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FTIR Studies of Mo/Al_2O_3-Based Catalysts

I. Morphology and Structure of Calcined and Sulfided Catalysts

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Quantitative FTIR studies of the alumina surface hydroxyl groups of unpromoted and promoted Mo/Al_2O_3 catalysts have been used to get new insight into the structure/morphology of calcined and sulfided catalysts. The interaction of Mo with surface OH groups in the calcined state is in agreement with previous studies seen to involve all the different types of OH groups, but the extent of interaction and the resulting Mo structural changes depend on the nature of these groups. At low Mo concentration, the interaction involves mainly the most basic OH groups, and as a result the relative concentration of the remaining OH groups in calcined Mo/Al_2O_3 catalyst is quite different from that observed for the alumina support. For the present calcined catalysts, monolayer-type structures dominate up to 12% Mo. The concentration of the OH groups determined by IR rather than the surface area of the alumina has been found to determine the upper limit for formation of the monolayer structures. CO_2 adsorption, which has previously been used to determine the coverage of the alumina surface by supported metals, was shown to have some inherent limitations in that too high coverages are typically obtained. Upon sulfiding, substantial regeneration of surface hydroxyl groups occurs involving predominantly the most basic OH groups. The resulting relative abundance of the various hydroxyl groups becomes quite similar to that observed for the alumina support. The results indicate that sulfiding leads to substantial rearrangement and lateral agglomeration of the supported Mo structures. However, for catalysts with up to 12% Mo, the monolayer dispersion is maintained and the MoS_2 phase appears to be predominantly present as 2D single-slab structures oriented flat-wise on the alumina support (*c*-axis perpendicular to alumina surface). The decrease upon sulfiding in the apparent coverages of the alumina by Mo is explained by the strong preference for Mo to interact with certain OH sites in the calcined catalysts, rather than due to contraction of the Mo phase upon sulfiding as suggested in the literature. For unpromoted catalysts, single-slab structures appear to be stable even after sulfiding at 873 K.

INTRODUCTION

The introduction of various physical and chemical characterization techniques has resulted in significant progress in the understanding of the surface structures present in calcined Mo-based catalysts supported on alumina (*1–3*). Regarding the formation of the surface structures, it is commonly accepted that Mo interacts in the calcined state with the hydroxyl groups on the alumina carrier surface (*4–11*), resulting in the formation of monolayer-type structures. The disappearance of surface hydroxyl species in the presence of Mo was directly observed by infrared spectroscopy (*8–10*), and such studies have therefore provided information regarding the fraction of the alumina surface covered by molybdenum. Upon sulfiding, EXAFS studies have shown that small MoS_2-type structures are formed (*12*). Furthermore, several studies (*10, 13–17*) have shown that a high coverage of the alumina by Mo is basically maintained after typical sulfiding conditions. In fact single-slab MoS_2 structures may dominate, as also observed by electron microscopy (*15, 18*). Electron microscopy studies (*19, 20*) of nonporous model systems have shown that the morphology and the orientation of the molybdenum phase relative to the support may change during sulfiding. These and other

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studies (*21, 22*) have indicated that the MoS_2 structures are oriented perpendicular to the alumina surface. However, the previous IR (*10*), XPS (*13*), and CO_2 adsorption studies (*17*) did not support this proposal. Rather, these studies gave good support for the MoS_2 structures lying flat on the Al_2O_3 support (i.e., with the *c*-axis perpendicular to the Al_2O_3 surface). Techniques such as XPS (*23*), EXAFS (*24*), and TPS (*25*) have provided further information on the nature of the sulfidation process, but several questions still remain unanswered. For example, the sulfidation into MoS_2 structures is expected to involve breaking of Mo–O–Al bonds, and this should result in significant structural rearrangements involving regeneration of surface alumina OH groups. A substantial increase in the free alumina surface upon sulfiding was indicated by CO_2 adsorption (*17*). If this is the case, it is puzzling why this has not been observed by infrared spectroscopy following typical sulfiding (*10*), but only after high-temperature sulfiding (*14*) or after other special sulfiding treatments (*26, 27*). It could be added that regeneration of OH groups should be especially pronounced if the MoS_2 structures are perpendicular to the alumina surface as suggested in some studies (*19–22*).

