

## A TEM study of Ni-MoS<sub>2</sub>- and Co-MoS<sub>2</sub>-based HDS catalysts supported on SBA 15

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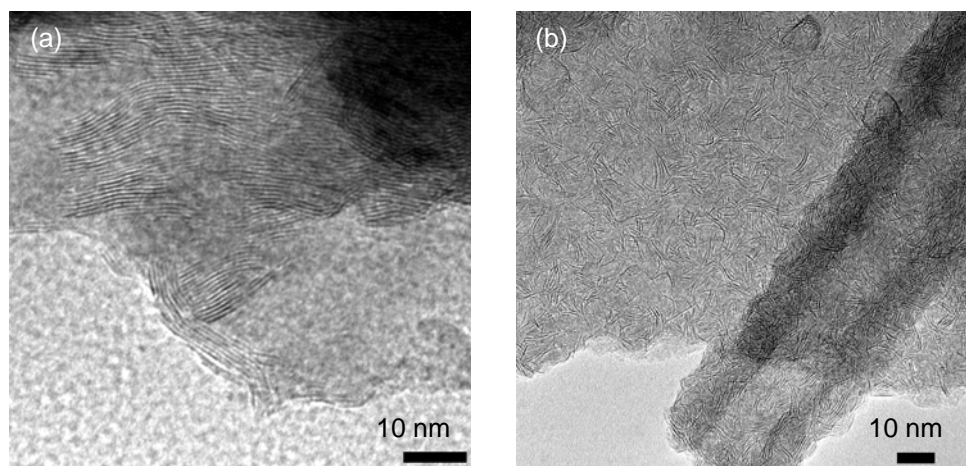
A hydrodesulfurization (HDS) processes is widely used in the petroleum refining industry. Commercially available HDS catalysts are based on MoS<sub>2</sub> promoted by Co or Ni. The HDS catalysts are usually supported on Al<sub>2</sub>O<sub>3</sub> and prepared from oxide precursors by sulfidation using either H<sub>2</sub>/H<sub>2</sub>S or an organic sulphur compounds. The improvements in the performance of HDS catalysts can be achieved by modifying the method of catalyst preparation or by changing the nature of the catalyst support. In this work, Ni-MoS<sub>2</sub> HDS and Co-MoS<sub>2</sub> HDS catalysts supported on mesoporous SBA-15 were synthesized using S-containing Mo (without C (ammonium thiomolybdate, ATM) or with C (tetramethyl ATM, TMATM)) and either Co or Ni thiocarbamate, as precursors. The catalysts were decomposed during the catalytic test in the presence of hydrocarbon solvent (in-situ activation) or under H<sub>2</sub>/N<sub>2</sub> (H<sub>2</sub>=10%) gas flow (ex-situ activation). The HDS reaction of dibenzothiophene was carried out in a Parr model 4522 high-pressure batch reactor while transmission electron microscopy (TEM) investigations were carried out in a Tecnai F30 STwin microscope.

Figures 1(a) and 1(b) show HRTEM micrographs of ex-situ and in-situ activated Ni-MoS<sub>2</sub> HDS catalyst, respectively. The MoS<sub>2</sub> slabs in Figure 1(b) are shorter and the number of their stacking is less compared to the MoS<sub>2</sub> shown in Figure 1(a). It was also found that the in-situ activated Ni-MoS<sub>2</sub> HDS has a higher catalytic activity ( $12.8 \times 10^{-7}$  mol/(s·g)) than the ex-situ one ( $8.1 \times 10^{-7}$  mol/(s·g)). Notably, the catalytic activity is slightly higher than the activity ( $12 \times 10^{-7}$  mol/(s·g)) of the industrial Ni-MoS<sub>2</sub> HDS catalyst supported on Al<sub>2</sub>O<sub>3</sub> [1]. The nature of the sites of catalytic activity remains an active area of investigation, but it is generally assumed that basal planes of the MoS<sub>2</sub> structure are not relevant to catalysis, rather the edges or rims of these sheets [2]. Thus, lower MoS<sub>2</sub> stacking presented on the in-situ activated catalyst will have the advantage of making more rim site available for the hydrogenation reaction [1], as was observed in this work.

