Microstructural Characterization of Highly HDS-Active
Co₆S₈-Pillared Molybdenum Sulfides

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In this work, we have used transmission electron microscopy (TEM) to study Co₆S₈(PPh₃)ₓ-
pillared MoS₂ and have directly observed that the Co clusters can either intercalate into
the bulk or can bind to defect sites at the edges of MoS₂. A distribution of discrete 0.87 nm
scattering centers has been assigned to remnants of the Co₆S₈(PPh₃)₆ clusters. On the basis
of X-ray diffraction (XRD) studies, a lattice expansion of 1.48 nm was expected if the
triphenylphosphine ligands remained intact. The distribution of Co scattering centers,
however, was consistent with that expected for a Co₆S₈ core (0.8 nm). The expansion of the
{001}-MoS₂ planes was almost always localized about a single Co cluster, and the degree of
lattice expansion (0.78 nm) was also consistent with the dimensions of the Co₆S₈ cores,
confirming that the ligands had been nearly completely removed. The organic ligands were
removed either during the vacuum pumpdown in the TEM specimen chamber or almost
immediately upon electron-beam exposure. Additional electron-beam exposures of up to 1 h
caused no further structural changes. The inorganic framework remained intact throughout
the duration of the experiment. The Co₆S₈-pillared MoS₂ materials possessed
dibenzo thiophene (DBT) hydrodesulfurization (HDS) activities that were slightly better than
that of a commercial sulfided Co–Mo/SiO₂ catalyst under low-severity HDS conditions.
However, the selectivity to biphenyl was somewhat poorer than that of commercial
Co–Mo and Ni–Mo catalysts under all conditions examined. The HDS and TEM results suggest
that the role of Co in sulfided Co–Mo catalysts is to prop apart MoS₂ layers, creating a
higher percentage of “rim” sites (in the Daage–Chianelli terminology) and enhancing
hydrogenation capability.

Introduction

Hydrodesulfurization Active Sites Models. Alu-
mina-supported cobalt- and nickel-promoted molybd-
enum sulfides have been the catalysts of choice for the
hydro treatment of crude oils for several decades. As one
progresses from left to right across the periodic table,
the HDS activities of transition metal sulfides pass
through a maximum near Os and Ir.2–5 Most commer-
cial hydro treatment catalysts consist of γ-Al₂O₃-
supported Mo or W sulfides promoted with Co or Ni.
The activity of these mixed-metal sulfides is substan-
tially greater than the weighted averages of the activi-
ties of the monometallic bulk sulfides.

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Mo sulfide raft bound to the support. It is believed that the promoter helps stabilize the Mo sulfide chain and increase the number of vacancies.

Delmon proposed that the active sites for HDS are Mo$^{5+}$ ions located at the interface of MoS$_2$ and Co$_9$S$_8$ domains. According to Delmon, the promotional effect of Co on both supported and unsupported MoS$_2$ catalysts was explained in terms of a "contact synergy" model. This model is based on experiments involving mechanical mixtures of MoS$_2$ and Co$_9$S$_8$ for which a synergistic increase in the activity was observed. It was proposed that the bulk promoter provides sites for hydrogen activation while the Mo sulfide sites utilize this hydrogen to activate aromatic C=S bonds. Inherent in this model is the spillover of hydrogen from the donor (bulk promoter sulfide) to the acceptor (bulk Mo sulfide).

According to the intercalation model, promoter atoms intercalate between layers of MoS$_2$ crystallites, and the primary function of the promoter is to reduce the Mo oxidation state. Topsøe’s "Co–Mo–S" model has many similarities with the intercalation model and has gained acceptance over the past decade. Their model, also known as the pseudointercalation or edge-decorated model, was postulated based on a linear relationship between the HDS activity and the amount of Co on both supported and unsupported MoS$_2$ catalysts prepared by conventional preparation techniques. Their model, activated MoS$_2$ pillared with small Co-containing pillaring agents, is more like clay delamination, with the major difference being that when days restack they form a "house-of-cards" structure, whereas with MoS$_2$ the restacking is more ordered. If prior to the restacking of the MoS$_2$ layers, the pillaring process is more complex. A CH$_2$Cl$_2$/H$_2$O emulsion is formed, with species migration across the liquid interface. Also, "exfoliation" of MoS$_2$ is more like clay delamination, with the major difference being that when days restack they form a "house-of-cards" structure, whereas with MoS$_2$ the restacking is more ordered. If prior to the restacking of the MoS$_2$ layers, one introduces a solution of Co$_9$S$_8$(PPh$_3$)$_6$ in CH$_2$Cl$_2$, then the Co-containing clusters act as pillars to open the MoS$_2$ layers.

DeBeer and co-workers were the first to suggest that the late transition metals, long considered to be "promoters" of Mo in sulfide hydrotreatment catalysts, were actually responsible for the catalysis. This was based upon the following trend in HDS activity: Co/C > Mo$_9$Al$_2$O$_3$ > Co$_9$Al$_2$O$_3$ > MoC (C = activated carbon). Vissers et al. demonstrated that activated carbon was relatively inert as a support compared to γ-Al$_2$O$_3$ and concluded that Co complexes with γ-Al$_2$O$_3$, forming inactive species. If Co is the active species, then the Mo sulfide on γ-Al$_2$O$_3$ is just a complex support for Co. Evaluation of this hypothesis is perhaps best accomplished by varying the degree of dispersion of the MoS$_2$. The Mo sulfide component in alumina-supported catalysts prepared by conventional preparation techniques is mostly S–Mo–S single layer sheets. Some of the MoS$_2$ is multilayered, and the number of MoS$_2$ layers per particle increases with catalyst age.

