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# The $MoO_3$–$Al_2O_3$ Interaction: Influence of Phosphorus on $MoO_3$ Impregnation and Reactivity in Thiophene HDS

JENNY M. LEWIS AND RONALD A. KYDD[1]

*Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4*

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Two series of catalysts, $Mo/Al_2O_3$ and 1 wt% P–$Mo/Al_2O_3$, containing between 0 and 4.7 wt% $MoO_3$ have been investigated by FT-IR spectroscopy of the $\nu(OH)$ region. It is seen that molybdena reacts preferentially with surface P–OH groups, and also that the Al–OH groups are more reactive towards these loadings of molybdena in the presence of phosphorus. This is interpreted as resulting in an increase in Mo dispersion for the P–$Mo/Al_2O_3$ catalysts. Sulphiding/reduction of the catalysts results in regeneration of few surface hydroxyls for the $Mo/Al_2O_3$ catalysts, but many are regenerated for the P-$Mo/Al_2O_3$ catalysts. This indicates that molybdena on $P/Al_2O_3$ is more easily sulphided/reduced than on $\gamma$-$Al_2O_3$; in particular, molybdena bonded to P–OH groups is readily sulphided. These factors may explain the improved thiophene HDS activities of the P–$Mo/Al_2O_3$ catalysts.

## INTRODUCTION

Recently, there has been much interest in determining the role of phosphorus as a secondary promoter in Ni–Mo and Co–Mo hydroprocessing catalysts. It has been found that phosphorus: Inhibits the formation of catalytically inactive $NiAl_2O_4$ (*1, 2*); increases the dispersion of both nickel and molybdenum (*3*); modifies the acid strength distribution of $\gamma$-alumina (*4*); ensures optimum composition of P–Ni–Mo heteropoly compounds (*3, 5*), with an increase in the $Ni^{2+}(Oh)$ content, a possible precursor to the sulphided active phase (*1, 3*).

There have been fewer studies investigating the reduced and sulphided catalyst systems, however. López Agudo and co-workers (*6, 7*) investigated the influence of phosphorus on the reducibility of $MoO_3/Al_2O_3$ and on the physicochemical properties of the sulphided phase. They found that phosphorus, particularly when impregnated first, increases the amount of reducible $MoO_3$ by promoting the formation of small $MoO_3$ clusters on the surface of alumina. This change in the surface distribution of $MoO_3$ accounted for the increased activity of the sulphided phase.

The present work extends our previous study into the $H_3PO_4$–$Al_2O_3$ interaction (*8*). It examines the interaction between $MoO_3$ and $P/Al_2O_3$ using FT-IR spectroscopy to investigate the changes in the OH stretching region, and compares these changes with those occurring for the $MoO_3$–$Al_2O_3$ interaction. The reduced/sulphided systems were also studied, since it is well known that reduction results in cleaving of the Al–O–Mo bonds and therefore a regeneration of the surface hydroxyls (*9*). From the degree of regeneration of the surface hydroxyls insight into the ease of sulphiding of $MoO_3$ bonded to different OH groups may be obtained. Implications of this in the thiophene HDS reaction were investigated. The interaction between $MoO_3$ and $Al_2O_3$ has been widely investigated by IR spectroscopy (*9–14*), but the $MoO_3$–P–$Al_2O_3$ system has been studied very little using this technique (*15*), and not in the reduced or sulphided forms.

## EXPERIMENTAL

The preparation of the $\gamma$-alumina (*16*) and the 1.0 wt% $P/Al_2O_3$ (*8*) have been described

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[1] To whom correspondence should be addressed.