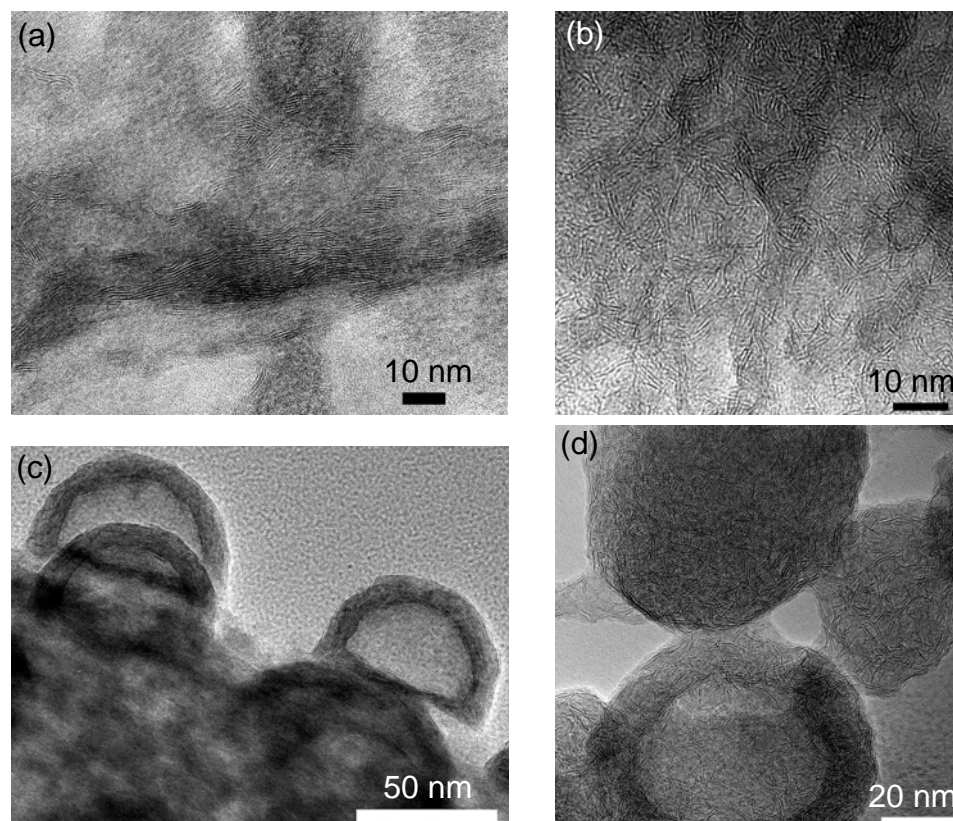
Figures 2(a) and 2(b) give HRTEM images of ex-situ and in-situ activated Co-MoS<sub>2</sub> HDS catalyst, respectively. The MoS<sub>2</sub> slabs in Figure 2(b) are shorter and the number of their stacking is less compared to the MoS<sub>2</sub> shown in Figure 2(a). The ex-situ activated Co-MoS<sub>2</sub> catalyst ( $13.9 \times 10^{-7}$  mol/(s·g)) shows higher HDS activity compared to an in-situ activated Co-MoS<sub>2</sub> catalyst ( $11 \times 10^{-7}$  mol/(s·g)). However, this situation is reverse when carbon-containing thiomolybdate complex is utilized. The in-situ activated Co-MoS<sub>2</sub> catalyst exhibits higher HDS activity ( $12.6 \times 10^{-7}$  mol/(s·g)) compared to the ex-situ activated Co-MoS<sub>2</sub> HDS catalyst

( $7.3 \times 10^{-7}$  mol/(s·g)). The MoS<sub>2</sub> slabs in Figure 2(d) are shorter and the number of their stacking is reduced compared to the MoS<sub>2</sub> shown in Figure 2(c). The MoS<sub>2</sub> morphology depends strongly on the activation condition and precursors used. But, the size and number of MoS<sub>2</sub> slabs are not the main prerequisite for the high HDS activity of Co-MoS<sub>2</sub> catalyst.

1. M. Poisot, W. Bensch, S. Fuentes, C. Ornelas, G. Alonso, *Catal. Lett.* **117** (2007) p43.
2. M. Daage, R.R. Chianelli, *J. Catal.* **149** (1994) p414.



**Figure 1.** HRTEM image of (a) an ex-situ activated Ni-MoS<sub>2</sub> HDS catalyst and (b) an in-situ activated Ni-MoS<sub>2</sub> HDS catalyst. The catalysts were prepared by decomposition of ATM precursor.



**Figure 2.** (a) and (c) HRTEM images of ex-situ activated Co-MoS<sub>2</sub> HDS catalysts. (b) and (d) HRTEM micrographs of in-situ activated Co-MoS<sub>2</sub> HDS catalysts. The catalysts in (a) and (b) were prepared by decomposition of ATM precursor. The catalysts in (c) and (d) were prepared by decomposition of TMATM precursor.