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Hydrodesulfurization Activity and EXAFS Characterization of Novel Ternary Tin and Lanthanum Molybdenum Sulfide Catalysts

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Reduced tin and lanthanum molybdenum sulfides prepared by a low-temperature synthesis route are active catalysts for hydrodesulfurization (HDS). Hydrogen pretreatment at temperatures below 600 °C produces amorphous materials, while higher temperature pretreatment results in the formation of Chevrel phases. Spectroscopic (FTIR, Raman, XPS) and EXAFS characterization have confirmed that the Mo_6S_8 clusters are the primary structural unit in these ternary molybdenum sulfide catalysts.

Introduction

The demand for low sulfur fuels and petroleum feedstocks and the need for a low aromatic content in diesel fuels and gasoline have stimulated an interest in new hydrodesulfurization (HDS) catalysts. Over the previous 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 studied a new series of hydroprocessing catalysts based on our discovery of the activity of Chevrel phases ($M_xMo_6S_8$).[2,3] The family of Chevrel phase compounds has a characteristic structural unit based on the Mo_6S_8 cluster. The somewhat elongated Mo_6 octahedral clusters are surrounded by eight triply bridging S atoms capping each face (Figure 1). The clusters are interlinked in three-dimensional rhombohedral or triclinic geometries, and cavities within the sulfur network incorporate the ternary metals. The oxidation state of the molybdenum in the Chevrel phases can be varied from +2 ($Mo_6S_8^{4-}$) to +2.67 (Mo_6S_8), depending upon the ternary metal ion stoichiometry. These materials can be described as reduced molybdenum sulfides, relative to MoS_2.

The Chevrel phase compounds have been found to exhibit high activity and selectivity for HDS, often exceeding the performance of unsupported Co−Mo catalysts.[2] Furthermore, Chevrel phases show remarkable stability under the HDS conditions, viz., the low oxidation states are maintained and decomposition or transformation to other Mo sulfides is not observed.[2] Previous synthesis procedures for the Chevrel phases have generally involved solid-state reactions at high temperatures (1000−1300 °C); materials with very low surface areas, typically around 1 m²/g, are formed. However, alternate routes via low-temperature solution precursors have been explored and produced materials that potentially are more useful for industrial applications.[4−8]

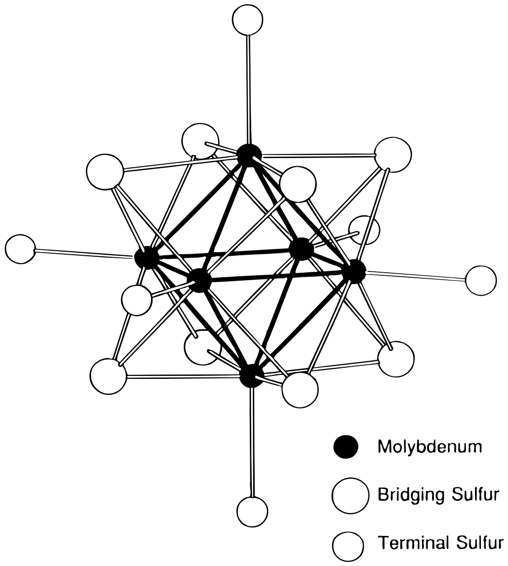

Figure 1. Structure of the Mo_6S_8 hexanuclear cluster unit that is formed by a molybdenum octahedron and eight triply bridging sulfur atoms capping each face. Additionally, six terminal positions are located at the vertexes of the octahedron and are occupied by S atoms upon interlinkage of the clusters.

Our research on the preparation of isolated $Mo_6S_8L_6$ cluster units as precursors to Chevrel phases[5] has

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Table 1. Thiophene Hydrodesulfurization Activities (400 °C) after 10 h Reactor Studies

						%C_4 products	
SnMoS catalyst	surface area, m^2/g	thiophene conversion	HDS rate (mol/m^2 s) × 10^8	*n*-butane	1-butene	*trans*-2-butene[a]	*cis*-2-butene
as-prepared							
no pretreatment	135/9[b]	3.80	1.90	[c]	42.1	25.0	32.9
H_2 pretreatment							
400 °C/3 h	20/7	2.10	1.32	[c]	58.4	19.0	22.6
400 °C/8 h	22/13	1.62	0.55	[c]	42.0	27.1	30.9
400 °C/20 h	7/8	1.19	0.66	[c]	44.9	22.6	32.5
500 °C/4 h	10/6	1.91	1.33	[c]	52.6	17.7	29.7
500 °C/6 h	7/8	1.51	0.70	[c]	47.2	22.5	30.3
500 °C/24 h	5/4	0.79	1.03	[c]	55.8	17.4	26.8
reference materials[d]							
$SnMo_6S_8$	0.39	1.72	3.24	0.5	63.1	21.3	15.1
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 were indicated by a single value. [c]Below detection limit. [d] Data from ref 2.

resulted in the development of a low-temperature synthetic route to a new family of ternary molybdenum sulfides [$M_{2x/n}{}^{n+}(Mo_6S_8)S_x$].[6] EXAFS and other spectroscopic techniques have been used to examine cluster stability during thermal deligation of the isolated $Mo_6S_8L_6$ complexes and to verify the formation of the binary Mo_6S_8 Chevrel phase.[7] Recently, we have reported HDS studies on the ternary lanthanum molybdenum sulfides (LaMoS): active catalysts having remarkably high surface areas were examined for thiophene HDS.[8] Characterization by Raman spectroscopy, FTIR spectroscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and electron microprobe analysis revealed that the catalysts were stable under HDS conditions, although some decrease in surface area was observed.[8] In this paper, EXAFS characterization is reported which was used to examine the structure of the ternary tin and lanthanum molybdenum sulfides prepared by the low-temperature synthesis route. In addition, the activity and selectivity of the tin molybdenum sulfide (SnMoS) compounds are reported for thiophene HDS.

Experimental Section

Materials. The reagents and products have been generally found to be air sensitive. Therefore, all manipulations were performed by the use of an inert-atmosphere drybox, a high-vacuum manifold, and Schlenk techniques, unless otherwise stated. High-yield preparations of the amorphous ternary molybdenum sulfide $Na_{2x}(Mo_6S_8)S_x{\cdot}y$MeOH (with $x = 1.0-1.5$, $y = 4-5$) were performed by the reaction of Mo_6Cl_{12} with NaSH and NaOBu in refluxing *n*-BuOH followed by a MeOH wash to remove the NaCl byproduct.[6] Ion-exchange reactions in methanol of the soluble tin dichloride and lanthanum nitrate hexahydrate salts with the insoluble $Na_{2x}(Mo_6S_8)S_x{\cdot}y$MeOH ($x = 1.0$ for Sn exchange and $x = 1.5$ for La) resulted in the formation of the ternary tin, $SnMo_6S_9{\cdot}x$MeOH (SnMoS), and lanthanum molybdenum sulfide compounds, $LaMo_6S_{9.5}{\cdot}x$MeOH (LaMoS), respectively.[6,8] 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.

