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Catalysis by Transition Metal Sulfides: A Theoretical and Experimental Study of the Relation between the Synergic Systems and the Binary Transition Metal Sulfides

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Both a systematic experimental study of the promoting effect of the first row transition metals on the hydrodesulfurization (HDS) activity of MoS_2 and a systematic theoretical study of the electronic structure of simple clusters which model these catalyst systems have been carried out. A comparison of measured trends in activity with calculated trends in electronic structure makes it possible to establish an electronic basis for the promotion effects observed in the MoS_2 systems. Both Co and Ni, which serve as promoters, have the ability to donate electrons to Mo, while Cu, which serves as a poison, withdraws electrons from Mo. The other first row transition metals, which have little effect on the HDS activity of MoS_2, do not have the ability to donate to or accept electrons from Mo. Thus promotion is associated with an increase in electron density on Mo while poisoning is associated with a decrease in electron density. These results are consistent with previous results which related particular electronic factors to the HDS activity of binary sulfide catalysts. © 1986 Academic Press, Inc.

INTRODUCTION

In a recent paper (*1*) we presented a relation between calculated electronic trends and experimental trends in the hydrodesulfurization (HDS) activity of the transition metal sulfides (TMS). The experimental trends had previously been measured using the HDS of dibenzothiophene (DBT) as a model reaction (*2*). The activities of the unsupported binary TMS (the simple TMS with one type of transition metal and sulfur as the two components) were determined in the model reaction, and the periodic trends for this reaction were established. The trends found in this reaction yield typical "volcano" plots similar to those observed for many other types of reactions and catalysts (*3*) The first row TMS are relatively inactive, but the second and third row TMS show distinct activity maxima in Group VIII with the peak of the maxima occurring at Ru in the second row and Os in the third row.

A theoretical basis for understanding the experimental trends was initiated by exploring the electronic structure of the first and second row TMS using the scattered-wave X_α technique (*4*). Calculations were carried out for a group of octahedral MS_6^{n-} clusters where the transition metal M was varied systematically across the first transition series from Ti to Ni and across the second transition series from Zr to Pd. Based on these calculations it was shown (*1*) that a relation exists between the calculated electronic structure of the sulfides and their activity as HDS catalysts. Several electronic factors were identified which appear to be related to catalytic activity. These are the orbital occupation of the highest occupied molecular orbital (HOMO), the degree of covalency of the metal–sulfur bond, and the metal–sulfur covalent bond strength. These factors were incorporated into a calculated activity parameter A_2, which correlates with the observed catalytic activity of the sulfides. If a particular sulfide has a high value of A_2 then it can be expected to have a high activity in the HDS reaction. In this

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paper we now extend both the experimental and theoretical approaches previously applied to binary sulfide systems to the promoted or "synergic" MoS_2 systems.

It is well known and of great industrial importance that the addition of a second transition metal such as Co or Ni to a binary sulfide such as MoS_2 or WS_2 can give rise to an enhancement of HDS activity. This enhancement can be quite pronounced. Tenfold increases in activity over the activity of the unpromoted sulfide are not uncommon. Industrially this effect is exploited in the common $Co/Mo/Al_2O_3$ and $Ni/Mo/Al_2O_3$ catalysts which are used for hydrotreating and heteroatom removal applications in virtually every refinery in the world. These systems have been studied intensively for many years (*5*), but progress toward understanding the origin of the promotion effect [through theoretical (*6*) as well as experimental studies] has been slow. A vast majority of the experiments done in this area have dealt with supported systems. Recent work has demonstrated with a fair degree of certainty that the active Mo component of the supported catalyst is found in a MoS_2-like structure, although the degree of dispersion and stoichiometry are still debated. The Co in these systems appears to be in a sulfided environment but its actual structural environment seems to be uncertain (*7*). It has been shown that the active form of the Co initially present in the catalyst gives a unique Mossbauer emission spectrum (MES) in both supported and unsupported promoted catalysts (*8*). This work has resulted in the discovery of a "CoMoS" phase which may be the active component in promoted catalysts. Although the precise structure of the CoMoS phase is still in question, the close association of the active Co with the MoS_2 seems clear. It is not clear, however, whether the CoMoS phase is the active phase present after a catalyst has been stabilized for long periods of time under reaction conditions or whether it is an active but metastable state. Nevertheless, the discovery of the CoMoS phase represents a significant advance in our understanding of these promoted systems.

Part of the difficulty in understanding the promotion effect arises from the fact that the industrially important supported catalysts are very complex systems containing a low percentage of the active material and many interfering phases. This difficulty can be partially overcome by studying unsupported systems. It has been known for some time that the promotion effect is not fundamentally related to the presence of the Al_2O_3 support. This is known because the effect can be observed quite strongly in unsupported catalysts (*9–11*). Delmon and co-workers have shown that the promotion effect can be observed if a mixture is made of either Co_9S_8 or Ni_3S_2 with MoS_2 or WS_2 (*11*). The mixture can be made either chemically or physically, with the effectiveness of promotion being dependent on the degree of intimacy provided by the mixing. When the amount of Co or Ni present is greater than some critical amount, then the bulk phases present, as determined by X-ray diffraction, are always Co_9S_8 or Ni_3S_2 and MoS_2 or WS_2. This observation led Delmon to attribute the promotion effect to the contact between the two phases, and thus the term "synergy by contact" was used to describe the promotion effect. Although this idea does not describe the microscopic origin of promotion it does express the idea that these pairs of compounds act together to produce the promotion effect. Topsøe and co-workers later showed that the CoMoS phase was present in these unsupported catalysts and that presumably the contact synergy could produce the CoMoS phase at the surface, at least in unsupported catalysts (*8*).