In an attempt to reconcile the different results regarding the surface structures of Mo/Al_2O_3 catalysts, we have reinvestigated in detail the infrared spectra of a series of catalysts with different Mo loadings and focused especially on the effects of sulfiding. The CO_2 adsorption technique is reevaluated in light of these findings.

EXPERIMENTAL

The catalysts studied were a 4, 8, 10, and 12 wt% Mo/Al_2O_3. They were prepared by depositing the active materials in appropriate concentrations onto η-Al_2O_3 (surface area, 230 m^2/g) via the incipient wetness method followed by drying and calcining in air at 773 K for 2 h. The catalysts were studied both in their oxidic precursor state and the active sulfided state.

To study the oxidic precursors, the calcined catalyst samples in the form of self-supporting wafers with a thickness corresponding to 4.7 mg/cm^2 were mounted into an *in situ* IR cell and evacuated at 723 K for 14 h to 10^{-6} mbar before cooling to room temperature, at which IR spectra were recorded. For the sulfided catalysts, the calcined sample wafers were sulfided *in situ* in the IR cell in a gas flow consisting of 1.7% H_2S in H_2 at 723 K for 2 h. This was followed by a N_2 flush treatment usually at 673 K for 14 h before cooling to rt at which temperature the samples were further evacuated for 1 h to 10^{-6} mbar. To study the effects of the post treatments following the sulfidation, the temperatures of the N_2 flush and evacuation treatment were also varied in particular cases. Nitrogen was purified by passage through Cu turnings at 523 K and a molecular sieve trap (Linde 5A) kept at 195 K.

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

Figure 1 shows the IR spectra of the OH stretching region of the series of oxidic Mo/Al_2O_3 catalysts were different Mo loadings. For comparison the spectrum of the η-alumina support (Fig. 1a) is also shown. The spectrum of the alumina exhibits well-defined OH bands at 3771, 3730, and 3684 cm^{-1}, and weak shoulder bands at around 3630 and 3590 cm^{-1}, in agreement with earlier findings (*10, 28*). As seen previously (*10*), the distinct OH stretching vibrational bands characteristic of the isolated hydroxyl groups on alumina progressively disappear with increasing Mo loading. Qualitatively, this observation is in accord with the literature (*4–11*) in that Mo interacts with the surface hydroxyl groups of alumina. The decreasing intensity of the OH bands therefore reflects the increase in the Mo coverage. At 12% Mo (Fig. 1e), all free hydroxyl groups

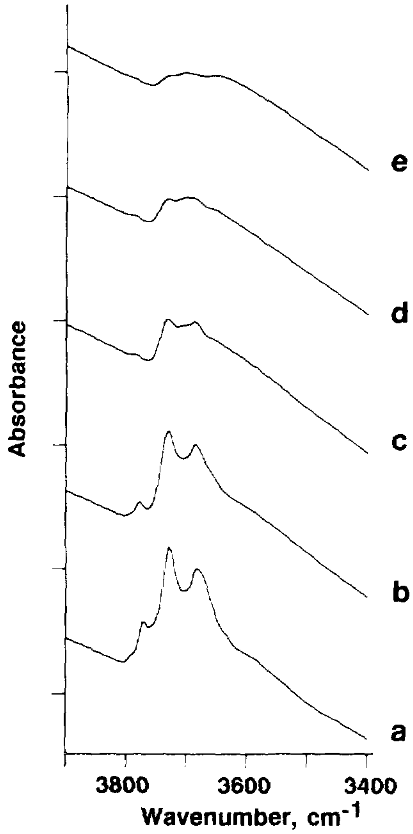

FIG. 1. Ir spectra of the OH band region of the (a) Al_2O_3 support and (b) 4%, (c) 8%, (d) 10%, and (e) 12% Mo supported on alumina after evacuation pretreatment.

are seen to be essentially removed leaving behind a broad background indicative of some bulk and H-bonded hydroxyls.

Figure 2 shows the spectra in the OH region of the same samples after sulfidation. For the Al_2O_3 support (Fig. 2a), the OH stretching bands due to free OH groups remain essentially unchanged after sulfiding as also reported earlier (*10*). The small increase in the surface OH concentration is probably due to the somewhat lower post treatment temperature (i.e., 673 K) used after sulfiding as compared to the evacuation pretreatment temperature (i.e., 723 K) used for the oxidic samples. The lower N_2 flush and evacuation temperatures were chosen in order to minimize possible changes in the phases formed by sulfidation.

