Metal cluster hydrodesulfurization catalysts based on ternary lanthanum molybdenum sulfides

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Abstract

Hydrodesulfurization (HDS) catalysis by a new group of reduced ternary molybdenum sulfides involving Mo_6S_8 clusters has been investigated. A low temperature synthesis route was used to produce LaMoS materials with initial surface areas near 200 m^2/g. Pretreatment at 200–700°C in flowing H_2 yielded amorphous materials that retained the lower Mo oxidation state characteristic of metal clusters (Mo_6S_8). Higher temperature pretreatment (800°C) resulted in formation of the corresponding Chevrel phase. The LaMoS materials prepared and pretreated at the lower temperatures had similar thiophene and benzothiophene HDS rates to those for Chevrel phases. After HDS reaction, the surface areas of the catalysts were near 30–50 m^2/g. © 1997 Elsevier Science B.V.

1. Introduction

The increasing demand for low sulfur fuels and chemical feedstocks from petroleum has continued to prompt research in hydrodesulfurization (HDS) catalysis. New requirements for diesel fuels and gasoline with a low aromatic content has further stimulated the need for improvements in processes and catalysts for hydrotreating. For nearly 60 years, catalysts based on Co(Ni)–Mo(W)/Al_2O_3 have been extensively investigated and developed for industrial HDS

applications [1]. In our research, we have investigated a new series of hydroprocessing catalysts based on our discovery of the activity of Chevrel phases [2–6]. This family of ternary molybdenum sulfide compounds has a characteristic structural unit based on the Mo_6S_8 cluster: the general composition is specified as $M_xMo_6S_8$, where M (the 'ternary' metal cation) includes over 40 different metallic elements. Chevrel phases are frequently considered to be reduced molybdenum sulfides because of the low molybdenum oxidation state relative to MoS_2.

Chevrel phase compounds have been shown

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to have high activity and selectivity for HDS, frequently exceeding the performance of unsupported Co–Mo catalyst materials [2–5]. Chevrel phases are also stable under HDS conditions: the low oxidation states are maintained, and no decomposition or transformation to other Mo sulfides has been detected for most compounds [2–5]. Previous methods for preparing Chevrel phases usually have involved solid state syntheses at high temperatures (1000–1300°C). The resulting materials have low surface areas, typically around 1 m^2/g. In order to produce materials which might be more useful for industrial applications, we have investigated alternate methods of synthesis which could produce catalysts with higher surface areas; these methods might also be useful in preparing supported Mo cluster catalysts [7–9]. The feasibility of preparing stable Chevrel phases on a representative oxide support has been demonstrated in principle using reactive sputtering techniques [10].

We have recently developed a low temperature synthesis route for ternary molybdenum sulfides based on work involving the preparation of isolated $Mo_6S_8L_6$ cluster units as pre-

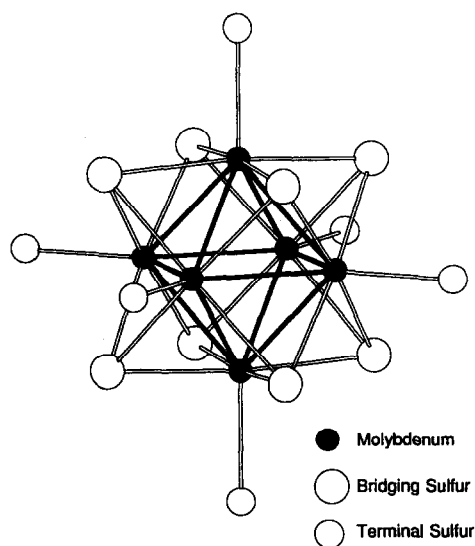● Molybdenum
○ Bridging Sulfur
○ Terminal Sulfur

Fig. 1. Structure of the Mo_6S_8 hexanuclear cluster unit which is formed by a molybdenum octahedron and eight triply bridging sulfur atoms capping each face. Additionally, six terminal positions are located at the vertices of the octahedron and are occupied by S atoms upon interlinkage of the clusters.

cursors to Chevrel phases [8,9,11]. The resulting materials are amorphous, but characterization has revealed that they are structurally similar to Chevrel phases because of the presence of Mo_6S_8 cluster units (Fig. 1). In this paper, we report the use of this preparative method and various pretreatment conditions to produce stable, high surface area materials for use as catalysts. The activity and selectivity of this new group of catalytic materials is reported for thiophene and benzothiophene HDS. This report will focus on ternary lanthanum molybdenum sulfide (LaMoS) compounds.