The following materials were used as model compounds for EXAFS analysis: MoS_2 (Cerac, 99%) was used as purchased, and $LaMo_6S_8$ was prepared by heating the prescribed mixture of La_2S_3, Mo, and S at 1200 °C for 2 days. Powder X-ray diffraction data for these model compounds were in agreement with prior results.[9,10]

Catalyst Pretreatment. The catalytic performance of SnMoS was examined as-prepared and following a variety of pretreatment conditions. Typical H_2 pretreatment involved placing the SnMoS powder in an alumina boat inside a quartz tube and heating to the desired temperature (400−700 °C) under flowing H_2. After cooling under this flow, the product was stored in an inert-atmosphere drybox. For clarity, a sample of SnMoS pretreated at 400 °C for 3 h will be noted as SnMoS/400 °C/3 h.

Hydrodesulfurization Activity Measurements. HDS activities were measured at atmospheric pressure using thiophene as a model organo−sulfur compound. The reactor system used in these studies has been described previously.[8] A 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 then replaced by a continuous flow of 2 mol % thiophene in H_2 at 22 mL/min (STP). Gas chromatographic analyses of the product stream were performed after 20 min and then at 1 h 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 characterization. Duplicate runs showed a maximum difference of 10% for each sample and the averaged results are given in Table 1.

Physical Characterization. The materials were characterized by infrared (FTIR), laser Raman (LRS), and X-ray photoelectron (XPS) spectroscopic techniques and by powder X-ray diffraction (XRD). 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 20 mW, was used to obtain spectra; a Princeton Instruments liquid nitrogen cooled CCD array detector was employed with an integration time of 200 s. The Raman spectra were obtained at ambient conditions for solid samples packed in capillary tubes. XPS data were collected with a Physical Electronics Industries 5500 multitechnique

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surface analysis system using a monochromatic Mg Kα 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 $\theta-2\theta$ diffractometer using Cu Kα radiation. The samples were loaded into a specially designed sample holder for reactive solids that could be sealed in a drybox.

The surface areas of the compounds were determined according to the BET method using either a Micromeritics 2100E Accusorb or ASAP 2010 instrument. Either N_2 or Kr (at −78 °C) was used as the adsorbate depending upon the surface area regime. Thermal analysis curves were obtained with a Seiko TG/DTA 300. Under flowing argon gas (100 cm^3/min), the samples were heated (3 °C/min) to 600 °C.

EXAFS Characterization. The model compounds and samples were individually ground to a particle size of less than 200 mesh while in an inert-atmosphere drybox. The fine powders were then placed between strips of Kapton tape in aluminum sample holders. All samples were kept under an argon atmosphere in sealed jars until the recording of the absorption spectra. The short-term stability of these samples was observed to be excellent.

Data Collection. The X-ray absorption spectra were recorded at the Cornell High Energy Synchrotron Source (CHESS) on beam-lines B2 and C1 under typical beam conditions of 6 GeV and 120−160 mA. The K absorption edge of Mo was studied using a channel-cut double-crystal monochromator [Si(220) on beam-line B2 and Si(111) on C1] detuned by 50% to avoid the effects of higher harmonics present in the X-ray beam. Energy calibration was performed with Mo metal foil by assigning the inflection point in the absorption edge as 20 000 eV. Measurements were obtained in three energy regions using a step size of 10 eV prior to the edge zone, 1−2 eV over the edge region, and 3−5 eV after this region. An 8 cm long argon-filled ionization chamber was used to measure the incident X-ray flux, while a 30 cm long argon-filled ionization chamber was utilized for the transmitted flux. For the LaMoS studies, transmission data from the Mo foil were further obtained for use as an internal standard. The foil was placed directly behind the sample ionization chamber and data collected with a separate argon-filled ionization chamber. For each sample, 6−10 spectra were obtained.

Data Analysis. The EXAFS data were reduced and analyzed using standard techniques with programs developed by Michalowicz[11] and the University of Washington.[12] The spectra were subjected to background removal and normalization using standard procedures involving application of a linear preedge function, removal of background curvature using a high-order (fifth−sixth) polynomial or spline polynomial, and division of the absorption spectrum into manually selected zones. These procedures were determined to give the best signal-to-noise ratio and minimum mean standard deviation. For all spectra, E_0 was chosen initially as the edge energy and refined during curve fitting of the data as described below.

After removal of the smooth atomic absorption contribution from the data and normalization to the step height, the EXAFS oscillations were Fourier transformed. The Fourier transformation was carried out over the range 4−14 $Å^{-1}$ for all data using a Hanning window function and k^3 weighting. The first two peaks in the transform were isolated and then back-transformed to k space. The filtered oscillations were then subjected to a nonlinear least-squares fit to a parametrized EXAFS expression using two (three where required) shells of Mo, S, and O scatterers. The phase shift and amplitude functions for the model compounds were calculated from the stated programs.[11] These values were then adopted for the samples. Parameters to account for the inelastic mean free Debye−Waller factor, overall scale factor, and photoelectron mean free path were determined from fits for the model compounds; these parameters were fixed for the samples in this study. Quantitative analysis was performed by systematically varying the coordination number N_i (fixed at crystallographic values for the model compounds), the Debye−Waller factor σ_i, and the distance of the ith shell of atoms from the absorber atom R_i.

Results

Previous Spectroscopic Characterization. The synthesis and characterization of the as-prepared tin and lanthanum molybdenum sulfide compounds have been reported.[6,8] X-ray diffraction studies showed only a broad radial distribution band indicative of their amorphous nature. Therefore, spectroscopic characterization was required. The infrared spectra exhibited bands for coordinated methanol (ν_{C-O}) at about 980 cm^{-1} (br); the antisymmetric T_{1u} Mo−S stretching modes characteristic of the Mo_6S_8 cluster unit were present at about 380−383 cm^{-1}. Laser Raman spectra of these ternary molybdenum sulfides showed only a very weak, broad band centered at about 450 cm^{-1}. Decomposition of the sample into MoS_2 was not believed to occur because of the absence of characteristic MoS_2 bands at 406 and 382 cm^{-1}.[2] Previous Raman studies have assigned a broad band at about 450 cm^{-1} to the Mo_6S_8 cluster unit.[2,6,7]

XPS is sensitive to changes in the oxidation state of molybdenum sulfides. A difference of approximately 1.5 eV was observed between the Mo $3d_{5/2}$ binding energies for the Mo_6S_8 cluster compounds and those for MoS_2, a possible decomposition product. Thus, mixtures of these two phases could be easily characterized. XPS characterization showed binding energies for the amorphous ternary molybdenum sulfides (MMoS, M = Na, Co, Ni, Sn, Pb, La, Ho) in the range 227.2−227.9 eV.[6] Crystalline Chevrel phase binding energies were found to be in the range 227.3−228.2 eV.[2b,13] In comparison, the binding energy of (crystalline) MoS_2 has been reported to be 229.5 eV.[14]

Surface Area. The as-prepared SnMoS compound had an initial surface area of about 135 m^2/g, which was lower than the values observed for either the NaMoS precursors (150−175 m^2/g) or the LaMoS phase (200 m^2/g). These surface areas were over 2 orders of magnitude greater than those observed for the crystalline Chevrel phases prepared by high-temperature synthetic techniques (about 0.4−1.0 m^2/g).[2]

