

NMR Study of the Adsorption of Phosphomolybdates on Alumina

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Received March 23, 1987; revised August 18, 1987

The adsorption of pentamolybdodiphosphate, 12-molybdophosphate and dimeric 9-molybdophosphate on γ -alumina during incipient wetness impregnation was studied by molybdenum-95 and phosphorus-31 NMR. Pentamolybdodiphosphate decomposes to phosphate and molybdate (MoO_4^{2-}) upon contact with the alumina. The phosphate adsorbs preferentially, giving the catalyst a phosphorus-rich shell and a molybdenum-rich core. The decomposition of pentamolybdodiphosphate can be inhibited by the addition of excess phosphate. The 12-molybdophosphate and the dimeric 9-molybdophosphate adsorb on the alumina intact. Thus, a catalyst impregnated with these compounds has a uniform phosphorus-to-molybdenum ratio throughout. © 1988 Academic Press, Inc.

INTRODUCTION

Many commercial cobalt-molybdenum and nickel-molybdenum hydrotreating catalysts contain a small amount (up to 5 wt%) of phosphorus (1-4). The promotional effect of phosphorus in desulfurization (5), and denitrogenation (6, 7) have been documented. Furthermore, phosphorus has the beneficial effect of increasing the solubility and stability of the molybdenum-containing impregnation solutions (8). For instance, while the solubility of ammonium heptamolybdate in water at room temperature is 21 wt% Mo, the solubility of 12-molybdophosphoric acid in water is 44 wt% Mo (9). While concentrated molybdate solutions tend to become turbid in a matter of hours, phosphomolybdate solutions are stable for several months. Numerous methods of preparing phosphomolybdate impregnation solutions have been disclosed in the patent literature (1-4).

Although the adsorption of molybdates on alumina has been studied by several investigators (10-14), the adsorption of phosphomolybdates on alumina has received little attention. Gishti *et al.* (15) studied the competitive adsorption between molybdates and phosphates on alumina, but they

failed to consider the interaction of the phosphomolybdate anions, which would be formed in the solution, with the support. In this paper, we report on the use of molybdenum-95 NMR and phosphorus-31 NMR to study the adsorption of phosphomolybdates on alumina during incipient wetness impregnation. We had previously used the NMR method to study the adsorption of molybdates on alumina (16).

EXPERIMENTAL METHODS

Reagent-grade ammonium heptamolybdate (ACS certified) was obtained from Fischer Scientific. Molybdenum trioxide and 12-molybdophosphoric acid were obtained from Aldrich. Concentrated phosphoric acid (85 wt%) was obtained from Baker Chemical. These reagents were used without further purification. The dimeric 9-molybdophosphate, $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$, and the dimeric 9-molybdophosphoric acid, $\text{H}_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$, were prepared according to the procedures of Tsigdinos (17).

The alumina used in the NMR study was obtained by crushing Davison's 1.6-mm-diameter γ -alumina extrudates (499-34-1A) into 20-40 mesh particles and calcining the particles for 2 h in air at 977 K. The alumina had a BET surface area of $190 \text{ m}^2 \text{ g}^{-1}$ and a

water pore volume of $0.96 \text{ cm}^3 \text{ g}^{-1}$. The 20–40 mesh alumina particles were impregnated to 95% incipient wetness. Details of the impregnation method were given in an earlier paper (16). All samples were prepared to give a MoO_3 loading of 8 wt%. The NMR study was carried out on a Bruker 400 AM spectrometer. Molybdenum-95 NMR spectra were obtained at 26.5 MHz with 20-mm sample tubes. Phosphorus-31 NMR spectra were obtained at 168 MHz with 10-mm sample tubes.

After the adsorption equilibrium had been established ($>18 \text{ h}$), deionized water was added to the impregnated alumina to form a slurry. The pH was measured and corrected for the dilution. This was taken as the final pH in the pores.

