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Properties of Fe, Co, Ni, Cu and Zn on S/Mo(110) surfaces and MoS$_x$ films: metal–metal interactions and the behavior of HDS catalysts

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Abstract—Recent studies on the physical and chemical properties of surfaces that contain sulfur, molybdenum and a second metal (X = Fe, Co, Ni, Cu or Zn) are discussed. The exposure of Mo(110) to large amounts of S$_2$ gas produces only a chemisorbed layer of sulfur, without forming molybdenum sulfides. The sulfidation of Mo occurs after exposing X/Mo(110) surfaces to S$_2$. Bimetallic bonding increases the reactivity of Mo toward sulfur. A good correlation exists between trends seen for the activity of XS$_y$/MoS$_2$ catalysts in hydrodesulfurization (HDS) reactions and trends found for the sulfidation of Mo in S/X/Mo(110) surfaces. Co and Ni exhibit a unique ability to promote Mo $\leftrightarrow$ S interactions that can be attributed to electronic effects induced by metal $\leftrightarrow$ metal interactions. On X/S/Mo(110) surfaces and X/MoS$_y$ films, the slow step in the H$_2$(gas) + S(solid) $\rightarrow$ H$_2$S(gas) reaction is the dissociation of molecular hydrogen. Co/MoS$_y$ and Ni/MoS$_y$ films interact strongly with atomic hydrogen, sorbing this element and forming gaseous hydrogen sulfide. The behavior of molybdenum sulfide catalysts in HDS processes is discussed in light of these results. © 1997 Elsevier Science Ltd

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The most frequently used hydrodesulfurization (HDS) catalysts consist of a mixture of MoS$_2$ and Co or Ni on a γ-alumina support [1]. After comparing the effects of different metals (V, Cr, Fe, Co, Ni, Cu 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 [2]. Several proposals have been offered to explain the behavior of CoMoS and NiMoS HDS catalysts [1–6]. In these systems, the active sites probably contain "CoMoS" or "NiMoS" units that may bond S weaker than Mo, facilitating in this way the formation of S vacancies where HDS reactions can occur [3]. Some workers attribute the high-turnover frequency of CoMoS and NiMoS catalysts to electronic interactions (Co $\rightarrow$ Mo or Ni $\rightarrow$ Mo electron transfers) that modify the reactivity of the metal components producing specially active HDS sites [2a,4,5]. In a different type of proposal, it has been suggested that the high activity of the catalysts results from their unique structural properties [1,6].

Part of the controversy in explaining the behavior of CoMoS and NiMoS catalysts arises from the fact that these systems are complex and very difficult to characterize, containing several interacting phases

and a small fraction of active sites [1,7]. In order to explain their behavior, it is necessary to understand the nature of the Co $\leftrightarrow$ Mo $\leftrightarrow$ S and Ni $\leftrightarrow$ Mo $\leftrightarrow$ S interactions at a fundamental level. Useful knowledge on this subject can be obtained by examining the properties of organometallic sulfur compounds [8] and well-defined surfaces generated by depositing Co or Ni on a single-crystal face of a molybdenum sulfide [9–12] or a S-covered face of metallic molybdenum [13–16].

In this article we discuss recent studies on the physical and chemical properties of surfaces that contain sulfur, molybdenum and a second metal (Fe, Co, Ni, Cu or Zn). In general, the interaction between sulfur and well-defined bimetallic surfaces has been the focus of considerable attention in recent years [13–23]. Depending on the nature of the metal $\leftrightarrow$ sulfur and metal $\leftrightarrow$ metal interactions, several phenomena can occur when sulfur reacts with a bimetallic surface. For some systems [19,21,22], one can observe the formation of bimetallic sulfides that exhibit chemical properties very different from those of the pure metals. In another type of system [17,18], the interaction between sulfur and one metal is repulsive, with sulfur inducing a weakening of the bimetallic bonds and

reducing the "mixing" of the metals. Finally, one can have bimetallic systems in which one of the metals increases or promotes the reactivity of the other toward sulfur [15,19]. In some situations, this phenomenon can accelerate the poisoning of catalysts for hydrocarbon reforming [19], while in others, the effect may be beneficial enhancing the activity of catalysts for HDS processes [15].