Earlier work on WS_2 by Voorhoeve and co-workers (*9*) and on MoS_2 by Farragher and co-workers (*10*) pointed to the importance of the edge planes of the layered compounds MoS_2 and WS_2 in the promotion by Ni and Co. Both groups of workers attributed promotion to "pseudo-intercalation" of Co or Ni at the edges of the layered compounds. Since that time most of the popular theories of promotion have involved association of Co or Ni with these edge planes, even though the precise location of the Co or Ni atoms is still unknown. Physical studies have also lent support to the idea of the promoter being associated with the edge planes. A recent scanning Auger study of single crystals of MoS_2 doped with Co clearly shows the edge Co enrichment of these crystals (*12*). A geometrical model which substantiates the idea of edge promotion was recently presented by Kasztelan and co-workers (*13*). Their study, which uses Co-decorated MoS_2 crystallites to fit experimental activity-versus-promoter concentration curves, indicates that the effect of the promoter is electronic (the quality of the site is promoted) and not structural (the number of sites is increased by the promoter). That the effect of the promoter is electronic (chemical) has been supported by Chianelli and co-workers who noted that the "synergic systems" are related to the simple binary sulfides through average heats of formation (*14*). This work suggests that the synergic systems behave at their surface as if they are hypothetical "pseudobinary" systems having average properties of their two components.

In the study reported here we further develop the idea that the basis for promotion is electronic in character. We have done this by using the same experimental and theoretical techniques which we used in our previous study of the binary TMS catalysts. We have carried out both a systematic experimental study of the promoting effect of the first row transition metals vanadium through zinc on the HDS activity of MoS_2 and a systematic theoretical study of the electronic structure of simple clusters which model these promoted catalyst systems. As discussed above, the importance of the edge planes and the proximity of the promoter and Mo atoms in MoS_2 catalyst systems have been established by previous experimental work. We have chosen the model clusters so that their structure is consistent with this established information. In the next two sections of this paper we describe the systematic preparation of MoS_2 promoted by the first row transition metals V through Zn and a study of the HDS activity for dibenzothiophene (DBT) of these catalyst systems. The results show that the effectiveness of the first row metals as promoters varies with the periodic position of the metal. In the fourth section we describe the makeup of the model clusters and the calculated electronic structure of these model systems. The results of these calculations show trends in electronic structure which are also related to the periodic position of the first row metal. These trends appear to correlate well with the activity of the corresponding promoted catalyst systems, and finally we discuss the apparent relation between catalytic activity and electronic structure. Thus we establish that there is an underlying fundamental electronic basis for the promotion effects observed in HDS catalysts.

EXPERIMENTAL

All catalysts were prepared by the reaction of a divalent or trivalent first row transition metal salt with ammonium thiomolybdate at 400°C in a flowing stream of $H_2/(15\%)H_2S$. The case of Mn is taken as an example:

$$MnCl_2 \cdot 4H_2O + (NH_4)_2MoS_4 \xrightarrow[H_2/H_2S]{400°C}$$
$$MnS + MoS_2 + H_2S\uparrow + 2NH_3\uparrow$$
$$+ 4H_2O\uparrow + S\uparrow + 2HCl\uparrow .$$

All first row transition metal salts were "Baker Analyzed" reagent grade, and the ammonium thiomolybdate was prepared by the method of Diemann and Müller (*15*). The resulting black powders were analyzed by standard X-ray diffraction powder methods and standard BET surface area analysis. All catalysts were prepared in a 1 : 1 stoichiometry (except for Cr and V where the Cr or V to Mo ratio was 2 : 3) as indicated above using the following divalent or trivalent salts of the first row transition metal: VCl_3, $CrCl_3 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$, $FeCl_2 \cdot 4H_2O$, $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot xH_2O$, and $ZnCl_2$. Standard MoS_2 catalysts were prepared by precipitation from nonaqueous solution (*16*). The reaction studied was the desulfurization of DBT, and the method used in this study has been previously reported (*2*). Catalyst activity measurements were made using a Carberry reactor modified to allow a flowing hydrogen atmosphere to remove product H_2S which may inhibit the HDS reaction at high concentrations. Rates were determined at 350°C and at 450 psi of hydrogen. Conversion of DBT with time was determined below 50% total conversion. Under these conditions the conversion with time plots are linear and pseudo-zero-order kinetics can be applied (*2*). In this paper only rates based on the total disappearance of DBT are reported and no effort is made to discuss selectivity effects (These effects are not important in these catalysts, the primary product being biphenyl.)

EXPERIMENTAL RESULTS

Catalysts were X-rayed after the DBT activity measurements in order to try to determine the stable states of the catalysts which are responsible for the activity and to avoid transient states which are changed in the reactor. The results of these X-ray measurements are indicated in Fig. 1. In all cases the diffraction shows "poorly crystalline" MoS_2 as the predominant Mo-containing phase. The pattern of this random layer lattice phase is easily recognizable by the broad hump appearing near 14° 2θ and the broad, assymetric peak beginning near 33° 2θ which tails to higher angles. The phase and its relation to catalysis have been previously described (*17*).

The catalysts chosen for this study were prepared in a convenient way which permitted all the first row transition metals to be prepared in the same manner. The result of choosing this method of preparation is that the stoichiometry of the catalysts is fixed at 1 : 1 or 2 : 3 (first row metal to molybdenum). Variation of this ratio for each

