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Catalysis by Transition Metal Sulfides: The Relation between Calculated Electronic Trends and HDS Activity

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Recent measurements of the catalytic activity of a series of transition metal sulfides showed that the ability of a particular sulfide to catalyze the HDS reaction is related to the position of the transition metal in the periodic table (Pecoraro, T. A., and Chianelli, R. R., *J. Catal.* **67**, 430 (1981)). In order to understand the specific origin of these periodic trends in activity, SCF-Xα calculations of the electronic structure of cluster models of the first and second row transition metal sulfides were carried out. The results of these calculations were used to identify several electronic factors which appear to be related to the catalytic activity of the transition metal sulfides. The computed quantities which measure these factors were combined to form an activity parameter for each sulfide. This parameter shows a direct correlation with the catalytic activity of the sulfides. A model for the binding of thiophenic molecules to the surface of the sulfide catalyst is suggested. This model is consistent both with the correlation between bulk electronic structure and catalytic activity of the sulfides and with the ligand properties of thiophene in transition metal complexes.

INTRODUCTION

In a previous paper we reported that the primary effect in the hydrodesulfurization (HDS) of dibenzothiophene (DBT) by transition metal sulfides is the "electronic effect," i.e., it is related to the position of the metal in the periodic table (*1*). This effect, which determines the ability of the transition metal sulfides to catalyze the HDS reaction, varies over 3 orders of magnitude across the periodic table. The first row transition metal sulfides are relatively inactive, but the second and third row transition metal sulfides show maximum activity with Ru and Os. HDS activity as a function of periodic position yields typical "volcano" plots. The catalysis literature contains numerous examples of model reactions which display periodic maxima or "volcano" relationships, and Sinfelt has reviewed broad relationships between the positions of various metals in the periodic table and the catalytic activity of these metals in hydrogenation, hydrogenolysis, isomerization, hydrocarbon oxidation, and ammonia synthesis–decomposition reactions (*2*). In general, the catalytic activity of the metal in these studies correlates with the metal *d* electronic configuration (as "percentage *d* character" of the metallic bond, as defined by Pauling from valence bond theory) or with the strength of the metal–adsorbate bond.

Similar correlations also apply to the transition metal sulfides and the observed periodic trends in their HDS activity. For example, a relation exists among the heats of formation of the transition metal sulfides, the metal–sulfur bond strengths, and the catalytic activity of the sulfides (*1*). The metal–sulfur bond strengths of the transition metal sulfides decrease continuously across the periodic table, and the most active sulfides from the second and third transition series have intermediate values of the heat of formation (30–55 kcal/mol). This suggests that in order to obtain the maximum desulfurization rate the strength of the metal–sulfur bond at the surface must be neither too strong or too weak. This reasoning is consistent with the commonly accepted idea that sulfur vacancies on the surface of the catalyst are the active HDS sites

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(*3*). The well-known principle of Sabatier (*4*) states that for catalysts exhibiting maximum activity in a given reaction the surface complexes formed by the reacting molecule will have intermediate heats of formation. Following this line of reasoning, the sulfides exhibiting maximum activity for the HDS reaction will have intermediate heats of formation, presumably because the surface complexes formed between the sulfur-bearing molecule and these sulfides will also have intermediate stabilities. This cannot be the entire picture, however, since even though the heat of formation of MnS from the first transition series falls within the required range (51 kcal/mol), MnS shows very low activity. Additionally, it is perplexing that Pauling percentage *d* character for the corresponding transition metals correlates very well with the catalytic activity of the transition metal sulfides. The most that can be concluded from these correlations is that both the strength of the metal–sulfur bond at the surface of the catalyst and the presence of 4*d* or 5*d* electrons in the catalyst are important in determining HDS activity.

As a first step toward understanding the basis for the catalytic activity of the metal sulfides, we undertook a series of calculations aimed at determining how the electronic structure of these sulfides varies as a function of the periodic position of the metal. Using scattered-wave Xα calculations we studied the electronic structure of a series of transition metal–sulfur clusters which serve as simple models for the first and second row transition metal sulfides. These cluster calculations and the resulting energy levels and charge distributions have been discussed in detail elsewhere (*5*). In this paper, we explore the relationship between the trends in the electronic structure of the metal sulfides and the trends in their activity as HDS catalysts. The next section summarizes the model cluster calculations and describes the calculated energy levels and charge distributions for these clusters. In the third section we identify several electronic factors which appear to be related to catalytic activity and, using quantities derived from our calculated results, we incorporate these factors into an activity parameter which correlates with catalytic activity. Finally, we discuss the possible implications of these correlations and propose a model for thiophene adsorption which is consistent both with the correlation between the electronic structure and HDS activity of the transition metal sulfides and with the ligand properties of thiophene in transition metal complexes.

CLUSTER CALCULATIONS AND RESULTS

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. The clusters carry a negative charge ($n-$) because enough electrons were included in each cluster so that every sulfur is formally S^{2-} and the transition metal has the formal oxidation state appropriate for the corresponding sulfide. All the calculations were carried out using the SCF-Xα scattered-wave method with tangent spheres (*6*). The metal–sulfur distances were taken from the experimental bond distances in the appropriate sulfides, and the atomic sphere radii were chosen using Norman's criteria (*7*). The atomic exchange parameter α values for the regions within the metal and sulfur spheres are those of Schwarz (*8*), and a weighted average of the atomic values was used for the intersphere and outersphere regions.

