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Adsorption Mechanism of Phosphoric Acid on γ-Alumina

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A series of P/Al_2O_3 catalysts with phosphorus loadings in the range 0–7 wt% P has been investigated by infrared spectroscopy. After pretreatment at 700°C, four types of hydroxyls were resolved in the OH stretching region of the IR spectrum for γ-alumina. Addition of phosphorus (as phosphoric acid) resulted in a reduction of all the different hydroxyls with the exception of the most basic, which increased to a maximum intensity at around 1 wt% P. A sharp band at 3676 cm^{-1} due to P–OH groups was also easily resolved, and this band increased in intensity with increasing phosphorus content. A mechanism for the adsorption of phosphoric acid on alumina is proposed on the basis of these results, whereby the different alumina hydroxyls react with H_3PO_4 preferentially depending on their basicity up to a critical surface concentration of around 10×10^{13} H_3PO_4 cm^{-2}. Above this concentration H_3PO_4 reacts not only with Al–OH groups but also with P–OH groups to form polyphosphate species. The intensity of the band due to the most basic alumina hydroxyls passed through a maximum since, at low phosphorus loadings, these sites may be generated by the reaction of H_3PO_4 with bridging and triply bridging alumina hydroxyls, but are not formed by this process at higher loadings. © 1991 Academic Press, Inc.

INTRODUCTION

Phosphorus has been recommended as a secondary promoter in Co–Mo and Ni–Mo hydroprocessing catalysts for many years. Recently, the mechanism of phosphorus promotion has been the subject of many investigations in the literature. Even so, many of the fundamental aspects of this question remain unanswered. Among these is the mechanism of interaction of phosphoric acid with the γ-alumina surface. On the basis of ammonia temperature programmed desorption, Stanislaus *et al.* (*1*) proposed a mechanism in which multiple bond formation between H_3PO_4 and Al_2O_3 occurs at low P content, but individual surface hydroxyls react at higher concentrations. In contrast, Morales *et al.* (*2*) proposed the reaction of H_3PO_4 with isolated basic alumina hydroxyls at low concentrations, followed by successive titration of the more acidic alumina hydroxyls. Finally, at higher concentrations condensation between adjacent P–OH groups is proposed to occur. The different types of hydroxyls on γ-alumina can be distinguished easily by infrared spectroscopy (*3–5*), and it occurred to us that investigation of the OH stretching region of P/Al_2O_3 catalysts would be a useful way of probing this adsorption process. There have been few studies of this type in the literature. Mennour *et al.* (*6*) characterized phosphated alumina for samples containing low phosphorus loadings (0–2 wt% P) by infrared spectroscopy. Also, Busca *et al.* (*7*) investigated the hydroxyl region for H_3PO_4/Al_2O_3 but for only one phosphorus loading of 2.4 wt% P. Very recently, van Veen *et al.* (*8*) investigated the adsorption of $(NH_4)H_2PO_4$ on γ-alumina and deduced that $H_2PO_4^-$ reacts with the basic hydroxyl groups by a ligand exchange mechanism. In the present work the adsorption of H_3PO_4 on γ-alumina is investigated for phosphorus loadings of 0–7 wt%.

METHODS

The preparation of the γ-alumina has been described previously (*9*) and resulted in a

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surface area of 198 m^2g^{-1}. The P/Al_2O_3 samples were prepared by impregnation of phosphoric acid solutions onto γ-alumina, using the minimum amount of water, to give 0–7 wt% P. In each case the pH of the impregnating solution was adjusted to pH 2 by the addition of NH_4OH solution, and the total volume of the impregnating solution was the same. After impregnation the sample was left to dry, first at room temperature overnight, and then at 110°C overnight, before being calcined at 475°C for 4 h.