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TABLE 1

Composition and Surface Areas of Catalysts

| Catalyst | Composition[a] | | Surface Area ($m^2g^{-1}$) |
|---|---|---|---|
| | Wt% P | Wt% $MoO_3$ | |
| 0MoAl | — | — | 193 |
| 1.2MoAl | — | 1.2 | 174 |
| 2.4MoAl | — | 2.4 | 175 |
| 4.7MoAl | — | 4.7 | 177 |
| 0MoPAl | 1.0 | — | 162 |
| 1.2MoPAl | 1.0 | 1.2 | 153 |
| 2.4MoPAl | 1.0 | 2.4 | 153 |
| 4.7MoPAl | 1.0 | 4.7 | 149 |

[a] Relative to the weight of γ-alumina.

previously. The source of phosphorus was ortho-phosphoric acid in all cases. The molybdenum-containing catalysts were prepared by incipient wetness impregnation of the γ-alumina or $P/Al_2O_3$ supports with aqueous $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions to give the nominal weight percents of the oxides (after calcination) given in Table 1. Calcination was achieved at 500°C for 4 h. The designations assigned to the different catalysts are also given in Table 1 together with their surface areas. The surface areas were measured by the BET method using a Micromeritics high speed surface area analyser after degassing the samples for 30 min at 200°C.

The infrared spectra were recorded on a Nicolet 8000 FT-IR spectrometer at 2 $cm^{-1}$ resolution using a liquid nitrogen cooled InSb detector. Approximately 15 mg of powdered catalyst was pressed into a self-supporting wafer and mounted in a cell for pretreatment. The cell design was such that four samples could be treated simultaneously and the IR spectra obtained without contacting the wafers to the atmosphere. The samples were cleaned under $\frac{1}{2}$ atm $O_2$ overnight at 500°C and then the cell was evacuated overnight at 600°C. Upon cooling a vacuum of around $1 \times 10^{-5}$ Torr was achieved. A high temperature is required in order to resolve the different surface OH groups (*12*), but this temperature is slightly lower than the 700°C used previously (*8*) because the higher temperature was nearing the melting point of $MoO_3$. Even so, we recognize the possibility that the molybdena is quite mobile on the alumina surface at 600°C. After the spectra of the oxides had been recorded, the samples were again heated to 500°C overnight, and then sulphided in 200 mmHg 10% $H_2S/H_2$ mixture at 500°C overnight. As before, the cell was evacuated at 600°C overnight, and a vacuum of around $1 \times 10^{-5}$ Torr was obtained upon cooling.

The thiophene HDS studies were performed in a bench-top flow reactor system equipped with on-line gas chromatography. The catalyst (0.150 g, 80–100 mesh) was sulphided for 90 min in a flow (30 ml $min^{-1}$) of 10% $H_2S/H_2$ at 500°C. After this time the reactor was cooled to 400°C under He and then the catalyst exposed to a thiophene-saturated $H_2$ flow (30 mL $min^{-1}$). The effluent stream was analysed every 20 min by on-line gas chromatography, and the HDS activity calculated from the % $C_4$ products in the effluent stream. The reaction was carried out for 4 h, after which time the HDS activity was approximately constant.

## RESULTS AND DISCUSSION

### *Compositions and Surface Areas of Catalysts*

The compositions and surface areas of the catalysts studied are given in Table 1 together with their designations and surface areas. Two support systems were used, γ-alumina and P/alumina, and molybdena loadings of 0–4.7 wt% were studied on each support. These low loadings of molybdena were chosen so that IR spectra with well defined OH stretching regions could be obtained. The addition of phosphorus to γ-alumina results in a decrease in surface area of about 15%. Further addition of molybdena results in smaller decreases in surface area of between 5–8%. The addition of molybdena to the bare γ-alumina support

