

## Structural Studies of Catalytically Stabilized Industrial Hydrotreating Catalysts

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As the world economy continues to expand the demand for petroleum based fuel increases and the price of these fuels rises. The rising price of fuel has another consequence: refiners tend to purchase cheaper fuels of poorer quality. These poor quality fuels contain increasing amounts of sulfur and other pollutants leading to a decline in air quality worldwide. A recent New York Times article described the major impact a growing Chinese economy will have on sulfur pollution causing an increase in acid rain and smog across the world.

Hydrodesulfurization (HDS) is a vital process to alleviate environmental effects, where the incoming petroleum feedstock is treated with hydrogen to remove sulfur from the petroleum as  $H_2S$ . Transition Metal Sulfide (TMS) catalytic materials, especially Molybdenum disulfide ( $MoS_2$ ) and promoted  $Co(Ni)/MoS_2$  catalysts normally supported on alumina ( $Al_2O_3$ ), are very good at removing sulfur from petroleum. Nevertheless, obtaining structural information about the changes of the metal/support interface is difficult because  $MoS_2$  has a highly anisotropic layered stacked structure (Figure 1).

Active  $MoS_2$  catalysts occur in stacks of four to five layers, when freshly prepared. A popular model of the reactivity of these catalyst, the “edge and rim” model, considers the differential reactivity of different exposed planes towards reactants. Basal planes are thought to be inert while edge planes are known to be reactive. The stack height of a  $MoS_2$  slabs of a given diameter influences selectivity by varying the ratio of rim sites (active in hydrogenation and C-S bond rupture) to edge sites (active only in C-S rupture) (Figure 2)<sup>1</sup>. However, there have always been some doubts on the

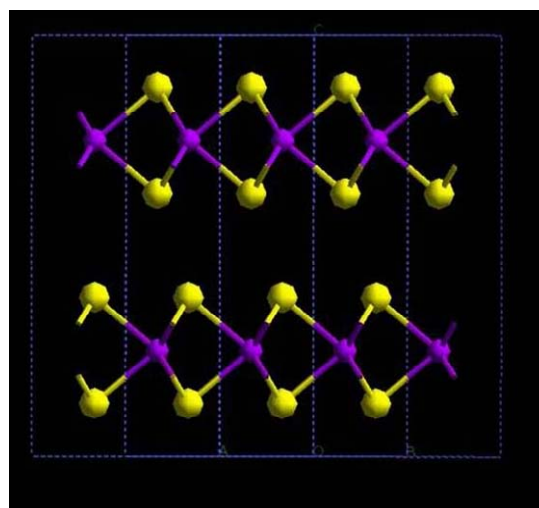


Figure 1:  $MoS_2$  layered structure.

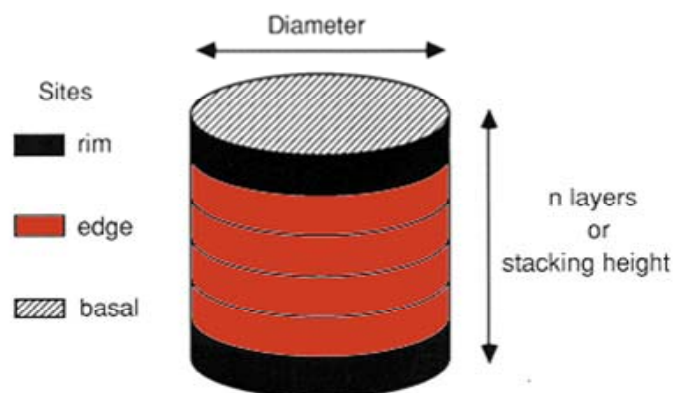


Figure 2: The “Rim-Edge” model. (reference 1)

<sup>1</sup> Daage M., Chianelli R.R., J. Catal. 149 (1994) 414.