In addition, 3.2-mm-diameter alumina beads (Davison HGSA) were used in the

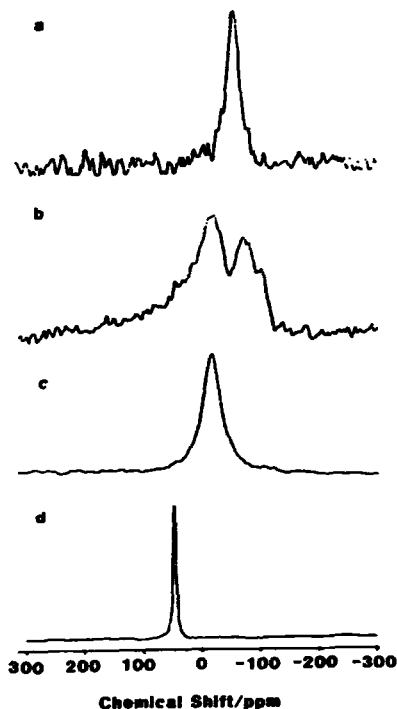


FIG. 1. Molybdenum-95 NMR spectra of phosphomolybdates. (a) 12-molybdophosphoric acid; (b) dimeric 9-molybdophosphoric acid; (c) pentamolybdodiphosphate; (d) ammonium heptamolybdate. Chemical shifts are referenced to $2 \text{ mol dm}^{-3} \text{ Na}_2\text{MoO}_4$.

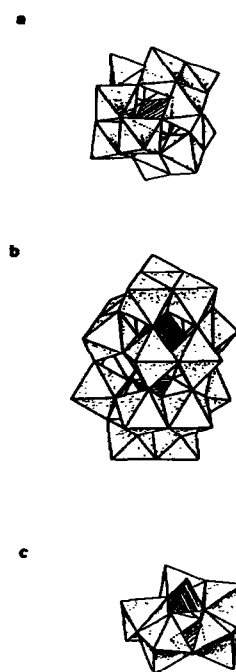


FIG. 2. Structures of (a) $\text{PMo}_{12}\text{O}_{40}^{3-}$; (b) $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$; (c) $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$.

electron microprobe studies. The alumina beads had a BET surface of $190 \text{ m}^2 \text{ g}^{-1}$ and a water pore volume of $1.1 \text{ cm}^3 \text{ g}^{-1}$. The alumina beads were impregnated to incipient wetness by spraying the solution with an atomizer. As with the NMR experiments, the beads were impregnated to give an 8 wt% MoO_3 loading. The elemental profiles of Al, Mo, and P were taken on a Cameca Electron Microprobe. The beads were first cut in half, mounted on an epoxy slide, and polished before being scanned under the electron beam.

RESULTS AND DISCUSSION

The molybdenum-95 NMR spectra of ammonium heptamolybdate and various phosphomolybdates are shown in Fig. 1. The structures of the phosphomolybdates are shown in Fig. 2. The chemical shifts are referenced to a 2 mol dm^{-3} sodium molybdate solution. The spectrum of 12-molybdophosphoric acid $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ is character-

ized by a single peak at a chemical shift of -59 ppm. The single peak is expected. As shown in Fig. 2a, all of the molybdenum atoms in 12-molybdophosphoric acid are equivalent. The spectrum of the dimeric 9-molybdophosphoric acid consists of two broad peaks centered around chemical shift values of -22 and -68 ppm. This is also as expected since in $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$ there are two types of molybdenum atoms, 6 in the capping position and 12 in the equatorial position, as shown in Fig. 2b. Pentamolybdodiphosphate, $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$, which is formed in a solution of ammonium heptamolybdate and phosphoric acid, is characterized by a single peak with a chemical shift of -15 ppm. Heptamolybdate, $\text{Mo}_7\text{O}_{24}^{6-}$, has a chemical shift of 51.6 ppm with respect to MoO_4^{2-} .