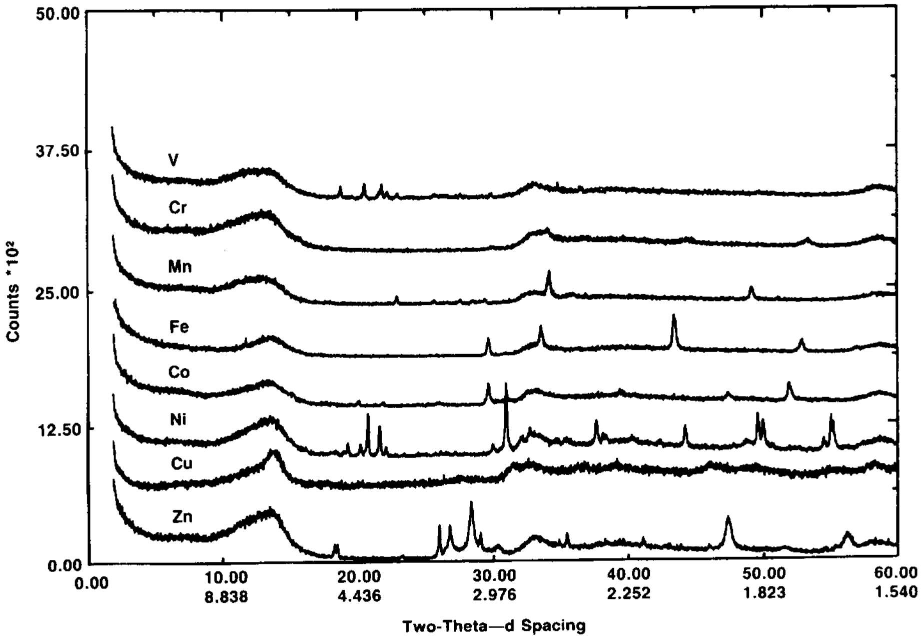

FIG.. 1. X-Ray diffraction patterns of sulfide catalysts as described in Table 1.

TABLE 1

Catalyst Properties

Catalyst phase		Surafce area (m^2/g)	Activity (molecules × $10^{16}/s \cdot m^2$)
V/Mo	$V_2S_3 + MoS_2$	21.9	1.13
Cr/Mo	$Cr_2S_3 + MoS_2$	45.8	0.65
Mn/Mo	$MnS + MoS_2$	15	1.07
Fe/Mo	$FeS_x + MoS_2$	18.2	1.55
Co/Mo	$Co_9S_8 + MoS_2$	20.8	2.60
Ni/Mo	$Ni_3S_2 + MoS_2$	10.8	4.01
Cu/Mo	$CuS_x + MoS_2$	23.1	0.41
Zn/Mo	$ZnS + MoS_2$	14.8	1.34
Mo	MoS_2	17.8	0.62
Mo	MoS_2	13.8	0.76

[a] Activity measurements were made at 350°C and 450 psi as described in Ref. (*2*).

metal is left to a future study. At these first row metal to molybdenum ratios it is well known (at least for Fe, Co, and Ni) that the first row metal will appear predominantly as a second phase (*18*). In all cases a second phase can be detected, and these phases are summarized in Table 1. It must be pointed out, however, that in many cases the second phases are difficult to absolutely determine, primarily because of the broadness of the diffraction peaks. All assignments are consistent with what appears in the literature about these mixed phases. Additionally, it has been shown that the first row metal may be present as an amorphous mixed phase (*19*). This phase would not appear as sharp Bragg peaks in the diffraction but would appear as diffuse scattering under the poorly crystalline scattering. In view of the fact that the scattering from the second phase is often weak and that the amount of first row metal is high, it is possible that an amorphous phase of this type occurs in many of these catalysts. Also it seems that there may be a small amount of an unidentified ternary oxide impurity in some of the catalysts.

The results of the activity measurements, normalized per unit surface area, are shown in Table 1. In the absence of further information regarding the surface composition of these catalysts we feel that the normalization to unit surface area is the best that can be accomplished with a set of catalysts prepared in the same manner. We believe that such a normalization, while not yielding a turnover number, will reflect the average surface composition of the catalysts as has been previously suggested (*14, 20*). Further information regarding the surface composition of these catalysts is the subject of an ongoing study. A normalization per gram of catalyst will also yield the same relation between the metals. The activity data are plotted in Fig. 2. We can see from the diagram that a "volcano plot" is the result. Standard MoS_2 catalysts of similar surface area yield relative values of activity in the range of 0.7. In this series it can be said that V, Cr, Mn, and Zn show no promotion and that Fe shows weak promotion although previous literature has not indicated any tendency of Fe toward promotion (*14*). In agreement with the literature Co and Ni are strong promoters. Cu shows a poisoning effect which to our knowledge has not been previously reported.

CLUSTER CALCULATIONS AND RESULTS

Calculations were carried out for a group of clusters $MoM'S_9^{n-}$, where the first row transition metal M' was varied systematically across the series from V to Zn. These

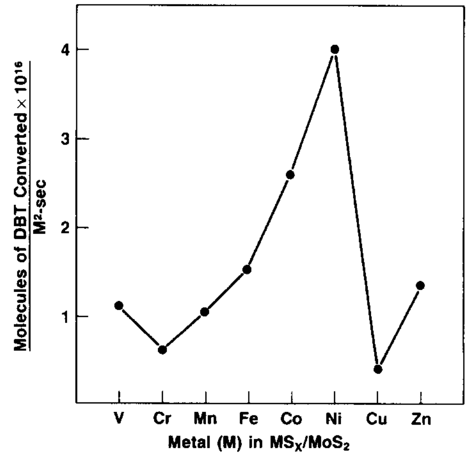

FIG. 2. Activity of sulfide catalysts described in Table 1. Activity measurements made at 350°C and 450 psi H_2 by the method described in Ref. (*2*).

clusters were chosen to model the catalyst systems whose preparation and activity were described in the previous sections. Each cluster carries a negative charge ($n-$) because enough electrons were included in each cluster so that each sulfur is formally S^{2-}, the molybdenum is formally Mo^{4+}, and the first row metal M′ has the formal oxidation state appropriate for the corresponding metal sulfide stable under reactor conditions. The geometry of the cluster can be seen in Fig. 3. Both metals are octahedrally coordinated by six sulfurs, three of which are shared between the two metals. Thus the model cluster is composed of two face-sharing octahedra. Within each cluster, all of the metal–sulfur bond distances were taken to be equal. These distances were determined for each cluster by averaging 2.42 Å, the Mo–S distance in MoS_2, and the M′–S distance in the corresponding first row transition metal sulfide. The choice of octahedral coordination around Mo allowed us to compare the Mo–S bonding and Mo electronic configuration in these model clusters with that in the simple binary cluster used previously (*4*). If the first row transition metal M′ occupies sites around the edges of MoS_2, an examination of a model of MoS_2 suggests that M′ could occupy either octahedral or tetrahedral sites and share sulfurs with an adjacent M′. Once again, we chose to use octahedral coordination for M′ because it allows us to make comparisons readily with our earlier calculations. We verified with selected calculations using tetrahedrally coordinated M′ that a change in geometry would not change the major conclusions of our calculations using octahedrally coordinated M′. The major purpose of this study was to systematically study the effect of the close proximity of a first row transition metal on the adjacent molybdenum atom. As in our previous calculations (*1*, *4*) all the calculations on these clusters were carried out using the SCF-X_α scattered wave method with tangent spheres (*21*). The atomic sphere radii were chosen according to Norman's criteria (*22*). The atomic exchange parameter values for the regions within the metal and sulfur spheres are those of Schwarz (*23*). A weighted average of these atomic values was used for the intersphere and outersphere region.

