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The Adsorption of Metal Oxyanions on Alumina

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The adsorption of perrhenate, permanganate, molybdate, tungstate, and chromate on alumina was studied at pH 4.5. The effect of nitrate in the impregnation solution on the adsorption of these ions was examined as well as the effect of washing the freshly prepared catalysts. The uptake of perrhenate and permanganate decreased with increasing nitrate in the impregnation solution; the uptake of molybdate, tungstate, and chromate was unaffected. Washing the catalysts almost completely removed perrhenate, permanganate, and chromate, but allowed a significant amount of molybdate and tungstate to remain on the alumina. It is concluded that tungstate and molybdate adsorb on two types of surface sites, producing loosely and tightly bound surface species. From the amounts of molybdate and tungstate adsorbed, and from EXAFS results from washed and unwashed Mo/Al_2O_3 samples, both loosely and tightly bound molybdate and tungstate are polymeric in nature. The results are discussed in terms of electrostatic and surface reaction models.

INTRODUCTION

The adsorption of metal oxyanions on metal oxide surfaces currently attracts significant attention. Studies have focused on catalytically important oxyanions and supports, particularly the molybdate–alumina system (*1–9*). The goals of many of these studies were to determine the structures of the adsorbing species, the nature of the adsorbed species–support interaction, and the effects of additives, pH, and isoelectric point on metal uptake from solution.

Although much has been learned about the adsorption of metal oxyanions on various supports, the establishment of a definitive adsorption model seems to be lacking. Electrostatic forces (*1, 3, 5, 9, 10*), condensation (*11, 12*) ion exchange (*11*), and other reactions (*4*) have been mentioned to describe the interactions of metal oxyanions with support surfaces. Meunier *et al.* (*10*) have noted that similar numbers of metal oxyanions were adsorbed on alumina in experiments carried out at the same pH, regardless of the nature of the metal.

The purpose of the present work was to elucidate the mode by which metal oxyanions adsorb on alumina. By changing the ratio of metal oxyanions to total anions in the impregnation solutions, it should be possible to distinguish electrostatic adsorption from other types. Also, washing samples containing adsorbed ions and determining the amount removed should give some indication of the strength of adsorbate–support interactions. Finally, the use of oxyanions of Cr, Mo, W, Mn, and Re should provide a variety of types of interactions so that distinctions between the different interactions can be observed.

EXPERIMENTAL

Sample Preparation

Harshaw γ-alumina (surface area = 170 m^2/g) was impregnated with ammonium heptamolybdate (Fisher Scientific), ammonium chromate (Mallinckrodt), ammonium metatungstate (Cerac), potassium permanganate (E. M. Science), and ammonium perrhenate (Alfa) by equilibrium adsorption. The standard preparation of samples was as follows: 1 g of alumina and 50 ml of 0.064 *M* (based on the monomeric anion) metal oxyanion solution were placed in a 125-ml Erlenmeyer flask along with a glass-coated stirring bar. Enough HNO_3, NH_4OH, and

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distilled water were added to the flask to bring the initial pH to about 2.5 and the solution volume to 58 ml. In order to change the metal oxyanion to total anions ratio (X_{oxy}) of the impregnating solutions, 0.125 *M* NH_4NO_3 was used as the solvent instead of distilled water in the preparation of several samples. For other samples, prepared in more dilute solutions, the number of moles of metal oxyanions in solution and the amount of support used were the same as those in the standard preparation. The solutions were stirred for 24 h and then filtered. Several samples were rinsed with 0.05 *M* potassium biphthalate buffer (pH 4) for 1/2 h, except for a permanganate preparation which was rinsed for only 1 min because permanganate oxidized the biphthalate buffer when rinsed for longer periods. The samples were filtered and then dried at room temperature in air.

