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FTIR Studies of Mo/Al_2O_3-Based Catalysts

II. Evidence for the Presence of SH Groups and Their Role in Acidity and Activity

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FTIR has been used to study the surface hydroxyl structures, the metal sulfide structures, and the acidic properties of Mo/Al_2O_3-based hydrotreating catalysts. The investigations of the functional group of the catalyst have been complemented by probe molecule studies using NO and pyridine. The different studies have provided evidence for the presence of SH groups in the sulfided state of both promoted and unpromoted catalyst. These SH groups are found to be associated with the Mo sulfide phase and they are involved in hydrogen bonding with surface alumina hydroxyl groups. It is concluded from a comparison with NO adsorption results that the SH groups are mainly associated with the edges of the MoS_2 phase. Furthermore, pyridine adsorption experiments have shown that Brønsted acidity is associated with the SH species. It is suggested that the SH groups may not only play a role determining the catalytic activity of reactions proceeding via Brønsted acid sites, but they may also be the source of hydrogen during a catalytic cycle. © 1993 Academic Press, Inc.

INTRODUCTION

Extensive studies of sulfided Mo/Al_2O_3 hydrotreating catalyst have provided evidence for that the HDS activity is related to the presence of sulfur vacancies (uncoordinated sites) at the edges of MoS_2 structures (*1*, *2*). The addition of Co or Ni leads to large increases in the activity which can be attributed to the promoter atoms decorating the edges of the MoS_2 phase in the so-called Co–Mo—S or Ni–Mo–S type structures (*2*, *3*). While agreement on the relative importance of various structures appears to have been reached, many questions regarding the detailed reaction mechanisms have not yet been answered. The importance of uncoordinated sites appears, as mentioned above, well established, but many models for the reaction mechanism also assume an important role of surface SH or sulfhydryl groups (e.g., (*4*–*9*)). In fact in a few instances, correlations between the HDS activity and estimations of the SH concentration have been reported for both promoted (*7*, *8*, *10*, *11*) as well as unpromoted catalysts (*12*). The formation of the SH groups may arise, as proposed by Schuit (*13*) and Wright *et al.* (*14*), from the adsorption and dissociation of H_2S on surface vacancies:

$$H_2S + \square + S^{2-} \Leftrightarrow H_2S_{ads} + S^{2-} \Leftrightarrow 2SH^- . \quad (1)$$

In view of this proposal, it is expected that the SH concentration should be related to both the overall vacancy concentration and the experimental conditions.

Regarding the evidence for the presence of SH groups, it has remained intriguing that such surface sulfhydryl groups have not been observed in infrared-spectroscopy-studies of supported catalysts (*15*), while deuterium exchange studies (*16*), chemical titration by silver ions (*5*), and Raman spectroscopy (*17*) have provided such evidence. For bulk MoS_2 samples, evidence for SH groups was provided by infrared spectroscopy (*18*) and inelastic neutron scattering spectroscopy (*14*), but for supported catalysts, no clear conclusions were obtained (*15*, *19*). The recent direct observation of Brønsted acidity (*20*) in sulfided catalysts

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can be taken as support for the presence of surface SH species. It should be mentioned that none of the studies, which have provided evidence for the presence of SH species, has given information on the location of such species.

In the present work, further evidence for SH has been obtained through an examination of the nature of the hydrogen bonding observed in sulfided Mo/Al_2O_3 and $Co-Mo/Al_2O_3$ catalysts. Furthermore, NO and pyridine adsorptions have been used in order to establish the detailed location and acid properties of the SH sites. The unpromoted catalysts studied are the same as those investigated in the preceding paper (*21*). The effects of Mo loading, sulfiding temperature, and the presence of promoter atoms are discussed.

EXPERIMENTAL

The Mo/Al_2O_3 catalyst studied, contained either 4, 8, 10, or 12 wt% Mo supported on a 230 m^2/g support. The promoted catalyst consisting of the same 10 wt% Mo with an additional 3 wt% Co added. Further details on the catalysts were given in the preceding paper (*21*). A separately prepared 8% Mo/Al_2O_3 based on a different alumina support having slightly lower surface area (220 m^2/g) was also studied for comparison. All the catalysts were studied in both the oxidic precursor and in the active sulfided states. Details of the experimental procedure for the *in situ* IR measurements and the sulfidation were also described in Ref. (*21*). In short, the samples were studied as self-supported wafers. The calcined catalysts were subjected to evacuation at 723 K for 14 h to 10^{-6} mbar before cooling to rt, at which temperature IR spectra were recorded. The catalysts were sulfided by passing a mixture of 1.7% H_2S in H_2 over the calcined sample wafers at 723 K for 2 h. This was followed by a N_2 flush post treatment at 673 K (if nothing else stated) for 14 h and an evacuation treatment for 1 h at rt to 10^{-6} mbar. To study the effects of the post treatments, the temperatures of the N_2 flush and evacuation treatments were varied in particular cases. The adsorptions of NO and pyridine were carried out at rt and 673 K, respectively.

