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On the structure of a nickel–molybdenum–alumina catalyst

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TEM pictures show that the MoS_2 of a sulfided NiMo–alumina catalyst preferentially agglomerates at steps of the alumina support. Catalyst samples aged during direct coal liquefaction either 2 or 26 days show single MoS_2 layers at steps of the support, and the length of the agglomerates is about the same in the two catalysts. The data is not consistent with models for the catalyst structure that include multi-layers of MoS_2.

Keywords: NiMo–alumina catalyst; structure; models for catalyst structure

1. Introduction

The structure of the sulfided form of the Co–Mo–alumina hydrotreating catalyst has been widely studied [1–7], and at least five models have evolved for the working catalysts. They can be summarized as:

(1) A model where molybdenum sulfide, the active component, covers the support in a monolayer [5]. The promoter, Co or Ni, is associated with this monolayer and could, in theory, be located on top of the Mo layer, incorporated into the Mo layer, or be between the Mo layer and the support.

(2) An intercalation model [8,9] where MoS_2 forms three-dimensional crystals. These crystals have a structure that, similar to graphite, has the strong chemical bonding restricted to two dimensions. Thus, the two-dimensional strong bonding forms planes of MoS_2 but the bonding in the third dimension of these MoS_2 layers is considerably weaker. Because of the weakness of the bonds

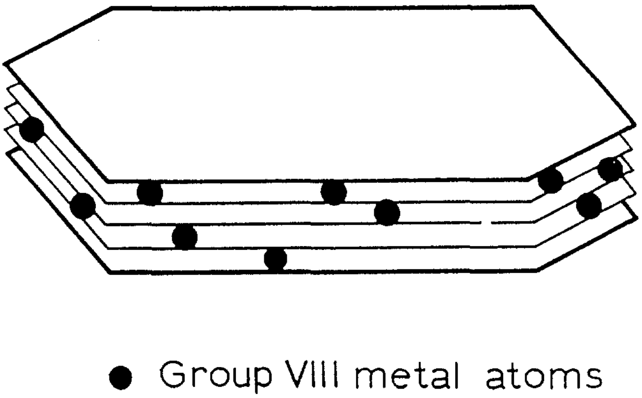

Fig. 1. Schematic representation of a pseudo-intercalated MoS_2 or WS_2 crystal (redrawn from ref. [2]).

between such layers substitution between any two layers is possible. It is postulated that Co or Ni is held at edge sites or intercalated between planes (fig. 1, ref. [2]).

(3) A mixed sulfide model [10] which has a formula corresponding to $(Co_xMo_{1-x})S_{2\pm y}$. For one region of the Co–S–Mo phase diagram only one phase exists, and the boundary of this region, with the highest possible Co content, has the highest catalytic activity. Catalysts with compositions that are outside this region are a mixture of at least two phases.

(4) A contact synergism model [11] where the two active components are present in separate phases. In this model the MoS_2 forms three-dimensional particles but rather than having the second component, Ni or Co, combined with the MoS_2, the second component, Ni or Co, is present as small particles of Co_9S_8 or NiS (fig. 2). To account for the promoting effort, it is postulated that these two particles make physical contact to effect the promotion.

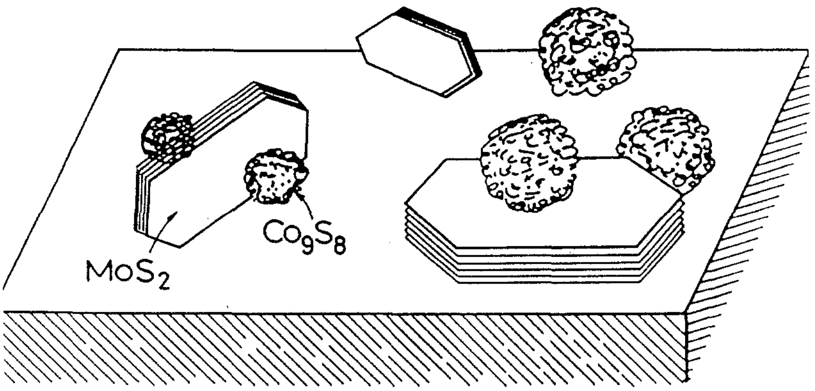

Fig. 2. Schematic representation of a biphasic MoS_2–Co_9S_8 system, and of the possible contacts between phases (redrawn from ref. [2]).