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 20 mg of catalyst was pressed into a self-supporting wafer and mounted in a cell for pretreatment. The cell design was such that four wafers could be treated simultaneously, and also, infrared spectra could be recorded without contacting the catalyst wafers to the atmosphere. The pretreatment conditions were as follows: First the wafers were cleaned overnight under $\frac{1}{3}$ atm. O_2 at 600°C. They were then evacuated for 24 h at 700°C, whereupon a vacuum of $<10^{-5}$ Torr was achieved upon cooling.

X-Ray diffraction powder patterns of the P/Al_2O_3 catalysts were determined using a Norelco X-ray diffractometer with graphite monochromated FeK_α radiation.

The catalyst testing was carried out in a stainless-steel continuous-flow microreactor operating at 400°C and under approximately atmospheric pressure. The reactant (cumene or *m*-diisopropylbenzene) was contained in a presaturator at 20 ± 1°C. Briefly, the catalyst was activated at 500°C before being exposed to the appropriate reactant in a sweep gas of He (cracking) or H_2 (hydrocracking) at 400°C. The effluent stream was analyzed by an on-line gas chromatograph. A detailed description of the catalyst testing is given in Ref. (*9*).

RESULTS AND DISCUSSION

The IR spectra for catalysts containing 0–5 wt% P are shown in Fig. 1. The OH stretching region for γ-alumina (Fig. 1(a)) can be resolved into four bands centered at 3795, 3780, 3736, and 3697 cm^{-1}. These values are in good agreement with those observed by Peri and coworkers (*3*, *4*) when γ-alumina is evacuated at 600–700°C. The different types of hydroxyls on alumina have been assigned by Knözinger and Ratnasamy (*5*). Figures 2(a–d) show the idealized low Miller index planes for γ-alumina, where the charge balance at the surface is maintained by hydroxide. The different types of OH groups are clearly demonstrated; OH may be bonded to either tetrahedral or octahedral Al leading to Types Ia (3780 cm^{-1}) and Ib (3795 cm^{-1}) hydroxyls, respectively. Alternatively, hydroxyl groups can bridge two Al centers resulting in Types IIa and IIb hydroxyls, which are observed unresolved at 3736 cm^{-1} in Fig. 1(a). Finally, OH can be triply bridging with an observed ν(OH) at 3697 cm^{-1}. Absent

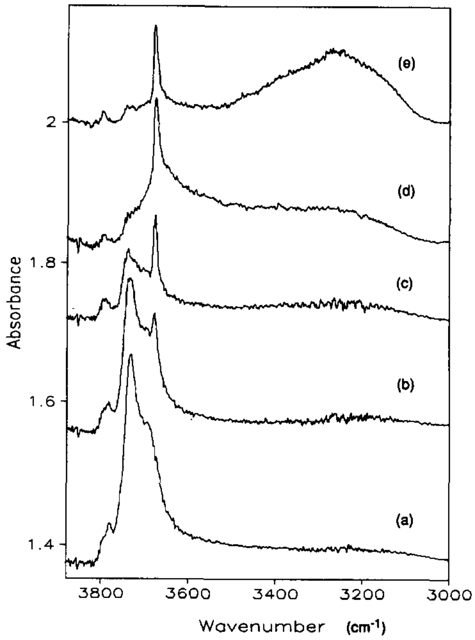


FIG. 1. FT-IR spectra of: (a) γ-alumina; (b) 0.3 wt% P/Al_2O_3; (c) 1.0 wt% P/Al_2O_3; (d) 3.0 wt% P/Al_2O_3; (e) 5.0 wt% P/Al_2O_3. Spectra were acquired after heating at 700°C *in vacuo* and have been offset along the absorbance axis for clarity.