A schematic diagram of the valence energy levels calculated for the clusters is shown in Fig. 1. In each cluster a group of levels arising from the sulfur 3*s* orbitals lies at the lowest energy. Somewhat higher in energy is a group of levels arising primarily from combination of the sulfur 3*p* orbitals. Included near the bottom of this group are the $2e_g$ and $1t_{2g}$ levels, which are mainly sulfur 3*p* in character but also contain some metal *d* character. It is these levels, the $2e_g$

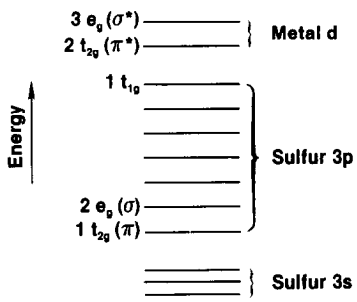

FIG. 1. Schematic valence energy level diagram for an octahedral MS_6^{n-} cluster.

and $1t_{2g}$, which are the sigma and pi bonding orbitals, respectively, between the metal d and sulfur p orbitals. Lying at the top of the group of sulfur levels is the $1t_{1g}$ level, a nonbonding combination of sulfur orbitals. Finally at the highest energy (in most of the clusters) are the levels which correspond primarily to the metal $3d$ or $4d$ orbitals. These orbitals, the $3e_g$ and $2t_{2g}$, also have a sulfur $3p$ component and are the sigma and pi antibonding counterparts of the bonding $2e_g$ and $1t_{2g}$ orbitals, respectively. A major effect of varying the transition metal in the clusters is a shift in the energy of the metal d orbitals relative to the energy of the sulfur $3p$ levels. This effect is illustrated in Fig. 2, where the separation in energy between the lowest energy metal d orbital ($2t_{2g}$) and the highest energy sulfur $3p$ orbital ($1t_{1g}$), denoted as ΔE in the diagram, is plotted versus the central metal in the cluster. For the second row transition metals a large decrease in the energy of the metal $4d$ orbitals relative to the energy of the sulfur $3p$ orbitals occurs from the left to the right side of the transition series. The only break in this trend occurs between Tc and Ru, where there is also an abrupt change in oxidation state. The decrease in energy of the metal d orbitals relative to the sulfur $3p$ orbitals is less regular in the $3d$ series, primarily because of the differing oxidation states of the metals on the left side of the series. On the right side of the $3d$ series, however, a decrease in the energy separation is apparent. The overall decrease is more pronounced for the second row metals, so that for Rh and Pd the filled $2t_{2g}$ orbitals actually lie at the same or lower energy than the uppermost filled sulfur $3p$ orbitals. Experimental photoelectron spectra are available for several of the transition metal sulfides, and these spectra are consistent with the calculated trends in relative metal and sulfur energies (*5*).

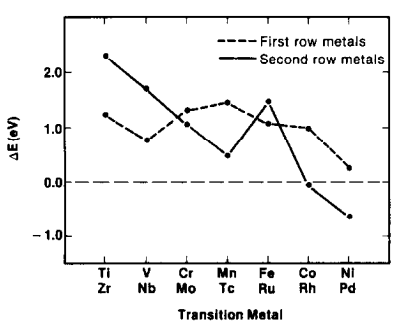

FIG. 2. Plot of the energy difference (ΔE) between the $2t_{2g}$ and $1t_{1g}$ levels in the octahedral cluster MS_6^{n-} for each central metal M.

Shifts in the energies of the metal d orbitals which bring them closer in energy to the sulfur $3p$ orbitals should result in a corresponding increase in covalent mixing of the metal d and sulfur p orbitals. In fact variations in d–p mixing do occur in the clusters as the metal changes across either the $3d$ or $4d$ transition series. This is illustrated in Fig. 3, where the metal contributions to the $2e_g$ (sigma) and $1t_{2g}$ (pi) metal–sulfur bonding orbitals (labeled D_σ and D_π, respectively) are plotted versus the central metal of the cluster. A larger metal contribution to these orbitals, which are primarily sulfur $3p$ in character, is an indication of a stronger metal–sulfur d–p interaction. It can be seen from Fig. 3a that although the metal orbitals in the 4d series generally make a larger contribution to the sigma-type bonding orbital, the metal orbitals in the 3d series also make a substantial contribution to this orbital. In fact, a comparison of Figs. 2 and 3a shows that both the $3d$ and $4d$ orbital contributions to the sigma bond-

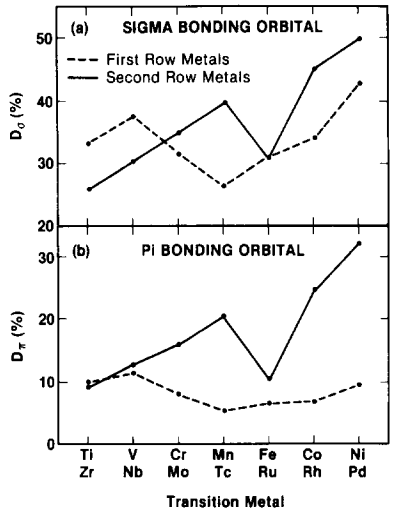

FIG. 3. Plots of the metal d orbital contribution to the (a) sigma bonding $2e_g$ and (b) pi bonding $1t_{2g}$ orbitals in the octahedral clusters MS_6^{n-}.

ing orbital exhibit an inverse correlation to ΔE. As expected, a smaller ΔE corresponds to greater d–p sigma mixing. On the other hand, it can be seen from Fig. 3b that while the $4d$ metals show the same type correlation between ΔE and the metal contribution to the pi bonding orbital, such a correlation is not observed for the $3d$ metals. Indeed, the metal $3d$ contribution to the pi-type bonding orbital is small across the entire $3d$ series. It is only for the larger $4d$ orbitals that a pi component to the metal–sulfur d–p bonding becomes important. The $4d$ metal sulfides are seen to be generally more covalent than their $3d$ counterparts, and this covalency is enhanced in the $4d$ metal sulfides by the pi contribution to the orbital mixing.