Nitrogen was purified by passage through Cu turnings at 523 K and a molecular sieve trap (Linde 5A) kept at 195 K. Nitric oxide, 99% (AGA A/S) and pyridine (spectroscopic grade) were purified by freeze–thaw cycles.

All spectra were recorded on a Digilab FTS-80 Fourier transform infrared spectrometer equipped with a liquid-nitrogen-cooled MCT (mercury–cadmium–telluride) detector.

RESULTS

The preceding paper (*21*) described the alumina surface hydroxyl groups in oxidic and sulfided catalyst. The analysis of the OH band intensities provided information regarding structural and morphological changes of the Mo phase. However, besides variations in OH band intensities, a significant broadening of the OH band envelope toward lower frequency was also observed in the Mo-containing sulfided catalysts and the origin of this will be addressed presently. These regions are conveniently examined as difference spectra, where the spectrum of the calcined and sulfided alumina support is subtracted from the respective spectra of the catalyst (Fig. 1). The difference spectra of the oxidic catalysts show mainly negative OH absorption bands reflecting the removal of surface OH species from the alumina support upon addition of Mo. This is due to the interaction of Mo with surface OH groups forming Mo–O–Al (see Discussion in Ref. (*21*)). It is also important to point out that these spectra clearly show no new bands are formed in the oxidic catalysts, indicating that the OH removal is the only process occurring. In contrast, a new band is formed in the spectra of the sulfided catalysts and the corresponding negative band areas are seen to be smaller as compared to those in the oxidic catalysts. These less negative bands are, as discussed in (*21*), due to break-

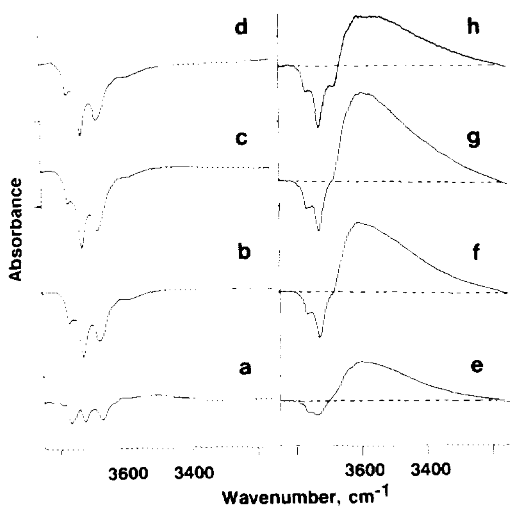


FIG. 1. Difference spectra (with the spectrum of the Al_2O_3 support subtracted) of the OH stretching region of (a)–(d) calcined 4%Mo, 10%Mo, 12%Mo, and 3%Co10%Mo/Al_2O_3, respectively; (e)–(h) are spectra of the same samples after sulfiding at 723 K.

age of Mo–O–Al bonds upon sulfiding and regeneration of some of the surface alumina OH groups which were removed during formation of the calcined catalysts. The new band in the sulfided samples appears to be centered around 3600 cm^{-1} and is most likely due to H-bonded OH to SH as will be discussed below. In agreement with earlier studies (*15*, *22*), the weak SH stretching vibration band around 2500–2600 cm^{-1} is not seen.

In order to examine closer the H-bonded contribution in the spectra of the sulfided Mo/Al_2O_3 catalysts, the band contributions due to the remaining OH groups on the exposed alumina surface were removed. This was done by subtracting an appropriate scaled spectrum of the sulfided alumina support, such that all the free OH bands are matched out (as also described in (*21*)). The resulting spectra shown in Fig. 2 now show a single broad band with a shape and position (around 3600 cm^{-1}) which remain quite constant for the different samples. It should be noted that all the essential features of this broad band are seen in Fig. 1, but they are shown more clearly in Fig. 2 and these data are more suited for a quantitative analysis. The intensity of the broad band is observed to increase for the sulfided Mo/Al_2O_3 samples upon increasing the Mo loading. For the series of catalysts prepared using the same alumina, the band intensity increases almost linearly with Mo concentration (Fig. 3) in the loading region studied. However, this relationship is not a general one since the catalyst prepared using the different alumina did not give results which fall on the same curve (point marked with an open circle in Fig. 3).

