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Composition of Impregnation Solutions and Wet Impregnated Mo–P/γ-Al_2O_3 Catalysts as Investigated by ^{31}P and ^{95}Mo NMR

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Impregnation solutions and wet impregnated Mo–P/γ-Al_2O_3 catalysts containing the impregnation liquid in the pores of the support were investigated by NMR spectroscopy. In phosphorus and molybdenum-containing solutions used for impregnation of γ-Al_2O_3 mainly $H_xP_2Mo_5O_{23}^{(6-x)-}$ and $H_yPO_4^{(3-y)-}$ ions were found. Great differences existed between the states of phosphorus during the last impregnation step of Mo–P/γ-Al_2O_3 catalysts which were coimpregnated or sequentially impregnated with or without intermediate calcination. In coimpregnated catalysts chemisorbed mono- and polyphosphates, physisorbed phosphates, as well as $H_xP_2Mo_5O_{23}^{(6-x)-}$ and $H_yPO_4^{(3-y)-}$ ions remaining in solution were observed. In sequentially impregnated catalysts which were calcined after the impregnation of P only chemisorbed phosphates and some amorphous $AlPO_4$ could be detected after the second impregnation with a Mo solution. Sequential impregnation without calcination after phosphorus impregnation is an intermediate case, especially since $NH_4H_2PO_4$ was used as phosphorus source which interacts less strongly with the alumina surface than H_3PO_4. During the second impregnation of these catalysts with a Mo solution, a loosening of the interaction of some phosphate ions with the surface and even desorption into the pore-filling liquid were observed.

INTRODUCTION

Many commercial cobalt–molybdenum and nickel–molybdenum hydrotreating catalysts contain a small amount of phosphate. Phosphate has the beneficial effect of increasing the solubility and stability of the molybdenum-containing impregnation solutions and of improving the mechanical and thermal stability of the support. In addition, a promotional effect of phosphorus in denitrogenation (HDN) has been documented (1–3). One of the fundamental questions of the phosphorus promotion is the interaction mechanism of phosphorus compounds with the γ-alumina surface and its influence on the molybdate adsorption. Conflicting results have been reported in the literature. Most authors proposed a strong interaction of the phosphate ion with alumina through a mechanism involving basic surface sites, at least at low loadings (4–7). Some authors suggested, however, that phosphate, especially at high loadings, primarily reacts with acidic hydroxyl groups (6, 8). Van Veen *et al.* showed that the interaction of phosphoric acid with the alumina surface is much stronger than that of $NH_4H_2PO_4$, leading to much more $AlPO_4$ formation (6). The study of phosphate adsorption is of relevance for catalysts which are sequentially impregnated, while for coimpregnation of phosphorus and molybdenum the adsorption of phosphomolybdate compounds has to be considered as well. Whereas van Veen *et al.* reported that both $P_2Mo_5O_{23}^{6-}$ and $PMo_{12}O_{40}^{3-}$ decompose upon adsorption on the alumina surface, Cheng and Luthra observed that $PMo_{12}O_{40}^{3-}$ adsorbs intact (9). The adsorption behavior of phosphates, molybdates, and phosphomolybdates on alumina has been studied with several different methods like IR and Raman spectroscopy, TPR, and chromatographic techniques. Cheng and Luthra (9, 10) and Sarrazin *et al.* (11, 12) used NMR spectroscopy of the impregnation liquid in the pores of the support to detect compounds remaining in the impregnation solution during catalyst preparation.

In the present study solid state NMR has been applied to freshly impregnated catalysts. Adsorbed species as well as solution compounds could be observed. The solution signals were assigned by comparison with liquid NMR spectra of pure solutions. Coimpregnated as well as sequentially impregnated samples with and without intermediate calcination were investigated immediately after the final impregnation. $NH_4H_2PO_4$ was used as phosphate source since its interaction with the alumina surface does not immediately lead to the formation of aluminum phosphate.

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EXPERIMENTAL

Different amounts of $NH_4H_2PO_4$ (or H_3PO_4) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were dissolved in water to obtain solutions with different phosphorus and molybdenum concentrations. Phosphorus concentrations were chosen between 0.06 and 1.97 mol/liter and molybdenum concentrations between 0.12 and 3.86 mol/liter. The pH was varied between 7.8 and 0.5 by adding HCl (38%), HNO_3 (65%), or NH_4OH (25%). Heptamolybdate solutions (1 *M*) with pH 8.2 and 5.2, a 1 *M* Na_2MoO_4 solution at pH 11.0 and another 1 *M* solution containing the complexing agent nitrilotriacetic acid (NTA) at pH 6.7 were prepared as well.

Three series of catalysts were prepared by pore-volume impregnation of γ-Al_2O_3 with aqueous solutions containing $NH_4H_2PO_4$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$. The first series was prepared by coimpregnation (notation $[Mo(x)P(y)]/\gamma$-Al_2O_3, where *x* and *y* indicate wt% of molybdenum and phosphorus). Catalysts of the second series were stepwise impregnated (P first) and dried for 12 h at 110°C after the first impregnation step (notation $Mo(x)P(y)/\gamma$-Al_2O_3). Catalysts of the third series were prepared by sequential impregnation with drying and calcination (2 h at 400°C) after the first impregnation step (notation $Mo(x)^{*}P(y)/\gamma$-Al_2O_3). A $P(2)/\gamma$-Al_2O_3 sample contained only phosphorus. All catalysts were investigated immediately after the last impregnation step when they still contained the impregnation solution in the pores of the γ-Al_2O_3.

^{31}P NMR spectra were acquired on a Bruker AMX400 spectrometer at a magnetic field of 9.4 T and a resonance frequency of 161.98 MHz. For the phosphorus containing solutions pulse lengths of 2 or 3 μs and relaxation delays of 1–5 s were used to acquire at least 32 scans for each spectrum. The chemical shifts were referenced to 85% phosphoric acid (0 ppm). The same spectrometer and a Bruker AM300 spectrometer with a magnetic field of 7.0 T were used to obtain solution ^{95}Mo spectra at resonance frequencies of 26.07 and 19.54 MHz, with pulse lengths between 5 and 15 μs and relaxation delays between 0.2 and 500 ms. At least 512 scans were acquired for each spectrum, and the ^{95}Mo chemical shifts were referenced to a 2 *M* Na_2MoO_4 solution at a pH of 11 (0 ppm).