Additional experiments were conducted to determine the effect of more extensive washing of samples containing molybdate and tungstate. Molybdate and tungstate were impregnated on alumina by the standard method described above. These samples were then washed by stirring for 24 h in 50 ml of 0.05 *M* potassium biphthalate solution. The samples were filtered and then rewashed (while still wet) with fresh biphthalate solution. This washing process was repeated five times.

Samples are denoted as *M*(*XY*), where *M* is the metal, and *X* = "*B*" for samples prepared in 0.125 *M* NH_4NO_3 solution, or *X* = "*U*" for samples which were prepared by the standard method. The symbol *Y* refers to the monomeric oxyanion concentration in the impregnation solution, which can be determined by multiplying *Y* by 10^{-3}. For example, Mn(B5.5) would denote a catalyst prepared from a solution which was 0.0055 *M* in $KMnO_4$ and 0.125 *M* in NH_4NO_3, and W(*U*55) refers to a sample prepared by the standard method from $(NH_4)_6H_2W_{12}O_{40}$ solution which was 0.055 *M* in WO_4^{2-}.

Metal contents of the samples were determined by X-ray fluorescence spectroscopy. The analyses were calibrated using catalyst samples prepared by incipient wetness. Reproducibility was ±5%, r.s.d.

Potentiometric Titration

Potentiometric titrations were carried out using an Orion model 201 pH meter and a gel-filled combination electrode. To 50 ml of 0.001, 0.01, and 0.1 *M* KNO_3 solutions was added 0.5 g of alumina. The mixtures were allowed to equilibrate for 1 day. Following this, 0.5 ml of 0.1 *M* KOH was added to each mixture and allowed to equilibrate. The mixtures were stirred to hasten equilibration. Nitric acid (0.1 *M*) was then added dropwise from a buret, with pH measurements made about 4 min after each addition. From these data, using the work of Breeuwsma (*13*) and Block (*14*), the quantity ($\Gamma_{H^+} - \Gamma_{OH^-}$), the change in the difference of the number of microequivalents of H^+ and OH^- adsorbed per square meter of alumina surface area, can be calculated. From the values of $\Gamma_{H^+} - \Gamma_{OH^-})_{zpc}$ at the zero point of charge (zpc), and $(\Gamma_{H^+} - \Gamma_{OH^-})_{pH}$ at any given pH, the surface charge at the given pH can be determined as $=F[(\Gamma_{H^+} - \Gamma_{OH^-})_{pH} - (\Gamma_{H^+} - \Gamma_{OH^-})_{zpc}]$, where *F* is Faraday's constant (*15*).

X-Ray Absorption Measurements

Transmission Mo *K*-edge spectra were collected at beamline X18B, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The catalyst samples were measured in powdered form and were mounted by placing small quantities in the space formed between the window of an aluminum holder and two pieces of Kapton tape, which held the powder in place. The path length (for transmission) was between $\frac{1}{32}$ and $\frac{1}{16}$ in. The spectra were collected at 77 K for scan times varying from 30 min to more than 6 h. The length of the scan time was determined by catalyst loading and the synchrotron beam intensity. Analysis of the EXAFS data was carried out using a previously described procedure (*16*). $\chi(k)$ was weighted by k^2 prior to Fourier transforming $\chi(k)$ into r-space and a 5% Hanning window function was used to select the Fourier transform range of $k^2\chi(k)$ which was approximately 3.5 to 16.0 k.

RESULTS

Table 1 shows the amounts of Re, Mn, Cr, Mo, and W which were deposited on the alumina surface at pH 4.5 by equilibrium adsorption. The Mo and W uptake for unrinsed catalysts was much greater than that for the other metals and agrees well with literature values (*1*). The amounts of adsorbed Cr, Mn, and Re ranged from 18 to 25 × 10^{19} atoms/g catalyst. Cr and Re were adsorbed in significantly higher quantities than those observed by other workers (*1, 2*), as shown in Table 1.