An alternate way to increase MoS$_2$ dispersion is to prop open the MoS$_2$ layers with small Co-containing clusters. For clay materials, this process of propping open sheets is known as pillaring and consists of swelling (or exfoliating) the layered material with a solvent containing a pillaring agent, followed by evacuation of the swelling solution. During the exfoliation of MoS$_2$, the pillaring process is more complex. A CH$_2$Cl$_2$/H$_2$O emulsion is formed, with species migration across the liquid interface. Also, "exfoliation" of MoS$_2$ is more like clay delamination, with the major difference being that when days restack they form a "house-of-cards" structure, whereas with MoS$_2$ the restacking is more ordered. If prior to the restacking of the MoS$_2$ layers, one introduces a solution of Co$_9$S$_8$(PPh$_3$)$_6$ in CH$_2$Cl$_2$, then the Co-containing clusters act as pillars to open the MoS$_2$ layers.

Daage and Chianelli recently reported a rim-edge model to explain the types of active sites in unpromoted Mo sulfides. If a MoS$_2$ particle is considered to be a stack of several disks, the "rim" sites are those sites that are associated with edges of the top and bottom disks in the stack, and the "edge" sites are those associated with edges of the disks that are "sandwiched" between the top and bottom disks.
Highly HDS-Active Co₆S₈-Pillared Molybdenum Sulfides

Daage and Chianelli, the rim sites are capable of both HDS and HYD (hydrogenation), whereas the edge sites are capable only of HDS. One way to evaluate the validity of Daage and Chianelli’s rim-edge model would be to exfoliate the MoS₂ in the absence of a pillaring agent. One would expect that an exfoliated and flocculated material would contain a higher density of rim sites because the exfoliation/flocculation process increases the basal plane area and hence increases the surface area of MoS₂. Thus, restacked MoS₂ would be expected to be more active but less selective than a nonexfoliated MoS₂ for direct desulfurization of dibenzothiophene to biphenyl. Unfortunately, the rim-edge model does not address the effects of Co or Ni.

Pillared Chalcogenides. Interest in the possibility of generating microporous chalcogenides has been increasing during the past few years, particularly in the field of electronic materials. Several groups, particularly those of Chianelli,37 Frindt,38 Nazar,39-41 Fuentes,42 Curtis,43 and Wypych44 have exfoliated LiₓMoS₂ in H₂O to form a restacked MoS₂, usually with surface areas of 10 m²/g but occasionally as high as 50 m²/g and much higher than the 5–6 m²/g MoS₂ obtainable from commercial vendors. Several reports,39-41,43,45 particularly those of Nazar, have appeared recently on the subject of pillared layered chalcogenides as well. Not until the preparation of this paper had intercalated chalcogenides been tested for hydrodesulfurization activity, however. Curtis43 and co-workers will soon report on materials prepared by exfoliation of LiₓMoS₂ in H₂O followed by flocculation in solutions of simple Co amine, and Co cyclopentadienyl complexes. These materials exhibit thiophene HDS activities comparable to conventionally prepared Co–Mo sulfides, but the Co complexes delintercalate during HDS.

Recently, we reported a new family of materials based on transition-metal dichalcogenides of the type [Co₆Q₈(PR₃)₆]MoS₂ (Q = S, Se; M = Mo, W; R = alkyl, phenyl) prepared as a first step toward pillared layered sulfides.46 The pillars in these materials are the cuboidal Co₆Q₈(PR₃)₆ clusters. The [Co₆Q₈(PR₃)₆]MoS₂ materials are of particular interest in HDS catalysis because they are compositionally similar to the commercial “Co–Mo–S” catalysts and simultaneously represent a structural arrangement between the Co and Mo centers which is different than previously studied. The pillaring process increases the surface area and, thus, may increase the dispersion of potentially active centers. Therefore, the [Co₆Q₈(PR₃)₆]MoS₂ family of compounds presents a unique opportunity to also probe several mechanistic HDS models. In this work, we have directly observed the presence of discrete cobalt-containing entities in the bulk MoS₂ lattice and along (001)-MoS₂ planes in an HDS-active material; in addition, the Co₆Q₈ cluster fragments appear to stay within the MoS₂ lattice during HDS.

Experimental Section

Materials Preparation. LiMoS₂ was prepared using procedures developed previously46 (in 0.25 g batches) under nitrogen in dried Schlenkware using one of two methods described below:

(A) After drying 2H–MoS₂ (Aldrich Chemical, 99+%) under vacuum overnight, the flask was placed under a nitrogen atmosphere. Hexane was refluxed, distilled over CaH₂, and then used to dilute 2.4 M n-BuLi (Aldrich) to 1.0–1.6 M. After stirring at least a 3-fold molar excess of n-BuLi with the 2H–MoS₂ for 3 days, the solution was poured under positive N₂ pressure through a Schlenk frit, filtered under N₂, and rinsed with copious amounts of hexane to remove byproducts and unreacted starting material.