For the Co-promoted Mo/Al_2O_3 catalyst (Fig. 2d), it is seen that the intensity of the 3600-cm^{-1} band is lower than that for the corresponding unpromoted catalyst (Fig. 2b). The intensity of the H-bonded band is seen to depend not only on the Mo loading (Fig. 4) but also for a given catalyst on the post treatment conditions such as the N_2

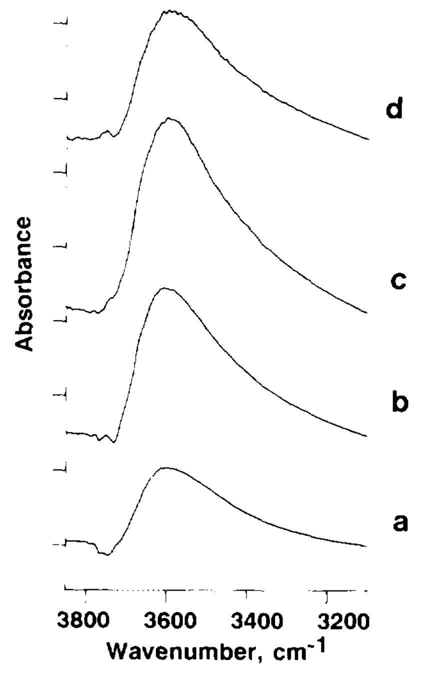


FIG. 2. IR spectral component after subtraction of free Al–OH bands for (a)–(d) 4%, 10%, 12% Mo/Al_2O_3, and 3%Co10%Mo/Al_2O_3, respectively.

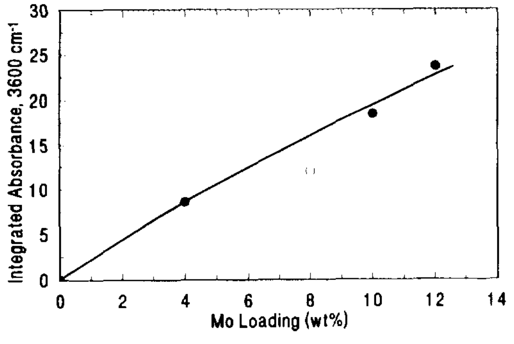


Fig. 3. Integrated absorbance of the 3600 cm^{-1} band vs. Mo loading.

flush condition and the evacuation temperature used following the sulfidation in the H_2S/H_2 gas mixture. A higher post treatment temperature was observed to lead to a lower band intensity. This effect appears to be most pronounced for the catalyst with the higher Mo concentration (Fig. 4a). It should be mentioned that the intensity of the free OH bands was not found to be very sensitive to these changes in post treatments, indicating that no sintering has occurred.

The adsorption of NO has been widely used to provide information on the nature of the active phases in hydrotreating catalysts (*23*). NO adsorbs mainly at the edge planes of MoS_2 and the adsorption of NO can therefore provide direct information on the Mo edge dispersion. The NO adsorption spectra of the sulfided Mo/Al_2O_3 catalysts are shown in Fig. 5. The positions of the two NO absorption bands (due to symmetric and asymmetric stretching vibrations of dinitrosyls) are seen to be very similar for the various catalysts. This indicates that the same

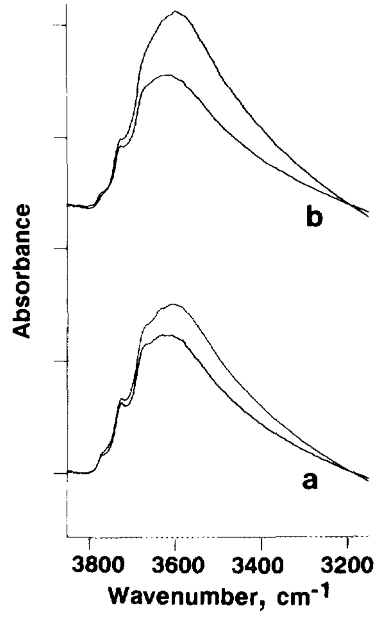


Fig. 4. IR spectra of the OH stretching region of the sulfided (a) 10%, and (b) 12% Mo/Al_2O_3 catalysts with different post treatment conditions. The spectra with the larger band areas are obtained after a lower N_2 flush at 673 K followed by rt evacuation, whereas those with smaller band areas are obtained after a N_2 flush and evacuation at 723 K.

