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# Pretreatment of new reduced ternary molybdenum sulfide catalysts

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## Abstract

Pretreatment of a new lanthanum molybdenum sulfide (LaMoS) hydrodesulfurization (HSD) catalyst in flowing H<sub>2</sub> has been investigated. Following pretreatment up to 800°C, the catalyst surface area decreased from 175 to 11 m<sup>2</sup>/g; the average pore diameter increased due to the loss of pore diameters smaller than 100 Å. TPD characterization of the as-prepared LaMoS was used to monitor the evolution of solvents and adsorbed materials up to 800°C. The Mo oxidation state was examined after various pretreatment procedures using X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR). Following temperature-programmed desorption (TPD), two types of surface oxygen were detected which could be reduced at 250°C and 950°C by a flow of 10% H<sub>2</sub> in N<sub>2</sub>. Transformation of the amorphous LaMoS to the corresponding crystalline Chevrel phase [La(Mo<sub>6</sub>S<sub>8</sub>)] was detected at 1000°C using TPR and x-ray diffraction (XRD). © 2000 Elsevier Science B.V. All rights reserved.

**Keywords:** Metal sulfide clusters; Hydrodesulfurization; Amorphous ternary molybdenum sulfides; H<sub>2</sub> pretreatment; Chevrel phases

## 1. Introduction

Hydrotreating of petroleum is receiving renewed attention due to legislation which has significantly reduced the allowable sulfur content of transportation fuels. These more stringent demands are requiring the development of more active hydrodesulfurization (HDS) catalysts, which can remove relatively

unreactive organosulfur compounds. In our previous research, we have investigated a new series of highly active hydroprocessing catalysts [1–3]. These new catalysts have a characteristic structural unit based on the Mo<sub>6</sub>S<sub>8</sub> cluster: the general composition is specified as M<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub>, where M is the ternary metal cation. Typically, two methods have been used to synthesize these catalysts. Solid state methods at high temperatures (1000–1300°C) produce highly pure, crystalline Chevrel phases [1–3]. However, these materials typically have low surface areas (1–2 m<sup>2</sup>/g). In our more recent research, we have discovered a new low temperature synthesis route for Mo cluster compounds [4,5]: the products are amorphous

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and have surface areas as high as 200 m<sup>2</sup>/g [6]. Both synthesis routes yield catalysts with similar activity for thiophene HDS [6].

Pretreatment of these new amorphous reduced ternary molybdenum sulfides in H<sub>2</sub> has been shown to stabilize the Mo<sub>6</sub>S<sub>8</sub> cluster unit and yield a more active HDS catalyst [6,7]. The pretreated materials also retain higher surface areas under HDS conditions. In this paper, we report further investigation of this pretreatment procedure for the LaMoS catalyst. Surface area and porosity measurements revealed changes in the physical structure of the materials. Characterization techniques such as temperature-programmed desorption (TPD) or reduction (TPR), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD) were also used. New information has been provided about the evolution of solvent and adsorbed species, the changes in the Mo oxidation state, and the conversion of the amorphous LaMoS to the crystalline Chevrel phase.

## 2. Experimental methods

High yields of the amorphous ternary Mo sulfide Na<sub>3</sub>(Mo<sub>6</sub>S<sub>8</sub>)S<sub>1.5</sub> · y(CH<sub>3</sub>OH) (y = 4–5) were obtained by the reaction of Mo<sub>6</sub>Cl<sub>12</sub> with NaSH and NaOBu in refluxing *n*-BuOH, followed by a CH<sub>3</sub>OH wash to remove the NaCl by-product [5]. Ion exchange reactions of the soluble lanthanum nitrate hexahydrate salt with the insoluble Na<sub>3</sub>(Mo<sub>6</sub>S<sub>8</sub>)S<sub>1.5</sub> · y(CH<sub>3</sub>OH) [NaMoS] produced the ternary lanthanum molybdenum sulfide compound, LaMo<sub>6</sub>S<sub>9.5</sub> · y(CH<sub>3</sub>OH) [LaMoS]. The sample stoichiometry was confirmed by microprobe analysis [6]. Compounds such as NaMoS and LaMoS were air-sensitive, and most manipulations were performed within an inert atmosphere dry box and with high-vacuum manifold or Schlenk techniques.

H<sub>2</sub> pretreatment studies were completed using a Lindberg/Blue 55035 tube furnace. Pretreatment involved placing 0.2–1.0 g of LaMoS in an alumina

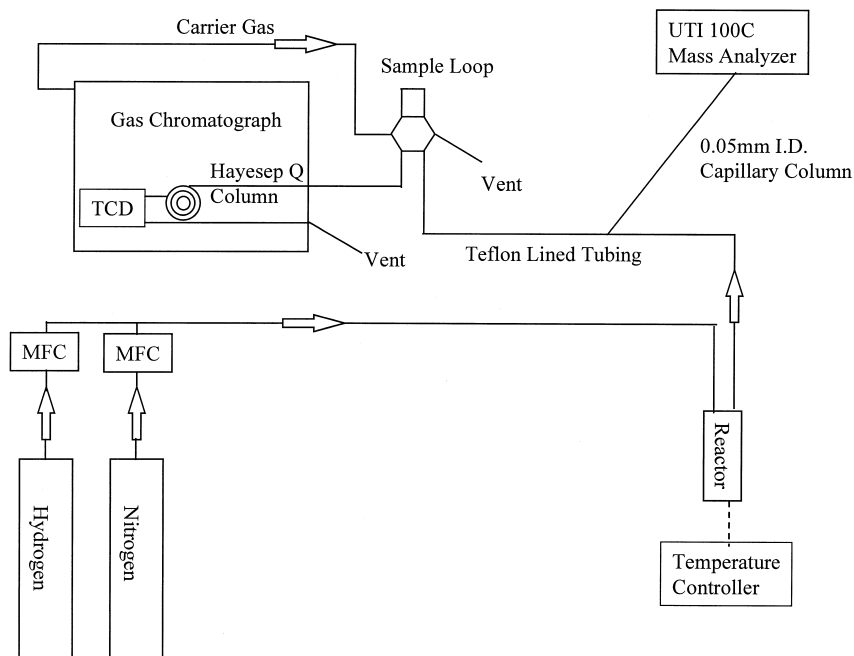


Fig. 1. Temperature-programmed analysis equipment.

boat inside a quartz tube. The furnace was heated at 20°C/min to the desired temperature (200–800°C) and held for 4 h at 1 atm in flowing H<sub>2</sub>. The catalyst was then cooled to room temperature in flowing H<sub>2</sub> and transferred to the dry box.