It is clear that variations in both the energy levels and charge distributions emerge when the results of the calculations are examined. The relative energies of the metal d and sulfur p orbitals show much greater variations across the $4d$ transition series than across the $3d$ series. At the same time, the bonding in the second row transition metal sulfides is seen to be more covalent than the bonding in the first row sulfides. A major factor in this increased covalency is the ability of the metal $4d$ orbitals to interact in a pi fashion with the sulfur $3p$ orbitals. Although the $5d$ metal sulfides were not included in these calculations, we would expect the trends in that series to be similar to the trends in the $4d$ series. Comparisons between these variations in energy levels and charge distributions in the metal–sulfur clusters and the trends in catalytic activity of the transition metal sulfides themselves suggest several correlations between the electronic structure of the sulfides and their catalytic activity. These correlations are discussed in the following section.

CORRELATIONS BETWEEN ELECTRONIC STRUCTURE AND ACTIVITY

We recall that the first row transition metal sulfides are relatively inactive as HDS catalysts and that the second and third row metal sulfides are considerably more active, with maximum activity at Ru and Os. These trends in activity are shown in Fig. 4, where the rate of HDS of dibenzothiophene (DBT) by various transition metal sulfides is plotted versus the periodic position of the transition metal (*1*). Note

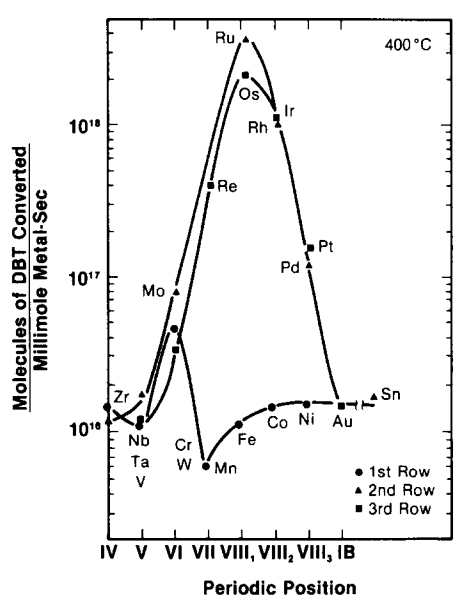

FIG. 4. Periodic trends for HDS of DBT/millimole of catalyst at 400°C (Ref. (*1*)).

that in this plot the activity is normalized per millimole of metal. The activities can also be normalized to BET surface areas, and on this basis the trends in activity change slightly (for example, in the surface area plot Rh and Ir are closer in activity to Ru and Os than they are in Fig. 4). However, the HDS activities of the sulfides do not, in general, correlate with BET surface areas. Normalization of activity on a per metal basis appears to give a better measure of the intrinsic activity of the sulfides, and we have therefore chosen this normalization for a basis of comparison. Considering both the experimental trends in catalytic activity of the sulfides and the calculated electronic structure of the model metal–sulfur clusters, we are able to relate catalytic activity to several calculated electronic factors. First, it was noted earlier that the higher activity of the second and third row sulfides emphasizes the importance of metal 4*d* or 5*d* electrons to catalytic activity. It is possible that a difference between the *d* electron configuration of the 3*d* metals and that of the 4*d* and 5*d* metals in the sulfides provides a basis for the difference in catalytic activity. Since the metal oxidation states vary somewhat between corresponding 3*d* and 4*d* metal sulfides, the difference in activity could be related to the total number of *d* electrons. However, an examination of Fig. 5a, where the formal *d* electron count is plotted for each of the first and second row sulfides, shows that this is not the case. In both transition series the *d* electron count increases across the series, and comparisons of pairs of first and second row sulfides having identical numbers of *d* electrons show that in each pair the second row sulfide exhibits higher activity. Thus the number of *d* electrons alone does not correlate with catalytic activity. If we instead consider the number of *d* electrons in the highest occupied molecular orbital (HOMO) of each cluster we find that a very different pattern emerges. This pattern can be seen in Fig. 5b, where the *d* electron count in the HOMO (labeled *n*) is plotted

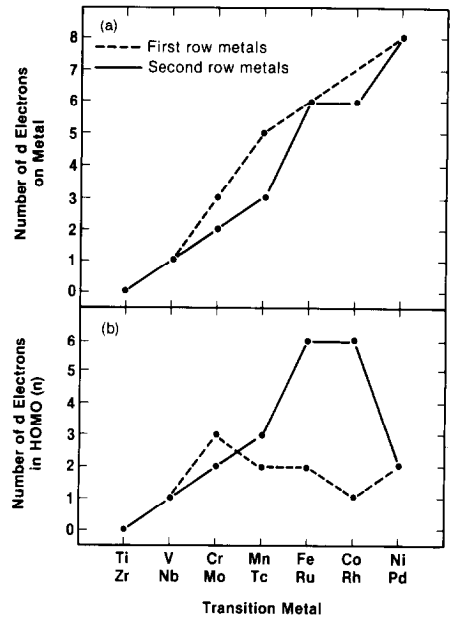

FIG. 5. (a) Formal *d* electron count for the central metal M in each octahedral cluster MS_6^{n-}; (b) Formal *d* electron occupation of the HOMO in each cluster.

