JOURNAL OF CATALYSIS **164,** 260–267 (1996)
ARTICLE NO. 0382

Proton NMR Investigations of Surface Hydroxyl Groups on Oxidic Mo–P/γ-Al_2O_3 Catalysts

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Received April 9, 1996; revised August 14, 1996; accepted August 15, 1996

Proton MAS NMR spectroscopy has been used to investigate the influence of the impregnation procedure on the surface hydroxyl structure of dehydrated γ-Al_2O_3 impregnated with varying amounts of molybdenum or phosphorus. Large differences were observed for catalysts prepared by coimpregnation, sequential impregnation, and sequential impregnation with intermediate calcination. A quantitative analysis of the spectra showed that molybdate ions preferentially reacted with basic OH groups at low molybdate loading, but also with acidic hydroxyl groups at higher. Phosphate ions adsorbed on both types of hydroxyl groups, even at low or moderate coverage, while at high surface coverage a nearly constant density of Al–OH and P–OH groups indicated $AlPO_4$ formation. Phosphorus and molybdenum were well dispersed after coimpregnation, whereas after sequential impregnation (phosphorus first) some pore-plugging occurred and Mo–O compounds adsorbed on underlying phosphates.

INTRODUCTION

Oxidic Mo/γ-Al_2O_3 and Mo–P/γ-Al_2O_3 are of interest as precursors for hydrotreating catalysts used for hydrodesulfurization or hydrodenitrogenation. In their final state after a sulfidation treatment, hydrotreating catalysts contain small MoS_2 crystallites, on the edges of which nickel or cobalt atoms are situated. In addition, such catalysts often contain phosphate. Phosphate is said to enhance the solubility and stability of molybdate in the impregnation solution and to improve the mechanical and thermal stability of the support. In addition, a beneficial effect of phosphorus on the activity for hydrodenitrogenation has been observed (1–3). The activity of these catalysts is connected with the dispersion of the active phases, i.e., the distribution of these phases over the support surface. Phosphates and Mo–O compounds interact with the surface hydroxyl groups of the support during the preparation of the catalysts. Therefore, a quantitative study of the disappearance of the hydroxyl groups as a function of molybdenum and phosphorus oxide loadings and impregnation procedures can give valuable information about the differences in dispersion induced by the addition of molybdenum and phosphorus. FTIR spectroscopy can be used for this purpose (4, 5). Unfortunately, poor resolution of the bands in the 3200–4000 cm^{-1} range often makes it impossible to determine unequivocally whether new hydroxyl groups have formed (giving rise to new bands), or if existing hydroxyl groups have been modified by the interaction with promoter species, thus causing the ν(O–H) stretching vibration to shift (6). Furthermore, quantification of the IR data is difficult, since IR extinction coefficients of the different OH groups are difficult to determine and are sensitive to the type of OH group.

An alternative to IR spectroscopy is the ^1H MAS NMR technique (7–9). Already in 1980 Cirillo *et al.* applied ^1H NMR on a wide-line cw spectrometer to alumina and a molybdena–alumina catalyst (10). Bronnimann *et al.* used combined rotation and multiple pulse spectroscopy (^1H CRAMPS) to study γ-Al_2O_3 and some silica–aluminas (11). Several studies of Mo/Al_2O_3 catalysts were conducted by Mastikhin *et al.* (8, 12, 13), but their spectra suffered from a low sample rotation frequency and prominent spinning sidebands. DeCanio *et al.* reported ^1H MAS NMR characterization studies of γ-Al_2O_3, modified γ-aluminas, and some P/γ-Al_2O_3 and P–Mo/γ-Al_2O_3 samples with varying phosphorus content (14). They applied partial deuteration of the samples to reduce dipolar interactions of the hydroxyl protons with protons of adsorbed water molecules. In a recent proton NMR study of η-Al_2O_3 and Mo/η-Al_2O_3 catalysts NMR data were correlated with IR measurements of the same samples (15).

In this study P/γ-Al_2O_3, Mo/γ-Al_2O_3, and Mo–P/γ-Al_2O_3 samples with varying P and Mo loadings were investigated by proton NMR in order to elucidate the effects of the P and Mo loading. Several samples with a fixed amount of P and different amounts of Mo were prepared by three different impregnation procedures, namely coimpregnation, sequential impregnation with intermediate

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0021-9517/96 $18.00

calcination, and sequential impregnation without calcination. With these samples the effects of the impregnation procedure could be investigated. $NH_4H_2PO_4$ was used as phosphorus source, since it was shown that its interaction with the γ-Al_2O_3 surface is weaker than that of H_3PO_4 (16).