The effect of rinsing on catalysts prepared by equilibrium adsorption is also shown in Table 1. It can be seen that rinsing removes most of the perrhenate, permanganate, and chromate deposited by adsorption. In the cases of tungstate and molybdate, however, approximately 50–60% of the adsorbed anions remain on the alumina after rinsing for ½ h.

TABLE 1

Comparison of Metal Loadings of Washed and Unwashed Catalysts; Concentration of Metal Anion (Monomeric) = 0.055 *M*

Metal	Loading ($\times 10^{19}$ at/g)		
	Unwashed	Washed[a]	Literature
Cr	24.9	1.97	14[b]
Mo	39.4	24.5	39[b]
W	64.0	33.5	56[b]
Re	21.3	0.32	13[c]
Mn	18.2	0.99	—

[a] All samples except Mn were washed for ½ h in 0.05 *M* potassium biphthalate. Mn was rinsed with the wash solution.

[b] Ref. (*1*).

[c] Ref. (*2*).

The effects of changing the X_{oxy} of the impregnation solution with nitrate are shown in Table 2. The X_{oxy} is determined as $X_{oxy} = [MO_4^{x-}]/([MO_4^{x-}] + [NO_3^-])$. $[MO_4^{x-}]$ is determined from the initial solution concentration and volume, and $[NO_3^-]$ from the amount of nitrate added as HNO_3 and NH_4NO_3. The X_{oxy} is expressed in terms of the monomeric anions for simplicity; $Mo_7O_{24}^{6-}$, $W_{12}O_{39}^{6-}$, $Cr_2O_7^{2-}$, MnO_4^-, and ReO_4^- are known to be the major species present in solution at pH 4.5 (*17*). The greatest effect of changing the X_{oxy} of the impregnation solution occurs for perrhenate and permanganate; less than half as many of these ions are adsorbed from solutions made with 0.125 *M* NH_4NO_3 relative to standard impregnation solutions. There is no significant effect of the X_{oxy} observed for molybdate, tungstate, or chromate.

DISCUSSION

Perrhenate and Permanganate Adsorption

An electrostatic model (*18*) has often been used to explain the adsorption of ions on metal oxide supports. This model considers the charge of the ion, the pH of the impregnation solution, and the isoelectric point (IEP) of the support to be the primary factors affecting adsorption (*18*). At a pH below the IEP of the support, the support acquires a net positive surface charge, which in turn attracts anions from bulk solution to the support–solution interface where the anions become electrostatically bound. Since the IEP of the alumina used in this study is 7.6 (*9*) and the pH of the impregnation had a final value of 4.5, the conditions were such that adsorption by an electrostatic mechanism could have occurred.

The fact that perrhenate and permanganate adsorption is affected by changing the X_{oxy} of the impregnation solution indicates that there is competition for adsorption sites between these metal oxyanions and nitrate. This should be expected if adsorption can be described by a simple electrostatic model, since all anions present in solution, including nitrate, would be attracted to the posi-

TABLE 2

Comparison of Metal Loadings Obtained from Standard and 0.125 *M* NH_4NO_3 Impregnation Solutions and Fraction of Anions Present in Solution as Metal Oxyanions (X_{oxy}).

Metal	Solution conc. (*M*)[a]	Loading ($\times 10^{19}$ at/g)		NO_3/standard	X_{oxy}[a]	
		Standard	NH_4NO_3		Standard	NH_4NO_3
Cr	0.055	24.9	24.9	1.00	0.449	0.240
Mo	0.055	39.4	39.7	1.01	0.640	0.290
W	0.055	64.0	66.9	1.04	0.762	0.306
Re	0.055	21.3	9.03	0.42	0.762	0.306
Mn	0.055	18.2	6.69	0.36	0.800	0.306
Mn	0.0055	9.54	4.61	0.48	0.727	0.300

[a] Based on monomeric anion concentration.