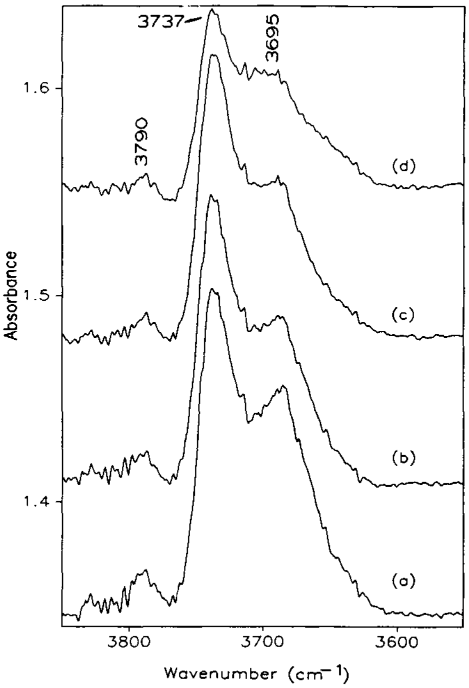


FIG. 1. FT-IR spectra of the oxide forms of: (a) 0MoAl; (b) 1.2MoAl; (c) 2.4MoAl; (d) 4.7MoAl. Spectra were acquired after heating at 600°C *in vacuo* and have been offset along the absorbance axis for clarity.

results in a drop in surface area of about 10% at low loadings, with no further change in surface area occurring at higher loadings.

### *FT-IR Spectra of Oxides*

Figures 1 and 2 show the OH stretching region in the IR spectra of the MoAl and MoPAl catalysts, respectively. Up to five different OH groups are expected to be present on the surface of γ-alumina (*17*) and suggested assignments for these have been given by Knözinger and Ratnasamy (*18*) as: Type Ib—terminal OH bonded to octahedrally coordinated Al, most basic (3785–3800 cm$^{-1}$); Type Ia—terminal OH bonded to tetrahedrally coordinated Al, next basic (3760–3780 cm$^{-1}$); Types IIa and IIb—doubly bridging hydroxyl (3730–3745 cm$^{-1}$); and Type III—triply bridging hydroxyls, least basic (3700–3710 cm$^{-1}$). In the spectrum of γ-alumina (Fig. 1a) three OH bands are resolved centered at 3790, 3737, and 3695 cm$^{-1}$. These are in good agreement with what we have seen previously (*8*), although the Ia and Ib sites have not been resolved for these pretreatment conditions. The bands can be assigned as Types Ib + Ia (unresolved), Types IIb + IIa (unresolved), and Type III, respectively. Addition of molybdena (Figs. 1b–d) results in a decrease in intensity of all three bands, indicating that the molybdenum species react with all types of hydroxyls. This is in agreement with other workers (*9–13*).

In the spectrum of 0MoPAl (Fig. 2a) an additional band is observed at 3676 cm$^{-1}$ which has been assigned to the P(O–H) stretch (*19*). All the spectra for the MoPAl catalysts have lower intensities than the MoAl catalysts since $H_3PO_4$ also reacts with

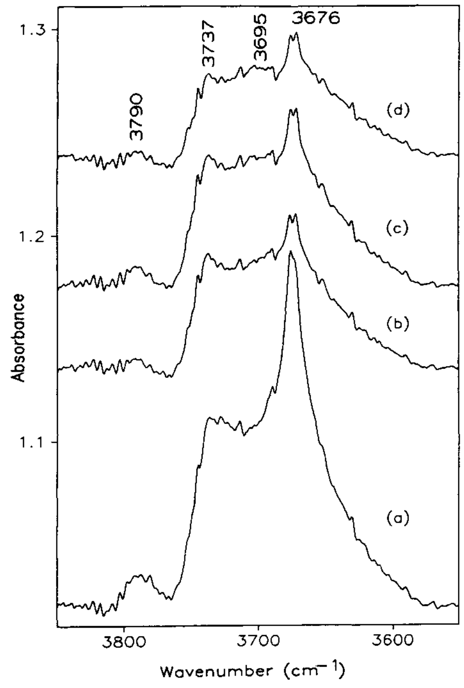


FIG. 2. FT-IR spectra of the oxide forms of: (a) 0MoPAl; (b) 1.2MoPAl; (c) 2.4MoPAl; (d) 4.7MoPAl. Spectra were acquired after the same treatment given to those in Fig. 1 and have been offset along the absorbance axis for clarity.

