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Molybdenum-95 NMR Study of the Adsorption of Molybdates on Alumina

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The equilibrium between $Mo_7O_{24}^{6-}$ and MoO_4^{2-}, and the adsorption of molybdates on γ-Al_2O_3 during incipient wetness impregnation were studied by molybdenum-95 NMR spectroscopy. The relative equilibrium concentrations of $Mo_7O_{24}^{6-}$ and MoO_4^{2-} at the pH range of 5.45 to 8.9 were determined. The effects of molybdenum concentration (loadings between 2 and 12 wt% MoO_3) and solution pH (5.45 to 8.9) on adsorption were investigated. The results indicate that $Mo_7O_{24}^{6-}$ decomposes to MoO_4^{2-} within minutes after coming into contact with alumina. The amount of unadsorbed MoO_4^{2-} increases with the pH of the impregnation solution. The results are consistent with the hypothesis that molybdate anions are attracted to the positively charged surface of the alumina and this attraction diminishes as the pH rises toward the isoelectric point of the alumina (pH 8.5).

INTRODUCTION

Molybdena on alumina catalysts have been the subject of numerous investigations. This has been due primarily to the importance of MoO_3/Al_2O_3 as an oxidation catalyst and as a precursor to a desulfurization catalyst. To date, Raman (*1–7*), UV reflectance (*1, 2, 5, 8*), and infrared spectroscopies (*1, 8*) have provided the most detailed information on the molecular nature of supported molybdena on alumina catalysts and the mechanism for the formation of such structures during the impregnation, drying, and calcination stages. However, there is still disagreement over whether the polymolybdates (e.g., $Mo_7O_{24}^{6-}$) present in the typical impregnation solution first dissociate to the monomer (MoO_4^{2-}) before adsorbing, thus forming a monolayer on the alumina surface (*3–5, 9*), or whether the polymolybdates adsorb intact and form molybdena clusters upon drying and calcination (*1, 2, 10*). Part of the reason for disagreement is that the molecular nature of molybdenum in the MoO_3/Al_2O_3 catalyst is strongly dependent on the method of preparation (*11–13*). This has important effects on the activity of these catalysts.

In the past several years our laboratory has been investigating the relationship between catalyst performance and the method of catalyst preparation. In this paper we report on the use of molybdenum-95 NMR spectroscopy to study the adsorption of molybdenum on the surface of γ-alumina. Due to the differences in the chemical shifts of various compounds NMR spectroscopy can differentiate among the species that are present in the system. Another benefit of NMR spectroscopy is that the motional state of the species can be determined from the linewidths and the relaxation times.

Molybdenum-95 is a quadrupolar nucleus with a spin-5/2 and a relatively high natural abundance of 15.8 at.%. It has a relatively small quadrupolar moment ($Q = 0.12 \times 10^{-24}$); therefore, linewidths are acceptably narrow. The fast relaxation rates allow rapid data accumulation.

Recent studies have reported molybdenum-95 NMR chemical shifts of Mo(VI), Mo(IV), Mo(II), and Mo(0) compounds (*14*). In this investigation we have extended the molybdenum-95 NMR work to study chemical phenomena inside the pores of alumina. This is done by ensuring that the total impregnation solution volume is less

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than the pore volume. Molybdenum-95 NMR resonance signals were observed for samples of alumina that have been impregnated with ammonium heptamolybdate solutions at 2, 4, 8, and 12 wt% MoO_3 equivalent loading. For the 8 wt% MoO_3 equivalent loading, the study was carried out at three pH values. To our knowledge this is the first report in which NMR has been used to study the dynamic adsorption process occurring during the preparation of molybdena-on-alumina catalysts.

EXPERIMENTAL METHODS

Materials and Impregnation Procedure

Alumina used in this study was obtained by crushing Davison 1.6-mm γ-alumina extrudates (499-34-1A) into 20- to 40-mesh particles and calcining the particles for 2 h at 977 K in air. The alumina after calcination had a BET surface area of 190 $m^2 g^{-1}$ and a water pore volume of 0.96 $cm^3 g^{-1}$. The ammonium heptamolybdate (ACS certified), obtained from Fisher Scientific, and ammonium hydroxide, obtained from Baker, were used without further purification.