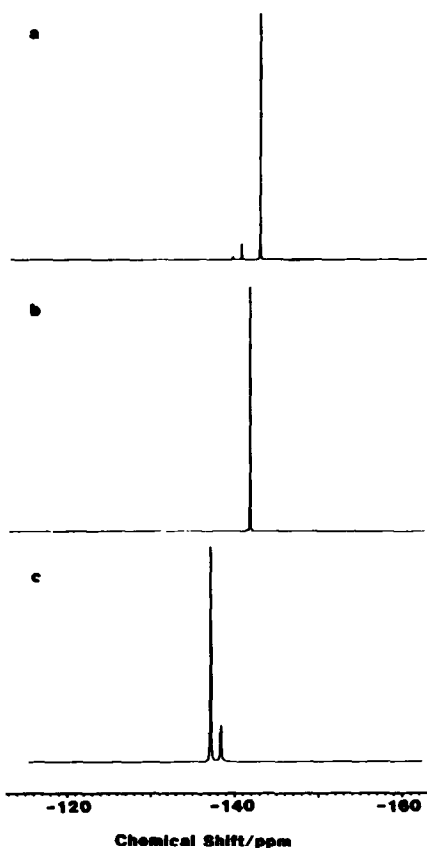


FIG. 3. Phosphorus-31 NMR spectra of (a) $\text{H}_3\text{PMo}_{12}\text{O}_{40}$; (b) $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$; (c) mixture of ammonium heptamolybdate and phosphoric acid, $\text{P}/\text{Mo} = 0.4$.

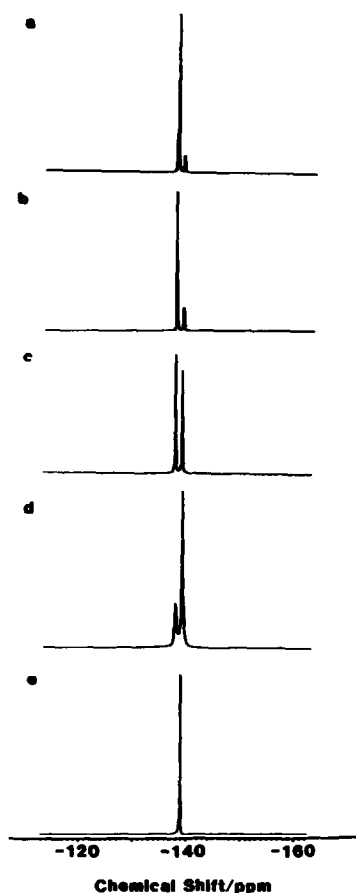
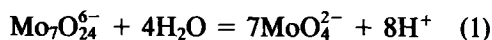


FIG. 4. Phosphorus-31 NMR spectra of ammonium heptamolybdate-phosphoric acid solutions. (a) $\text{P}/\text{Mo} = 0.4$; (b) $\text{P}/\text{Mo} = 0.5$; (c) $\text{P}/\text{Mo} = 0.68$; (d) $\text{P}/\text{Mo} = 1.0$; (e) H_3PO_4 .

The equilibrium between $\text{Mo}_7\text{O}_{24}^{6-}$ and MoO_4^{2-} ,

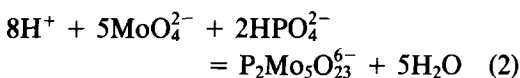


is established rapidly (16).

The phosphorus-31 NMR spectra of 12-molybdophosphoric acid, $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$, and pentamolybdodiphosphate are shown in Fig. 3. The chemical shifts are referenced to a trimethyl phosphite external standard. The 12-molybdophosphoric acid has a chemical shift of -142.1 ppm, the $(\text{NH}_4)_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ has a chemical shift of -141.6 ppm, and the pentamolybdodiphosphate has a chemical shift of -137.4 ppm.

The phosphorus-31 NMR spectra of am-

monium heptamolybdate– H_3PO_4 solutions of varying Mo to P ratio are shown in Fig. 4. The peak at a chemical shift of -137.4 ppm is due to the phosphorus in $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$, and that at a chemical shift of -138.9 ppm is due to the phosphate. In a solution containing the stoichiometric P/Mo ratio of 0.4 (Fig. 4a), a small amount of phosphorus remains in the form of phosphate. This suggests that there exists an equilibrium between phosphate and molybdate as shown in Eq. (2).