TPD and TPR studies were completed using the apparatus shown in Fig. 1. A 6-mm O.D., 4 mm I.D. quartz reactor was constructed, and Teflon-lined stainless steel tubing was used between the reactor and the gas analysis equipment. The sample temperature was controlled using an Omega 2010 programmable temperature controller. A Varian 3600cx gas chromatograph with a thermal conductivity detector and a UTI 100C residual gas analyzer were used for gas analyses. Product separation for chromatographic analyses required an 8 ft. × 1/8 in. glass-lined Hayesep-Q packed column. For the TPD studies, the flow rate of the N<sub>2</sub> carrier gas was 10 sccm, and the heating rate was 5°C/min. For the TPR studies, a 10% mixture of H<sub>2</sub> in N<sub>2</sub> was used at a total flow rate of 11 sccm. The heating rate for the TPR studies was 10°C/min, which provided acceptable signal-to-noise ratios while maintaining good peak resolution. Prior to TPR, the LaMoS catalyst first underwent TPD to 800°C and then was cooled in flowing N<sub>2</sub>. XRD and XPS analyses were performed at various stages of the temperature programming experiments.

Characterization of the LaMoS compounds using infrared spectroscopy (FTIR), electron microprobe analysis, and Extended X-ray Absorption Fine Structure (EXAFS) analysis have been reported previously [6,7]. In our current work, we have focused on laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy (XPS), and powder X-ray diffraction (XRD). Laser Raman spectra were obtained using a Coherent 532-50 diode-pumped solid state laser (532 nm, 50 mW at the source), a Kaiser HoloSpec f/1.8 spectrometer, and a Princeton Instruments CCD (1100 × 330). XPS data were collected with a Physical Electronics Industries 5500 multi-technique surface analysis system using a monochromatic MgK $\alpha$  source; binding energies were calibrated with adventitious carbon assuming C 1s = 284.6 eV, and all reported binding energies have been corrected to this value. XRD was performed using a Scintag 2000 diffractometer with CuK $\alpha$  radiation.

Surface area and porosity data were examined using a Micromeritics ASAP 2010C adsorption instrument. N<sub>2</sub> at 77 K was used as the adsorbing gas for both surface area and porosity studies. The BET equation was employed for the surface area calculations. The average pore diameter was determined using analysis based on the method developed by Barrett, Johner and Halenda (BJH method) for pores with diameters greater than 20 Å [8,9]. Repeated measurements of the surface areas and porosity indicated that the reproducibilities were within 5%.

### 3. Results

#### 3.1. Surface area and porosity characterization

Surface areas and average pore diameters of the LaMoS materials were examined after nine different pretreatment temperatures (Fig. 2). The initial surface area of LaMoS was 175 m<sup>2</sup>/g; this surface area decreased as the pretreatment temperature increased. After pretreatment at 800°C for 4 h, the surface area was 11 m<sup>2</sup>/g. The average pore diameter increased with the pretreatment temperature (Fig. 2) from 60 Å for the as-prepared material to nearly 300 Å after pretreatment at 800°C.

Surface area and porosity data were also obtained after exposure to HDS conditions for 10 h. Following HDS reaction, these catalysts were transferred under inert conditions to a dry box and then were placed in adsorption sample tubes to minimize oxygen contamination. Fig. 3 illustrates the trends in the

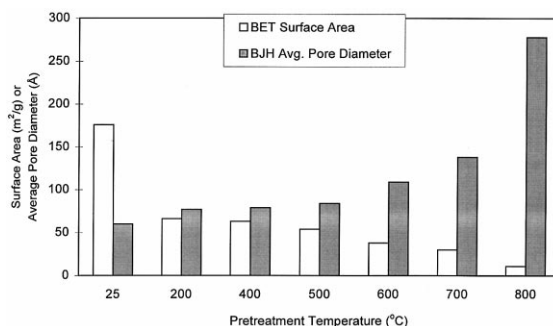


Fig. 2. Effect of pretreatment temperature on surface area and average pore diameter.

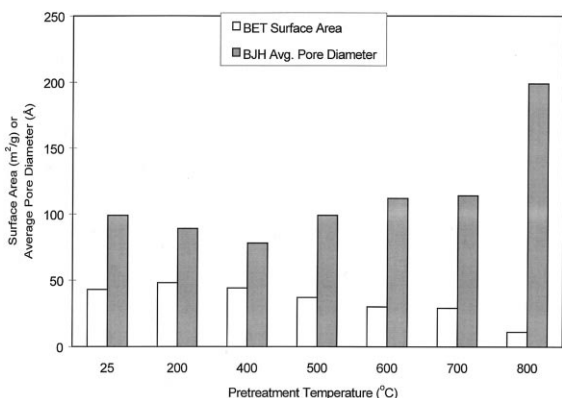


Fig. 3. Effect of pretreatment temperature on surface area and average pore diameter after HDS reaction studies.

surface area and average pore diameter data for the post-HDS reaction samples. At temperatures less than 400°C, surface areas did not change significantly. Surface areas decreased for pretreatment temperatures above 400°C. The average pore diameter of the post-HDS catalyst decreased from 100 Å for the as-prepared material to 78 Å after pretreatment at

400°C. The average pore diameter increased to 200 Å for pretreatment at 800°C.

### 3.2. Temperature-programmed analysis

TPD studies of the as-prepared material were used to examine the nature of gas evolution (Fig. 4). For all temperature program analysis data shown in the figures, the intensity scale represents the output signal from the gas chromatograph detector. The low temperature catalyst synthesis route results in the presence of solvents (from the ion exchange reaction) and H<sub>2</sub>O (from the La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O). CH<sub>3</sub>OH was removed from the catalyst at temperatures between 50°C and 250°C (Fig. 4). The peak at 100°C resulted from CH<sub>3</sub>OH trapped in the pore structure of the catalyst. CH<sub>3</sub>OH detected at 165°C was believed to be associated with the coordination sphere of the ternary metal cation. H<sub>2</sub>O peaks were observed at 125°C, 195°C, and 325°C. The low temperature peak resulted from water released from the pore structure of the catalyst while the second and third peaks resulted from water evolution from the

