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Chemical Properties of Zn/S/Mo(110) and Co/S/Mo(110) Surfaces: Reaction with Hydrogen and Formation of Hydrogen Sulfide

J. A. Rodriguez,* S. Y. Li,[†] and J. Hrbek*

Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973

H. H. Huang and G.-Q. Xu

Department of Chemistry, National University of Singapore, Singapore 119260, The Republic of Singapore

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The chemical and electronic properties of a series of Zn/S/Mo(110) and Co/S/Mo(110) systems have been investigated using photoemission, thermal desorption mass spectroscopy, and hydrogen (H₂, D₂, or D) chemisorption. Sulfur multilayers supported on Mo(110) are very reactive toward admetals like Zn and Co. The behavior of the Zn/S/Mo(110) and Co/S/Mo(110) systems indicates that Zn and Co promote Mo ↔ S interactions, inducing the formation of molybdenum sulfide films. The ZnMoS and CoMoS films were unreactive toward H₂ or D₂ under ultrahigh vacuum conditions. As gas-phase hydrogen atoms (D) impinged on the surfaces, gaseous hydrogen sulfide was formed. Thus, the slow step in the D_{2,gas} + S_{solid} → D₂S_{gas} reaction is the dissociation of molecular hydrogen. A good correlation exists between trends seen in the hydrodesulfurization (HDS) activity of ZnMoS and CoMoS catalysts and trends found for the sulfidation of Mo and hydrogenation of S in ZnMoS and CoMoS films. The systems that contain Co show the larger HDS activity, the stronger metal ↔ metal interactions with a subsequent increase in the reactivity of Mo toward S-containing molecules, and the bigger tendency to create unsaturated Mo sites through the hydrogenation of Mo-bonded S atoms.

I. Introduction

Metal sulfides are catalytically active for numerous reactions that are also catalyzed by pure metals.^{1–3} The most active metal sulfides are frequently orders of magnitude less active than the most active metals.^{1–2} However, metal sulfide catalysts are not poisoned by sulfur and are therefore widely used in the petroleum industry for the treatment of feedstocks that contain sulfur compounds.^{1,4,5} By far the most important application of metal sulfide catalysts involves hydrodesulfurization (HDS) processes, where sulfur-containing molecules are removed from petroleum by reaction with hydrogen to form H₂S and hydrocarbons.^{1–4}

The industrial HDS catalysts typically consist of a mixture of Mo and Co sulfides on a γ -alumina support.^{1,4,6} When Co is added to molybdenum sulfide catalysts, the turnover frequency of the HDS process can be increased by a factor of 10.⁶ Several proposals have been offered to explain the behavior of CoMoS catalysts.^{6–12} Some workers attribute their high turnover frequency to electronic interactions between the components of the system that produce especially active HDS sites.^{7–10} In a different type of proposal, it has been suggested that the high activity of the CoMoS catalysts results from the special structural properties of these systems.^{6,11,12} After comparing the effects of different metals (V, Cr, Mn, Fe, Co, Ni, and Zn) on the HDS activity of molybdenum sulfide catalysts, it was found that Co and Ni were strong promoters, whereas the rest of the metals showed very weak promotional effects.^{7a,13}

On molybdenum sulfide catalysts, the HDS reactions occur on metal sites that are not covered with sulfur.^{10a} In principle, a metal promoter can raise the activity of a HDS catalyst by

enhancing the reactivity of the unsaturated Mo sites toward organosulfur compounds or by increasing the number of unsaturated Mo sites in the surface. These “tasks” can be accomplished by changing the strength of the Mo ↔ S interactions or the rate of hydrogenation of sulfur. In this article, we examine if these phenomena occur in model CoMoS and ZnMoS systems.

Here, the effects of Co (a good HDS promoter) and Zn (a poor HDS promoter) on the chemical properties of S/Mo(110) surfaces and MoS_x films are investigated using core-level photoemission, X-ray excited Auger electron spectroscopy (XAES), thermal desorption mass spectroscopy (TDS), and hydrogen (H₂, D₂, or D) chemisorption. Recently, we have found that thick sulfur films can be grown on top of transition-metal substrates by dosing S₂ gas at temperatures below 200 K.¹⁴ The results presented below show that these sulfur films are very reactive toward Co and Zn and useful for studying the effects of metal promoters on the S affinity of Mo. The CoMoS and ZnMoS systems exhibit very different reactivities for the adsorption of hydrogen and the formation of hydrogen sulfide.

II. Experimental Methods

The equipment used in these experiments has been described before.^{14,15} The XPS and XAES spectra were acquired using a Mg K α X-ray source and a hemispherical electron-energy analyzer with multichannel detection. The binding-energy scale in the spectra was calibrated using the Co 2p_{3/2} and Mo 3d_{5/2} peaks of pure Co and Mo, which were set at binding energies of 778.1 and 227.9 eV, respectively.¹⁶ During the photoemission experiments, the electron-energy analyzer was positioned at $\sim 30^\circ$ from the normal of the surface. The total instrumental resolution in these studies was ~ 0.8 eV.

For the preparation of the ZnMoS and CoMoS systems we used a Mo(110) crystal as substrate. The crystal was cleaned

* To whom all correspondence should be addressed.

[†] Permanent address: Department of Chemistry, National University of Singapore.

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following standard procedures reported in the literature.¹⁵ It was mounted in a manipulator capable of resistive heating to 1500 K and liquid nitrogen cooling to 80 K. Heating to 2400 K was achieved by electron bombardment from behind the sample. A W-5%Re/W-26%Re thermocouple was spot welded to the edge of the sample for temperature measurements.

Sulfur multilayers were prepared by exposing the Mo(110) crystal to S₂ gas at temperatures around 100 K. The S₂ gas was generated in situ by the decomposition of Ag₂S in a solid-state electrochemical cell: Pt/Ag/AgI/Ag₂S/Pt.¹⁷ Zn and Co were deposited on the S/Mo(110) systems by sublimation from high-purity wires of Zn and Co, which were heated by W filaments. The atomic flux from the metal dosers was calibrated following the methodology described in our previous studies for Zn/Mo(110)¹⁸ and Co/Mo(110).¹⁹ In this work, the amount of admetal dosed is reported with respect to the number of Mo(110) surface atoms. One equivalent monolayer (ML) of the admetal corresponds to the deposition of 1.43×10^{15} atoms cm⁻² of Zn or Co.

In a set of experiments, Zn/S/Mo(110) and Co/S/Mo(110) systems were exposed to a beam of D atoms generated in situ by dissociating D₂ with a hot W wire. The D doser was retractable and consisted of a leak valve attached to a stainless steel tube that housed a tungsten coil.²⁰ When operated at a temperature of 1850 K, we estimate that 1–2% of the D₂ molecules that went through the doser dissociated into D atoms.^{20a} All the hydrogen exposures reported here are based on the pressure of D₂ measured inside the ultrahigh vacuum (UHV) chamber.

III. Results

III.1. Interaction of Sulfur and Mo(110). Thick sulfur films can be grown on Mo(110) or Ru(001) by dosing S₂ at temperatures below 200 K.¹⁴ Under these conditions the S₂ molecules react on the surface forming S_n species. The sulfur multilayers sublime at temperatures between 250 and 400 K, with S, S₂, S₄, and S₈ evolving into gas phase.¹⁴ At temperatures above 400 K only a chemisorbed layer of sulfur is left on the Mo(110) or Ru(001) surface.