2. Experimental method

2.1. Catalyst synthesis

Preparation of the ternary lanthanum molybdenum sulfide catalysts involved the ion-exchange reaction of a soluble lanthanum salt with insoluble $Na_3Mo_6S_{9.5}(MeOH)_y$ (NaMoS) in methanol [11]. Stoichiometric replacement of the Na with La by ion-exchange should be accomplished with 1 equivalent of La salt. Several La sources were used including anhydrous lanthanum trichloride (prepared according to Ref. [12]) and two hydrated salts, $LaCl_3 \cdot 7H_2O$ and $La(NO_3)_3 \cdot 6H_2O$. A typical procedure involved the following: $Na_3Mo_6S_{9.5}(MeOH)_y$ (1.00 g) and 1 equivalent of the lanthanum nitrate hexahydrate (0.39 g) were weighed in a drybox and transferred to a 100 mL Schlenk reaction flask; 30 mL of methanol (MeOH) were vacuum-distilled onto the solids. After the mixture was stirred at room temperature under N_2 for 1 day, a blackish solid and light yellow solution were obtained. The resulting solid was extracted with solvent distilled from the filtrate in order to remove the sodium chloride byproduct and any unreacted metal salt. After drying under dynamic vacuum, the black powder (1.05 g) was stored in an inert-atmosphere drybox. The product was insoluble in noncoordinating solvents and was amorphous by XRD.

Stoichiometric La compounds (La/Mo_6 ~

Table 1
Microprobe elemental analyses on LaMoS samples prepared with various lanthanum salts

LaMoS catalyst	% La	% Mo	% S	La/Mo$_6$	S/Mo$_6$
La(NO$_3$)$_3$ · 6H$_2$O preparation					
No pretreatment	13.22	51.99	24.79	1.05	8.80
400°C, H$_2$, 4 h	11.80	51.42	25.37	0.96	8.90
LaCl$_3$ · 7H$_2$O preparation	13.00	51.21	23.06	1.07	8.05
LaCl$_3$ preparation	4.08	57.70	25.60	0.30	7.97

1.0) were obtained when either the hydrated lanthanum nitrate or chloride salt was used (Table 1). However, lower La contents (La/Mo$_6$ ~ 0.30) were observed for exchange reactions with solutions prepared from the anhydrous lanthanum chloride salt. Therefore, materials based on the nitrate preparation (referred to as LaMoS) were investigated in the catalytic studies reported here.

2.2. Catalyst pretreatment

The catalytic performance of LaMoS was examined as-prepared and following a variety of pretreatment conditions. Powders having approximately 0.15–0.425 mm particle size (40–100 mesh) were selected for all pretreatment studies, activity measurements, and surface area determinations. Typical H$_2$ pretreatment involved placing the LaMoS powder in an alumina boat inside a quartz tube and heating to the desired temperature (200–800°C) under flowing H$_2$. After cooling under this flow, the product was stored in an inert-atmosphere drybox. An alternative pretreatment was performed in the reactor system. This procedure involved heating samples in varying H$_2$S–H$_2$ gas streams (3 or 10 mol% H$_2$S in H$_2$) at 400°C for 4 h.

2.3. Catalyst characterization

The materials were characterized by infrared (FTIR), laser Raman (LRS), and X-ray photoelectron (XPS) spectroscopic techniques, by powder X-ray diffraction (XRD), and by electron microprobe analyses. Infrared spectra

(4000–200 cm^{-1}) were recorded with a Bomem MB-102 Fourier transform infrared spectrometer equipped with CsI optics. Samples were prepared as Nujol mulls and mounted between CsI windows. Laser Raman spectra were obtained with a Spex Triplemate monochromator. The 514.5 nm line of an argon laser, operated at approximately 100 mW, was used to obtain spectra; a Princeton Instruments liquid nitrogen-cooled CCD array detector was employed with an integration time of 30 s. The Raman spectra were obtained at ambient conditions from solid samples packed in capillary tubes. XPS data were collected with a Physical Electronics Industries 5500 multitechnique surface analysis system using a monochromatic MgK α source; binding energies were calibrated with adventitious carbon assuming C 1s = 284.6 eV. Powder X-ray diffraction data were obtained with a Philips ADP3520 θ–2θ diffractometer using CuK α radiation. The samples were loaded into a specially designed sample holder for reactive solids and sealed while in a drybox.

Quantitative elemental analyses for La, Mo, and S were completed with an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers and operated at 10 kV and 25 nA. All powder samples were loaded in a drybox on double-stick carbon discs and placed in a sealed sample holder designed for air-sensitive samples prior to transfer to the microprobe instrument. Peak profiles and backgrounds were measured for standards immediately before the analyses. At least ten regions for each sample were analyzed, and the compositional data were averaged.

The surface areas of the catalysts were determined according to the BET method using a Micromeritics ASAP 2010 instrument. N$_2$ (at −78°C) was used as the adsorbate.

2.4. Reactor design and analytical equipment

The reactor system used in these studies consisted of a 1/4 in. diameter stainless-steel reac-

tor fitted with Nupro valves to allow for catalyst loading in an inert atmosphere drybox. All gas flows were metered through Tylan RC-260 mass flow controllers, and the thiophene was fed with a Sage 341 syringe pump. Product separation and analysis were performed on an n-octane/Porasil C column and an Antek 310 gas chromatograph with flame ionization detector. Peak areas were measured by a Hewlett-Packard 3390A integrator.