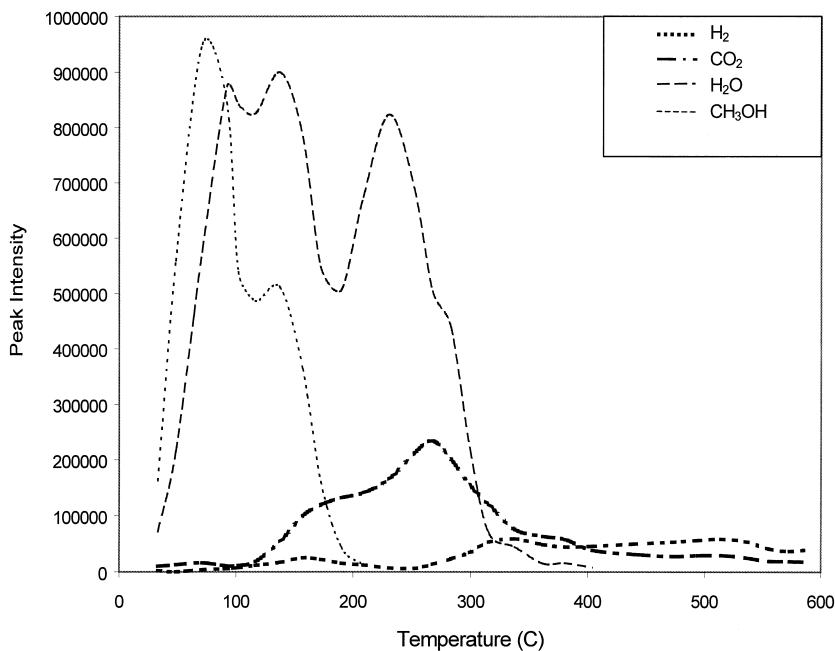


Fig. 4. TPD for as-prepared LaMoS.

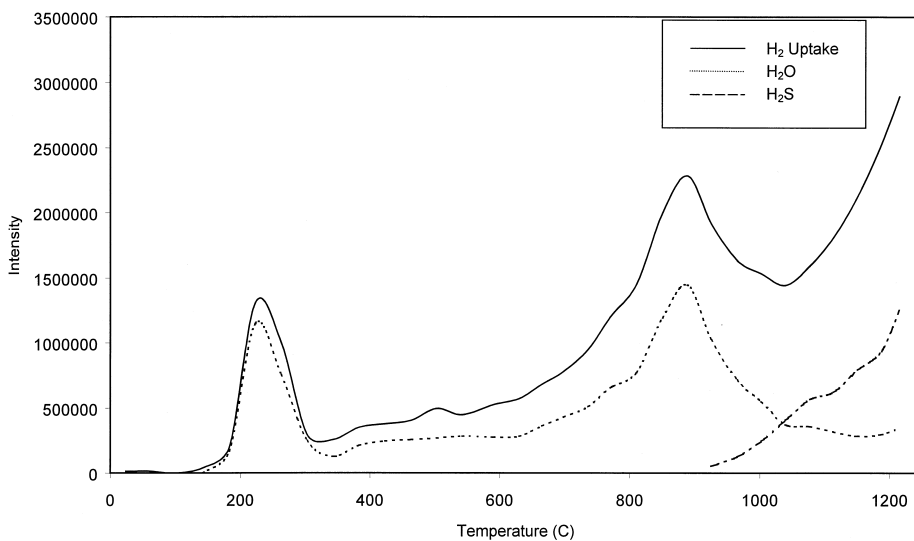


Fig. 5. TPR after TPD using a 10%  $H_2$  in  $N_2$  feed.

coordination sphere of the ternary metal cation.  $CO_2$  was released from the catalyst between 125°C and 325°C, with a maximum occurring at about 280°C.

Small amounts of  $H_2$  evolved throughout the TPD experiment: two peaks were observed at 180°C and 320°C.

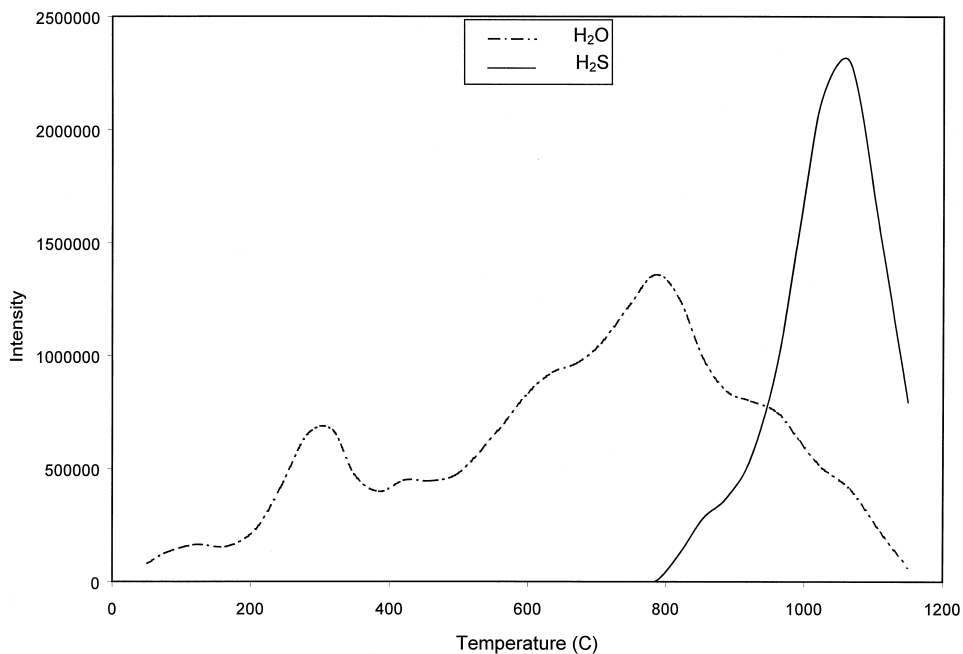


Fig. 6. TPR after TPD using a 100%  $H_2$  feed.