Thermolysis Studies. TG/DTA curves for the as-prepared SnMoS and LaMoS are shown in Figure 2. Only a small weight loss (∼2%) below 150 °C was observed in the TG/DTA curves, which indicated that little free methanol was present in these materials. The curves also showed that methanol was removed from SnMoS at lower temperatures than for LaMoS: about 50% of the total weight loss occurred at about 300 °C for SnMoS and about 400 °C for LaMoS. The observed weight loss of 12.3% for SnMoS corresponded to the removal of about four methanol molecules or three methanol molecules and one sulfur atom, while the weight loss of 15.0% for LaMoS corresponded to the

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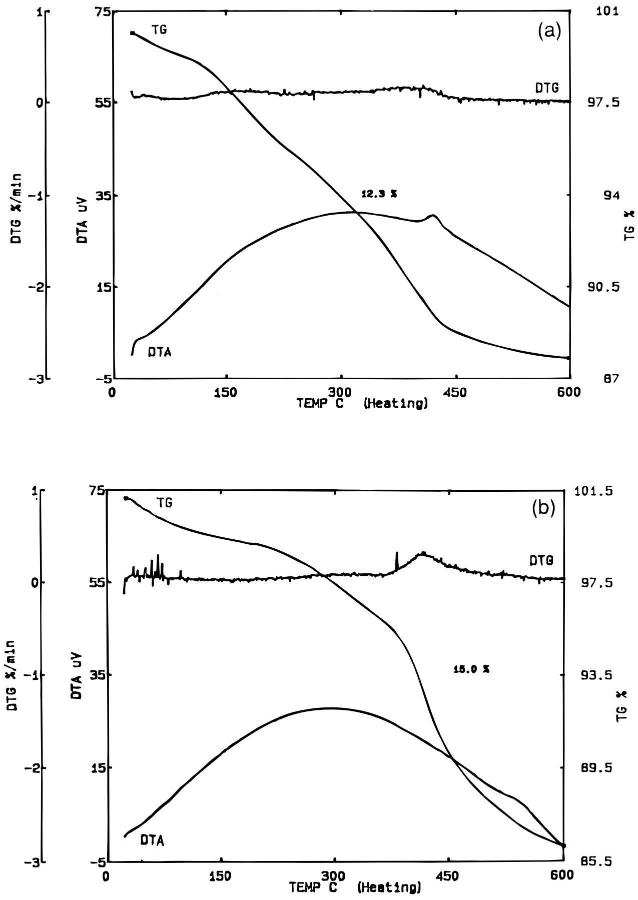

Figure 2. Thermogravimetric analyses of the as-prepared (a) SnMoS and (b) LaMoS.

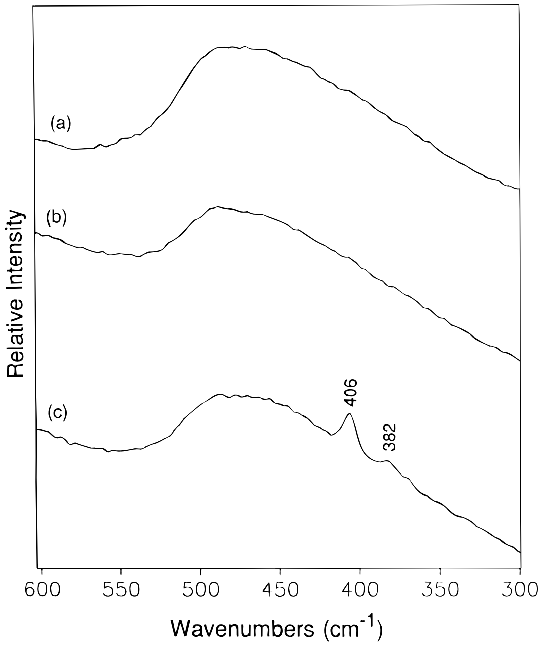

Figure 3. Laser Raman spectra of SnMoS samples after H_2 pretreatment at 400 °C for 3 h (a) and following HDS reactor study (b). The broad peak is characteristic of the Mo_6S_8 cluster unit. The presence of MoS_2 is shown by the peaks at 406 and 382 cm^{-1} for SnMoS after pretreatment at 400 °C for 20 h and HDS study (c).

removal of about five methanol molecules or four methanol molecules and 1.5 sulfur atoms. Temperature-programmed gas evolution studies[15] demonstrated noticeable gas evolution at higher temperatures (200–400 °C) which further supported the presence of strongly held methanol.

Hydrogen Pretreatment. Pretreatment conditions for SnMoS materials were studied in an attempt to stabilize higher surface areas while retaining the low Mo oxidation state of the Mo_6S_8 cluster. If this pretreatment could also remove methanol and excess sulfide and produce materials similar to $SnMo_6S_8$, then stabilization of the Mo_6S_8 cluster might be achieved.[6] In previous studies, hydrogen pretreatment of the LaMoS compounds at 200–700 °C yielded amorphous materials that retained the lower Mo oxidation states characteristic of the Mo_6S_8 clusters. A fairly high surface area (40–70 m^2/g) was maintained.[8]

BET surface area measurements (Table 1) indicated that the surface areas of the SnMoS materials decreased from 135 (as-prepared) to about 20 m^2/g following H_2 pretreatment at 400 °C for up to 8 h. A larger surface area loss (to 5–10 m^2/g) was observed for longer pretreatments at 400 °C or for a pretreatment temperature of 500 °C.

XRD characterization after H_2 pretreatment at temperatures up to 500 °C indicated that the SnMoS materials apparently remained amorphous, while pretreatment at 600 °C or above produced a product with crystalline phases.[6] The XRD pattern of this higher temperature product showed diffraction peaks for $SnMo_6S_8$, Sn, and Mo; lattice parameters calculated from the observed reflections were in excellent agreement with those reported for the tin Chevrel phase.[6] In comparison, hydrogen pretreatment of LaMoS at 800 °C was necessary to produce $LaMo_6S_8$.[8]

FTIR, LRS, and XPS were used to verify Mo_6S_8 cluster stability with respect to disproportionation (formation of MoS_2 and Mo metal). The characteristic infrared Mo–S stretching band was observed at about 375–385 cm^{-1} for the SnMoS samples after H_2 pretreatment. Laser Raman characterization of the samples did not indicate any detectable degree of MoS_2 formation (Figure 3a). For almost all of the pretreated SnMoS materials, two separate bands were required to fit the XPS Mo $3d_{5/2}$ envelope, as shown in Figure 4a. In these cases, a band due to the Mo_6S_8 cluster unit was generally in the range 227.4–227.8 eV, while a second weaker component at higher binding energy was likely due to an oxidized surface state. The higher binding energy of this second state was indicative of either an intermediate oxidation state (Mo^{3+}) or a still higher oxidation state characteristic of MoS_2 (Mo^{4+}). Similar results were observed for the pretreatment studies on the ternary lanthanum molybdenum sulfides.[8]

HDS Activity Measurements. Results for continuous-flow reaction studies involving thiophene (Table 1) conversion are summarized for the as-prepared SnMoS and for materials after hydrogen pretreatment. Results for the lanthanum materials have been reported previously.[8] The conversion rates are expressed on the basis of the catalyst surface area. Related results for three reference materials are offered for comparison.