for each of the first and second row sulfides. This plot exhibits the same general features as the experimental activity plot for the sulfides. That is, the number of electrons, *n*, for the first row sulfides peaks with Cr while for the second row sulfides this number peaks at Ru and Rh. The maximum value of *n* for the second row is twice the maximum value for the first row. Thus the maximum in catalytic activity for the sulfides occurs in those sulfides with the maximum number of *d* electrons in the highest occupied energy level. It is informative to ask why the number of electrons in the HOMO varies so between corresponding 3*d* and 4*d* metals while the total number of *d* electrons does not. A major reason for this difference is the weaker metal–sulfur interaction for the 3*d* metals. This results in weaker *d* orbital splittings in the 3*d* series so that for Mn and Fe both the $2t_{2g}$ and $3e_g$ levels are partially occupied in a high spin configuration. For the 4*d* metals (Ru and Rh) where both of these levels might also be occupied, only the $2t_{2g}$ level is occupied in a

low spin configuration. For the other metals on the far right of both transition series (Co, Ni, and Pd) occupancy of the $3e_g$ level is forced by the total d electron count. Thus in the less active $3d$ metal sulfides (Mn, Fe, Co, and Ni) the HOMO is the $3e_g$ (sigma antibonding) level. For the $4d$ sulfides the HOMO for all the metal sulfides except Pd is the $2t_{2g}$ level, and the activity increases as the number of electrons in the $2t_{2g}$ level increases. Therefore not only do the more active catalysts have more electrons in the HOMO, but also the HOMO in these active catalysts is the $2t_{2g}$ level.

Although there is a correlation between n, the number of electrons in the HOMO of each cluster, and the activity of the sulfide, a comparison of the plot of n in Fig. 5b with the activity plot in Fig. 4 suggests that n is not the only electronic factor related to activity. For example, comparisons between Cr and Mo and between Mn and Tc show that while n differs by only one electron in either pair, the activities of Cr and Mo are similar while the activities of Mn and Tc (or Re)[1] are very different. Further comparisons show that for both Cr and Mo the HOMO is the $2t_{2g}$ level, while for Mn and Tc the HOMO's are different. These observations suggest once again that not only the number of electrons in the HOMO but also the nature of the HOMO itself may be related to the catalytic activity of the sulfides. It is important to note, however, that the changes in the orbital occupations of the HOMO's and the differences in the nature of the HOMO from the $3d$ to the $4d$ transition series reflect significant changes in the metal–sulfur bonding interactions. It is likely that the strengths of the metal–sulfur covalent interactions are also related to the catalytic activities of the sulfides. In order to explore whether such a relationship does exist, we compare variations in the metal–sulfur covalency with changes in the catalytic activity of the sulfides.

[1] Since Tc is not a naturally occurring element and is radioactive it was not included in the catalytic measurements (*1*). In this paper, Tc calculations are assumed to correlate to Re measurements since TcS_2 and ReS_2 are isostructural and isoelectronic.

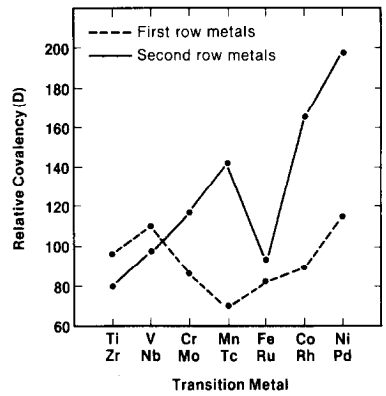

FIG. 6. Relative metal–sulfur covalency, D, for each MS_6^{n-} cluster.

Before we can make such comparisons, however, we must define a quantity which measures the metal–sulfur covalency. Increased covalency is indicated by increased mixing of the metal d and sulfur p orbitals in the $2e_g$ and $1t_{2g}$ bonding molecular orbitals. As was illustrated in the previous section, a larger metal contribution to these orbitals indicates stronger mixing and increased covalency. Therefore the simplest measure of covalency in the clusters is just the sum of the metal d orbital contributions to the $2e_g$ (sigma) and $1t_{2g}$ (pi) bonding molecular orbitals. We define a quantity

$$D = 2(D_\sigma) + 3(D_\pi)$$

where D_σ and D_π are the metal contributions (plotted in Figs. 3a and b), to the $2e_g$ and $1t_{2g}$ orbitals, respectively, and the factors 2 and 3 take into account the degeneracies of these orbitals. The sum of the sigma and pi contributions, D, measures the overall covalent contribution of the metal d orbitals to the M–S bonding orbitals. Consequently, it provides an approximate measure of the relative covalency of the various sulfides; a larger D corresponds to increased covalency. Figure 6 shows a plot of D versus the central metal in each cluster. Not unexpectedly, it shows that the $4d$ metal sulfides are generally more covalent