This is in accord with the results of Pettersson (18), who has measured the equilibrium constant for the above reaction.

The time-dependent molybdenum-95 NMR spectra of ammonium heptamolybdate– H_3PO_4 solution (P/Mo = 0.4) impregnated to 95% incipient wetness on alumina is shown in Fig. 5. Within the first several minutes after impregnation, the signal of MoO_4^{2-} was observed, and the intensity of this signal increased with time. This indicated that $\text{P}_2\text{Mo}_5\text{O}_{23}^{6-}$ was decomposing into simple molybdate, MoO_4^{2-} , and phosphate, as shown by the reverse of Eq. (2). Table 1 shows that although the initial pH of this solution was 3.52, the pH of the solution after impregnation was 6.26. The rise in pH is most likely due to the release of hydroxyls from the alumina surface upon adsorption by ion-exchange of phosphate, molybdate, and phosphomolybdate anions. The ion-exchange mechanism has been pro-

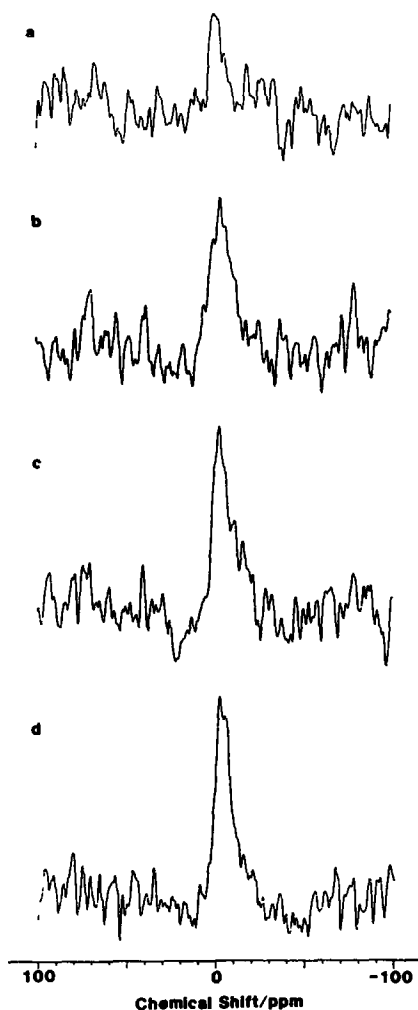


FIG. 5. Molybdenum-95 NMR spectra of a solution of ammonium heptamolybdate and phosphoric acid (P/Mo = 0.4) in the pores of the alumina as a function of time after impregnation. (a) 1800 s; (b) 7200 s; (c) 10,800 s; (d) 18,000 s. A line broadening of 50 Hz has been applied.

TABLE I
Comparison of Initial and Final pH Values of Impregnation Solutions

	Ammonium heptamolybdate + H_3PO_4				
	H_2O	P/Mo = 1	P/Mo = 0.4	$\text{H}_3\text{PMO}_{12}\text{O}_{40}$	$(\text{NH}_4)_6\text{P}_2\text{MO}_{18}\text{O}_{62}$
Initial pH	7.00	1.73	3.52	1.48	3.51
Final pH	8.36	5.63	6.26	4.62	4.86

Note. All solutions contain 6.36×10^{-4} mol Mo cm^{-3} .

posed by Iannibello and Mitchell (12) for the adsorption of MoO_4^{2-} on alumina. A rise in pH would push the equilibrium of Eq. (2) to the left and cause the decomposition of pentamolybdodiphosphate.