In each experiment, 10 g of alumina was placed in a 120-cm^3 wide-mouth bottle. Ammonium heptamolybdate was dissolved in enough water to obtain a solution with a volume of 9.2 cm^3 (equivalent to 95% of the alumina pore volume). The pH was adjusted by adding NH_4OH to the heptamolybdate solution. The impregnation solution was added to the alumina in three portions. After each addition the bottle was shaken vigorously to obtain a more uniform distribution of the liquid. The impregnated alumina was then transferred to the NMR tube and loaded into the magnet. The volume of the impregnation solutions was less than the pore volume; this ensured that the spectra represented only the molybdenum inside the pores.

After the adsorption equilibrium had been established (>18 h), 10 cm^3 of water was added to the impregnated alumina to form a slurry. The pH of the slurry was measured and corrected for the dilution. This was taken as the final pH in the pores.

Spectroscopy

The molybdenum-95 Fourier transform NMR spectra were obtained at 26.1 MHz on a superconducting Bruker AM-400 spectrometer, using 20-mm NMR tubes. All chemical shifts are reported with respect to an external reference of 2.0 M Na_2MoO_4. Data acquisition parameters were as follows: sweepwidth, 6666 Hz; data points, 4K; digital resolution, 3.3 Hz; pulse width, 48 μs (50° pulse); and pulse repetition rate, 0.31 s. A 500-μs delay was used between the end of each RF pulse and the beginning of data collection. Line broadening factors of 10, 50, and 100 Hz were introduced to improve the signal-to-noise ratio during the Fourier transformation. All spectra represent an average of 1800 scans (10 min) unless otherwise stated.

RESULTS AND DISCUSSION

The molybdenum-95 NMR spectra of a 2 M Na_2MoO_4 solution and 0.095 M solutions of $(NH_4)_6Mo_7O_{24}$ at pH values of 5.45, 6.7, and 8.9 are shown in Fig. 1. At pH 5.45 the predominant species is $Mo_7O_{24}^{6-}$ which is characterized by a broad peak (linewidth, 185 Hz) at a chemical shift of 35 ppm. At pH greater than 6.7 the predominant species is MoO_4^{2-}. At intermediate pH values both $Mo_7O_{24}^{6-}$ and MoO_4^{2-} are observed. The hydrolytic instability of polymolybdate has been well documented. The exchange rate between MoO_4^{2-} and $Mo_7O_{24}^{6-}$ at room temperature is of the order of 10^{-3} s (*15*). This is much slower than the NMR time scale; therefore, the signals of both species are observed.

The linewidth of the MoO_4^{2-} lies in the range of 3 to 150 Hz (Table 1) with the narrowest signal being observed at pH above 8, where the molybdate ion is completely ionized. At that point the electric

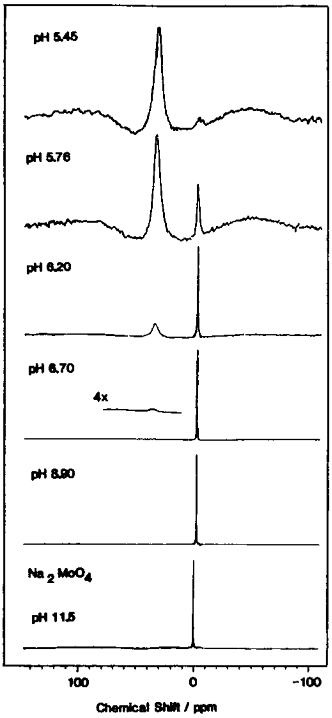

FIG. 1. Molybdenum-95 NMR spectra of molybdate solutions at various pH values. Spectra are referenced to 2 M Na_2MoO_4. An exponential multiplication producing a line broadening of 10 Hz was applied to each FID before Fourier transformation.

TABLE 1

Linewidths of Molybdates as a Function of pH

pH	Linewidth of MoO_4^{2-} (Hz)	Linewidth of $Mo_7O_{24}^{6-}$ (Hz)
5.45	150	185
5.76	60	160
6.00	27	150
6.20	15	150
6.46	13	150
6.70	7	140 ± 5
8.90	3	[a]

[a] No $Mo_7O_{24}^{6-}$ signal was observed.

field gradient is close to zero as a result of the tetrahedral symmetry of the anion. At lower pH the protonation of the anion introduces asymmetry which increases the electric field gradient and causes an increase in the linewidth (*16*). A previous study (*17*) has reported a similar increase in the linewidth with the lowering of pH, although in that study the signals of heptamolybdate and MoO_4^{2-} were not observed at pH 5.4. No apparent change in the linewidth is observed for heptamolybdate for pH greater than 6.0. The linewidth increases from 150 to 185 Hz as the pH is decreased from 6.0 to 5.45. The p*K*a for the protonation of $Mo_7O_{24}^{6-}$ to $HMo_7O_{24}^{5-}$ is 4.3 (*18*); therefore, above pH 5.45 (our experimental condition), greater than 93% of heptamolybdate is in the form of $Mo_7O_{24}^{6-}$. Thus for pH above 5.45, we do not expect a very large variation in the linewidth of the heptamolybdate.