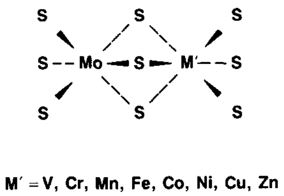

FIG. 3. Geometry of a model cluster $MoM'S_9^{n-}$ used for the molecular orbital calculations. This geometry, two face-sharing MS_6 octahedra, remained constant as the 3*d* transition metal M′ was varied. Variations in bond distances are described in the text.

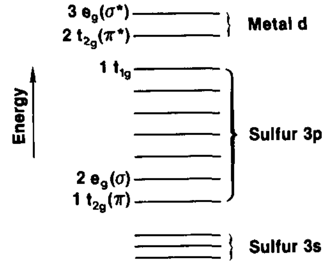

FIG. 4. Schematic valence energy level diagram for an octahedral MS_6^{n-} cluster.

In our previous reports we described in detail the electronic structure and bonding in the model octahedral first and second row transition metal–sulfur clusters. Figure 4 shows a schematic diagram of the valence energy levels calculated for those clusters. Lying at the lowest energy is a group of orbitals arising from the sulfur 3*s* orbitals. The next group of orbitals arises primarily from combinations of sulfur 3*p* orbitals. Included in this group are the $1t_{2g}$ and $2e_g$ orbitals. Although these orbitals are primarily sulfur 3*p* in character, they do contain some metal *d* character, and it is these orbitals which are π and σ bonding, respectively, between the metal *d* and sulfur 3*p* orbitals. At the top of this group of sulfur levels is the $1t_{1g}$ level, a nonbonding combination of sulfur 3*p* orbitals. Finally at highest energy (in most of the clusters) are the $2t_{2g}$ and $3e_g$ levels. These levels correspond primarily to the metal 3*d* or 4*d* orbitals, but they also contain a sulfur 3*p* component and are the antibonding counterparts of the $1t_{2g}$ and $2e_g$ levels. We found that a major effect of varying the transition metal in these octahedral clusters is a shift in energy of the metal d orbitals relative to the energy of the sulfur 3*p* orbitals. As measured by the difference in energy between the $2t_{2g}$ and $1t_{1g}$ levels, it was found that from Ti to Ni in the first transition series the energy of the 3*d* orbitals shifts downward in energy (i.e. closer in energy to the sulfur 3*p* orbitals) by about 1.5 eV. This shift is expected when moving from left to right in the transition series and is confirmed by available photoelectron spectra of the transition metal sulfides (*4*).

For the face-sharing octahedral clusters considered here, we can also draw a schematic energy level diagram showing the main features and patterns of the energy levels resulting from the calculations. One feature to note immediately is the change in point group symmetry of the face-shared clusters (C_{3v}) in comparison to the octahedral clusters (O_h). In the C_{3v} point group there are no triply degenerate representations. Consequently the triply degenerate t_{1g} and t_{2g} representations now split into a_2 plus *e* and a_1 plus *e* representations, respectively. We see these changes in the labels of the energy levels in Fig. 5, where a schematic level diagram for a MoM'S$_9^{n-}$ cluster is shown. In this case, because of the increase in number of sulfur levels, the groups of levels which are primarily sulfur 3*s* and 3*p* in character are simply drawn as blocks. These blocks represent 6 and 20 levels, respectively in the 3*s* and 3*p* blocks. Once again the sulfur 3*s* levels lie below the broader group of levels resulting from the sulfur 3*p* levels. Although not shown specifically there is a group of levels lying toward the bottom of the 3*p* group which contain some Mo and/or M' character and are the Mo–S and M'–S bonding orbitals. The top of the sulfur 3*p* group of levels is once again delineated by a nonbonding combination of sulfur 3*p* orbitals, in this case the $2a_2$ level, as shown on the diagram. The really notable feature of this level diagram is the presence, above the sulfur 3*p* levels, of levels resulting from both the Mo 4*d* and M' 3*d* metals. Each set of five *d* orbitals forms one a_1 and two *e* sets of levels so that on the diagram we see an a_1 plus two *e* levels for each set of metal orbitals. Although the set of 3*d* or 4*d* orbitals which in O_h symmetry transforms as the t_{2g} representation is no longer degenerate in these clusters having C_{3v} symmetry, the remnants of the octahedral splitting between the t_{2g} (now a plus e) and e_g (now *e*) orbitals are still apparent in these lower symmetry clusters so that we can talk about "t_{2g}" and "e_g" sets of orbitals. The schematic diagram in Fig. 5 would correspond to the case where the M' levels lie low enough in energy that the M' 3*d* "t_{2g}" and "e_g" sets of levels each lie below the corresponding Mo 4*d* sets of orbitals but not so low in energy that the entire 3*d* manifold of levels lies below the 4*d* levels. This relative energy separation applies to most of the clusters considered here. The relative energies of these levels, the numbers of electrons and their distributions within

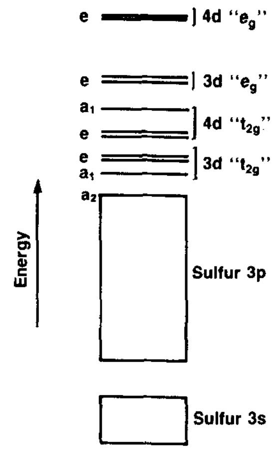

FIG. 5. Schematic valence energy level diagram for an MoM'S$_9^{n-}$ cluster made up of two face-sharing MS_6 octahedra. The blocks labeled sulfur 3*s* and sulfur 3*p* represent 6 and 20 energy levels, respectively.

these levels, and the mixing of the 3*d* and 4*d* orbitals all depend on M′. As we vary M′ it is the changes in these quantities which are really of interest to us, and we next describe these changes in some detail.