(5) A defect structure [12,13] was used to explain the synergism where promotion results from a change of the defect structure of MoS_2 that results from doping with Co^{2+} ions.

Topsøe et al. [14–16] have recently suggested that cobalt is located at the edge of a molybdenum disulfide crystallite; however, in contrast to the pseudointercalation model, there is no stacking of MoS_2 to form multiple layers. For Co–Mo–alumina catalysts that have been sulfided at a high temperature, there appear to be two types of Co–Mo–S structures, one a low temperature (type I) and a high temperature (type II) form [16].

Ryan et al. [17] proposed a structure for a catalyst that contains phosphorous at the 2–3% level that differs from a phosphorous-free catalyst. The Co–Mo–P–alumina catalyst appears to contain molybdenum disulfide primarily as monolayers (fig. 3A). For the Ni–Mo–P–alumina catalyst, the molybdenum disulfide consists of stacks of 5–6 layers (fig. 3B).

Crajé et al. [18] made Mössbauer emission spectroscopic studies of sulfided Co or Co–Mo supported on carbon or alumina. They found that the spectra of all of the materials were similar and the fitting parameters for a material containing only highly dispersed cobalt sulfide and for a material containing Co–Mo sulfide were essentially the same. Thus, the authors imply that

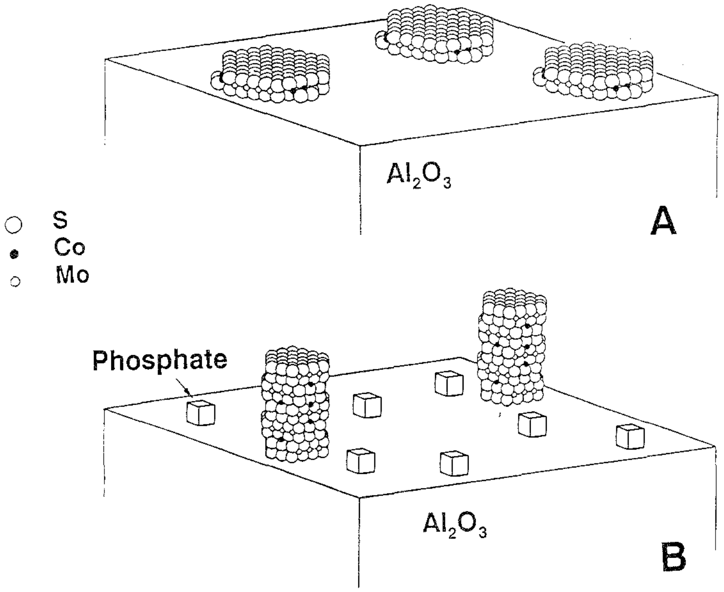

Fig. 3. (A) Illustration of sulfided Co/Mo catalyst supported on alumina showing the cobalt tetrahedrally coordinated at the edge of a single crystal of MoS_2 (redrawn from ref. [17]). (B) Illustration of sulfided Ni/Mo catalyst supported on alumina and promoted with phosphorous. The Ni is shown as octahedrally coordinated between MoS_2 layers and the phosphate occupies a portion of the alumina surface. All sulfurs are not shown on the nickel ion (redrawn from ref. [17]).

Mössbauer measurements may not be appropriate for defining the state of Co in a Co–Mo–alumina catalyst, and therefore do not provide data adequate to define the structure of the active components of the catalyst. These authors also examined the influence of phosphorous on the structure of carbon-supported Ni and Ni–Mo sulfide hydrotreating catalysts [19]. They reported that the introduction of phosphorous changed the type of Ni-compound present following sulfidation. Instead of a bulk Ni-sulfide or "Ni–Mo–S", both catalysts contained a "Ni(thio)phosphate"-like phase (they could not distinguish between the phosphate or thiophosphate anion). The authors also reported that the "Ni-(thio)phosphate" structure appeared to have a low activity for hydrodesulfurization but a high activity for hydrodenitrogenation.