In the sulfided catalysts, an increase in the intensity of the free OH bands is seen compared to the calcined state. This shows that some of the alumina OH groups which disappeared upon the interaction with Mo in the calcined catalysts are regenerated after sulfiding. At the same time the OH bands are shifted to slightly lower frequencies (i.e., 3768 and 3728 cm^{-1} in the sulfides vs 3771 and 3730 cm^{-1} in the oxides). It is also observed that there is a broad band centered around 3600 cm^{-1}. This further enhancement of a band in this region, therefore, reflects an increased extent of H-bonding. Since it is only a dominant feature for the Mo containing catalysts, it is related to the presence of the MoS_2 phase.

In order to examine more quantitatively the free surface OH structures in the calcined and sulfided state, the contributions

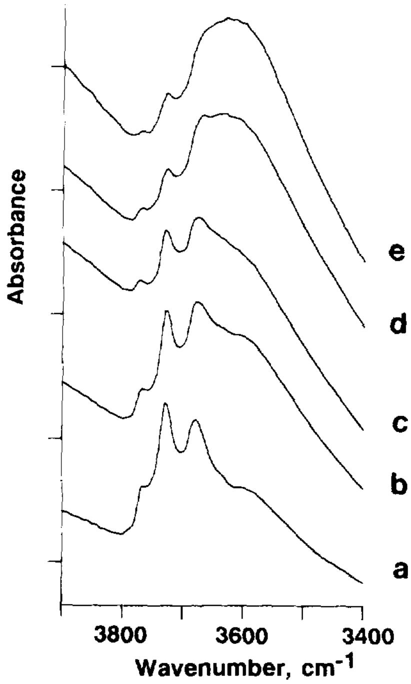

FIG. 2. Ir spectra of the OH band region of the (a) Al_2O_3 support and (b) 4%, (c) 8%, (d) 10%, and (e) 12% Mo supported on alumina after sulfidation.

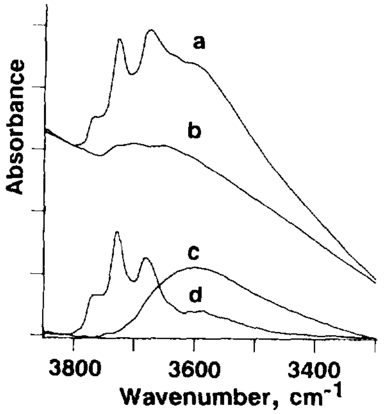

FIG. 3. Illustration of the spectral calculation procedure using the sulfided 4% Mo/Al$_2$O$_3$ as an example. (a) The total spectrum, (b) the alumina background contribution (using the 12% Mo/Al$_2$O$_3$ calcined spectrum), (c) the H-bonding contribution, and (d) the free OH groups contribution which is simply that remaining after subtracting (b) and (c) from (a).

from the background (arising from bulk OH groups, etc.) have been subtracted. For the sulfided catalysts, the contribution from the above-mentioned H-bonded structures were also removed. The background correction was in all cases done by subtracting the spectrum of the 12% Mo/Al$_2$O$_3$ catalyst, which is a good reference for the alumina without significant amounts of free surface hydroxyl groups. The shape of the band in the H-bonding region which was used for the correction of the spectra of the sulfided catalysts was found from an analysis of the spectrum of the sulfided 12% Mo/Al$_2$O$_3$, which displays the most extensive H-bonding and the weakest intensity of free OH groups. In order to arrive at the pure H-bonding spectrum, the free OH bands were removed by subtracting a scaled amount of the spectrum of the sulfided Al$_2$O$_3$ support. Figure 3 further illustrates the procedures used to obtain the spectral contributions using the sulfided 4% Mo/Al$_2$O$_3$ catalyst as an example. The resulting spectra of the free OH groups are shown in Figs. 4a and 4b for all the calcined and sulfided catalysts, respectively.