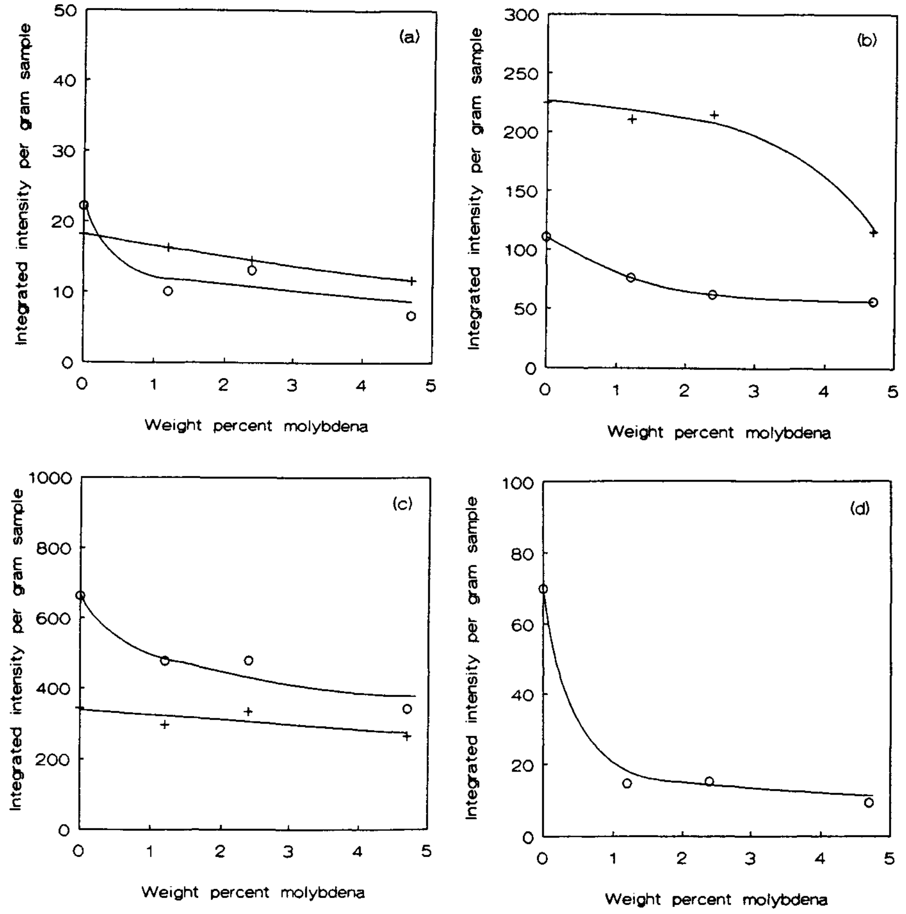
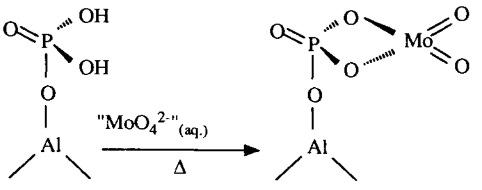


FIG. 3. Effect of the wt% $MoO_3$ on the OH stretching region of MoAl (+) and MoPAl (O) oxide catalysts: (a) 3795 + 3780 $cm^{-1}$ bands (Ib and Ia sites); (b) 3737 $cm^{-1}$ band (IIb and IIa sites); (c) 3695 $cm^{-1}$ band (III sites); (d) 3676 $cm^{-1}$ band (P–OH groups). Band areas were obtained from the curve-fitted spectra in Figs. 1 and 2, and have been normalized with respect to sample weight.