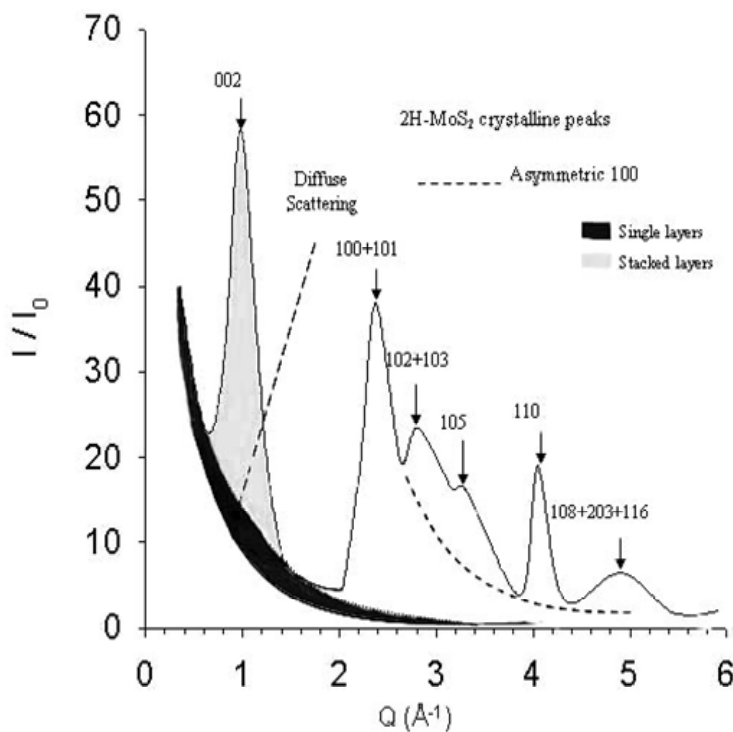
applicability of the “edge and rim” model to Co and Ni promoted MoS<sub>2</sub> catalysts used in industrial HDS process, as the initial model was developed for a simple “unpromoted” MoS<sub>2</sub> system. The work reported here is the first attempt to determine the catalytically stable state of a HDS catalyst after 4 years of use in an industrial reactor. The knowledge of the CSS of any catalysts forms the basis for an understanding of its reactivity and the mechanisms for its eventual aging and demise.

Often transmission electron microscopy (TEM) is used to visualize the catalyst morphology. However, ability to see poorly crystalline MoS<sub>2</sub> slabs, in TEM, strongly depends on how the slabs are bonded to the support. Edge-bonded layers are clearly visible,

whereas flat thin slabs are often missed. Another alternative is to probe the structure via EXAFS/XAFS. However, due to the elimination of low  $k$  data in EXAFS analysis and the highly disordered nature of the MoS<sub>2</sub> slab, EXAFS/XAFS is not very useful in probing medium range order and thus the morphology of MoS<sub>2</sub> slabs. X-ray diffraction pattern is the fourier transform of a material in reciprocal space. Further, diffraction patterns are easy to measure between  $Q$  of 0.1 – 10 Å<sup>-1</sup> (d- spacing of 0.6 to 60 Å). Further a x-ray diffraction pattern probes all orientations of the MoS<sub>2</sub> slabs, albeit as a fourier transform of the real space morphology, and thus gives an unbiased picture of the catalyst morphology. Therefore, x-ray diffraction appears to be the ideal probe for the determination of the CSS of promoted MoS<sub>2</sub> catalyst. Never the less, because of the poor crystallinity of the MoS<sub>2</sub> slabs, the overall diffraction signal is weak and the alumina support contributes significantly to the overall diffraction and therefore conventional lab based diffractometers have failed.

In this work, every effort was made to reduce the background of the diffraction pattern, by using « zero » background sample holders, a high brightness x-ray source, and tightly aligned beam collimators. The contributions of the Al<sub>2</sub>O<sub>3</sub> were eliminated by carefully measuring the diffraction from support alone and then subtracting it from the supported catalyst diffraction pattern by employing the appropriate normalizations. The resulting patterns after subtraction resembled those found for the poorly crystalline unsupported MoS<sub>2</sub> phase, therefore validating the subtraction procedure.

Liang and coworkers<sup>2</sup> have established a procedure for quantitatively determining the size of the MoS<sub>2</sub> slabs from the analysis of the width of the diffraction peaks. Their procedure was followed to determine the average height and the diameter of the MoS<sub>2</sub> slab from the