In Figs. 5a and 5b, the OH band intensities are normalized with respect to those found in the pure Al$_2$O$_3$ support and are plotted against the Mo loading for the calcined and sulfided catalysts respectively. For the calcined catalysts, Figs. 4a and 5a show that the relative intensities of both the 3684- and 3730-cm^{-1} bands decrease almost linearly to the same extent with Mo loading. In contrast to this, the intensity of the 3771-cm^{-1} band decreases much more steeply initially at low Mo loadings while leveling off at a low intensity for higher Mo loadings. For the sulfided catalysts (Fig. 5b), the relative intensities are higher than those of the calcined catalysts. The intensities decrease almost linearly with Mo loading, but they do not approach zero absorbance at 12% Mo loading. These results clearly show that some regeneration of all types of OH groups has occurred during the sulfiding process. Furthermore, the difference in the relative

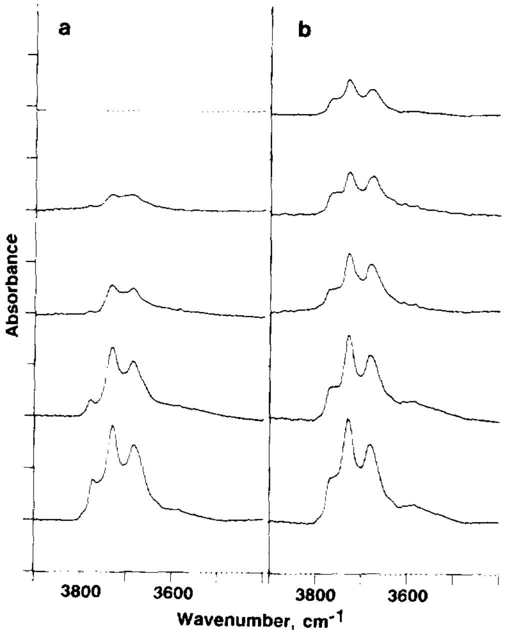

FIG. 4. Ir spectra of the OH band region of the (a) calcined samples (as in Fig. 1) after subtraction of bulk alumina contrbution, and (b) sulfided samples (as in Fig. 2) after subtraction of both bulk alumina and H-bonded components.

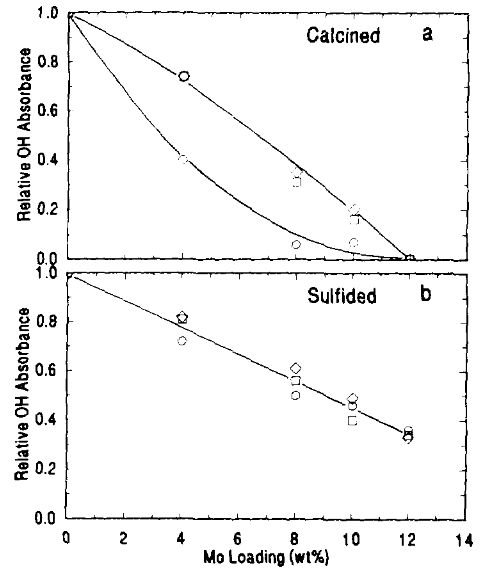

FIG. 5. Relative OH band absorbance vs Mo loadings for (a) calcined and (b) sulfided catalysts. The symbols ○, □, and ◇ represent the 3771-cm^{-1}, 3730-cm^{-1}, and 3680-cm^{-1} bands, respectively.

intensities of the different bands is not as substantial for the sulfided catalysts as that seen for the calcined catalysts. Thus, the regeneration of the OH groups is most pronounced for the 3771-cm^{-1} band. It is also evident from these results that independent of the coverage by Mo, the free alumina surface in the sulfided catalysts has about the same distribution of OH groups as that of the alumina support itself. This was certainly not the case for the calcined samples.