(B) 2H–MoS₂ was ground in a N₂ atmosphere glovebox with a 2.5 molar excess of LiBH₄ and then placed in a quartz tube. The resulting material was heated in a furnace to 300 °C for

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LiMoS$_2$ exfoliates in water via a redox reaction, generating LiOH and H$_2$. After exfoliation of the resulting LiMoS$_2$ in water, centrifugation, and washing three times to remove excess LiOH (final pH $\approx$ 7), the [Co$_{6}$S$_{8}$(PPh$_{3}$)$_{n}$]$_{x}$MoS$_2$ materials were then prepared via the addition of a CH$_2$Cl$_2$ solution of Co$_{6}$S$_{8}$(PPh$_{3}$)$_{n}$ to the aqueous, exfoliated suspension of MoS$_2$ (1:40 or 1:20 molar ratio of cluster to MoS$_2$; $x$ = 0.025 or 0.050 by molar ratio, respectively). Values of $x$ = 0.02 and 0.05 in [Co$_{6}$S$_{8}$(PPh$_{3}$)$_{n}$]$_{x}$MoS$_2$ were determined by elemental analysis, respectively. After 2 days of stirring, the MoS$_2$ flocculated, encapsulating the clusters and collecting at the interface between the solvents. The products were isolated by vacuum filtration and washed with CH$_2$Cl$_2$ to remove any external cluster. The products were then dried under vacuum overnight. For comparison purposes, an Al$_{13}$O$_{4}$(OH)$_{24}$(H$_2$O)$_{12}$$^{7+}$ pillared material was prepared by substituting Al$_{13}$O$_{4}$(OH)$_{24}$$^{7+}$.
(H₂O)₁₂⁷⁺ for Co₆S₈(PPh₃)₆ during the intercalation step.

To deconvolute the effects of structural and electronic promotional effects of the Co₆S₈(PPh₃)₆ clusters on MoS₂, two additional reference samples x-[Co₆S₈(PPh₃)₆]-MoS₂-R (x = 0.02 and 0.05, R = reference) were prepared. For these materials, the MoS₂ layers were restacked prior to the addition of the Co-containing clusters. Because the MoS₂ layers were restacked prior to addition of the Co₆S₈(PPh₃)₆ clusters, and because of the relatively low surface area of the restacked material (10 m²/g), intercalation of the Co₆S₈(PPh₃)₆ into the MoS₂ layers would not be expected to take place. As a result, the morphology of these reference materials would parallel Topsøe’s edge-decoration model,⁶,¹⁵ if the Co-containing clusters did not aggregate. If the Co₆S₈ in the x-[Co₆S₈(PPh₃)₆]-MoS₂-R materials segregated into large, distinct Co₆S₈ domains and if any promotional effect for Co on the HDS activity of MoS₂ was exhibited in these materials, such results would support Delmon’s “contact synergy” hypothesis.⁹ In this hypothesis, Delmon claims that the most active HDS sites lie at the interface between Co₆S₈ and MoS₂ domains. The synthesis of the Co-containing reference materials consisted of exfoliating LiMoS₂, washing twice (by centrifuging, decanting the supernatant, and adding fresh deionized H₂O) to remove the LiOH generated upon exfoliation, and drying the product on a glass slide to yield restacked MoS₂ in 85% yield. After dissolving the Co₆S₈(PPh₃)₆ cluster in CH₂Cl₂, the resulting solution was added to the MoS₂ powder and stirred at room temperature in an open Erlenmeyer flask in the hood until the solvent was evaporated. After adding more solvent and evaporating the additional solvent, the product was stored under N₂ until further use.

Prior to use as a catalyst, the [Co₆S₈(PPh₃)₆]-MoS₂ materials were purged in N₂ at 20 °C for 30 min at 1000 cm³/min, dried in N₂ at 150 °C for 60 min and at 200 °C for 60 min, and then reduced in H₂ for 2 h at 200 °C. Subsequent runs were conducted after prereduction at 250, 300, and 400 °C and after presulfiding in 8% H₂S/H₂ at 300 °C. No substantial differences were observed between the activities after reduction and/or presulfiding. Commercially available oxidized Co–Mo (Crosfield 465) and Ni–Mo (Crosfield 504) were purged in N₂ at 20 °C for 30 min at 1000 cm³/min, dried in N₂ at 150 °C for 60 min and at 400 °C for 60 min, and finally sulfided in a 8% H₂S/H₂ at 400 °C mixture prior to use.

Transmission Electron Microscopy. Approximately 0.01 g of fresh [Co₆S₈(PPh₃)₆]-MoS₂ was placed into a vial containing ~3 mL of 2-propanol. After sonicating for 30 min, several drops of the resulting slurry were pipetted onto 3 mm holey carbon on Cu grids. Once dry, the grids were inserted into nontilt holders and loaded into a JEOL 4000EX II (line-to-line resolution = 0.14 nm, point-to-point resolution = 0.17 nm). The micrographs were in all cases taken at magnifications of either 150000 or 500000 x. The morphologies of the [Co₆S₈(PPh₃)₆]-MoS₂ materials were not noticeably affected by exposure to the 2-propanol when compared to the materials prepared by dipping the grids into the [Co₆S₈(PPh₃)₆]-MoS₂ powder.

After scanning in the micrographs at 400 dpi using an Epson ES-1000C scanner, the measuring tool function in NIH Image 1.59 was used to determine the particle diameters. The distances have been referenced to those for the (001)-1T-MoS₂.
These conditions were chosen so as to mimic those of an industrial middle distillate desulfurization unit. The weight loadings of the Co$_{0.02}$-pillarared MoS$_2$ materials (0.1 g) and the commercial catalysts (1.0 g) have been adjusted so as to make the total metal (Co or Ni + Mo) loadings equivalent.