^{31}P MAS NMR measurements were performed on the catalysts with the impregnation solution in the pores of the support. Chemical shifts were referenced to 85% phosphoric acid, using $NH_4H_2PO_4$ (0.9 ppm (13, 14)) as secondary reference. Rotors were spun at 14 kHz and 2-μs pulses (40° flip angle) were applied to obtain ^{31}P MAS spectra with proton high power decoupling. For each spectrum with a recycle time of 5 s, 8192 scans were acquired. ^{1}H-^{31}P cross-polarization (CPMAS) experiments were performed on the coimpregnated samples with a contact time of 5 ms and a proton 90° pulse length of 7.4 μs. The other conditions were the same as for the single pulse spectra.

RESULTS AND DISCUSSION

Impregnation Solutions, ^{31}P NMR

Using potentiometric titrations, differential pulse polarography, Raman spectroscopy, and NMR spectroscopy, two groups were able to characterize the different molybdophosphate complexes present in solutions containing phosphorus and molybdenum (15–17). These studies showed that ^{31}P NMR is a convenient technique for screening a phosphorus molybdenum solution for the number of phosphomolybdate species and to assign these species. Since these studies were conducted with much lower phosphorus and molybdenum concentrations ($[P] \leq 0.07$ mol/liter $[Mo] \leq 0.72$ mol/liter) than used in catalyst preparations, we first investigated solutions at varying pH with a similarly low phosphorus concentration $[P] = 0.06$ mol/liter and with a $[P]:[Mo]$ ratio comparable to that in impregnation solutions for coimpregnated catalysts ($[Mo] = 0.12$ mol/liter). The analyzed solutions were prepared with ammonium salts, whereas the other groups (15–17) used sodium salts, partly in 3 *M* $NaClO_4$.

^{31}P NMR spectra of some of our solutions are shown in Fig. 1. Most of these spectra were measured under conditions normally used for solid state NMR measurements in order to check whether compounds in solution are also detectable under these conditions. The solutions in the pH range from 5.9 to 2.1 exhibited two signals with a nearly constant 3 : 1 intensity ratio (Fig. 1a). The larger signal is situated at 2.0 ppm, whereas the smaller signal shifts from 1.1 to 0.6 ppm with decreasing pH. According to the above-mentioned studies (15–17) these signals should be assigned to $H_xP_2Mo_5O_{23}^{(6-x)-}$ (2.0 ppm) and free phosphate ($H_yPO_4^{(3-y)-}$) ions. Because of the 3 : 1 intensity ratio, 0.045 mol/liter of the phosphorus is present in the $H_xP_2Mo_5O_{23}^{(6-x)-}$ anions. As a consequence, practically all molybdenum in the solutions must be bound in these complexes. In solutions with $pH < 2$ only one signal at 0.5 ppm is found which is due to free phosphate ions (Fig. 1b). In these solutions a yellow precipitate was formed which removed any phosphomolybdate complex from the solution. In Fig. 1c the spectrum of a solution with the higher $[P] = 0.47$ mol/liter and $[Mo] = 1.19$ mol/liter concentrations at $pH = 3.0$ is presented. More than 92% of the intensity is found in a signal at 2.0 ppm due to $H_xP_2Mo_5O_{23}^{(6-x)-}$, the rest in a very weak signal at 0.7 ppm (free phosphate ions). A similar spectrum was obtained for the same solution at pH 1.0. Since the $[P]:[Mo]$ ratio in these solutions is about 0.4, the equivalent amount of molybdenum ($\geq$92%) has to be part of the diphosphopentamolybdate complexes.

^{31}P NMR spectra of solutions actually used for impregnation of catalysts are shown in Fig. 2. The spectrum in Fig. 2a is that of a solution used for preparing the

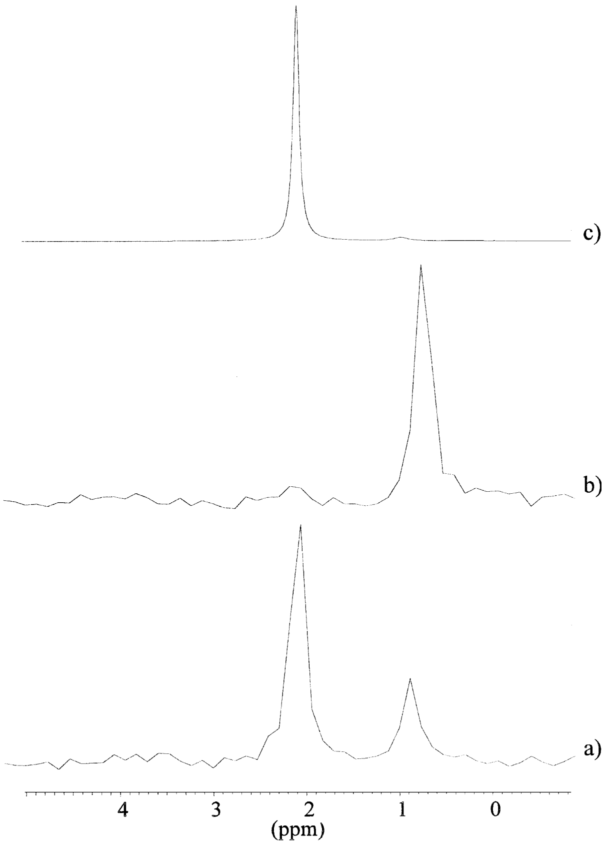


FIG. 1. ^{31}P NMR spectra of P–Mo solutions. (a and b) [P] = 0.06 mol/liter and [Mo] = 0.116 mol/liter, pH 3.1 and 1.5, respectively; (c) [P] = 0.47 mol/liter, [Mo] = 1.19 mol/liter; pH 3.0.