As we noted earlier, the metal 3*d* orbitals become more stable upon proceeding from the left to right side of the transition series; i.e., they drop in energy relative to the sulfur 3*p* orbitals. This means that in these clusters, which also contain Mo, the metal 3*d* orbitals also drop in energy relative to the Mo 4*d* orbitals. Proceeding across the 3*d* series from V to Zn this shift in energy is quite large, as is illustrated in Fig. 6. This figure illustrates the relative energies of the sulfur 3*p*, the M′ 3*d* "t_{2g}" and "e_g", and the Mo 4*d* "t_{2g}" sets of orbitals for all the $MoM'S_9^{n-}$ clusters considered here. (Since the Mo 4*d* "e_g" orbitals lie above the 3*d* "e_g" orbitals and are unoccupied for all these clusters, they are not important to our discussion and are omitted from the diagram.) For ease of comparison, all the energies shown on the diagram are measured relative to the nonbonding $2a_2$ combination of sulfur 3*p* orbitals which always lies at the top of the sulfur 3*p* group of orbitals. It is obvious from this diagram that the relative energies of the Mo 4*d* and M′ 3*d* orbitals do change dramatically in going from the left to the right side of the 3*d* transition series. For V, on the left, the 3*d* levels are slightly higher in energy than the Mo 4*d* levels. For Cr, Mn, and Fe the 3*d* levels shift downward somewhat. Moving to the right this shift becomes larger so that finally for Cu and Zn the 3*d* levels lie well below the Mo 4*d* levels.

At the same time that the 3*d* levels decrease in energy, the number of 3*d* electrons occupying the orbitals increases. For all the clusters, Mo contributes two "*d*" electrons while the number of "*d*" electrons contributed by the first row metal depends on the metal. Thus the total number of "*d*" electrons in the clusters varies from 4 in the V–Mo cluster all the way up to 12 in the Zn–Mo cluster. The distribution of electrons among the metal orbitals depends on both the relative energies of the orbitals and spin effects. Although the "up" and "down" spin orbitals are not shown in Fig. 6, the actual occupations of the orbitals shown in the figure were determined by a series of spin unrestricted calculations. In a series of model clusters such as these, the spin states obtained by our calculations are not the important feature of our results. What is important is the obvious trend in

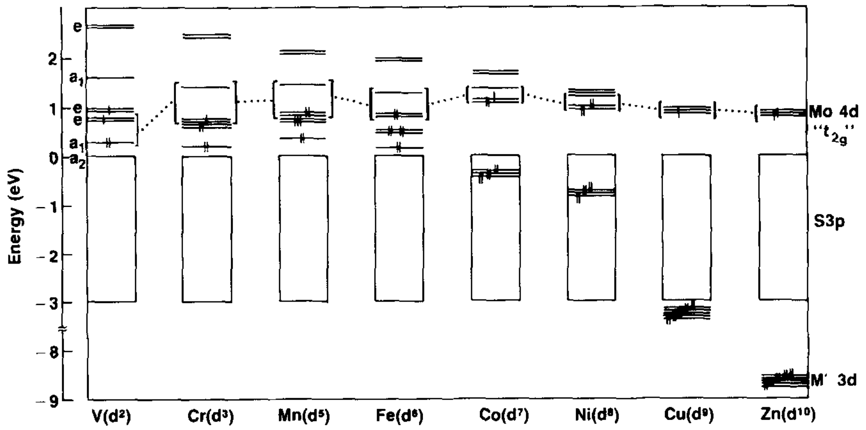

FIG. 6. Calculated valence energy levels for the $MoM'S_9^{n-}$ clusters, where M′ is the 3*d* metal shown below each level diagram. The sulfur 3*s* levels and the Mo 4*d* "e_g" levels have been omitted. The block labeled sulfur 3*p* represents 20 levels. For ease of comparisons, the energies of all the levels are shown relative to the energy of the nonbonding a_2 level lying at the top of the sulfur 3*p* group of orbitals. The three Mo 4*d* "t_{2g}" levels are bracketed so as to distinguish them from the M′ 3*d* levels.

occupations which accompanies the simultaneous shift in energy of the $3d$ levels and increase in number of "d" electrons. To describe this trend we follow Fig. 6 from left to right and observe the changes.

In the clusters containing V, Cr, and Mn the "t_{2g}" sets of $3d$ and $4d$ orbitals lie very close in energy, and, particularly for the a_1 orbitals, there is considerable mixing of the $3d$ and $4d$ orbitals. As can be seen from the diagram in Fig. 6, this mixing pushes one a_1 orbital down and one a_1 orbital up in energy, relative to the e orbitals of these sets. These e orbitals, on the other hand, remain quite close in energy. In these clusters the number of electrons varies from 4 to 7, and because of the near degeneracy of these two sets of e levels numerous occupations and spin states are possible. Any attempt to really assign these states in these simple model systems would be fruitless and not particularly meaningful. Instead, it is important to note that it is only in these three systems that the $3d$ and $4d$ "t_{2g}" orbitals lie so close in energy. Because of the closeness of these levels it is very difficult to assign with any certainty an actual configuration of electrons in the metal d orbitals. These results suggest that in a catalyst system such a manifold of d orbitals would also be present to accommodate a number of electrons, but it is difficult to predict with any certainty the effect of the $3d$ metal on the molybdenum.

