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HREM studies of layered transition metal sulfide catalytic materials

Russell R. Chianelli [a,*], Albert F. Ruppert [a], Miguel José-Yacamán [b], Armando Vázquez-Zavala [b]

[a] *Corporate Research Laboratories, Exxon Research and Engineering Co., Annandale, NJ 08876, USA*

[b] *Instituto de Física, Universidad Nacional Autónoma de México, Apartado Postal 20-364, Delegación Alvaro Obregón 01000, México DF, Mexico*

Abstract

Recent studies using HREM techniques are yielding new insight into the nature of the layered transition metal sulfide (LTMS) catalytic materials. While the insight being generated is still at an early stage, HREM techniques are showing promise in solving complex problems in this field which have been studied for many years. HREM techniques are beginning to elucidate the structure of the catalytically active 'edge' sites and to reveal the atomic structure of these edge terminations. HREM is also generating new insight into the problem of disorder in the layered TMS which has hindered understanding of these systems. Finally, HREM is yielding an insight into the very complex 'promotion' problem. Evidence is presented that the older idea of pseudo-intercalation resulting in charge transfer and thus promotion may be correct.

1. Introduction

LTMS (Layered Transition Metal Sulfide) catalysts have played a crucial role for many years in the petroleum and chemical industry. Early in this century, it was discovered that sulfur containing compounds poisoned many metallic catalysts but that transition metals such as Mo and W while converting to sulfides during use, retained their ability to hydrogenate aromatic compounds. Thus, one of the first uses of LTMS catalysts was for the hydrogenation of coal liquids. Developed in Germany in the early 1920's for this purpose the LTMS were later applied to petroleum and tar upgrading as well. The LTMS were originally used in an unsupported form. The alumina supported catalysts first appeared just before War II and emerged shortly after as the modern petroleum processing catalyst and are used today in virtually every refinery in the world [1].

TMS catalysts fall into a special category due to their exceptional resistance to poisons. In fact, the presence of sulfur compounds, the most common poison of metallic and oxide catalysts, does not decrease their catalytic activity, but is needed to maintain high activity. Sulfide catalysts are also very resistant to carbon deposition, which is illustrated by their use for converting resids. Arsenic, as well as nickel and vanadium contained in heavy petroleum fractions, are some of the few substances which cause significant deactivation, and this only occurs by physical blockage of pore structure in supported catalysts.

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* Corresponding author.

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The major reactions catalyzed by LTMS are: hydrogenation of olefins, ketones and aromatics, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodemetallization (HDM), dealkylation and ring opening of aromatics. But the LTMS catalysts have many other uses as well, including: reforming, isomerization of paraffins, dehydrogenation of alcohols, Fisher–Tropsch and alcohol synthesis, hydration of olefins, amination, mercaptan and thiophene synthesis, and direct coal liquefaction. More esoteric applications can also be found in polymer synthesis and in inorganic synthesis (synthesis of silanes and metal hydrides). A more comprehensive list of the LTMS catalyzed reactions is found in Weisser and Landa [1].

In commercial applications of the LTMS, they almost always occur as Al_2O_3 supported, extruded pellets with the Mo or W present in the range of 10 to 20% by weight of the metal. They are usually 'promoted' by Co or Ni which is present in the range of 20 to 30 atomic per cent with respect to the Mo or W. The metals are sulfided and activated prior to use by in-situ sulfiding techniques at temperatures in the range of 300 to 400°C. H_2S is the commonly used sulfiding agent but other agents are also used. Catalyst prepared in this manner are commercially prepared in large quantities every year. The $Co/Mo/Al_2O_3$, $Ni/Mo/Al_2O_3$ and $Ni/W/Al_2O_3$ catalysts of this type have become refinery 'work-horses' and because of this have been the subject of intense research in the past. Research interest in these catalysts promises to remain important due to increasing environmental pressures which will require improved LTMS catalysts.

Fifteen years ago Massoth reviewed the field of Mo and W based hydrotreating catalysts [2]. At the time of the Massoth article, it was not clear what role the alumina support played in the activity of these catalysts. We now know that the activity and selectivity of these catalysts originates in the sulfide phase. Since the availability of probes such as EXAFS (Extended X-Ray Fine Structure), it has become clear that the alumina's primary function is to disperse and stabilize the MoS_2 and WS_2 based hydrotreating catalyst [3]. The role of the Co and Ni promoter phase has been extensively studied with much progress being made in elucidating its role. However, a clear picture of this role awaits further study. A more recent review of the state of understanding of the fundamental origins of the catalytic activity and selectivity of the LTMS can be found in ref. [3].

CTEM (Conventional Transmission Electron Microscopy) and more recently HREM (High-Resolution Electron Microscopy) has played and will continue to play a key role in developing an understanding of the relation between the catalytic activity and selectivity of the LTMS and their structures. In fact, it is precisely the atomic level structural information which is provided by HREM, that is needed for developing further insight into the origin of the catalytic activity and selectivity of these catalytic materials.

The LTMS discussed in this report are MoS_2, WS_2 and ReS_2 with the first two being the most important sulfide commercial sulfide catalysts. These three catalytic materials all have layered structures with layers of the metal sandwiched between close-packed layers of sulfur as described in detail below. In this report, we review the role played by CTEM in understanding the relation between structure and catalytic activity and review recent results from HREM studies. In order to understand the impact of CTEM and HREM studies of LTMS catalytic materials, we have divided this report into four sections, which address fundamental structural problems and the relation of these problems to catalytic activity and selectivity:

(1) The atomic structure of crystalline LTMS and their active catalytic planes which terminate the crystallites and stabilize the catalytic sites.

(2) The supported LTMS catalytic materials and the role of the Al_2O_3 support.

(3) The role of structural disorder in LTMS catalytic materials.

(4) Biphasic LTMS systems including the promoted LTMS.

By dividing a study of the LTMS into these sections we are able to simplify considerably the study of these very complex commercial catalyst systems.