ADMETAL-PROMOTED SULFIDATION OF Mo(110) AND TRENDS IN THE ACTIVITY OF HDS CATALYSTS

In order to optimize the activity of Mo-based HDS catalysts, one needs to understand how metals like Co and Ni affect the reactivity of Mo toward S-containing molecules. This issue has been the motivation for a series of works that examine the behavior of Co/Mo and Ni/Mo surfaces [13–16]. The structural and electronic properties of Co/S/Mo(100) [13], Co/S/Mo(110) [14–16], Ni/S/Mo(110) [12,15] and Ni/S/W(100) [20] surfaces have been examined in detail. For submonolayer coverages of sulfur, the S atoms remain close to the surface of these systems in a chemisorbed state and no formation of sulfides of the admetals (Co and Ni) or metal substrates (Mo and W) has been observed. After depositing a Co or Ni monolayer on S/Mo and S/W surfaces ($\theta_s < 0.8$ monolayer) and heating above 500 K, the admetals form three-dimensional clusters and a large fraction of the sulfur migrates from the Mo and W substrates to on-top of the Co or Ni producing systems with a sulfur–admetal–substrate configuration [12,13,15,20]. The "driving-force" for this migration is the very low surface-free energy of sulfur (0.08 J M^{-2}) [24].

S/Ni/Mo(110) surfaces exhibit a reactivity toward H$_2$, CO and H$_2$S that is much smaller than that of Ni, Mo and Ni/Mo surfaces [12]. Studies dealing with the adsorption of Co on S/Co/Mo(110) surfaces reveal that sulfur weakens the CO $\leftrightarrow$ metal interactions in these systems by acting as a site blocker and an electron-withdrawing agent [14]. A comparison of the reactivities of Ni(100), W(100) and Ni/W(100) surfaces for methanethiol decomposition shows that a bilayer of pseudomorphic Ni and W(100) exhibits the lowest temperature for C—S bond cleavage and the highest selectivity for methane formation [25]. On the other hand, the trends in the desulfurization of methanethiol on Co/Mo(110) and Mo(110) surfaces are very similar [16]. The reaction of methanethiol with S/Co/Mo(110) surfaces indicates that the presence of sulfur decreases the reactivity of cobalt [16].

The exposure of Mo(110) to S$_2$ gas at 500–700 K under ultrahigh-vacuum conditions produces a chemisorbed layer of sulfur without the formation of molybdenum sulfides [10,15]. In principle the formation of MoS$_x$ from metallic molybdenum and sulfur should occur spontaneously ($\Delta G = -200$ to -370 kJ mol^{-1}) [26], but there is a large kinetic barrier for the pen-

etration 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 $\leftrightarrow$ metal interactions [15,21b].

Figure 1 shows Mo $3d$ XPS spectra acquired after dosing S$_2$ to clean Mo(110) [15] and Mo(110) surfaces with similar coverages (~ 1.5 monolayers) of Ni [15], Cu [21b], Zn [27] and Ag [21b]. The Mo $3d$ peak at ~ 228 eV corresponds to metallic Mo, while the peak at ~ 229.2 eV denotes the formation of molybdenum sulfides (MoS$_x$) in these systems [15]. The amount of MoS$_x$ formed depends strongly on the nature of the admetal (bottom of Fig. 1). In general, Ni and Co have a unique ability to promote Mo $\leftrightarrow$ S interactions and the formation of molybdenum sulfide [15].
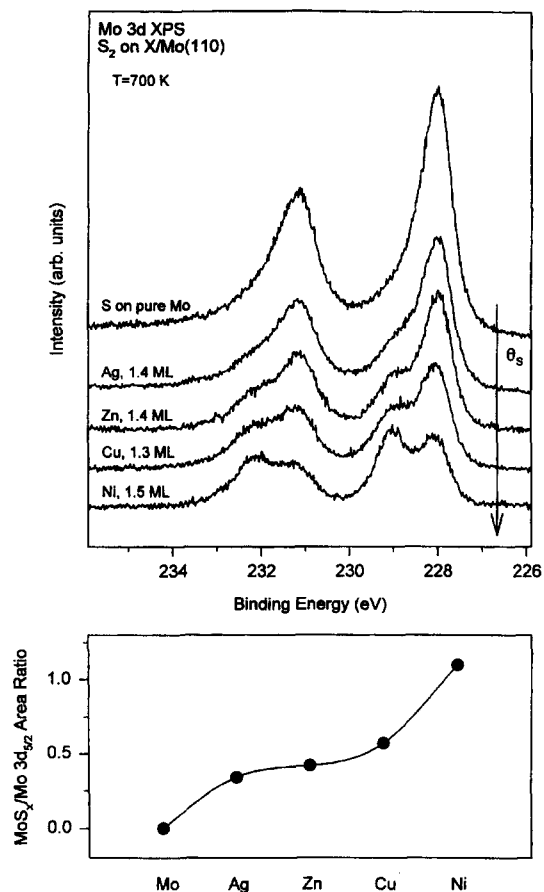