The liquid products (typically 60 g at 15 g/h per temperature) were weighed for later determination of mass balance closure (95–102%). A small aliquot (≈1 g) and a vial (≈20 g) of product was saved each hour for later analysis. From the small aliquot, 100 mg of product was diluted to 10 mL with hexane, of which 30 μL was diluted further with hexane to 1.00 mL for GC-MS analysis. The diluted products were separated using a DBS-MS column and analyzed using an HP 5890 GC-MS Series II Plus. Random errors associated with GC-MS concentration measurements were less than 5% of the reported values, and the reproducibility of activity measurements was ±15%. The percentage conversions consistently leveled off after less than 2 h time-on-stream. Selectivity is defined as the percentage of biphenyl yield divided by the dibenzothiophene conversion.

**Results**

**Transmission Electron Microscopy.** The pristine MoS$_2$ was composed of highly ordered crystals (Figure 4a). Exfoliation of the MoS$_2$, followed by evacuation of H$_2$O solvent, increased the MoS$_2$ surface area and shortened the length scale for MoS$_2$ ordering, but substantial MoS$_2$ order still remained. In neither the pristine nor restacked MoS$_2$ materials (Figure 4b) were any discrete scattering centers observed, and the number of dislocation faults was relatively low. In contrast to the materials that contained no cobalt clusters, dispersed among the (hk0)-MoS$_2$ planes found in the [Co$_{0.02}$PPh$_3$]$_0$MoS$_2$ were some discrete scattering centers of weak intensity (Figure 4c) of 0.5–1.5 nm in diameter. The Co-containing species in the x[Co$_{0.02}$PPh$_3$]$_0$MoS$_2$–R materials distinctly segregated into large, Co-rich domains (Figure 4d).

The microstructure of the Co$_{0.02}$-intercalated MoS$_2$ material consisted of crystal facets containing the following types of planes: (001)–[Co$_{0.02}$PPh$_3$]$_0$MoS$_2$, (001)-1T-MoS$_2$, {hk0)-1T-MoS$_2$, (002)-2H–MoS$_2$, and (hk0)-2H–MoS$_2$. The 1T and 2H forms of MoS$_2$ cannot be distinguished clearly by the (001) spacings but can be distinguished by their (hk0) planes.

Figure 5 is an image and optical diffraction pattern obtained by Fourier transform, respectively, of a representative region of [Co$_{0.02}$PPh$_3$]$_0$MoS$_2$ containing (hk0), or basal, planes. The inner ring of brighter spots correspond to the (hk0)-1T–MoS$_2$ planes (a = 0.327 nm), and the few faint spots slightly further away from the center of the diffraction are associated with (hk0)-2H–MoS$_2$ planes (a = 0.316 nm). The relative intensities suggested that the percentage of 2H–MoS$_2$ in this material, while present, was low. X-ray diffraction of a freshly restacked material appears to contain only one phase, 1T–MoS$_2$, but this phase is transformed with heat, pressure, or time to the 2H form.

The region of [Co$_{0.02}$PPh$_3$]$_0$MoS$_2$ in Figure 6 appeared to be nearly completely pillared and partially delaminated, although a section within the same pristine (white arrow) was not intercalated at all. This was the only region for which lattice expansion was continuous over any distance longer than a single Co$_{0.02}$PPh$_3$ cluster in the low-loaded [Co$_{0.02}$PPh$_3$]$_0$MoS$_2$ material. Here, the distance between the layers which were...
obviously pillared was $1.39 \pm 0.10$ nm. Arrows indicate scattering centers of 0.5–1.5 nm in diameter.

Several micrographs of the $[\text{Co}_6\text{S}_8\text{(PPh}_3)_n]_{0.02}\text{MoS}_2$ material appeared very similar to those reported for unintercalated MoS$_2$; however, upon closer inspection, the material was composed of locally disturbed MoS$_2$ layers. Arrows in Figures 7 and 8 point to local disruptions in the $\{001\}$-$1\text{T}$-$\text{MoS}_2$ planes.

The size distribution of the discrete scattering centers has been summarized in Figure 9 and Table 2. This distribution was constructed by grouping the data into logarithmically evenly spaced bins ranging from 0.17 to 100 nm. The smallest of these scattering centers was 0.32 nm, barely above our ability to confidently assign such a feature as real. Scattering centers greater than 0.40 nm are certainly real. The size distribution of scattering centers was fitted with a log-normal distribution using the commercially available program PeakFit (Jandel Scientific). The particle size distribution data (points), the computer fit of the data (solid line), and the 95% prediction intervals (dashed lines) have been reported. This 95% prediction interval defines the confidence interval for an individual curve fit. Thus, one would expect that 95 out of 100 individual curve fits would fall within the 95% prediction interval. The abscissa of this histogram has been scaled logarithmically to make the particle size distribution appear Gaussian.

Representative regions of the $[\text{Co}_6\text{S}_8\text{(PPh}_3)_n]_{0.05}\text{MoS}_2$ material appeared quite similar to that observed for the $[\text{Co}_6\text{S}_8\text{(PPh}_3)_n]_{0.02}\text{MoS}_2$. As in Figures 7 and 8, local disruptions in the $\{001\}$-$1\text{T}$-$\text{MoS}_2$ planes (Figure 10) as well as lattice expansions of about 0.9 nm (Figure 11) were common. In the $[\text{Co}_6\text{S}_8\text{(PPh}_3)_n]_{0.05}\text{MoS}_2$ material, the higher loading of Co sometimes resulted in some slightly larger Co$_x$S$_y$ aggregates at the external surface of MoS$_2$ (Figure 10) as well as longer range pillaring of the MoS$_2$ layers. Expulsion and subsequent aggregation of the Co$_6$S$_8$ guests from octahedral $1\text{T}$-$\text{MoS}_2$ occurred concomitantly with the conversion to $2\text{H}$-$\text{MoS}_2$. Such guest expulsion has also been observed for other $[\text{Co}_6\text{Q}_8\text{(PR}_3)_n]_x\text{MS}_2$ ($Q = S, \text{Se}, \text{Te}; M = \text{Mo}, \text{W}; \text{R} = \text{alkyl, phenyl}$) systems.46