The HDS results showed catalysts having rates from 0.55 to 1.90 × 10^{-8} mol/m^2 s, depending on the specific pretreatment conditions. These rates indicated high activity, but they were lower than those for the $SnMo_6S_8$

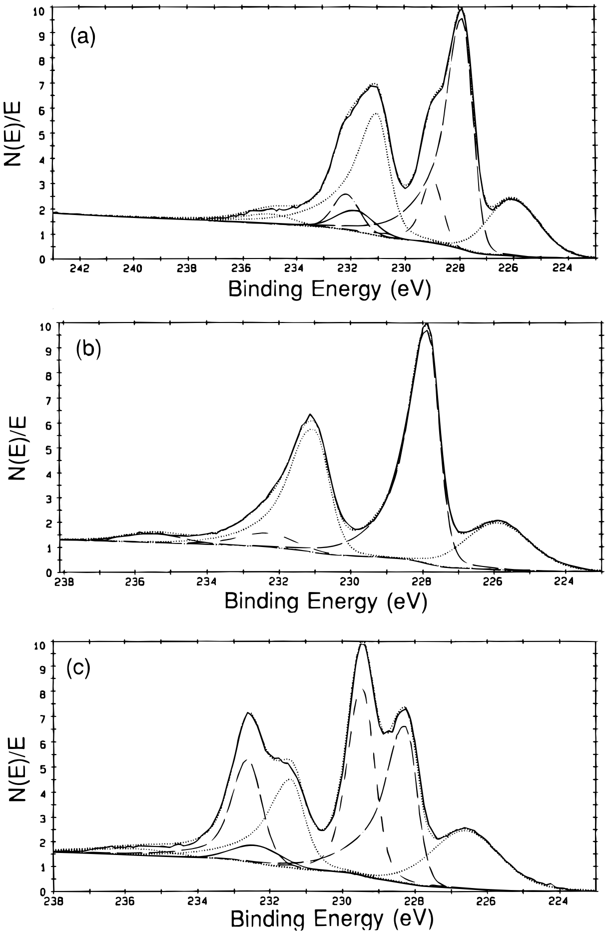

Figure 4. Uncorrected molybdenum 3d XPS spectra of SnMoS samples after H_2 pretreatment at 400 °C for 3 h (a), SnMoS/400 °C/3 h following the HDS reactor study (b), and for SnMoS/400 °C/20 h following the HDS reactor study (c). Corrected Mo 3d binding energies consistent with the Mo_6S_8 cluster unit (227.7 eV) and an intermediate oxidation state species (228.8 eV) are observed for (a), while only the peak for the Mo_6S_8 cluster (227.8 eV) is detected after HDS (b). Peaks for the Mo_6S_8 cluster (228.3 eV) and MoS_2 (229.4 eV) are noted in (c). The broad band observed at the lower binding energy side of the Mo 3d doublets arises from the sulfur 2s peak.

Chevrel phase, expressed on a surface area basis. The C_4 hydrocarbon product distributions for these catalysts were somewhat variable with general ranges of 0% *n*-butane, 42−58% 1-butene, 17−27% *trans*-2-butene, and 23−33% *cis*-2-butene. In comparison to the conventional $SnMo_6S_8$ Chevrel phase, the 1-butene production was noticeably lower and the *cis*-2-butene production was larger. Hydrogenation activity with respect to *n*-butane production was negligible. The LaMoS pretreated catalysts had lower HDS rates in general, but the hydrogenation activity (3−11% *n*-butane production) was higher.[8]

Laser Raman characterization (Figure 3b,c) showed the presence of only the Mo_6S_8 cluster unit in the SnMoS/400 °C/3 h sample and a mixture of the cluster unit and MoS_2 in the SnMoS/400 °C/20 h sample. Three other samples indicated the presence of MoS_2: SnMoS/no pretreatment, SnMoS/400 °C/8 h, and SnMoS/500 °C/6 h. Confirmation of the Raman results was provided by an examination of the XPS data (Figure 4b,c). Characterization after HDS indicated that the SnMoS samples were less stable than the LaMoS materials. Furthermore, the resulting surface areas (4−13 m^2/g) were noticeably lower.

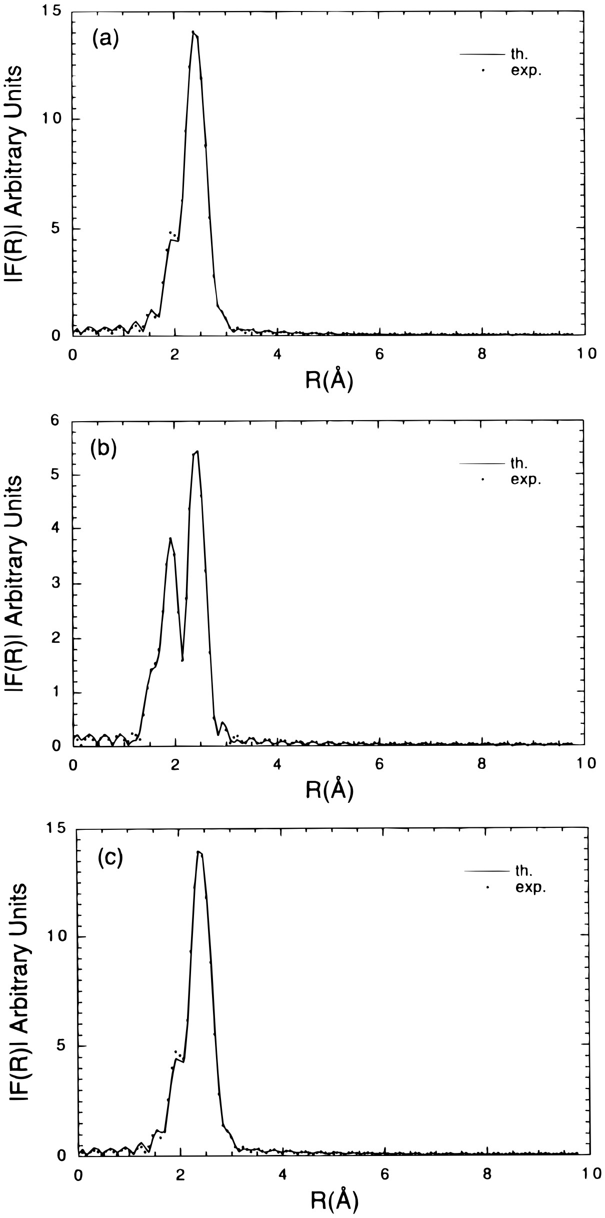

Figure 5. Fourier transformed EXAFS data (dotted curve) and best-fit results of curve fitting (solid curve) for (a) LaMoS, (b) LaMoS/700 °C/4 h, and (c) $LaMo_6S_8$.