Fig. 1. Mo $3d$ XPS spectra acquired after dosing large amounts of S$_2$ to clean Mo(110) and X/Mo(110) surfaces (X = Ag, Zn, Cu or Ni) at 700 K. The spectra correspond to systems in which the rate of S$_2$ adsorption has become equal to zero under UHV conditions. In the bimetallic systems the total amount of adsorbed sulfur is much larger than a monolayer and increases when going from Ag/Mo(110) to Ni/Mo(110). The bottom part of the figure shows the ratio between the $3d_{5/2}$ signals of MoS$_x$ and Mo in each spectrum (from ref. [15]).

Results for the reaction of S_2 with a series of X/Mo(110) surfaces (X = admetal) indicate that the "promotional effect" of an admetal on the sulfidation of Mo increases following the sequence: Ag $\approx$ Zn < Cu < Fe < Co < Ni [10,15,28]. This trend correlates with the strength of the bimetallic bond in X/Mo(110) surfaces: the stronger the admetal $\leftrightarrow$ molybdenum interactions, the larger the promotional effect of the admetal on the sulfidation of Mo [15]. All the admetals in Fig. 1 form sulfides that are less stable than those formed by molybdenum [26].

Figure 2 compares trends observed in the activity of a series of XS_y/MoS_2 catalysts (X = Zn, Cu, Fe, Co or Ni) during the desulfurization of dibenzothiophene [2] with trends found for the sulfidation of Mo in X/Mo(110) surfaces. In general, a good correlation is observed between the changes in the two properties. The presence of Ni leads to a significant enhancement in the Mo $\leftrightarrow$ S interactions and a very large HDS activity. In contrast, the effects of Zn, Cu and Fe on the Mo $\leftrightarrow$ S interactions and HDS activity are less pronounced.

It has been proposed that the difference in the HDS activity of FeMoS and NiMoS catalysts is a consequence of a change in the electronic interactions between the metals, with Ni being more effective than Fe at increasing the electron density and reactivity of Mo toward S-containing molecules [2]. The same argument can explain the difference in the reactivity of Fe/Mo(110) and Ni/Mo(110) toward S_2. Table 1 list the results of *ab initio* SCF calculations [15,28] for Fe/Mo_9 and Ni/Mo_9 clusters that model the bonding of a Fe and Ni atom to a hollow site of Mo(110), and Fe_4Mo_4 and Ni_4Mo_4 cubic clusters that model 1:1 alloys of the metals (see Fig. 3). A positive charge indicates a depletion of electrons at the metal center. The *ab initio* SCF calculations show that Ni is a much better electron donor than Fe. In Ni/Mo(110) the electron density of the Mo atoms should be larger than in Fe/Mo(110), making an S electrophilic attack on Mo and the formation of Mo $\rightarrow$ S dative bonds easier [28].