EXPERIMENTAL

Two model compounds and five series of catalysts were used in this investigation. γ-Al_2O_3 was commercially available (Condea, surface area 230 m^2/g, pore volume 0.53 cm^3/g), whereas a sample of amorphous $AlPO_4$ was prepared by the method of Kehl (17, 18). This sample has a surface area of 86 m^2/g and a pore volume of 0.87 cm^3/g. A series of Mo(x)/γ-Al_2O_3 catalysts was prepared by pore-volume impregnation of γ-Al_2O_3 with an aqueous solution of $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$. The value in brackets (x) indicates the loading of the sample in number of Mo atoms per nm^2 of support surface area (1 Mo atom/$nm^2 \approx 3.1$ wt% Mo). Impregnation of the support with a $NH_4H_2PO_4$ solution resulted in a corresponding series of P(x)/γ-Al_2O_3 samples, containing phosphorus instead of molybdenum (1 P atom/$nm^2 \approx 1.1$ wt% P). Three more series with a fixed amount of phosphorus (about 1.9 atoms/nm^2) and varying amounts of molybdenum were prepared, one by coimpregnation of the two elements (denoted by [Mo(x)P(y)]/γ-Al_2O_3) and two by sequential impregnation (Mo(x)P(y)/γ-Al_2O_3 and Mo(x)*P(y)/γ-Al_2O_3). In the sequentially impregnated samples phosphorus was applied first. Thereafter the samples were dried, and in one case calcined at 400°C for 2 h (indicated by the asterisk *), before molybdenum was added. All samples were dried after each impregnation step at 110°C in air for 12 h.

Before these samples were investigated by proton NMR, they were dehydrated by evacuation in a BET apparatus overnight at 400°C and at a pressure below 1 Pa. After transferring them in helium atmosphere to a moisture-free nitrogen glove box, the samples were filled into ZrO_2 rotors with tight fitting Kel-F caps. The rotors were spun at 10 kHz during MAS NMR experiments in a Bruker AMX400 NMR spectrometer. The resonance frequency for ^1H NMR measurements was 400.13 MHz at a magnetic field of 9.4 T. Single pulse excitation with pulse lengths of 6.0 μs (69° flip angle) and 10-s relaxation delays was applied. T_1 relaxation times were found to be shorter than 5 s. Chemical shifts were referenced to TMS (0 ppm). At least 256 scans were acquired for each spectrum. For the determination of quantitative results, all samples were weighed and the spectra were calibrated by measuring a known amount of 1,1,1,3,3,3-hexafluoro-2-propanol under the same conditions. By measuring an empty rotor it was observed that the probe and rotor themselves gave rise to a broad background signal which had to be subtracted from the ^1H spectra measured for the different samples.

RESULTS AND DISCUSSION

OH Groups on γ-Al_2O_3 and $AlPO_4$

The spectra of hydrated and dehydrated γ-Al_2O_3 are markedly different. The spectrum of the untreated (hydrated) sample consists of a single broad line at about 4.6 ppm due to physisorbed and chemisorbed water at the γ-Al_2O_3 surface. After dehydrating a much smaller signal is obtained which is dominated by a narrow signal at −0.2 ppm and a broader signal at 2 ppm. This spectrum could very well be deconvoluted with Voigt lineshapes as displayed in Fig. 1. Four parameters, the amplitude, the center of the peak and two width parameters have to be fitted for each Voigt line. The second width parameter w_2 gives an indication as to whether the line is similar to a Gaussian line due to inhomogeneous broadenings ($w_2 = 0$) or to a Lorentzian line due to homogeneous broadenings ($w_2 \geq 1$). Four Voigt lines were used for the deconvolution of the ^1H NMR spectrum of γ-Al_2O_3 with w_2 values between 0 and 1, indicating that the lineshapes are Lorentzian with a Gaussian distribution. The first line has its center at −0.2 ppm and is ascribed to OH groups which are end-on bonded to octahedrally coordinated Al centers (Al_o–OH) (8). The high-field shift of this line indicates the basic character of these OH groups (9). The two lines at 0.6 and 1.9 ppm are due to more acidic

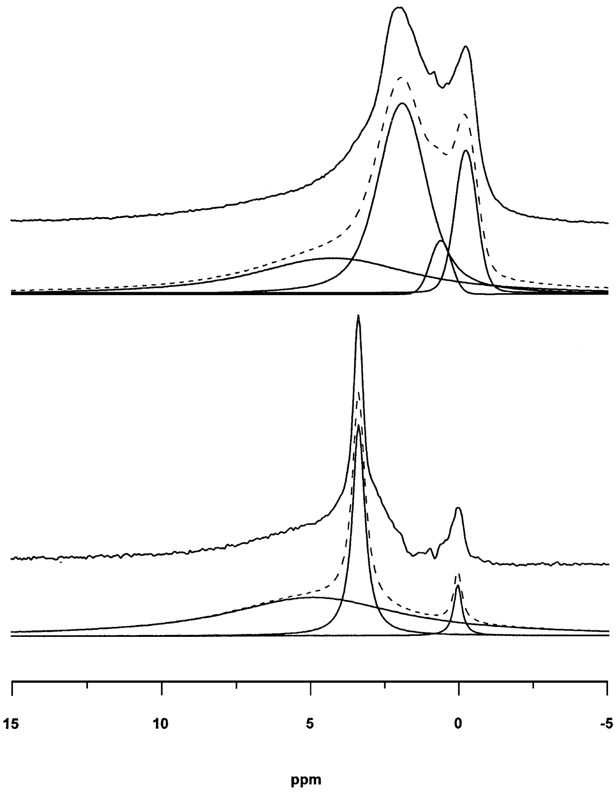

FIG. 1. ^1H MAS NMR spectra of dehydrated γ-Al_2O_3 (top) and dehydrated amorphous $AlPO_4$ (bottom) with deconvolutions.