P(2)/γ-Al_2O_3 sample, with a phosphorus concentration of 1.29 mol/liter and a pH of 3.7; the single signal at 0.9 ppm is due to free phosphate ions. One or two signals were also observed in three solutions used for preparing the [Mo(x)P(2)]/γ-Al_2O_3 samples containing [P] = 1.35, 1.54, and 1.97 mol/liter and [Mo] = 0.88, 2.01 and 3.86 mol/liter, respectively (Figs. 2b–2d). Since these solutions were used without further acidification, the pH increased with increasing molybdenum concentration from 5.5 to 6.0. In the solution with the lowest concentration (Fig. 2b) about 1/4 of the ^{31}P NMR intensity is found in the phosphomolybdate signal at 2.1 ppm, corresponding to 0.33 mol/liter of phosphorus. The stoichiometric amount of molybdenum in this heteropolyanion ($2.5 \times 0.33 = 0.825$ mol/liter) corresponds to more than 94% of the total molybdenum concentration. A second signal due to free phosphate ions is observed at 1.2 ppm. The solution with medium concentrations displayed two nearly equal ^{31}P NMR signals at 2.1 and 1.5 ppm (Fig. 2c). Again, the intensity distribution corresponds to a situation where the maximum possible amount of phosphorus atoms is complexed with molybdenum atoms in protonated $P_2Mo_5O_{23}^{6-}$ type anions, so that nearly no molybdenum is present in other complexes. The spectrum of the solution with the highest concentrations (Fig. 2d) consists of only one signal at 2.2 ppm. At first sight this suggests that all phosphorus is present in phosphomolybdate ions, but this is stoichiometrically not possible. From the data of Pettersson *et al.* it can be deduced, however, that at the applied concentrations and at a pH of 6.0 the signals of $H_xP_2Mo_5O_{23}^{(6-x)-}$ and $H_yPO_4^{(3-y)-}$ ions overlap (15). Therefore, we assume that the situation is similar to that in the other investigated solutions, so that about 80% of the phosphorus atoms participate in the formation of $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions, and the remaining phosphorus is present as free phosphate.

Since an increase of the pH value is expected after contact of the solutions with the γ-Al_2O_3 surface, the three [Mo(x)P(2)] solutions have also been measured after addition of ammonia. The pH values thus obtained were 7.8, 7.6, and 7.7. The spectra are shown in Figs. 2e–2g. In each spectrum two signals are observed. The signal at 2.2–2.5 ppm can again be assigned to diphosphopentamolybdate complexes. With increasing pH the signal of free phosphate ions shifts to the downfield side of the diphosphopentamolybdate signal (15). Indeed, signals at 2.9, 3.0, and 3.2 ppm due to free phosphate ions are observed in the spectra

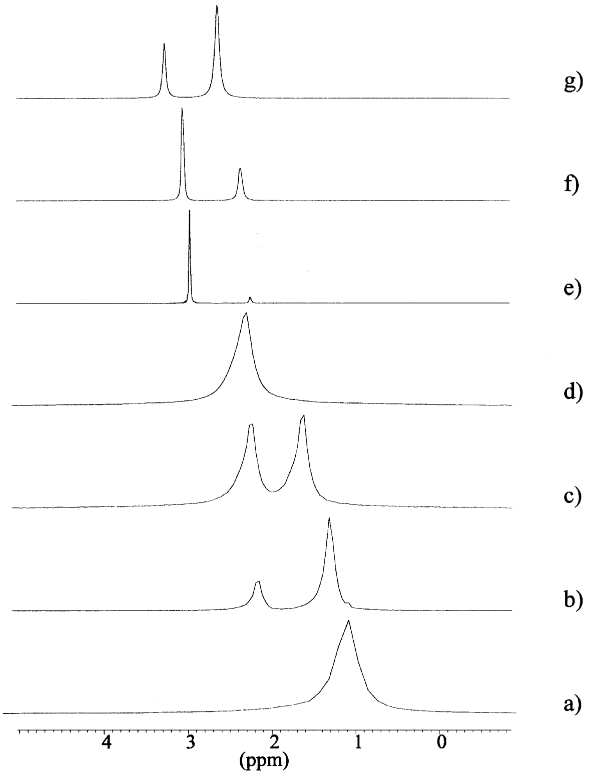


FIG. 2. ^{31}P NMR spectra of solutions used for coimpregnation. (a) Solution with [P] = 1.29 mol/liter, pH 3.5; (b–d) solutions with [P] = 1.35, 1.54, and 1.97 mol/liter and [Mo] = 0.88, 2.01, and 3.86 mol/liter at pH 5.5, 5.7, and 6.0, respectively; (e–g) the same solutions at pH 7.8, 7.6, and 7.7, respectively.

of these solutions. The intensity of this phosphate signal relative to the $H_xP_2Mo_5O_{23}^{(6-x)-}$ signal is larger in these spectra than in the corresponding spectra of solutions at lower pH. The signal intensities show that the amount of Mo bound in diphosphopentamolybdate rises from 38% at low concentrations to 91% at high concentrations in the solutions at pH $\approx$ 7.7, while in the solutions at lower pH practically all Mo is bound in these complexes. This means that part of the diphosphopentamolybdate decomposes at higher pH.

Impregnation Solutions, ^{95}Mo NMR

Some solutions have also been measured by ^{95}Mo NMR spectroscopy. Figure 3a shows the spectrum of the 2 *M* Na_2MoO_4 reference solution at pH 11, with a single signal at 0 ppm due to monomolybdate ions. A similar spectrum is obtained for a 1 *M* Na_2MoO_4 solution at pH 8.8, but shifted to 1.4 ppm. Figures 3b and 3c were obtained from 1 *M* $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ solutions at pH 8.2 and 5.2. According to Luthra and Cheng (10) and to Sarrazin *et al.* (11) the signal at −0.9 ppm (Fig. 3b) can be assigned to tetrahedrally coordinated molybdenum atoms in monomolybdate ions, whereas the broad signal at 33.5 ppm (Fig. 3c) is due to octahedrally coordinated molybdenum atoms in heptamolybdate complexes. A molybdate solution ([Mo] = 1 mol/liter, pH 6.7) containing the complexing agent nitrilotriacetic acid (NTA) shows two ^{95}Mo NMR signals (Fig. 3d): a very narrow one at 2.5 ppm which is again assigned to monomolybdate and a broad signal at 67.2 ppm due to octahedrally coordinated molybdenum atoms in $[MoO_3(NTA)]^{3-}$ complexes. The spectra of solutions containing phosphorus (0.47 mol/liter) and molybdenum (1.19 mol/liter) at a pH of 1.0 and 3.0 contain only one broad signal at about −18 ppm (Fig. 3e). From the ^{31}P spectra of the same solutions (Fig. 1c) it was deduced that these solutions mainly consist of $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions. Therefore the signal in the ^{95}Mo spectra should also be assigned to these ions. Molybdenum is octahedrally coordinated in these complexes, but not all octahedra are structurally equivalent and they are rhombohedrally distorted (18). The inequivalence of the Mo octahedra and their distortion explains the rather large linewidth in the NMR spectrum. The shift of the signal to −18 ppm must be due to the presence of phosphorus in the complexes. This assignment is in accordance with the literature (9).