Information regarding the coverage of the support by the Mo species may be obtained from an analysis of the changes in the concentration of surface OH sites which reflect the amount of uncovered Al_2O_3 surface. Recently, Zmierczak *et al.* (*17*) used CO_2 to titrate the uncovered Al_2O_3 surface area and the principles for the present analysis of the coverages are similar to those given by these authors. The experimental coverages, Θ_{exp}, are in the present study calculated directly from the OH absorbances, taking into account the fact that the weight fraction of alumina in the different catalysts decreases with increasing Mo loading. For both calcined and sulfided catalysts, Θ_{exp} is given by the expression

$$\Theta_{exp} = 1 - \frac{A_{cat}}{A_{supp}(1-1.5\,m/100)} \qquad (1)$$

where A_{cat} and A_{supp} are the absorbances of the OH groups for the catalyst and support, respectively, m is the wt% of Mo metal in the calcined catalysts, and 1.5 is the factor converting this to the oxide form assuming three oxygens per Mo. Θ_{exp} can be calculated from an analysis of each of the different OH bands. The resulting experimental coverages are plotted in Fig. 6 against the monolayer coverages, Θ_{mono}, which are the

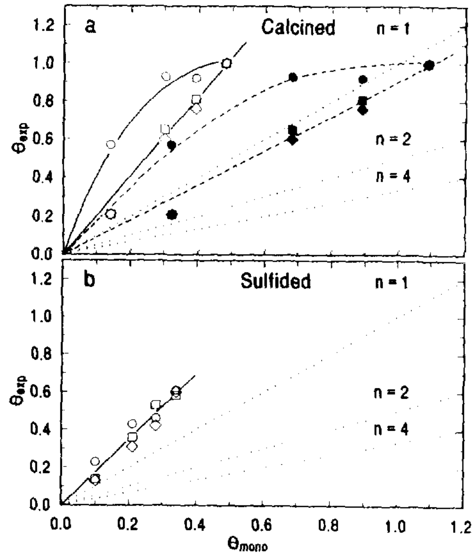

FIG. 6. Experimental coverages, Θ_{exp} vs the calculated coverages, Θ_{mono} assuming the Mo species present as monolayers; (a) and (b) give data for calcined and sulfided Mo/Al_2O_3 catalysts, respectively. The symbols ○, □, and ◇ represent the 3771-cm^{-1}, 3730-cm^{-1}, and 3680-cm^{-1} bands, respectively. The open symbols represent Θ_{mono} calculated based on Mo structures spread over the whole alumina surface, whereas the solid symbols represent Θ_{mono} calculated based only on the fraction of the alumina surface involving OH groups. The dotted lines are theoretical lines expected for monolayer (n = 1), bilayer (n = 2), and four-layer (n = 4) structures.

coverages expected if the Mo species are present as monolayers. In the case of the sulfided catalysts, it is known that Mo is present as MoS_2 (*12*) and Θ_{mono} can therefore be calculated using the average size of Mo in a single MoS_2 slab (8.65 Å^2/Mo atom). For the oxidic catalyst, the situation is slightly more complicated, since both the exact structure of Mo is not known and the average size of Mo^{6+} in oxides also varies somewhat (for example, in MoO_3, the Mo–O distance varies from 1.85–2.35 Å). For the present purpose, it is not very important which of these distances is used, and a size of 12 Å^2/Mo was chosen. This, for example, corresponds to the density in a staggered chain of edge-shared MoO_6 octahedra (one of the building blocks of MoO_3) oriented flat on the surface. It should be pointed out that in Ref. (*17*), a much larger average size of Mo (34 Å^2/Mo) was used, but this does not appear realistic from a crystallographic point of view. With the above average sizes for Mo, Θ_{mono} is given by

$$\Theta_{mono} = \frac{7.53\,m}{\text{Area}_{supp}(1-1.5m/100)} \quad (2)$$

for the calcined catalysts, and

$$\Theta_{mono} = \frac{5.41\,m}{\text{Area}_{supp}(1-1.5m/100)} \quad (3)$$

for the sulfided catalysts. The constant in the numerator contains the average sizes of Mo and a unit conversion factor. Area_{supp} is the BET area of the support given in m^2/g.

Thus, monolayer-type structures prevail when Θ_{exp} equals to Θ_{mono}, whereas multilayer and bulk like structures are present when Θ_{exp} is significantly smaller than Θ_{mono}. The lines expected for monolayer ($n = 1$), bilayer ($n = 2$) as well as for four-layer ($n = 4$) structures are also indicated in Fig. 6.