The mole fractions of molybdenum existing in the forms of $Mo_7O_{24}^{6-}$ and MoO_4^{2-} were obtained by integrating the areas under the peaks. The results, shown in Fig. 2, indicate that the equilibrium constant, log *K*, for the reaction

$$7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O \quad (1)$$

is 59. The solid lines of Fig. 2 were obtained by calculation using this value as the equilibrium constant. This is in good agreement

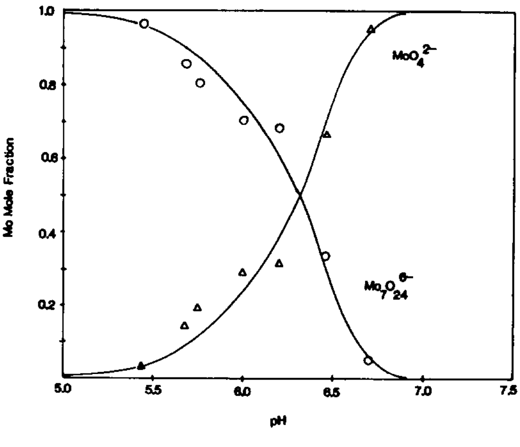

FIG. 2. Equilibrium mole fractions of MoO_4^{2-} and $Mo_7O_{24}^{6-}$ as determined by molybdenum-95 NMR. Solid lines represent calculated values with log *K* = 59 for the equilibrium $7MoO_4^{2-} + 8H^+ = Mo_7O_{24}^{6-} + 4H_2O$.

with the value of 57.7 obtained by Sasaki *et al.* (*19*), using an electrochemical titration method.

Ammonium heptamolybdate solutions containing the equivalent of 2, 4, 8, and 12 wt% MoO_3 were impregnated on γ-alumina. The molybdenum-95 NMR spectra were then acquired at various times after impregnation. The spectra of 4 and 8 wt% MoO_3 impregnations are shown in Fig. 3. In the first few minutes a signal of MoO_4^{2-} was observed. The intensity of the MoO_4^{2-} singal increased slightly with time. This is most evident in the sample with 4 wt% MoO_3. At loadings of 2, 4, and 8 wt% MoO_3 we did not observe any resonance signals of $Mo_7O_{24}^{6-}$. The strong dipolar interactions that exist in the absence of rapid molecular motion increase the linewidth of the adsorbed species. Therefore, adsorbed species show very broad signals. The absence of a heptamolybdate signal indicates that all of the heptamolybdate has either adsorbed on the surface or has decomposed to MoO_4^{2-}.

TABLE 2

Comparison of Initial and Final pH Values, and Molybdenum-95 NMR Linewidth of MoO_4^{2-} in Equilibrium with the Alumina Surface

wt% MoO_3 loading	Initial pH	Final pH	Linewidth (Hz)
2	5.35	7.43	[a]
4	5.40	7.18	330
8	5.45	6.82	280
12	5.50	6.58	230
8	6.70	8.20	114
8	8.90	8.50	104

[a] Insufficient signal to noise.

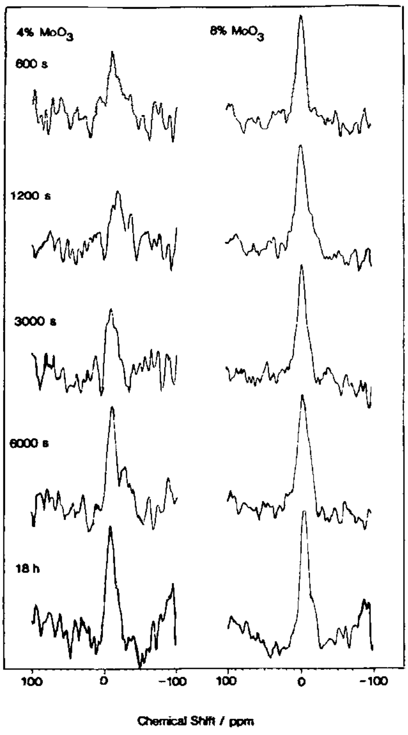

FIG. 3. Molybdenum-95 NMR spectra taken at various times after impregnation on alumina. Spectra are averaged over 1800 scans. An exponential multiplication producing a line broadening of 100 Hz was applied to each FID before Fourier transformation.