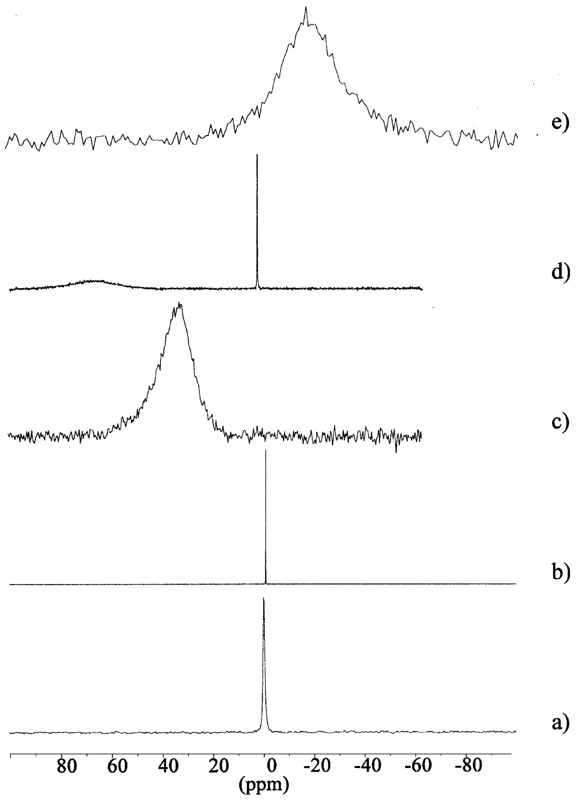


FIG. 3. ^{95}Mo NMR spectra of model solutions, (a) 2 *M* Na_2MoO_4 at pH 11; (b and c) 1 *M* $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at pH 8.2 and 5.2, respectively; (d) Mo–NTA solution, [Mo] = 1 mol/liter, pH 6.7; (e) Mo–P solution, [P] = 0. 47 mol/liter, [Mo] = 1.19 mol/liter, pH 3.0.

^{95}Mo NMR spectra were also acquired for the three [Mo(*x*)P(2)] solutions at two different pH values. At lower pH values (5.5–6.0) only one very broad signal could be detected, whose linewidth increased with increasing concentration (Figs. 4a–4c). This signal should again be assigned to $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions, since it was deduced from the corresponding ^{31}P NMR spectra that practically all Mo must be bound in such ions. At higher pH only a very narrow signal was observed at about −4 ppm (Figs. 4d–4f). The line position and the narrow width indicate that monomolybdate has been formed (compare Fig. 3). This is in accordance with the findings of the ^{31}P NMR measurements where a partial decomposition of the $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions was observed. Nevertheless, part of the molybdenum should still be bound in diphosphopentamolybdate ions, but could not be detected in the ^{95}Mo NMR spectra. Probably the corresponding signal is lost in the baseline when compared to the sharp peak of the monomolybdate. The signal/noise ratio in the spectrum of the solution with the highest concentration (Fig. 4f) is much lower than in the other two spectra although all three spectra were measured under the same conditions. This indeed indicates that not all of the molybdenum is observed in these spectra. Nevertheless, the spectra clearly show that besides $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions as observed by ^{31}P NMR also monomolybdate is present in the three solutions at a higher pH, whereas only $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions are present at lower pH.

Wet Coimpregnated Catalysts

After establishing the composition of the impregnation solutions the freshly impregnated catalysts could be investigated. The solid state ^{31}P NMR spectra of these catalysts were measured directly after impregnation without drying or calcination of the catalysts, so that the impregnation solution was still in the pores of the support. Spectra of samples impregnated with solutions containing a fixed amount of phosphorus and different amounts of molybdenum are shown in Fig. 5, together with the spectra of the corresponding impregnation solutions. Several features can be observed in the spectra of the catalysts. A very broad component ranges from 5 to −20 ppm, while a second also rather broad component observed in all samples is centered at about −3.7 ppm (−3.2 ppm in the P(2)/γ-Al_2O_3 sample). In addition, all samples exhibit signals at exactly the same positions as the corresponding impregnation solutions with peak widths decreasing with increasing Mo loading.

Three different peaks were observed for the sample which contained only phosphorus, although the impregnation solution contains only monophosphate. After drying of this catalyst for 12 h at 110°C one broad signal ranging from 5 to −25 ppm is observed (Fig. 5a) which was assigned to a distribution of mono- and polyphosphates adsorbed on the γ-Al_2O_3 surface (19). This signal is similar to the broadest feature in the spectrum of the freshly impregnated sample, which is therefore assigned to mono- and polyphosphates which have reacted with the surface hydroxyls of the alumina by replacement of water and are thus chemisorbed on the surface. The other two signals must be due to structures which can exist only in the presence of the solution in the pores of the support. On the other hand, they are broader than the solution signals. These two signals might be due to complexes which are physisorbed on the surface, e.g., by hydrogen bonding. Such physisorbed compounds can exist only before drying of the sample, since removal of water will transfer them to chemisorbed compounds. The physisorption restricts the mobility and gives rise to a dipolar or chemical shift broadening. The signal at 1.5 ppm in the P(2)/γ-Al_2O_3 catalyst is thus assigned to monophosphate hydrogen bonded to a surface OH group. The somewhat broader signal at −3.2 ppm can be explained in two ways, either by condensation of two phosphate groups physisorbed on neighboring sites to a diphosphate, or by a monophosphate group which is doubly hydrogen bonded to the surface. This physisorbed phosphate could be the intermediate state in a mechanism proposed by van Veen *et al.* for monophosphate adsorption on the basic hydroxyl groups on the alumina surface (6):