The HDS reactor set-up was modified for benzo[b]thiophene (BT) studies without contamination of the existing thiophene system. Since BT is a solid at room temperature (mp 30–33°C), the BT reservoir was heated to 40°C; the liquid BT was fed with a Sage 341 syringe pump. The BT saturator and all lines to the GC were maintained at 230–250°C. Product separation and analysis were performed using 3% SP-2100DB on a 100–120 mesh Supelcoport packed column in a Varian 3600 gas chromatograph with flame ionization detector and internal integrator.

High-purity He (99.997%) and H_2 (99.997%) were further purified by using copper traps for O_2 removal and 4 Å molecular sieves for drying. Thiophene (99%, Alfa) and benzothiophene (99%, Aldrich) were used as obtained.

2.5. Hydrodesulfurization activity measurements

HDS activities were measured at atmospheric pressure using thiophene and benzothiophene in H_2. The reactor was loaded with fresh catalyst of 0.15–0.425 mm particle size in a drybox and heated from room temperature to 400°C in a mixed He (19 mL/min)–H_2 (22 mL/min) gas flow (STP). This gas flow was replaced by a continuous flow of 2 mol% thiophene or 0.75 mol% benzothiophene in H_2 at 22 mL/min (STP). Gas chromatographic analyses of the product stream were performed after 20 min and then at one hour intervals during the 10 h reaction study. The reactor was purged and cooled in a He stream. The catalysts were removed and stored in an inert-atmosphere drybox

for further characterization by XPS, LRS, and FTIR and for surface area measurements.

3. Results

This research has investigated aspects of the preparation, pretreatment, and catalytic properties of a new family of ternary molybdenum sulfides for use in hydroprocessing. The ternary molybdenum sulfides examined in this research are representative of a new class of compounds having a structural similarity to the Chevrel phases — namely, the Mo_6S_8 cluster unit. An important goal has been to preserve this unique metal cluster structure in the new catalytic materials since the Chevrel phases have been determined to be active and selective materials for HDS. A previously reported [11] low temperature synthetic route has been used to develop stable, high-surface-area metal cluster catalysts which retain molybdenum in a low oxidation state. Stabilization of higher surface areas is very important for industrial applications. The low temperature synthesis route may also lead to further applications of these materials.

3.1. As-prepared LaMoS

The activity, selectivity, and stability of the high surface area LaMoS materials was expected to depend on achieving a stoichiometry similar to that of the Chevrel phase ($LaMo_6S_8$). Several methanol-soluble lanthanum salts were examined for the ion-exchange procedure in order to obtain the desired stoichiometry ($La/Mo_6 = 1$). The results of the microprobe analyses are given in Table 1. Anhydrous $LaCl_3$ in methanol produced materials that were consistently La-deficient ($La/Mo_6 \sim 0.3$), even with use of excess lanthanum chloride. The desired La stoichiometry was obtained using methanol solutions of $LaCl_3 \cdot 7H_2O$ or $La(NO_3)_3 \cdot 6H_2O$ for the ion-exchange reaction. Slightly low sulfur ratios ($S/Mo_6 < 9.5$) were always observed and appeared to be due to a small amount of surface oxygen contamination.

Characterization of the resulting material after ion-exchange was challenging because the samples were amorphous powders. As shown in Fig. 2a, only a broad radial distribution band indicative of the amorphous nature was observed by XRD.

The infrared spectra of both the NaMoS precursor and the as-prepared LaMoS had bands for coordinated alcohol (v_{C-O}) at about 980 cm^{-1} (br); the anti-symmetric T_{1u} Mo–S stretching modes characteristic of the Mo_6S_8 cluster unit were present at about 385 cm^{-1} (Fig. 3).

XPS has been demonstrated to be sensitive to changes in the oxidation state of molybdenum sulfides. A difference of approximately 1.5 eV was observed for the Mo $3d_{5/2}$ binding energies of the Mo_6S_8 cluster compounds and MoS_2.

Fig. 3. FTIR spectra of: (a) the NaMoS precursor and (b) the as-prepared LaMoS showing only bands attributable to coordinated MeOH and the Mo–S stretching mode characteristic of the Mo_6S_8 cluster unit.

Ternary molybdenum sulfides (MMoS) (M = Na, Co, Ni, Sn, Pb, La, Ho) exhibit binding energies in the range 227.2–227.9 eV [11], and Chevrel phases typically have binding energies of 227.3–228.2 eV [3],[13]. The binding energy of (crystalline) MoS_2 has been reported as 229.5 eV [14]. XPS characterization of LaMoS (Fig. 4) indicated that Mo was in a reduced oxidation state (227.6 eV, corrected with respect to the C 1s value). The broad band observed at the lower binding energy side of the Mo 3d doublet was due to the sulfur 2s peak. These results were interesting since the use of a potential oxidizing agent (nitrate) in this preparation apparently did not result in oxidation of the Mo_6S_8 cluster.