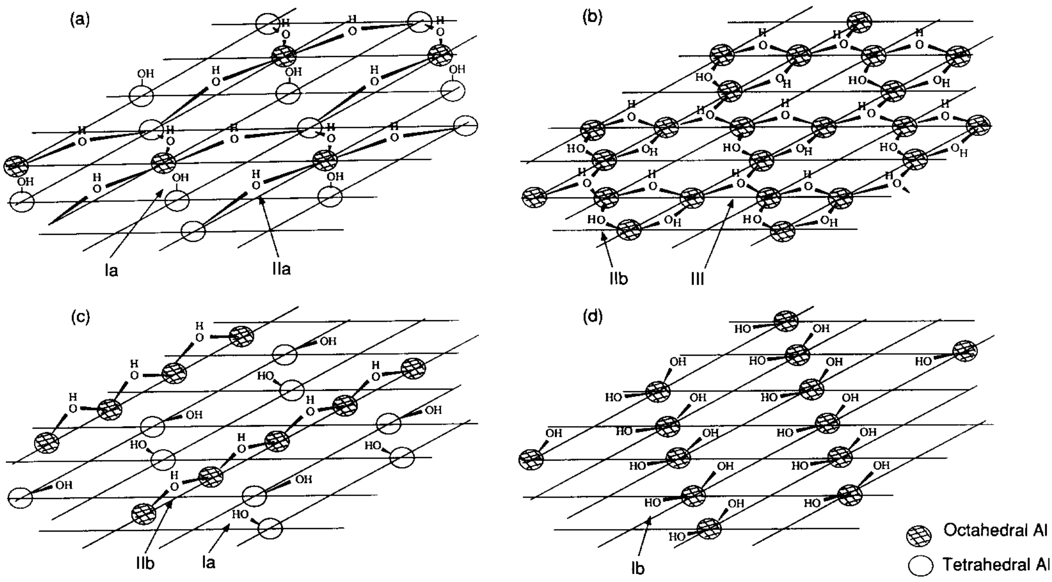


FIG. 2. Idealized low Miller index surface planes of γ-alumina, where the charge balance at the surface is maintained by hydroxide: (a) *A* layer, parallel to the (111) plane; (b) *B* layer, parallel to the (111) plane; (c) *C* layer, parallel to the (110) plane; (d) *D* layer, parallel to the (110) plane.

from Fig. 2 is the (100) plane, which in the ideal case would be a plane of Ib sites only. Since four, and possibly all five, of these OH types are observed in Fig. 1(a) it seems probable that all five of these planes are present in our γ-alumina sample.

Inspection of the IR spectra of the P/Al_2O_3 samples (Figs. 1(b–e)) shows a decrease in the Al–OH band intensities with increasing P content, with the exception of the 3795 cm^{-1} band. This indicates that H_3PO_4 reacts with all but the most basic Type Ib OH groups. In fact, the band due to Type Ib hydroxyls appears to increase in intensity up to 1 wt% P. Also apparent is a new band at 3676 cm^{-1}, which has been assigned to P–OH groups (*6*); this band increases in intensity with increasing H_3PO_4 content. Finally, for high loadings of H_3PO_4, a broad region at around 3250 cm^{-1} is observed, which becomes even broader for the 7 wt% P sample (not shown), and suggests interaction between OH groups on the surface (either between P–(OH) and Al–(OH) or between neighboring P–(OH) groups).

In order to gain more quantitative information on the reactivities of the different hydroxyls, the ν(OH) regions of the spectra were curve-fitted for the five hydroxyl bands. A sample curve fit is given in Fig. 3 for the catalyst containing 0.3 wt% P. The band areas, normalized with respect to sample weight, were plotted against the surface H_3PO_4 concentrations and are given in Figs. 4(a–e).

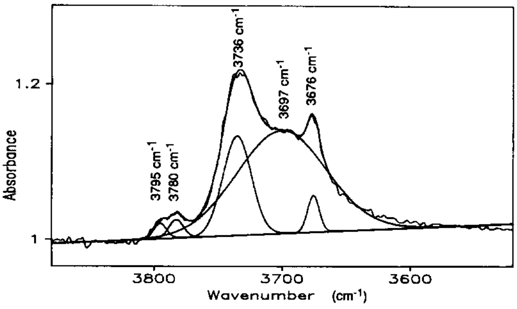


FIG. 3. OH stretching region in the IR spectrum of 0.3 wt% P/Al_2O_3 curve-fitted for five different hydroxyl bands.