Figure 1 displays S 2p and Mo 3d XPS spectra taken after depositing a sulfur film (6–7 layers thick) on Mo(110) at 80 K with subsequent annealing to 340 and 900 K. At 80 K, the S 2p region shows only two peaks (a single well-defined doublet) with the S 2p_{3/2} level appearing at ~163.2 eV. The corresponding Mo 3d spectrum exhibits peak positions that are very close to those of clean Mo(110), which implies that the Mo substrate serves as an inert support for the sulfur film. After annealing to 340 K part of the sulfur multilayer desorbed,¹⁴ and one can see now the S 2p_{3/2} features of sulfur atoms bonded to Mo, which appear around 161.6 eV.¹⁵ Further annealing to temperatures above 400 K led to a complete desorption of the sulfur multilayer, and a chemisorbed layer of sulfur ($\theta_s \approx 0.9$ ML) remained on top of the Mo(110) substrate. In Figure 1, the Mo 3d features have binding energies that are always very close to those of metallic Mo, indicating that no molybdenum sulfide was formed during the heating of the S/Mo(110) system.²¹

In general, we were unable to form molybdenum sulfide films by dosing S₂ to Mo(110) at temperatures between 80 and 700 K, or by annealing S_{>1}/Mo(110) systems from 80 to 900 K.

III.2. Chemical Behavior of Zn/S/Mo(110) Systems. The deposition of Zn on sulfur multilayers at temperatures lower than 200 K led to the formation of ZnS_x compounds. Complete sulfidation of Zn was observed only when the amount of Zn deposited was below 2 ML. For higher doses of Zn, there was

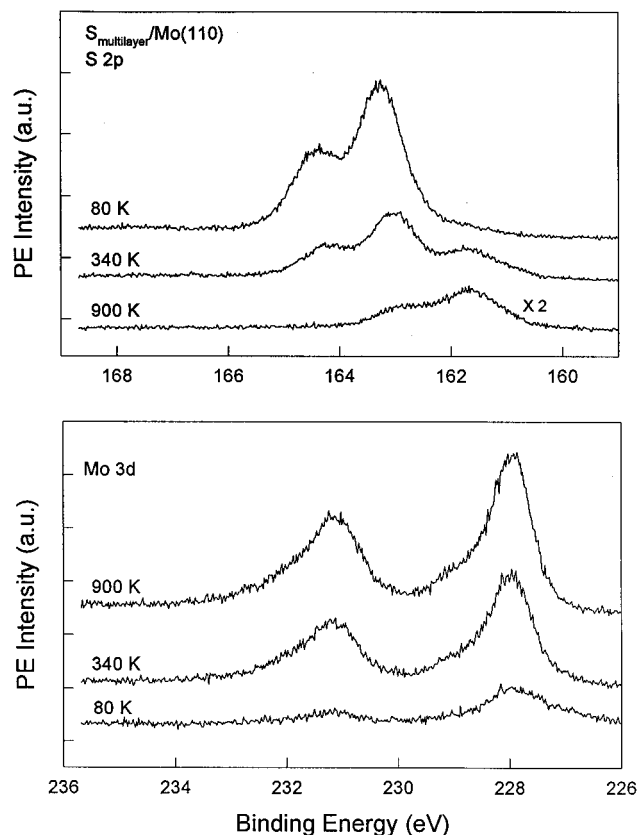


Figure 1. S 2p and Mo 3d XPS spectra for a sulfur film deposited on Mo(110) at 80 K and annealed to 340 and 900 K.

coexistence of metallic Zn and ZnS_x on top of the sulfur multilayer. At the low temperature of these experiments, the metallic Zn was not able to diffuse deep inside the film.

Photoemission results for a typical Zn/S_{>1}/Mo(110) system are shown in Figure 2. In the first step, a sulfur film (>10 layers) was deposited on Mo(110) at ~200 K. At this point there was a complete attenuation of the Mo 3d signal, and a well-defined doublet of peaks appeared in the S 2p region. After dosing Zn (~5 ML) at 200 K, one sees a significant change in the line shape of the S 2p spectrum and new features appear at ~162 eV. The corresponding Zn LMM Auger spectrum is a convolution of spectra reported for metallic Zn and zinc sulfides.^{18,22} Heating from 200 to 1050 K induced the desorption of zinc and the total disappearance of the signal from the Zn LMM Auger spectrum. At this stage, extra peaks in the Mo 3d region (bottom of Figure 2) indicate the presence of significant amounts (3–4 ML) of molybdenum sulfides²¹ in the system. The area under the S 2p features is ~3.6 times larger than the area measured for the saturation coverage of chemisorbed sulfur on Mo(110), $\theta_s = 0.91$ ML.²³ After annealing the Zn/S_{>1}/Mo(110) system to 1050 K, the doublet of peaks in the S 2p spectrum exhibits binding energies that match those reported for MoS_x films¹⁵ and bulk MoS₂.^{21,24} By comparing the data in Figures 1 and 2 for S_{>1}/Mo(110) and Zn/S_{>1}/Mo(110), we can conclude that the presence of zinc facilitates Mo ↔ S interactions and the formation of several layers of molybdenum sulfide.

In a previous work examining the adsorption of S₂ on Zn/Mo(110) surfaces at 500–700 K,¹⁸ we also found that Zn promoted the synthesis of molybdenum sulfides, but the amounts of MoS_x formed were much smaller than those seen after annealing Zn/S_{>1}/Mo(110) systems from 200 to 700 K. Using the properties of the Zn/S_{>1}/Mo(110) systems, we developed an efficient procedure for the preparation of MoS_x films. First,

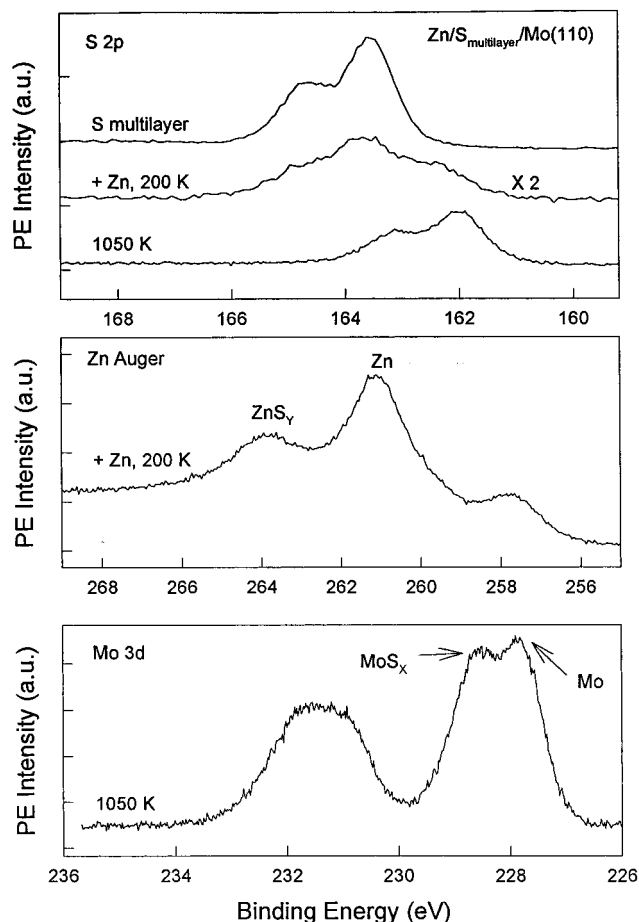


Figure 2. S 2p (top), Zn LMM (center), and Mo 3d (bottom) spectra acquired after dosing Zn (~ 5 ML) to a sulfur film (> 10 layers) at 200 K followed by annealing to 1050 K.