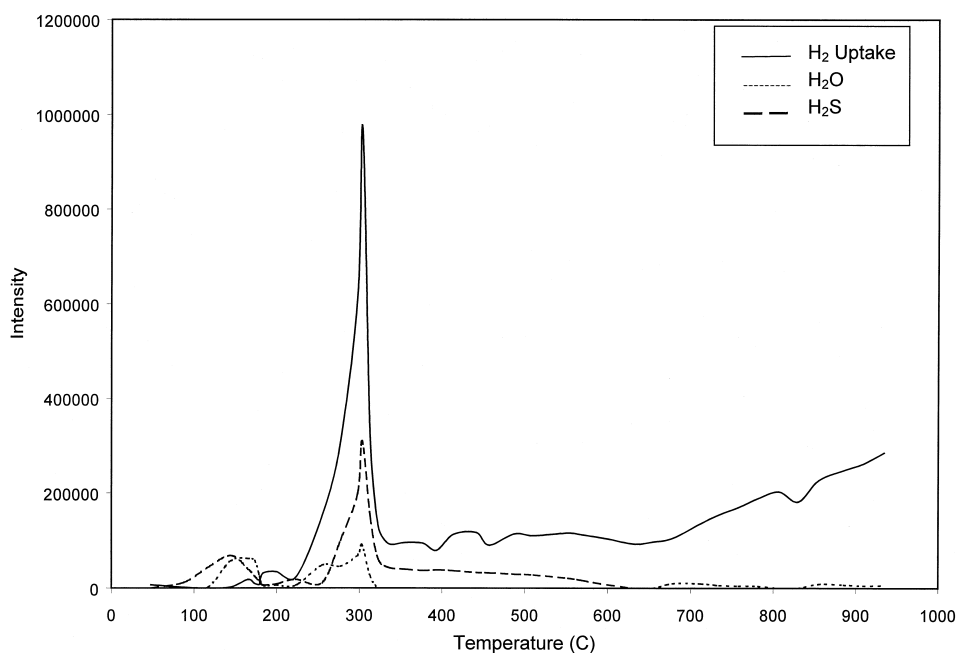


Fig. 7. TPR after TPD and H<sub>2</sub>S exposure at 400°C for 15 min.

TPR studies were conducted after the catalysts had undergone TPD to 800°C. Experiments involving 10% H<sub>2</sub> in N<sub>2</sub> revealed peaks due to H<sub>2</sub> consumption, H<sub>2</sub>O production, and H<sub>2</sub>S production (Fig. 5). At 250°C, H<sub>2</sub> consumption and H<sub>2</sub>O production indicated the reduction of an oxygen-containing species in the catalyst. A second combination of H<sub>2</sub> consumption and H<sub>2</sub>O production occurred at 850°C.

This high temperature was due to the reduction of a strongly bound oxygen species in the catalyst. Reduction of a sulfur species to form H<sub>2</sub>S began at around 950°C and continued at temperatures up to 1200°C (the maximum temperature attainable).

A second series of TPR experiments was conducted in pure H<sub>2</sub> (Fig. 6). It was not possible to determine the H<sub>2</sub> uptake under these conditions due

Table 1

XPS characterization after pretreatment conditions: TPD was performed with N<sub>2</sub> and TPR was performed with 5% H<sub>2</sub> in N<sub>2</sub>

Pretreatment	Mo <sub>6</sub> S <sub>8</sub> Mo 3d <sub>5/2</sub> peak	Oxidized MoS Mo 3d <sub>5/2</sub> peak	% Mo <sub>6</sub> S <sub>8</sub> <sup>a,b</sup>
As-prepared	227.5	–	100
800°C TPD	227.5	228.9	47
800°C TPD/100°C TPR	227.5	228.8	49
800°C TPD/300°C TPR	227.5	228.8	53
800°C TPD/500°C TPR	227.5	228.7	55
800°C TPD/700°C TPR	227.5	228.7	57
800°C TPD/900°C TPR	227.5	228.8	65
800°C TPD/1100°C TPR	227.2	228.6	75
800°C TPD/1200°C TPR	227.0	–	100

<sup>a</sup> MoO<sub>3</sub> present in most samples was excluded from these calculations.

<sup>b</sup> Quantitative calculations are based on the fitted Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> peak areas.

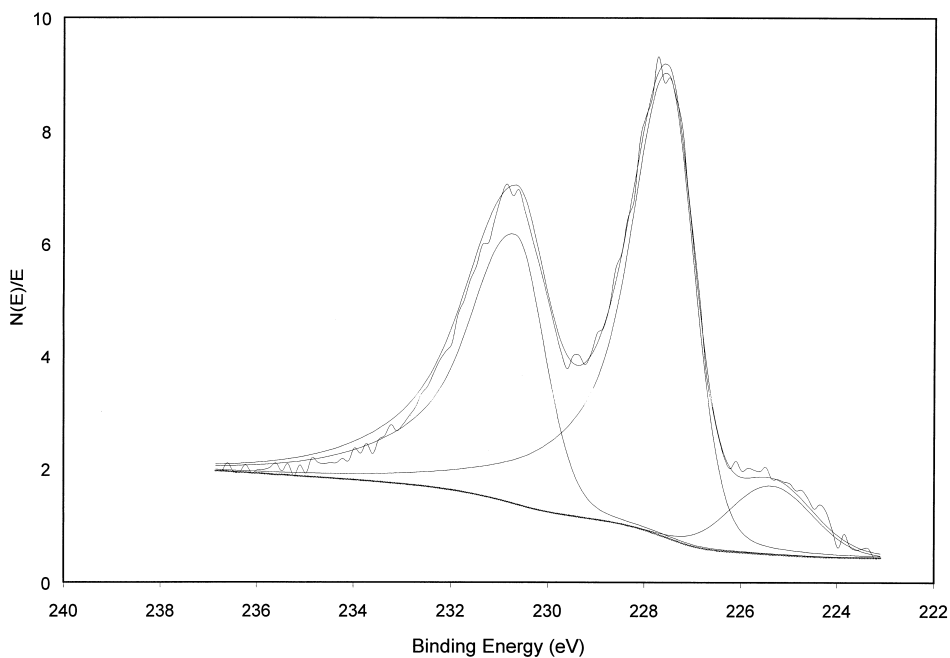


Fig. 8. Molybdenum 3d XPS spectra of as-prepared LaMoS.

to the large amount of  $H_2$  present in the system. However, the TPR results did reveal both  $H_2O$

production and  $H_2S$  production. For  $H_2O$  production, a low temperature peak occurred at  $250^\circ C$ , and