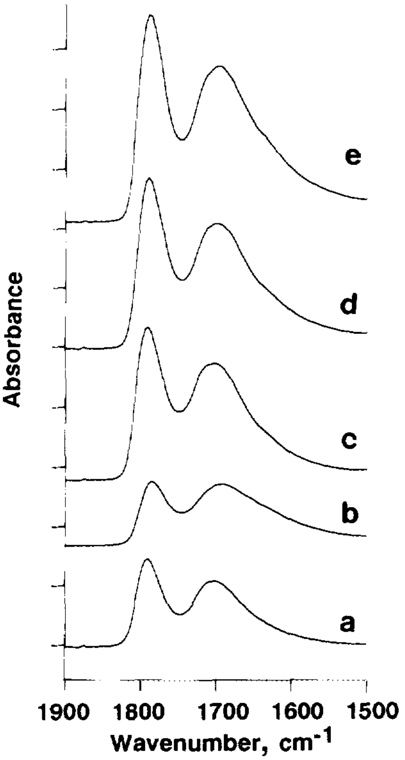


Fig. 5. NO absorption spectra of sulfided (a) 4%, (b) 8%, (c) 8%, (d) 10%, and (e) 12% Mo/Al_2O_3, where the 8% Mo/Al_2O_3 sample in (b) is not from the same batch of preparation as the others.

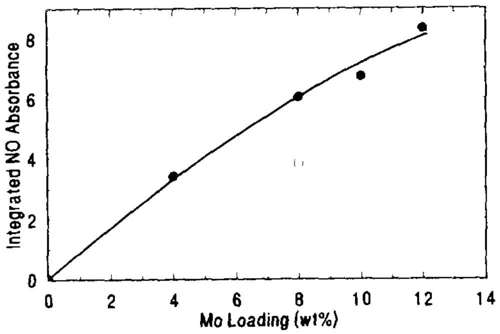


FIG. 6. Integrated absorbance of NO absorption bands vs Mo loading.

type of adsorption complex is formed on the different samples. The intensity ratio of the symmetric to asymmetric NO stretching bands tends to increase slightly with increasing Mo concentration, reflecting a decreasing bond angle between the dinitrosyl species on the higher loading catalysts. A plot of the integrated absorbance of the Mo-NO bands versus the Mo loading (Fig. 6) shows for the series of similar catalysts a nearly linear increase in the amount of NO adsorbed with the Mo loading. Thus, the MoS_2 edge dispersion stays quite constant for the present concentration range. The 8% Mo/Al_2O_3 catalyst from the different batch (corresponding to the point marked with the open circle in Fig. 3) was also investigated with NO adsorption. The results (relatively low integrated absorbance and I_{sym}/I_{asym} ratio) again show that this catalyst behaves differently from the rest. The lower intensity of the NO absorption bands observed for this 8% Mo sample indicates a lower Mo edge dispersion as compared to the other samples.

In Fig. 7, the integrated absorbance of the 3600-cm^{-1} band, indicative of the SH groups, is plotted against the integrated absorbance of the NO bands. A good linear relationship is displayed, and it is observed that the Mo catalyst with the lower edge dispersion which did not fall on the curves in Figs. 3 and 6 now falls quite nicely on the same general curve. Thus, the SH sites and the vacancies for NO adsorption appear both to be associated with the MoS_2 edges. The results further show that increasing the post treatment severity, a treatment, which will increase the number of vacancies, leads to a decrease in the concentration of SH sites (Fig. 4). Thus, the relationship displayed in Fig. 7 will probably only apply for one set of post treatment conditions.