EXAFS Study. EXAFS was utilized to gain an understanding of the local environment in these amorphous ternary tin and lanthanum molybdenum sulfide compounds. The spectroscopic techniques (FTIR, LRS, XPS) strongly supported retention of the Mo_6S_8 cluster unit in the majority of the compounds examined. Yet, these tools did not unambiguously prove that the cluster unit was retained in materials treated at higher temperatures (400−700 °C). Earlier studies in our labs showed the efficacy of using EXAFS in conjunction with these other spectroscopic techniques in order to examine the changes occurring upon thermal deligation of isolated molybdenum sulfide cluster units and formation of the binary Mo_6S_8 Chevrel phase.[7] Fourier transformed EXAFS data for the lanthanum and tin molybdenum sulfides are shown in Figures 5 and 7, respec-

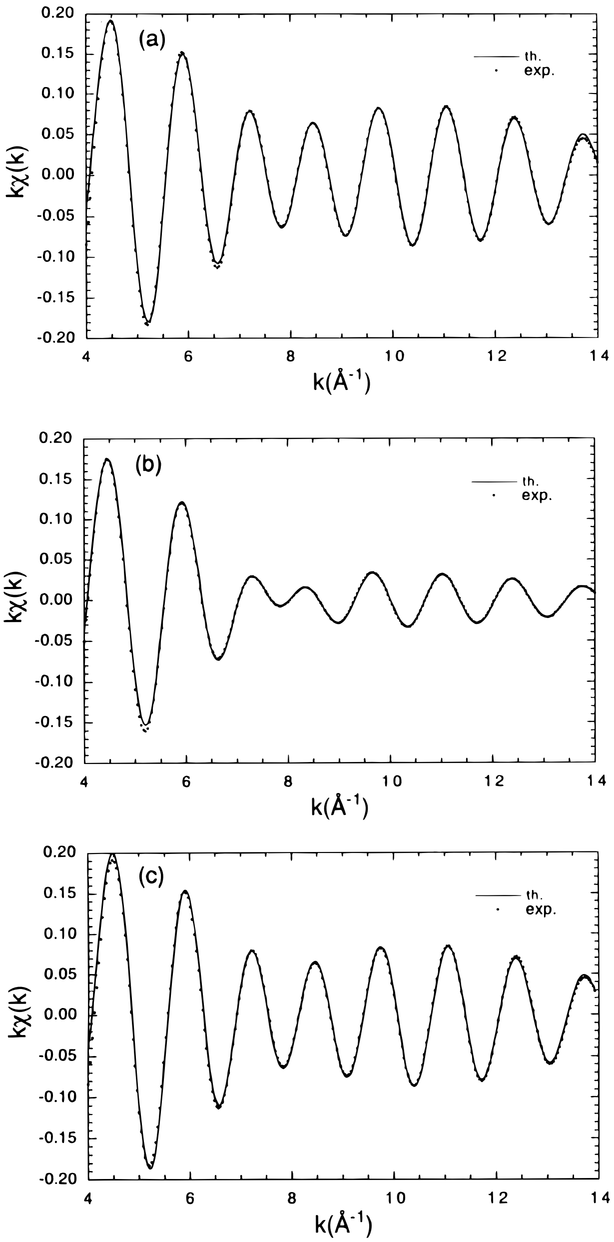

Figure 6. Filtered data (dotted curve) and best-fit results of curve fitting (solid curve) for EXAFS of (a) LaMoS, (b) LaMoS/700 °C/4 h, and (c) $LaMo_6S_8$.

tively, while the background subtracted and normalized data are shown in Figures 6 and 8.

A. Model Compounds. The results of nonlinear least-squares fitting for the MoS_2 data (Table 2) were consistent with bond distances derived from the reported crystallographic structure determinations[9b] and previous studies.[7]

The bond distances derived from fitting the EXAFS data for the $LaMo_6S_8$ Chevrel phase were in excellent agreement with crystallographic values. Elongation of the Mo_6S_8 cluster unit along the 3-fold axis was observed to be smaller in the ternary Chevrel phases, which causes less distortion of the cluster units in $LaMo_6S_8$ as compared to Mo_6S_8.[7] This phenomenon allowed for the consolidation of two Mo–Mo distances (2.67, 2.71 Å) into a single shell and produced a large inequivalency in the Mo–S distances. Thus two S shells were needed to fit the data. The powder XRD pattern was entirely consistent with that expected for hexagonal $LaMo_6S_8$. In this structure, each Mo atom is bonded to one Mo atom from a neighboring cluster at a distance of 3.24 Å. However, the Mo shell representing this feature exhibited a low *N* value of 0.2 when the occupancy was allowed to vary. Attempts to fix this occupation number at the expected value of 1.0 led to consistent misfitting of the data curves. This result could imply that the EXAFS fitting is much less sensitive to the longer range intercluster Mo–Mo bonding interactions and thus leads to greater uncertainties in the occupation number.

B. LaMoS Compounds. LaMoS materials (as-prepared and after H_2 pretreatment at 700 °C for 4 h) were examined to determine the effect of pretreatment conditions on the formation of the $LaMo_6S_8$ Chevrel phase. The bond distances derived from nonlinear least-squares fitting on these compounds (Table 2) were consistent with those found in previous EXAFS studies.[7]

As-Prepared LaMoS. Since the Mo_6S_8 clusters are the primary structural unit in the ternary molybdenum sulfides, it was expected that the EXAFS characterization of LaMoS should be quite similar to that of compounds containing the isolated $Mo_6S_8L_6$ cluster units examined previously.[7] The derived bond distances from the intracluster Mo–Mo and Mo–S shells were in good agreement with the values found for the isolated $Mo_6S_8L_6$ clusters. An observed difference was the presence of a S shell characteristic of an intercluster Mo–S bond arising from interactions between the Mo_6S_8 cluster units. The Fourier transformed (FT) and EXAFS spectra (Figures 5a and 6a) were virtually identical with the spectra observed for $LaMo_6S_8$ (Figures 5c and 6c). These results indicated that the local environment around the Mo in the amorphous LaMoS material and the crystalline $LaMo_6S_8$ Chevrel phase were very similar and that the Mo atoms were not bonded to the oxygen atoms of the methanol.

H_2 Pretreated at 700 °C. A previous study showed that H_2 pretreatment at 700 °C resulted in the formation of an amorphous material and that pretreatment at 800 °C was necessary to produce the crystalline $LaMo_6S_8$ Chevrel phase.[8] Since other ternary molybdenum sulfides were converted to the corresponding crystalline Chevrel phases at 600–800 °C,[6,8] the structural nature of this sample was unclear. The local structure could resemble that for $LaMo_6S_8$ and be considered as “poorly crystalline” Chevrel phase; or the materials could exist in a “pre-Chevrel phase” state with an intermediate structure.

EXAFS fitting of the 700 °C pretreated sample produced similar bond distances to the $LaMo_6S_8$ Chevrel phase, yet the larger Debye–Waller factors indicated a more disordered local environment and gave rise to distinct FT and EXAFS spectra (Figures 5b and 6b). The larger degree of disorder may be indicative of the material existing as an intermediate phase, rather than “poorly crystalline” $LaMo_6S_8$. An additional difference was the partial substitution of oxygen for sulfur in the bridging sulfur sites. The significance of the oxygen substitution will be discussed below.