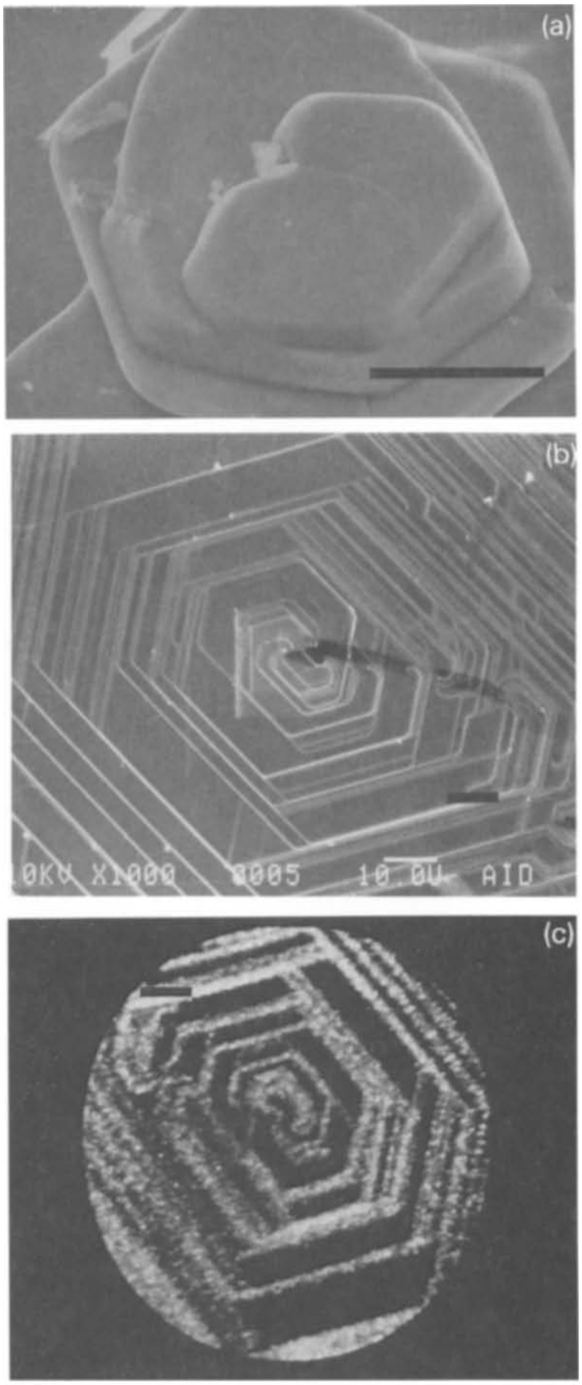

Fig. 1. (a) SEM of MoS_2 crystallite showing smooth basal planes terminated by edge planes. (b) SEM of MoS_2 crystallite showing edge planes and screw dislocation. (c) SIM of MoS_2 crystallite showing chromium impurity at edge plane.

2. Experimental

CTEM was performed using a Philips EM400 electron microscope and HREM was performed on a JEOL 4000 EX electron microscope with a 0.17 nm point-to-point resolution. The samples were prepared by depositing a drop of sulfide suspended in hexane on a carbon covered copper grid and drying it at room temperature (296 K) in air. The sample was then transported to the microscope stage and the microscope was pumped down for several hours before observation. SEM micrographs were taken with an ISI-40 (International Scientific Instruments) scanning electron microscope. Secondary ion mass spectrographic images (SIMS) were taken using a Cameca 3F instrument.

3. Atomic structure of crystalline LTMS and active catalytic planes which terminate the crystallites

The layered structure of MoS_2, WS_2, and ReS_2 is highly anisotropic. It is this anisotropy which gives rise to many of the important catalytic properties of the LTMS and also to substantial difficulties in characterizing them and relating their structure to activity and selectivity [4]. Each metal atom in the bulk structure is strongly bound to three sulfur atoms. The sulfur atoms form two close-packed two-dimensional arrays which sandwich the metal atoms between them. This particularly stable environment for the sulfur atoms results in weak Van der Waals interaction between adjacent layers. The close-packed layers, which terminate a crystallite perpendicular to the c-axis, are the basal planes and can be seen in Fig. 1a. The basal plane exhibits a low reactivity for adsorption and catalytic activity and leads to the ability of MoS_2 to act as a very effective lubricant [5]. ReS_2 has a similar layered structure but is highly distorted due to the fact that Re has one more electron than Mo or W. It crystallizes in a single layer stacking configuration (1T) rather than a two layer polytype (2H) as in MoS_2 and WS_2. ReS_2 consists of ReS_2 layers made up of ReS_6 octahedra sharing their edges. In each ReS_2 layer, the metal-atom sheet is sandwiched by chalcogen-atom sheets, and the metal atoms of an undistorted ReS_2 layer form a hexagonal lattice. ReS_2 has a d^3 electron count, and their metal-atom sheets exhibit a clustering pattern of 'diamond-chains'. Because of this distortion, the chalcogen-atom sheets deviate from the perfect planarity. The structure of ReS_2 has [6] recently been refined and the compound has been studied by AFM and STM techniques [7]. Though not used commercially, ReS_2 is important as a model catalyst because of its potential relation to the promoted systems as discussed below.

In contrast, the 'edge planes' which terminate the close-packed sulfur planes in their growth direction, are highly reactive. Much evidence now exists to indicate that the catalytically active sites are located on these edge planes. Therefore, accurate determination of the amount of edge plane area present relative to the basal plane area is of primary importance for developing catalytic structure/function relationships in anisotropic systems [3]. Until recently, it has been very difficult to do this.

Currently the atomic structure of the edge planes which terminate the two dimensional layers is unknown and forms part of the investigation presented in this paper. Edge planes are seen at low resolution in Fig. 1b and often are the results of screw dislocations which are thought to cause crystals of layered sulfides to grow in the third dimension parallel to the c-axis. These planes (because of their activity) tend to react with second metals during preparation. The metal impurities tend to accumulate at the edges often at very low concentrations. These metal impurities terminate and stabilize the edges. A SIMS map of a chromium impurity at the edge of an MoS_2 crystal is seen in Fig. 1c. The effect of these metal impurities on the catalytic activity of supposedly 'pure' has generally not been addressed in the literature and may be one factor in the large variability in activity seen in a survey of the literature.