The decomposition of pentamolybdodiphosphate is aided by the strong interaction between the phosphate anion and the alumina. Phosphorus-31 NMR of the impregnated sample showed no evidence of any phosphorus species remaining in the pores. Furthermore, no phosphorus-31 NMR signal was observed when the alumina was impregnated with a solution containing only phosphoric acid. This indicated that all of the phosphate had adsorbed on the alumina. The strong interaction between phosphate and alumina has been attributed to the formation of the very stable aluminum phosphate (19). Indeed, Gishti *et al.* (15) have shown by adsorption chromatography that phosphate anions cannot be eluted when alumina is used as an adsorbent. Furthermore, when alumina is coimpregnated with a solution of phosphate and molybdate, there is complete adsorption of the phosphate which inhibits the

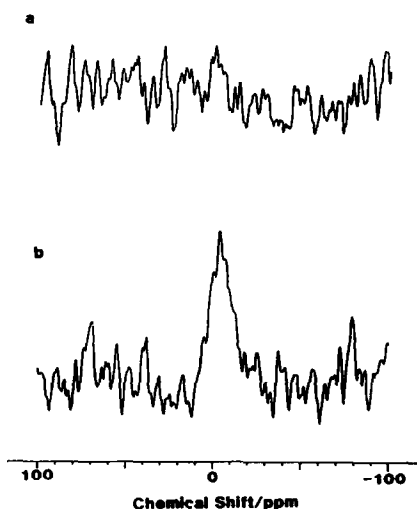


FIG. 6. Molybdenum-95 NMR spectra of solutions of ammonium heptamolybdate and phosphoric acid in the pores of alumina 7200 s after impregnation. (a) $\text{P}/\text{Mo} = 1$; (b) $\text{P}/\text{Mo} = 0.4$. A line broadening of 50 Hz has been applied.

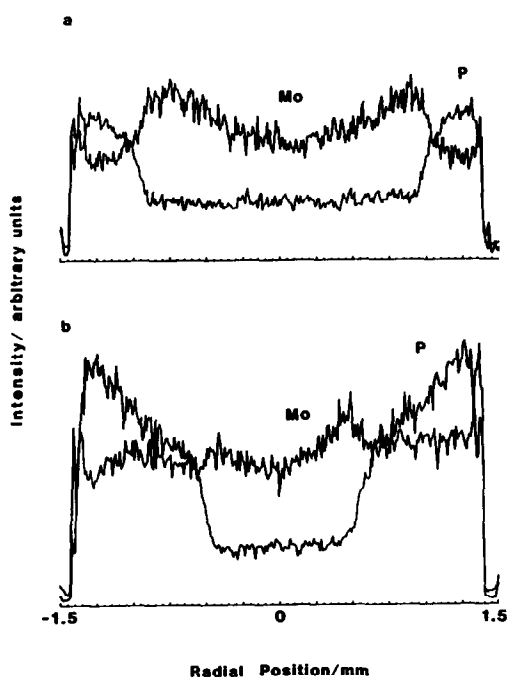


FIG. 7. Electron microprobe profiles of Mo and P on 3.2-mm-diameter alumina spheres impregnated with solutions of ammonium heptamolybdate and H_3PO_4 . (a) $\text{P}/\text{Mo} = 0.4$; (b) $\text{P}/\text{Mo} = 1$.

adsorption of molybdate. This is in agreement with our NMR results.

At a higher phosphorus loading ($\text{P}/\text{Mo} = 1$), molybdenum-95 NMR did not show the presence of any soluble molybdenum species in the pores of the alumina (Fig. 6). Furthermore, as with the case of P/Mo molar ratio of 0.4, there was no signal from phosphorus-31 NMR. This suggested that all of the phosphate, molybdate, and phosphomolybdates had adsorbed on the alumina. Table 1 shows that the final pH of this impregnation solution, 5.63, is lower than that for the solution with a P/Mo ratio of 0.4. The lower pH, which was due to the greater amount of phosphoric acid used to prepare the impregnation solution (Fig. 4d), would favor greater adsorption of the anions on the alumina (16, 20).