Moving across the periodic table the effects are more clear-cut, because the interactions of the $3d$ and $4d$ orbitals decrease and the $3d$ orbitals begin to shift to energies significantly below the Mo $4d$ orbitals. In the Fe-containing cluster the energy of the Fe "t_{2g}" set of orbitals falls below the Mo set, the mixing of the levels decreases, and we can describe molybdenum formally as Mo(IV). These results suggest that in an Fe–Mo catalyst system, the electronic configuration of the Mo will be little affected by the presence of the Fe. In the Co–Mo and Ni–Mo clusters, there are two observable effects. First, because the Co and Ni "t_{2g}" orbitals lie well below the Mo orbitals, there is negligible mixing of the "t_{2g}" sets. On the other hand, Co and Ni provide seven and eight "d" electrons, respectively, to the cluster. In a pure Co–S or Ni–S cluster, the higher lying set of e orbitals, the descendents of the octahedral e orbitals, would be occupied. In these clusters containing Mo, however, we find that the lower energy Mo "t_{2g}" orbitals are available and that therefore a net transfer of charge from the Co or Ni to the Mo occurs. This is a result of the Mo "t_{2g}" orbitals lying energetically between the $3d$ "t_{2g}" and "e_g" orbitals and Co and Ni having a high enough d electron count that the $3d$ "e_g" orbitals would normally be partially occupied. The electron transfer of this type occurs only because both of these effects are present. In both the Co–Mo and Ni–Mo, the Mo is formally reduced relative to the Mo present in MoS_2.

If we proceed to the Cu–Mo cluster, we now find another change. All five of the Cu $3d$ orbitals now lie well below the Mo $4d$ levels—so low in fact that there is virtually no interaction between the Mo and Cu orbitals. On the other hand, Cu contributes only nine "d" electrons to the cluster. As a result a net transfer of electrons from Mo to Cu occurs. This is not entirely surprising because it is known that in CuS (*24*) (which contains nominally Cu^{2+} and S^{2-}) there are in fact present Cu^+ and S_2^{2-} as well as Cu^{2+} and S^{2-}. This has been interpreted in terms of the relative energies of the Cu $4d$ and S $3p$ levels. The Cu $4d$ levels lie low enough in energy that some of the Cu's are reduced to Cu^+ while sulfurs are oxidized. In our Cu–Mo cluster the Mo electrons are even more available than the sulfur $3p$ electrons and thus the Mo is oxidized relative to the Mo in MoS_2. Proceeding one element further in the transition series, we can see that in the Zn–Mo cluster the Zn $3d$ orbitals are now so low in energy that they are not really involved in M–M or M–S bonding. Zn formally contributes ten "d" electrons to the cluster, and thus the Zn $3d$ orbitals are fully occupied and have no effect on the Mo in the cluster. This Mo should be very similar electronically to the Mo in MoS_2.

In summary, when the first row transition metal M′ is varied in these Mo–M′ clusters, the changes in electronic structure depend on changes in both the relative energies of the Mo 4*d* and M′ 3*d* orbitals and the number of "*d*" electrons which M′ contributes to the cluster. As the 3*d* levels drop in energy across the first transition series, the number of 3*d* electrons occupying these levels increases. It is only when M′ is Co, Ni, or Cu, however, that these effects combine in such a way that the electronic state of Mo is formally affected. It is of course important to note that these three first row metals also have a measurable effect on the HDS activity of MoS_2. The apparent relation between these electronic effects in the model clusters and the HDS activity of the corresponding catalyst systems is the subject of the next section.

RELATION BETWEEN ELECTRONIC STRUCTURE AND TRENDS IN CATALYTIC ACTIVITY

In our previous work on binary sulfides, we found several electronic factors which appear to relate strongly to the catalytic activity of a particular sulfide. One factor is the ability of the transition metal to bond covalently, in both a σ and π fashion, to the 3*p* orbitals of sulfur. This factor serves to differentiate the 3*d* from 4*d* transition metals, since the 3*d* metals covalently bond much less effectively to sulfur than do the 4*d* metals. This is particularly true for π bonding. We defined a quantity called B, which measures the covalent contribution to the metal–sulfur bond strength and found that a large value of B, and thus a strong covalent contribution to the metal–sulfur bonding, correlates with high activity. Another important factor is the number of "*d*" electrons in the highest occupied orbital. We called this number n, and we observed that a large value of n also correlates with high activity. Thus the most active catalysts have large values of n and/or B. We combined these quantities to form an activity parameter "A_2", where

$$A_2 = nB.$$

This parameter provided us with a simple quantitative relationship between the calculated electronic structure and the HDS catalytic activity of the transition metal sulfides. A metal sulfide with a large value of A_2 will have high HDS activity. The correlation between this parameter and HDS activity suggests that we successfully identified electronic properties which exert an important influence on catalytic activity.

The combined experimental and theoretical results presented in this paper allow us not only to establish whether there is an underlying electronic basis for the promotion effect exerted by certain first row metals, but also to test our theory developed for the binary sulfides. The periodic nature of the effect of the first row metals (Fig. 2) on the HDS activity of MoS_2 suggests that the basis for promotion is indeed electronic in nature. In that case, if the electronic factors identified earlier really do influence HDS activity, then we should find that these factors are influenced by the presence of the promoter.

The experimental catalytic results described above show that only particular first row transition metals have a really marked effect on the HDS activity of MoS_2. Both Co and Ni exert a true promoting effect, in that the HDS activity of the Co/Mo and Ni/Mo systems is markedly greater than that of pure MoS_2. On the other hand Cu exerts a negative influence, in that the HDS activity of the Cu/Mo system is less than that of pure MoS_2. This is not a result that has been previously observed, but this work and other work from our laboratory suggest that this poisoning effect is real. The experimental results also suggest that Fe may serve as a weak promoter. Again, this is not a result that has been observed previously. The results of the calculations on the model clusters show that in the clusters containing Co, Ni, and Cu (and only in these three clusters) a distinct electronic effect is observed. This effect is the formal reduction or oxidation of Mo. In the presence of Co or Ni, Mo is reduced relative to the Mo present in MoS_2. That is, the formal Mo 4*d* orbital occupation increases from 2 in MoS_2 to 3 and 4 in the presence of Co and Ni, respectively. In the presence of Cu, on the other hand, Mo is formally oxidized so that the formal 4*d* occupation decreases to 1. These effective reductions and oxidation of Mo correlate with an increase and decrease in catalytic activity. Thus the combined experimental and theoretical observations suggest that the promotion effect is indeed electronic in origin and that it arises from the ability of the effective promoters to donate electrons to Mo and thus increase the number of "4*d*" electrons. Likewise, a poison such as Cu has the ability to remove electrons from Mo and thus decrease the number of "4*d*" electrons.