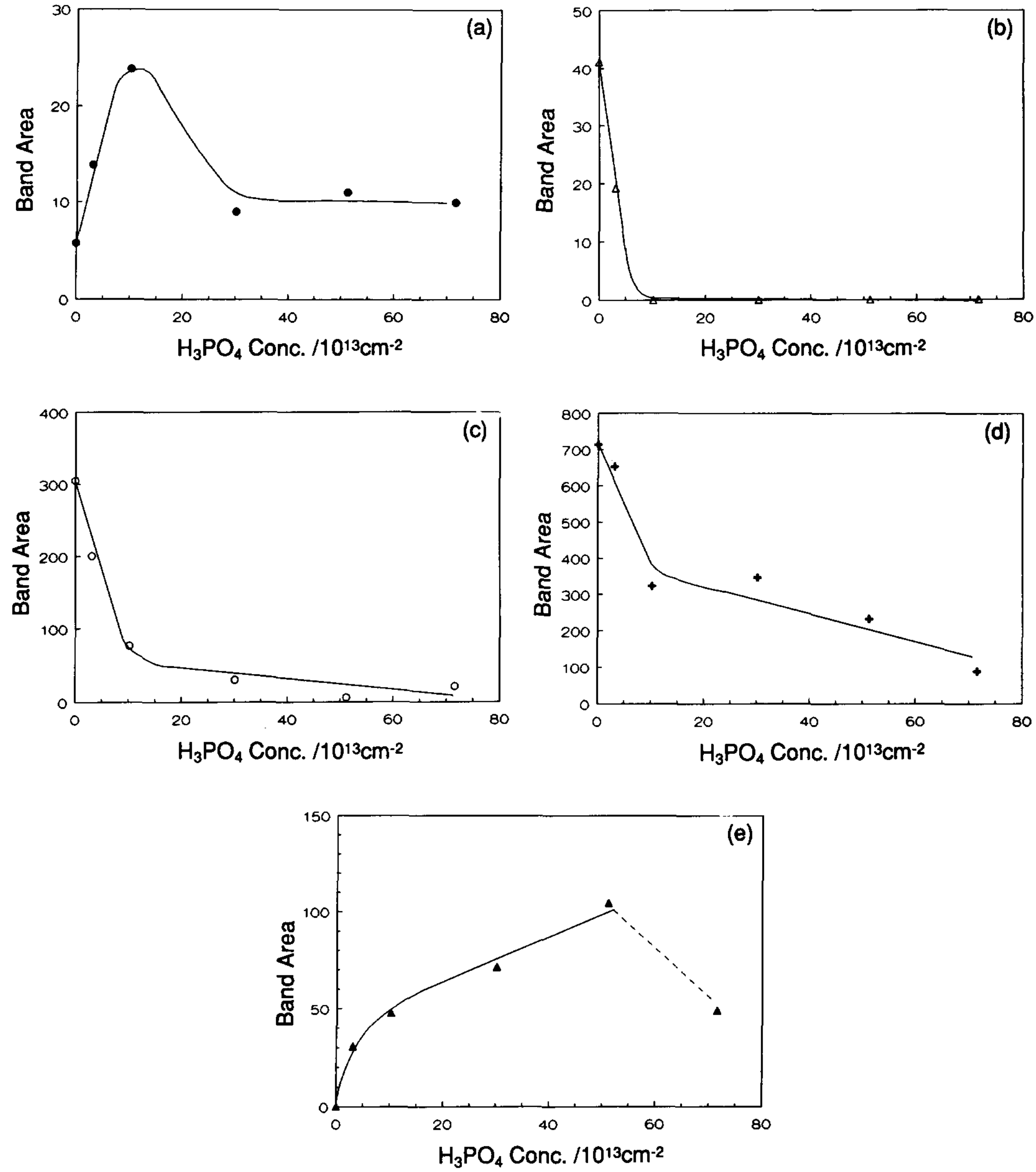
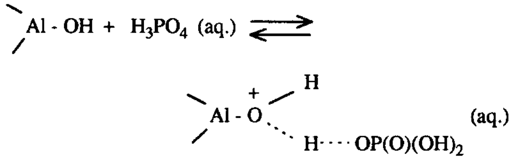