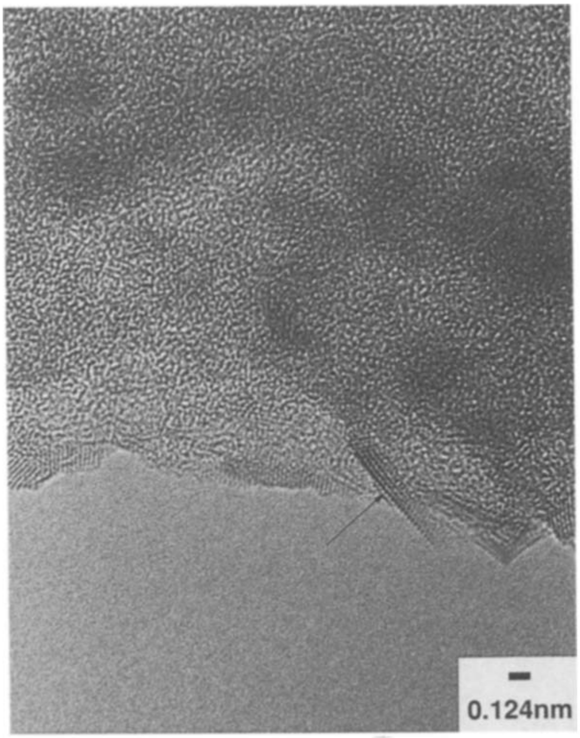

Fig. 2. HREM of ultrasonically produced MoS_2 crystallite. Note atomic resolution near edge showing edge structure.

Metals at the edge of MoS_2 are also thought to be at the origin of the promotion effect which is central to the catalytic importance of layered transition metal sulfides. Cobalt and nickel 'promote' molybdenum and tungsten sulfide catalyst and are of great commercial importance [2]. The interaction of Co and Ni at the edges of the LTMS appears to be quite strong resulting in charge transfer from the Co or Ni to the Mo and W. One theory of promotion attributes the increase in the activity to this charge transfer causing a reduction in the Mo or W which causes these metals to behave like the more active metal to their right in the Periodic Table [3].

Direct images of the important edge planes are now being obtained. In Fig. 2 for example we are able to observe the atomic structure of freshly prepared MoS_2 edges. In this case large crystals were reduced to flakes by ultrasound techniques [8]. Though not yet completely analyzed, the termination of the edge in this case seem to be similar

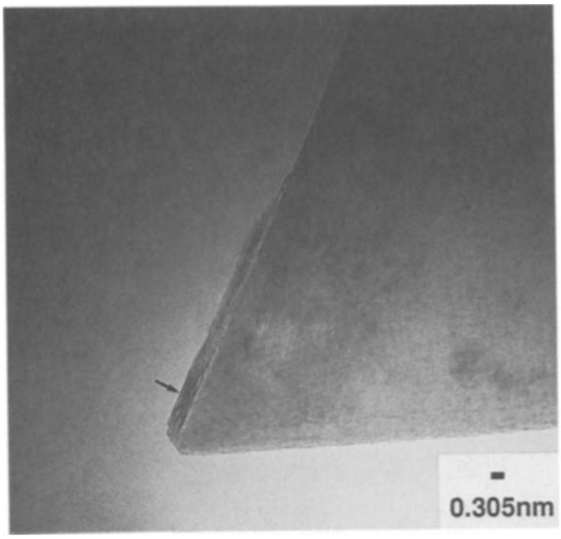

Fig. 3. HREM of MoS_2 crystallite near the edge. In this case the crystallite has been treated with H_2/H_2S at 400°C prior to use as a catalyst. Note the 'booklike' structure near the edge typical of layered sulfide catalytic materials.

to that expected based on knowledge of the crystal structure. The MoS_2 prepared in this manner has not been catalytically activated in H_2/H_2S and therefore the edges are 'pristine'. As discussed below catalytic activation with H_2/H_2S has a pronounced effect on the structure. In Fig. 3 we can see an edge which has been activated in H_2/H_2S. The 'booklike' structure can clearly be seen and the atomic arrangements of the edge atoms are quite clear. The structure of these edges is now being modeled.

4. Supported LTMS catalytic materials

Commercial catalysts based on the LTMS are almost always found today supported on Al_2O_3. The Al_2O_3 serves to spread out the active phase and lessen the amount of metal required to obtain a given activity. Thus, its role is primarily to reduce the cost of the catalyst and to ease the handling and loading of refinery reactors [3]. Many studies have attempted to apply CTEM techniques to the supported materials but with generally ambiguous results [9–12]. The ambiguities arise because of the anisotropy of the MoS_2. The layer stacking spacing of 0.613 nm (002) are large enough for easy resolution with many microscopes available over the past 20 years and have been observed many times on supported materials. However, as described below the observation of these planes alone can lead to misinterpretation of crystallite size and orientation.

HREM considerably improves the situation and Cruz-Reyes et al. [13], performed such a study on a series of Al_2O_3 supported promoted and unpromoted MoS_2 catalysts. They also compared preparation methods which are commonly found in the literature. The MoS_2 'rag' structure appeared in all cases with only slight differences appearing between methods of preparation and with the addition of a promoter phase. The authors were also able to determine an average particle size and stack height. The catalyst had a typical stack height of between 4–6 layers and a typical particle length of 10 to 25 nm. This later number is quite high showing that the catalysts are not well dispersed and calls into question the existence of small (0.1 nm) cluster which have been reported to exist on these catalysts. The effect of varying the support has also been studied [14,15].