a sulfur multilayer is deposited on Mo(110) at 80–200 K. Then, a Zn film is vapor-deposited on the $S_{>1}/\text{Mo}(110)$ system at ~ 200 K. This is followed by a full sulfidation of the zinc by exposing it to S_2 gas. Finally, the sample is annealed to 1000–1050 K to desorb Zn and leave a pure MoS_x film. Following this methodology we were able to produce systems that had between 2 and 6 ML of MoS_x . These systems exhibited Mo 3d spectra that were very similar to those of molybdenum sulfides.^{21,25} They decomposed at 1150–1300 K, with S_2 evolving into gas phase and a chemisorbed layer of sulfur remaining on top of the Mo(110) substrate. The exact structure of the MoS_x films was unknown. They exhibited no reactivity toward CO, O_2 , and H_2 at 80–300 K. This indicates that they did not expose metallic Mo or edge planes similar to those of MoS_2 , which contain Mo sites and are able to adsorb CO, O_2 , and H_2 .^{26–29} Our films probably exposed surfaces similar to the sulfur-basal plane of MoS_2 that is unreactive toward CO, O_2 , and H_2 .^{26,27,30}

The MoS_x films were also unreactive toward zinc. Upon the deposition of zinc (0.1–4.4 ML) on MoS_x films, we observed Zn LMM Auger spectra identical with that of pure metallic zinc (for an example, see Figure 3). The same result was found after depositing zinc on $S_{0.9-0.7}/\text{Mo}(110)$ surfaces. Thus, it appears that zinc does not react with sulfur atoms bonded to molybdenum. However, the Zn atoms supported on the MoS_x films or $S_{0.9-0.7}/\text{Mo}(110)$ surfaces were very reactive toward S_2 gas (see Figure 3).

After exposing MoS_x , Zn/MoS_x , and $\text{ZnS}_y/\text{MoS}_x$ films to large amounts of H_2 or D_2 (< 400 L (Langmuir)) at temperatures between 80 and 300 K, we saw no evidence for the adsorption or reaction of these molecules with the films. In contrast, atomic

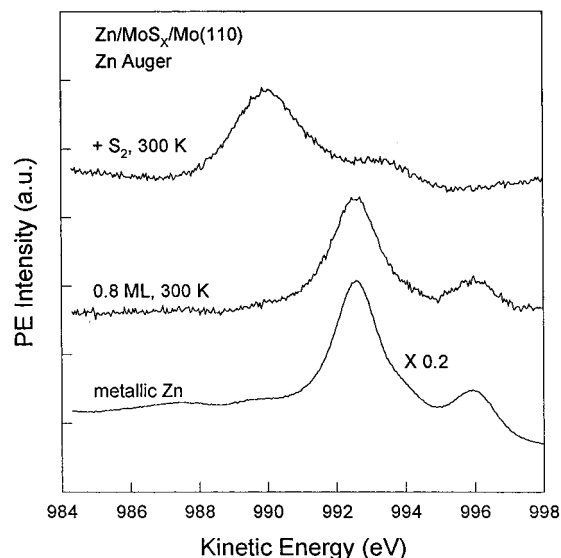


Figure 3. Zn LMM Auger spectra taken before and after dosing S_2 to 0.8 ML of Zn supported on a molybdenum sulfide film (MoS_x/Mo 3d ratio = 1.1; 3–4 ML of MoS_x). For comparison, at the bottom of the figure, we also include the corresponding spectrum for metallic zinc.

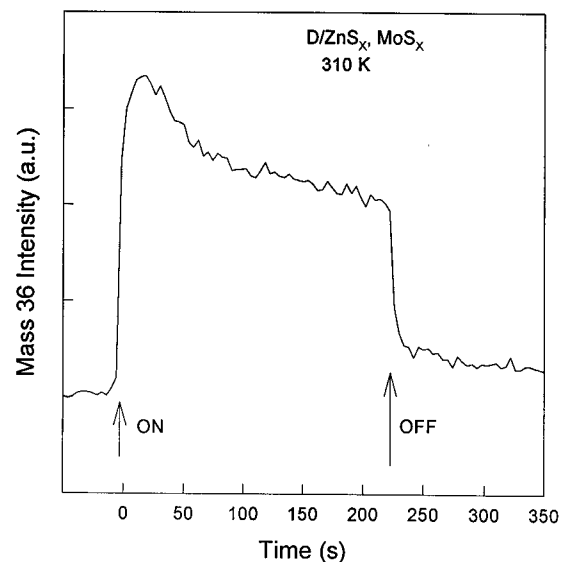


Figure 4. MS signal for D_2S gas while dosing D to a $\text{ZnS}_y/\text{MoS}_x$ film ($\theta_{\text{Zn}} = 0.6$ ML; MoS_y/Mo 3d ratio = 0.96) at 310 K. Labels “ON” and “OFF” indicate the times at which the D doser was turned on and off. Total dose of D_2 between these times was ~ 110 L, and an estimate of 1–2% of the D_2 molecules that went through the doser dissociated into D atoms.

hydrogen (D) was very reactive, forming gaseous hydrogen sulfide ($2D_{\text{gas}} + S_{\text{solid}} \rightarrow D_2S_{\text{gas}}$). This is illustrated by the data in Figure 4. After a $\text{ZnS}_y/\text{MoS}_x$ film ($\theta_{\text{Zn}} = 0.6$ ML; MoS_y/Mo 3d ratio = 0.96) was set in front of the mass spectrometer and exposed to D_2 gas ($\sim 5 \times 10^{-7}$ Torr), there was no change in the background signal for mass 36 (D_2S). After the D doser was turned on, there was a large increase in the D_2S signal that disappeared when the D doser was switched off. Similar results were obtained for MoS_x films. Thus, in the reaction between molecular hydrogen and the MoS or ZnMoS films, there is a very large activation energy for the dissociative adsorption of the molecule. Once atomic hydrogen is available, the formation of bonds between hydrogen and sulfur to produce hydrogen sulfide occurs relatively fast.