the alumina hydroxyls. This has been discussed in detail elsewhere (*8*), and it was seen in that study that $H_3PO_4$ reacts preferentially with Type Ia hydroxyls, and that these types of hydroxyls are almost completely removed by loadings of 1.0 wt% P. In the present study a lower degassing temperature was used (see Experimental), and some Type Ia hydroxyls still remain, as shown by the position of the highest wavenumber band in Fig. 2a (3790 $cm^{-1}$). This is lower than would be seen if only Type Ib hydroxyls were present (3795 $cm^{-1}$, see Ref. (*8*)). The addition of molybdena results in a decrease in intensity of all bands, but most dramatically for the P(O–H) stretch. Therefore, it is clear that the molybdenum species react preferentially with the P–OH groups on the alumina surface. A similar conclusion was made by van Veen *et al.* (*15*). The band at 3790 $cm^{-1}$ also shifts to 3795 $cm^{-1}$ for Figs. 2b–d, indicating that the Ia hydroxyls are removed and only Ib sites remain after the addition of molybdena to $P/Al_2O_3$.

The eight spectra in Figs. 1 and 2 were curve-fitted for the different hydroxyl stretches in order to examine the $MoO_3$-



SCHEME 1

$Al_2O_3$ and $MoO_3$-P/$Al_2O_3$ interactions more closely. Figs. 3a–d show the variation in the band areas, normalized with respect to sample weight, as a function of $MoO_3$ content. Differences between the two interactions are clearly evident: In all cases, low loadings of molybdena react with many of the surface hydroxyls on the P/$Al_2O_3$ surface. After the addition of 1.2 wt% $MoO_3$, a 79% decrease in the area of the P–OH band (Fig. 3d), a 54% decrease in the 3790 $cm^{-1}$ band (Fig. 3a), and 31 and 28% decreases in the 3737 and 3695 $cm^{-1}$ bands, respectively (Figs. 3b and c) are observed. Since the P–OH band intensity decreases much more rapidly with increasing molybdenum content compared to the Al–OH groups, this implies that the molybdenum species reacts in a bidentate fashion with the –$P(OH)_2$ groups, possibly in the manner similar to that shown in the Scheme 1, at least to some extent. However, as discussed in the next section, these species are sulphided to a greater extent than Mo bonded to other surface hydroxyls, suggesting they may be in the form of polymolybdate ($Mo_{Oh}$) species (e.g., see Ref. (*10*)).

The higher area of the 3700 $cm^{-1}$ band in the MoPAl catalysts compared to the MoAl catalysts probably is just an artifact of the curve-fit program used, which tends to broaden this band in the former case.

The hydroxyls on the surface of γ-alumina react much less than those on the P/alumina surface with increasing molybdenum content. The band at 3790 $cm^{-1}$ is slightly more reactive than the 3737 and 3695 $cm^{-1}$ bands, at low molybdena loadings; the decreases in intensities upon addition of 1.2 wt% molybdena are approximately 18, 6 and 5%, respectively. Above 2.4 wt% $MoO_3$ a greater number of the type II hydroxyls (3737 $cm^{-1}$) start to react (Fig. 3b); a reduction in intensity/g of 48% is observed for this band for the highest Mo loading studied. Other workers have reported simultaneous consumption, by molybdena, of basic and nonbasic hydroxyls (*13*), and preferential reaction of basic hydroxyls with molybdena (*14*). This work suggests only slight preferential reactivity of the most basic groups with molybdena (and only at low loadings) and similar reactivity of the next most basic hydroxyls at the same loading. The different results of these three studies seem to arise from the various outgassing temperatures and times used, which leads to different OH stretching frequencies and different resolution of the OH group types on the surface. Thus, comparison of the change in intensities of the same types of alumina hydroxyls for these three studies is not possible.

Some conclusions may be drawn from these results. First, molybdena clearly reacts preferentially with the P–OH groups on the surface of alumina, and second, the presence of phosphorus influences the other surface hydroxyls so that they are more reactive towards molybdena. The inference from these conclusions is that phosphorus increases the dispersion of $MoO_3$, at least for these low loadings studied. Although no dispersion measurements were made in this study, an increased dispersion of molybdenum in the presence of phosphorus is well established in the literature (*3*).