As shown in Table 2, the final pH of the impregnation solution tends to rise toward the isoelectric point of the alumina surface (pH 8.5). This is attributable to the equilibrium

$$\text{Al-OH} + H^+ = \text{Al-OH}_2^+ \qquad (2)$$

which gives the alumina surface a large buffering capacity (*13*). The rise in pH causes the equilibrium of Eq. (1) to shift to the left and MoO_4^{2-} to be formed. A possible explanation for the increase in the amount of MoO_4^{2-} in the pores with time is that due to the low initial pH of impregnation there is initially a large amount of adsorption of molybdates, some of which is possibly in the form of $Mo_7O_{24}^{6-}$. However, as the pH increases the surface charge of the alumina decreases, and thus the attraction for the molybdate anions decreases. With time some of the molybdate must desorb back into the solution in the pores so as to satisfy the adsorption equilibrium at the final pH.

The molybdenum-95 NMR spectra of the impregnated samples after 18 h aging in a sealed NMR tube are shown in Fig. 4. The MoO_4^{2-} peak is present in all the samples.

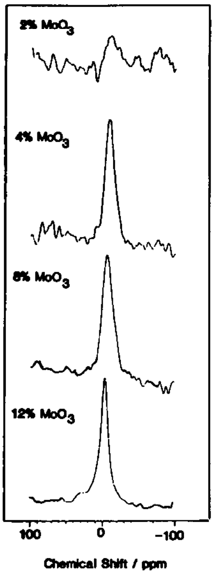

FIG. 4. Effect of molybdenum loading on the molybdenum-95 NMR spectra at >18 h after impregnation. Spectra are averaged over 7200 scans. An exponential multiplication producing a line broadening of 50 Hz was applied to each FID before Fourier transformation.

At the highest loading (12 wt% MoO_3), a small amount of $Mo_7O_{24}^{6-}$ (shoulder at a chemical shift of 35 ppm) is observed. Table 2 shows that the final pH decreases with increasing molybdenum loading. The final pH for the sample with 12 wt% MoO_3 is 6.58. As shown in Fig. 2, at this pH about 15% of the molybdenum would still be in the form of $Mo_7O_{24}^{6-}$. For the samples with lower loadings, the higher final pH values dictate that only MoO_4^{2-} would be present at equilibrium. The amount of unbound molybdate increases with the concentration of molybdate in the initial impregnation solution as evidenced by the increase in the signal to noise as the concentration of molybdate increases. The linewidth decreases from greater than 330 Hz to 230 Hz as one goes from 2 wt% equivalent MoO_3 loading to 12 wt% MoO_3 (Table 2). The linewidth of the MoO_4^{2-} signal in a solution of ammonium heptamolybdate adjusted to pH 6.7, which is close to the final pH of these loadings, was found to be 7 Hz. The increase in the linewidth by more than 200 Hz in all the loadings can be attributed to (1) the exchange occurring between the molybdate in solution and the adsorbed molybdate and (2) the restricted motion of molybdates in the pores of alumina which causes an increase in the reorientational correlation time, and a decrease in the transverse relaxation time (*16*). Since the linewidth increases with a decrease in the amount of loading, the exchange phenomenon is more responsible for an increase in the linewidth.

Figure 5 shows the effect of impregnation pH. As the impregnation pH increases, the intensity of MoO_4^{2-} signal increases, indicating that less of the molybdate is adsorbed. The linewidth becomes narrower, indicating that the molybdate species are less strongly adsorbed on the surface. This suggests that the strength of adsorption