Figure 5 shows photoemission spectra taken after exposing a $\text{ZnS}_y/\text{MoS}_x$ system to atomic hydrogen. Before D was dosed, 0.8 ML of Zn were deposited on the molybdenum sulfide film

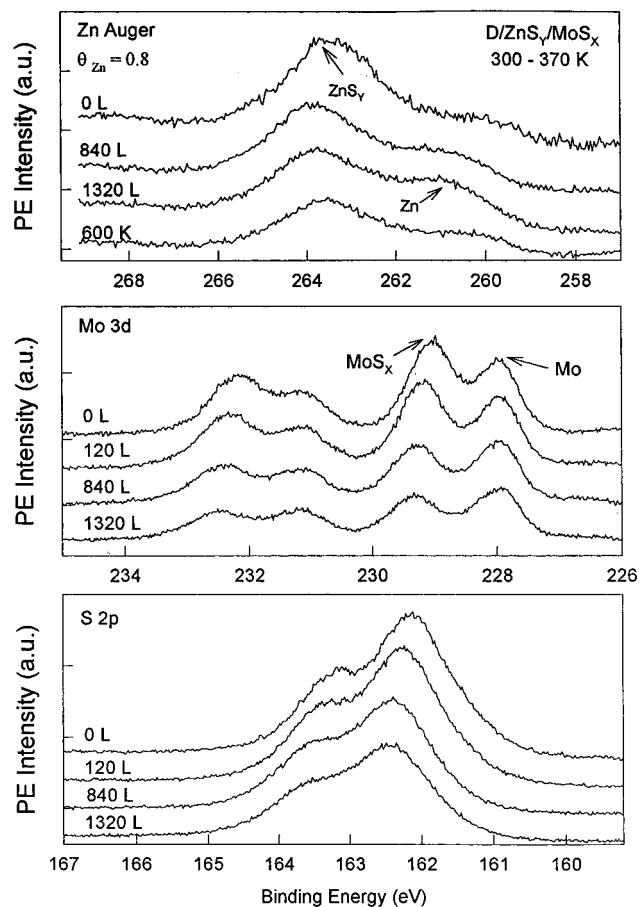


Figure 5. Zn LMM, Mo 3d, and S 2p spectra acquired after dosing atomic hydrogen (D) to a $\text{ZnS}_y/\text{MoS}_x$ film ($\theta_{\text{Zn}} = 0.8$ ML; MoS_x/Mo 3d ratio = 1.28) at 310–370 K. Labels on the left side of the spectra indicate the exposures of D based on the total pressure of D_2 in the chamber before switching on the D doser. 1–2% of the D_2 molecules that went through the doser dissociated into D atoms. In the final step, after 1320 L of D/D_2 were dosed, the film was annealed to 600 K.

(MoS_x/Mo 3d ratio = 1.28; 3–4 ML of MoS_x) at 300 K and exposed to S_2 gas. A dose of 360 L of D_2 to the $\text{ZnS}_y/\text{MoS}_x$ film at room temperature produced no change in its Zn LMM, Mo 3d, and S 2p features, and there was no evolution of hydrogen in a TDS spectrum covering the range 300–600 K (the sample was not heated to higher temperature to avoid the decomposition of the ZnS_y overlayer¹⁸). In the experiments of Figure 5, the dosing of atomic hydrogen was carried out at 310–370 K. The sample was initially at ~ 300 K, but thermal radiation from the hot filament of the D doser produced a temperature increase of 10–70 K. After exposing the $\text{ZnS}_y/\text{MoS}_x$ system to D, one sees a simultaneous increase of 0.3–0.4 eV in the binding energy of the Zn LMM, Mo 3d, and S 2p peaks. (However, the Mo 3d peaks of metallic Mo are not affected.) This type of behavior indicates that hydrogen diffuses into the “bulk” of the film, forming compounds and changing the electronic properties of the film in a uniform way. The $2\text{D}_{\text{gas}} + \text{S}_{\text{solid}} \rightarrow \text{D}_2\text{S}_{\text{gas}}$ reaction decreases the amounts of sulfur, MoS_x , and ZnS_y present in the film. After the last dose of D, we annealed the system in Figure 5 from 350 to 600 K observing desorption of metallic Zn (450–520 K) and D_2 (400–500 K) and no desorption of D_2S . Thus, all the hydrogen sulfide produced during the dosing of D desorbs into gas phase as soon as it is formed.

In a set of experiments, we investigated the interaction between H_2S and the “final” film in Figure 5 (i.e., after partially reducing the $\text{ZnS}_y/\text{MoS}_x$ film with 1320 L of D/D_2 and annealing it to 600 K). TDS spectra taken upon dosing 1, 5, and 10 L of

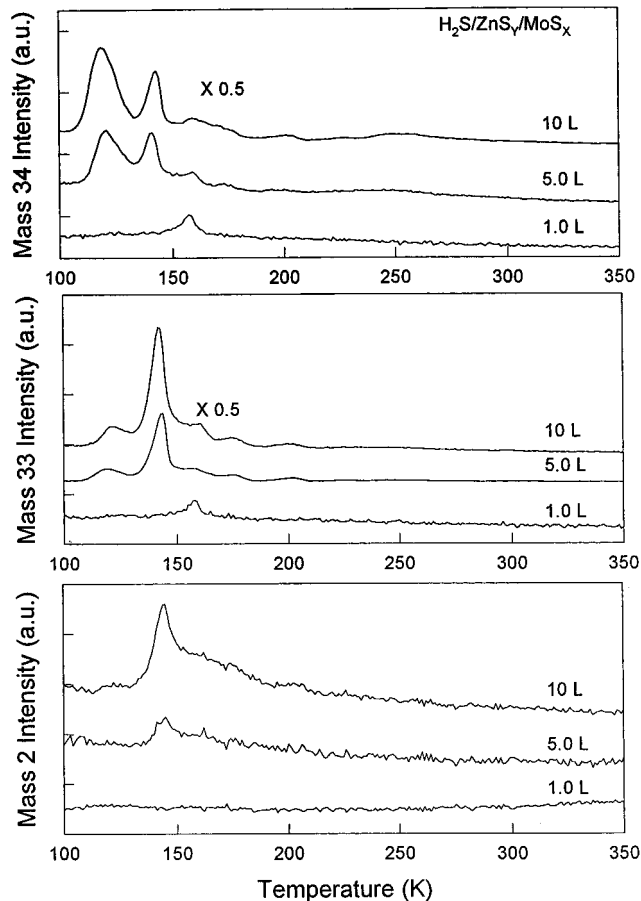


Figure 6. Thermal desorption spectra acquired after adsorbing H_2S on the $\text{ZnS}_y/\text{MoS}_x$ film of Figure 5 (H_2S , mass 34; HS , mass 33; H_2 , mass 2). Before H_2S (1, 5 or 10 L) was dosed at 80 K, the $\text{ZnS}_y/\text{MoS}_x$ film was exposed to 1320 L of D/D_2 at 370 K and annealed to 600 K. Heating rate = 2 K/s.

H_2S at 80 K are shown in Figure 6. No desorption of hydrogen sulfide (or HS) was observed from 300 to 600 K. As the exposure of H_2S is raised, well-defined peaks for desorption of the molecule appear at 160, 140, and 120 K. For a 10 L exposure, one finds the largest signal for mass 34 at ~ 120 K, which can be attributed to desorption of H_2S molecules that were weakly adsorbed on top of the $\text{ZnS}_y/\text{MoS}_x$ film. At temperatures between 135 and 180 K strong signals are observed for masses 34, 33, and 2. By comparing the pattern of intensities for masses 34 and 33, we conclude that there is simultaneous desorption of H_2S and HS (i.e., the HS signal does not come from the fragmentation of H_2S in the mass spectrometer). At 80 K, part of the adsorbed H_2S molecules dissociate into HS and H fragments. A fraction of these fragments recombine between 135 and 180 K, producing H_2S that desorbs. At the same time part of the H fragments form H_2 gas, forcing in this way the desorption of SH species from 135 to 180 K. In the $\text{H}_2\text{S}/\text{ZnS}_y/\text{MoS}_x$ system most of the “chemistry” takes place at temperatures below 300 K, as it has been previously reported for the adsorption of H_2S on $\text{Mo}(100)$ ³¹ and many other metal surfaces.^{32–37} When D is dosed to a $\text{ZnS}_y/\text{MoS}_x$ film, the hydrogen-rich environment favors the formation of D_2S , which cannot make bonds with the film if the temperature is higher than 250 K.