### *IR Spectra of the Sulphided Catalysts*

The IR spectra of the sulphided MoAl and MoPAl catalysts are given in Figs. 4 and 5, respectively. The reduction/sulphiding process regenerates some of the surface hydroxyls by cleaving the Al–O–Mo (*9*) and presumably P–O–Mo bonds. Furthermore, the water generated by these processes, or reduction of oxide surface species, may also rehydrate the surface. Therefore, the intensities of the hydroxyl stretches of the sul-

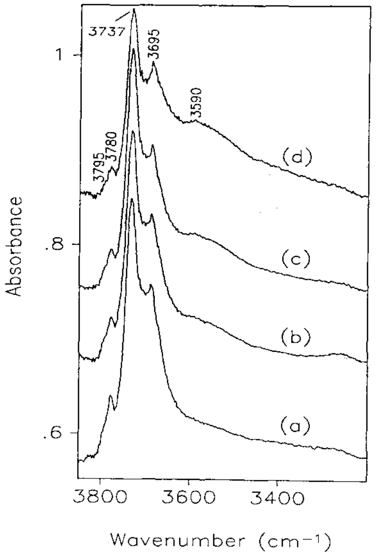


FIG. 4. FT-IR spectra of the sulphided forms of: (a) 0MoAl; (b) 1.2MoAl; (c) 2.4MoAl; (d) 4.7MoAl. Spectra were acquired after sulphiding at 500°C under 200 mmHg 10% $H_2S/H_2$ mixture, and then heating at 600°C *in vacuo*. They have been offset along the absorbance axis for clarity.

phided catalysts are higher than those of the corresponding oxide catalysts. The Types Ib and Ia hydroxyls are now resolved at 3795 and 3780 $cm^{-1}$, respectively; these band positions are in good agreement with those we have seen previously (*8*). In addition, one other band at 3590 $cm^{-1}$ is apparent in the spectra of the reduced/sulphided Mo-containing catalysts. This band has been assigned to Al–OH groups (*9*). However, this band is not present in the spectra of the oxide forms of the catalysts (which were subjected to the same pretreatment conditions, i.e., evacuated at 600°C overnight), and it also increases in intensity with increasing Mo content in the spectra of the reduced/sulphided Mo.

These spectra were also curve-fitted for the different hydroxyl stretches and it was apparent from these results that certain of the alumina hydroxyls are regenerated to a greater extent than others. Figure 6 shows the % increase in band area per gram for the MoAl and MoPAl catalysts. An increase in the "% increase in band area per gram" with increasing molybdena content does not mean that there are more sites than on the $Al_2O_3$ (or $P/Al_2O_3$) surface, but rather that there are more sites present on the sulphided catalyst *compared to the respective oxide* surface. For γ-alumina, sulphiding results in a substantial increase in the intensities of Types Ib and Ia hydroxyl stretches and a large increase in the band intensity associated with the Type III hydroxyls, while the number of Type II hydroxyls is unchanged with sulphiding (Fig. 6a). These increases in intensity are presumably associated with reduction of surface oxide species, or hydration of c.u.s. $Al^{3+}$ centres. This makes complete interpretation of these figures difficult since increases in intensity for Mo-containing catalysts could be due both to sulphiding of the $MoO_3$ species, creating surface Al–OH groups, and to rehydration of the γ-alumina surface, as described above. In cases where the % increases in intensity are greater for Mo-containing catalysts than for the support alone, then it can

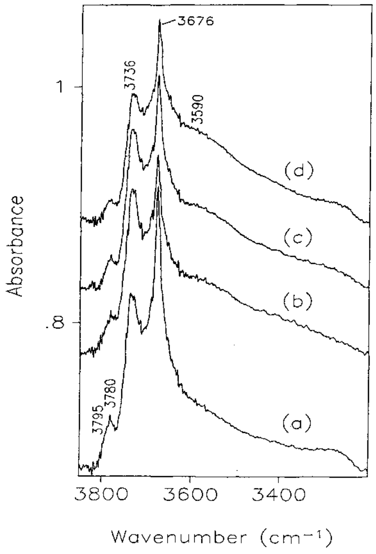


FIG. 5. FT-IR spectra of the sulphided forms of: (a) 0MoPAl; (b) 1.2MoPAl; (c) 2.4MoPAl; (d) 4.7MoPAl. Spectra were acquired after the same treatment given to those in Fig. 4 and have been offset along the absorbance axis for clarity.