Catalytic materials often change during or after use. Figure 12 displays a typical micrograph of the $[\text{Co}_6\text{S}_8\text{(PPh}_3)_n]_{0.02}\text{MoS}_2$ material after use as an HDS catalyst. The degree of Co$_6$S$_8$ pillaring remained relatively constant. The lattice expansion of the MoS$_2$ edge planes appeared to be slightly higher than the expansion before use as a catalyst (0.85 vs 0.78 nm), but certainly this difference is within the experimental error of the measurements. Likewise, it is difficult to say whether the increase in the log-mean diameter of the scattering centers (from 0.87 nm before use to 0.94 nm after use)

**Table 2. TEM Size Distribution of Cobalt Clusters**

<table>
<thead>
<tr>
<th>Material</th>
<th>Log mean (nm)</th>
<th>FWHM (nm)</th>
<th>No. of scatterers</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co}_6\text{S}_8\text{(PPh}_3)<em>n]</em>{0.02}\text{MoS}_2$</td>
<td>0.87 ± 0.03</td>
<td>0.75 ± 0.08</td>
<td>160</td>
</tr>
<tr>
<td>$[\text{Co}_6\text{S}_8\text{(PPh}_3)<em>n]</em>{0.02}\text{MoS}_2$ used</td>
<td>0.94 ± 0.06</td>
<td>0.85 ± 0.10</td>
<td>79</td>
</tr>
<tr>
<td>$[\text{Co}_6\text{S}_8\text{(PPh}_3)<em>n]</em>{0.05}\text{MoS}_2$</td>
<td>0.92 ± 0.07</td>
<td>0.90 ± 0.15</td>
<td>53</td>
</tr>
</tbody>
</table>

*a Reported errors are standard deviations.
attributed to the Co₆S₈ cluster cores was significant. Therefore, from these results, it can be concluded that the Co₆S₈ cluster core pillars remain essentially intact with respect to HDS.

Figures 13 and 14 show the same region of the [Co₆S₈(PPh₃)ₙ]₉₀⁵MoS₂ material after 2 min and after 1 h of electron-beam exposure at 20 pA/cm². There were no substantial differences in the region. Thus, after the first 2 min, there was no detectable electron-beam damage. Electron-beam degradation of the organic ligands during the first 2 min cannot be ruled out, however. The inorganic framework was stable throughout the duration of the experiment.

HDS Activity. Hydrodesulfurization activities for the Co₆S₈-pillared MoS₂ and the commercially available sulfided, promoted Mo catalysts were severely mass-transfer limited at all liquid hourly space velocities tested, at temperatures below 350 °C (Table 3). In the absence of mass-transfer limitations, activity should be independent of liquid hourly space velocity (LHSV).

Figure 10. Edge planes in the [Co₆S₈(PPh₃)ₙ]₉₀⁵MoS₂ material contain even more local disruptions of approximately 1.0 nm in diameter than the [Co₆S₈(PPh₃)ₙ]₉₀²MoS₂ material.

Figure 11. Percentage of completely pillared and partially delaminated layers of [Co₆S₈(PPh₃)ₙ]₉₀⁵MoS₂ increases with Co cluster loading.
Mass-transport limitations were not nearly so dramatic at or above 350 °C, where industrial hydrotreating units typically operate. We have observed this trend for a wide variety of catalysts.\textsuperscript{52}

Despite the mass transport limitations, the Co\textsubscript{6}S\textsubscript{8}-pillared MoS\textsubscript{2} materials possessed higher dibenzothiophene HDS activities than commercial, sulfided Co–Mo and Ni–Mo catalysts at 300 °C and below. Most of this high activity could be attributed to enhanced hydrogenation functionality as indicated by the relatively low selectivities to biphenyl. Biphenyl is the desired, direct desulfurization (C=S bond cleavage) product from dibenzothiophene. The other primary reaction pathway proceeds through saturation of one of
the non-sulfur-containing aromatic rings prior to desulfurization, resulting in cyclohexylbenzene. Such aromatic ring saturation requires more costly hydrogen and is, therefore, not desirable. The direct desulfurization and aromatic ring saturation reaction pathways are shown in eqs 1 and 2, respectively. At higher temperatures where mass-transport limitations were not as significant, the activities and selectivities of the Co$_6$S$_8$-pillared MoS$_2$ materials were competitive with the commercial catalysts.

![Figure 14. Region of [Co$_6$S$_8$(PPh$_3$)$_n$]$_{0.02}$MoS$_2$ shown in Figure 14 after an electron-beam exposure of 1 h at 20 pA/cm$^2$.](image)

**Table 3. Mass Transport Limitations**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[Co$_6$S$_8$(PPh$_3$)$<em>n$]$</em>{0.02}$MoS$_2$</th>
<th>Crosfield 465 (Co–Mo)</th>
<th>Crosfield 504 (Ni–Mo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHSV (h$^{-1}$)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>% conversion at 300 °C</td>
<td>59</td>
<td>31</td>
<td>5</td>
</tr>
<tr>
<td>HDS activity$^a$ at 300 °C</td>
<td>0.40</td>
<td>0.21</td>
<td>0.24</td>
</tr>
</tbody>
</table>

$^a$ Run-to-run conversion reproducibility = ±15% (e.g., 20 ± 3%). Amount of “active” metals in each run = 0.10 g in all cases. $^b$ Activity in g of DBT converted/(g of catalyst) h.