OH groups. The line at 1.9 ppm is the most intense of these three lines and much broader than the other two. It is possible that more than one type of OH group contributes to this line. Knözinger and Ratnasamy developed a model for the five peaks which can be observed in the hydroxyl region of the IR spectrum of γ-Al_2O_3 (19). As well as the basic OH groups mentioned above, there are OH groups end-on bonded to tetrahedrally coordinated Al centers (Al_t–OH), bridging OH groups between tetrahedrally and octahedrally coordinated Al centers (Al_t–OH–Al_o), bridging ones between two Al_o centers (Al_o–OH–Al_o), and finally an OH group bonded to three Al_o centers ($3Al_o$–OH). It can be concluded that the NMR signal at 1.9 ppm is due to the three (or at least two) most acidic OH groups, that is Al_t–OH–Al_o, Al_o–OH–Al_o, and $3Al_o$–OH. In the ^1H NMR spectrum of our γ-Al_2O_3 a fourth, very broad signal was found at 4.4 ppm and assigned to physisorbed water (11, 14). This signal is found in all of the measured spectra with nearly the same intensity and has not been included in the quantitative analysis. The two signals of acidic Al–OH groups were combined for the quantitative analysis. The fits of the spectra did not improve when using two signals instead of one broadened signal which was shifted a little bit (to 1.8 ppm). From a comparison of the total intensity of the three OH group signals with the intensity of 1,1,1,3,3,3-hexafluoro-2-propanol an OH group density of 8.5 OH/nm^2 is calculated, 1.8 basic OH/nm^2 and 6.7 acidic OH/nm^2. The whole sideband pattern of each spectrum has been included for this intensity comparison, not, however, for the deconvolution, since it was found that the difference would be much smaller than the overall uncertainty of about 8% of these measurements. The value of 8.5 OH/nm^2 is somewhat higher than the value found by Jacobsen *et al.* (15) and the values collected by Knözinger and Ratnasamy (19). Jacobsen *et al.* used η-Al_2O_3 instead of γ-Al_2O_3 and dehydrated it at 500°C for 18 h. For a sample pretreated at 400°C which gives a larger NMR signal they did not note the OH group density. Furthermore, different aluminas might have different numbers of OH groups, depending on their different structure as well as crystallite sizes, number of defect sites, etc.

The spectrum of amorphous $AlPO_4$ exhibits mainly two resonances, a small one at −0.3 ppm and a larger one at 3.0 ppm. The small upfield signal can again be assigned to rather basic Al–OH groups. In studies of $AlPO_4$–Al_2O_3 systems and of $AlPO_4$ type molecular sieves signals at about 3 ppm were assigned to P–OH groups (8, 9). It is not possible to conclude from the downfield position of this signal relative to the signals of the Al–OH groups of γ-Al_2O_3 that the P–OH group is more acidic, because the nuclei to which the OH groups are attached are different. The total ^1H NMR intensity of the two signals of amorphous $AlPO_4$ corresponds to an OH group density of 2.2 OH/nm^2 (0.3 Al–OH/nm^2 and 1.9 P–OH/nm^2).

Molybdate Adsorption

Upon adsorption of Mo–O compounds on the γ-Al_2O_3 surface the basic and acidic OH groups are differently affected. This can be seen in Fig. 2, where the number of (remaining) OH groups/nm^2 is plotted versus the number of adsorbed molybdenum atoms per nm^2. At low molybdate loadings only the basic sites are affected, at higher loadings the number of acidic sites decreases too. Similar results were reported by Jacobsen *et al.* (15), confirming the results of Topsøe and Topsøe (5). With Raman spectroscopy it was found that molybdenum atoms are mainly present as tetrahedrally coordinated monomolybdate on the surface of γ-Al_2O_3 when the loading is low. At higher loadings octahedrally coordinated molybdenum atoms are observed, probably as part of polymolybdates (4, 20–22). In solutions monomolybdates are found at pH values of 8 or higher, while at lower pH values polymolybdates are found, mainly $Mo_7O_{24}^{6-}$ or $Mo_8O_{26}^{4-}$. Our starting impregnation solutions had a pH of 5.5 and therefore heptamolybdate complexes should dominate in these solutions. The γ-Al_2O_3 surface has a point of zero charge (PZC) of 8–9 and has a buffering influence on the impregnation solution when it is brought into contact with the support. The pH of the impregnation solution in the pores of the γ-Al_2O_3 rises and heptamolybdate complexes close to the surface decompose to monomolybdates:

$$Mo_7O_{24}^{6-} + 8\ OH^- \rightarrow 7\ MoO_4^{2-} + 4\ H_2O. \qquad [1]$$

These monomolybdates preferentially react with basic surface sites,

$$Al_s\text{–}OH + MoO_4^{2-} \rightarrow [Al_s\text{–}MoO_4]^- + OH^-, \qquad [2]$$