A typical HREM micrograph of Al_2O_3 supported WS_2 is shown in Fig. 4. Large particles of

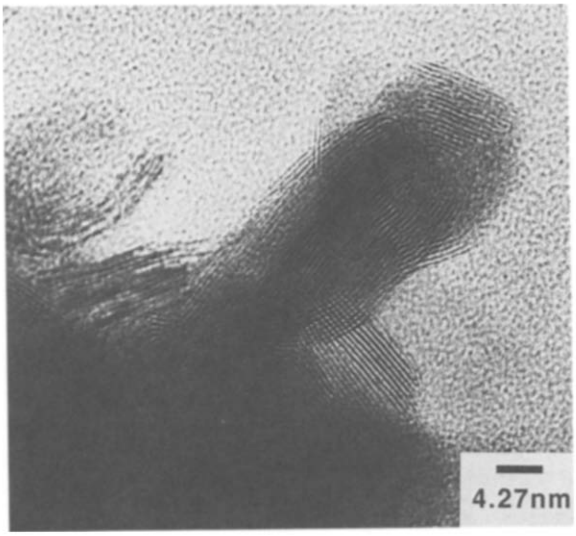

Fig. 4. HREM of Al_2O_3 supported WS_2 showing highly folded and disordered layers.

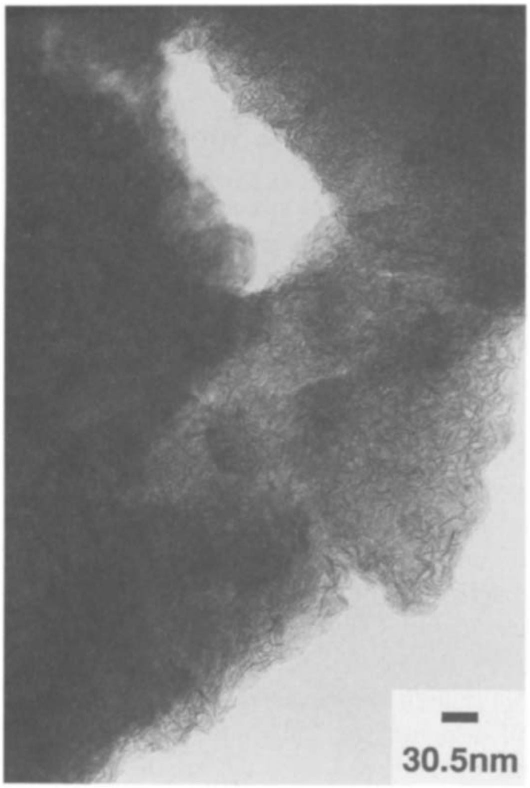

Fig. 5. TEM of MoS_2 catalyst showing the rag structure. Each folded line represents a single layer of MoS_2 which is 0.62 nm thick.

WS_2 can easily be seen in the micrograph with many layers of WS_2 stacked and curved. Stacks of WS_2 are seen which exceed 15 layers. While this catalyst is not particularly well dispersed, particles such as this are typical in micrographs of supported WS_2 and MoS_2. However, extensive literature evidence as described above suggests that only part of the MoS_2 is contained in these particles. This occurs in part because the presence of the Al_2O_3 masks highly disordered MoS_2 and in part because the anisotropic structure of the MoS_2 causes difficulties in the interpretation of TEM images as described by Srinivasan et al. who concluded that the crystallites always occurred with their basal planes parallel to the support surface [16]. Therefore most of the Mo or W occurs in these catalysts as large folded rags of MoS_2 or WS_2.

In a recent article Pollack et al. describe a method for dissolving the Al_2O_3 with HF, leaving just the active metal sulfide for examination [17]. Two important results were obtained. Firstly, the freshly sulfided catalyst contained MoS_2 very similar to that described above: 'books' of MoS_2 with stacking height of 5–10 layers which the authors refer to 'high reflectance' MoS_2. Secondly, and most importantly the catalyst is quite different after exposure to the catalytic conditions: the catalyst now contains large amounts of carbon and the stacking height has been reduced to mostly single layers. Though this method is fairly new and many more experiments are needed, fundamental new insight has been generated. Leading two important conclusions:

(1) Carbon plays a crucial role in stabilizing and creating an active catalyst. Future studies dealing with the basis for activity and selectivity in these systems should be performed on catalysts stabilized in catalytic environments.

(2) The crystallite sizes of 'real' stabilized catalysts are much greater than much of the literature suggests and models based on small clusters of the order of 1 nm are clearly incorrect.

5. Role of structural disorder in LTMS catalytic materials

To further complicate the situation, MoS_2 produced under conditions leading to good catalytic properties is in a poorly crystalline and highly disordered state best described below as the 'rag structure.' A quick look at an electron micrograph rapidly convinces the researcher of the difficulty in estimating the particle size of such a material [18]. In Fig. 5 we can see many folded single layers of MoS_2. Fig. 6 shows a closer view of the polymeric and highly folded nature of MoS_2 catalytic materials. In extreme cases 'rolls' and possibly tubes are formed as seen in Fig. 7. Also seen in this figure is a single sheet folded over on itself. This disordered nature of MoS_2 and WS_2 has recently been 'rediscovered' and an attempt has been made to connect it to disordered fullerene structures [19].

Because of this disorder it is a very difficult problem to measure the dispersion of these materials, therefore, many catalytic correlations which appear in the literature do not yield reliable information regarding these systems. X-ray diffraction may be used but the line broadening will depend upon the bending/folding of the layer and not be representative of the particle size as it is in the isotropic materials. When applying the Debye–Scherrer line broadening equation to the 002 diffraction peak, a reasonable value of the coherence length of the crystallites is obtained for the stacking of the layers along the c-axis agreeing within a factor of 2 with that estimated from TEM. However, the same analysis applied to the 100 or 110 peaks results in values of the coherence length along the a axis of between 70 and 100 Å, whereas the real dimension can be as large as several microns.