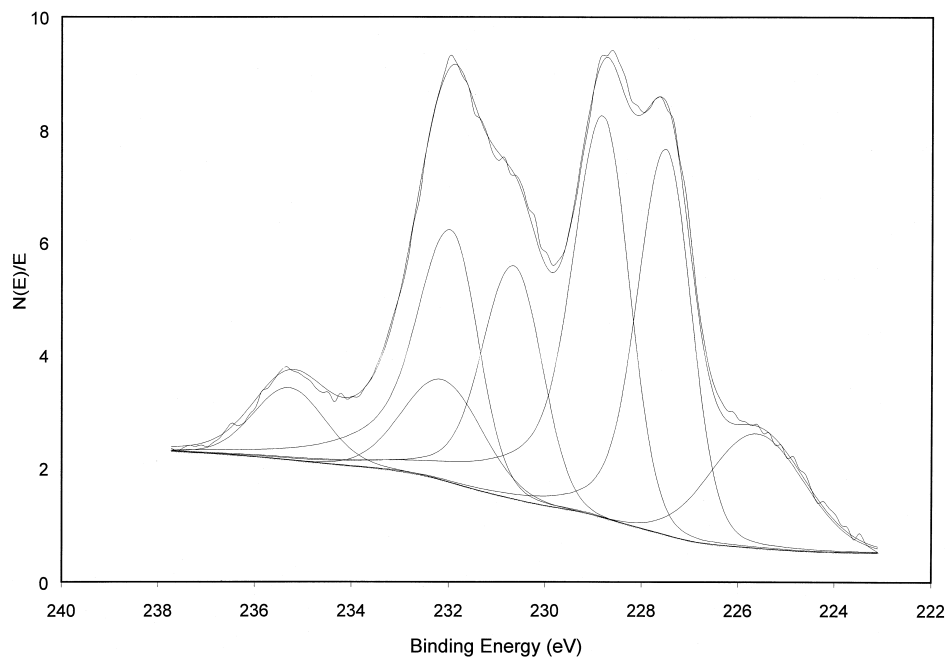


Fig. 9. Molybdenum 3d XPS spectra of LaMoS after heating to  $800^\circ C$  in flowing  $N_2$  at  $5^\circ C/min$ .

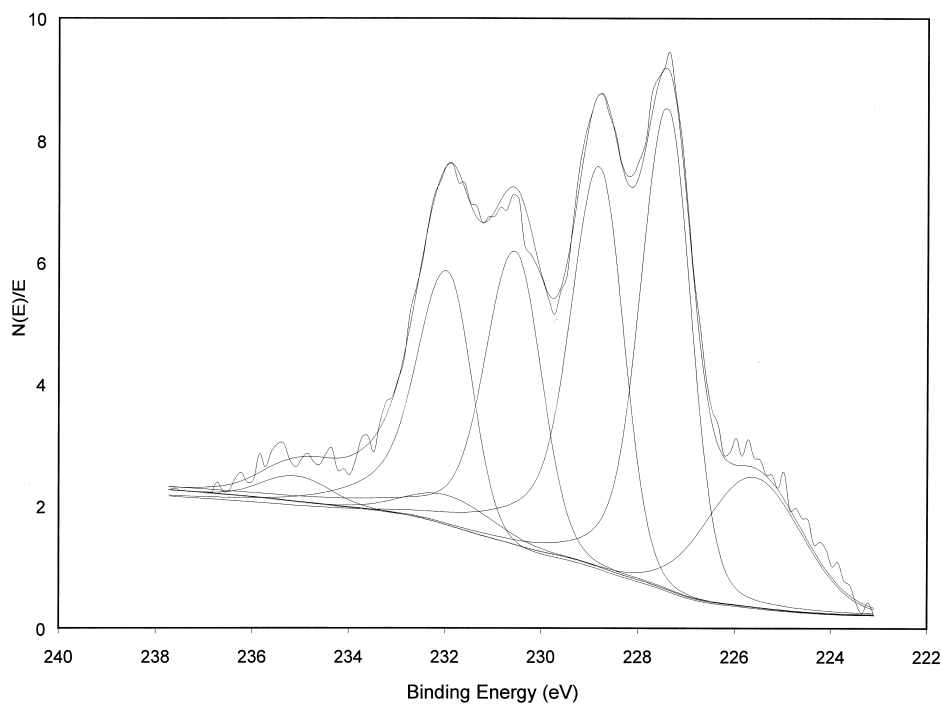


Fig. 10. Molybdenum 3d XPS spectra of LaMoS after TPD to 800°C and TPR to 900°C.

a high temperature peak was present at 780°C.  $H_2S$  evolution began at 800°C and reached a maximum at

1050°C. Most of the TPR results with pure  $H_2$  were very similar to the studies completed using the 10%

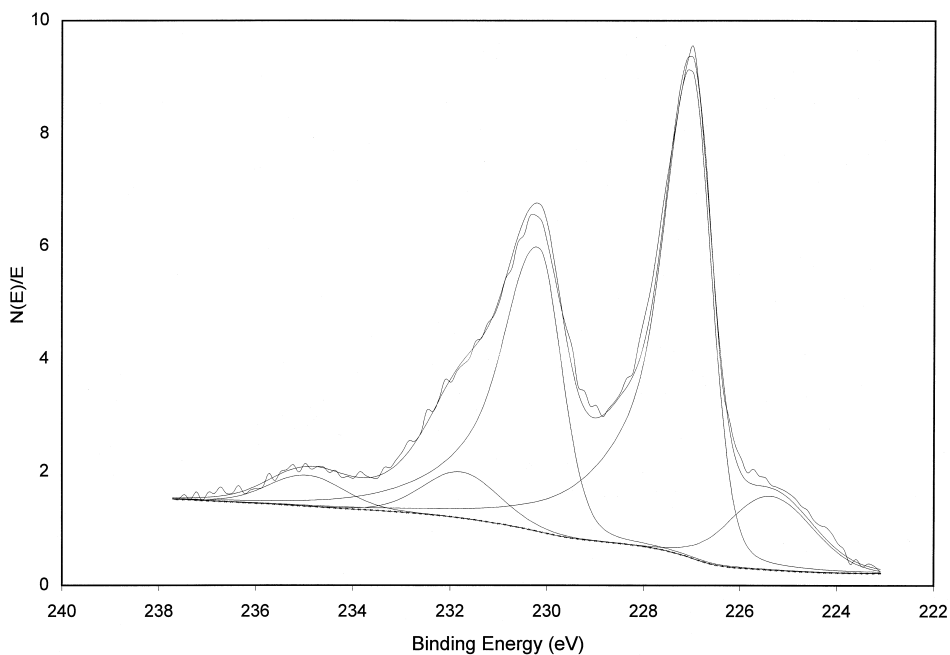


Fig. 11. Molybdenum 3d XPS spectra of LaMoS after TPD to 800°C and TPR to 1200°C.