C. SnMoS Compounds. A series of SnMoS materials were examined under a range of reaction conditions: as-prepared, H_2 pretreated at 400–600 °C, and after 10 h HDS reactor studies. A complete listing of the struc-

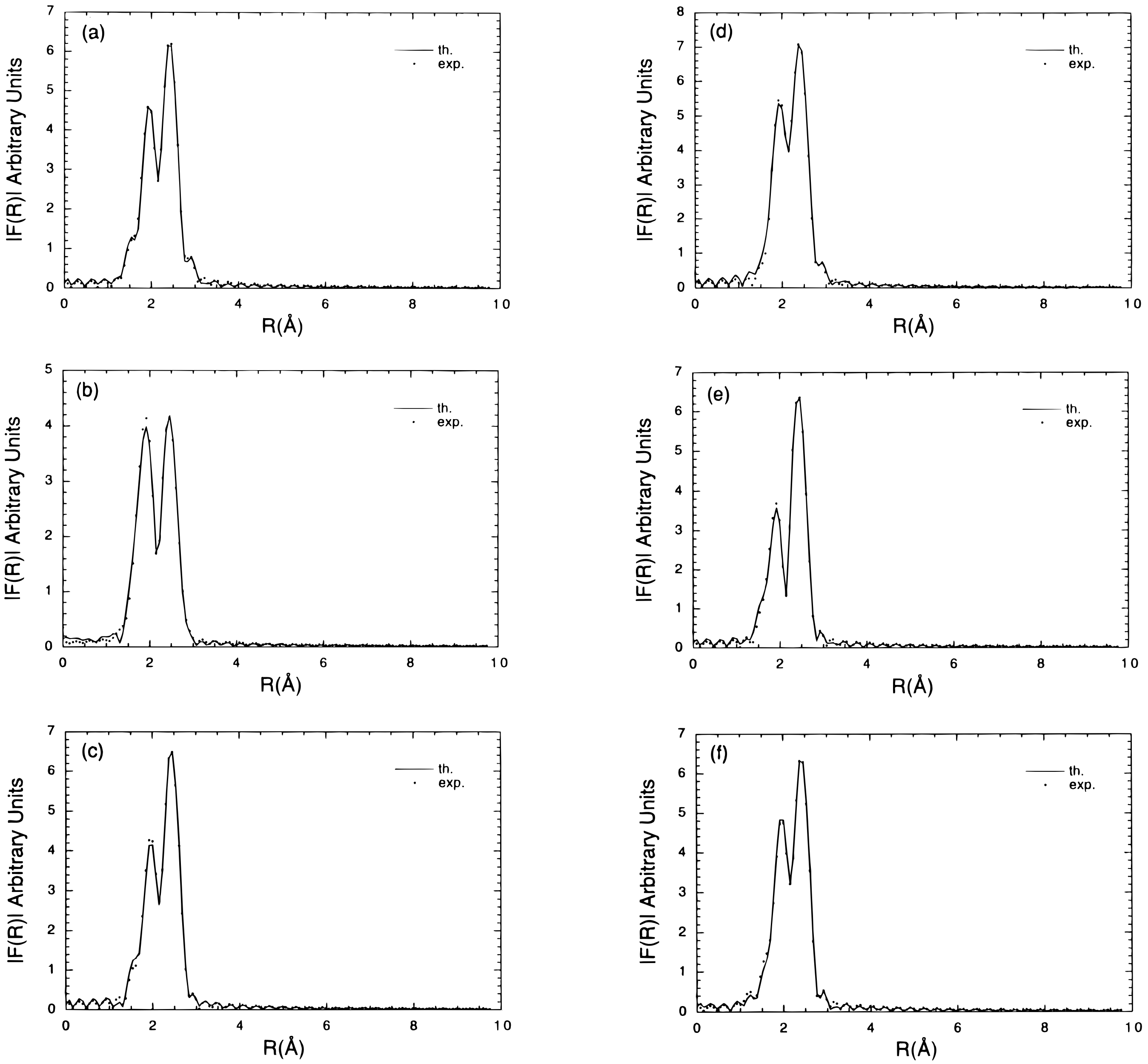

Figure 7. Fourier transformed EXAFS data (dotted curve) and best-fit results of curve fitting (solid curve) for (a) SnMoS, (b) SnMoS/400 °C/3 h, (c) SnMoS/400 °C/20h, (d) SnMoS/500 °C/4 h, (e) SnMoS/400 °C/3 h/HDS, and (f) SnMoS/500 °C/24 h/HDS.

tural parameters is given in Table 3. In the early treatment of data for every sample (except SnMoS/500 °C/24 h/HDS), a misfitting in the smaller *R* (distance) region of the EXAFS spectra was observed. Variation of fitting parameters could not account for this misfit. However, the addition of a Mo−O shell resulted in dramatic improvement in the fitting. At the derived Mo−O distances, this oxygen was concluded to substitute for the triply bridging sulfur (Figure 1), so the oxygen population ($N_{\mathrm{Mo-O}}$) was tied to the sulfur population and allowed to vary from 0 to 0.5 ($N_{\mathrm{Mo-S}} = 3.5-4.0$ for sulfur). Fitting with the addition of the Mo−O shell led to unreasonably large ΔE values in the range 18−20 eV. However, the results were quite comparable when the Debye−Waller factor (σ) and ΔE were fixed at reasonable values for oxygen, viz., $\sigma = 0.066$ Å and $\Delta E = 8.0$ eV. This result indicated that the fitting was relatively insensitive to these oxygen fitting parameters.

As-Prepared SnMoS. As discerned from the data in Tables 2 and 3, the derived structural parameters for the as-prepared SnMoS were quite similar to LaMoS (within experimental error). The only distinct difference noted for the as-prepared SnMoS was the need for a Mo−O shell. The Mo−O distance of 1.78 Å is deceptively short. The average Mo−O distance derived from all of the materials examined, 1.88 Å, is more representative. This value is close to the expected value when O replaces S in the cluster units, based on covalent radii of S (1.04 Å) and O (0.66 Å). The second distance for the Mo−Mo shell is near the expected value for an intercluster bond characteristic of the Chevrel phases.