Stacking faults in MoS_2 and WS_2 have been extensively studied in a recent series of articles using HREM techniques [20–22]. These papers contain many atomic resolution micrographs of stacking faults within these materials which are models using calculations. Limitations in determining the exact nature of the stacking faults using HREM are also described. The papers are also restricted to modeling stacking faults which can be described as defects in normal infinite arrays of atoms of highly ordered crystallites. Ignored in these papers and most others is the disorder described above which results in highly folded and curved structures. There remains the fundamental question of how layers with such a degree of folding are formed and what is their structure? This question is being addressed by HREM studies and micrographs of the atomic structure occurring in these highly folded layers can be seen in the lead article of this issue [23]. However, further elucidation of these types of structures will require new modes of calculation and modeling

While this is still an open question, one further disorder problem arises in the formation of the active catalyst. As mentioned above, Pollack et al. reported that the structure of the catalyst changed on exposure to the catalytic environment [17]. It has also been observed that an H_2/H_2S activated MoS_2 will exfoliate in high vacuum presumably because residual carbon in the vacuum reacts with the activated catalyst [24]. This effect may be seen in Fig. 8 and remains a basic unanswered question in this field. It is expected that HREM studies now in progress will shed new light on the role of carbon in stabilizing and activating layered transition metal sulfide catalysts.

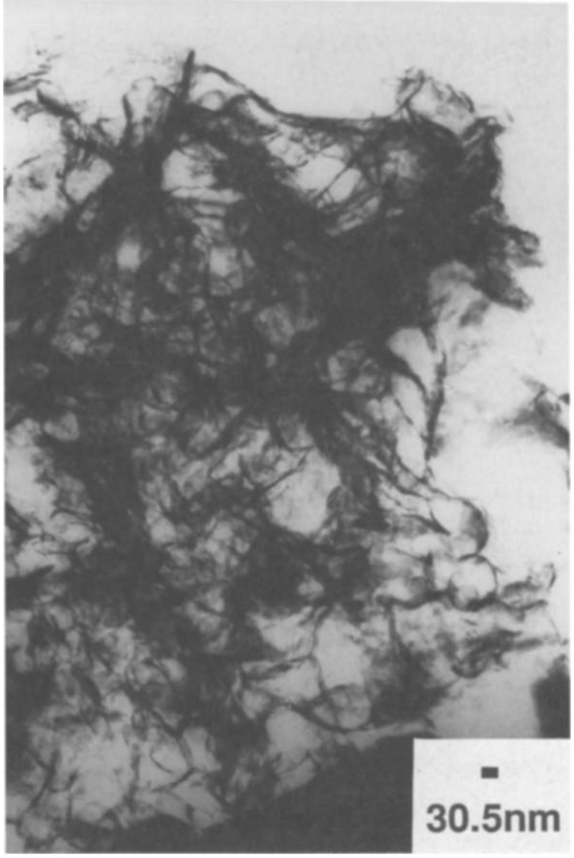

Fig. 6. TEM of MoS_2 showing the highly disordered and folded nature of the layers (from ref. [18]).

6. Biphasic systems including the promoted LTMS

In 1959, Beuther et al. of Gulf published the first systematic study of the HDS activity of CoMo and NiMo supported on alumina as a function of the atomic ratio Co(Ni)/Mo [25]. As a result,

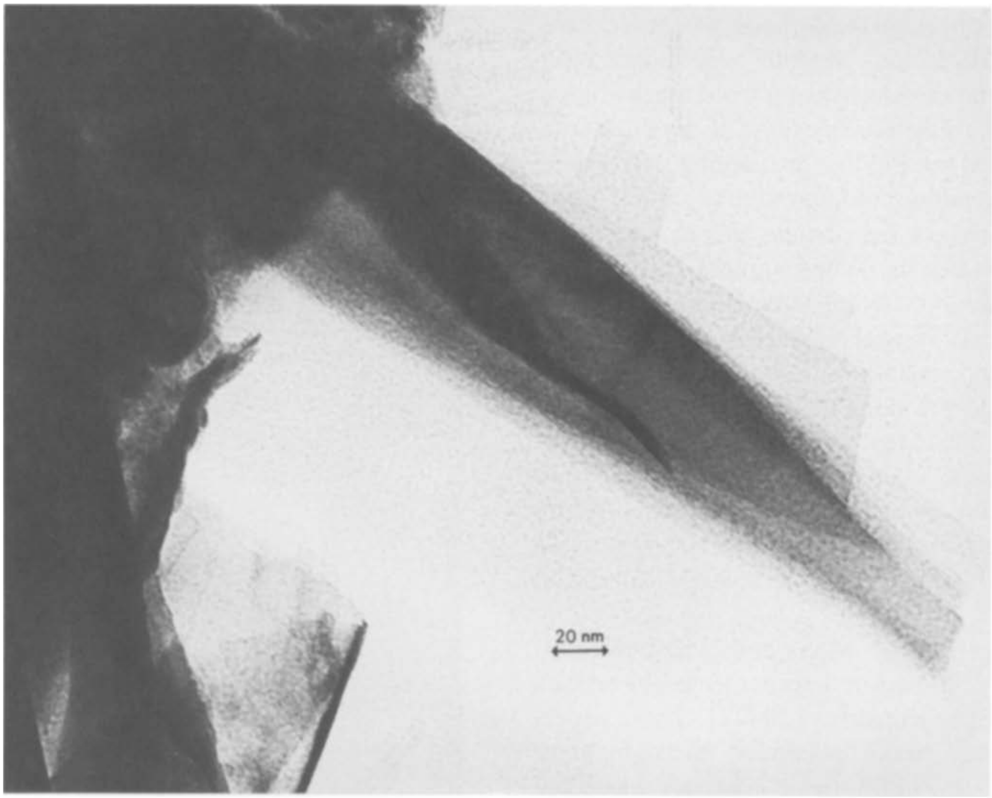

Fig. 7. TEM of MoS_2 showing 'roll' structure of layers. Note single layer of MoS_2 folded over on itself (from ref. [18]).

they showed what they called a 'promoter effect' of the cobalt (or nickel) on the molybdenum for atomic ratios Co/Mo = 0.3 and Ni/Mo = 0.6. At these ratios a maximum was observed in the catalytic activity curves which was significantly greater than the activity of a simple mixture of the two components leading to the equivalent term of 'synergistic effect', indicating that the two phases are working together. The promotion effect has tremendous industrial significance and has been the subject of intense scientific scrutiny.