At 300–400 K, the $\text{D} \leftrightarrow \text{ZnS}_y/\text{MoS}_x$ and $\text{D} \leftrightarrow \text{MoS}_x$ interactions were similar in many aspects. In both types of systems, there was adsorption and diffusion of D into the “bulk” of the film, with the sorbed hydrogen evolving into gas phase at temperatures between 400 and 500 K. In addition, the sulfur atoms of these systems reacted with atomic hydrogen to yield

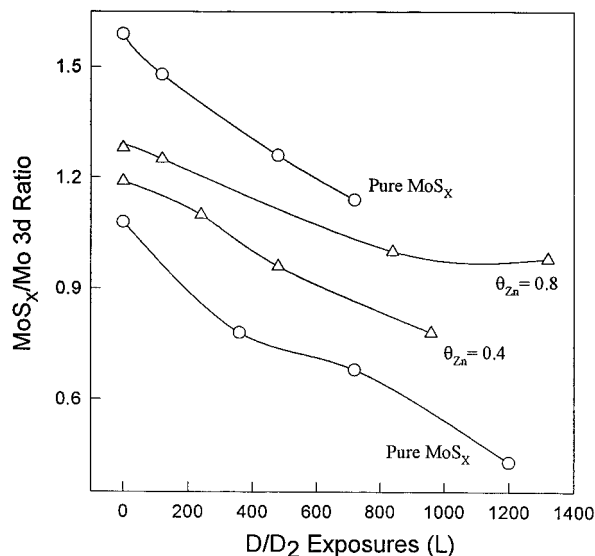


Figure 7. Hydrogenation of Mo-bonded S atoms in MoS_x (○) and $\text{ZnS}_y/\text{MoS}_x$ films (△). MoS_x and $\text{ZnS}_y/\text{MoS}_x$ films were exposed to a given mixture of D and D_2 . Hydrogen was then pumped out from the chamber, and the ratio of the MoS_x and Mo peaks in the corresponding Mo $3d_{5/2}$ XPS spectrum was measured. Dosing of hydrogen was carried out at 300–370 K. 1–2% of the D_2 molecules that went through the doser dissociated into D atoms. Lines connecting the points are drawn to guide the eyes.

hydrogen sulfide molecules that immediately desorbed. However, there were significant differences in the reactivity of the $\text{ZnS}_y/\text{MoS}_x$ and MoS_x films toward hydrogen. Figure 7 compares the effects of atomic hydrogen on the MoS_x/Mo 3d XPS ratio of $\text{ZnS}_y/\text{MoS}_x$ and MoS_x films. (In this work, the “ MoS_x/Mo 3d XPS ratio” represents the ratio of peak intensities for the $3d_{5/2}$ level of the sulfide and metal in the Mo 3d spectrum.) In the first stage of these experiments, MoS_x films were prepared by heating $\text{ZnS}_{>1}/\text{Mo(110)}$ systems from 200 to 1050 K (see above). Then, on some of the MoS_x films, we vapor-deposited zinc at 300 K and exposed it to S_2 gas until it was transformed into ZnS_y . Finally, the $\text{ZnS}_y/\text{MoS}_x$ and MoS_x films were exposed to D at 300–370 K. In Figure 7, the “hydrogenation” curves for the $\text{ZnS}_y/\text{MoS}_x$ systems exhibit initial slopes (at 0–400 L D/D_2 exposures) that are substantially smaller than those of the curves for the MoS_x systems. Furthermore, the $\text{ZnS}_y/\text{MoS}_x$ ($\theta_{\text{Zn}} = 0.8$ ML) system reaches a point at which the rate of hydrogenation of Mo-bonded S atoms is negligible. Thus, under the hydrogen-rich conditions of a HDS process, one can expect a lower probability for the existence of unsaturated (or sulfur “free”) Mo sites in a ZnMoS catalyst than in a pure MoS catalyst.

III.3. Chemical Behavior of Co/S/Mo(110) Systems. Figures 8 and 9 display Co $2p_{3/2}$ and S 2p spectra taken after depositing Co (1.8, 2.5, and 3.4 ML) on a sulfur film (>10 layers) at 80 K. The deposited Co atoms exhibited Co $2p_{3/2}$ binding energies that are very close to that of metallic Co. Previous studies indicate that the Co core levels are rather insensitive to Co–S bonding.^{24,25} For example, changes in the position of the Co $2p_{3/2}$ level are too small to allow for a clear separation of Co_9S_8 and metallic Co ($\Delta\text{BE} \approx 0.1$ eV²⁴). On the other hand, the S 2p spectra in Figure 9 indicate that cobalt reacts with sulfur at 80 K. Upon the deposition of Co there is a strong feature around 162 eV that is not seen for pure solid sulfur (see Figure 2). This feature dominates the S 2p region after heating to 500 K. (This heating induced the desorption of the sulfur multilayer.) At this point, there is no molybdenum sulfide present in the system (see bottom of Figure 8), and most of the sulfur is bonded to cobalt. The area under the S 2p features is ~ 4.1 times larger

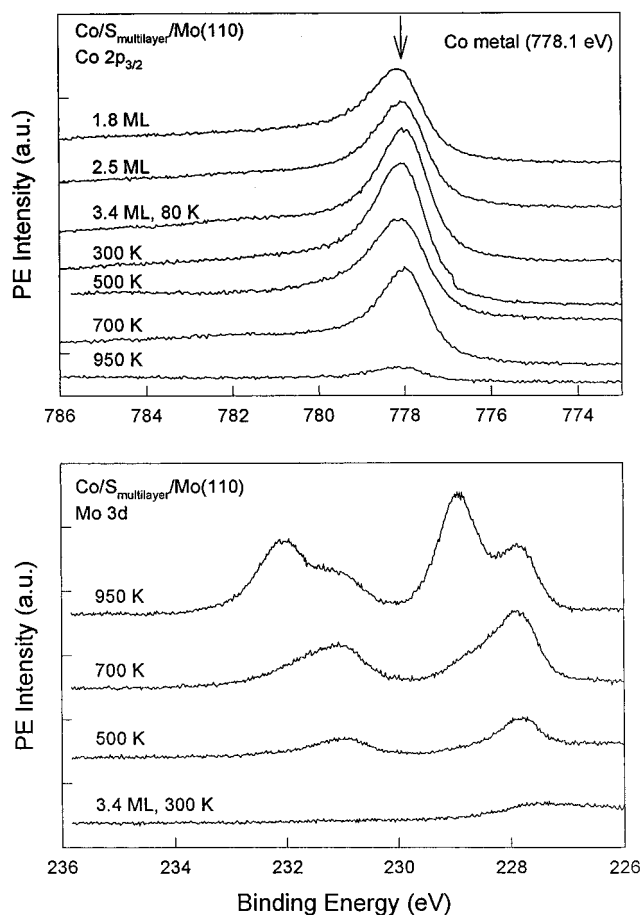


Figure 8. Co $2p_{3/2}$ and Mo 3d XPS spectra acquired after dosing Co (1.8, 2.5 or 3.4 ML) to a sulfur multilayer supported on Mo(110). Co was vapor-deposited at 80 K, and this was followed by annealing of the sample to 300, 500, 700, and 950 K. In the top part of the figure, the arrow indicates the position for the Co $2p_{3/2}$ level of pure metallic Co.