The elemental profiles as determined by electron microprobe of the impregnated beads are shown in Fig. 7. In the case of

$P/Mo = 0.4$, the phosphorus is more concentrated at the edge of the bead while the molybdenum is more concentrated at the center. This confirms the NMR results, which show that some of the $P_2Mo_5O_{23}^{6-}$ decomposes to phosphate and molybdate and that the phosphate adsorbs more strongly on alumina than does the molybdate. In the case of $P/Mo = 1$, the phosphorus is again more concentrated at the edge of the bead. However, the concentration of molybdenum is mostly uniform throughout the pellet. This suggests that at a higher concentration of phosphate there is less decomposition of $P_2Mo_5O_{23}^{6-}$ and that most of the $P_2Mo_5O_{23}^{6-}$ anions are adsorbing intact. This is made possible by the excess phosphate which pushes the equilibrium of Eq. (2) to the right in favor of $P_2Mo_5O_{23}^{6-}$. The P-rich shell is due to adsorption of the excess phosphate. The greater adsorption is due to the lower pH of the solution in the pores. This agrees well with the fact that no molybdenum species was observed by NMR during impregnation.

In contrast to the behavior of pentamolybdodiphosphate are those of 12-molybdophosphate and dimeric 9-molybdophosphate. Molybdenum-95 and phosphorus-31 NMR did not show the presence of any soluble Mo- or P-containing species in the pores of the alumina. This is not surprising as the final pH of these two impregnation solutions are very low (Table 1). Thus, we expect the anionic species to be more strongly adsorbed on the surface of the alumina. Figure 8 shows the electron microprobe scans of 3.2-mm alumina beads impregnated with solutions of $H_3PMo_{12}O_{40}$ and $(NH_4)_6P_2Mo_{18}O_{62}$. The elemental profiles of Mo and P in these samples are identical, suggesting that the precursors $P_2Mo_{12}O_{40}^{3-}$ and $P_2Mo_{18}O_{62}^{6-}$ adsorb on the alumina intact.

The difference in the adsorption behavior between $P_2Mo_5O_{23}^{6-}$ and that of $PMo_{12}O_{40}^{3-}$ and $P_2Mo_{18}O_{62}^{6-}$ may be understood from examining their molecular structure. As shown in Fig. 2c, the two phosphate groups

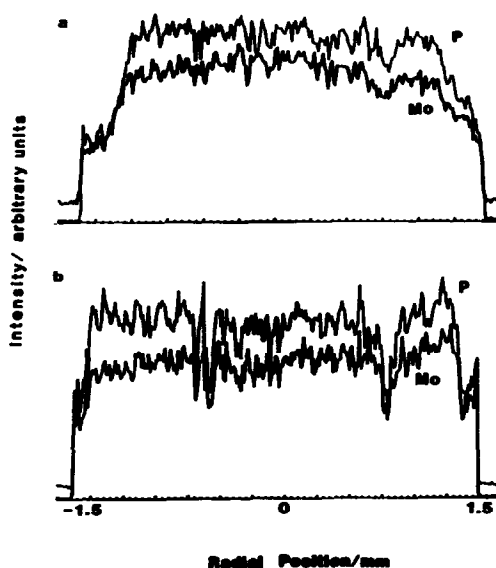


FIG. 8. Electron microprobe profiles of Mo and P on 3.2-mm-diameter alumina spheres impregnated with solutions of (a) $H_3PMo_{12}O_{40}$ and (b) $(NH_4)_6P_2Mo_{18}O_{62}$.

in $P_2Mo_5O_{23}^{6-}$ located above and below the planar 5-member ring of MoO_6 octahedra are free to interact with the alumina. Reaction between the phosphate and alumina would lead to the break-up of $P_2Mo_5O_{23}^{6-}$. However, the phosphate groups in $PMo_{12}O_{40}^{3-}$ and $P_2Mo_{18}O_{62}^{6-}$ are completely enclosed by a shell of MoO_6 octahedra and are therefore shielded from the alumina surface. Thus, these anions are more stable and adsorb intact on the alumina.

These findings will be useful in the preparation of hydrotreating catalysts of uniform metal distribution and high metal dispersion.

ACKNOWLEDGMENTS

The authors are grateful to K. O. MacFadden for helpful discussions, T. A. Boyer for performing the impregnation experiments, M. A. Peters for the microprobe analysis, and W. R. Grace and Co. for permitting us to publish this work.

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