Voorhoeve and Stuiver [26], and Farragher and Cossee [27] from Shell proposed a model derived from the structure of sulfides called intercalated solids. In these type of compounds, the group VIII transition metals of the first row of the Periodic Table (Fe, Co, Ni) can penetrate the Van der Waals layers of the lamellar tungsten sulfide to occupy the octahedral symmetrical voids. However, for MoS_2 in the presence of Co or Ni, these intercalated compounds could only be prepared at temperatures greater than 800°C resulting in surface areas too low for catalytic measurements. Furthermore, it was difficult to prove that intercalates existed under catalytic conditions, and the authors of the model had to make the assumption that only the sites located on the edges of the MoS_2 crystallites were occupied by the Co^{2+} and Ni^{2+} ions under catalytic conditions. They called this model the 'pseudo-intercalation' model to incorporate this idea.

At about the same time Delmon and co-workers at Louvain-la-Neuve University proposed a simple model which explained their experimental observations [28]. Since they often found that the unsupported catalysts they prepared had the phases MoS_2 and Co_9S_8 present, the model was based on the interaction of these phases. They proposed that the MoS_2 and Co_9S_8 acted together by being in close contact, from which came the

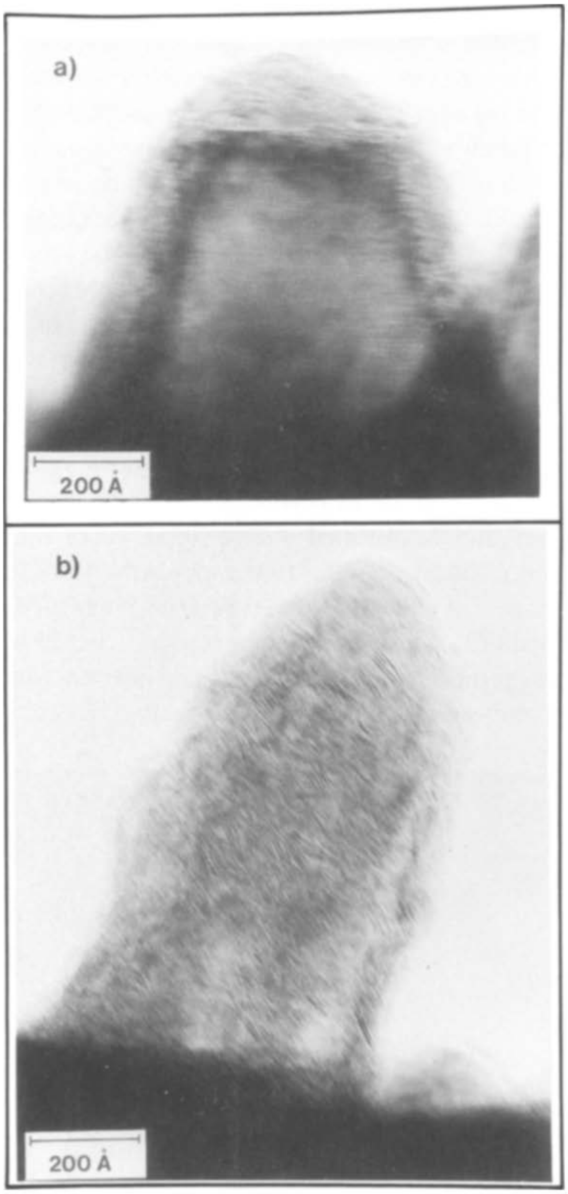

Fig. 8. TEM of MoS_2 'posts' after activation with H_2/H_2S: (a) during exfoliation and (b) after exfoliation (from ref. [20]).

term 'contact synergy'. The HDS reaction took place at the interface between the two sulfides with each phase 'helping.'

The concept of a mixed phase containing both cobalt and molybdenum which was responsible for the synergy was considered seriously, but the first physical proof of a specific Co environment was present by Topsøe et al. The introduction of very small amounts of Co into bulk MoS_2 allowed the observation of a specific EMS (Emission Mössbauer Spectroscopy) signal from a new Co site different from the usual signal characteristic of Co_9S_8 [29]. Topsøe et al. located the cobalt inside or on the edges of MoS_2 crystallites and called this Co the 'CoMoS phase'. Only microanalysis on MoS_2 crystallites, containing small amount of Co, showed convincingly that the Co atoms were located on the edges of the MoS_2 platelets [30], leading to a model very close to the pseudo-intercalation model with similar limitations. One very interesting but relatively unknown paper is a paper by Phillips and Fote [31]. The authors take the view that the promoted systems may be viewed as mixtures of two immiscible phases (Co_9S_8 and MoS_2) which interact by forming surface phases or surface complexes. This behavior has been termed 'symmetrical synergy' [3].

Electron microscopy has failed so far to give a clear picture of the CoMoS or NiMoS phase supported on alumina because of interference from the alumina support itself and because of the high dispersion of the sulfide. However, Pratt and Sanders [32] for bulk NiMo sulfide and Vrinat and De Mourgues [33] for bulk CoMo sulfide were able to produce pictures from electronic microscopes, showing a high dispersive effect of cobalt and nickel added to molybdenum sulfide. However, Ledoux et al. [34] were able to measure the activity of catalysts, highly dispersed on carbon support, and at the same time to observe the size and shape of the active particles by high-resolution transmission electron microscopy, since the carbon support is almost transparent to electrons. On the most highly dispersed form of MoS_2, the average size of the particles was 100 Å with 1/8 of the molybdenum atoms located on the edges. By adding to the same catalyst the exact amount of cobalt or nickel to reach maximum activity, they observed two kinds of particles: circular with an average diameter of 36 Å, and chain-like, 150 Å long and 14 Å wide. From these observations two structures were proposed for the promotion site. When HDS activity was measured on these