Table 1. Charge in Fe–Mo and Ni–Mo clusters (electrons)

| | Fe or Ni Orbital populations | | | |
	$3d$	$4s$	$4p$	Atomic charge
Fe/Mo_9[a]	6.89	0.75	0.23	+0.13
Ni/Mo_9[b]	8.77	0.74	0.28	+0.21
Fe_4Mo_4[a,c]	6.91	0.79	0.21	+0.09
Ni_4Mo_4[b,c]	8.80	0.82	0.22	+0.16

[a] From ref. [28].

[b] From ref. [15].

[c] The listed values are for one of the Fe or Ni atoms in the cluster (see Fig. 3).

After exposing X'/Mo(110) surfaces (X' = Zn, Cu, Fe or Ni) to large amounts of S_2 (θ_s > 1 monolayer), photoemission spectroscopy allows a clear analysis of the chemical state of each metal under various conditions. Such analysis is not possible for the S/Co/Mo(110) systems, since there is no clear difference in the core-level binding energies of metallic cobalt and cobalt sulfides [10,15]. In the case of S/Ni/Mo(110), the admetal exhibits a large tendency to remain in a metallic state [15]. On the other hand, for S/Zn/Mo(110) [27], S/Cu/Mo(110) [21b] and S/Fe/Mo(110) [28], one finds that the admetals are fully sulfidized. If we extrapolate these results to XS_y/MoS_2 catalysts, we can expect that the probability of finding a S-free adsorption site around a Ni atom is larger than that of finding a similar site around Zn, Cu or Fe atoms. Thus, three factors can contribute to the large HDS activity of NiMoS catalysts [12,15]: (1) the existence of Ni centers that have S-free sites on which an S-containing molecule can adsorb; (2) the presence of Ni–Mo sites that are very reactive for the desulfurization of the adsorbed molecule; (3) on the S-free Ni sites hydrogen molecules can dissociate, producing in this way a source of hydrogen atoms that will help to remove sulfur from the surface and keep a large number of unsaturated Mo and Ni sites (see below).

SYNTHESIS OF MOLYBDENUM SULFIDE FILMS

To investigate the chemical properties of surfaces of molybdenum sulfide using modern techniques of surface science, one needs an efficient route to prepare these systems under ultrahigh vacuum (UHV) conditions. Thick sulfur films can be grown on surfaces of Mo [29,30] and other metals [31] by dosing S_2 at temperatures below 200 K. Under these conditions the S_2 molecules react on the surface forming S_n rings [30,31]. Results of photoemission and IR spectroscopy suggest that S_8 is the dominant species in these films [31]. The sulfur films sublimate at temperatures between 250 and 400 K, with S, S_2, S_4 and S_8 evolving into gas phase [30,31].
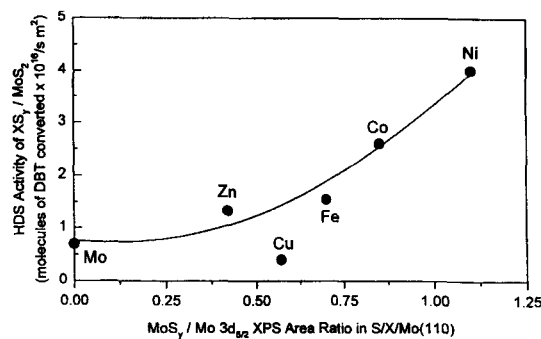

Fig. 2. X axis: relative amount of MoS_y formed after exposing $X_{1.5}$/Mo(110) surfaces (X = Zn [27], Cu [21b], Fe [28], Co [15] and Ni [15], with θ_x = 1.5 monolayer) to S_2 at 700 K. Y axis: activity of MoS_2 and XS_y/MoS_2 catalysts for the desulfurization of dibenzothiophene (DBT) [2].
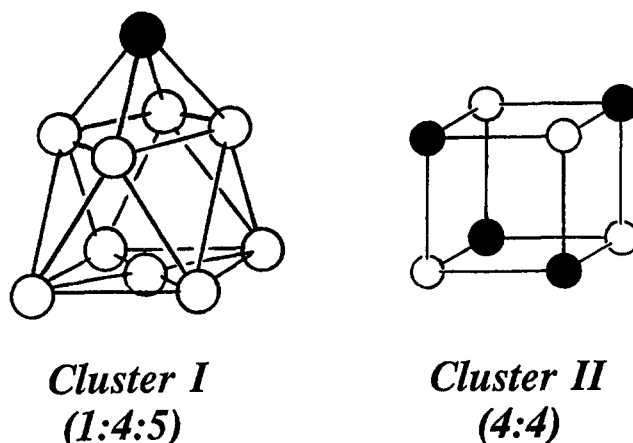
Cluster I
(1:4:5)