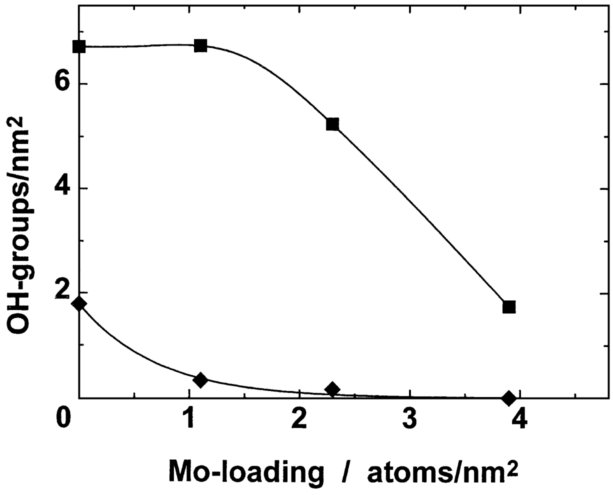

FIG. 2. OH-group density as a function of Mo loading for Mo(x)/γ-Al_2O_3 samples. ◆, Basic Al–OH groups; ■, acidic Al–OH groups.

where Al_s is a surface aluminum atom. The combination of reactions [1] and [2] leads to a decrease of the solution pH, so that no more polymolybdate is decomposed. Finally the polymolybdates adsorb on the remaining acidic sites (20, 23). The density of the basic Al–OH groups is reduced from 1.8 to 0.3 OH/nm^2 when 1.1 Mo-atoms/nm^2 are adsorbed. Thus the ratio of consumed OH groups per Mo atom is slightly higher than 1. The larger part of the molybdate groups is only bonded via one oxygen atom to the alumina surface, a smaller part via two oxygen atoms (after drying and calcination/dehydration). Note that the compounds were applied as NH_4^+-salts. During the dehydration pretreatment of the investigated samples ammonia was lost and the surface species were probably stabilized by aggregation.

At higher molybdate loadings up to 1.8 OH groups (mainly acidic) are replaced per Mo atom. This is in accordance with findings of Hall (4). Most Mo atoms which are in an octahedral coordination at high loadings are therefore bonded to two surface oxygen atoms. As the density of the acidic Al–OH sites which are the adsorption sites for octahedrally coordinated molybdenum atoms is much higher than the density of the basic adsorption sites of monomolybdates, this is not unexpected. The O–O distances within the octahedra of the $Mo_7O_{26}^{6-}$ ion ($\approx$ 0.33 nm) and the distances between oxygen atoms of octahedra which share corners ($\approx$ 0.40 nm) (24, 25) match rather well with the distances between neighboring oxygen atoms within a row ($\approx$ 0.28 nm) and between oxygen atoms of every second parallel row ($\approx$ 0.48 nm) (26) in the (111) faces of the spinel lattice of γ-Al_2O_3, respectively. It therefore seems possible that at high molybdena loadings phases with structures similar to that of the $Mo_7O_{26}^{6-}$ anion are formed on alumina surfaces in such a way that several MoO_6 octahedra are anchored via oxygen bridges onto the support surface, the oxygen atoms of these bridges being aligned in parallel rows (27). Recently Mastikhin *et al.* (13) published the ^1H NMR spectrum of bulk MoO_3. Signals were found at about 3 ppm. They claim that part of the proton signal observed in high-loading MoO_3/γ-Al_2O_3 catalysts is not due to surface Al–OH groups, but to Mo–OH or Al–OH–Mo groups, and that this proton signal overlaps with the signal of acidic Al–OH groups. In our spectra no additional signal or shoulder is found in this spectral region, but it cannot be ruled out that Al–OH and Al–OH–Mo groups cannot be discriminated in ^1H NMR spectra of Mo/Al_2O_3 catalysts.

Phosphate Adsorption

After adsorption of a moderate amount of phosphate (1.7 P-atoms/nm^2) on γ-Al_2O_3 the number of both basic and acidic OH groups decreased, and an additional signal at 3.2 ppm appeared (Fig. 3). At higher loadings this additional signal reached a maximum, and shifted to 3.0 ppm. The Al–OH signals first decreased with increasing loading and then leveled off. The observed influence of phosphate groups on both types of Al–OH groups even at low or moderate loadings is in contradiction with an IR investigation of P/Al_2O_3 catalysts by DeCanio *et al.* (28). They reported that phosphate reacts at low loadings preferentially with the most basic surface sites and only at higher loadings with more acidic sites. They used phosphoric acid as the phosphate source in their impregnation solutions, whereas the present study was done with a $NH_4H_2PO_4$ solution. This solution has a higher pH ($\approx$4) than a phosphoric acid solution (pH $\leq$ 1). The protonation state of the two solutions is different and the interaction of $H_2PO_4^-$ with the surface, especially with basic surface sites, is much weaker than that of H_3PO_4.

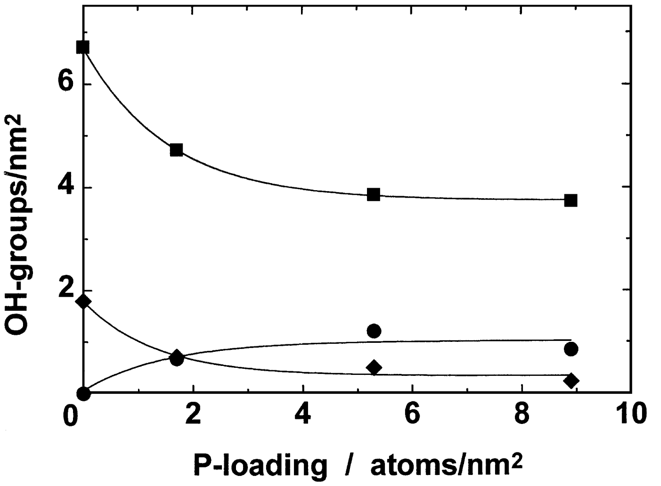

FIG. 3. OH-group density as a function of P loading for P(x)/γ-Al_2O_3 samples. ◆, Basic Al–OH groups; ■, acidic Al–OH groups; ●, P–OH groups.