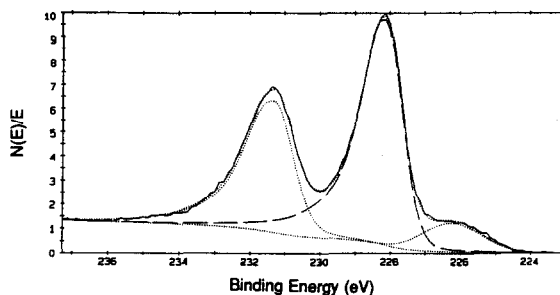Fig. 2. Powder XRD spectrum of: (a) as-prepared LaMoS and (b) the material after a 4 h H_2 pretreatment at 800°C.

Fig. 4. Uncorrected molybdenum 3d XPS spectrum of the as-prepared LaMoS. The broad band observed at the lower binding energy side of the Mo 3d doublet arises from the sulfur 2s peak.

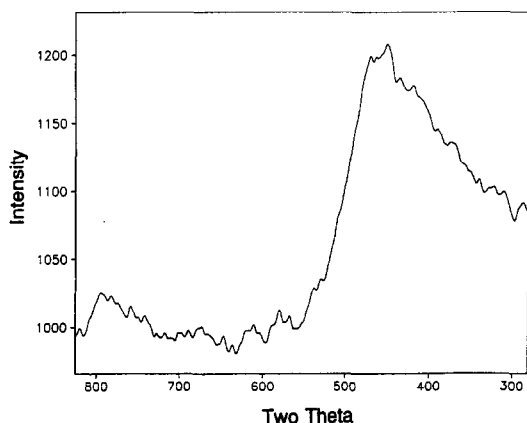Fig. 5. Laser Raman spectrum of the as-prepared LaMoS showing only a broad band attributable to the Mo_6S_8 cluster unit.

Laser Raman spectroscopic characterization (Fig. 5) of the amorphous LaMoS revealed only a very weak, broad band centered about 450 cm^{-1}. Previous studies [8,15] supported the attribution of this broad 450 cm^{-1} band to the Mo_6S_8 cluster unit. The Raman technique has also been used to detect the presence of crystalline or amorphous MoS_2 in catalysts. MoS_2 has Raman bands at 408 and 384 cm^{-1}, which can be observed for unstable Chevrel phase materials after HDS catalysis [3]. No indication of the formation of MoS_2 was apparent in the as-prepared material.

These unsupported LaMoS compounds had initial surface areas of 200 m^2/g; the surface area of the NaMoS precursor was also large (150–175 m^2/g). The low temperature preparation route, therefore, resulted in the production of materials with surface areas that are about two orders of magnitude greater than that observed for the crystalline lanthanum Chevrel phase ($LaMo_6S_8$) prepared by solid state synthesis techniques (about 1 m^2/g) [5]. Use of the three different La(III) salts for ion-exchange resulted in only small changes in the surface areas.

3.2. Pretreatment

Pretreatment studies were undertaken in an attempt to stabilize the higher surface areas while retaining the low Mo oxidation state of the Mo_6S_8 cluster. Stabilization of the Mo_6S_8 cluster with respect to disproportionation (leading to formation of MoS_2) was also important [11]. Pretreatments with H_2 or with a H_2S-H_2 mixture were examined.

Stoichiometric samples ($La/Mo_6 \sim 1.0$) were present after H_2 pretreatment of LaMoS (prepared by ion-exchange from lanthanum nitrate hexahydrate). Table 1 shows nearly identical La/Mo_6 and S/Mo_6 ratios for the as-prepared LaMoS and the product after H_2 pretreatment at 400°C for 4 h.

Surface area measurements (Table 2) indicated that the surface areas decreased from 200 to about 70 m^2/g following H_2 pretreatment at 200°C. A larger surface area loss was observed as the pretreatment temperature was raised; however, even after the 700°C pretreatment, the surface area was high (40 m^2/g).

XRD characterization after the 4 h H_2 pretreatments at temperatures up to 700°C indicated that the materials remained amorphous. Direct H_2 pretreatment at 800°C or further heating of previously pretreated amorphous samples in a sealed tube at 800°C for 2 days produced a crystalline product. The XRD pattern of this product (Fig. 2b) showed diffraction peaks for the $LaMo_6S_8$ Chevrel phase; a few peaks could not be identified. The lattice parameters calculated from the XRD data of this sample ($a_H = 9.131$ and $c_H = 11.550$ Å) were in reasonable agreement with the values reported by Yvon [16] for $LaMo_6S_8$ ($a_H = 9.120$ and $c_H = 11.554$ Å).

A combination of FTIR, XPS, and LRS characterization was used to verify Mo_6S_8 cluster stability with respect to disproportionation (the formation of MoS_2 and Mo metal). The Mo–S stretching band (which could potentially be too diffuse to be apparent with FTIR) was observed for LaMoS after H_2 pretreatment for 4 h at 700°C (Fig. 6a). The characteristic anti-symmetric T_{1u} Mo–S stretching modes were observed at about 375–380 cm^{-1}. This band was similar to that observed for the as-prepared LaMoS and NaMoS precursors (Fig. 3).