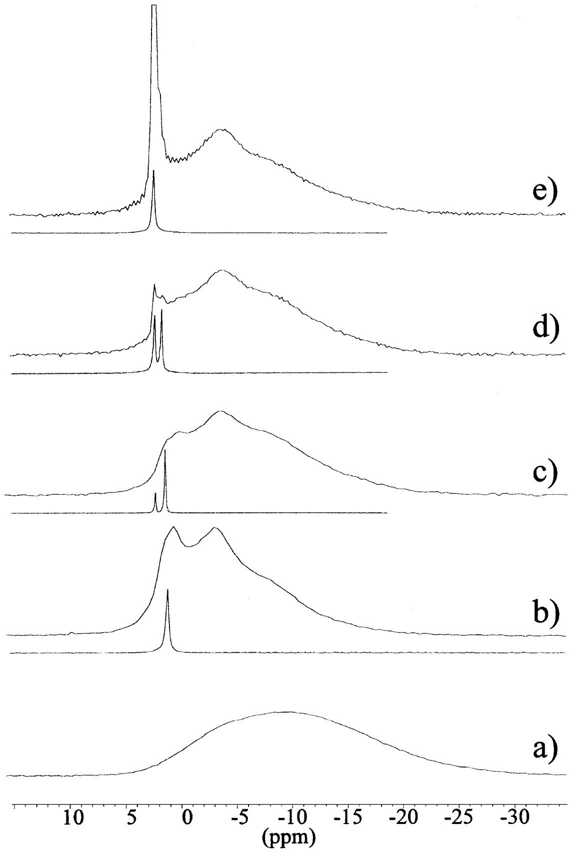


FIG. 5. ^{31}P MAS NMR spectra of one dried and of several wet coimpregnated catalysts together with the ^{31}P NMR spectra of corresponding impregnation solutions. (a) Dried P(2)/γ-Al_2O_3; (b) P(2)/γ-Al_2O_3; (c) [Mo(4)P(2)]/γ-Al_2O_3; (d) [Mo(8)P(2)]/γ-Al_2O_3; (e) [Mo(12)P(2)]/γ-Al_2O_3.

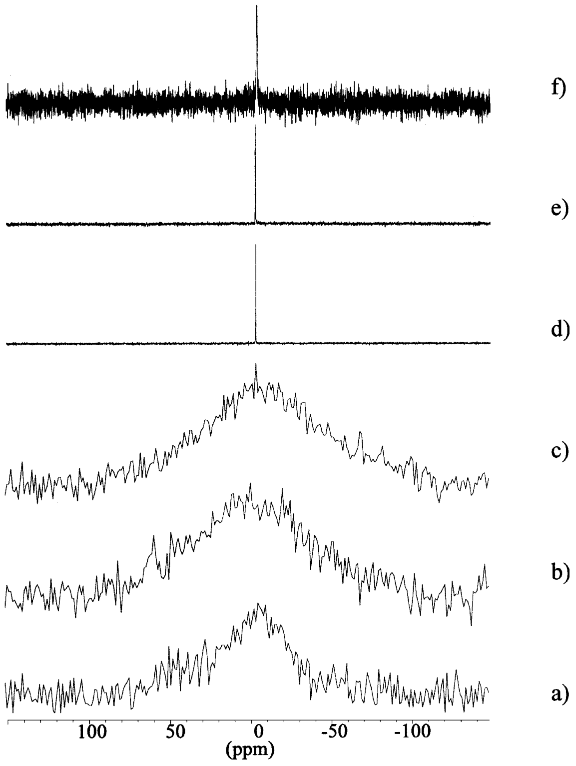
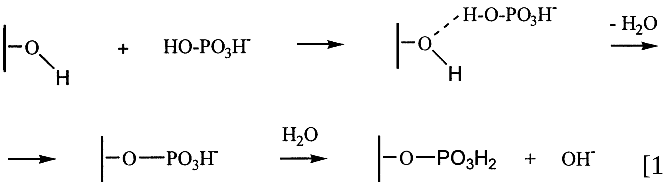


FIG. 4. ^{95}Mo NMR spectra of solutions used for coimpregnation; composition and pH of (a–f) are the same as those in Figs. 2b–2g, respectively.



$$|\!-\!OH + HO\text{-}PO_3H^- \longrightarrow |\!-\!O(H)\cdots H\text{-}O\text{-}PO_3H^- \xrightarrow{-H_2O} |\!-\!O\!-\!PO_3H^- \xrightarrow{H_2O} |\!-\!O\!-\!PO_3H_2 + OH^-$$ [1]

Instead of a proton a NH_4^+ group could be attached to the phosphate group as well. Similar mechanisms would be involved in the reaction of a phosphate with two hydroxyls or of a diphosphate with neighboring OH groups. Proton NMR (20) and IR measurements (6, 7) showed that at the loading applied in this study neutral or acidic surface OH groups are affected by phosphate adsorption as well. The mechanism for this reaction is not yet known.

The broad signal due to chemisorbed mono- and polyphosphates and the signal at −3.7 ppm, due to diphosphates or doubly bonded phosphates which are only physisorbed, are not only observed in the P(2)/γ-Al_2O_3 sample, but in the coimpregnated [Mo(x)P(2)]/γ-Al_2O_3 samples as well. In the spectra of the [Mo(8)P(2)]/γ-Al_2O_3 and [Mo(12)P(2)]/γ-Al_2O_3 samples with high molybdenum loading two additional signals at 1.5–2.2 ppm are observed which are much narrower than the signal of the P(2)/γ-Al_2O_3 sample in the same region. These two signals resemble those of the impregnation solutions. The overall loading of these two coimpregnated samples is higher than the loading which would correspond to monolayer coverage of the alumina surface, suggesting that the narrow signals are due to compounds which are not adsorbed on the surface but still in solution. As mentioned above, some solution spectra have been measured under the same conditions as the solid state spectra, so that we know that solution compounds are detectable under these conditions. The slightly larger width of the signals found in the catalysts compared to the solution signals may result from a lifetime broadening due to rapid exchange between free and adsorbed anions (12). Evidence for this explanation is presented by the CPMAS results. In the ^1H-^{31}P CPMAS spectrum of the [Mo(12)P(2)]/γ-Al_2O_3 catalyst only a small signal at 2.2 ppm is observed (Fig. 6b). Since no CPMAS signal was detected in the corresponding impregnation solution under the same measurement conditions, we assume that a small part of the 2.2 ppm signal in the single pulse spectrum of the wet impregnated sample must be due to an adsorbed (probably physisorbed) compound, whereas the largest part is due to a compound in solution.