and that the covalency in the 4*d* series increases from left to right, with a break only at Ru. Clearly, the plot of *D* does not show the same behavior as the plot of experimental activities. It does show, however, that in several cases there are marked differences in metal–sulfur bonding in pairs of 3*d* and 4*d* metals with similar values of *n* but different activities. For example, both the metal–sulfur covalency and the catalytic activity are considerably larger for Tc than for Mn, while the value of *n* differs by only one electron. This and other comparisons suggest that both *n*, the number of electrons in the HOMO, and *D*, the metal–sulfur covalency, are related to activity. The more active catalysts have larger values of *n* and/or *D*, and the activity appears to be directly related to both these quantities. If we assume that both *n* and *D* are directly related to activity, we can obtain a correlation between the calculated electronic structure and the experimental catalytic activity of the sulfides. The simplest relationship between these quantities and activity is found by defining a parameter A_1, which is just the product of *n* and *D*,

$$A_1 = nD$$

and then comparing the trends in A_1 to the experimental trends in activity. A plot of A_1 for the metal sulfides is shown in Fig. 7, and it can be seen from the plot that this parameter does correlate with the activity of the corresponding sulfides. In general, the changes in A_1 across both the 3*d* and 4*d* transition series are very similar to the observed changes in activity, although some differences are observed. For example, the peak in A_1 for the 4*d* series lies at Rh rather than Ru, and the peak in A_1 for the 3*d* series at Cr is somewhat smaller, relative to the other 3*d* metals, than we might expect from the corresponding changes in activity. (Both of these features in A_1 are similar, however, to activities which are normalized to surface area.) On the other hand, several features of the plot are very satisfying. For example, the values of A_1 for Cr and Mo are

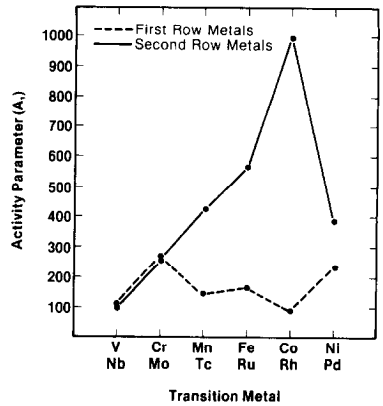

FIG. 7. Calculated activity parameter A_1 for each transition metal sulfide.

very similar while the value of A_1 for Tc is about three times larger than that for Mn. It is only because A_1 includes both *n* and *D* that this behavior is observed. Comparisons of Tc and Mn and of Mo and Cr show that for Tc both *n* and *D* are larger but for Mo *n* is smaller while *D* is larger. Thus for Tc, where these two factors reinforce one another, A_1 as well as the activity of Tc sulfide is considerably larger than that of Mn sulfide. For Mo, however, where these two factors compete, we find similar values of A_1 and similar activities for the Cr and Mo sulfides.

Although the parameter A_1 appears to correlate with activity, a slightly better correlation can be obtained if we take one more factor into account. It was pointed out in the introduction that for the second and third row sulfides intermediate heats of formation and intermediate metal–sulfur bond strengths correlate with high activity. It was also noted that although the heat of formation of MnS falls within the optimum range for high activity, the actual activity of MnS is one of the lowest of any of the sulfides tested. The cluster results indicate why heat of formation and metal–sulfur bond strength data alone cannot predict catalytic activity. These quantities do not give any indication of the relative sizes of the ionic and covalent components of the metal–sulfur bond. Our calculations sug-

gest that it is the covalent component which is related to activity; thus for MnS, where this covalent component is low, it is not surprising that the activity is also low. For the second row sulfides, where the covalent component to the metal–sulfur bond is higher, we would expect better correlations between heats of formation, bond strengths, and activity. This suggests that a better correlation between the calculated electronic structure and catalytic activity can be obtained if we take into account some measure of not only the relative covalency, but also the covalent bond strength. Although our model calculations do not allow us to calculate quantitative bond strengths, we can, using calculated quantities, define a parameter which provides a measure of the relative metal–sulfur *d–p* covalent bond strengths in the different sulfides. This parameter will take into account both the net number of bonding electrons as well as the covalency of the bonds. We define

$$B = n_\sigma D_\sigma + n_\pi D_\pi$$

where D_σ and D_π have been defined previously as the metal *d* orbital contribution to the sigma and pi bonding orbitals and n_σ and n_π are the net number of sigma and pi bonding electrons, respectively. That is,

$$n_\sigma = (4 - n_{3e_g})$$

where 4 is the number of electrons in the $2e_g$ (sigma bonding) orbital and n_{3e_g} is the number of electrons in the $3e_g$ (sigma antibonding) orbital. Likewise,

$$n_\pi = (6 - n_{2t_{2g}})$$

where 6 is the number of electrons in the $1t_{2g}$ (pi bonding) orbital and $n_{2t_{2g}}$ is the number of electrons in the $2t_{2g}$ (pi antibonding) orbital. Since D_σ and D_π provide a measure of the sigma and pi covalency and n_σ and n_π measure the net number of electrons which take part in the *d–p* sigma and pi bonds the products $n_\sigma D_\sigma$ and $n_\pi D_\pi$ provide a relative measure of the metal *d*–sulfur *p* sigma and pi bond strengths. The sum of these quantities, *B*, gives a relative measure of the overall metal *d*–sulfur *p* covalent bond strength. This parameter takes into account the fact that the covalent bond strength depends on both the magnitude of the metal sulfur interaction and the net number of bonding electrons. In general, since throughout either the 3*d* or 4*d* transition series D_σ and D_π increase as n_σ and n_π decrease, the behavior of *B* is somewhat different from that seen earlier for *D*. A plot of *B* versus transition metal is shown in Fig. 8. It can be seen that there are several differences between *D* and *B*. First, the relative difference in the size of *B* between the 3*d* and 4*d* metals tends to be larger than that for *D*. Thus the variations in relative metal–sulfur bond strength between the first and second transition series are even larger than the variations in covalency, and the parameter *B* differentiates more effectively between the bonding in the metal sulfides. Also, *B* takes into account the fact that although the metal–sulfur orbital mixing is stronger on the right-hand side of the transition series the number of antibonding electrons is also larger, so that the actual covalent bond strength decreases. The parameter *B* thus includes information contained in *D* about covalent interactions as well a new information about the actual covalent bond