FIG. 4. Effect of the surface concentration of phosphoric acid on the OH stretching region of P/Al_2O_3 samples: (a) 3795 cm^{-1} band (Ib sites); (b) 3780 cm^{-1} band (Ia sites); (c) 3736 cm^{-1} band (IIa and IIb sites); (d) 3697 cm^{-1} band (III sites); (e) 3676 cm^{-1} band (P–OH groups). Band areas are normalized with respect to sample weight.

From the initial areas (i.e., in γ-alumina) it appears that after the pretreatment procedure described above there is a far greater number of Type III hydroxyls and Type II hydroxyls than either Type Ia or Ib. While the extinction coefficient is expected to increase with increasing acidity of OH (*10*) (i.e., for the lower wavenumber hydroxyl bands), it seems unlikely that this would contribute a 10-fold difference in the band areas. Therefore, it seems that the numbers of Types II and III OH groups on the surface are of the same order of magnitude, but there are fewer Ia sites by a factor of approximately 10, and still fewer Ib sites. The most basic hydroxyls (Ib most basic, then Ia) are expected to be lost most easily by dehydroxylation, and so it is perhaps not surprising that these are the least abundant OH groups after heating γ-alumina at 700°C under vacuum. Also, as discussed by Knözinger and Ratnasamy (*5*), dehydroxylation of the (111) plane (*A* and *B* layers, Figs. 2(a) and (b), respectively) may result in a situation where the more frequently occurring IIa and IIb sites predominate. However, the large area of the Type III hydroxyl ν(OH) band leads one to the suggestion that the (111) plane is preferentially exposed on the γ-alumina surface.

There are a number of features in Figs. 4(a–e) which need to be explained by any adsorption mechanism. First, in the initial portion of the curves, the area of the band due to Ia OH groups (Fig. 4(b)) decreases more rapidly than the Type II sites (4(c)), which in turn decrease more rapidly than the Type III sites (4(d)). Second, at a surface concentration of about 10×10^{13} H_3PO_4 cm^{-2} there follows a more gradual decrease in the areas of the latter two bands, while the band due to Type Ia OH groups has been removed completely. Similarly, for the P–OH band at 3676 cm^{-1} (Fig. 4(e)) there is an initial sharp increase in the area of this band with increasing P content, and a change in slope of this curve occurs at a surface concentration of about 10×10^{13} $H_3PO_4\,cm^{-2}$. Also, a sudden decrease in the integrated intensity of the P–OH band at the highest phosphorus concentration is observed. Finally, the number of Type Ib hydroxyls (3795 cm^{-1}) increases to a maximum value at around 10×10^{13} $H_3PO_4\,cm^{-2}$ (1 wt% P) and then decreases again to around the original number at higher P loadings (Fig. 4(a)).

To explain the first of these observations, i.e., Type Ia reacting faster than Type II which react faster than Type III hydroxyls, it is necessary to consider the acid–base chemistry of the preparation procedure. γ-alumina develops strong acidity only upon heat treatment above 470°C in a vacuum, and furthermore there is strong evidence that this acidity is due to the development of Lewis acid centers (not Brønsted acid sites) through dehydroxylation (*11*). Therefore, it is reasonable to assume that during the preparation procedure, the aqueous phosphoric acid will protonate all types of alumina hydroxyls by an acid–base reaction:



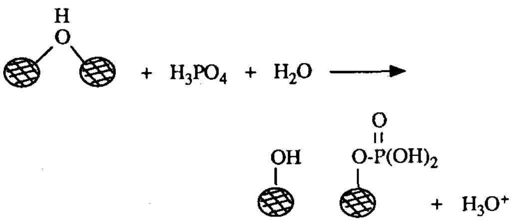
$$\rangle Al\text{-}OH + H_3PO_4\ (aq.) \rightleftharpoons \rangle Al\text{-}\overset{+}{O}(H)\cdots H\cdots OP(O)(OH)_2\ (aq.)$$

Presumably water is lost either before or during the calcination process, resulting in the formation of Al–O–P bonds and in the elimination of the bands associated with the O–H stretching vibration of these groups. Clearly the most basic hydroxyls of alumina would be expected to react preferentially with phosphoric acid and hence one would expect Types Ia and Ib to react more quickly than Types II and III. This explains the slopes of the curves in the initial portion of Figs. 4(b–d); the unusual behavior of the intensity of the Type Ib hydroxyls as phosphoric acid is added (Fig. 4(a)) is discussed later. While this order of reactivity is not surprising, it is worth noting that it is not the same as that found for $(NH_4)H_2PO_4$; van Veen *et al.* (*8*) found that the $H_2PO_4^-$ ion did not adsorb on the basic hydroxyl groups.

At phosphoric acid surface concentrations above 10×10^{13} H_3PO_4 cm^{-2} the alumina hydroxyl groups start to react more slowly, as reflected in the change in slope of Figs. 4(c) and (d) (and (b)). This shape of curve was also observed for the addition of MoO_3 or SO_4^{2-} to alumina (*12*) and was explained in terms of the formation of polymolybdate species in the former case. We propose therefore that at concentrations above 10×10^{13} H_3PO_4 cm^{-2} phosphoric acid reacts with P–OH groups on the alumina surface in addition to Al–OH groups. Thus polyphosphate species are expected to be formed on the alumina surface. There is some evidence in support of this in the literature. Cordero *et al.* (*13*) observed excellent phosphorus dispersion for samples containing up to 0.9 wt% P (9.2×10^{13} phosphate species cm^{-2}) which then decreased at higher loadings, due to the formation of phosphate multilayers.

Consistent with this model is the shape of the P–OH band area–concentration curve (Fig. 4(e)). Up to 10×10^{13} H_3PO_4 cm^{-2} the area of the P–OH band increases rapidly, which is expected since for every Al–OH which reacts with phosphoric acid two P–OH groups are formed. However, above this surface concentration phosphoric acid reacts with some P–OH groups, in addition to Al–OH, and the rate of increase in the P–OH band area becomes less. At still higher phosphorus loadings ($>51 \times 10^{13}$ H_3PO_4 cm^{-2} (5 wt% P)) a sudden drop in the P–OH band intensity occurs, possibly signifying a surface phase change to $AlPO_4$. Indeed, XRD patterns of the catalysts resembled that of γ-alumina for samples containing low loadings of phosphoric acid, but at high loadings of phosphorus (5 and 7 wt% P samples) there is an additional, very broad peak near $2\theta = 27°$ (possibly the 111 diffraction peak of $AlPO_4$), which is consistent with the presence of $AlPO_4$. Furthermore, van Veen *et al.* (*8*) observed the formation of an $AlPO_4$-type phase at above 4.5 wt% P, as evidenced by solid-state NMR spectra of calcined P/Al_2O_3 samples.

The effect of phosphoric acid on the band at 3795 cm^{-1} (Ib OH groups) is quite different to that on the other alumina surface OH groups. According to our proposed mechanism this hydroxyl should have greater reactivity than the more acidic OH groups, for example Types II and III. However, the number of Ib sites first increases and then decreases and, furthermore, over and above this effect the Ib sites do not appear to react with H_3PO_4 at all. The apparent increase in the number of these sites may be explained by inspection of Fig. 2(b). Reaction of a Type IIb or Type III site with phosphoric acid may result in the formation of Ib sites at low loadings of phosphorus by:



Similarly, reaction of Type IIa with phosphoric acid (Fig. 2(a)) will tend to generate Ib sites (rather than Ia) since the "tetrahedral Al" Lewis center generated is stronger than the "octahedral Al" center and will therefore react preferentially with the $H_2PO_4^-$ ion. At higher loadings of H_3PO_4 these reactions will occur to a lesser extent since first, both Al centers may react with phosphoric acid thus leading to a decrease in the number of Ib sites, and second, phosphoric acid starts to react with P(OH) groups on the surface in addition to Al(OH) groups. The fact that above around 30×10^{13} H_3PO_4 cm^{-2} the number of Ib sites appears to remain constant is difficult to explain. Possibly steric factors come into play at these high loadings, so that it is more favorable for H_3PO_4 to react with P(OH) groups than certain Al(OH) groups. Alternatively, an equilibrium situation may have arisen such that Ib sites do react but they are also formed from the reactions described above.

It should be noted that Peri (*14*) observed a very intense band at 3800 cm^{-1} in an $AlPO_4$ aerogel after drying at 600°C which he assigned to OH groups bonded to tetrahedral aluminum. At high loadings, such OH groups could contribute to the residual intensity seen in our spectra at 3795 cm^{-1} (see Fig. 4(a)). (Recall that at high surface concentrations of H_3PO_4 a surface $AlPO_4$ phase starts to form.) However, there are many different aluminum orthophosphates, and Mennour *et al.* (*6*) observed no bands at all in this region for a commercial, anhydrous

$AlPO_4$ sample. Clearly, the type of $AlPO_4$ phase formed on the surface of the P/Al_2O_3 samples will have a strong influence on the intensity of the band at 3795 cm^{-1}. In view of the relative intensities of the Al–OH and P–OH bands in our samples containing high loadings of phosphorus, we conclude that the $AlPO_4$ surface phase contains few OH groups attached to tetrahedral aluminum.

Some catalytic studies were performed to assess the surface acidity of the H_3PO_4/Al_2O_3 surfaces. Three reactions were studied, cumene hydrocracking and 1,3-diisopropylbenzene cracking and hydrocracking. Cumene is a common probe reaction to assess Brønsted acidity since it is cracked to benzene in the presence of these acid sites. 1,3-diisopropylbenzene was chosen since it is cracked more easily (to cumene) than cumene is to benzene. For all of the P/Al_2O_3 catalysts the amount of cracking in these reactions was low, indicating that any Brønsted acidity developed by the addition of H_3PO_4 to Al_2O_3 is too weak to crack cumene or 1,3-diisopropylbenzene to any great extent. However, some small differences were observed and some tentative conclusions can be drawn from the results; low P loadings leave the surface acidity of γ-alumina unchanged or possibly increase it slightly, while high P loadings decrease the acidity by a small amount. Since the effect of phosphorus on surface acidity is so small, this is clearly not the major role of P as a secondary promotor in Co–Mo and Ni–Mo catalysts.

CONCLUSIONS

Inspection of the OH stretching region of the infrared spectra of the P/Al_2O_3 catalysts gives rise to the following conclusions regarding the mechanism for the reaction of H_3PO_4 with γ-alumina: (1) Phosphoric acid reacts with the alumina hydroxyls in an acid–base reaction during the impregnation process; the most basic hydroxyls are expected to react in preference. (2) At higher phosphorus loadings ($>10 \times 10^{13}$ H_3PO_4 cm^{-2}) phosphoric acid reacts not only with surface Al–OH but also with P–OH groups to form polyphosphate surface species. (3) Above 51×10^{13} H_3PO_4 cm^{-2} an $AlPO_4$-type surface phase starts to form. (4) Ib sites are generated at low phosphorus content by the reaction of H_3PO_4 with Types II and III hydroxyls. Catalytic studies indicate that any Brønsted acidity that may be developed by the addition of H_3PO_4 to γ-alumina is too weak to crack cumene or 1,3-diisopropylbenzene to any great extent. There is some indication, however, that phosphorus may increase the acidity at low loadings and decrease the acidity at higher loadings.

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