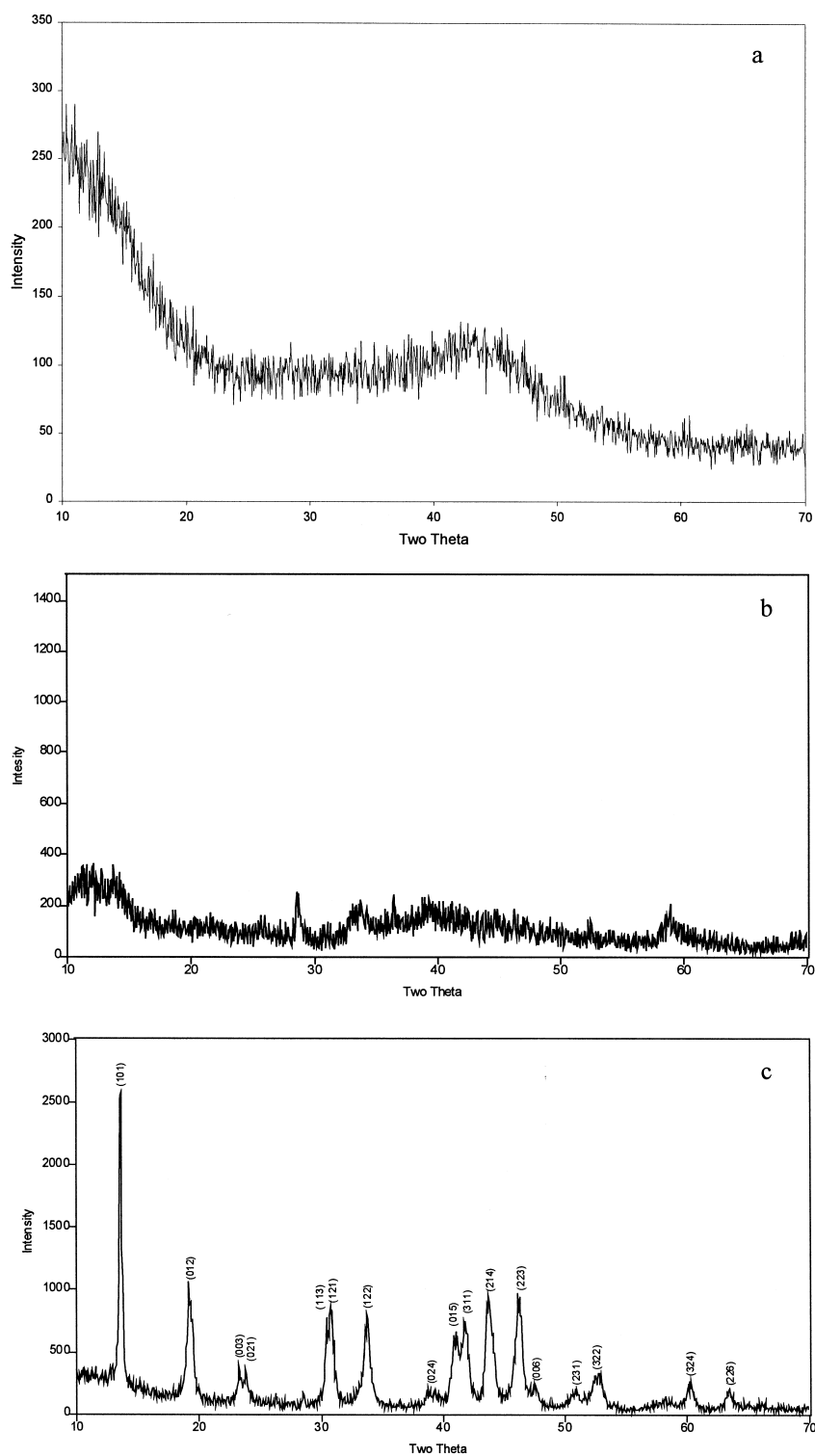


Fig. 12. XRD data for a) as-prepared LaMoS, b) after TPD to 800°C, c) after TPR to 1200°C.

H<sub>2</sub> in N<sub>2</sub> mixture. However, the high temperature H<sub>2</sub>O and H<sub>2</sub>S peaks shifted to lower temperatures, and a H<sub>2</sub>S peak was clearly present at 1050°C.

TPR studies have also been completed for samples, which were pre-reduced in 10% H<sub>2</sub> in N<sub>2</sub> at 400°C (Fig. 7). The flow over these catalysts was then changed to a 10% H<sub>2</sub>S in N<sub>2</sub> mixture at 400°C for 15 min, followed by cooling to room temperature in this gas mixture. The TPR studies showed a large H<sub>2</sub>S production peak and H<sub>2</sub> consumption peak at 300°C. A small H<sub>2</sub>O peak was also seen at this temperature. No higher temperature reduction peaks were observed for the H<sub>2</sub>S-pretreated samples.

### 3.3. Characterization by XPS and XRD

Changes in Mo oxidation state due to TPD or TPR were examined with XPS (Table 1). For the as-prepared material (Fig. 8), the Mo oxidation state was consistent with the presence of the Mo<sub>6</sub>S<sub>8</sub> cluster [5]. (A broad band observed at the lower binding energy side of the Mo 3d doublet spectra was due to the S 2s peak.) LaMoS, which had undergone TPD and TPR, typically had three distinct oxidation states. The Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> doublet bands due to the Mo<sub>6</sub>S<sub>8</sub> cluster unit were generally near 227.5 and 230.6 eV. A second oxidation state was observed at higher binding energies of 228.7–228.9 and 231.9–232.1 eV. A third set of doublet peaks was present at 232.3 and 235.4 eV and was characteristic of MoO<sub>3</sub>. This relatively small amount of MoO<sub>3</sub> was likely a surface phenomenon: it could not be detected by laser Raman spectroscopy or XRD. The second oxidation state (as illustrated in Fig. 9 for a LaMoS sample following TPD) was due to surface oxidation. The binding energies indicated the formation of Mo<sup>3+</sup> or Mo<sup>4+</sup>, such as is present for Mo<sub>2</sub>S<sub>3</sub> (Mo 3d<sub>5/2</sub> = 228.7 eV).

The relative amount of Mo present on the catalyst surface in the various oxidation states was quantified by determining the Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub> peak areas. Surface MoO<sub>3</sub> was likely due to sample contamination during catalyst handling and from small amounts of oxygen present during pretreatment. No MoO<sub>3</sub> was detected by laser Raman spectroscopy or XRD, and the amount detected by XPS varied randomly for different samples. For these reasons, XPS

peaks associated with MoO<sub>3</sub> were excluded from the analysis of the effects of pretreatment on surface oxidation. After heating to 800°C, over 50% of the surface Mo was present in the (non-MoO<sub>3</sub>) oxidized state. The amount of Mo with a binding energy consistent with the existence of the Mo<sub>6</sub>S<sub>8</sub> cluster (227.5 eV) slowly increased as TPR temperatures increased from 100°C (47%) to 700°C (57%). At higher reduction temperatures, the reduced state (227.5 eV) accounted for 65% of the surface for 900°C, 75% for 1100°C, and 100% for 1200°C. The Mo 3d<sub>5/2</sub> binding energy for the cluster was 227.5 eV for all of the sample, which had been reduced at temperatures less than 900°C. After reduction at 900°C, the binding energy shifted from 227.5 to 227.2 eV (Fig. 10); after reduction at 1200°C the binding energy of the cluster shifted even further to 227.0 eV (Fig. 11).