Cluster II
(4:4)

Fig. 3. Clusters employed to study the interaction between Mo atoms (open circles) and Fe or Ni atoms (closed circles). Cluster I represents the adsorption of Fe or Ni on the center of a hollow site of Mo(110). Cluster II was used to model metal–metal bonding in 1:1 FeMo and NiMo alloys (from ref. [15]).

In the $S_{film}/Mo(110)$ systems, no molybdenum sulfide is formed [30]. Recently, an efficient method has been reported for the preparation of molybdenum sulfide films under UHV conditions using zinc as a promoter for the sulfidation of molybdenum [10]. First, a sulfur multilayer is deposited on Mo(110) at 80–200 K. Then, a Zn film is vapor-deposited on the $S_{film}/Mo(110)$ system at ~ 200 K. This is followed by a full sulfidation of the zinc by exposing it to S_2 gas at 250–300 K. Finally, the sample is annealed to 1000–1050 K to desorb Zn and leave a *pure* MoS_x film. Following this methodology, films that have between 2 and 6 monolayers of MoS_x can be prepared [10]. These films exhibit Mo $3d$ and S $2p$ XPS spectra that are very similar to those of MoS_2 [10]. They show no reactivity toward CO, O_2 and H_2 at 80–300 K [10]. This indicates that they do 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 [32–34]. The films probably expose surfaces similar to the sulfur-basal plane of MoS_2 that is unreactive toward CO, O_2 and H_2 [32,35].

ADMETALS ON MOLYBDENUM SULFIDE SURFACES

It is important to establish how metals like Co and Ni interact with surfaces of molybdenum sulfide. Figure 4 shows Ni $2p_{3/2}$ and Mo $3d$ XPS data taken after depositing 0.4 monolayers of Ni on a pure molybdenum–sulfide film (12–15 Å in thickness) at 80 K [12]. The deposition of Ni did not induce any change in the line shape or binding energy of the Mo $3d$ and S $2p$ features [12]. The Ni adatoms remained in a metallic state. An identical result was found for the deposition of Ni on the sulfur-basal plane of MoS_2 [9], where the admetal was not able to remove S from

Mo to form NiS_y. In a similar way, for the adsorption of Co, Ag and Zn and MoS_x films at 80–300 K there was no formation of CoS_y, AgS_y or ZnS_y compounds [10,36]. In contrast, Fe atoms deposited on the S-basal
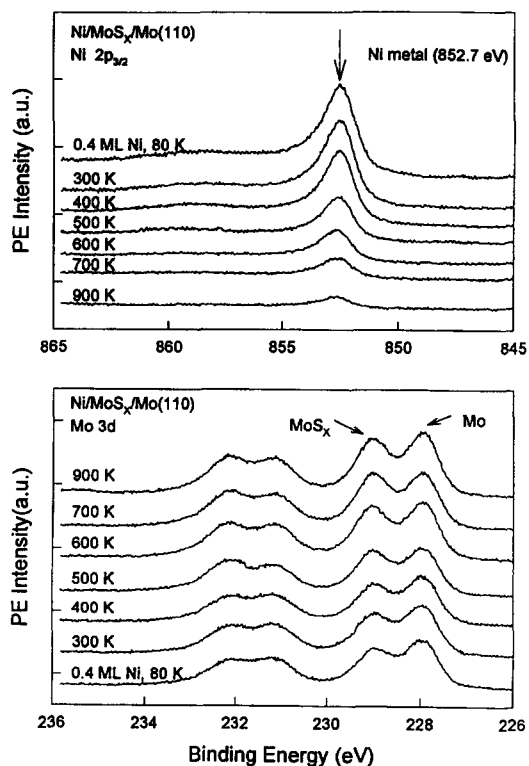