Previous FTIR studies (*20*) have provided evidence for the presence of weak Brønsted acid sites on both the sulfided promoted and unpromoted Mo/Al_2O_3 catalysts at temperatures typical of the hydrotreating reaction. These weak Brønsted acid sites were proposed to be associated with surface SH species formed via dissociation of H_2S. At the reaction temperatures, pyridine may activate a proton transfer from these sites to form an adsorbed pyridinium (or pyridonium) ion. In order to investigate whether or not these sites are associated with the SH sites, adsorption of pyridine at reaction temperature (673 K) was carried out on the 8% Mo/Al_2O_3 sample. In view of the above results, different post treatment temperatures after sulfiding were chosen in order to vary the concentration of H-bonded species. Figure 8 shows, as expected, more H-bonding in the OH spectrum of the catalyst after a post treatment at the lower temperature (i.e., 623 vs 723 K). Figure 9 shows the IR spectra recorded after pyridine adsorption on the catalyst after post treatments at

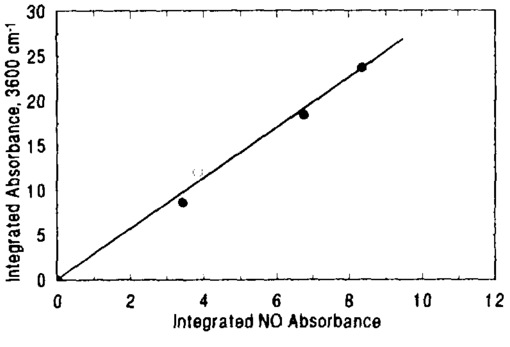


FIG. 7. Integrated absorbance of the 3600-cm^{-1} band vs integrated absorbance of NO absorption bands.

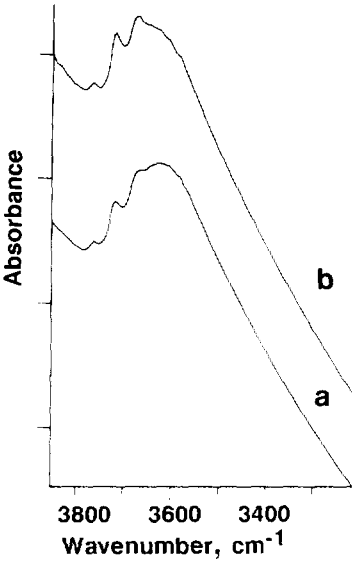


FIG. 8. IR spectra of the OH region of the sulfided 8% Mo/Al_2O_3 after post treatment at (a) 623 K and (b) 723 K.

either 723 or 623 K. It can be seen that the sample which had received the lower post treatment temperature displayed a higher absorbance of adsorbed pyridinium (or pyridonium) ion as compared to that after the higher post treatment temperature. Thus, these results are in agreement with the proposal that the Brønsted acidity is associated with the edge SH groups. The assignment of Brønsted acidity to the SH groups is also in accordance with the results for promoted catalysts which show a lower concentration of Brønsted acid sites (*20*), as well as SH groups (Fig. 2).

DISCUSSION

The present studies suggest that SH groups are present and can be evidenced through the strong hydrogen bonding band observed around 3600 cm^{-1}. The absence of the SH stretching band in the 2500–2600 cm^{-1} region is probably due to that this band is typically very weak in the infrared region. The evidence and the assignment of the 3600-cm^{-1} band to SH has already been mentioned above, and we discuss in the following the genesis of this band and the results which indicate that the SH species are located at the edges of the MoS_2 phase. It is also discussed that the hydrogen bonded SH species may be a quite special feature of the single-slab (monolayer) MoS_2 structures which dominate the present catalysts (see preceding paper (*21*)). Finally, the relationship between the SH groups and the Brønsted acidity and the possible importance of SH groups for catalytic activity and selectivity are discussed.

Properties and Location of SH Groups

A special feature of the sulfided catalysts is the formation of a H-bonding band (Figs. 1 and 2). This is not observed for the sulfided support and is thus clearly related to the presence of the Mo. However, the mere presence of a H-bonding band can obviously not be taken as evidence for SH groups, but in view of our various results, it seems reasonable to attribute the observed H-