tively charged alumina. The maximum amounts of Mn and Re expected to adsorb by a simple electrostatic model in the absence of competition from other anions are shown in Table 3 for impregnation solutions having different X_{oxy} ratios. Maximum possible loadings (MPLs) were calculated using the X_{oxy} in solution and the amount of metal adsorbed on alumina. Even though nitrate, perrhenate, and permanganate differ in ionic radius and charge density, for simplification of the model it is assumed in these calculations that the metal oxyanion and nitrate have the same affinity for positively charged surface sites and that the adsorbate–surface interaction is entirely electrostatic. As an example, 50 ml of NH_4ReO_4 solution containing 0.0032 mol of ReO_4^- was used to prepare sample Re(*U*55). To the perrhenate solution, 0.25 ml of 4.0 *M* HNO_3 was added to adjust the pH, adding 0.0010 mol of NO_3^- to the number of moles of anions in the solution. Thus, ReO_4^- accounts for 0.0032/0.0042, or 76%, of the anions in the perrhenate solution used to prepare sample Re(*U*55). The amount of perrhenate which would be adsorbed if the solution contained 100% ReO_4^- is (100/76)(21.3 $\times$ 10^{19} at/g) = 28.0 $\times$ 10^{19} at/g. Mathematically, MPL = $X/(X_{oxy})$, where X is the experimentally observed loading. According to the model, MPLs calculated for a particular metal oxyanion should be independent of X_{oxy}, since nitrate and the metal oxyanion are assumed to have equal affinities for the alumina surface. Agreement of MPLs for adsorption of the same oxyanion from solutions having different X_{oxy} values is good, as is shown in Table 3. There is less than 6% difference between the samples prepared in 0.055 *M* $KMnO_4$, about 5% difference between those impregnated with NH_4ReO_4, and 15% difference between the samples prepared from 0.0055 *M* $KMnO_4$.

For such a simple electrostatic model, it might be expected that the amount of charge on the alumina surface would be equivalent to the amount of charge carried by the adsorbed ions; i.e., each surface charge should be balanced by an anion

TABLE 3

Calculated Maximum Possible Amounts of Re and Mn Adsorbed on Alumina at pH 4.5

Sample	Metal loading ($\times 10^{19}$ at/g)	X_{oxy}	Maximum possible loading (MPL) ($\times 10^{19}$ at/g)
Mn(U55)	18.2	0.800	22.8
Mn(B55)	6.69	0.306	21.9
Mn(U5.5)	9.54	0.727	13.2
Mn(B5.5)	4.61	0.300	15.4
Re(U55)	21.3	0.762	28.0
Re(B55)	9.03	0.306	29.5

TABLE 4

Variation in Alumina Surface Charge as a Function of KNO_3 Concentration and Amount of Charge Carried by Adsorbed Oxyanions at pH 4.5

KNO_3 concentration (*M*)	Surface charge (*C*/g)	Sample	Charge carried by adsorbed anions (*C*/g cat.)
0.1	43	Re(*U*55)	46
0.01	32	Mn(*U*55)	35
0.001	24	Mn(*U*5.5)	22

adsorbed from solution. The maximum expected perrhenate and permanganate loadings shown in Table 3 are in fair agreement with the amounts to be expected on the basis of charge on the alumina surface at the pH of impregnation. Table 4 shows a comparison of net positive charge per gram of alumina at the pH of impregnation (pH 4.5) with the amount of charge carried by the MPLs of perrhenate and permanganate. The surface charge/g was determined by potentiometric titration as outlined in the Experimental section. Three concentrations of KNO_3 were used to bracket the concentrations of $KMnO_4$ and NH_4ReO_4 used in the impregnating solutions. The average amounts of negative charge borne by the maximum possible loadings of ReO_4^- and MnO_4^- calculated in Table 3 for 0.055 *M* MO_4^- impregnating solutions (46 and 35 *C*/g, respectively) are in good agreement with the amount of positive charge on the surface of alumina in bracketing 0.01 and 0.1 *M* KNO_3 solutions (32 and 43 *C*/g, respectively) shown in Table 4. For adsorption from 0.0055 *M* MnO_4^- solution, the charge for the maximum amount of MnO_4^- expected to adsorb (22 *C*/g) is only slightly less than the net amount of positive charge present on alumina in 0.001 *M* KNO_3 solution at pH 4.5 (24 *C*/g).