Hydrogen Pretreatment Effects. Data are presented for the pretreatment of SnMoS at 400−600 °C for time periods ranging from 3 to 24 h. Previously, it was observed that at 600 °C, the first evidence for the

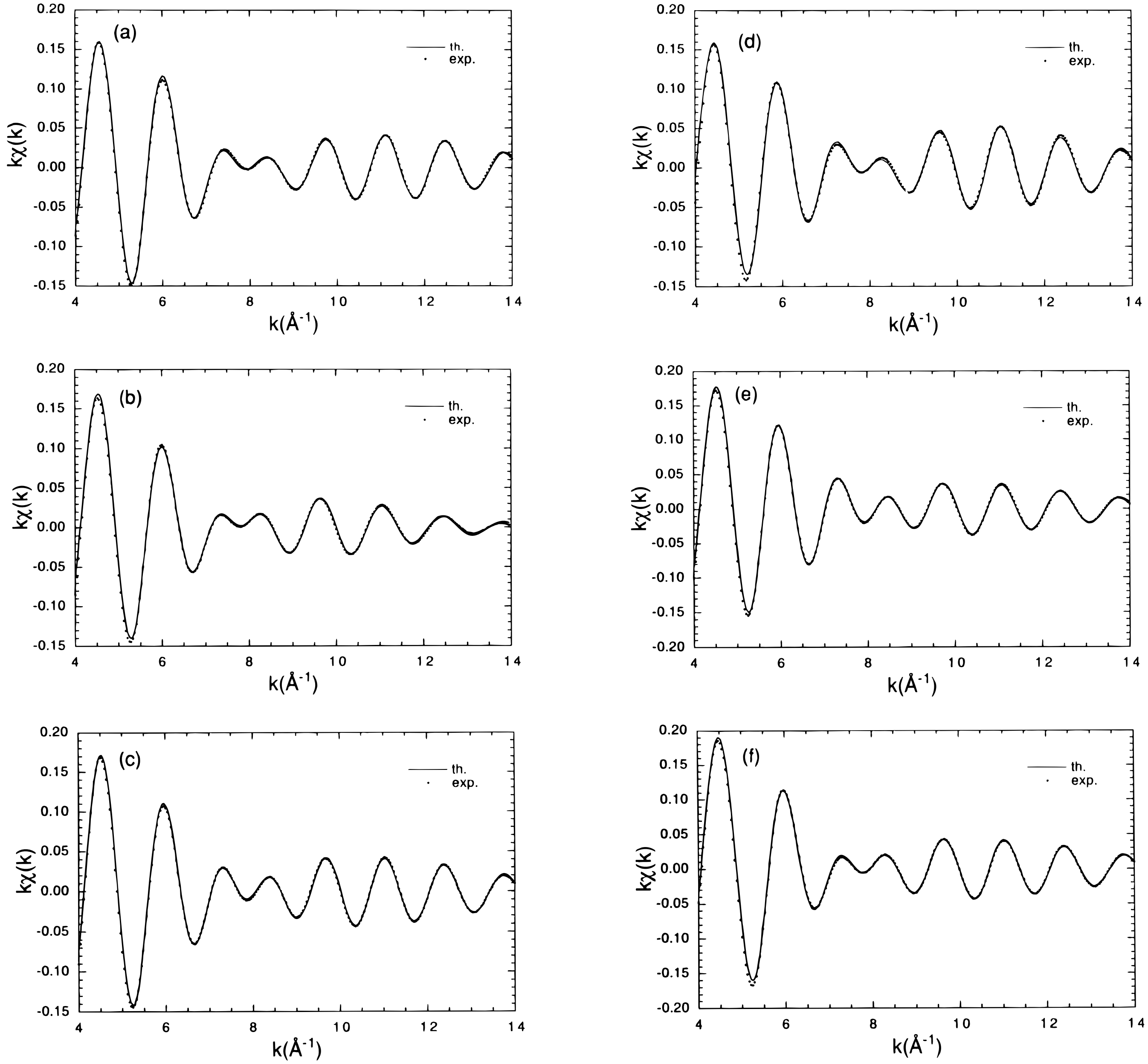

Figure 8. Filtered data (dotted curve) and best-fit results of curve fitting (solid curve) for EXAFS of (a) SnMoS, (b) SnMoS/400 °C/3 h, (c) SnMoS/400 °C/20 h, (d) SnMoS/500 °C/4 h, (e) SnMoS/400 °C/3 h/HDS, and (f) SnMoS/500 °C/24 h/HDS.

formation of the crystalline $SnMo_6S_8$ phase was detected by XRD (along with some reduction and formation of Mo and Sn metal).[6] At lower temperatures (even under extended heating periods of 20−24 h), XRD indicated that the compounds were still amorphous.

Figures 7b−d and 8b−d show very similar FT and EXAFS spectra for samples pretreated at 400 and 500 °C. Only slight changes were observed in intensity and peak positions. The effects are noticeable in the 7−9 $Å^{-1}$ region in Figure 8b−d. Differences in the Mo−S intercluster bond distance seemed to affect these changes.

HDS Reaction Effects. The exposure of the catalysts to thiophene apparently had little effect on the SnMoS sample pretreated at 400 °C for 3 h since the EXAFS structural parameters were very similar. However, the results indicated that the oxygen present in the 500 °C/24 h sample was removed during the HDS reaction. Attempts to fit the data with a Mo−O shell led to a much poorer solution (least-squares fitting diverged). This result indicated that structural differences in the longer pretreated sample allowed for easier reexchange of sulfur for the oxygen. Characterization of these samples by other spectroscopic techniques indicated that MoS_2 was absent.

Discussion

Ternary Molybdenum Sulfide Structural Considerations. On the basis of the EXAFS studies and spectroscopic characterization, insight can be drawn about the structure of the ternary molybdenum sulfides. EXAFS clearly shows that the Mo_6S_8 cluster units are retained under all of the conditions examined. The Mo_6S_8 cluster units are interconnected by Mo−S intercluster bonds. These Mo−S bonds are somewhat longer (2.65−2.70 Å) than found in the Chevrel phases (2.55−2.59 Å), yet the bonding is strong enough to interconnect these clusters and lead to Mo−Mo intercluster bonding.

Table 2. Comparison of Model Compound and LaMoS Structural Parameters Derived from EXAFS Mo-Edge Data[a]

	shell	N	R_{EXAFS}, Å[b]	R_{cryst}, Å	σ, Å	ΔE, eV
models						
MoS_2	S	6	2.43	2.42	0.061	6.7
	Mo	6	3.18	3.16	0.061	3.3
$LaMo_6S_8$	S	4	2.48	2.46	0.068	6.1
	S	1	2.61	2.59		
	Mo	4	2.68	2.67, 2.71	0.061	0.7
	Mo	0.2^c	3.25	3.24		
LaMoS						
as-prepared	S	4	2.48		0.062	6.4
	S	1	2.65			
	Mo	4	2.68		0.062	0.7
	Mo	0.2^c	3.26			
700 °C/4 h	S	3.7^c	2.46		0.068	5.3
	S	1	2.63			
	Mo	4	2.66		0.093	−2.8
	Mo	0.2^c	3.19			
	O	0.3^c	1.83		0.066	8.0

[a] N, number of atoms in the shell; R, distance from Mo absorber; σ, Debye−Waller factor; ΔE, shift in energy origin. [b] Error in the experimental bond distances based on fitting is on the order of ±0.03 Å. [c] Error in the number of atoms based on fitting is on the order of ±0.5.

EXAFS fitting of the SnMoS compounds showed the necessity of adding a Mo−O shell. The short Mo−O distances of 1.8−1.95 Å support substitution of O for S into the triply bridging sites of the cluster unit. Previous studies on the tin Chevrel phase have reported that oxygen could be substituted for sulfur into the triply bridging sites.[16] A number of different compositions were examined for which the maximum degree of oxygen substitution was found to be two, such as M_x-$Mo_6S_6O_2$ (M = Co, Ni, Cu, Pb).[17] Substitution of two oxygens for sulfurs (in the unique positions on the 3-fold axis of the cluster unit) would be equivalent to an EXAFS occupancy (N) equal to 3.0 for sulfur and 1.0 for oxygen. From the oxygen occupancy number, $N = 0.3$, we can estimate a composition of $SnMo_6S_{7.4}O_{0.6}$ for the average degree of substitution in the cluster compounds.