XRD data for as-prepared LaMoS were consistent with the presence of amorphous material (Fig. 12a). Broad powder patterns were also observed after heating to 800°C in flowing N<sub>2</sub> and after TPR to 900°C (Fig. 12b). However, after TPR to 1000°C, distinct XRD peaks appeared (Fig. 12c), which were due to the LaMo<sub>6</sub>S<sub>8</sub> Chevrel phase [10]. Calculated lattice parameters for this sample ( $a_H = 9.120 \text{ \AA}$  and  $c_H = 11.550 \text{ \AA}$ ) were in reasonable agreement with the values reported by Yvon [10] for LaMo<sub>6</sub>S<sub>8</sub> ( $a_H = 9.120 \text{ \AA}$  and  $c_H = 11.554 \text{ \AA}$ ). In previous work, we have shown that following pretreatment of the as-prepared LaMoS for 4 h in pure H<sub>2</sub> at 800°C, conversion to the Chevrel phase occurred [7].

## 4. Discussion

In previous papers, we have shown that H<sub>2</sub> pretreatment stabilizes the amorphous Mo cluster catalysts for HDS; relatively higher surface areas were also retained [6,7]. Furthermore, there was no appreciable MoS<sub>2</sub> formation when the preparation and pretreatment procedures outlined above were followed. By examining the changes that these catalysts undergo during pretreatment, a better understanding of the active form of these HDS catalysts has been obtained. The physical nature (surface area and pore

structure) of these catalysts was modified through pretreatment. In addition, the chemical composition of the catalysts changed during pretreatment. The amorphous LaMoS could ultimately be transformed into the crystalline Chevrel phase, a highly active HDS catalyst [1–3].

#### 4.1. Physical structure of the catalyst

The surface area of LaMoS decreased as the pretreatment temperature increased, and the average pore diameter also increased. The largest decrease in surface area occurred for pretreatment from 25°C to 200°C (175 to 71 m<sup>2</sup>/g): CH<sub>3</sub>OH and H<sub>2</sub>O evolved over this range (Fig. 4). Small pores were destabilized concomitant with the evolution of these molecules. As the pretreatment temperature increased to 800°C, the decrease in surface area continued, probably due to sintering. After pretreatment at 800°C for 4 h in H<sub>2</sub>, the surface area decreased from 175 to 11 m<sup>2</sup>/g, and the average pore diameter increased from 60 to 300 Å as the crystalline LaMo<sub>6</sub>S<sub>8</sub> formed (Fig. 2).

Surface areas after HDS catalysis were lower than for the as-prepared or pretreated catalysts. Surface area loss after 10 h of HDS reaction was less significant for samples pretreated at higher temperatures (Fig. 3). A more stable structure may be produced by these higher temperature pretreatments. The post-HDS surface area was fairly stable for pretreatment up to 400°C (44 m<sup>2</sup>/g), but a significant decrease (11 m<sup>2</sup>/g) occurred after pretreatment at 800°C. The average pore diameter after HDS decreased for pretreatment temperatures up to 400°C and then increased for pretreatment temperatures up to 800°C. Similar changes in the average pore diameter were not observed for samples prior to HDS reaction. Samples pretreated at 400°C in H<sub>2</sub> had the lowest average pore diameter after HDS, indicating that more of the small pores (less than 100 Å) remained. At temperatures above 400°C, the effects of sintering probably became dominant.

#### 4.2. Gas evolution

The low temperature synthesis route used to prepare these materials results in the presence of solvent

molecules in both the pore structure of the catalyst and in the coordination sphere of the ternary metal cation. TPD studies revealed three H<sub>2</sub>O peaks at 125°C, 195°C, and 325°C (Fig. 4). These catalysts were synthesized under inert atmosphere using primarily anhydrous reagents. The only hydrated reagent for the synthesis was La(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O, which was used in the ion exchange reaction with Na<sub>3</sub>Mo<sub>6</sub>S<sub>9.5</sub>. The H<sub>2</sub>O peaks were due to water released from the pore structure of the catalyst (125°C) and the coordination sphere of the La (195°C and 325°C). CH<sub>3</sub>OH evolution was also observed in these TPD experiments: this process began at room temperature, rose to a maximum at 100°C, exhibited a shoulder at 165°C, and ended by about 250°C. During synthesis of these materials, the ion exchange reaction between La(NO<sub>3</sub>)<sub>3</sub> and NaMoS was performed in CH<sub>3</sub>OH solution. CH<sub>3</sub>OH can apparently displace some of the H<sub>2</sub>O coordinated with La in LaMoS. Above 200°C, some residual CH<sub>3</sub>OH was thought to still be present which could react with H<sub>2</sub>O to form CO<sub>2</sub> and H<sub>2</sub>. CO<sub>2</sub> production peaks observed at 350°C provided an indication of this reaction. Broad peaks for H<sub>2</sub> evolution were observed at high temperatures for TPD, indicating that the H<sub>2</sub> produced was adsorbed on the catalyst surface.

#### 4.3. Surface oxidation

XPS characterization revealed that surface oxidation occurred during TPD. For the as-prepared catalyst (Fig. 8), the binding energy (227.5 eV) was consistent with the presence of La(Mo<sub>6</sub>S<sub>8</sub>)S<sub>1.5</sub>, and only one oxidation state was necessary to fit the data. Previous work has shown that ternary molybdenum sulfides (MMoS) (M = Na, Co, Ni, Sn, Pb, La, Ho) exhibit binding energies between 227.3 and 228.2 eV [5]. The XPS spectrum for LaMoS after TPD to 800°C indicated formation of another oxidation state (Fig. 9). The Mo 3d<sub>5/2</sub> binding energy (228.7 eV) was considerably lower than MoS<sub>2</sub> (229.5 eV) and was about 1 eV higher than the binding energies for as-prepared material. Mo<sub>2</sub>S<sub>3</sub> has a similar binding energy (228.7 eV) and has a Mo oxidation state of +3. The formation of this surface oxidized species probably resulted from reactions that accompanied the evolution of CH<sub>3</sub>OH and H<sub>2</sub>O. These oxy-

genates could react with the surface of the material to form surface oxides and  $H_2$ . The XPS data indicated that over 50% of the surface was present in this oxidized state after undergoing TPD to 800°C.