It should be noted that the observed dependence of perrhenate adsorption on the presence of nitrate may explain the disagreement between the perrhenate uptake observed in the present study and that observed previously (*2*), since it is likely that different amounts of nitrate were used in the preparation of perrhenate samples in the previous study.

Molybdate, Tungstate, and Chromate Adsorption

Although the present work agrees with the data of Wang and Hall (*1*) (Table 1) for tungstate and molybdate adsorption, the uptake of chromate is about twice as large as that observed by these workers (*1*). The reason for this discrepancy is not clear, but the present results for chromate adsorption indicate that the difference cannot be explained by the dependence of uptake on the presence of nitrate ion.

The absence of any effect of changing X_{oxy} on the amounts of chromate, molybdate, and tungstate adsorbed suggests that a simple electrostatic model cannot account for adsorption of these anions. Therefore, it appears that adsorption of the three metal oxyanions must involve some additional step or a different mechanism. One possibility is that electrostatic ion pairing occurs first, followed by a condensation reaction between the ions and the alumina surface, such as the following:

$$\mathrm{Al - OH_2^+ + Mo_7O_{24}^{6-} \rightleftharpoons Al - OH_2^+Mo_7O_{24}^{6-}}$$

$$\mathrm{Al - OH_2^+Mo_7O_{24}^{6-} \rightleftharpoons Al - O - Mo_7O_{23}^{5-} + H_2O.}$$

This scheme is very similar to one proposed by Knoezinger (*19*). Similar reactions have been proposed to occur during impregnation (*4, 7*), drying, and calcination (*11, 12*) of molybdenum–alumina catalysts. An analogous reaction could occur between $W_{12}O_{39}^{6-}$ and alumina.

Chromate adsorption appears to be an intermediate case between perrhenate and permanganate adsorption on the one hand and tungstate and molybdate adsorption on the other. Since no effect of X_{oxy} is observed for chromate, a reaction similar to the above might be responsible for chromate adsorption. However, the interaction which occurs must be relatively weak since chromium is almost completely removed from the sample by rinsing.

The reaction proposed above between molybdate and alumina is one in which the metal oxyanion associates with and then reacts with protonated hydroxyl groups on alumina. As a gauge of the strength of this type of interaction, equilibrium constants (K) were obtained from literature for reactions of metal oxyanions with positively charged ions in solution:

$$H^+ + Mo_7O_{24}^{6-} \rightleftharpoons HMo_7O_{24}^{5-} \qquad K = 3.8 \times 10^4 \quad (20)$$

$$H^+ + Cr_2O_7^{2-} \rightleftharpoons HCr_2O_7^- \qquad K = 1.18 \quad (21)$$

$$H^+ + ReO_4^- \rightleftharpoons HReO_4 \qquad K = 5.6 \times 10^{-2} \quad (22)$$

$$H^+ + MnO_4^- \rightleftharpoons HMnO_4 \qquad K = 5.6 \times 10^{-3}. \quad (23)$$

The equilibrium constant for the formation of $HW_{12}O_{39}^{5-}$ by a similar reaction could not be found in the literature. However, on the basis of the similarities of molybdate and tungstate equilibria, the value of the formation constant for protonated tungstate should be of the same magnitude as that of protonated molybdate. Assuming that the equilibrium constants of these reactions can be used as an indication of the strength of interaction between an anion and a protonated hydroxyl group on alumina, one would predict that molybdate should form a strong bond with alumina, chromate a substantially weaker bond than molybdate, and perrhenate and permanganate should have little tendency to bond to alumina. The effects of rinsing as well as the effect of ionic strength of the impregnation solution show this trend in bond strength: molybdate and tungstate are difficult to remove by rinsing, evidencing a strong interaction with alumina; permanganate and perrhenate are almost completely removed from alumina by rinsing and are greatly affected by the ionic strength of the impregnation solution, indicating a weak interaction with alumina. Bonding of chromate to alumina appears to be of intermediate strength, since chromate is rinsed from alumina but is unaffected by changes in the ionic strength of the impregnation solution.