Table 3. Comparison of SnMoS Structural Parameters Derived from EXAFS Mo-Edge Data[a]

	shell	N[c]	R_{EXAFS}, Å[b]	σ, Å	ΔE, eV
SnMoS	S	3.8	2.44	0.062	5.9
as-prepared	S	1	2.70		
	Mo	4	2.64	0.085	−0.9
	Mo	0.4	3.20		
	O	0.2	1.78	0.066	8.0
400 °C/3 h	S	3.7	2.43	0.081	4.7
	S	1	2.58		
	Mo	4	2.68	0.103	2.0
	O	0.3	1.91	0.066	8.0
400 °C/3 h/HDS	S	3.7	2.46	0.069	6.8
	S	1	2.62		
	Mo	4	2.66	0.089	−0.3
	Mo	0.2	3.23		
	O	0.3	1.87	0.066	8.0
400 °C/20 h	S	3.8	2.46	0.063	6.7
	S	1	2.69		
	Mo	4	2.65	0.087	−1.8
	Mo	0.2	3.26		
	O	0.2	1.84	0.066	8.0
500 °C/4 h	S		2.45	0.058	2.6
	S	1	2.66		
	Mo	4	2.66	0.089	−2.3
	Mo	0.4	3.22		
	O	0.5	1.95	0.066	8.0
500 °C/24 h	S	3.7	2.42	0.070	4.2
	S	1	2.56		
	Mo	4	2.68	0.091	2.1
	Mo	0.1	3.25		
	O	0.3	1.92	0.066	8.0
500 °C/24 h/HDS	S	4	2.45	0.067	5.1
	S	1	2.66		
	Mo	4	2.66	0.091	−1.8
	Mo	0.2	3.19		
600 °C/6 h	S	3.6	2.45	0.067	5.5
	S	1	2.67		
	Mo	4	2.67	0.089	−0.4
	Mo	0.3	3.15		
	O	0.4	1.90	0.066	8.0

[a] N, number of atoms in the shell; R, distance from Mo absorber; σ, Debye−Waller factor; ΔE, shift in energy origin. [b] Error in the experimental bond distances based on fitting is on the order of ±0.03 Å. [c] Error in the number of atoms based on fitting is on the order of ±0.5.

The source of oxygen is not completely discernible, yet its presence could arise from the use of alcohols in the preparation. Several different routes of oxygen incorporation can be considered. During the initial preparation of NaMoS, alkoxide species may substitute for sulfides and then convert to oxide by homolytic O−R bond dissociation. Support can be found in the need for an oxygen shell in the fitting of the as-prepared SnMoS. Yet, the absence of an oxygen shell for the as-prepared LaMoS raises equally valid doubts. Lack of EXAFS data on the NaMoS phase prevents a confirmation of this hypothesis. It may be possible for oxygen to be incorporated in the NaMoS but then be removed during the ion-exchange process. However, this result is not very likely considering the low-temperature conditions involved during the ion-exchange process. Similarly, oxygen might also be incorporated during the ion-exchange reaction. Also, the presence of coordinated methanol could lead to solvolysis of the sulfur atoms. This result is more likely at higher temperatures. Thus, questions remain concerning the incorporation of oxygen into the triply bridging sites of the Mo_6S_8 cluster unit. On the other hand, the involvement of cluster atoms, either oxygen or sulfur, in the HDS process is indicated by the removal of cluster-bound oxygen in the SnMoS/500 °C/24 h/HDS sample.

However, the bonding of methanol in these materials is now clarified. It was initially thought that irregular bonding interactions between clusters in these amorphous materials could lead to vacant terminal coordination sites where MeOH could reside and bond weakly to Mo. These sites then would not be involved in intercluster Mo−S bonding between adjacent Mo_6S_8 cluster units. However, the short Mo−O distances (1.8−1.95 Å) found in the EXAFS fitting preclude the presence of terminal Mo−MeOH interactions. For methanol coordinated to molybdenum, the Mo−O distance should be in the range 2.1−2.2 Å. The presence of methanol in these ternary molybdenum sulfides must then arise solely from solvation of the ternary metal ions. Methanol in the coordination sphere of the metal ion is consistent with the method of preparation by ion exchange in methanol, detection of MeOH by FTIR, gas

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evolution at higher temperatures in the thermolysis (TG/DTA and gas evolution) studies, and the absence of longer Mo−O shells in the EXAFS fitting.

Upon removal of methanol by H_2 pretreatment, a material with greatly reduced surface area is obtained. The reduction in surface area may not be caused directly by loss of methanol; rather it may be a result of surface "sintering". Methanol loss and an even larger reduction in surface area are observed when these ternary molybdenum sulfides are washed with H_2O or undergo ion-exchange reactions in H_2O.[18] The loss of MeOH in these two processes may lead to rather different materials. Thus these processes are of considerable interest and are still under investigation.

Conclusions

This paper describes catalytic studies on the ternary tin molybdenum sulfide and EXAFS characterization on the lanthanum and tin molybdenum sulfides after a variety of pretreatment conditions. These materials were found to be active hydrodesulfurization catalysts that are quite different from the conventional cobalt- and nickel-promoted molybdenum disulfide catalysts in terms of composition, structure, oxidation state, etc. They are similar to Chevrel phase catalysts because of the common hexanuclear Mo_6S_8 cluster units. The as-prepared tin and lanthanum molybdenum sulfides represent a new family of compounds that can be considered as "pre-Chevrel phase" materials. After low-temperature (200−500 °C) hydrogen pretreatment, the tin molybdenum sulfide catalysts remained amorphous, although a large loss of surface area was observed. Pretreatment at 600 °C or above resulted in formation of the crystalline tin Chevrel phase.

Tin molybdenum sulfide catalysts were found to be more active (on the basis of catalyst surface area) than the similar lanthanum molybdenum sulfides.[8] However, the tin compounds were also observed to be less stable under the HDS reactor conditions. The EXAFS fitting for the lanthanum and tin molybdenum sulfides clearly showed that the Mo_6S_8 cluster units were the critical structural factor affecting the chemistry of these phases. However, a Mo−O shell with coordination number $N < 1$ was needed to properly fit the data. The short Mo−O bonds indicated that oxygen partially replaced sulfur in the triply bridging cluster positions. The lack of longer Mo−O bonds and the presence of reasonably short intercluster Mo−S bonds provided evidence that the Mo_6S_8 clusters are connected by Mo−S bonding. Methanol was detected by the use of FTIR and was deduced to be coordinated to the ternary metal cations by EXAFS and thermolysis studies. The solvated metal cations may lead to a structural expansion and a larger surface area for the as-prepared ternary molybdenum sulfides. Hydrogen pretreatment at elevated temperatures removed the MeOH and decreased the surface area. Subsequent research involving gas evolution and porosity studies is being conducted to more fully understand the effects of pretreatment conditions and the use of other solvents on the structure and surface area of the ternary molybdenum sulfides.

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