Fig. 4. Ni $2p_{3/2}$ and Mo $3d$ XPS spectra taken upon the deposition of 0.4 monolayers of Ni on a molybdenum–sulfide film at 80 K, followed by heating to 300, 500, 700 and 900 K. The arrow in the top part of the figure denotes the position for the Ni $2p_{3/2}$ level of pure metallic Ni (from ref. [12]).

plane of MoS_2 removed S from it, leaving islands of uncovered Mo in the surface [9b]. These differences in the behavior of the admetals probably reflect variations in the thermodynamic stability of the sulfides that they can form [10,12]. Thus, Fe is able to form sulfides that are more stable than those formed by Co, Ni, Ag and Zn [26].

The bonding interactions between several admetals (Co, Ni, Ag and Zn) and MoS_2 were investigated using INDO/S and *ab initio* SCF calculations [15,36]. The S-basal plane of MoS_2, (0002) face, plus the Mo- and S-terminated ($10\bar{1}0$) faces were modeled using 18–36 atom clusters: Mo_6S_{12}, Mo_9S_{18} and $Mo_{12}S_{24}$. In all the cases investigated, there was an admetal → MoS_2 charge transfer that increased the negative charge on sulfur and reduced the positive charge on molybdenum. Zn and Ag were poor electron donors when compared with Co and Ni [15,36]. This is consistent with the results of previous theoretical studies that explain the high catalytic activity of CoMoS and NiMoS catalysts in terms of an electron transfer from Co or Ni to Mo [2a,4,5a].

In Fig. 4, heating to temperatures above 400 K induces a reduction in the Ni $2p_{3/2}$ signal as a consequence of clustering of Ni into three-dimensional islands and penetration of the admetal into the MoS_x substrate [12]. The same phenomena are observed when heating $Ni/MoS_2(0002)$, $Fe/MoS_2(0002)$, Ag/MoS_x and Co/MoS_x surfaces to high temperature [9,10,36]. The migration of the admetals from the surface into the bulk of molybdenum sulfide leads to a minimization of the total surface-free energy [10].

HYDROGENATION OF SULFUR AND MOLYBDENUM SULFIDE SURFACES

On molybdenum sulfide catalysts, the HDS reactions occur on metal sites that are not covered with sulfur [3a]. Unsaturated metal sites are generated through the hydrogenation of surface S atoms. Studies using scanning transmission electron microscopy have revealed that the sulfur-basal plane of MoS_2 is virtually unreactive toward H_2 [32]. Hydrogen attacks only the edge planes of MoS_2 [32].

The reaction of hydrogen (H_2, D_2 or D) with sulfur multilayers, $S/Mo(110)$ surfaces, and MoS_x films has been investigated at temperatures between 100 and 400 K [30]. All these systems were unreactive toward molecular hydrogen under UHV conditions. However, they showed a large reactivity toward atomic hydrogen. As gas-phase hydrogen atoms impinged on the surfaces, gaseous hydrogen sulfide was formed. This is illustrated by the data in Fig. 5 [30]. In this experiment, a sulfur film ($\theta_s \sim 8$ monolayers) was set in front of a mass spectrometer an exposed to D_2 gas ($\sim 5 \times 10^{-7}$ Torr, 300 s) at 100 K. This did not produce any significant change in the background signal for mass 38 (D_2S). Upon turning on the D doser ($\sim 1 \times 10^{-8}$ Torr, 170 s), there was a
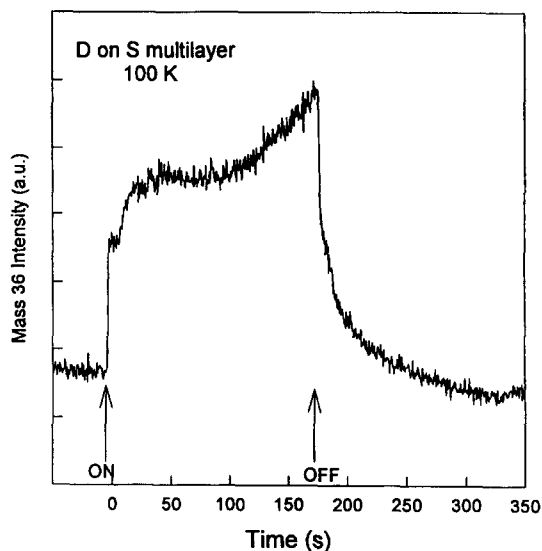