The two solution signals of the [Mo(8)P(2)]/γ-Al_2O_3 sample are found at the same positions as the signals of the corresponding impregnation solution, but with a different intensity ratio (Fig. 5d). The downfield signal of the freshly impregnated catalyst is relatively more intensive. In solution this signal was assigned to $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions, and the whole amount of molybdenum and about half of the phosphorus was contained in these complexes. After contact with alumina most of the phosphorus is adsorbed as mono- or polyphosphates on the surface. This indicates that the diphosphopentamolybdate complexes decompose during the adsorption process. The decomposition is probably induced by an increase of the pH of the solution after contact with the γ-Al_2O_3 surface (9). In the ^{31}P NMR spectra of the impregnation liquids it was observed that a pH increase leads to such a decomposition (see above). As a consequence of the decomposition of $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions mono- or polymolybdates must have been formed as well. Van Veen *et al.* (6) and Cheng and Luthra (9) also reported the decomposition of diphosphopentamolybdate during impregnation on a γ-Al_2O_3 support. In addition, Cheng and Luthra observed that monomolybdate stayed in solution, but could not detect phosphorus compounds. A possible explanation could be a lower pH of their solutions since they used phosphoric acid instead of $NH_4H_2PO_4$ for the preparation of the $H_xP_2Mo_5O_{23}^{(6-x)-}$ solution. This might lead to a stronger adsorption of phosphates, as was reported from a comparison of a phosphoric acid with a $NH_4H_2PO_4$ solution (6). Whether the decomposition of the diphosphopentamolybdate results in the formation of monomolyb-

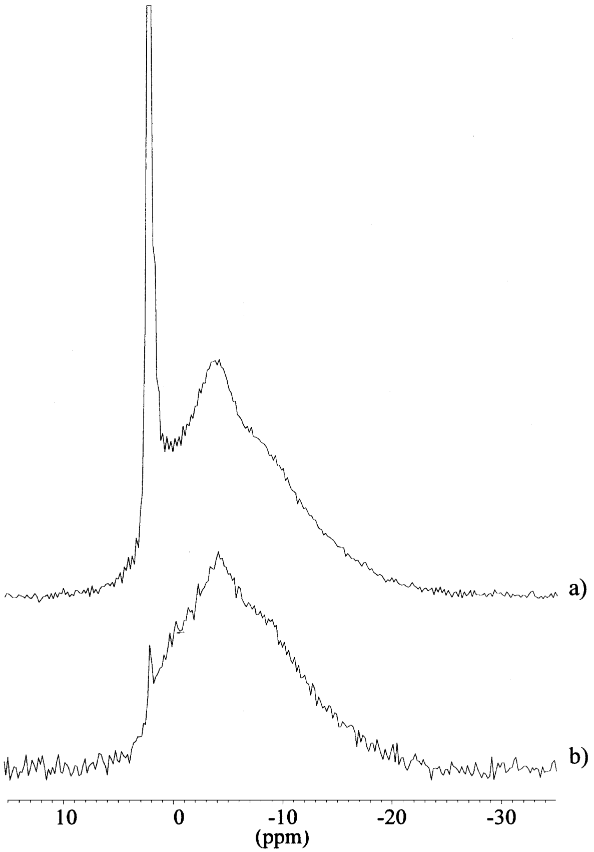


FIG. 6. ^{31}P MAS NMR spectrum (a) and ^1H-^{31}P CPMAS NMR spectrum (b) of wet impregnated [Mo(12)P(2)]/γ-Al_2O_3.

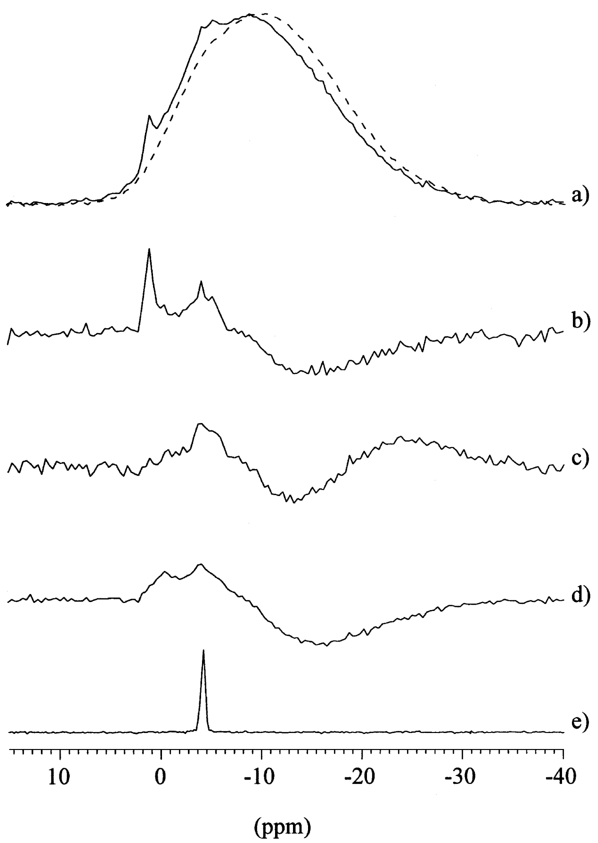


FIG. 7. (a) ^{31}P MAS NMR spectra of wet impregnated Mo(12)P(2)/γ-Al_2O_3 (solid line) and dried P(2)/γ-Al_2O_3 (dashed line); (b) difference between the two spectra in (a); (c) difference between wet impregnated Mo(8)P(2)/γ-Al_2O_3 and dried P(2)/γ-Al_2O_3; (d) difference between wet impregnated Mo(4)P(2)/γ-Al_2O_3 and dried P(2)/γ-Al_2O_3; (e) ^{31}P MAS NMR spectrum of $H_3PMo_{12}O_{40}$; the spectra are on different scales.

date, as observed by Cheng and Luthra, or in the formation of heptamolybdate as proposed by van Veen *et al.* (Eq. [6] in Ref. 6) depends on the initial and final pH of the impregnation solution. The initial pH of the solutions used in our study was rather high (≈6). When the decomposition is initiated by an exchange mechanism with basic surface hydroxyls the pH will increase. As shown above, an increase of the solution pH from about 6 to about 7.7 leads to the formation of monomolybdate. Therefore it can be expected that in the pores of γ-Al_2O_3 monomolybdates were formed as well.