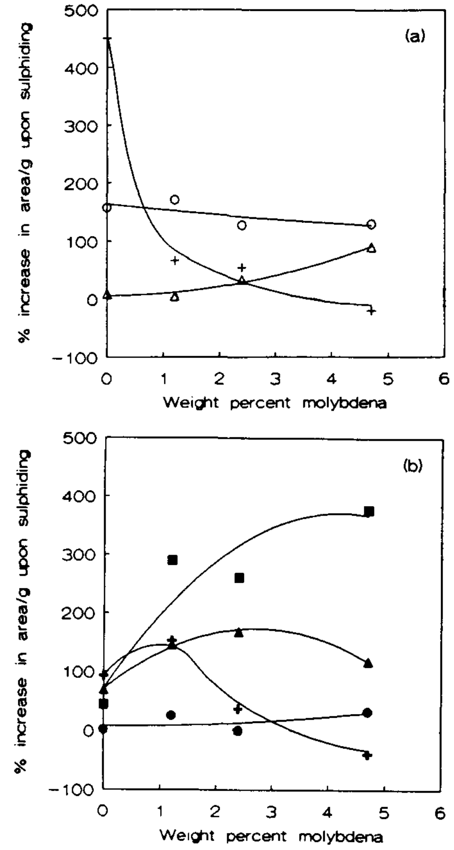


FIG. 6. Change in band areas of: (a) 3795 + 3780 $cm^{-1}$ (+), 3737 $cm^{-1}$ (△), and 3695 $cm^{-1}$ (○) bands upon sulphiding of the MoAl catalysts; (b) 3795 + 3780 $cm^{-1}$ (+), 3737 $cm^{-1}$ (▲), 3680 $cm^{-1}$ (●), and 3676 $cm^{-1}$ (■) bands upon sulphiding of the MoPAl catalysts. Plotted is the % increase in band area (normalized with respect to sample weight) of the sulphided catalyst as compared to the respective oxide catalyst.

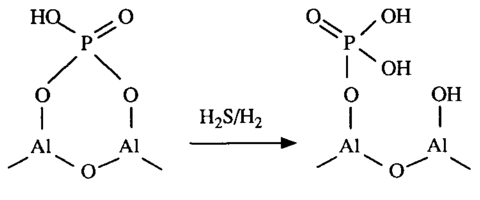
be stated unambiguously that sulphidation of the $MoO_3$ species is occurring. In Fig. 6a this is observed only for the band at 3737 $cm^{-1}$ (Type II) and therefore we may conclude that molybdena which reacts with these hydroxyls can be sulphided to some extent. Interestingly these sites only start to react significantly with molybdena at higher loadings (Fig. 3b). This suggests that the molybdenum species impregnated on these sites at lower loadings may be wasted, i.e., may not be convertable to the active form. These findings are in agreement with those of other workers (*20*) in that at very low $MoO_3$ loadings tetrahedral molybdate species are formed which are difficult to sulphide, while at higher loadings octahedral Mo in polymolybdate is present, which can be converted to the active phase.

Sulphiding of 0MoPAl (Fig. 6b) results in an increase in intensity of all but the Type III hydroxyls. Since the number of P–OH groups also increases with sulphiding, the process in Scheme 2 is implied. The possibility that this reaction proceeds further to produce free $H_3PO_4$ cannot be dismissed on the basis of the IR spectra.