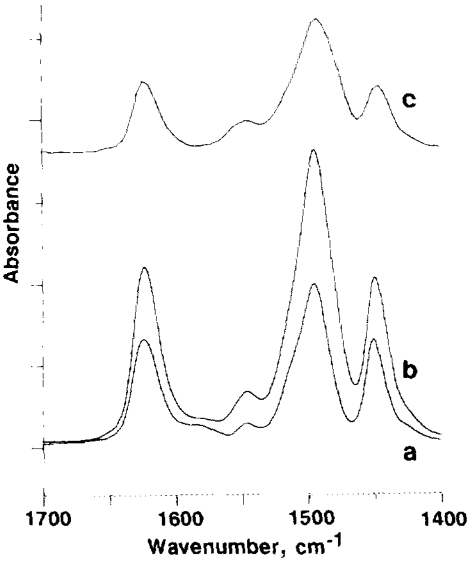
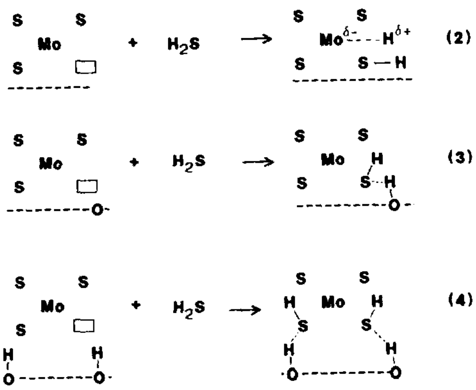


FIG. 9. IR spectra of pyridine adsorbed on sulfided 8% Mo/Al_2O_3 (a) after N_2 flush and evacuation at 723 K (spectrum with lower intensity), and (b) after post treatment at 623 K (spectrum with higher intensity); (c) is the difference spectrum between (b) and (a).

bonding to an interaction between SH associated with the MoS_2 phase and neighboring surface alumina OH groups.

The correlation found between the extent of H-bonding and the Mo loading (Fig. 3) again suggests that the SH groups are associated with the MoS_2 phase. This is in agreement with the proposal made earlier by Burch and Collins (*24*). Furthermore, it is clear from Fig. 3 that the SH groups are not associated with all the Mo atoms but only a certain fraction of them. These could, for example, be the Mo atoms at either the edge or the basal plane of MoS_2. The NO adsorption experiments which titrate Mo edge atoms may be used to discriminate between these two possibilities. The results in Fig. 6 show that the sample (open circle) which gave results that deviate from the overall "correlation" in Fig. 3 has indeed a significantly lower MoS_2 edge dispersion. Nevertheless, in spite of the differences in edge dispersion, a good linear correlation is observed between the band intensity related to the SH groups and the concentration of the Mo edge atoms (Fig. 7). Thus, it can be concluded that the SH groups are associated with the MoS_2 edge. The fact that both the SH groups and the vacancies titrated by NO are found to be related to the MoS_2 edges should not lead to the conclusion that they are at the same sites, but merely indicates that both sites are located at the MoS_2 edges. In fact, the SH groups and the vacancy sites may be interrelated according to a scheme like that given in Eq. (1). For example, it is seen (Fig. 4) that increasing the post treatment severity—a treatment which will increase the number of vacancies—results in a decrease in the concentration of SH sites (Fig. 4). SH groups may also be produced by adsorption of H_2 and reduction of molybdenum. As a consequence, the type of correlation displayed in Fig. 7 is expected to depend on the process (temperature, pH_2S/pH_2, etc) and treatment conditions. It could be added that the present assignment of the location of the SH groups to the MoS_2 edges is also consistent with the single-crystal experiments which showed that the basal planes are inert toward many reactions including adsorption of H_2S (*25*).



SCHEME 1

Let us consider the case where SH groups are formed by H_2S dissociation on a vacancy site. In one proposal, the H from the dissociation is suggested to remain at the same Mo sites as the SH group (*7*, *20*) and this hydrogen could act as the source for Brønsted acidity (this is very schematically illustrated in Scheme 1, part (2) looking at a $(10\bar{1}0)$ edge of MoS_2). It should be mentioned that positively charged H coordinated to a metal atom is not a favorable situation from a chemical point of view. Alternatively, the proton may be located on a neighboring S^{2-} ion forming another SH group (e.g., corresponding to Eq. (1)) and Scheme 1, part (4). The above schemes, however, do not by themselves account for the observed H-bonding. This must involve neighboring surface hydroxyl groups which are either formed as a product of the dissociation of H_2S (i.e., reaction of H with a surface oxygen ion of the alumina as depicted in Scheme 1, part (3)) or are present on the alumina surface (Scheme 1, part (4)). In these different cases, the SH groups will most likely point out perpendicular from the $(10\bar{1}0)$ edge. The results indicating that there may be more OH groups on the surface of the catalyst than those readily observed (*21*) would seem to favor Scheme 1, part (3).