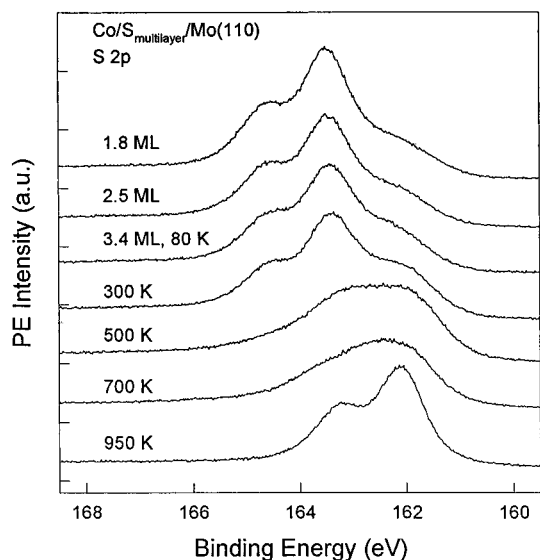


Figure 9. S 2p spectra recorded during the experiments that produced the Co $2p_{3/2}$ and Mo 3d spectra displayed in Figure 8.

than the area measured for the saturation coverage of chemisorbed sulfur on Mo(110), $\theta_{\text{S}} = 0.91$ ML.²³

Heating from 700 to 950 K induces a transfer of S from Co to Mo and a change in the morphology of the CoS_y overlayer that leads to a decrease in the Co $2p_{3/2}$ signal and an enhancement in the Mo 3d signal (Figure 8). The reduction in

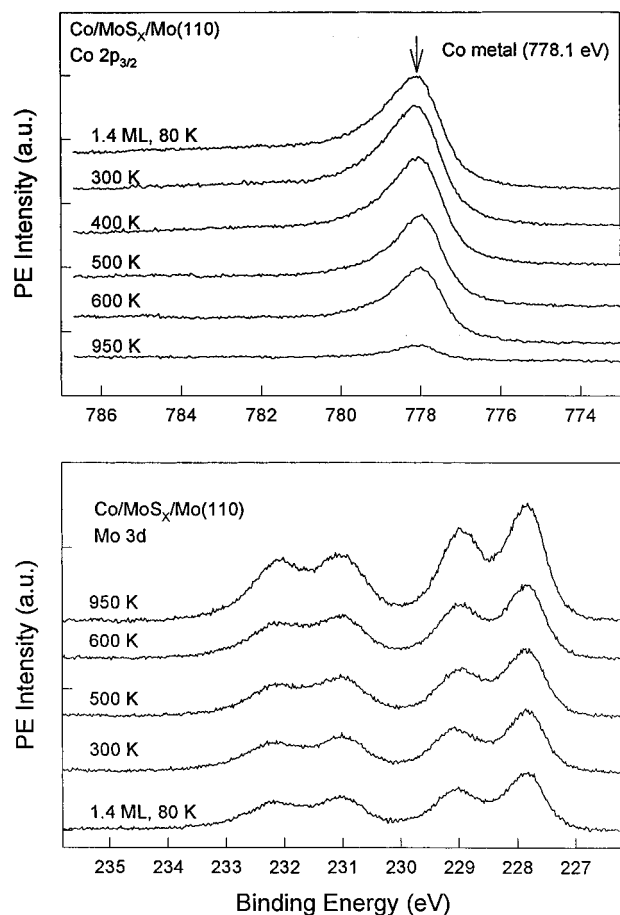


Figure 10. Co $2p_{3/2}$ and Mo 3d XPS spectra taken upon the deposition of 1.4 ML of Co on a molybdenum sulfide film (MoS_x/Mo 3d ratio = 0.7; 2.5–3.5 ML of MoS_x) at 80 K followed by annealing to 300, 400, 500, 600, and 950 K. Arrow in the top part of the figure denotes the position for the Co $2p_{3/2}$ level of pure metallic Co.

the Co $2p_{3/2}$ intensity cannot be attributed to the desorption of cobalt. It is probably a consequence of the formation of three-dimensional (3D) clusters of Co or CoS_y that are dissolved in a matrix of molybdenum sulfide. At 950 K, MoS_x is the dominant molybdenum species within the escape depth probed by XPS (Figure 8), and there is a well-defined doublet of peaks in the S 2p region (Figure 9). The S $2p_{3/2}$ binding energy (~ 162.1 eV) is close to those reported for bulk MoS_2 (162.2 eV;²¹ 161.9 eV²⁴) and Co_9S_8 (162.1 eV²⁴).

After the results in Figures 1 and 8, typical of $\text{S}_{>1}/\text{Mo}(110)$ and $\text{CoS}_{>1}/\text{Mo}(110)$ systems, are compared, it is obvious that the presence of Co greatly enhances $\text{Mo} \leftrightarrow \text{S}$ interactions. Data for the adsorption of S_2 on $\text{Co}/\text{Mo}(110)$ surfaces at 700–900 K also show that Co promotes the formation of molybdenum sulfides,¹⁹ but this route is less effective for the synthesis of MoS_x than the annealing to high temperature of $\text{Co}/\text{S}_{>1}/\text{Mo}(110)$ systems. In addition, a comparison of the behavior of $\text{Zn}/\text{S}_{>1}/\text{Mo}(110)$ and $\text{Co}/\text{S}_{>1}/\text{Mo}(110)$ systems that contained similar amounts of sulfur and the admetals indicates that on a per atom basis Co is 2–3 times more effective than Zn at promoting the formation of MoS_x .

In a set of experiments, we investigated the interaction of Co with MoS_x films synthesized by annealing $\text{Zn}/\text{S}_{>1}/\text{Mo}(110)$ systems from 200 to 1050 K (see above). Figures 10 and 11 show photoemission data taken after depositing 1.4 ML of Co on a molybdenum sulfide film (MoS_x/Mo 3d ratio = 0.7; 2.5–3.5 ML of MoS_x) at 80 K. The deposition of Co did not induce any change in the line shape or binding energy of the Mo 3d and S 2p features of the film. This suggests that the deposited

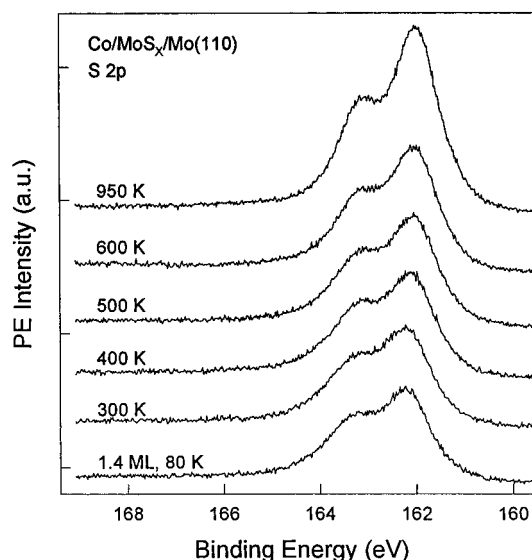
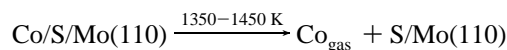
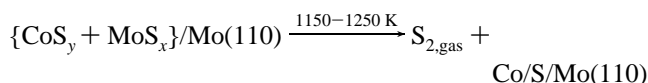


Figure 11. S 2p spectra taken during the experiments that produced the Co $2p_{3/2}$ and Mo 3d spectra displayed in Figure 10.