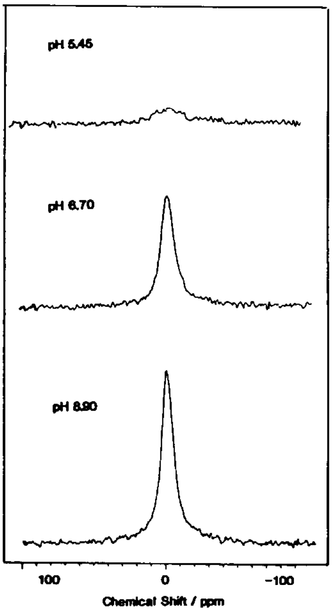

FIG. 5. Effect of initial pH of impregnation solution on the molybdenum-95 NMR spectra at >18 h after impregnation. Spectra are averaged over 1800 scans. An exponential multiplication producing a line broadening of 50 Hz was applied to each FID before Fourier transformation.

decreases as the pH nears that of the isoelectric point of alumina. Our results are in accord with those of Wang and Hall (*2*) and Houalla *et al.* (*20*), which showed higher equilibrium molybdate adsorption on alumina at lower pH and is consistent with D'Aniello's model for adsorption of anions on alumina (*21*).

The picture of molybdenum on alumina catalysts most often proposed is that MoO_3 forms a monolayer on the alumina surface (*9, 22*). Iannibello and Mitchell (*13*) have proposed that the adsorption of molybdate on alumina involves ion exchange of surface hydroxyl groups with MoO_4^{2-}. This was also the conclusion of Jeziorowski and Knozinger (*5*), who further proposed that the ion-exchange adsorption of molybdate caused the local pH within alumina pores to increase, thereby causing $Mo_7O_{24}^{6-}$ to disaggregate to MoO_4^{2-}. Wang and Hall (*2*) have prepared molybdena on alumina samples using an equilibrium adsorption method and characterized them with Raman spectroscopy. They have shown that by carefully controlling the pH, isopolymolybdates ($Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$) can be made to adsorb intact on the alumina surface, and that the actual MoO_3/Al_2O_3 catalyst consists of patches of molybdena with seven or eight Mo atoms per cluster. The MoO_3 monolayer envisioned by earlier workers was found not to exist. These authors argued that the conditions of Jeziorowski and Knozinger's experiments (incipient wetness impregnation and initial pH values of 6 and 11) were unfavorable for adsorption, and the catalyst thus made would be inhomogeneous. Indeed, Kasztelan *et al.* (*10*), who followed the guidelines set forth by Wang and Hall and devised a method of preparing equilibrium adsorption catalysts in a fluidized bed, found that washing the just-impregnated samples with water removed all of the molybdenum from the sample impregnated at pH 11 and only 5% of the molybdenum from the samples impregnated at pH 2 and 7. This indicated that the adsorption of molybdate at a pH greater than the isoelectric point of alumina is weak. Kasztelan *et al.* have shown that upon drying, the unadsorbed MoO_4^{2-} will precipitate and/or polymerize to form bridging species, and upon calcination, these form "free" MoO_3 crystallites. The "free" MoO_3 crystallites are not observed in samples which have been washed after impregnation.

In this study we have prepared catalyst samples by incipient wetness impregnation. We have observed that unadsorbed MoO_4^{2-} is present in the pores under a wide variety of conditions (loading from 2 to 12 wt% MoO_3 and initial pH values from 5.45 to 8.9). The concentration of MoO_4^{2-} in the pores increases with increasing pH of impregnation solution. Drying and calcining of these samples would indeed lead to inhomogeneous molybdate species as suggested by Wang and Hall. Due to the small volume of impregnation solution used, the change in pH when the solution comes into contact with alumina is quite large (Table 2). The increase in pH would shift the equilibrium to favor MoO_4^{2-} as suggested by Jeziorowski and Knozinger. Iannibello and Mitchell (*13*) have shown that catalysts prepared by pore-filling contain a smaller proportion of strongly bound molybdenum than those prepared by equilibrium adsorption. This is consistent with our finding that a substantial fraction of molybdates remain unadsorbed in the pores of catalysts prepared by incipient wetness impregnation.

CONCLUSIONS

We have used molybdenum-95 NMR spectroscopy to study the adsorption of molybdates on alumina during incipient wetness impregnation. The decomposition of $Mo_7O_{24}^{6-}$ to MoO_4^{2-} was observed and was believed to be caused by the increase in the pH of the impregnation solution inside the pores of the alumina. The amount of unadsorbed MoO_4^{2-} increases with the pH of the impregnation solution. This is consistent with the idea that molybdate anions are attracted to the positively charged surface of the alumina and this attraction diminishes as the pH rises toward the isoelectric point of the alumina. Finally, we believe that NMR can be a useful tool for studying the impregnation chemistry inside the pores of catalyst supports.

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