Of particular importance in Fig. 6b is that many of the OH groups are regenerated in the MoPAl catalysts to a greater extent than they are for the blank $P/Al_2O_3$ support. In particular, molybdena which reacted with the P–OH groups is greatly sulphided as evidenced by the large % increase in band area upon sulphiding. Similarly, Mo bonded to Type II OH groups is sulphided. The conclusions drawn from the data for the sulphided catalysts are, therefore, that phosphorus clearly increases the sulphidibility/reducibility of molybdenum both directly (Mo bonded to P–OH groups is sulphided) and indirectly (Mo bonded to Type II OH groups is also sulphided more readily); i.e., although some of the Mo is still present in a form which is difficult to sulphide, as it is in the MoAl catalysts, some of it, in particular that bonded to phosphorus, is readily sulphided.

### *Thiophene HDS Studies*

The sulphided catalysts were studied in the thiophene HDS reaction and the results



SCHEME 2

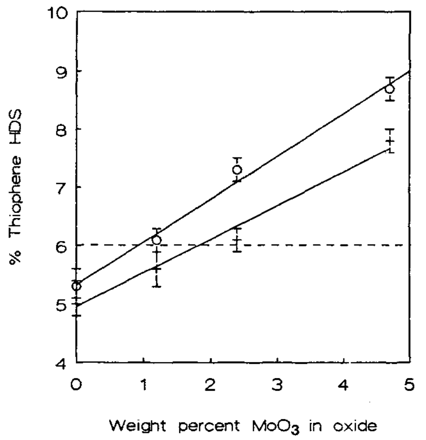


FIG. 7. Influence of phosphorus on the thiophene HDS activity of MoAl (+) and MoPAl (O) catalysts; % conversions were after 4 h on stream at 400°C. Error bars show reproducibility between experiments and the dashed line indicates the thermal % conversion in this reaction.

are shown in Fig. 7. The thermal conversion in this reaction was around 6% as indicated by the dashed line in Fig. 7. The activities of the catalysts were quite low (5–9% conversion, uncorrected for thermal conversion) because of the low loadings of molybdenum present, but nevertheless, differences were apparent. These differences were confirmed to be significant from repeated experiments. The maximum error between repeated experiments is shown by the error bars in Fig. 7. At very low or zero loadings of molybdenum the % conversion in thiophene HDS is actually less than that obtained thermally. Thus, it appears that in the absence of catalytic sites a thermal mechanism occurs, but the support provides sites for termination of this mechanism. In agreement with de Beer *et al.* (*21*) loadings of above 4 wt% $MoO_3$ were required to see any appreciable activity (above thermal conversion) in thiophene HDS over MoAl catalysts. However, for the phosphorus-containing catalysts, the activity exceeded the thermal % conversion at lower loadings of Mo, i.e., 2.4 MoPAl and 4.7 MoPAl catalysts. Also, these catalysts had higher activities than their analogous MoAl counterparts. This demonstrates that in the presence of phosphorus the impregnated molybdenum has a higher activity in this reaction. Clearly, the ability of phosphorus to increase the molybdenum dispersion and reducibility/sulphidability results in catalysts which are more active in thiophene HDS.

## CONCLUSIONS

Phosphorus influences the surface distribution of molybdenum both directly, since molybdena reacts preferentially with P–OH groups, and indirectly, since more alumina OH groups react with molybdena in the presence of P than in its absence. It is suggested that these interactions account for the increased molybdenum dispersion seen in P–Ni–Mo/$Al_2O_3$ catalysts. Molybdena in the P–Mo/$Al_2O_3$ catalysts, particularly that bonded to P–OH groups, is more easily sulphided/reduced compared to Mo/$Al_2O_3$ catalysts. Both these influences of phosphorus result in improved thiophene HDS activities for P–Mo/$Al_2O_3$ as compared to Mo/$Al_2O_3$ catalysts.

## ACKNOWLEDGMENTS

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