Table 2
Thiophene hydrodesulfurization activities (400°C) after 10 h reactor studies

Catalyst	Surface area, m^2/g	Thiophene conversion, %	HDS rate $(mol/m^2 \cdot s)$ $\times 10^8$	n-butane	1-butene	% C_4 products trans 2-butene [a]	Cis 2-butene
LaCl$_3$ preparation							
No pretreatment	201/64 [b]	12.12	1.51	17.1	22.7	35.1	25.1
H$_2$ pretreatment							
400°C, 4 h	42/15	11.57	3.53	7.4	27.8	38.4	26.4
500°C, 6 h	31/13	3.86	1.41	4.4	33.1	38.4	24.2
600°C, 4 h	34/32	6.86	1.19	4.3	21.9	33.5	40.3
La(NO$_3$)$_3$ preparation							
No pretreatment	200/54	2.62	0.32	5.5	41.0	32.4	21.1
H$_2$ pretreatment							
200°C, 4 h	71/48	2.22	0.27	10.9	41.8	28.0	19.3
200°C, 2 h/400°C, 2 h	68/42	6.59	0.90	5.7	34.7	35.3	24.4
400°C, 4 h	56/29	5.28	1.02	4.2	47.6	32.6	15.6
500°C, 4 h	55/37	5.62	0.87	3.3	33.3	39.0	24.3
600°C, 4 h	40/29	2.86	0.54	3.3	45.2	30.1	21.4
700°C, 4 h	44/33	4.54	0.68	8.0	46.2	26.7	19.1
800°C, 4 h	13/12	1.37	0.51	5.3	45.9	29.2	19.5
H$_2$S/H$_2$ pretreatment							
400°C/3% H$_2$S, 4 h	48	7.88	0.73	7.5	30.9	36.3	25.3
400°C/10% H$_2$S, 4 h	46	9.78	0.93	8.6	30.2	35.8	25.4
Reference materials [c]							
LaMo$_6$S$_8$	0.99	0.95	1.18	— [d]	49.4	33.9	16.7
Co–Mo–S	10.83	0.89	3.36	1.5	36.4	41.1	21.0
MoS$_2$	3.40	0.88	1.06	1.8	46.0	34.9	17.3

[a] Trans 2-butene and 1,3-butadiene exhibit identical retention times and are therefore grouped together.
[b] Surface areas reported before and after HDS runs, or after HDS runs where indicated by a single value.
[c] Data from [2–5].
[d] Below detection limit.

For all of these pretreated LaMoS materials, two separate bands were required to fit the XPS Mo 3d$_{5/2}$ envelope, as shown in Fig. 7. In these cases, the bands due to the Mo$_6$S$_8$ cluster unit were generally in the range of 227.4–227.6 eV, while a second state was indicated by higher binding energies of 228.4–228.8 eV. This second component was likely due to an oxidized surface state: the binding energies indicated the formation of an intermediate oxidation state (Mo^{3+}) or a still higher oxidation state characteristic of MoS$_2$ (Mo^{4+}). The binding energy of the intermediate Mo^{3+} species is similar to that of Mo$_2$S$_3$ (Mo 3d$_{5/2}$ = 228.7 eV). An ion-etching experiment in the XPS spectrometer provided evidence that this second species was formed only on the surface and that the bulk material was not oxidized. Studies of LaMoS which had been pretreated with H$_2$ at 500°C showed that the bulk material exclusively had the lower oxidation state for the cluster (227.9 eV).

The LRS spectra of these H$_2$ pretreated samples showed no indication of MoS$_2$ formation up to 800°C (Fig. 8). The spectra show only a broad band centered at about 450 cm^{-1} indicative of the Mo$_6$S$_8$ cluster unit, while peaks for MoS$_2$ at 408 and 387 cm^{-1} are absent.

3.3. HDS activity measurements

Results for continuous-flow reaction studies involving thiophene (Table 2) and benzothiophene (Table 3) conversion are summarized for
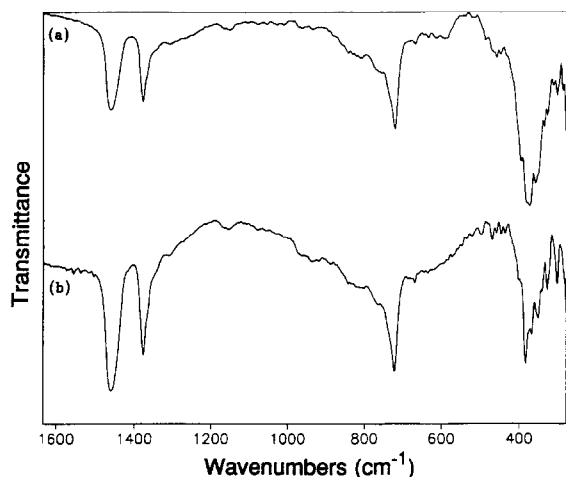
Fig. 6. FTIR spectra of: (a) the LaMoS sample following H_2 pretreatment at 700°C for 4 h and (b) after the HDS reactor study. Both spectra confirm the presence of the Mo–S stretching mode characteristic of the Mo_6S_8 cluster unit.