Fig. 5. Increase in the MS signal for D_2S gas as a consequence of dosing D to a sulfur film at 100 K. The labels "ON" and "OFF" indicate the times at which the D doser was turned on and off, respectively. When a similar experiment was carried out dosing D_2, there was no change in the MS signal for D_2S (from ref. [30]).

large increase in the D_2S signal that disappeared when the D doser was switched off.

On MoS_x films the $2D(gas) + S(Solid) \rightarrow D_2S(gas)$ reaction was 3–4 times slower than on sulfur multilayers, and at least six times faster than on $S/Mo(110)$ surfaces [30]. A good correlation was found between the rate of formation of gaseous hydrogen sulfide and the stability of the S—S and S—Mo bonds in a surface [30]. Reaction with atomic hydrogen is a very effective way to remove sulfur atoms from molybdenum sulfide. Figure 6 shows Mo $3d$ XPS spectra acquired before and after dosing atomic hydrogen to a film that contained between 2.5 and 3 monolayers of MoS_x. Similar doses of pure D_2 did not produce any modification in the intensity or line shape of the Mo $3d$ features. After exposing the $MoS_x/Mo(110)$ system to atomic hydrogen there is a monotonic decrease in the signal for MoS_x. By dosing D one can achieve a complete reduction of the sulfide [30].

From the results in Figs 5 and 6, one can conclude that the slow step in the $H_2(gas) + S(solid) \rightarrow H_2S(gas)$ reaction is the dissociation of molecular hydrogen [30]. Thus, if a metal promoter enhances the concentration of atomic hydrogen on the surface of a MoS_2 catalyst, one can expect an increase in the number of unsaturated Mo sites and in the HDS activity [36]. Experiments examining the interaction of H_2 with Co/MoS_x and Ni/MoS_x surfaces under UHV conditions at 200–300 K showed that a significant amount of hydrogen molecules dissociated on the Co and Ni overlayers [10,12]. However, the chemisorbed hydrogen did not migrate onto the MoS_x substrate and, therefore, no sulfur was removed from the surfaces
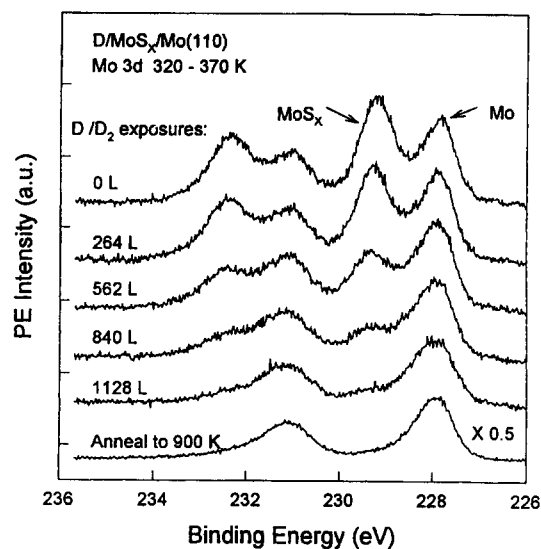
Fig. 6. Mo 3d spectra taken after dosing a mixture of atomic and molecular hydrogen to a MoS_x film at 320–370 K (from ref. [30]) ; 1–2% of the D_2 molecules that went through the doser dissociated into D atoms. Dosing of pure D_2 did not induce any significant change in the Mo 3d features of the MoS_x film. 1 langmuir (L) = 10^{-6} Torr s.
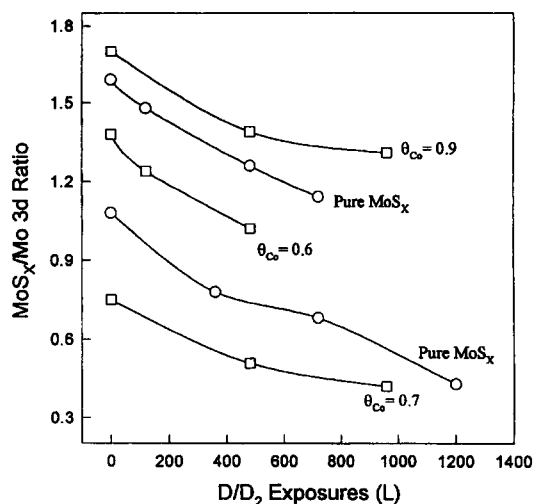
Fig. 7. Hydrogenation of Mo-bonded S atoms in MoS (○) and CoMoS films (□). The films were exposed to a mixture of D_2 and D ($\sim 1\%$) at 300–370 K. Dosing of pure D_2 did not produce any significant change in the MoS_x/Mo 3d XPS ratio of the films. The lines connecting the points are drawn to guide the eyes. 1 langmuir (L) = 10^{-6} Torr s (from ref. [10]).