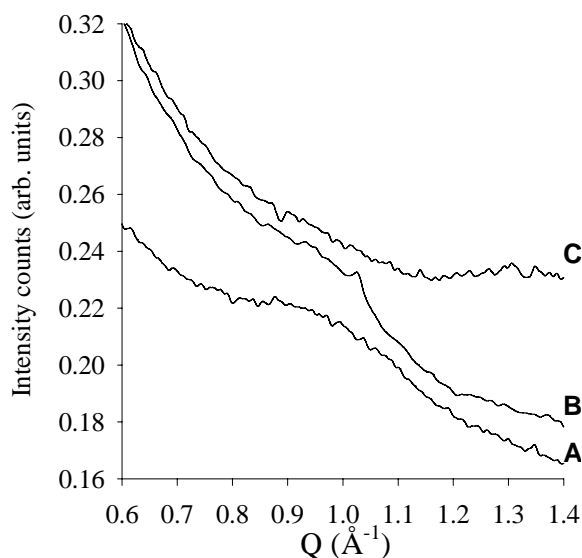


**Figure 3:** Typical x-ray diffraction of the poorly crystalline MoS<sub>2</sub> phase. (reference 5)

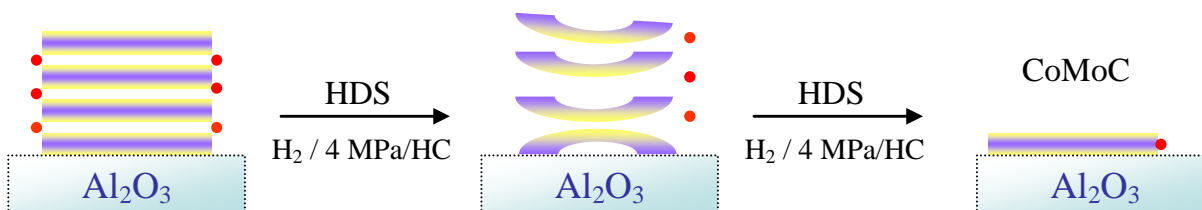
<sup>2</sup> Liang K.S., Chianelli R.R., Chien F.Z., Moss S.C., J. Non-Cryst. Solids 79 (1986) 251.

width of the (002) and (110) peaks. Liang *et al*'s line broadening analysis was complemented by a full scattering model. The full scattering model evaluates the area of the 002 peak and the diffuse scattering area under the 002 peak to determine the fractions of stacked and unstacked layers. The resulting areas of the (002) peak and the diffuse area under the peak correspond to the respective contributions of stacked and unstacked layers of the commercial catalysts. The relative proportions of stacked and unstacked layers were then directly obtained from the XRD data (see figure 3)<sup>3</sup>. This approach allows identification of significant features of the diffraction pattern.

After four years of industrial hydro-treating operations synchrotron scattering patterns of these catalysts show that the catalytic material is on average composed of 7nm diameter slabs. The determination of the average diameter of the MoS<sub>2</sub> is in very good agreement with statistically average sizes obtained from HRTEM photographs of several MoS<sub>2</sub> slabs. The very surprising result is that a very large fraction of these MoS<sub>2</sub> slabs are completely de-stacked<sup>3</sup> (see figure 4). The high pressure applied during the hydrotreating conditions and the strong interaction of adsorbed substances (in this case, hydrocarbon molecules), we believe, provides the stabilization of single MoS<sub>2</sub> layers and is the main cause for the destacking process observed in commercial catalysts under industrial conditions. Similar pressure-crystallization effect, of decreasing stacking with increasing pressure, inside the reactor during the hydrothermal synthesis of MoS<sub>2</sub> in an autoclave have been reported by Peng *et al*<sup>4</sup>. The de-stacking of the MoS<sub>2</sub> slabs, according to the "edge and rim" model, should result in significant decrease in activity since the de-stacked slabs have much lower proportion of Mo active edge sites. However, the activity of the commercial catalysts changed insignificantly over 4 years in a commercial reactor and the process of almost complete de-stacking.



**Figure 4:** Low-angle X-ray synchrotron patterns for the commercial CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst at the three different stages of its catalytic life: one week (A), one month (B), and four years (C). (reference 5)



**Figure 5:** Hydrodesulfurization effect

<sup>3</sup> Perez De la Rosa M., Texier S., Berhaut G., Camacho A., Yacaman M.J., Mehta A., Fuentes S., Montoya J.A., Murrieta F., Chianelli R.R., :J. Catal. 225 (2004) 288.

The result is highly significant not only because for the first time a clear picture of the catalytically stabilized MoS<sub>2</sub> phase is described, but also because it calls into question previous models based on fresh MoS<sub>2</sub> catalyst. The newly determined catalytically stabilized MoS<sub>2</sub> phase structure appears to indicate that the activity/selectivity of a promoted catalyst is related to the size but not to the height of the MoS<sub>2</sub> slab. Therefore, it appears that the promoter cations, such as Co or Ni, tend to reduce the difference between the reactivity of the edge and the rim sites, perhaps by preferentially enhancing the reactivity of the edge sites. This insight suggests pathways to making improved catalysts to address the sulfur pollution problem.

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