Irrespective of the mode of formation of the SH groups and the detailed origin of the H-bonding, the latter is expected to be an especially dominating feature for the single slab MoS_2 structures lying flat on the alumina support as is indeed the prevailing situation for the catalysts studied here (*21*). High-temperature sulfiding studies which transform the MoS_2 phase into multislab structures have shown as expected a drastic decrease in the H-bonded species (*26*). Whether one in this case may observe free SH groups directly is also presently being investigated. Studies on bulk unsupported samples (*18*) suggest that this may be possible. The hydrogen bonding is also expected to be a special feature for the single slab structures supported on alumina. For other supports or multislabs structures, such hydrogen bonding may be absent or may only affect a minor fraction of the atoms. Thus, it is possible that the hydrogen bonding may be the origin of some of the observed catalytic differences between the socalled Type-I and Type-II MoS_2 (and Co–Mo–S) structures (*27*).

Surface Acidity

Although many of the catalytic properties of sulfided Mo catalysts have shown strong indications for the presence of Brønsted acid sites (*28*), direct evidence for their presence has first been obtained recently from pyridine adsorption studies carried out at temperatures similar to those of the reaction (*20*). The present study has provided support for the proposals that the Brønsted acidity is associated with the presence of SH groups (*9*, *20*). Furthermore, the acidity may for example be generated via dissociative H_2S adsorption as depicted above.

The association of Brønsted acidity to the SH groups associated with the MoS_2 phase is also supported by the experiments on the promoted Co–Mo/Al_2O_3 catalysts. Such catalysts are known to have a decrease in the number of exposed Mo edge sites (*23*) and the results show that the addition of the Co promoter atoms to the Mo/Al_2O_3 catalyst results in a decrease in both the extent of H-bonding (Fig. 2) and in the concentration of Brønsted acid sites (*20*). These results therefore suggest that in the promoted catalysts, the Brønsted acid sites are mainly associated with the unpromoted Mo edge sites in MoS_2 and not the Co–Mo–S promoter atoms. It could be added that the presence of SH groups is not expected to be favored at the Co edge sites due to the lower metal sulfide bond strength of the Co promoter edge atoms compared to that of the Mo edge atoms (*29*).

Catalytic Implications

In view of the observed occurrence of SH groups in Mo/Al_2O_3 and CoMo/Al_2O_3 catalysts, it is relevant to examine the proposed models (*4–9*) and studies (*7*, *8*, *10–12*, *30*, *31*) which dealt with the role of these groups in the hydrotreating reactions. The observation that the SH groups are located at the MoS_2 edges is particularly interesting, since it provides basis for relating such models to the catalyst structure. Another interesting observation is the result which indicates that one may have an interconversion between SH and vacancies at the edges. Thus, both types of sites may coexist at the edges in the vicinity of each other. This may be an attractive situation from a catalytic point of view, since the vacancies can be the sites for the coordination of the heteroatom of the reactant and the neighboring SH groups may be the source for providing the hydrogen. For unpromoted Mo catalysts, both the vacancies and the SH groups are associated with the Mo atoms, whereas for the promoted catalysts, recent results (*32*, *33*) suggest that the vacancies which are important to consider are those associated with the Co edge atoms. A structural model of thiophene adsorbed on a Mo sites at the $(10\bar{1}0)$ edge of a small MoS_2 single slab is shown in Fig. 10a. Two neighboring SH groups and a vacant Mo site are also included in the model. The atoms are drawn to scale and it should be noted that the sulfurs in thiophene and SH are smaller than

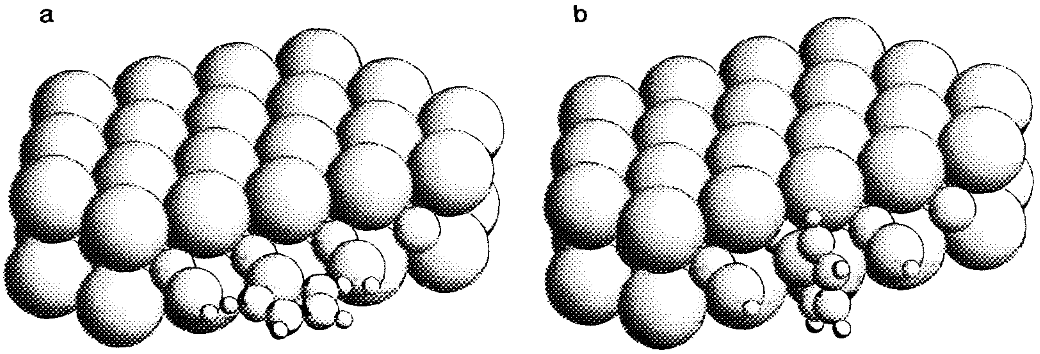


FIG. 10. Schematic views of thiophene adsorbed at a Mo sites at the $(10\bar{1}0)$ edge of a small MoS_2 single slab showing two neighboring SH groups and a vacant Mo site (the atoms are drawn to scale): (a) shows a parallel orientation and (b) shows perpendicular orientation of thiophene on a Co edge (Co–Mo–S) site.