The decrease in the Al–OH groups levels off at higher phosphorus loading. The question arises as to where the remaining phosphate adsorbs. In the ^{27}Al-^{31}P REDOR NMR study on the same samples (29) it was found that at this high loading an amorphous $AlPO_4$ phase had formed already after drying of the samples. At low loading phosphate groups (mono- and polyphosphates) were found to be well dispersed over the alumina surface. When the loading increases from low to moderate amounts of phosphates, the number of consumed OH groups increases too. When it is assumed that the phosphate has a P_2O_5-like structure, a density of 4.7 P atoms/nm^2 can be calculated for monolayer coverage. Such a P_2O_5-like monolayer does not necessarily mean that all the OH groups of the surface are covered by this layer. After adsorption of an amount of phosphate corresponding to this monolayer coverage, the formation of $AlPO_4$ begins. Additionally added phosphate adsorbs on this $AlPO_4$ phase, thus leaving the remaining Al–OH groups of the γ-Al_2O_3 unaffected. This might have happened in the P(5.3)/γ-Al_2O_3 and P(8.9)/γ-Al_2O_3 samples, since the amount of phosphate in these two samples is larger than monolayer coverage. The fact that $AlPO_4$ is formed implies that its formation is preferred over a denser packing or a stacking of phosphate. The formation of an amorphous $AlPO_4$ phase can also explain why the number of P–OH groups (signal at 3–3.2 ppm) does not increase with increasing phosphate loading. When more phosphate is supplied, more bulk $AlPO_4$ is formed, but the surface of this phase and the number of phosphorus atoms at its surface does not increase. It can be imagined that some mono- or polyphosphate groups are adsorbed on this $AlPO_4$ surface without having yet reacted to $AlPO_4$. The number of these groups can vary with the phosphate loading, which explains why in fact a small decrease in the density of P–OH groups is observed between the two samples with the highest loading. At moderate loadings 3.1 Al–OH groups/nm^2 are replaced by 1.7 P-atoms/nm^2. Most phosphorus atoms must therefore be bonded via two oxygen atoms to the alumina surface, either at one former basic and one acidic site or at two acidic sites. For the sample with the highest loading a value of 0.5 OH groups replaced per P atom is calculated, but as discussed before, the formation of $AlPO_4$ does not consume any more Al–OH groups. Furthermore, the basic Al–OH groups present on the high loading samples can be either Al–OH groups of γ-Al_2O_3 or hydroxyl groups on the surface of the $AlPO_4$ phase, as found on the $AlPO_4$ reference sample.

The number of P–OH groups on the low loading sample is surprisingly small, only 0.4 per P atom. As mentioned above, most phosphorus atoms must be bonded via at least two oxygen atoms to the alumina surface. Dimeric phosphate species without any OH group could account for such doubly bonded P atoms. To account for the P–OH groups some species with such groups must exist, however. We therefore assume that after a dehydration treatment some phosphate groups are connected with one bond to the alumina surface and with another to each other, to form polyphosphate. OH groups are present at each end of such a polymeric row. The polymerization may be induced by the dehydration treatment, and less polymeric and more monomeric phosphates may be found on samples which are only dried or calcined. Recently DeCanio *et al.* published ^{1}H NMR results on P/Al_2O_3 catalysts prepared with H_3PO_4 solutions (14). Besides the P–OH signal at 3.2 ppm they observed a signal at 1.6 ppm in low loading catalysts. They assigned the latter signal to P–OH groups of monophosphate and the signal at 3.2 ppm to hydroxyls of polyphosphate. In our samples no separate signal at 1.6 ppm was observed, but such a signal can be obscured by the Al–OH signal in the same region. Furthermore, it is possible that after an impregnation of the alumina with a phosphoric acid solution the phosphate groups have reacted more strongly with the surface than after an impregnation with a $NH_4H_2PO_4$ solution. Therefore less polymerization of the phosphate groups occurs during the dehydration treatment.

Coadsorption of Phosphate and Molybdate

When molybdenum and phosphorus were coimpregnated at constant P loading (1.9 atoms/nm^2), the density of the basic and acidic Al–OH sites decreased nearly linearly with increasing Mo loading. This correlation is shown in Fig. 4. The choice of the values for zero Mo loading in this figure is somewhat arbitrary, since only the Mo loading has been varied. It could be argued that the values obtained for the P(1.7)/γ-Al_2O_3 sample are the appropriate choice for zero Mo loading. On the other hand, this choice could give rise to the impression that molybdenum compounds in the impregnation solution have to interact with a surface on which phosphate has already adsorbed. Contrary to that, during coimpregnation, all compounds can theoretically interact with the free alumina surface, independent of the loading. Therefore, we have chosen the γ-Al_2O_3 values as reference for this figure and these values have also been used for calculating the number of OH groups replaced per P or Mo atom. The situation is different when Mo is impregnated subsequent to P. Consequently, in Figs. 6 and 8 the P(1.7)/γ-Al_2O_3 sample has been chosen as reference (see below). Nevertheless, a P–OH signal on the coimpregnated samples can be compared with that of the P(1.7)/γ-Al_2O_3 sample. Such a P–OH signal was indeed observed. It decreased in intensity at higher Mo-loadings, and it was always smaller than the P–OH signal of the molybdenum free P(1.7)/γ-Al_2O_3 sample. At the highest molybdenum loading the basic Al–OH sites had vanished, whereas a small amount of acidic Al–OH groups remained. The chemistry of Mo–P solutions is somewhat more complicated than