DISCUSSION

Calcined Catalysts

The IR spectra of the OH region of the calcined alumina supported Mo catalysts containing different Mo concentrations show in accordance with previous studies (*4–11*) that Mo interacts with the surface OH groups of the alumina, leading to the disappearance of these groups. However, the different OH bands are not randomly removed and do not disappear at the same rate, and the resulting distribution of the different types of OH groups in the catalysts is therefore quite different from that of the alumina support (Fig. 5a). For example, it is clear that the hydroxyl group giving rise to the OH band at the highest frequency (i.e., 3771 cm^{-1}) is removed preferentially. This agrees with the earlier findings by Okamoto and Imanaka (*11*), who also observed that fluorine anions react exclusively with these hydroxyl groups and decrease the subsequent adsorption capacity of molybdate anions. The OH band with the highest frequency can be attributed to the most basic hydroxyl group (*29, 11*) as also proposed earlier by Peri (*28*). Such basic OH groups are therefore the preferred interaction sites for the molybdate anions. The OH groups giving rise to the lower frequency bands at 3730 and 3684 cm^{-1} (Fig. 4a) disappear at about the same rate in the whole concentration range. This could indicate that both OH groups are involved in interaction with the same molybdate species (e.g., bidentate chain-like structures). Alternatively, the similarity in the relative concentrations of these two OH species may be due to a similarity in interaction strength with the Mo species.

The density of the OH groups is according to the literature about 4.4×10^{14} cm^{-2} for the alumina support (*30, 31*). Based on this value, the average OH/Mo ratio (OH consumed per Mo added) is estimated to be about 1.4 for the lowest loading catalyst (4% Mo/Al_2O_3), whereas this ratio drops progressively to about 1.1 for the highest loading catalyst (12% Mo/Al_2O_3). The high values of the ratios confirm the high dispersion of the Mo structures and the preferred interaction of Mo with the OH groups on the Al_2O_3 surface. Furthermore, these ratios are in agreement with the observations (*32–34*) that upon increasing the Mo loading the Mo coordination changes from mainly tetrahedral to octahedral, since the tetrahedrally coordinated Mo is generally believed to be bonded to the alumina surface via two oxygen atoms, whereas the octahedrally coordinated Mo atoms are probably more extensively bridged to each other. The latter could for example be in the form of staggered chains of edge-shared MoO_6 octahedra as mentioned earlier. The above results therefore indicate that the tetrahedrally coordinated Mo species on the Al_2O_3 surface are mainly formed via interaction with the hydroxyl groups, giving rise to the OH bands at the highest frequency.

It is furthermore clear from the data in Fig. 6a that the molybdenum is not present as multilayer structures in the catalysts. The data points are actually observed to lie considerably above the line corresponding to the presence of monolayer structures. Also the points for the different OH bands do not coincide. These observations can be rationalized by a situation where Mo is not distributed over the whole alumina surface but preferentially at the locations of the OH sites. The present results support this view and the Θ_{exp} values for the calcined catalysts do therefore not provide a measure of the extent of coverage of the whole alumina surface but only the coverage of the fraction of the alumina surface covered with OH groups. In fact, the results suggest that the molybdenum oxide structures may be exclusively located at the positions of the OH sites, since if the calculations of Θ_{mono} are based on the fraction of the alumina surface covered with OH groups (about 44%) rather than the whole alumina surface area, then the data points for the 3730- and 3680-cm^{-1} bands fall nicely on the monolayer line (Fig. 6a, filled symbols).

The above results indicate that the limit for the presence of monolayers is governed by the OH group density rather than by the alumina surface area as such. This makes FTIR a very useful technique and Θ_{exp} a useful parameter from a catalysis point of view, since it directly reflects the actual extent of monolayer formation. The Mo concentration corresponding to $\Theta_{exp} = 1$ is an important value since it probably represents the limit above which authors have observed (see, e.g., (*13*, *17*)) multilayer growth and leveling off in the catalytic activity.