The signal at −3.7 ppm in the three coimpregnated samples is slightly broader than in the P(2)/γ-Al_2O_3 sample. In the same spectral region the resonance of solid $H_3PMo_{12}O_{40}$ is observed (Fig. 7e). Therefore it cannot be excluded that in the coimpregnated samples (but not in the P(2)/γ-Al_2O_3 sample) the −3.7 ppm signal is not due only to physisorbed phosphates, but also due to compounds which have some structural similarity with the Keggin anion or at least P–O–Mo bonding (21). After drying only the broad signal due to chemisorbed compounds remains. It is somewhat more broadened to the upfield site, indicating enhanced formation of polyphosphates (or amorphous $AlPO_4$). No specific signal of P–Mo compounds can be found after drying. P–Mo compounds which still exist in the pore-filling solution or as physisorbed compounds during the impregnation step decompose at last during the drying step.

Wet Sequentially Impregnated Catalysts

Figure 8 shows the spectra of several sequentially impregnated Mo–P/γ-Al_2O_3 catalysts immediately after the last impregnation step, together with the spectrum of P(2)/γ-Al_2O_3 after drying (top spectrum) and the spectrum of the freshly impregnated Mo(12)*P(2)/γ-Al_2O_3 sample which was calcined after the impregnation of phosphorus. The latter spectrum (Fig. 8b) consists of only one broad line ranging from 5 to −33 ppm. The upfield tail relative to the spectrum of the P(2)/γ-Al_2O_3 sample suggests that besides chemisorbed mono- and polyphosphate also some amorphous $AlPO_4$ has been formed after calcination (19). No physisorbed phosphorus-containing compounds or compounds in solution are observed, however. The spectrum is the same as that after calcination of the P(2)/γ-Al_2O_3 sample. The interaction between phosphate ions and the alumina surface after calcination is so strong that no changes of the phosphate structure and distribution occur during the second impregnation with Mo. This does not mean that changes are excluded during the following drying and calcination steps of such a catalyst.

Some changes can be observed in the spectra of the Mo(x)P(2)/γ-Al_2O_3 samples (Figs. 8c–8e) taken immediately after the last impregnation step compared to the dried P(2)/γ-Al_2O_3 sample (Fig. 8a). The spectrum of the sample with the highest Mo loading (Mo(12)P(2)/γ-Al_2O_3) has a small narrow signal at 1.4 ppm. The spectra of all three samples contain the broad signal ranging from 5 to −25 ppm and a shoulder at about −4 ppm. In Fig. 7 the difference spectra between the dried P(2)/γ-Al_2O_3 sample and the Mo(x)P(2)/γ-Al_2O_3 samples are displayed, together with the spectrum of $H_3PMo_{12}O_{40}$ for comparison. A positive signal in the difference spectra means that this signal is less strong or does not exist in the P(2)/γ-Al_2O_3 sample. A negative signal indicates that the intensity at this frequency was reduced by the impregnation with a molybdate solution. Positive signals are found at 1.4 ppm for the Mo(12)P(2)/γ-Al_2O_3 sample and at about −4 ppm in all three samples, negative signals are found for parts of the broad signal, while in the Mo(8)P(2)/γ-Al_2O_3 sample an additional positive signal at the upfield tail of the broad peak is found. It can be concluded that during the second impregnation of the catalysts with a molybdate solution changes in the type and the dispersion of the phosphates occur. Assuming that the signal assignment for the coimpregnated samples is valid in this case too, it can be concluded

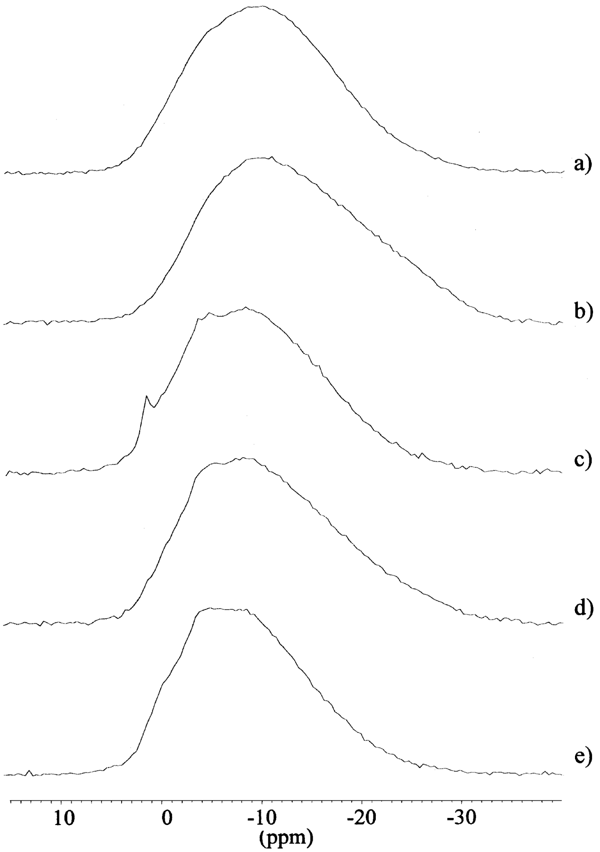


FIG. 8. ^{31}P MAS NMR spectra of several wet impregnated samples and of one dried sample: (a) dried P(2)/γ-Al_2O_3; (b) Mo(12)*P(2)/γ-Al_2O_3; (c) Mo(12)P(2)/γ-Al_2O_3; (d) Mo(8)P(2)/γ-Al_2O_3; (e) Mo(4)P(2)/γ-Al_2O_3.