Coal liquefaction provides severe conditions for hydrotreating catalysts. For a Co–Mo–alumina catalyst, it was definitely shown that Co_9S_8 was formed during operation for 15 days in an ebullated bed H-Coal reactor maintained at 450–455°C [20]. The hydrotreating catalyst experiences less severe conditions in the two-stage liquefaction process but even in this case the temperature of the catalytic ebullated reactor may be as high as 430°C. Samples of a Shell 317 Ni–Mo–alumina and a special preparation of a Ni–Mo–alumina Amocat catalyst that had been exposed to coal liquefaction conditions during 32 days of operation were shown to retain about 60–70% of the sulfur added during pretreatment after the initial contact with coal; furthermore, extrapolation of the sulfur isotope data for the latter catalyst indicated that it would take 90 days of continuous operation before the sulfur isotopes on the catalyst would be in equilibrium with those of the coal liquids [21]. Therefore, it appears that the sulfur combined with the Ni–Mo portion of the catalyst exchanges very slowly, and that the "metal sulfide cluster" formed during the pretreatment survives for a period of up to several weeks. Thus, it was of interest to use high resolution transmission electron microscopy (TEM) to identify the structure of these "metal sulfide clusters" and to determine the extent of change that they undergo during exposure to these severe operating conditions.

2. Experimental

Catalyst samples used in this study were for run 257 at the Wilsonville, Al six ton/day coal liquefaction pilot plant. The samples for day 2 and 24 were withdrawn from the second reactor which was operated so that the catalyst was exposed to ash-containing coal liquids generated in the first stage reactor. The reactor was operated for 31 days before catalyst addition and withdrawal was initiated; only small amounts of the total sample were withdrawn daily for characterization. The catalyst was a special bi-nodal preparation of a Ni–Mo–alumina formulation of the Amocat series. The average catalyst composition was: S, 6.57%; Mo, 7.10% and Ni, 1.60%. The catalysts contained approximately

13% carbon which, for these coal liquefaction catalysts, has been shown to be present predominantly as strongly adsorbed nitrogen heterocycles [22]. The catalyst samples were shipped to the CAER covered with a viscous coal liquid that was withdrawn with the sample. Catalyst samples were extracted with tetrahydrofuran in a soxhlet apparatus for approximately 48 h during which time they were maintained under a nitrogen blanket, then dried overnight in vacuum oven at 80°C, and then ground with a mortar and pestle. The ground sample was prepared for transmission electron microscopic (TEM) examination.

A suspension of finely ground sample in ethanol was placed on a carbon film supported on a Cu-grid. Thin areas were examined using a Jeol 4000 EX electron microscope operated at 400 kV with a point resolution of 0.17 nm.

3. Results and discussion

Pictures of the catalyst samples withdrawn on day 2 and day 26 of operation are shown in figs. 4 and 5, respectively. Consider first the sample withdrawn