Rinsing and Washing of Catalysts

The purpose of rinsing catalysts with biphthalate solution was to determine the reversibility of the adsorption of metal oxyanions. Rinsing the catalysts not only removed metal oxyanions which were trapped in the alumina pores but also extracted those adsorbed metal oxyanions which were capable of being replaced with biphthalate. Perrhenate, permanganate, and chromate were especially susceptible to removal by rinsing, indicating that these anions were either easily ion-exchanged or that formation of perrhenate, permanganate, and chromate ions in solution was favored by the equilibria involved.

The results of rinsing molybdate and tungstate catalysts are interesting in that only part of the molybdate and tungstate was removed from the alumina. When molybdate and tungstate were washed for longer periods of time than those indicated in Table 2 or were washed repeatedly for 24-h periods with fresh biphthalate solutions, increasing amounts of molybdate and tungstate were removed until a limit was reached. Subsequent washing had little effect, as is shown in Table 5 and Fig. 1. Such behavior indicates that two types of surface molybdate and tungstate species exist on the support: a tightly bound species which cannot be ion-exchanged with biphthalate and a more loosely bound species which can be removed by washing with biphthalate solution. This finding is consistent with the work of Van Veen *et al.* (*4, 7, 23*), who have suggested that two types of alumina sites (coordinatively unsaturated Al^{3+} sites and basic hydroxyl groups) are responsible for the adsorption of molybdate.

TABLE 5

Variation in Molybdate and Tungstate Remaining after Washing as a Function of the Number of Times Washed (Time for one Wash = 24 h)

Times washed	Loading ($\times 10^{19}$ atoms/g)	
	Mo	W
0	40.5	60.6
1	16.3	25.5
2	12.9	20.3
3	12.6	18.7
4	11.3	17.0
5	11.0	16.0

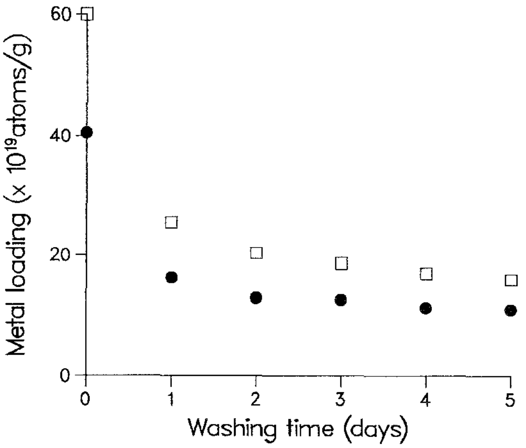

FIG. 1. Variation in molybdate (●) and tungstate (□) loading as a function of washing time. Wash solution (0.05 *M* potassium biphthalate) was changed every 24 h.

The data of Table 5 provide an opportunity for conjecture with regard to the nature of adsorption sites and adsorbed species on alumina. For instance, the ratios of the number of atoms removed by washing to the number remaining after washing five times (*L*/*R*) in molybdate and tungstate samples are very similar ($L/R = 29.5/11.0 = 2.68$ for Mo, $44.6/16.0 = 2.78$ for W; see Table 5), indicating that for molybdate and tungstate the ratio of loosely bound to tightly bound species is the same. This observation indicates that the primary difference between loosely bound and tightly bound molybdate and tungstate species lies in the sites to which these species are bound, rather than in a difference in the type of species (octahedral or tetrahedral) bound to the surface. Strongly bound molybdate and tungstate species may adsorb at sites occupied by the most basic hydroxyl groups of the alumina surface (*7*, *9*). Since alumina has five types of hydroxyl groups (*24*), perhaps less basic types of hydroxyl groups are responsible for the adsorption of weakly bound molybdate and tungstate.