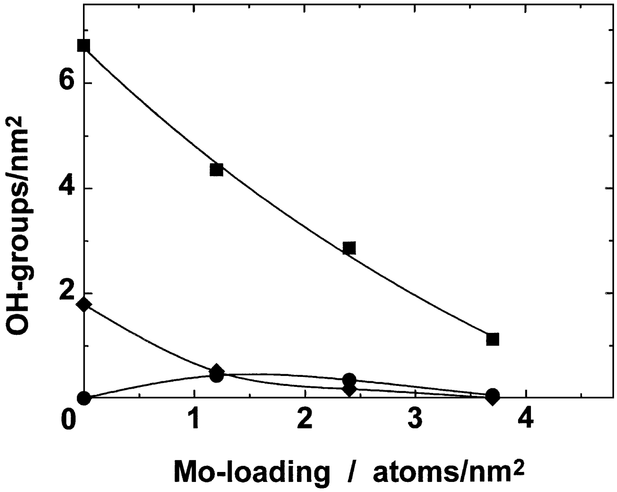

FIG. 4. OH-group density as a function of Mo loading for coimpregnated samples with constant P loading ([Mo(x)P(1.9)]/γ-Al_2O_3). ◆, Basic Al–OH groups; ■, acidic Al–OH groups; ●, P–OH groups.

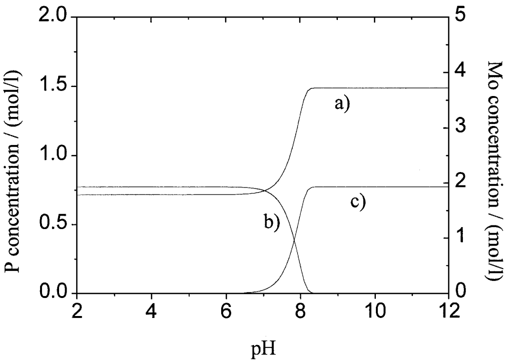

FIG. 5. P and Mo concentrations in different complexes in the impregnation solution of the [Mo(2.4)P(1.9)]/γ-Al_2O_3 sample as a function of the pH. (a) $H_xPO_4^{(3-x)-}$, (b) $H_yP_2Mo_5O_{23}^{(6-y)-}$, (c) $H_zMoO_4^{(2-z)-}$.

that of solutions containing only phosphates or Mo–O compounds. Using equilibrium constants of Pettersson *et al.* (30) the composition of the impregnation solutions can be simulated. At all molybdenum contents used in this study molybdenum should be present as $H_xP_2Mo_5O_{23}^{(6-x)-}$ complexes at a pH of 5–6. A corresponding amount of phosphorus is present in these complexes, and the remaining phosphorus is present as phosphate groups. Figure 5 shows what should happen to the composition of a solution like that used for impregnation of the [Mo(2.4)P(1.9)]/γ-Al_2O_3 sample with changing pH. In contact with the γ-Al_2O_3 surface the pH of the solution rises to 8 or higher. At such values the diphosphopentamolybdate complexes decompose to monomolybdates and monophosphates. As discussed above, the monomolybdates preferentially adsorb on basic sites, while the phosphate groups adsorb also on more acidic sites (16). After coverage of all basic sites, which may happen in samples with higher molybdenum loading, the pH of the solution will decrease and two situations may occur. The first situation is that some phosphomolybdates will adsorb intact on the alumina surface, probably on acidic sites. It is improbable that these complexes remain intact during the calcination/dehydration treatment. Nevertheless, part of the Mo–O compounds will be bonded to phosphate and not directly to the surface and vice versa. This can explain the low number of P–OH groups in these samples and a lower number of OH groups consumed per P and Mo atom than in the samples discussed above with comparable P or Mo loadings. The same results are obtained for the second situation: during the adsorption of monomolybdate on basic surface sites, all phosphate ions adsorb on acidic sites. Some remaining Mo–O compounds which will then be heptamolybdate ions due to the decreasing pH cannot find enough surface adsorption sites. These will partly adsorb on phosphate groups already on the surface. The number of OH groups replaced per phosphate or molybdate group is 1.3 in all three coimpregnated samples. As expected this value is lower than that of the P(1.7)/γ-Al_2O_3 sample, or that of the Mo/γ-Al_2O_3 samples with medium and high molybdenum loading.