In addition to being competitive with the commercial catalysts, the two Co$_6$S$_8$-pillared MoS$_2$ catalysts were far more active than pristine MoS$_2$, restacked MoS$_2$, and Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}^{7+}$-pillared MoS$_2$ on a per gram of metal basis. Within experimental error, the two Co$_6$S$_8$-pillared MoS$_2$ materials possessed approximately the same reactivity, so no clear relationship between the amount of the Co$_6$S$_8$(PPh$_3$)$_6$ clusters in the material and reactivity could be determined. The restacked MoS$_2$ provided a modest conversion and was significantly better than the pristine MoS$_2$ on a per gram of catalyst basis. Most importantly, if one normalizes the activities by surface area, one finds that the pristine MoS$_2$, restacked MoS$_2$, and the two Co$_6$S$_8$-pillared MoS$_2$ materials all possessed very similar reactivities (Figure 15). The large error bars (95% confidence intervals) in Figure 15 are mostly attributable to a high region-to-region variability in the number of near-edge vacancies. When combined with the relatively low conversions observed for the x-[Co$_6$S$_8$(PPh$_3$)$_n$]–MoS$_2$–R materials (Table 4), our results suggest that, at least in pillared MoS$_2$ materials, the HDS promotional role of Co is largely structural.
Highly HDS-Active Co$_8$S$_8$-Pillared Molybdenum Sulfides

For MoS$_2$, a one would expect the pillaring to separate the layered material over crystal-wide length scales. If the cluster loading were near the stoichiometric limit, the layered material might be very localized. Conversely, one would expect that the disturbance in the structure of the lattice. If the cluster loading was sufficiently low and the clusters were uniformly dispersed, then one would expect the pillaring density and the rigidity of the host lattice. The large error bars for the concentration of edge lattice disruptions take into account not only the error associated with variability in the concentration of lattice disruptions within the edge planes but also region-to-region variability in the percentage of edge planes.

Discussion

Transmission Electron Microscopy. Whether or not the intercalated regions would be separated by regions with unexpanded lattice spacings is dependent on the pillaring density and the rigidity of the host lattice. If the cluster loading was sufficiently low and the clusters were uniformly dispersed, then one would expect that the disturbance in the structure of the layered material might be very localized. Conversely, if the cluster loading were near the stoichiometric limit, one would expect the pillaring to separate the layered material over crystal-wide length scales. For MoS$_2$, a lubricant, the critical pillar concentration is likely higher than for more rigid compounds such as pillared clays.

The presence of Co clusters could be theoretically detected in two ways. Because of the lower atomic number (relative to Mo) and the molecular nature of the clusters, one would certainly expect the Co scattering to be relatively weak in intensity (if detectable) and discrete relative to the MoS$_2$ layers. For crystals in which the (h0I)-MoS$_2$ planes were observed, Co might be detected as discrete scattering centers of the size of the Co$_8$S$_8$ core. (The PPh$_3$ ligands, if still there, would not likely scatter sufficiently to be detected by TEM). As can be seen in Figure 16, the diameter of the Co$_8$S$_8$ core is approximately 0.8 nm, whereas the diameter of the Co$_8$S$_8$(PPh$_3$)$_6$ cluster precursors is 1.48 nm.

The encapsulation of the Co cluster expands the MoS$_2$ lattice spacing only locally for the most part at low Co cluster loadings (0.12 Co atoms per Mo), whereas at intermediate loadings (0.30 Co atoms per Mo), MoS$_2$ layers were often separated by 0.8 nm for lengths of 5–10 nm. No evidence for Co-containing phases was observed external to MoS$_2$ domains. In fact, the excellent agreement between the size of the intercalating center and the size of a Co$_8$S$_8$ cluster core (0.8 nm) is strong evidence that the clusters were, for the most part, molecularly dispersed throughout the MoS$_2$ matrix.

The presence of Co$_8$S$_8$ clusters could be detected far more easily by the expansion of the (001)-1T–MoS$_2$ planes from 0.615 nm to some larger distance. Such lattice expansion would be consistent with Co cluster intercalation between MoS$_2$ lamellae near the edges of the MoS$_2$ layers. The distance associated with such expansion—0.615–MoS$_2$ planes could vary from approximately 1.4 nm (for sections from which the triphenylphosphine ligands have been completely removed) to 2.1 nm, the distance for 001-|Co$_8$S$_8$-(PPh$_3$)$_6$|MoS$_2$ planes determined from X-ray diffraction (XRD). Lengths between 1.4 and 2.1 nm would indicate partial loss of the triphenylphosphine ligands. The average distance between layers in the region which appeared to be nearly completely pillared was 1.46 ± 0.10 nm, corresponding to a lattice expansion of 0.78 ± 0.10 nm and confirming that the triphenylphosphine ligands had been completely removed either prior to or during TEM examination. In the case of the |Co$_8$S$_8$-(PPh$_3$)$_6$|MoS$_2$ materials, vacuum pumpdown might have evolved the triphenylphosphine ligands. Electron-beam degradation of the triphenylphosphine ligands cannot be ruled out during the first 2 min of the TEM experiments, however.