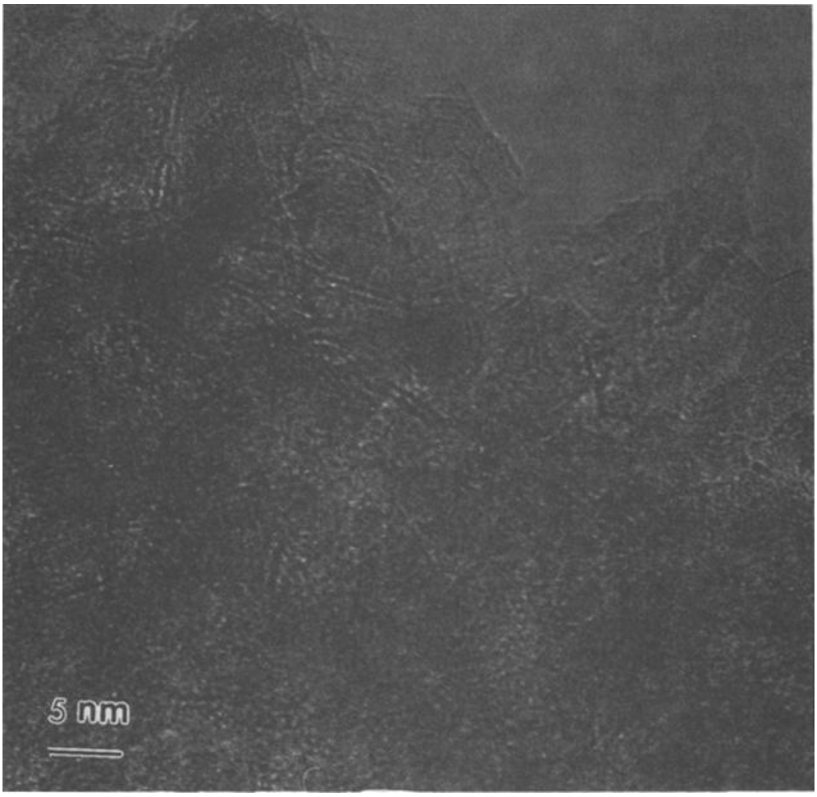

Fig. 4. TEM sample (48597) of Ni-Mo alumina catalyst withdrawn from the second stage hydrotreater after day 2.

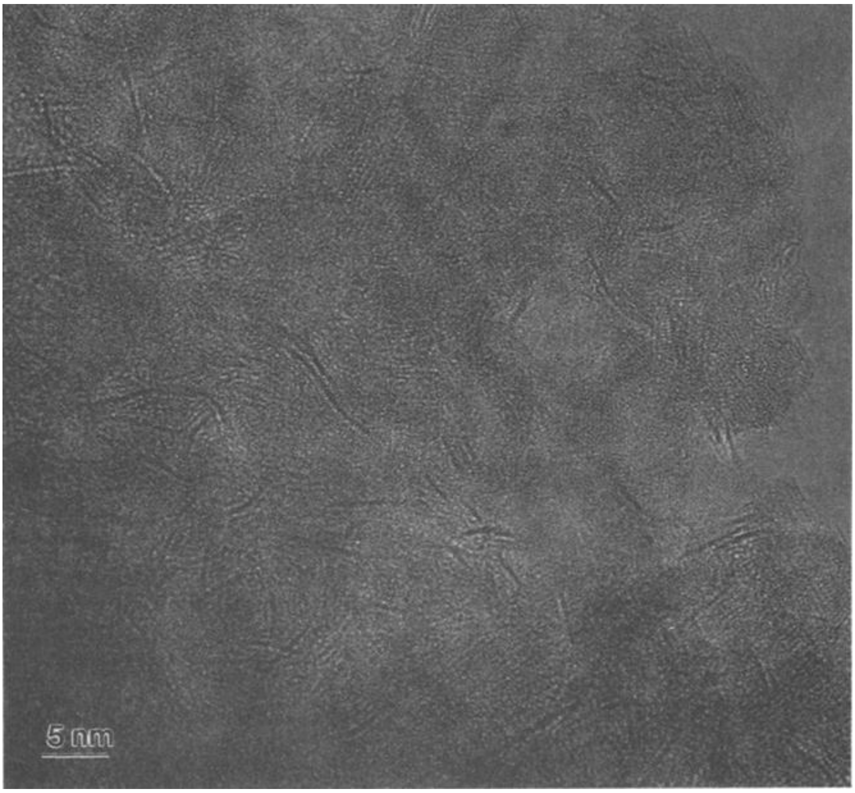

Fig. 5. TEM sample (48604) of Ni–Mo alumina catalyst withdrawn from the second stage hydrotreater after day 2.