EXAFS studies of the washed and unwashed catalysts support the idea that the difference between tightly and loosely bound species lies in the sites to which they are adsorbed. The similarity of the washed and unwashed samples is demonstrated in Fig. 2, which shows that the $\chi(k)$ spectra are essentially identical. Considering that approximately $\frac{2}{3}$ of the Mo is removed by washing, it is unlikely that the Mo species which is washed from the catalyst is structurally different from the species which remains.

The pseudo-radial distribution functions (PRDF) from washed and unwashed molyb-

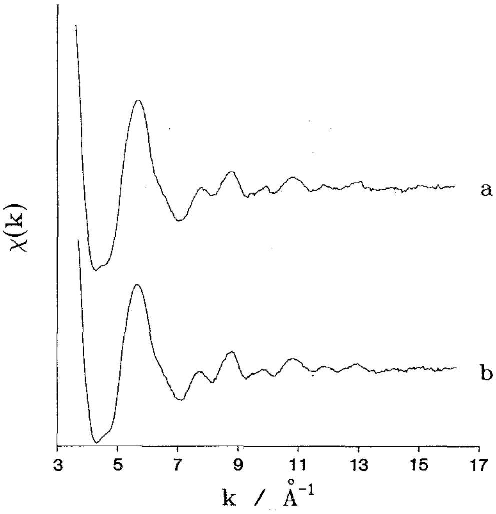

FIG. 2. $\chi(k)$ spectra from (a) washed Mo/Al_2O_3 and (b) unwashed Mo/Al_2O_3.

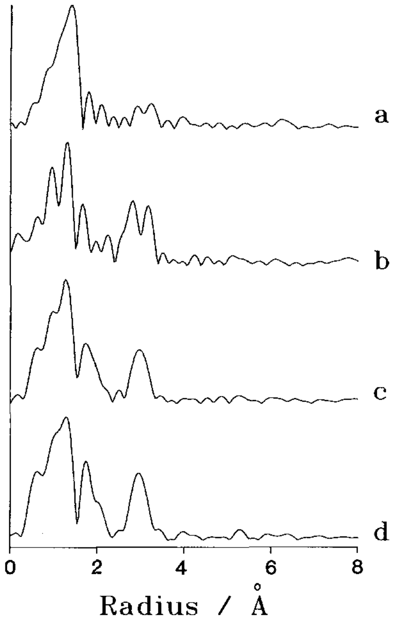

FIG. 3. Pseudo-radial distribution functions (PRDF) of (a) $Na_2MoO_4 \cdot 2H_2O$, (b) $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, (c) washed Mo/$Al_2O_3$, (d) unwashed Mo/$Al_2O_3$.

denum catalysts prepared by equilibrium adsorption, sodium molybdate ($Na_2MoO_4 \cdot 2H_2O$), and ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 2H_2O$) are shown in Fig. 3. The structure of sodium molybdate basically consists of tetrahedral MoO_4^{2-} anions, sodium ions, and water (*25*). This is evident in the sodium molybdate PRDF which is dominated by a large first shell peak at about 1.8 Å. A pair of small second shell peaks at 3.0 Å are primarily due to the contribution of Mo and Na scattering atoms (O and H_2O scatterers are also found in this region). The Mo atoms in the heptamolybdate ion have a distorted octahedral coordination with Mo–O nearest neighbor distances between 1.675 and 2.424 Å (*26*). The distorted nature of the heptamolybdate ion is evidenced by the multitude of first shell peaks in the ammonium heptamolybdate PRDF. The pair of second shell peaks at 3.0 Å is due to a combination of Mo–Mo and Mo–O interactions.