Fig. 8. Laser Raman spectra of LaMoS samples (nitrate salt preparation) after the following H_2 pretreatment conditions (4 h): (a) 200°C, (b) 400°C, (c) 500°C, (d) 600°C, and (e) 700°C.

the as-prepared LaMoS and for materials after pretreatment. The conversion rates are expressed on the basis of the catalyst surface area.
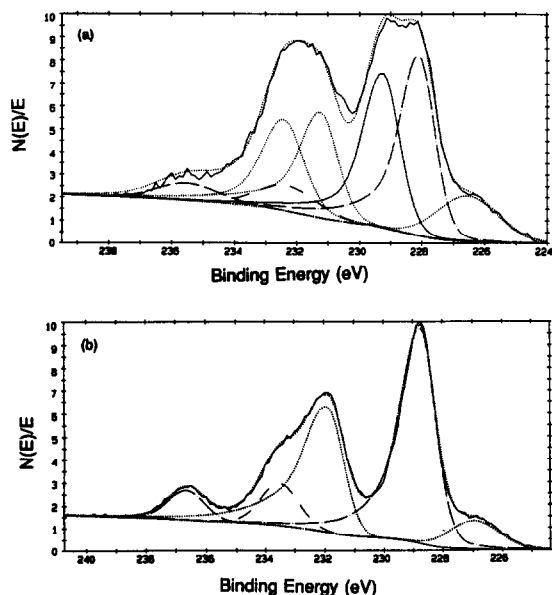

Fig. 7. Uncorrected molybdenum 3d XPS spectra of LaMoS samples (nitrate salt preparation) after H_2 pretreatment (4 h): (a) LaMoS pretreated at 400°C and (b) LaMoS pretreated at 800°C. Corrected Mo 3d binding energies consistent with the Mo_6S_8 cluster unit (227.4 eV) and an intermediate oxidation state species (228.6 eV) are observed for (a), while peaks for Mo_6S_8 and a small amount of surface MoO_3 are noted in (b).
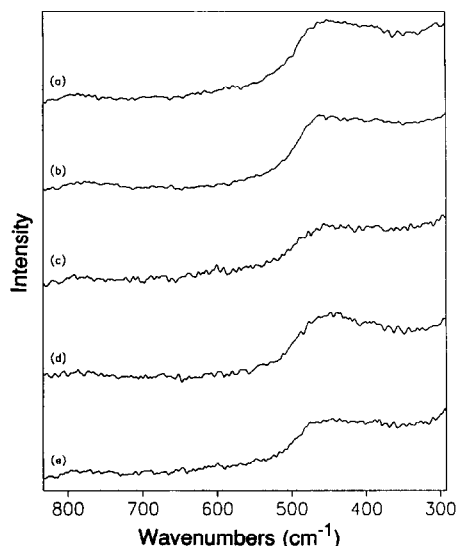
For the thiophene studies, data from two preparative methods are included: the hydrated lanthanum nitrate route and the anhydrous lanthanum chloride. Related results for three unsupported reference materials are offered for comparison.

3.3.1. Hydrogen-pretreated catalysts

The lanthanum nitrate route for preparing LaMoS produced catalysts having rates from $0.3–1.0 \times 10^{-8}$ mol/m$^2 \cdot$ s, depending on the specific pretreatment conditions. The C_4 hydrocarbon product distributions for these catalysts were also somewhat variable. Several materials exhibited product selectivities that were comparable to the conventional $LaMo_6S_8$ Chevrel phase. The hydrogenation activity (with regard to n-butane production) appeared to be noticeably higher for LaMoS: 3–11% n-butane was produced together with moderately large amounts of 1-butene. In contrast, the $LaMo_6S_8$ Chevrel phase exhibited no measurable n-butane production.

Laser Raman characterization of the samples after HDS reaction showed that MoS_2 was not present (Fig. 9). However, some surface oxida-

Table 3
Benzothiophene hydrodesulfurization activities (400°C) after 10 h reactor studies

Catalyst	Surface area, m^2/g	Benzothiophene conversion, %	HDS rate $(mol/m^2 \cdot s) \times 10^8$
La(NO$_3$)$_3$ preparation			
No pretreatment	200/55 [a]	14.0	0.84
H$_2$ pretreatment			
400°C, 4 h	56/40	19.5	0.78
700°C, 4 h	40/31	15.0	1.21
Reference materials			
LaMo$_6$S$_8$	2.2/1.1	11.3	8.55

[a] Surface areas reported before and after HDS runs.

tion had occurred as indicated by XPS (Fig. 10a). The XPS binding energies for the Mo$_6$S$_8$ cluster unit were apparent for the band in the range of 227.5–227.9 eV; but a higher binding energy band was also present at 228.7–229.0 eV. LRS characterization (Fig. 11a) indicated that this second band was not due to MoS$_2$. FTIR examination (Fig. 6b) further confirmed the presence of the Mo$_6$S$_8$ cluster unit.