Several TEM studies of pillared days have been reported. Typically, these have involved the addition of an aluminum Keggin ion, Al$_{13}$O$_4$(OH)$_{24}$(H$_2$O)$_{12}$H$_2$O, into a clay matrix. Gil et al. have reported mean percent conversion (biphenyl selectivity)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>400 °C</th>
<th>350 °C</th>
<th>300 °C</th>
<th>250 °C</th>
<th>surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co$_8$S$_8$(PPh$_3$)$<em>6$]$</em>{0.02}$MoS$_2$</td>
<td>85 (50)</td>
<td>38 (61)</td>
<td>15 (7)</td>
<td>26.8</td>
<td></td>
</tr>
<tr>
<td>[Co$_8$S$_8$(PPh$_3$)$<em>6$]$</em>{0.05}$MoS$_2$</td>
<td>88 (52)</td>
<td>42 (41)</td>
<td>12 (25)</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>0.05-</td>
<td>Co$_8$S$_8$</td>
<td>-(PPh$_3$)$_6$</td>
<td>MoS$_2$–R</td>
<td>25 (73)</td>
<td>25 (72)</td>
</tr>
<tr>
<td>0.05-</td>
<td>Co$_8$S$_8$</td>
<td>-(PPh$_3$)$_6$</td>
<td>MoS$_2$–R</td>
<td>30 (70)</td>
<td>15 (48)</td>
</tr>
<tr>
<td>Al$_{13}$-pilled MoS$_2$</td>
<td>6 (89)</td>
<td>&lt;5 (NM)</td>
<td>5 (NM)</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>restacked MoS$_2$</td>
<td>22 (75)</td>
<td>9 (78)</td>
<td>&lt;5 (NM)</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>pristine MoS$_2$</td>
<td>8 (88)</td>
<td>&lt;5 (NM)</td>
<td>5 (NM)</td>
<td>5 (NM)</td>
<td></td>
</tr>
<tr>
<td>Crossfield 465 (Co–Mo)</td>
<td>82 (80)</td>
<td>20 (85)</td>
<td>&lt;5 (NM)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crossfield 504 (Ni–Mo)</td>
<td>96 (44)</td>
<td>27 (76)</td>
<td>10 (55)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ NM = not meaningful (conversion too low that selectivity could not be reliably determined). Run-to-run conversion reproducibility = ±15% (e.g., 20 ± 3%). Amount of “active” metals (Co + Mo) in each run = 0.10 g in all cases.
lattice spacings from TEM of 0.3–0.5 nm less than those reported from XRD for Keggin ion-pillared clays. They attributed these decreased lattice spacings to dehydration of the water-soluble Keggin ion during vacuum pumpdown in the TEM specimen chamber. Perhaps for this reason, the use of TEM to study pillared materials has been quite limited. Like previous workers studying the intercalation of the Keggin ion into pillared clays, we were unable to detect the Keggin ion in \( \text{Al}_{13}\text{O}_{4}(\text{OH})_{24}^{-}(\text{H}_{2}\text{O})_{22}^{+} - \text{MoS}_2 \) directly as a scattering center but, like Gil,\(^ {54} \) we were able to see a distribution of lattice expansions due to its presence.

X-ray diffraction suggests the presence of pillared \( \text{[Co}_6\text{S}_8(\text{PPh}_3)_6]_{0.02}\text{MoS}_2 \) and little if any unpillared \( \text{MoS}_2. \)\(^ {46} \) However, the unpillared \( \text{MoS}_2 \) edge lattice spacing overlaps with one of the XRD peaks for the pillared \( \text{[Co}_6\text{S}_8(\text{PPh}_3)_6]_{0.02}\text{MoS}_2, \) so interpretation based solely on XRD is somewhat ambiguous. Partial population of unpillared \( \text{MoS}_2 \) edge sites with the Co clusters would destroy much of the coherence in the X-ray diffraction.

Thus, the regions that are completely pillared would be expected to give rise to most of the signal in X-ray diffraction patterns.

The major advantages of the use of TEM over XRD for studying pillared materials are that one can determine the degree and uniformity of the pillaring in localized regions. As has been shown in the micrographs, there were distinct heterogeneities in the degree of pillaring of MoS2 not visible by XRD. Moreover, in cases where the pillaring is partial, XRD may give an incorrect interpretation of the pillaring behavior. In our case, TEM suggests that the disruptions in the MoS2 lattice were highly localized at the surface, whereas XRD suggests that the predominant structure is that of a perfectly pillared material.46 Of course, the two techniques probe different regions and consequently provide complementary information. Only the edges were observed by TEM, while XRD samples the entire material. We suggest that the presence of large internal areas of pillared MoS2 could be observed by examination of a microtomed, resin-embedded sample.

**HDS Activity.** The activities of the Co6S8-pillared molybdenum disulfides at low temperatures (≤300 °C) were the highest per gram of catalyst of the many materials that we have tested and were still slightly more active than commercially available sulfides on a per gram of metal basis. This activity benefit is partially offset by a relatively low selectivity to biphenyl, implying a more significant hydrogenation function for the pillared materials as compared to the commercial catalysts. The effect of mass transport at low severity HDS conditions, while very significant, was also less important for the Co6S8-pillared MoS2 than for the commercial catalysts, suggesting that the pillaring may have enhanced the accessibility of the active sites.