during day 2 (fig. 4). Careful examination of the picture reveals contrasts indicating facets in the alumina, and these are obtained when steps are present in the sample. It is inferred from the picture that the MoS_2 filaments that are visible are located at these steps of the support. Two observations support this view: (1) the distance between pairs of filaments is variable and does not match that of MoS_2, and (2) many pairs of filament are not aligned parallel along the length as would be expected for crystalline MoS_2. The clusters appear to be in the form of long filaments that are on the order of one MoS_2 in width and on the order of 3–10 nm in length. MoS_2 is used in discussing these filaments; however, the chemical composition of the filaments could not be determined. Some of these filaments may have a uniform structure along the length; however, most of the filaments appear to be made up of clusters of "metal sulfide" of a much shorter length. It therefore appears that the steps trap small clusters of "metal sulfide" and, once a cluster is trapped, it provides a mechanism for causing additional clusters to be trapped along the length of the step. It further appears that there are certain regions of the alumina surface that cause a concentration of these "metal sulfide" clusters.

Numerous efforts were made to focus on a region of the catalyst sample that contained a filament and to use EDX to learn whether Ni was present with the Mo in the filaments. However, the number of atoms in the area of the small focussed electron beam was insufficient to permit a determination of either the S/Mo or the Ni/Mo ratio. Thus, the current data do not provide information about the chemical composition of the material that makes up these filaments.

The sample withdrawn after 26 days of operation yielded the picture shown in fig. 5. The physical features shown in fig. 5 are similar to those shown in fig. 4. The average length of the filaments appear to be about the same in the two pictures. Likewise, essentially all of the filaments are the width of a single MoS_2 unit. It does appear that there are regions of the picture for the 26 day sample that has a higher density of the filaments than was the case with the 2 day sample. To the extent that this is the case, it would indicate that a fraction of the molybdenum sulfide was present in isolated, essentially molecular MoS_2 units, and that these units had undergone agglomeration during the period between day 2 and day 26. However, it does not appear that the filaments present in the 26 day sample have larger dimensions than those in the 2 day sample, either in width or length. Thus, if agglomeration occurs during the 24 day interval between collection of the two samples used in this study, the agglomeration is predominantly to form new filaments rather than to cause growth of the filaments already present in the 2 day sample.

A mechanism of nucleation and growth of MoS_2 can be inferred from these observations. The MoS_2 molecules nucleate at the steps of the support and grows until the step is covered by a monolayer of MoS_2. But the next layer does not grow on top of the first layer; instead growth begins on another step and covers it. The growth of the monolayer appears to be limited by the length of the steps.

It was noted in ref. [20] that if the sulfur is combined only with Mo the stoichiometry of the second-stage catalyst is $MoS_{2.78}$; assuming that all Ni is sulfided to the stoichiometry of NiS reduces the stoichiometry to only $MoS_{2.41}$. Even if we assume that all of the Ca, Fe and Ni are present as $M^{II}S$ in the sample withdrawn during day 26, the stoichiometry is still greater than that corresponding to MoS_2. Massoth [4] concluded that the sulfided catalyst is deficient in sulfur with respect to the compounds MoS_2 and Co_9S_8, and that the sulfided catalyst consists of a mixed surface oxysulfide species or some bulk MoS_2 and another oxysulfide species. Combining the elemental analyses from ref. [20] and the TEM pictures shown in figs. 4 and 5, we conclude that it is likely that the “molybdenum sulfide clusters”, even if they contain Ni and NiS, are sulfur-rich compared to MoS_2.

The present data with only one catalyst formulation are inadequate to define a complete model for the complex Ni–Mo– or the Co–Mo–alumina catalyst system. However, they appear to severely limit any of the models in which the molybdenum sulfide forms three-dimensional materials in which two-dimensional rafts that are several MoS_2 units in width or three-dimensionsal crystals of MoS_2 are utilized. Thus, the current data are not consistent with the models that consist of a large monolayer (raft), a multi-layer of MoS_2 with intercalated Ni or Co, or with separate bulk metal sulfide crystals which acquire their synergistic properties by intimate contact unless they are both present along a step of the support. In the case of the Ni–Mo–alumina catalyst examined in this study, most of the earlier models have been based upon two- and/or three-dimensional sizes that are much larger than are present in a real catalyst that has been exposed for up to 26 days to the extremely severe reaction conditions encountered in coal liquefaction.

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