Sequential Adsorption of Phosphate and Molybdate

In the Mo(x)*P(2.0)/γ-Al_2O_3 samples phosphorus was impregnated first. Thereafter the samples were dried and calcined, and then different amounts of molybdenum were impregnated. After the calcination step (without molybdenum) the catalysts are expected to be very similar to the moderate loading P(1.7)/γ-Al_2O_3 sample discussed above. In this sample phosphate has adsorbed on about 60% of the basic sites and on 30% of the acidic sites. The bonds between the phosphate groups and the alumina surface are already quite stable; it is not expected that during the second impregnation (with molybdenum) these bonds are broken. Therefore a reduced number of Al–OH sites and some new P–OH groups remain for adsorption of Mo–O compounds. With increasing Mo loading all of the basic OH groups which were left after phosphate adsorption vanished due to replacement by monomolybdates. The number of acidic OH groups was also reduced, but less so at higher loading, as shown in Fig. 6. Heptamolybdate groups are expected to adsorb on these sites. Probably some of these sites could not be reached because of steric hindrance by already adsorbed Mo–O compounds or because they exist in pores which were (partly) plugged by the phosphates. Apparently, basic sites which might be in the same pores could still be reached by the smaller monomolybdate groups. Especially at high molybdenum loadings not enough Al–OH sites remained for Mo–O compound adsorption. The Mo–O compounds had to adsorb on phosphate groups too. Therefore the number of P–OH groups is much lower than in the P(1.7)/γ-Al_2O_3 sample and also lower than in the coimpregnated samples, where some competition of Mo–O compounds and phosphates for the surface Al–OH sites could take place. Lewis and Kydd even reported that molybdena reacts preferentially with surface P–OH groups (31). The

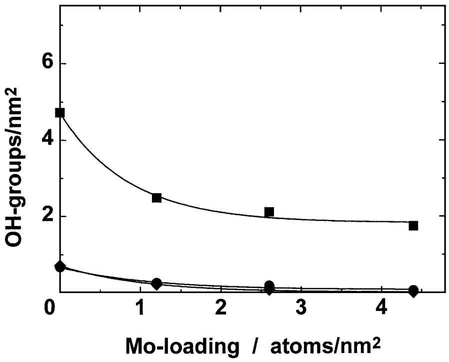

FIG. 6. OH-group density as a function of Mo loading for Mo(x)*P(2.0)/γ-Al_2O_3 samples. ◆, Basic Al–OH groups; ■, acidic Al–OH groups; ●, P–OH groups. The values for the sample without molybdenum are those of the P(1.7)/γ-Al_2O_3 sample.

number of P–OH groups per P atom is lower than 0.15 in all three samples. The number of Al–OH groups replaced per Mo atom is about 2 for the low loading sample. This is in accordance with the number found for the Mo(3.9)/γ-Al_2O_3 sample, in which mainly octahedrally coordinated Mo–O compounds are expected as well. At higher molybdenum loadings the number of replaced hydroxyls is lower, just 1.2 and 0.8 per Mo atom. The additionally supplied Mo–O compounds in this sample must be adsorbed in a second layer on phosphate or molybdate groups of the first layer.

The ^{1}H NMR spectra of Mo(x)P(y)/γ-Al_2O_3 samples are displayed in Fig. 7, and the OH group density as a function of Mo loading obtained after quantitative analysis of these spectra is shown in Fig. 8. These samples were not calcined, but only dried after the impregnation with $NH_4H_2PO_4$. After drying, the interaction of the phosphate groups with the alumina surface is much weaker than in the samples which were calcined before molybdenum impregnation. Some of the weakly bonded phosphates even desorb into the molybdate solution during the second impregnation step (32). Thus a complex situation exists. A substantial part of the basic sites are already occupied by phosphates, and a phosphated alumina surface has a lower PZC than the pure alumina surface (33). The pH of the second impregnation solution is lower than 8 and the solution contains mainly octahedrally coordinated Mo–O compounds, either heptamolybdate or phosphomolybdate which is formed with phosphate desorbed from the surface. These complexes compete for the free (mainly acidic) adsorption sites. Furthermore they can also adsorb on phosphate already on the surface. Some pore-mouth plugging by adsorbed phosphate may also occur. This may hinder especially large phosphomolybdate complexes from diffusing into these pores. Therefore the number of Al–OH groups replaced by Mo–O compounds or phosphate is even lower than in the samples which were calcined after the first impregnation step. Values of 1.0 and 0.7 OH groups replaced per Mo atom were found. The number of P–OH groups per P atom is also quite low, always smaller than 0.15. This indicates that stacking of phosphates and/or Mo–O compounds may occur in these samples. Indeed some crystalline $PMo_{12}O_{40}^{3-}$ was found by ^{31}P NMR on the highest loading sample after a calcination following the second impregnation step.