Sulfided Catalysts

Upon sulfiding, it is observed that a significant fraction of the OH bands which were removed by the addition of Mo in the calcined state reappears (Figs. 2 and 4b). This regeneration is observed for all the catalysts and can be, for example, easily seen in the spectrum of the 12% Mo/Al_2O_3 catalyst where distinct OH bands are observed in the sulfided while not in the calcined state. It therefore follows that the Mo–O–Al bonds present in the calcined catalysts must be broken during sulfiding. The fact that regeneration of OH groups was not observed in the first infrared study of such catalyst (*10*) is probably related to the lower sensitivity of the IR instrument used in the previous study. From a comparison of Fig. 5b with Fig. 5a, it is seen that the intensities of both high- and low-frequency OH bands have increased for the sulfided catalysts. This shows that the OH regeneration involves breaking of all types of Mo–O–Al bonds. As discussed above, some of the OH groups in the sulfided catalysts are involved in hydrogen bonding (giving rise to the broad contribution around 3600 cm^{-1}), thus the OH regeneration is even more extensive than indicated in Fig. 5b.

Although the absolute intensity of the OH bands in the sulfided catalysts are smaller than that of the support, the relative concentration of the OH groups is quite similar. This is observed for all the catalysts and reflects a more statistical distribution of the MoS_2 phase over the alumina support. Thus, these results indicate that the molybdenum structures which were interacting with specific support sites and not statistically distributed in the calcined state have become mobile upon sulfiding due to breaking of the Mo–O–Al bonds. In view of the EXAFS results (*12*) which showed that the MoS_2 structures on the average contain more Mo atoms per unit than the structures in the calcined state, it appears that the rearrangement on the alumina surface also leads to significant agglomeration. It is interesting that this agglomeration is mainly lateral as discussed below with very small tendency towards formation of three dimensional structures.

The data in Fig. 6b clearly show that although Mo–O–Al bonds are broken and some agglomeration takes place, the MoS_2 is not found as multilayer structures in the sulfided catalysts. The presence of quite large MoS_2 layers oriented perpendicular to the alumina surface as proposed previously (*19–21*) can thus be excluded since this will give Θ_{exp} values below Θ_{mono}. Similar conclusions were reached by Zmierczak *et al.* (*17*) using the CO_2 titration method which will be discussed further below. The straight line in Fig. 5b indicates that monolayer structures dominate in the sulfided catalysts with a molybdenum loading up to about 12%. This is in broad agreement with the results presented in some previous studies (*10, 13, 15*).

The present results suggest that the monolayer structures are most likely small single-slab MoS_2 structures lying flat on the alumina support. (The presence of some single-atom chains of MoS_2 attached to the Al_2O_3 via the edges will of course also be consistent with a monolayer coverage). It is noteworthy that for the sulfided catalysts the data points lie somewhat above the monolayer line. This may be due to some remaining preferential interactions with the OH groups (or some preferential coverage of these regions of the alumina surface after sulfiding). Furthermore, it should be noted that the calculated Θ_{exp} overestimates the coverages (or underestimates the number of surface OH groups) due to the presence of hydrogen-bonded OH groups which are not included in Θ_{exp}.

The predominant presence of 2D single-slab structures rather than multislab bulk-like MoS_2 structures may be related to both the existence of monolayer structures in the calcined catalysts and to an interaction between the MoS_2 structures and the support thereby stabilizing the single slabs. Previously (*16*), it was suggested that this interaction which results in the so-called Type-I structures involves some residual Mo–O–Al linkages to the support. The observation that the relative intensity of the 3771-cm^{-1} band has a tendency to fall slightly below that of the other bands (Fig. 5b) could be taken as an indication of such residual support interactions. Studies on the 10% Mo/Al_2O_3 catalysts have shown no extensive regeneration of free OH groups upon increasing the sulfiding temperature from 723 to 873 K. This is in agreement with earlier results which showed that the Type I–Type II transition (i.e., 2D to 3D structures) does not readily take place in unpromoted catalysts.

It is important to realize that the present measurements of Θ_{exp} do not by themselves provide information on changes in lateral size or edge dispersion on the MoS_2 structures. The same holds for CO_2 adsorption and XPS experiments. Information on the edge dispersion, however, can be obtained from NO adsorption (*35*) or EXAFS (*12, 15*) measurements. It is interesting that the latter techniques, on the other hand, do not provide information on the number of layers. Consequently, a combination of both types of techniques may therefore provide valuable complementary information. NO adsorption experiments on the present catalysts will be reported in the following paper (*36*).