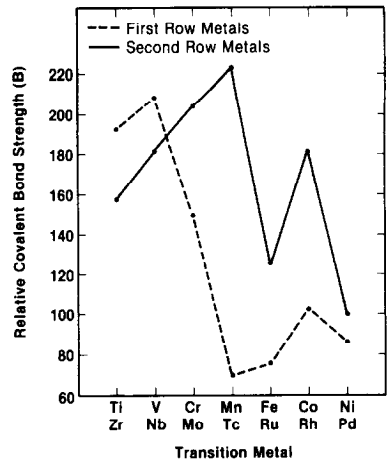

FIG. 8. Calculated relative metal–sulfur covalent bond strength, *B*, for each transition metal sulfide.

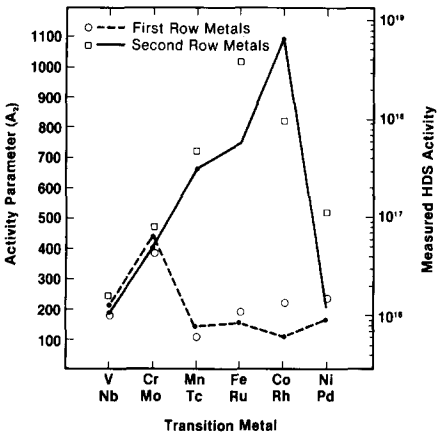

FIG. 9. Calculated activity parameter A_2 for each transition metal sulfide. Shown for comparison, using the right-hand scale, are the measured HDS activities of the transition metal sulfides.

strength. Finally, the shape of the plot of B, in comparison to the shape of the experimental activity plot, suggests a closer relation between B and activity than between D and activity. We would expect then that a new parameter which is the product of n and B should give an even better correlation with the activity of the sulfides than did A_1. We define this parameter

$$A_2 = nB$$

and show a plot of A_2 versus transition metal in Fig. 9. Also shown on this figure, plotted against the scale on the right, are the experimentally measured activities. It can be seen from Fig. 9 that trends in A_2 are very similar to the trends in activity of the sulfides. The difference within the $3d$ series between Cr and the remaining $3d$ metals is apparent, as are the differences between the $3d$ metals Mn, Fe, and Co and the $4d$ metals Tc, Ru, and Rh. Once again, however, the maximum in A_2 for the $4d$ series falls at Rh rather than Ru. Also, we note that the values of A_2 for Pd and Ni are nearly the same, suggesting that we would expect the activities for these two sulfides to be closer than is actually observed. In spite of these discrepancies between calculated and measured activities, the plots shown in Figs. 8 and 9 are really quite satisfying. The general behavior of both of these plots suggests that we have identified electronic factors which are related to the catalytic activity of the metal sulfides. These factors include the number of electrons in the highest occupied orbital, the degree of covalency in the metal–sulfur bond, and finally, the metal–sulfur covalent bond strength. Since the parameter A_2 takes into account all three of these factors, it provides a good criterion for catalytic activity. That is, a sulfide with a large calculated value of A_2 would be expected to have high activity. The existing discrepancies in this correlation, however, suggest that as our knowledge of the HDS process increases we will be able to make further modifications to our activity parameters. For example, as noted above, the similar values of A_2 for Pd and Ni suggest similar activities, while the actual activity of Pd is higher. It may well be that for Pd, where the number of antibonding electrons is large, the parameter B overemphasizes the weak metal–sulfur bond and underemphasizes the very strong metal–sulfur covalency. A refinement of the weighting of these two factors may be necessary. Another discrepancy is the maximum in A_2 at Rh rather than at Ru. Again, although this may indicate a need for refinement of the activity parameter, it should be remembered that the available experimental data provides only a good indication of intrinsic activities. It is very likely that when true intrinsic activities are measured there will be some changes in the relative activities of the sulfides. The important result to be noted is the general agreement obtained here between the behavior of A_2 and the trends in activity. This agreement is sufficient to convince us that we have identified electronic factors which are related to activity.

DISCUSSION

The previous section clearly indicates that there exists a correlation between the electronic structure of the bulk transition

metal sulfides and their catalytic activity. Several questions immediately come to mind about these correlations. Why do the particular electronic factors identified above correlate with the activity? What is the relation between the bulk electronic structure and the surface interactions which directly affect the catalytic process? Finally, since the bulk electronic factors do appear to correlate with catalytic activity, what do these correlations suggest about the important surface interactions? A dominant factor in the correlations is n, the number of electrons in the HOMO. Why does this number appear to correlate so closely with activity? The most obvious answer is simply that the number of electrons available at the metal center (in solid state terminology, the metal d electron density of states at the Fermi level) is particularly important. That is, greater available d electron density on the metal leads to higher activity. This simple answer ignores, however, the symmetry of the occupied orbitals. The active sites in these catalysts are probably sulfur vacancies, i.e., exposed metal atoms, and if this is the case both the occupancies and the symmetries of the metal orbitals at the active sites may be important. The fact that in the more active catalysts the HOMO is the $2t_{2g}$ level suggests that the symmetry of the HOMO is indeed important. These observations are all suggestive, but a better understanding of the nature of the metal sulfide surfaces, the active sites, and the interactions between these sites and the reacting molecules will be necessary before we can completely understand the relation between HOMO occupancy and activity.

