DOI: 10.1017/S1431927605509115
Microsc Microanal 11(Suppl 2), 2005


# Morphological Study of Nanostructured $MoS_2$ bulk catalysts

Camacho-Bragado, G. A.[*], Olivas, A.[**]; Fuentes, S.[**] and Jose Yacaman, M. [*,***]

* Texas Materials Institute, 1 University station C2201, University of Texas at Austin, Austin, TX, 78712, USA
** Centro de Ciencias de la Materia Condensada - UNAM, Ensenada, B. C., CP 22800, México
*** Department of Chemical Engineering and Center for Nano and Molecular Science and Technology, University of Texas at Austin, Austin, TX, 78712, USA

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, 2]. 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 regulations for 2006-2010 limits the sulfur content to 15 ppm in diesel and 30 ppm to gasoline. The problem becomes more complicated when one takes into account that the oil consumption keeps on increasing and the average sulfur content in the current crude oils has been increasing in the last two decades.
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 [3] 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 $\alpha$-$MoO_3$ nanoribbons that were prepared by hydrothermal synthesis [4]. 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. For TEM analysis, the samples were sonicated in isopropanol and deposited on lacey carbon copper grids. 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 $MoO_2$ and $MoS_2$.
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 HREM images of the resulting sulfides showed two kinds of terminations, one corresponds to regular hexagonal $MoS_2$ and the other

consists of bundles of nanowires of a $MoS_2$ phase (figure 2). The samples were analyzed by HAADF, the $MoS_2$ wires showed a very strong contrast in this mode even though they were measured to be one to two unit cells across.
Preliminary results of these materials showed a good selectivity for hydrogenation. It is in process a morphological study of these materials after catalytic testing, in order to obtain an insight of the deactivation mechanism of this kind of catalysts.

[1] K. L. Riley, D. P. Klein, Z. Hou, S. L. Soled, M. C. Kerby, G. B. McVicker, E. S. Ellis, M. S. Touvelle, S. Miseo, Hydrotreating using bulk multimetallic catalysts, in: '(Ed.)'^'(Eds.)', vol Exxon Mobil Research and Engineering Company, US, 2004, p.^pp. 22.
[2] C. Song, Catalysis Today 86 (2003) 211-263.
[3] M. Perez De la Rosa, S. Texier, G. Berhault, A. Camacho, M. José Yácaman, A. Mehta, S. Fuentes, J. A. Montoya, F. Murrieta, R. R. Chianelli, Journal of Catalysis 225 (2004) 288-299.
[4] X. L. Li, J.-F. Liu, Y. D. Li, Applied Physics Letters 81 (2002) 4832-4834.
[5] Authors want to thank JEOL, Ltd for the access to the Cs corrected SEM. Funding was provided by SEMATECH and CONACyT.

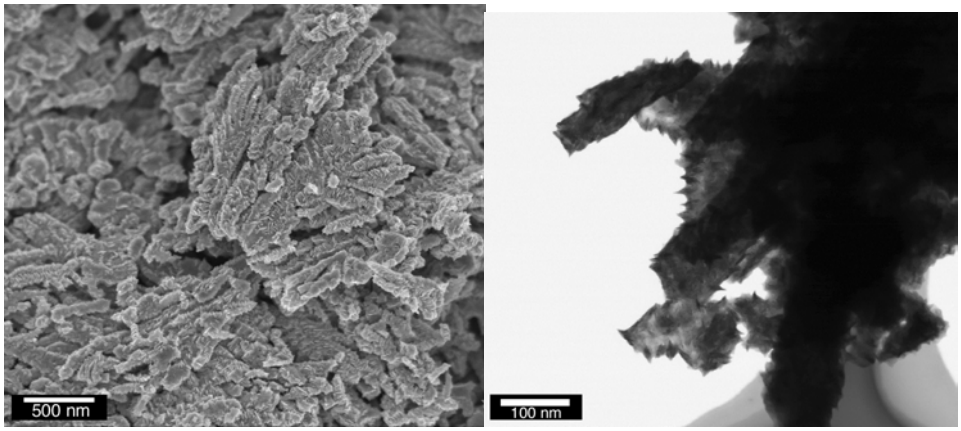

Figure 1. (Right) SEM image of the nanostructured sulfides, the rod-like particles are visible. (Left) bright field image where the high contrast on the edges were the nanowires are located is clearly visible.

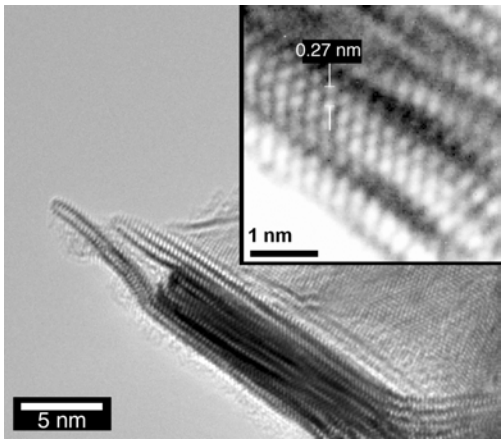

Figure 2. HREM image of a bundle of $MoS_2$ nanowires, the inset shows the hexagonal array of the atoms in one of the wires.

https://doi.org/10.1017/S1431927605509115 Published online by Cambridge University Press