Comparisons with Previous CO_2 Adsorption Studies

As mentioned above, CO_2 adsorption is another technique which has been widely used to titrate the free alumina surface and provide information about the coverage of the alumina surface by metals (*37, 27, 17*).

A detailed study of the surface coverage and its loading dependence for both calcined and sulfided Mo/Al_2O_3 catalysts was carried out by Zmierczak *et al.* (*17*). In spite of many general similarities, there are some apparent differences between the CO_2 adsorption results and the present IR results on surface hydroxyl structures. These differences are addressed in the following.

For calcined catalysts, both Millman *et al.* (*27*) and Zmierczak *et al.* (*17*) observed the disappearance of CO_2 adsorption sites at about the same Mo loading (i.e., 8% Mo on a 186 m^2/g Al_2O_3 (*27*) and 7.7% Mo on a 194 m^2/g Al_2O_3 (*17*)). However, in the present case, all the hydroxyl groups are not removed until a loading of 12% Mo on a 230 m^2/g Al_2O_3 which corresponds to about a 30% higher average Mo surface density than in the CO_2 adsorption studies. Zmierczak *et al.* (*17*) found in their CO_2 adsorption studies that after sulfiding the 7.7% Mo catalyst which was assumed to have a full monolayer coverage in the calcined state, the coverage of the alumina dropped to a value of 23%. The authors interpreted this as a substantial reduction in size of the Mo phase upon sulfiding (from about 35 Å^2/Mo to 8.65 Å^2/Mo). As discussed above, this does not seem reasonable from a crystallographic point of view and in view of the present results, an alternative explanation of the CO_2 adsorption results may be proposed. First of all, the present results show that the complete "monolayer coverage" will not correspond to a monolayer coverage of the whole alumina surface but rather to a "monolayer coverage" of the fraction of the surface covered with OH groups. If this is taken into account, a more reasonable average size of the Mo oxide phase is indeed obtained. Second, it should be pointed out that the CO_2 adsorption only occurs on a small fraction of the surface sites. In the pure alumina support they only account for about 2.5% of the total number of surface sites. Consequently, the concentration of such sites may not always represent the same fraction of the available free alumina surface, and this may lead to errors in the estimated coverages. Large errors would, for example, result if the supported species react with the CO_2 adsorption sites. Such specific interactions seem in fact very likely for the calcined catalysts since CO_2 adsorption has been observed to involve the most basic OH groups (the 3770-cm^{-1} band) yielding bicarbonate species (*11*). These OH groups have in the present study shown (Fig. 5a) to be the preferred interaction sites for Mo and more than 90% of these sites are removed at 8% Mo. Thus, if the determination of the "monolayer" capacity is based on these OH groups (or the CO_2 adsorption sites) it is expected to give about a 30% lower Mo concentration than that used to interaction with all the OH groups. Taking also this into account, the differences between the previous CO_2 adsorption results (*27, 17*) and the present results appear readily explainable. It could be pointed out that for the sulfided catalysts where the uncovered alumina surface has a more statistical distribution of adsorption sites, the CO_2 adsorption method is expected to provide much better estimations of surface coverages than those for the calcined catalysts.

CONCLUSIONS

The present studies on surface hydroxyl structures have shown that the interaction of Mo with the surface hydroxyls of alumina support in an oxide catalyst is not an entirely random process since the different hydroxyl groups are not removed to the same extent at a given Mo concentration. Especially, at low Mo concentrations there appears to be a preference for the most basic hydroxyl species which interact with Mo to form mainly tetrahedrally coordinated Mo species. Upon sulfiding, a rearrangement of the surface Mo structures occurs resulting in some regenerations of hydroxyl groups on the alumina surface which were removed due to interaction with Mo in the oxide catalysts. Such regeneration apparently involves breaking of all types of Mo–O–Al bonds and the support surface exposed after sulfidation has a more alumina-like OH group distribution than the corresponding oxide catalysts. The results suggest a significant lateral agglomeration of Mo phase, but the MoS_2 phase formed is present mainly as 2D single-slab structures oriented flat on the alumina surface. CO_2 adsorption which has previously been used to estimate the coverage of the alumina surface by metals has been shown to have some limitations for the calcined catalysts due to nonrandom interaction of Mo with the same hydroxyl groups involved in the CO_2 adsorption.

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