The relation between covalency, covalent bond strength, and activity can be interpreted in terms of possible surface interactions. As mentioned above, a number of proposed mechanisms for the HDS reaction assume that the active catalytic site is a sulfur vacancy on the transition metal sulfide. Our calculations suggest that it is not only the formation of this vacancy but also the bonding capability of the metal at the vacancy which is important for high activity. In the proposed HDS mechanisms a sulfur-containing molecule such as thiophene, benzothiophene, or dibenzothiophene binds to the catalyst surface through the metal atom exposed by the sulfur vacancy. The nature of this interaction has not been well established, but one likely mode of binding, especially for thiophene, is through the sulfur atom of the heterocyclic ring. Since our results clearly indicate that a metal's ability to bond covalently with sulfur is related to catalytic activity, we propose that the sulfur-bearing heterocycle does bind to the catalyst through the ring sulfur atom. In fact the observed correlations between metal–sulfur bonding and activity suggest that the activity of the metal sulfide depends strongly on whether the metal atom at the vacancy can bind effectively to the sulfur in the heterocycle.

How might this binding of the heterocycle occur? An examination of the level structure of thiophene, the simplest sulfur heterocycle of interest, provides an answer to this question. Figure 10 shows schematically the form of the three highest energy occupied molecular orbitals and the first unoccupied molecular orbital of thiophene. Assuming that the thiophene ring binds perpendicular to the catalyst surface, binding of the ring sulfur to the metal could occur through electron donation from the filled $6a_1$ (sigma) or $2b_1$ (pi) orbital to the metal d orbitals and/or back donation from a metal d orbital into the empty $3b_1$ (pi*) orbital. From the previous discussion of metal–sulfur interactions in the metal sulfides we can predict which interactions would be important for binding of the ring sulfur to the metal. We expect that sigma interactions between the metal and the ring sulfur could occur for either the $3d$ or $4d$ metals, but that the sigma interactions would be stronger for the $4d$ metals. On the other hand, we expect that pi interactions would be significant only for the $4d$ metals and that if pi interactions are necessary, binding would

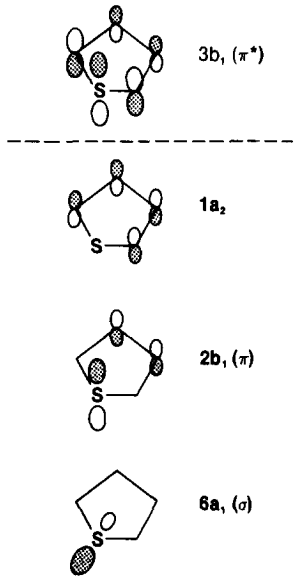

FIG. 10. Schematic representation of the three highest energy occupied molecular orbitals ($6a_1$, $2b_1$, $1a_2$) and the lowest energy unoccupied molecular orbital ($3b_1$) of thiophene.

only occur for the 4*d* metals. A quantitative description of how such binding occurs of course requires more detailed calculations and experiments. We do know, however, that the 4*d* metal sulfides are in general more active and that the metals in these sulfides are capable of both sigma and pi interactions. This suggests that effective binding of thiophene to the catalyst does require both pi and sigma interactions. Further evidence for this type of binding is found if we examine the ligand properties of thiophene in transition metal complexes.

It is well known that when bound to transition metals, sulfur-containing molecules generally act as donor ligands. Aromatic molecules such as thiophene, however, are not particularly good ligands, and the explanation usually given for their poor ligand properties is that the sulfur electrons are tied up in the aromatic system and therefore less available for donation. Certainly, there are few known transition metal complexes containing thiophene ligands, and most of these are in fact weak pi complexes containing first row transition metals (*9*). In these complexes binding does not occur through the sulfur. The thiophene ring binds flat through the ring pi system, so that the bonding between the ring and the first row metal is similar to the bonding between a cyclopentadiene ring and a transition metal. No pi complexes of this type contain second row transition metals. On the other hand, the only complexes containing thiophene bound through the ring sulfur atom contain the second row metal Ru (*10*). These complexes are $Ru(NH_3)_5(SC_4H_4)^{2+}$ and $Ru(NH_3)_5(SC_4H_4)^{3+}$, and the experimental evidence for the nature of the metal–sulfur binding in these complexes is consistent with our conclusions concerning the ability of 4*d* metals to interact with the ring sulfur. In a comparison of the two Ru complexes, Kuehn and Taube (*10*) found that although thiophene is only weakly bound to Ru, the affinity of Ru(II) for thiophene is approximately 10^8 greater than the affinity of Ru(III) for thiophene. They attributed this greater affinity of Ru(II) to the pi acceptor ability of thiophene. That is, the metal–sulfur pi interaction plays an important role in the binding of the ring sulfur to the 4*d* metal Ru, and it is the empty thiophene $3b_1$ (pi*) orbital which takes part in this interaction.