Co remained in a metallic state. (A similar result was found for the deposition of Zn on MoS_x films (see above), where the admetal was not able to remove S from Mo to form ZnS_y .) Annealing from 80 to 300 K did not produce any modification in the Co $2p_{3/2}$, Mo 3d, and S 2p spectra. Further heating to temperatures above 500 K led to a reduction in the intensity of the Co $2p_{3/2}$ signal and negative binding-energy shifts in the S $2p_{3/2}$ (0.3–0.4 eV, Figure 11) and Mo $3d_{5/2}$ (0.2–0.3 eV, Figure 10) levels of MoS_x . Since there is no desorption of cobalt at these temperatures, the trends in Figures 10 and 11 indicate that Co is migrating from the surface into the “bulk” of the MoS_x film, probably forming 3D clusters of CoS_y . In general, after examining the thermal stability of a series of Co/MoS_x systems, we found that the Co overlayers showed a large tendency to penetrate into the MoS_x substrate at temperatures above 400 K.

The CoMoS systems formed by annealing $\text{Co}/\text{MoS}_x/\text{Mo}(110)$ and $\text{Co}/\text{S}_{>1}/\text{Mo}(110)$ films to high temperature decomposed in an identical way:



Thus, in a CoMoS system, it is impossible to induce the desorption of Co without inducing first the decomposition of the molybdenum sulfides.

After dosing H_2 or D_2 (<400 L) to Co/MoS_x and $\{\text{CoS}_y + \text{MoS}_x\}$ films at 80 or 300 K, we saw no evidence for the formation of gaseous hydrogen sulfide and there was no change in the S 2p and Mo 3d spectra of the films. In contrast, exposure of the films to atomic hydrogen (D) at 300–370 K produced D_2S gas and positive binding-energy shifts of 0.3–0.4 eV in the S 2p and Mo $3d_{5/2}$ levels. TDS spectra taken after exposing the films to D showed desorption of D_2 in a broad peak from 400 to 500 K, and no evolution of D_2S . As in the case of MoS and ZnMoS systems, one has a situation in which some of the impinging D atoms react with S atoms on the surface to form D_2S gas and some are sorbed on/into the CoMoS system. Over all these systems, the slow step for the $\text{D}_{2,\text{gas}} + \text{S}_{\text{solid}} \rightarrow \text{D}_2\text{S}_{\text{gas}}$ reaction is the dissociation of molecular hydrogen.

In general, the Co/MoS_x and $\{\text{CoS}_y + \text{MoS}_x\}$ films exhibited initial rates of hydrogenation that were comparable to those seen

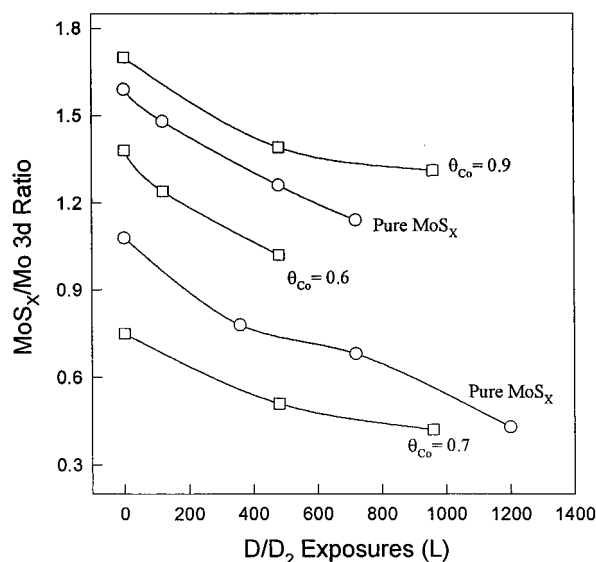


Figure 12. Hydrogenation of Mo-bonded S atoms in MoS (○) and CoMoS films (□). Mo and CoMoS films were exposed to a given mixture of D and D₂. Hydrogen was then pumped out from the chamber, and the ratio of the MoS_x and Mo peaks in the corresponding Mo 3d_{5/2} XPS spectrum was measured. Dosing of hydrogen was carried out at 300–370 K. 1–2% of the D₂ molecules that went through the doser dissociated into D atoms. Lines connecting the points are drawn to guide the eyes.

for MoS_x films. This is illustrated by the data in Figure 12. The figure shows how the MoS_x/Mo 3d XPS ratio of CoMoS and MoS systems changes after dosing atomic hydrogen. The CoMoS systems with 0.6 and 0.9 ML of Co were prepared by depositing Co on MoS_x films at 300 K followed by exposure to S₂ gas at the same temperature (CoS_y on MoS_x). On the other hand, the system with 0.7 ML of Co was synthesized by annealing a Co_{0.7}/S_{>1}/Mo(110) film to 800 K (CoS_y on/in MoS_x). In Figure 12, the “hydrogenation” curves for the CoMoS and MoS systems show initial slopes (at 0–400 L D/D₂ exposure) that are very similar. Differences in the rate of hydrogenation are observed only at very high exposures of hydrogen, when the rate of formation of D₂S becomes somewhat slower on the CoMoS systems. However, before this occurs, one can hydrogenate between 20 and 30% of the molybdenum sulfide present in a CoMoS system at a rate close to that observed in a MoS system.

IV. Discussion

In the solid state, sulfur forms S_n clusters (4 < n < 20) that adopt linear or cyclic configurations.³⁸ When S₂ is dosed to Mo(110) at temperatures below 200 K, the S₂ molecules react on the surface forming S_n rings or chains.¹⁴ The results described above show that these sulfur species are very reactive toward admetals like Zn and Co. This large reactivity can be very useful for the preparation of ultrathin films of metal sulfides.

The results for the Zn/S_{>1}/Mo(110) and Co/S_{>1}/Mo(110) systems indicate that zinc and cobalt promote Mo ↔ S interactions and the subsequent formation of molybdenum sulfides. The promotional effect of Co in a per atom basis is 2–3 times larger than that of Zn. In principle the formation of MoS_x from metallic molybdenum and sulfur should occur spontaneously (ΔG = −50 to −90 kcal/mol³⁹), but there is a large kinetic barrier for the penetration of S into the bulk of the Mo(110) sample. An admetal can promote the sulfidation of molybdenum by facilitating the migration of S from the surface into the Mo lattice or by increasing the reactivity of Mo toward

S through metal ↔ metal interactions.^{18,19} It is well-established now that bimetallic bonding can induce dramatic changes in the chemical and catalytic properties of a metal.^{40–45} Indeed, in theoretical studies examining the effects of Zn and Co on the HDS activity of molybdenum sulfide catalysts,⁷ it has been proposed that Co is a much better promoter because it is more efficient than Zn at increasing the electron density and reactivity of Mo.