LaMoS catalysts prepared by the LaCl$_3$ route exhibited HDS rates that were comparable to or even higher than the unsupported reference compounds (Table 2). However, characterization by XPS (Fig. 10b) and LRS (Fig. 11b) following HDS reaction indicated that both MoS$_2$ and the Mo$_6$S$_8$ cluster unit were present

in these materials. The use of hydrated lanthanum chloride resulted in a higher La stoichiometry which aided in the stabilization of the cluster; however, some MoS$_2$ was still detected after the HDS reactor studies.

3.3.2. Hydrogen sulfide / hydrogen-pretreated catalysts

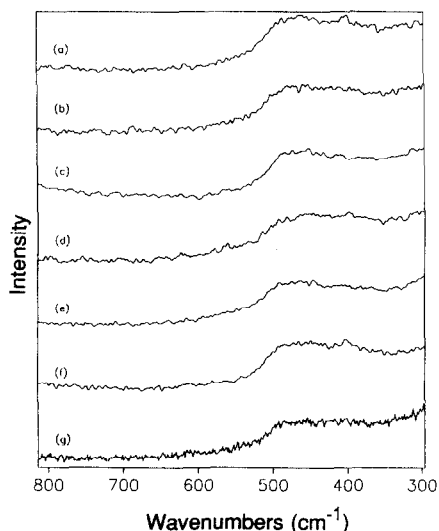The results for mixed gas pretreatment of materials synthesized by the lanthanum nitrate

Fig. 9. Laser Raman spectra of LaMoS samples after the following H$_2$ pretreatment conditions (4 h) and HDS studies: (a) no pretreatment, (b) 200°C, (c) 400°C, (d) 500°C, (e) 600°C, (f) 700°C, and (g) 800°C.
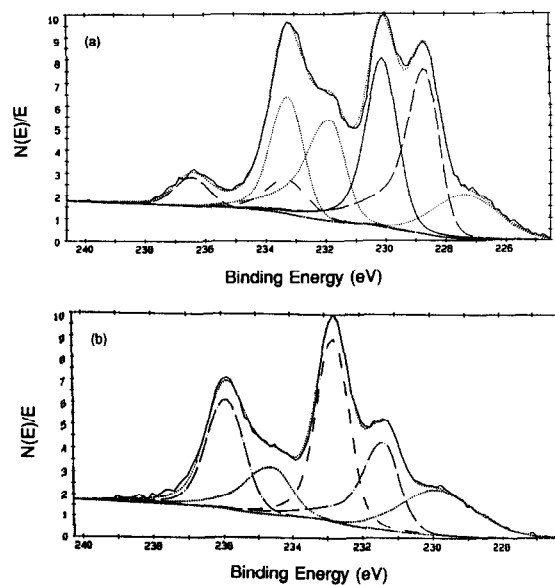
Fig. 10. Uncorrected molybdenum 3d XPS spectra of LaMoS samples after H$_2$ pretreatment (4 h) and HDS studies: (a) nitrate salt preparation of LaMoS and 400°C pretreatment and (b) chloride salt preparation and 600°C pretreatment. Corrected Mo 3d binding energies consistent with the Mo$_6$S$_8$ cluster unit (227.7 eV) and an intermediate oxidation state species (228.8 eV) are observed for (a), while peaks for both Mo$_6$S$_8$ and MoS$_2$ are noted in (b). The broad band observed at the lower binding energy side of the Mo 3d doublets arises from the sulfur 2s peak.
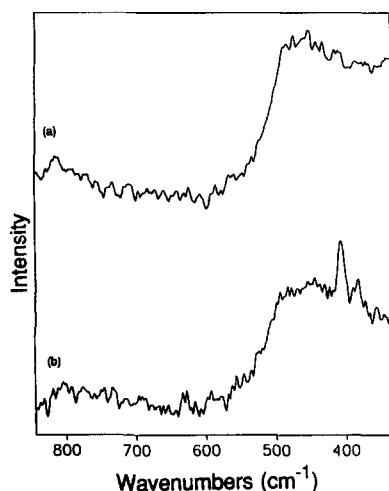
Fig. 11. Laser Raman spectra of LaMoS samples after the following H_2 pretreatment conditions (4 h) and HDS studies: (a) nitrate salt preparation of LaMoS and 400°C pretreatment and (b) chloride salt preparation and 600°C pretreatment. Both spectra show a broad band centered at about 450 cm^{-1} indicative of Mo_6S_8 cluster unit; peaks for MoS_2 at 408 and 387 cm^{-1} are only detected in sample (b).

preparation route are shown in Table 2. Lower HDS activity rates and differing product distributions were detected as compared to the H_2 pretreatment. The addition of H_2S appeared to increase the hydrogenation activity as noted by the higher n-butane production and the lower 1-butene yield. However, characterization of these catalysts by LRS and XPS indicated that MoS_2 was present.