that parts of the chemisorbed mono- and polyphosphates become disconnected from the surface in the presence of a molybdenum-containing solution. In all three samples physisorbed compounds are found instead. As mentioned above, the signal at about −4 ppm may be due either to physisorbed monophosphate with a double bond to the surface, to physisorbed diphosphates, or to compounds having P−O−Mo bonds. In the Mo(12)P(2)/γ-Al_2O_3 sample some physisorbed monophosphate or monophosphate driven back into solution is observed (narrow signal at 1.4 ppm). This clearly shows that a competition between molybdate and phosphate for surface adsorption sites exists, even when phosphate has been impregnated first. It cannot be concluded whether monophosphate or polyphosphate is more affected by the presence of the molybdate solution.

Van Veen *et al.* investigated the adsorption of molybdates on a phosphated alumina surface as well (6). They concluded from TPR results of calcined samples that heptamolybdate anions react with P–OH groups to form PMo_7 or P_2Mo_5 species. No reaction with remaining basic Al–OH groups was observed. This was independent of the phosphate precursor, being either a H_3PO_4 or a $NH_4H_2PO_4$ solution. Such reaction of heptamolybdate with P–OH groups may in fact occur on our samples too, since the signal at −4 ppm may be (partly) due to species with a P–O–Mo bonding. Furthermore, after calcination of the Mo(12)P(2)/γ-Al_2O_3 sample a distinct narrow signal at −4.0 ppm due to $H_3PMo_{12}O_{40}$ was observed. No similar signal was observed in the other samples. Van Veen *et al.* did not report such signals in their ^{31}P NMR spectra, either. Moreover, proton NMR studies of our samples after dehydration (20) showed that basic Al–OH groups which remained after $H_2PO_4^-$ adsorption were removed by the subsequent molybdate adsorption. The number of P–OH groups was reduced, too. Therefore we do not think that reaction with P–OH groups is the only adsorption mechanism of molybdates with a phosphated alumina surface. The fact that van Veen *et al.* did not observe reaction with basic Al–OH groups may be explained by pore plugging due to $AlPO_4$ formation, especially when H_3PO_4 has been used for phosphate adsorption.

The Mo(*x*)P(2)/γ-Al_2O_3 samples were prepared by impregnation with a $NH_4H_2PO_4$ solution, drying, and a second impregnation with a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution. The ^{31}P NMR results showed that during the second impregnation some phosphate ions were present in the impregnation solution. It is not clear what caused the desorption of phosphorus compounds into solution. The results for the coimpregnated samples established that diphosphopentamolybdate remained preferentially in solution. Such P_2Mo_5 compounds may be formed by reaction of molybdates with P–OH groups on the stepwise impregnated samples as well, but if such species desorb afterward they should be detected as a solution compound. A hydrolysis of some monophosphate during the second impregnation is a more likely explanation for the desorption of phosphorus compounds into solution. This removal of phosphate groups from the surface makes more sites available for molybdate adsorption and reduces the danger of pore plugging. This behavior may depend on the pH of the impregnation solutions, especially of the phosphate solution. In this study the $NH_4H_2PO_4$ solution was used at its natural pH, that is at about 3.5. Acidified solutions of $NH_4H_2PO_4$ may behave more similar to phosphoric acid solutions, resulting in dissolution of alumina which precipitates as $AlPO_4$ during drying or at least resulting in the formation of more stable surface compounds which are not hydrolyzed during the second impregnation. It is clearly seen that calcination of the phosphated alumina before the second impregnation leads to the formation of more stable mono- and polyphosphates; even some $AlPO_4$ is formed. This may be connected to the removal of ammonia from the phosphate groups and to a redistribution of the phosphate groups during the calcination. Although no ^{31}P NMR evidence was found for the formation of P–Mo species in the freshly impregnated Mo(*x*)*P(2)/γ-Al_2O_3 samples, nor for the formation of

P–Mo species in the dried or calcined samples, a P–O–Mo interaction cannot be excluded, since a removal of P–OH groups after Mo adsorption was observed by ^{31}H NMR (20).

CONCLUSIONS

It has been shown that large differences in the distribution and structure of phosphorus compounds exist during the last impregnation step of Mo–P/γ-Al_2O_3 catalysts when different impregnation methods are applied. This is related in part to the use of $NH_4H_2PO_4$ instead of H_3PO_4 solutions for P impregnation.

As a consequence, after impregnation of γ-Al_2O_3 with a solution containing only phosphorus chemisorbed phosphates and physisorbed intermediates, probably hydrogen bonded, were observed. In the corresponding impregnation solution only $H_yPO_4^{(3-y)-}$ ions were detected.

Solutions used for coimpregnation contained $H_yPO_4^{(3-y)-}$ ions as well as $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions. During coimpregnation some of the diphosphopentamolybdate ions decomposed; as a result, these ions and the phosphate ions had to compete with molybdate ions for surface adsorption sites. The adsorption of molybdate ions seemed to be stronger. Therefore $H_xP_2Mo_5O_{23}^{(6-x)-}$ ions and to a lower degree $H_yPO_4^{(3-y)-}$ ions could be observed in the pore-filling solution during the coimpregnation. Furthermore physisorbed intermediates, probably hydrogen bonded, were observed. Some Mo–P compounds may have been present as well. Nevertheless, chemisorbed phosphates contained most of the phosphorus.

Physisorbed intermediates or some Mo–P compounds were also detected during the second impregnation (with Mo) of catalysts which were stepwise impregnated (P first) without a calcination between the first and the second impregnation step. Some phosphates even desorbed back into solution, thus indicating a stronger interaction of molybdate ions with the alumina surface.

Only in catalysts which were calcined after the impregnation with a phosphorus solution did the phosphates and some $AlPO_4$ remain stable; their structure or connection to the surface in the presence of the Mo-containing solution applied in the second impregnation step did not change.

Thus by changing the impregnation procedure and by using phosphate salts instead of H_3PO_4 it is possible to influence the P and Mo distribution.

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