For the deposition of Zn and Co on MoS_x films at 300 K, we found that the admetals were not able to remove sulfur from the substrate to form ZnS_y or CoS_y compounds. An identical result has been reported for the deposition of Ni on the S basal plane of MoS₂.⁴⁶ In contrast, Fe atoms deposited on the same substrate removed S atoms from it, leaving islands of uncovered Mo in the surface.⁴⁷ These differences in the behavior of the admetals probably reflect variations in the thermodynamic stability of the sulfides that they can form. Thus, Fe is able to form sulfides that are more stable than those formed by Mo,³⁹ whereas the sulfides formed by Zn, Co, or Ni are less stable than those formed by Mo.³⁹ After annealing Co/MoS_x surfaces to temperatures above 500 K, we observed clustering of Co into 3D islands and penetration of the admetal into the MoS_x substrate. The same phenomena have been seen after heating Ni/MoS₂(0001) and Fe/MoS₂(0001) surfaces to high temperatures.^{46a,47} The exact cause behind these phenomena is unknown at the present time. They lead to a minimization of the total surface-free energy.⁴⁸ In the case of Zn/MoS_x surfaces, the penetration of the admetal into the substrate upon heating is not possible because metallic zinc sublimates at temperatures between 450 and 500 K.¹⁸

Upon exposure of ZnMoS and CoMoS films to atomic hydrogen at 300–400 K, the films sorbed significant amounts of hydrogen. The sorption of hydrogen produced uniform changes in the electronic properties of the films, with simultaneous positive binding-energy shifts in the core levels of the admetal, molybdenum, and sulfur (for example, see Figure 5). Previous studies have shown the formation of H_xMoS₂ (or D_x-MoS₂) compounds after exposing bulk MoS₂ to high pressures (0.5–50 atm) of H₂ (or D₂).⁴⁹ It has been proposed that several reactions carried out over molybdenum sulfide catalysts under hydrogen-rich conditions (olefin hydrogenation, synthesis of alcohols from CO, HDS, HDN, HDO, etc.) are actually catalyzed by H_xMoS₂ compounds.⁵⁰ This raises the question of the catalytic effect of the sorbed hydrogen. In the ZnMoS and CoMoS films, most of the sorbed hydrogen evolved into gas phase at temperatures between 400 and 500 K. These temperatures are higher than those typically used during the hydrogenation and isomerization of olefins⁵¹ but lower than those used for the synthesis of alcohols from CO^{26,52} and the hydrotreatment of oil-derived feedstocks (HDS, HDN, or HDO processes).⁶

Under UHV conditions, our ZnMoS and CoMoS films did not react with molecular hydrogen to produce hydrogen sulfide. On the other hand, the films showed a large reactivity toward atomic hydrogen. This result suggests that the slow step in the H_{2,gas} + S_{solid} → H₂S_{gas} reaction over ZnMoS and CoMoS catalysts is the dissociation of molecular hydrogen. The results found for the interaction of D with ZnMoS and CoMoS films are similar in many aspects to those reported for the interaction of D with O/Ru(001).^{20a} As gas-phase hydrogen atoms impinge on O/Ru(001) surfaces, water is formed.^{20a} More than 50% of the saturation coverage of oxygen can be removed by means of gas-phase atomic hydrogen.^{20a} The trends in Figures 7 and 12 for the hydrogenation of the ZnMoS and CoMoS systems are consistent with a mechanism in which the impinging D

atoms react with S or SD species in the film to yield gaseous hydrogen sulfide. The hydrogen sorbed in the films did not seem to be active in the production of D_2S , since upon heating, it desorbed as D_2 instead of forming hydrogen sulfide. This behavior suggests that the sorbed hydrogen may have been bonded to coordinatively unsaturated metal atoms formed after removing sulfur from the films.

Comparing the initial rates for the $2D_{\text{gas}} + S_{\text{solid}} \rightarrow D_2S_{\text{gas}}$ reaction on MoS_x , ZnS_y/MoS_x , and CoS_y/MoS_x films (Figures 7 and 12), one finds that zinc significantly reduces the rate of hydrogenation of Mo-bonded S atoms. Once ZnS_y particles are formed on top of a MoS_x substrate, the direct interaction between D and the MoS_x is probably blocked, and the D atoms that adsorb on the ZnS_y particles are not able to diffuse toward the MoS_x substrate fast enough. In contrast, CoS_y particles are not effective at preventing the interaction between D atoms and a MoS_x substrate, and the initial rates of hydrogenation of Mo-bonded S atoms in CoS_y/MoS_x and MoS_x films are very similar. Therefore, when a source of atomic hydrogen is available, it could be more difficult to create Mo sites with sulfur vacancies on $ZnMoS$ catalysts than on $CoMoS$ or MoS catalysts.

In a previous work examining the effects of several metal promoters on the hydrodesulfurization of dibenzothiophene over MoS_2 catalysts,^{7a} it was found that the enhancement in the catalytic activity induced by Co was ~ 2 times larger than that produced by Zn. In general, several models have been proposed to explain the promotional effects of Co in HDS processes.^{3,6-12,19,53-55} Part of the difficulty in understanding the behavior of $ZnMoS$ and $CoMoS$ catalysts arises from the fact that these systems are complex, containing a low percentage of the active material and several interacting phases.^{6,12} On the basis of our results, the differences in the HDS activity of the $ZnMoS$ and $CoMoS$ catalysts could be a consequence of two factors. First, Co is more efficient than Zn at increasing the reactivity of Mo toward S-containing molecules. And second, the number of Mo centers that have sulfur vacancies on which an organosulfur molecule can adsorb and dissociate is probably larger on a $CoMoS$ catalyst than on a $ZnMoS$ catalyst.

V. Conclusions

Sulfur multilayers are very reactive toward admetals like zinc and cobalt. The behavior of the $Zn/S_{>1}/Mo(110)$ and $Co/S_{>1}/Mo(110)$ systems indicates that zinc and cobalt promote $Mo \leftrightarrow S$ interactions and the subsequent formation of molybdenum sulfides. The promotional effect of cobalt in a per atom basis is 2–3 times larger than that of Zn.

On $ZnMoS$ and $CoMoS$ films, the slow step in the $D_{2,\text{gas}} + S_{\text{solid}} \rightarrow D_2S_{\text{gas}}$ reaction is the dissociation of molecular hydrogen. The $2D_{\text{gas}} + S_{\text{solid}} \rightarrow D_2S_{\text{gas}}$ process is very efficient for the removal of sulfur from the films. The addition of ZnS_y particles to a MoS_x film leads to a reduction of 30–50% in the initial rate of hydrogenation of Mo-bonded sulfur. In contrast, CoS_y particles are unable to prevent the interaction between hydrogen and a MoS_x substrate, and the initial rates of hydrogenation of Mo-bonded S atoms in CoS_y/MoS_x and MoS_x films are very similar.

A good correlation exists between trends seen in the HDS activity of $CoMoS$ and $ZnMoS$ catalysts and trends found for the sulfidation of Mo and hydrogenation of S in $CoMoS$ and $ZnMoS$ films. The systems that contain Co exhibit the larger HDS activity, the stronger metal \leftrightarrow metal interactions with a subsequent increase in the reactivity of Mo toward S-containing molecules, and the bigger tendency to create unsaturated Mo sites through the hydrogenation of Mo-bonded S atoms.

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