The Co6S8-pillared molybdenum disulfides were only active, however, once the triphenylphosphine ligands had been evolved. Following a 300 °C H2 reduction, the evolution of these ligands was detected readily by a color change in the KOH scrubbing solution. This initially clear solution, meant to trap H2S as K2S precipitate, turned bright orange. Pyrolysis mass spectroscopy experiments46 indicated that the majority of the volatile product from the Co6S8-pillared molybdenum disulfides were phosphine sulfide fragments (both PhPS and Ph2PS) that, when combined with the fact that only triphenylphosphine was observed during pyrolysis of the neat cluster, suggests that the phosphines attacked the MoS2 layers by extracting sulfur as they departed from the solid. Extraction of sulfur from the MoS2 layers during thermal pretreatment prior to catalysis or during e-beam exposure in the TEM would create vacancies at which the Co6S8 cluster cores would be preferentially stabilized; such a mechanism would certainly help to explain the fact that the Co6S8 cluster cores did not aggregate into large cobalt sulfide domains.

The sulfur extraction during the evolution of the triphenylphosphine ligands creates sulfur anion vacancies, which have long been associated with HDS-active sites. Certainly, there are localized disruptions in the MoS2 lattice (in Figures 7, 8, and 10) which are about 0.9 nm. These disruptions are too big to be the sulfur anion vacancies that have been associated with HDS activity and are more likely associated with remnants from the Co6S8 cluster fragments. Nevertheless, the removal of Ph3P ligands may be an interesting activation step for introducing additional reactivity in the MoS2 layers.

**Structure–Reactivity Relationships.** Some of the local lattice disruptions in MoS2 edge structures observed in this work, such as those in Figures 7, 8, and 10, might be due to defects induced by cobalt-containing clusters. These local lattice disruptions seem barely present, if at all, in the restacked and pristine MoS2 materials, as compared to the significant number in the Co cluster-loaded materials. Although screw dislocations and Moire fringes are commonly observed in MoS2 catalysts,46–60 the appearance of circular scattering regions (in 2-D) of 0.5–1.5 nm, to our knowledge, has not been reported for unpromoted MoS2 and was not observed in our work for either the pristine or the restacked MoS2 materials. However, structures such as those in Figures 7, 8, and 10 in our paper have been reported in Figure 9 of a recent paper by Chianelli et al.59 for bulk MoS2 doped by 1 wt % Co.

In the Co6S8-pillared materials, both the 1T and 2H forms of MoS2 were detected. The 1T form, more common in our materials but not as thermodynamically stable as the 2H form, has a highly distorted sulfur close-packed layer42,43 and is related to that of highly HDS active ReS2.59 Chianelli et al.59 also reported 1T superlattices within their Co-doped MoS2 single crystals. They concluded that near-edge Co distorts the sulfur close-packed layer, inducing lattice strain and a slight rotation of one sulfur close-packed layer with respect to another. This rotation further results in regular Moire fringes that have been observed in the micrographs of several researchers.59,60 This Co-induced lattice strain is absent away from the edges of Co-doped MoS2 single crystals,60 as the intercalation of Co into Mo sulfides is mostly a surface phenomenon, with the deepest penetration of Co being only a few layers.61

Daage and Chianelli4 have argued that the "rim" sites, in addition to possessing the desulfurization capability of "edge" sites, are efficient at hydrogenation. If Daage and Chianelli's rim-edge model is correct, a restacked MoS2 would be expected to be more active but less selective for direct desulfurization of dibenzothiophene to biphenyl because the exfoliation and flocculation processes decrease the basal plane area effectively increasing the rim:basal plane ratio. The restacked MoS2 gave rise to a higher conversion and a lower hydrogen selectivity than the pristine MoS2. The Co6S8-pillared MoS2 catalysts produced higher conversions and lower hydrogen selectivities than the restacked or pristine MoS2 materials. On a surface area-specific activity basis, however, the activities of the Co6S8-pillared MoS2 catalysts and the activities of the pristine

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and restacked MoS2 materials were essentially constant (Figure 15). In addition, the concentration of these 0.9 nm disruptions in the MoS2 lattice also roughly correlates with the activity of the material (Figure 15). The large error bars (95% confidence intervals) for the concentration of edge lattice disruptions take into account not only error associated with variability in the concentration of lattice disruptions within the edge planes but also region-to-region variability in the percentage of edge planes, the latter of which is more significant. Despite the large uncertainty, these results suggest that the exfoliation and flocculation processes increase the MoS2 surface area, thereby increasing hydrogenation capability, and that the presence of Co clusters both decreases the degree of stacking while increasing the degree of hydrogenation. In this respect, Co props apart MoS2 layers, thereby increasing dispersion and hydrogenation activity in a manner consistent with Daage and Chianelli's “rim-edge” model1 of hydrodesulfurization active sites, and acts as a structural promoter in the current catalyst.62

Conclusions

Evidence for intercalation of Co6S8(PPh3)6 clusters into MoS2 was observed by both expansion of the (001)-IT−MoS2 d spacing and by observation of discrete scattering centers. Both the size of the discrete scattering centers and the observed average lattice expansion between MoS2 layers were consistent with the size expected for the Co6S8 cores of the Co6S8(PPh3)6 clusters, indicating that the phosphine ligands had been nearly completely removed. Transmission electron microscopy revealed not only domains of crystal-wide pillaring but also large regions of randomly pillared MoS2. The Co6S8 cluster remnants were readily visible along the edges of (001)-IT−MoS2 edge planes.

The activities of the Co6S8-pillared MoS2 materials were competitive with those of commercial, sulfided Co−Mo and Ni−Mo hydrotreating catalysts and even slightly superior at low temperatures. However, the selectivity to biphenyl was relatively poor compared to the commercial catalysts. The HDS reactivity results are consistent with the Daage−Chianelli rim-edge model1.

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References