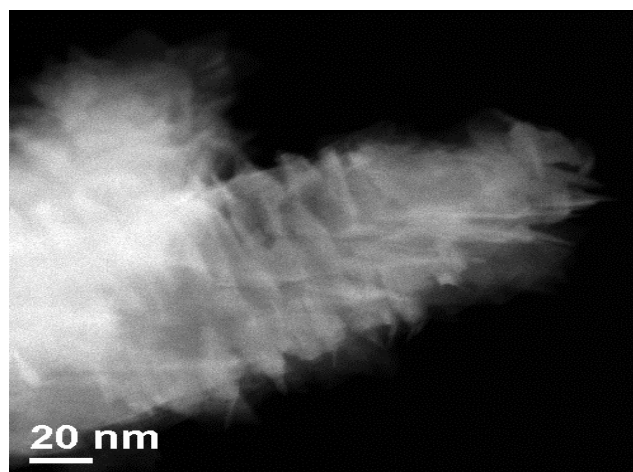


Fig. 2. HAADF image of a bundle of MoS₂ nanowires on a MoO₃ substrate.

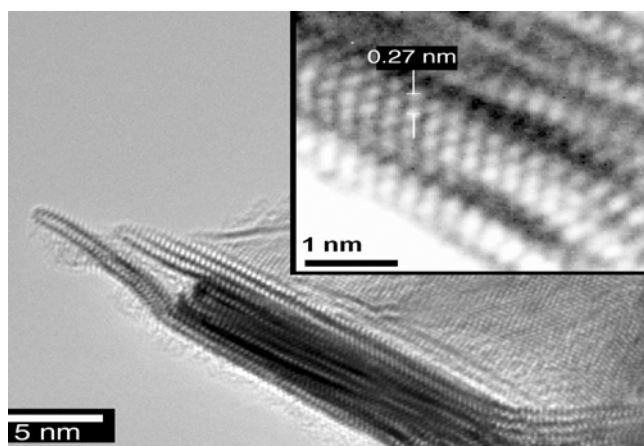


Fig. 3. HREM of a sample of MoS₂+x showing the structure of the nanowires edges nanowires are located is clear.

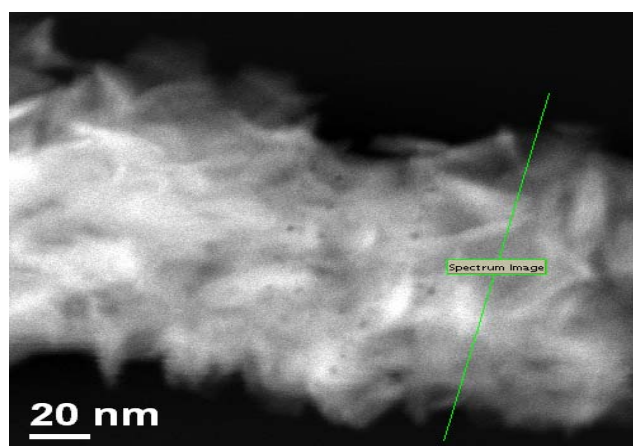


Fig. 4. Plasmon Image of the sample in which the MoS₂ nanowires can be seen.