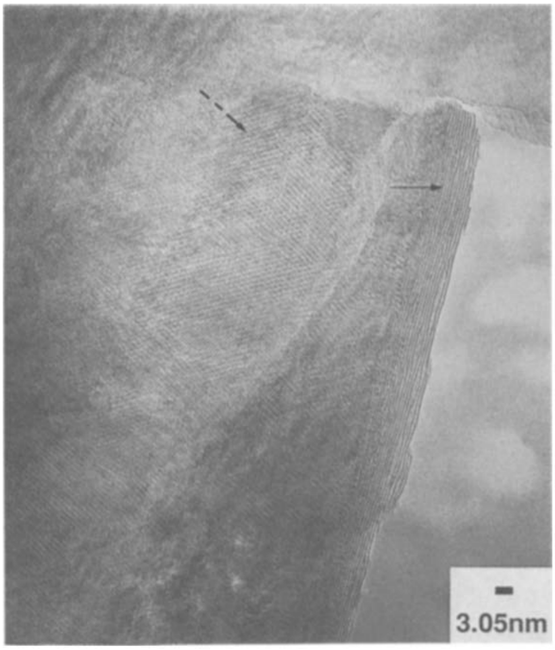

Fig. 9. HREM of Co doped MoS_2 near the edge. Solid arrow indicates area with pseudo-intercalated area and broken arrow indicates hexagonal superlattice area.

catalysts, an activity seven times higher than that of the MoS_2 of 100 Å catalyst was found. However, the chains reported were imaged using CTEM techniques and though complementary techniques indicate that the proposed structures are reasonable, HREM techniques need to be applied to these catalysts for confirmation. Recently Hansen et al. described some of the problems in trying to model HREM in promoted sulfide systems [35].

Model catalyst are beginning to yield valuable insight because they allow simplification of the complex catalyst system. With HREM techniques, Yacamán et al. [36] were able to localize Co at the edge of bulk MoS_2 single crystals which had been doped with 1% Co. In Fig. 9 can be seen a HREM micrograph of a single crystal of MoS_2 of a crystal doped with Co from this study. The edge structure of this crystal is clearly seen in the micrograph with possible areas of Co insertion between the layers of MoS_2. This area might also be defects in the stacking of the MoS_2 layers. Further study and modeling is required to settle this point however, the micrograph illustrates the wealth of information revealed by HREM.

Also seen in the figure is a superstructure away from the edge but still near the edge and not present far away from the edge. The atomic resolution which is obtained in these regions can be seen in Fig. 10. The regions often appear as hexagonal arrays as seen in Fig. 11. In this case the repeat distance between regions is approximately 3 nm. It has been reported that these structures can be obtained as Moiré patterns caused by rotating two close-packed sulfur lattices slightly with respect to each other [23]. However, Fig. 12 which shows an enlargement of one of these hexagonal regions indicates that the array is not a regular hexagonal array and is distorted with a short (0.23 nm) atomic distance. At this time we take short atomic distance as indicative of the presence of a Mo–Mo bond. The pairing of the Mo atoms is caused by the presence of Co as an intercalate near the edge of the crystallite (pseudo-intercalate). Electron

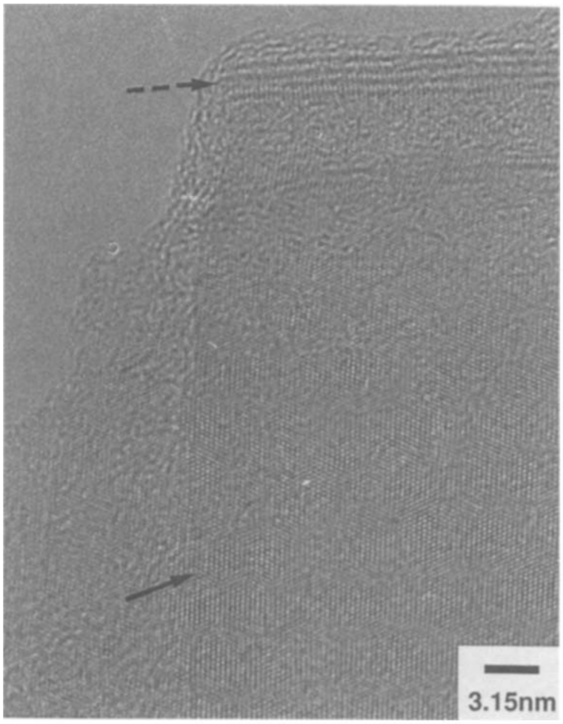

Fig. 10. HREM of Co doped MoS_2 near the edge. Broken arrow indicates edge area and solid arrow indicates hexagonal superlattice area.

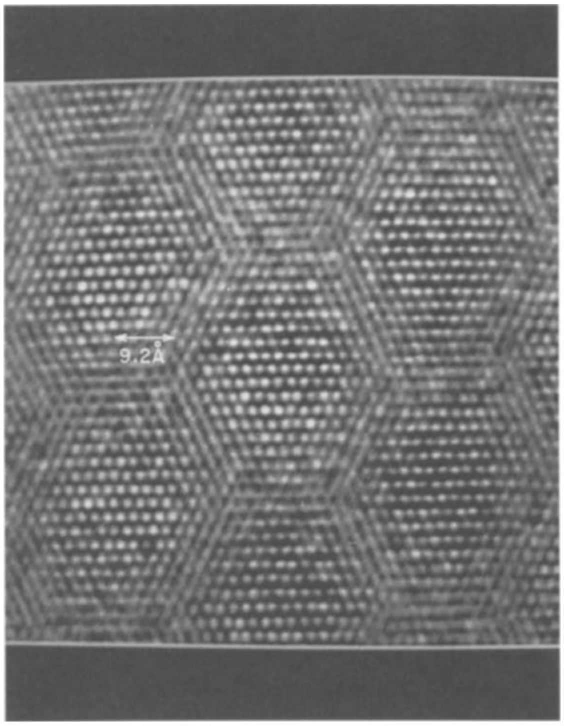

Fig. 11. HREM of superlattice area in Co doped MoS_2.

transfer occurs from the Co to the Mo causing the Mo to be reduced from 4+ to 3+. This reduction causes the Mo pairing resulting in the MoS_2 layer becoming isostructural with ReS_2 which has a highly distorted sulfur close-packed layer. It seems reasonable that the strain introduced by the distortion of the lattice results in a slight rotation of one layer of close-packed sulfur with respect to another and thus the regular Moiré patterns observed. It should also be keep in mind that this strain occurs within a single crystal which is unstrained and regular away from the edge of the crystal. Though more work is needed to confirm this model HREM techniques are beginning to yield information regarding this complex problem. If this interpretation it correct is would be a dramatic physical confirmation of the earlier ideas of pseudo-intercalation and charge transfer promotion reviewed in ref. [3].

