doi:10.1017/S1431927614011532
Microsc. Microanal. 20 (Suppl 3), 2014

Sulfidation of Molybdenum Oxide and Tungsten Oxide Crystallites: an Ex-Situ TEM Study

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With environmental considerations mandating ever-increasingly lower sulfur levels in fuels, it is necessary to develop more robust hydrodesulfurization (HDS catalysts).[1-3] In order to improve upon the current commercial catalytic systems, it is critical to first develop an understanding of the morphological transformations that occurs during activation (sulfidation) of the catalyst.[4-8] Because commercial HDS catalysts are highly complex systems containing promoters and supports,[4-8] this initial work follows the sulfidation of two simple (unpromoted, and unsupported) systems (molybdenum oxide and tungsten oxide) to gain an overall, fundamental understanding of the transformations that occur within these materials.

In this investigation, oxide particles of both Mo and W were crushed into fines and dusted onto standard, 200 mesh, holey-carbon-coated TEM grids. The grids were transferred into a Philips CM200F TEM where individual oxide particles were examined in the bright field imaging mode at an accelerating voltage of 200 kV. Following the ex-situ TEM protocols described previously,[9] the locations of the oxide particles being imaged during the initial examination of each grid were "mapped" so that those same particles could be re-located and re-examined subsequent to various thermal treatments.

Examination of the fresh Mo oxide crystallites revealed well-defined lattice structures (Figure 1a). The TEM grid holding the Mo oxide crystallites was then given a series of thermal treatments under a 10% H2S / H2 environment. After each treatment, the grid was inserted into the TEM via an inert transfer protocol developed specifically for ex-situ work.[9] Areas of the material that had been examined initially were re-examined (Figure 1b) and (Figure 1c). These images reveal that the outer layers of the bulk Mo oxide particles sulfide prior to the inner portion of the crystallites (Figures 1a-1c). With time, the interior of the metal oxide particles transforms to the sulfide via the diffusion of oxygen and sulfur ions. This diffusion is hypothesized to occur through pathways created by defects (point, line) in the crystallites. A similar study was conducted on W oxide particles and presented identical results (Figure 2a-2c). These data suggest that the basic architecture of HDS catalysts (i.e., tailored edge and rim sites for catalysis[10]) may be created by controlling the oxide phase morphology.

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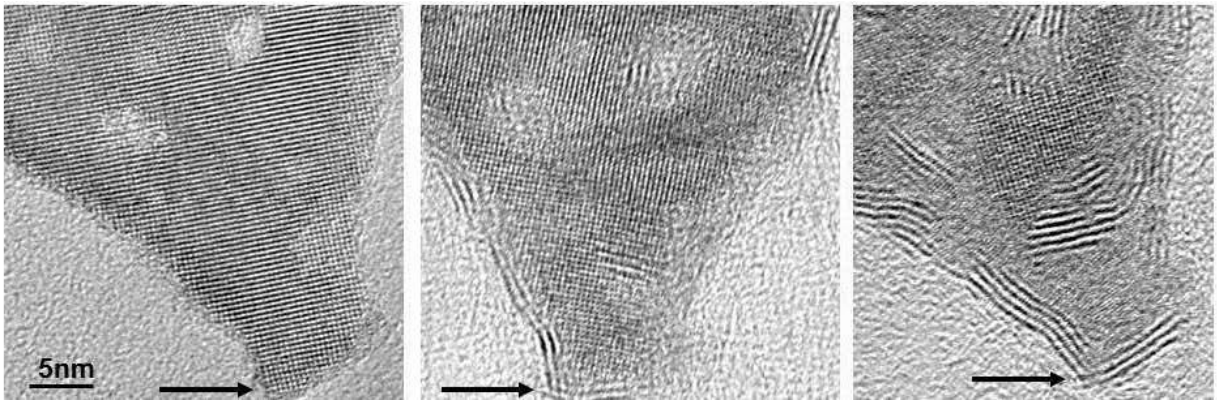

Figure 1: BF TEM image showing: (a) Mo oxide crystal lattice, (b) original Mo oxide crystallite after three separate 350 °C, 3 h treatment in 10% H2S / H2 environment, and (c) original Mo oxide crystallite after a 400 °C, 1 h treatment in 10% H2S / H2 environment. Arrow indicates the same region of crystallite in each image.

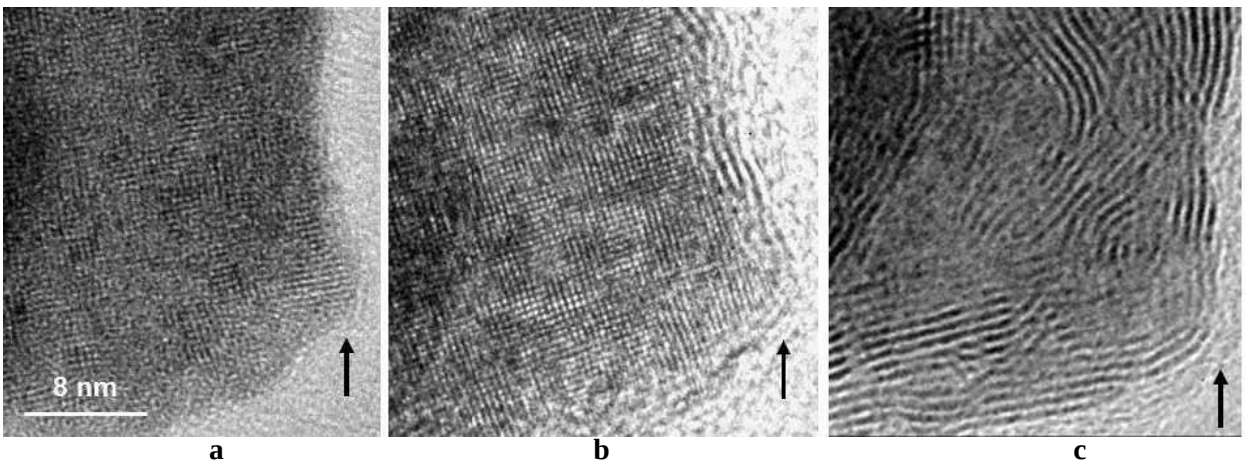

Figure 2: BF TEM image showing: (a) W oxide crystal lattice, (b) original W oxide crystallite after a 350 °C, 2 h treatment in 10% H2S / H2 environment, and (c) original W oxide crystallite after a 450 °C, 2 h treatment in 10% H2S / H2 environment. Arrow indicates the same region of

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