Returning to the discussion of HDS catalysis, we know that one step in the catalytic process must be the binding of the heterocyclic molecule to the catalyst. If the heterocycle binds to an exposed metal at a sulfur vacancy, then the available evidence from transition metal thiophene complexes suggests that for the 3*d* metals binding of the heterocycle through the ring sulfur atom would occur with difficulty. For the 4*d* metals, however, this mode of binding is more likely. This is consistent with the results of our calculations, which indicate that for the 4*d* metals bonding between the metal of the catalyst and the sulfur in the ring could have both a sigma and pi component, while for the 3*d* metals this type of bond would have only a weaker sigma component. Since we know that the 4*d* metal

sulfides are more active and that the activity appears to be related to the ability of the metal to form covalent bonds with sulfur, we conclude that (1) the heterocyclic molecule does bind to the active catalyst through the ring sulfur atom and (2) it is the ability of the metal to bond covalently with sulfur which determines whether this binding can actually occur. The more active 4*d* metal sulfides have this ability. It is probably the ability of the 4*d* metals to form both sigma and pi bonds with sulfur which is important for catalytic activity. Neither of these interactions will be really strong, but the combined sigma and pi interactions could enable the heterocycle to bind to the catalyst for reaction. As mentioned above, thiophene can function as a sigma donor, and it is potentially either a pi donor or pi acceptor, depending on the relative energies of the metal and thiophene pi orbitals. The importance of these effects will vary for the different metals, and they cannot be determined from the information at hand since the correlations between the covalency of the sulfides and their activity tell us only that a metal–sulfur pi interaction is possible. One very intriguing observation can be made, however, if we return to the correlation between HOMO occupation and activity. We recall that for the 4*d* metals the occupation of the $2t_{2g}$ level correlates with activity. That is, increased $2t_{2g}$ occupation corresponds to greater activity. If thiophene binds to the metal, it is through one of these $2t_{2g}$ type metal orbitals that metal–sulfur pi interactions will occur. We saw earlier that for $Ru(NH_3)_5(SC_4H_4)^{2+}$ pi back donation from the metal to the ring pi* orbital is apparently the important metal–sulfur pi interaction. The fact that increased occupation of the $2t_{2g}$ level in the sulfides corresponds to increased activity suggests that pi backdonation from the metal to the ring sulfur is also the important pi interaction when the heterocyclic ring bends to the catalyst. Finally, we should note that pi backdonation would not only make it possible for the binding to occur, but would also aid in the carbon–sulfur bond breaking which takes place in the HDS process. It can be seen from Fig. 10 that the pi* orbital is antibonding between the sulfur and adjacent carbon atoms. Therefore, population of this orbital through backdonation from the metal would result in a net weakening of the carbon–sulfur bonds which must ultimately be broken.

CONCLUSIONS

In this report we have attempted to lay a theoretical foundation for understanding HDS catalysis by transition metal sulfides. In particular, we have explored the bulk electronic structure of the first and second transition series sulfides and shown that a relation exists between the calculated bulk electronic structure of the transition metal sulfides and their activity as HDS catalysts. We have identified several electronic factors which appear to be related to catalytic activity. These are the orbital occupation of the HOMO, the degree of covalency of the metal–sulfur bond, and the metal–sulfur covalent bond strength. Using quantities derived from the results of our calculations, we have incorporated these factors into an activity parameter A_2 which correlates with catalytic activity. That is, if the calculated value of A_2 for a particular metal sulfide is large, we would predict that this sulfide should exhibit high activity as an HDS catalyst. This is the first time, to our knowledge, that such a parameter has been obtained.

A true understanding of the fundamental basis for the observed correlations between electronic structure and catalytic activity will require better experimental and theoretical knowledge of the HDS process. We have shown, however, how the relation between catalytic activity and metal–sulfur covalency in the sulfides, combined with experimental observations of thiophene–transition metal bonding, suggests a specific surface binding model for thiophene. This model invokes binding of the ring sulfur of the thiophene to an exposed transi-

tion metal on the surface of the catalyst, and it is consistent with the relation between metal–sulfur covalency in the bulk sulfides and their activity. If the metal is able to bind effectively to sulfur in the bulk, it is more likely to be able to bind effectively to the sulfur in a heterocyclic ring. This model thus suggests why the bulk electronic structure of the sulfide may be related to the surface properties and ultimately to the catalytic properties of the sulfide.

Two remaining fundamental questions are (1) what is the actual surface electronic structure of the bulk catalyst and (2) what is the relation of this structure to the catalytic activity of the sulfide? In an attempt to answer these questions we are carrying out calculations on extended neutral metal–sulfur clusters which serve as better models for the transition metal sulfides. This approach will give us a clearer understanding of the surface electronic structure of the sulfides and allow us to examine various types of vacancies on the surface as potential active sites. Perhaps most importantly, these model systems will allow us to study the interaction between a reacting molecule such as thiophene and the model catalyst surface. The cluster calculations reported in this paper have made it possible to propose a model for this interaction which is consistent with both the trends in catalytic activity of the sulfides and the bulk electronic properties of the sulfides. Other theoretical studies have also proposed models for this interaction (*11, 12*), but these too have been based on very simplified model systems. The extended cluster systems should allow us to develop a much more definitive model for the interaction between a thiophenic molecule and the catalyst surface. Finally, another area of particular interest is the relation between the "promoted" transition metal sulfide systems and the binary transition metal systems. In particular, what is the basis for this promotion? Preliminary results indicate that calculations on clusters which model these promoted systems will yield considerable insight into this problem. These promoted systems will be discussed in a future report.

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