Finally, the interaction of layered sulfides with a second phase is a problem of general interest which includes the problem of sulfide support interaction and the promotion problem. In both cases a layered sulfide such as MoS_2 is immiscible with a second phase such as Al_2O_3 or Co_9S_8. Ternary phases are not formed under catalytic conditions. Yet, important interactions exist at the interface between the two phases. In the case of promotion at high concentrations of Co the interaction occurs between MoS_2 and Co_9S_8. At low Co concentrations the Co_9S_8 phase is not present and only the pseudo-intercalation phase described above is present. Thus, when describing these catalytic systems it is important to remember that the specific structural problem being addressed may change according to the portion of the catalytic phase diagram being addressed.

Another manifestation of this phenomenon is indicated in Fig. 13. This CTEM micrograph is of a mixed Fe/Mo sulfide catalyst [3]. The composition of this phase is approximately 50% FeS_{1-x} (phyrrotite) and 50% MoS_2 and it is exceptionally stable and selective as a catalyst. Examination of the micrograph and complementary X-ray diffraction data clearly indicate that the catalyst consists of single layers of MoS_2 bound to the phyrrotite

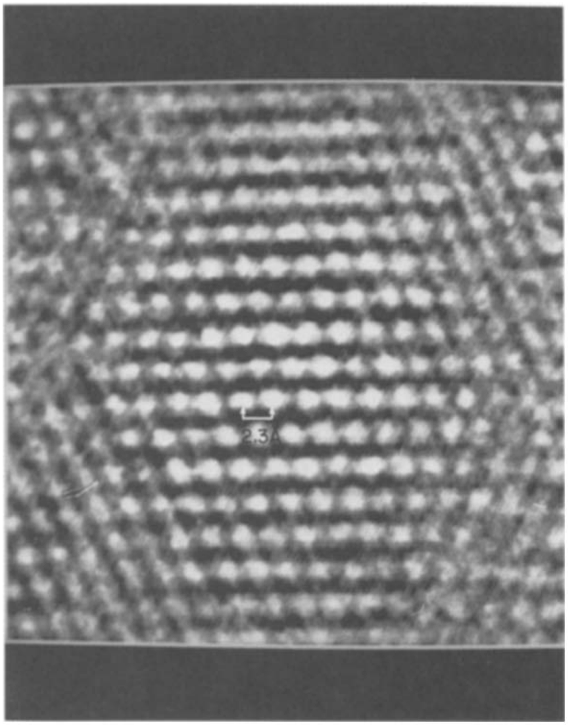

Fig. 12. Close up of one superlattice region.

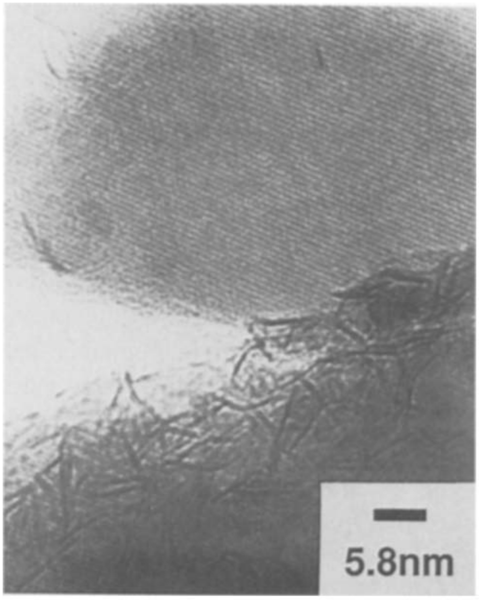

Fig. 13. FeMo catalyst showing single MoS_2 layers 'supported' on FeS_{1-x} (pyhrhottite) phase (from ref. [3]).

phase. Because of the exceptional stability of this catalyst the interaction between the two phases at the interface must be quite strong allowing the stabilization of single MoS_2 layers. The structure of the interface and the single layers or 'chains' is the subject of future HREM microscopy studies. The study of these interfaces may be the most important problem in the field of layered transition metal catalysts for the next period of investigation using HREM techniques, promising to yield both fundamental insight and information leading to improved catalytic systems.

7. Conclusions

Recent studies using HREM techniques have yielded a new insight into the nature of layered transition metal sulfide catalytic materials. While it is still very early, HREM techniques already show promise for solving some of the complex problems which have confronted this field for many years.

It has been well established that the active sites of layered LTMS catalysts are located at the edges of the anisotropic crystallites. HREM techniques are beginning to elucidate the structure of these sites and reveal the atomic structure of these edge terminations.

Disorder in real layered LTMS catalysts is another problem which has caused great difficulty when trying to interpret catalytic data. Again HREM is generating a new insight into this problem. It remains, however, a problem to understand how, at an atomic level, layers of MoS_2 can fold and bend at such acute angles and still retain their original atomic structure.

Finally, HREM is yielding an insight into the very complex 'promotional' problem. Evidence is growing that the older idea of pseudo-intercalation resulting in charge transfer and thus promotion is correct. Though much work remains to be done, HREM is giving a new impetus to this field and knowledge is being gained again at a rapid pace due to the fact that atomic level structural information is being gained by application of HREM techniques. It is exactly this type of information which will enable further progress to be made.

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