Although the effect of the 3*d* transition metals to the left of Co, i.e., V, Cr, Mn, and Fe, is much less clear-cut, it is certainly different from the effect of Co, Ni, or Cu. Our calculations indicate that in the systems containing V, Cr, or Mn, the "t_{2g}" sets of orbitals resulting from the Mo 4*d* and first row metal 3*d* orbitals are nearly degenerate in energy. Thus numerous levels lying very close together in energy are available for occupation by the "*d*" electrons, and calculation of the actual electronic configuration would require precise knowledge of the structure of the promoted catalyst systems. Clearly we are lacking this knowledge, and our simple cluster models were designed to enable us to identify gross differences in electronic structure rather than to understand the detailed electronic structure of any one system. Thus, while the exact electronic configuration of the clusters containing V, Cr, and Mn should be viewed with some caution, it is important to note that the electronic structures of all of these clusters are similar, in that none of these first row metals affects the Mo in the same way that Co, Ni, or Cu does. That is, these metals do not have the ability to unambiguously formally donate or withdraw electrons from Mo. We use the term unambiguous here, because if we consider Fig. 6 we can see, for example, that in the model Cr/Mo cluster the calculated results indicate that Mo is formally oxidized relative to Mo in MoS_2. As we have just discussed, however, the Mo- and Cr-based energy levels are so close together that this result is highly dependent on our choice of cluster and is not unambiguous. Likewise, although the experiments suggest that Fe can act as a weak promoter, our results for the model Fe/Mo cluster indicate that Fe will have no effect on Mo. Again, although the 3*d* and Mo 4*d* orbitals appear to lie slightly further apart in energy when the 3*d* metal is Fe rather then V, Cr, or Mn, changes in the model cluster could also affect these results. Therefore we again stress that the important result is the difference between the electronic structure of these systems and that of the systems containing Co, Ni, or Cu, namely, that for V, Cr, Mn, and Fe the relative energies of the 3*d* and 4*d* orbitals and the electronic configuration of the 3*d* transition metal are not those necessary for unambiguous donation of electrons to, or withdrawal of electrons from, Mo. Since these metals also do not serve as very effective promoters or poisons, this is consistent with our above argument that the donation or withdrawal of electrons from Mo is responsible for the promotion or poisoning of HDS catalytic activity. Finally, if we consider the Zn/Mo system we see that the Zn 3*d* levels lie far below the Mo 4*d* levels so that there is virtually no interaction between the 3*d* and 4*d* orbitals. Furthermore, since the Zn 3*d* orbitals are fully occupied there is no donation or withdrawal of electrons from Mo. The electronic structure of the Zn/Mo systems is thus consistent with our description of an electronic basis for promotion and poisoning, since the presence of Zn is seen to have little effect on the catalytic activity of MoS_2.

Not only do these results suggest that there is an electronic origin for the promotion effect, but they are also consistent with our earlier theory relating catalytic activity to several electronic factors for the binary sulfides. Our model cluster calculations indicate that in the promoted Co/Mo and Ni/Mo systems one of these electronic factors for Mo, n, the number of electrons in the HOMO, is increased by the presence of the promoter. Since these extra electrons occupy an antibonding orbital the Mo–S bonds are somewhat weakened. Thus the factor B which enters the activity parameter and measures the relative Mo–S covalent bond strength decreases in the presence of the promoter. On the other hand, the presence of a poison such as Cu has just the opposite effect on both these factors. To a first approximation, for all the other systems considered here (except for Cr/Mo, as discussed above) the two electronic factors n and B for Mo are unaffected by the presence of the $3d$ transition metal. We can calculate an activity parameter for the model clusters treated here. The simplest way of doing this is to first take n as the occupation number of the highest occupied Mo-based set of orbitals. If n is the same as in MoS_2, we assume that B is unchanged from the value for MoS_2 and the activity parameter A_2 is thus the same as in MoS_2. If n is different from MoS_2 we take our previous results for MoS_2 and recalculate the value of B taking into account the increase or decrease in the number of antibonding electrons. We could attempt to redefine and calculate B for these mixed metal clusters, but this would not be very straightforward because of the sulfur atoms which are shared between the two metals. Moreover, since any change in B is considerably smaller than the corresponding change in n (in the Ni/Mo cluster, for example, B decreases by only 15% while n increases by 100%) the variations in A_2 are dominated by changes in n, and we would not expect a new definition of B to have a large effect on these variations. The activity parameter for the model clusters, calculated by the method just described, is plotted in Fig. 7 along with the experimental HDS activities of the real catalyst systems. We see that the trends in activity are reproduced by the trends in the value of the activity parameter. It is important to note that the scales on this plot were chosen to illustrate the *overall* correlation between the calculated and experimental trends and not the agreement for any one system. (We note once again the uncertainty in the value of A_2 for the Cr/Mo cluster and point out that the agreement here with the decreased activity for the Cr/Mo catalyst is probably fortuitous. The low experimental value results from the normalization to surface area and should also be viewed with some caution.) The qualitative correlation obtained here indicates that promotion does indeed have an electronic basis and that the electronic factors identified earlier in our study of the binary sulfides are influenced by the presence of a promoter.