#### 4.4. Reduction of oxidized surface

In previous work, we have found that  $H_2$  pretreatment stabilized the chemical structure of the LaMoS materials. Our TPR studies have revealed peaks for  $H_2$  consumption and  $H_2O$  production centered at 250°C (Fig. 5). The low temperatures associated with these peaks suggest that a weakly bound oxygen species on the surface of the catalyst reacts with  $H_2$  to produce  $H_2O$ . Table 1 indicates that no dramatic change in the Mo oxidation state occurred at these temperatures: apparently, the weakly bound surface oxygen does not dramatically effect the Mo oxidation state.

A second broad TPR peak was observed beginning at around 600°C and with a maximum at about 950°C. XPS data indicated that the amount of surface oxidized species decreased at these temperatures, falling from 45% of the surface at 500°C to 25% of the surface at 1100°C. Eventually, the surface was completely reduced by 1200°C. At the same time that the amount of this surface oxidized species was decreasing, the surface oxidation state corresponding to the Mo cluster increased from 55% at 500°C to 65% at 900°C. At 1200°C, this conversion reached 100%. The ability of these materials to reversibly change from  $La(Mo_6S_8)S_{1.5}$  to  $La(Mo_6S_8)S_{1.5}O_x$  indicated that the cluster unit is not completely destroyed even by surface oxidation. It is possible that the easily reduced oxide species (after TPD at 250°C) is present as a terminal oxo- or hydroxyl-groups on the  $Mo_6S_8$  cluster units. The oxide species reduced at approximately 900°C likely arises from oxygen that has displaced sulfur in bridging positions of the cluster, as evidenced by previous EXAFS studies [7].

#### 4.5. Conversion to the chevrel phase

Chevrel phase materials are structurally similar to these new reduced ternary molybdenum sulfides in

that both materials contain the  $Mo_6S_8$  cluster unit. In previous work, we have shown that after pretreatment in 100%  $H_2$  at 800°C, the new reduced ternary Mo sulfides were converted to the Chevrel phase. In our current studies, TPR, XRD, and XPS were all used to examine this transformation more closely.

The new reduced ternary Mo sulfide catalysts have the stoichiometry  $La(Mo_6S_8)S_{1.5}$  while the composition of the crystalline Chevrel phase is known to be  $LaMo_6S_8$ . In order to convert  $La(Mo_6S_8)S_{1.5}$  to crystalline Chevrel phase, it was necessary to remove the labile sulfur. For TPR using 10%  $H_2$ , a large  $H_2$  uptake peak and a  $H_2S$  production peak were observed starting at 950°C; both continued to increase up to 1200°C (Fig. 5). XRD (Fig. 12) showed that after TPR to 900°C, these materials were still amorphous, but after TPR to 1000°C the crystalline Chevrel phase formed. These results indicated that under TPR conditions, amorphous  $La(Mo_6S_8)S_{1.5}$  began to convert to crystalline  $LaMo_6S_8$  at 950°C and continued to undergo transformation at temperatures up to 1200°C. A downward shift in Mo  $3d_{5/2}$  binding energy, from 227.5 to 227.0 eV, indicated that these materials were reduced at 1200°C. This shift resulted from the removal of excess sulfur as these materials were converted from  $La(Mo_6S_8)S_{1.5}$  to the Chevrel phase ( $LaMo_6S_8$ ). No further reduction to produce Mo metal was observed in these experiments.

The higher temperature at which  $La(Mo_6S_8)S_{1.5}$  was converted to the Chevrel phase in TPR was a result of the decrease in  $H_2$  partial pressure used (10% for TPR vs. 100% for pretreatment studies). A TPR study was also conducted in pure  $H_2$ . In this study, the high temperature reduction peak was shifted to lower temperatures, and the  $H_2S$  evolution began at 800°C (Fig. 6). These data were consistent with our previous work showing conversion of amorphous  $La(Mo_6S_8)S_{1.5}$  to the crystalline Chevrel phase at 800°C in pure  $H_2$ . A peak for  $H_2S$  evolution was observed at 1050°C, indicating that  $H_2S$  evolution ends when sulfur in excess of the Chevrel phase stoichiometry has been removed. XRD characterization of this sample indicated that the crystalline Chevrel phase was present and there was no further reduction to Mo metal. This suggests that the removal of excess sulfur and conversion of  $La(Mo_6S_8)S_{1.5}$  to the Chevrel phase  $La(Mo_6S_8)$  are

completed in pure  $H_2$  under TPR conditions by  $1100^\circ\text{C}$ , without removing sulfur from the  $\text{Mo}_6\text{S}_8$  cluster unit.

#### 4.6. $H_2S$ pretreatment

$H_2$  pretreatment of the post-TPD samples have shown the presence of oxygenates in these catalysts. For TPR studies of catalysts pretreated in  $H_2S$ , a large  $H_2S$  peak was present at  $250^\circ\text{C}$  (Fig. 7). This peak occurred in the same temperature region where the  $H_2O$  peak was observed for the previous TPR studies. These data indicated that  $\text{LaMoS}$  can adsorb either sulfur or oxygen. The ability to remove these species from these sites at low temperatures could be an important aspect of the HDS activity of these catalysts.

### 5. Conclusions

Pretreatment of these new reduced Mo sulfide catalysts produced a more stable surface structure for HDS reaction at  $400^\circ\text{C}$ : smaller surface area losses occurred, and the average pore diameter was larger. TPD indicated that at  $400^\circ\text{C}$  gas evolution was nearly complete, which apparently produced a stable environment for HDS catalysis. TPR demonstrated that two types of reducible anions were present: one species could be reduced at  $250^\circ\text{C}$ , but another species could not be reduced until  $950^\circ\text{C}$ . The lower temperature reducible anion could be present as either oxygen or sulfur. The reduction of these anions might free adsorption sites necessary for HDS catalysis.

The conditions under which these new reduced ternary molybdenum sulfides were transformed to crystalline Chevrel phase have also been determined. For the as-prepared materials, the stoichiometry was  $\text{La}(\text{Mo}_6\text{S}_8)\text{S}_{1.5}$ . TPR in a 10%  $H_2$  environment showed a  $H_2S$  production peak beginning at  $950^\circ\text{C}$

indicating sulfur removal. XPS also revealed a shift in the Mo  $3d_{5/2}$  binding energies corresponding to the conversion of these amorphous ternary molybdenum sulfides ( $\text{La}(\text{Mo}_6\text{S}_8)\text{S}_{9.5}$ ) compounds to the crystalline Chevrel phase ( $\text{LaMo}_6\text{S}_8$ ).

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