3.3.3. Benzothiophene HDS studies

Benzothiophene (BT) reaction studies for as-prepared LaMoS and after pretreatment at 400°C and 700°C in H_2 demonstrated that the materials were active catalysts (Table 3). As the pretreatment temperature increased, the HDS rate also increased. Neither of the pretreated materials showed rates as high as the $LaMo_6S_8$ Chevrel phase. As expected, the surface areas decreased with increasing pretreatment temperature. XPS and LRS characterization of these samples indicated that the Mo_6S_8 cluster unit was retained; no MoS_2 was detected. Some surface oxidation was observable by XPS, but LRS confirmed that MoS_2 was not present.

4. Discussion

The low temperature synthesis route developed in these studies was based on the observation of a structural similarity between Mo_6Cl_{12} and the Chevrel phases: both contain hexanuclear cluster units as shown in Fig. 1, although the overall structures of the two compounds are quite different. This observation prompted studies of Mo_6Cl_{12} sulfidation in an effort to prepare isolated $Mo_6S_8L_6$ cluster units as precursors to the Chevrel phases [8,9]. During this attempt, the new ternary molybdenum sulfides discussed in this report were discovered.

These reduced ternary lanthanum molybdenum sulfides were determined to be active hydroprocessing catalysts which differ (in terms of composition, structure, oxidation state, etc.) from conventional cobalt- and nickel-promoted molybdenum sulfide catalysts but which are similar to Chevrel phase catalysts. This new synthetic route allows for the preparation of high surface area, amorphous 'pre-Chevrel phase' ternary molybdenum sulfides. For low temperature (200–600°C) pretreatment, the catalysts remained amorphous, although some loss of surface area was observed. Pretreatment at a higher temperature (800°C) resulted in the formation of the crystalline Chevrel phase. Two distinct advantages can be anticipated based on this low temperature synthesis technique: (1) a wide variety of ternary metal ions can potentially be incorporated into these materials [11]; and (2) materials can be produced which have higher surface areas compared to the products of solid state syntheses which can entail sintering of the product.

Surface areas of up to 200 m^2/g were obtained for the as-prepared LaMoS samples, regardless of La source. Hydrogen pretreatment led to some lowering of the surface area but probably helped to prevent disproportionation. This method of pretreatment resulted in active catalysts with surface areas of 30–50 m^2/g after the HDS reactor studies. These surface areas compare with the 1 m^2/g seen for

$LaMo_6S_8$ prepared by the conventional high temperature solid state preparation method.

Characterization of these LaMoS compounds confirmed retention of the Mo_6S_8 octahedral cluster unit. However, after pretreatment of materials prepared by the anhydrous $LaCl_3$ route, some surface decomposition was detected by XPS and LRS; formation of MoS_2 was likely. The low La content of these materials ($La/Mo_6 = 0.3$) could be responsible for the instability. Pretreatment of samples with cation (La) vacancies may destabilize the Mo_6S_8 clusters and result in oxidation of the surface molybdenum. An increase in La content may prevent the formation of these higher Mo oxidation states. Previous work has also revealed this behavior for the Chevrel phases [2–5]. For materials prepared by using the $La(NO_3)_3 \cdot 6H_2O$ ion-exchange procedure, a stoichiometric incorporation of La could be achieved, and subsequent formation of MoS_2 was not observed. The observation of increased stability by using lanthanum nitrate as the La source in the ion-exchange further emphasizes the importance of precursor choice.

The LaMoS materials examined in this study exhibit high activity and selectivity for thiophene HDS at 400°C. Previous studies have shown that some Chevrel phase materials exhibit activities comparable to or greater than the unpromoted and cobalt-promoted MoS_2-based model catalysts [2–5]. Several of the LaMoS catalysts exhibited similar activities to the conventional $LaMo_6S_8$ Chevrel phase. For example, the rate for the 400°C pretreated sample was comparable to that for $LaMo_6S_8$; the 30-fold increase in surface area was maintained. Pretreatment at higher temperatures (400–800°C) appeared to result in catalysts with activities which did not fit an obvious pattern. The apparent lower relative activity of the high surface area LaMoS for the benzothiophene HDS reaction may be due to restricted access of this reactant to surfaces within the small pores. Further work is addressing the porosity and pore structure of these materials.

These LaMoS catalysts are likely to be members of a large family of reduced ternary molybdenum sulfides. Examination of the synthesis and pretreatment conditions will aid in optimization of their composition, surface areas, and catalytic activities. While structurally similar to the Chevrel phases, the as-prepared LaMoS and lower temperature pretreated materials represent a new group of catalytic materials. Higher temperature pretreatment (700–800°C) of these materials to produce the Chevrel phase results in products with much higher surface areas than those found for materials prepared by conventional high temperature methods.

Acknowledgements

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