The results obtained here are also consistent with the physical picture and model which we described earlier for the binary sulfide systems. That is, we found that in

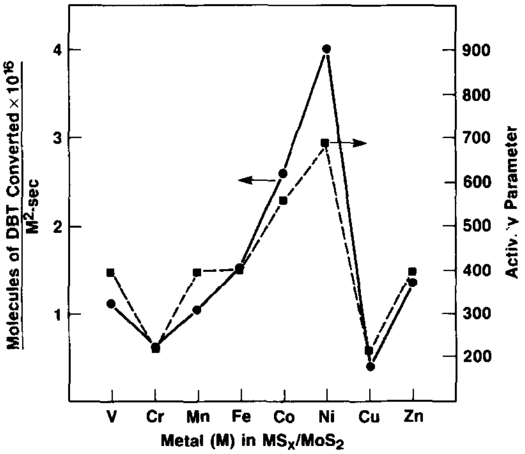

FIG. 7. Calculated activity parameter for each mixed metal sulfide system (right-hand scale). Shown for comparison, using the left-hand scale, are the measured HDS activities.

the active binary sulfide catalysts (those containing 4*d* transition metals) the transition metals are able to covalently bond very effectively (in both a σ and π manner) to sulfur. We also observed that in the best catalysts this ability to covalently bond with sulfur is combined with a high electron density in the metal *d* orbitals. We observed that a transition metal which can bind effectively to sulfur in the sulfide should also be able to bind to the sulfur atom in a heterocycle ring. Thus if the active site is a sulfur vacancy on the surface of the catalyst, we suggested a model for thiophene binding to the catalyst surface in which thiophenic molecules bind through the ring sulfur atom to a metal at a sulfur vacancy. This model invoked metal–sulfur σ and π interactions and the back-donation of metal electrons into a thiophenic π^* orbital. In this model, effective binding of the heterocyclic ring to the catalyst surface also results in weakening of the C–S bonds within the heterocyclic ring—an effect which can only aid the HDS reaction.

We now find in this study that the dominant electronic factor related to promotion of MoS_2 is the increase in the number of "*d*" electrons on Mo. We saw above that this effect, rather than the smaller changes in the covalency factor *B*, dominates the changes in the value of the activity parameter for the promoted Mo systems. More importantly, the dominance of this factor fits the physical model just described and indicates that for a 4*d* metal such as Mo, which does bind covalently to sulfur, an increase in *d* electron density will result in increased HDS activity. This is completely consistent with our model for thiophene binding as well, since an increase in number of electrons on Mo would result in stronger binding to the heterocyclic ring sulfur and further weakening of C–S bonds in the ring through further back-donation into the ring π^* orbital. By combining the results of our previous studies on the binary sulfides with the results of the experimental and theoretical studies presented here for the synergic systems it is thus possible to develop a unified theory which not only identifies electronic factors which are related to catalytic activity in the binary sulfide catalysts but also describes how these factors are related to promotion effects in the synergic systems.

CONCLUSIONS

By combining measured trends in the HDS activity of promoted MoS_2 catalysts with calculated trends in the electronic structure of cluster models of these catalyst systems, we have established that there is an electronic basis for the promotion effects observed in MoS_2-based HDS catalysts. The measured HDS activities show that only Co and Ni serve as effective promoters, while Cu functions as a poison. The other 3*d* transition metals have little effect on the activity of MoS_2. The calculated electronic structure of the cluster models of these promoted catalyst systems indicates that Co and Ni have the ability to formally reduce Mo in these systems, while Cu has the ability to formally oxidize Mo. None of the other 3*d* metals has this ability. The number of 3*d* electrons which Co, Ni, or Cu contributes to the cluster and the energies of their 3*d* orbitals relative to the Mo 4*d* orbitals make these metals unique when combined with Mo. Thus we associate promotion of MoS_2 with formal reduction of Mo and poisoning with oxidation of Mo.

These results are consistent with our earlier identification of electronic factors which are related to the HDS activity of binary sulfide catalysts. For the binary sulfides these factors are the covalent contribution to the metal–sulfur bond strength and the metal *d* orbital occupations. For the promoted MoS_2 catalysts, both of these factors are affected by the presence of a 3*d* metal promoter or poison, although the dominant effect of a promoter is the increase in the number of "*d*" electrons formally associated with Mo. This is consistent with our model for thiophene bonding to the catalyst since an increase in *d* electron density on Mo would strengthen the interaction between Mo and the ring sulfur atom in thiophene.

It is interesting to note that while the increase in the number of *d* electrons on Mo appears to be the dominant electronic factor influencing the HDS activity, the accompanying change in the metal–sulfur covalent bond strength may provide us with an explanation for the earlier observation (*14*) that the "synergic" systems appear to be related to the binary systems through an average heat of formation. In the Co/Mo system, for example, the formal transfer of an electron from Co to Mo involves an electron transfer from a Co–S antibonding orbital to a Mo–S antibonding orbital. This results in a weakening of the Mo–S bonds and a strengthening of the Co–S bonds relative to the metal–sulfur bonds in the binary sulfides. A sulfur which is shared between Mo and Co would be expected to behave much like a sulfur in a binary sulfide having some intermediate metal–sulfur bond strength. Thus for systems where such electron transfers occur it is reasonable to see a correlation between average heats of formation and activity.

We should also note that our conclusions are consistent with a recent study of carbon-supported transition metal sulfide catalysts (*25*). In that study, Prins and co-workers showed that the trends in activities of these carbon-supported sulfides, where interactions with the support are weak, are very similar to trends measured earlier (*2*) for unsupported sulfides. Furthermore, they suggested that discrepancies between the activities of alumina- and carbon-supported transition metal sulfides (i.e. the lower activities of alumina-supported sulfides) result from the strong interaction between alumina and the sulfides. These interactions will increase the charge and thus decrease the electron density on the transition metal and lower the HDS activity. This is in accord with our results which indicate that HDS activity is strongly influenced by an increase or decrease of *d* electron density on the transition metal.

The work reported here has allowed us to understand trends in the HDS activities of promoted MoS_2 catalysts in terms of the electronic structure of models of these systems. The picture which emerges is consistent with the results of our previous studies of trends in the catalytic activity of binary sulfide catalysts. All of our calculated results are based on simple models for the catalyst systems, and although these results are sufficient to understand trends in activity we would like to be able to establish a more detailed understanding of the electronic basis for HDS activity. Such a detailed understanding depends, however, on a much more precise understanding of the structure of the catalysts themselves. The characterization of these catalyst systems is an active area of research in many laboratories, and we expect that as our knowledge of the details of the structure of these materials increases we will also be able to better understand their electronic structure.

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