those in MoS_2. A parallel orientation of thiophene is shown in this figure, although there may not be a strong preference for such orientation. It is seen that even in the case of single MoS_2 slab lying on an alumina support, a perpendicular orientation poses no steric constraints in the case of thiophene adsorption as illustrated in Fig. 10b. In this example, thiophene is considered to coordinate to a Co atom located at the $(10\bar{1}0)$ MoS_2 edge (i.e., a Co–Mo–S Co atom). For larger reactant molecules, however, steric constraints will be much more important.

The above type of "bifunctional" mechanisms are close to those presented by Lipsch and Schuit (*4*) and Topsøe (*6*) for unpromoted and promoted catalysts, respectively. The supply of hydrogen in these mechanisms is however occurring quite differently from that envisaged in the remote control model involving spill over of hydrogen from Co_9S_8 (*34*). Theoretical calculations (*29*) suggest that in the case of HDS, the rate-limiting step is not the supply of hydrogen but the creation of the vacancies (*29*). These calculations further showed that this situation holds not only for Mo based catalysts but for HDS on many other elements in the periodic system.

In the case of HDN and other hydrotreating reactions such as hydrocracking, the SH sites may also play a different catalytic role from that discussed above. This role may be to provide Brønsted acid sites for acid catalyzed reactions. Studies in the literature (*11, 30, 31, 37, 38*) have shown that the partial pressure of H_2S during the hydrotreating reaction plays a significant role in the selectivity in that increasing H_2S concentration enhances the hydrogenolysis of C–N bonds in HDN reactions. This has been proposed (*7*) to be due to the generation of weak Brønsted acid sites by dissociative adsorption of H_2S on anionic vacancies. Our earlier observation of Brønsted acidity (*20*), as well as the present results have supported that such a mechanism may result in Brønsted acidity. Weak Brønsted acidity is observed at typical hydrotreating reaction temperatures on these catalysts and a correlation is seen between these acid sites and the surface SH species. Thus, in view of the observation reported in the literature on the reactivity correlation, it is reasonable to conclude that these SH sites are the sites which facilitate the C–N bond cleavage in HDN reactions and other acid catalyzed reactions. In fact, recently evidence for this has been obtained for the isomerization of N-dodecane (*39*).

The present results show that the number of SH and vacancy sites for different Mo/Al_2O_3 catalysts is proportional to the total concentration of edge sites in the sample.

For a given catalyst, however, the relative concentration of the SH and vacancy sites is expected to change depending on the reaction conditions. Such changes are also expected to influence the catalytic properties.

Breysse and co-workers (*35, 36*) have recently presented interesting results which show that the relative role of the different types of sites in HDN reactions may depend strongly on the given elements in the periodic system investigated. In view of the present results which show that interconversion between SH groups and vacancies may take place, it is not unexpected that H_2S was observed to promote reactions over some elements and poison the same reaction over other elements. Also a change from promotion to poisoning has been observed when changing the H_2S/H_2 ratio for a given catalyst (*40*).

CONCLUSIONS

The present studies have provided further evidence for the presence of SH groups associated with the MoS_2 phase in sulfided Mo/Al_2O_3 catalysts. The SH groups are involved in hydrogen bonding to surface alumina OH groups giving rise to a broad IR band around 3600 cm^{-1}. The formation of SH is proposed to occur for example via dissociative adsorption of H_2S on Mo vacancies. By comparison with NO adsorption results, it can be concluded that the SH groups are located at the edge positions of the MoS_2 structures. The edge location of both the SH groups and vacancies is seen to have interesting catalytic consequences. Furthermore, the SH groups and the vacancies are found to interconvert and coexist in close proximity. Adsorption of pyridine at reaction temperature further shows that the SH species give rise to Brønsted acidity. The concentration of these SH has been found to depend closely on the sulfiding and pretreatment conditions and is therefore expected to depend on the reaction conditions as well. Finally, the SH groups may both have a role in the supply of H and provide Brønsted acidity for acid catalyzed reactions.

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