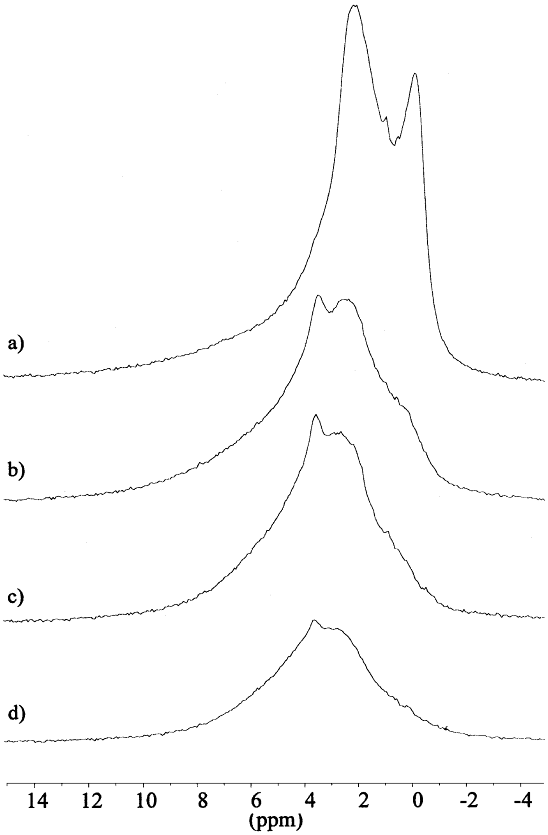

FIG. 7. ^{1}H MAS NMR spectra of (a) γ-Al_2O_3, (b) Mo(1.2)P(1.9)/γ-Al_2O_3, (c) Mo(2.5)P(2.0)/γ-Al_2O_3, and (d) Mo(4.2)P(2.0)/γ-Al_2O_3.

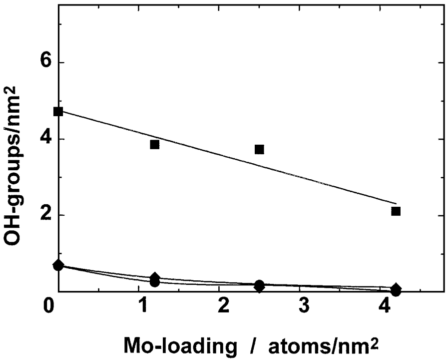

FIG. 8. OH-group density as a function of Mo loading for Mo(x)P(2.0)/γ-Al_2O_3 samples. ◆, Basic Al–OH groups; ■, acidic Al–OH groups; ●, P–OH groups. The values for the sample without molybdenum are those of the P(1.7)/γ-Al_2O_3 sample.

Although the above-described values for the hydroxyl groups on the surface of γ-Al_2O_3 are certainly trustworthy in a qualitative sense, one should be cautious when interpreting them in a quantitative way, because they depend on the conditions of dehydration. Thus, Jacobsen *et al.* (15) studied dehydrated Al_2O_3 and Mo/Al_2O_3 samples with ^{1}H NMR and found 4.7 OH/nm^2 on their η-Al_2O_3 after dehydration at 500°C, whereas in this study 8.5 OH/nm^2 were found on γ-Al_2O_3 after dehydration at 400°C. Differences also exist after adsorption of molybdates on the surface. Jacobsen *et al.* obtained a linear correlation between the loss of OH sites and the adsorbed amount of Mo with an OH/Mo ratio of 1.16. On our samples only at low molybdenum loadings an OH/Mo ratio close to 1 is found. This ratio increases to 1.8 for the samples with higher loading, when Mo–O compounds adsorb mainly on acidic sites. For the pure alumina support a correlation between dehydration temperature and number of observed OH groups was found (19). For alumina loaded with Mo or P the correlation might be different, since the mobility of the OH groups and thus the possibility for hydroxyl condensation and subsequent water vaporization might be reduced by the presence of phosphate of Mo–O compounds on the surface. Furthermore, OH groups still visible after a 400°C dehydration of the pure support may be removed after a 500°C dehydration. Consequently, their replacement by adsorbates may only be observed if both the pure support and the catalyst are dehydrated at a not too high temperature. On the other hand, dehydration at too low a temperature leaves too much water on the samples which disturbs the interpretation of the data. The same difficulties will of course also occur in IR studies of the hydroxyl region of such Mo–P/Al_2O_3 samples.

The oxidic Mo–, P–, and Mo–P/γ-Al_2O_3 samples in the present study are only precursor states of actual NiMoP/γ-Al_2O_3 catalysts used for HDN reactions. However, the effects described in the present paper are relevant for understanding the structure of (oxidic) NiMoP/γ-Al_2O_3 samples. An investigation of such systems and a discussion of the catalytic relevance will be reported in another paper.

CONCLUSIONS

The ^1H NMR investigations of molybdenum or phosphorus impregnated γ-Al_2O_3 after (partial) dehydration provided quantitative information about the hydroxyl groups at the surface of these oxidic catalysts. It was found that molybdate adsorbed on basic sites at low loading. At higher loadings acidic OH groups were replaced by aggregated species with a octahedral Mo coordination, probably heptamolybdates. Phosphate, supplied in the form of a $NH_4H_2PO_4$ solution, adsorbed on both basic and acidic sites, even at low loading. At higher loadings formation of an amorphous $AlPO_4$ can explain why the number of Al–OH and P–OH groups did not change significantly with increasing loading. After coimpregnation of phosphorus and molybdenum both types of hydroxyls were replaced simultaneously. Since molybdates preferentially adsorb on basic sites, it is assumed that phosphates adsorbed on acidic sites in these samples. When phosphorus was impregnated first, the phosphates occupied most of the basic sites before molybdenum was supplied. The Mo–O compounds could adsorb on remaining acid sites or on phosphate groups. Not all of the hydroxyls were replaced, probably because polymolybdate complexes could not reach all of them due to pore-plugging by the phosphate or to steric hindrances.

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