[10,12]. This result does not rule out the possible existence of a migration of atomic hydrogen from Co or Ni to MoS_x when CoMoS and NiMoS surfaces are exposed to high pressures of H_2 or D_2, which can produce large coverages of hydrogen on the admetals and force in this way hydrogen diffusion toward the molybdenum sulfide. This "spillover" of atomic hydrogen will help to remove sulfur from the molybdenum–sulfide surface, creating unsaturated Mo site on which HDS reactions can take place [36].

In general, Co/MoS_x and Ni/MoS_x films exhibit initial rates of sulfur hydrogenation that are comparable to those seen during the exposure of MoS_x films to atomic hydrogen [10,12]. This is illustrated by the data in Fig. 7. The figure shows how the MoS_x/Mo 3d XPS ratio of MoS and CoMoS systems changes after dosing atomic hydrogen [10]. The "hydrogenation" curves for the MoS and CoMoS systems show initial slopes (at 0–400 L D/D_2 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 D_2S 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.

Upon exposure of MoS_x and Y/MoS_x films (Y = Co or Ni) to atomic hydrogen at 300–400 K, the films sorb significant amounts of hydrogen [10,12]. This is consistent with experiments that show the formation of H_xMoS_2 (or D_xMoS_2) compounds after exposing bulk MoS_2 to high pressures (0.5–50 atm) or

H_2 (or D_2) [37]. 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 catalysed by H_xMoS_2 compounds [38]. This raises the question of the catalytic effect of the sorbed hydrogen. In the MoS_x and Y/MoS_x films, most of the sorbed hydrogen evolves into gas phase at temperatures between 400 and 500 K [10,12]. These temperatures are higher than those typically employed during the hydrogenation and isomerization of olefins [39], but lower than those used for the synthesis of alcohols from CO [40] and the hydrotreatment of oil-derived feedstocks (HDS, HDN or HDO processes) [1].

CONCLUSIONS

Bimetallic bonding increases the reactivity of molybdenum toward sulfur. A good correlation exists between trends seen for the activity of XS_y/MoS_2 catalysts (X = Fe, Co, Ni, Cu or Zn) in HDS reactions and trends found for the sulfidation of Mo in S/X/Mo(110) surfaces. Co and Ni exhibit a unique ability to promote Mo $\leftrightarrow$ S interactions that can be attributed to electronic effects induced by metal $\leftrightarrow$ metal interactions.

On S/Mo(110) and MoS_y films, the slow step in the H_2(gas) + S(solid) $\rightarrow$ H_2S(gas) reaction is the dissociation of molecular hydrogen. If a metal promoter enhances the concentration of atomic hydrogen on the surface of a MoS_2 catalyst, one can expect an

increase in the number of unsaturated Mo sites and in the HDS activity. Co/MoS_y and Ni/MoS_y films interact strongly with atomic hydrogen, sorbing this element and forming hydrogen sulfide.

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