Also shown in Fig. 3 are the PRDFs of the washed (five times) and unwashed catalysts. The overall shape of the peaks and their relative intensities are approximately the same for these two samples. The PRDFs of the washed and unwashed catalysts both exhibit broad first shell peaks indicative of a distorted first coordination shell. The second shell peaks in the PRDFs of the catalysts at 3.0 Å were curve fit using theoretical Mo–Mo and Mo–O amplitude and phase functions (*27*). The fitted k^2 (k) spectra are shown in Fig. 4, illustrating the goodness of fits. The Mo–O nearest neighbor distances were 2.89 Å for the washed catalyst and 2.85 Å for the unwashed sample. The Mo–Mo nearest neighbor distance was 3.15 Å for both catalysts and is similar to the Mo–Mo distances in the heptamolybdate ion (3.076–3.500 Å) (*26*). The presence of the Mo–Mo interaction in these catalysts indicates the presence of polymeric Mo species. However, the presence of monomeric Mo species in addition to the polymeric species cannot be ruled out.

The presence of polymeric molybdate species on the Mo catalysts prepared by

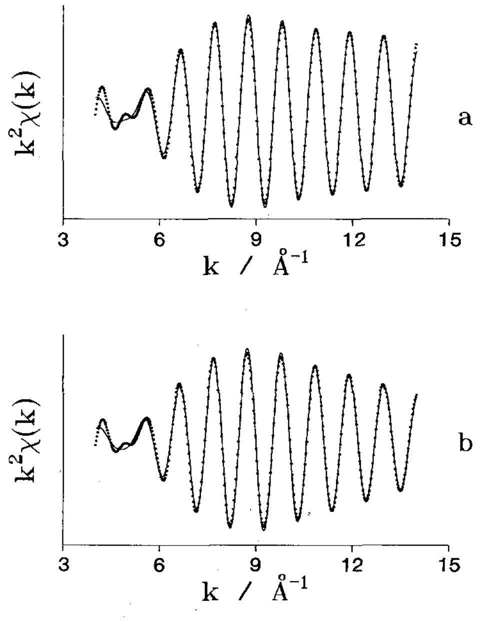

FIG. 4. Curve fit (●) and experimental (solid) k^2 $\chi(k)$ from the second shell peak in the PRDF of (a) washed and (b) unwashed Mo/Al_2O_3 samples.

equilibrium adsorption is also suggested by comparison of the amounts of molybdenum and tungsten present on washed and unwashed samples. If it is assumed that molybdates and tungstates adsorb on the same types of sites, the relative amounts of molybdate and tungstate adsorbed may be useful in determining the identity of the adsorbed species. The ratio of loosely bound (removable by washing) Mo to W is 29.5/44.6 = 0.66 (see Table 5). For tightly bound species (not removed after 5 days of washing) the Mo/W ratio is 11.0/16.0 = 0.69. If molybdate and tungstate species adsorb on the same kinds of sites to the same extent, the ratio of Mo/W adsorbed should be 7/12 (0.58) if the species are adsorbed as polymeric anions or 1/1 if they are adsorbed as monomeric species. The measured ratios are consistent with the adsorption of polymeric anions. Thus, it appears that both loosely and tightly bound tungstate and molybdate species are formed by the adsorption of polymeric octahedral tungstates and molybdates when the pH of the impregnating solution is low enough to form these polymeric anions.

Determining that molybdates and tungstates are adsorbed as polymeric species at pH 4 is important, since there has been a question whether strongly adsorbed molybdates are monomeric or polymeric species. The adsorption of molybdate conducted by Van Veen *et al.* (*4, 7*) at pH 5–6 indicated that strongly adsorbed molybdates were monomeric and that the monomers were produced by reaction of basic alumina hydroxyl groups with polymeric molybdate. The work of Van Veen *et al.* (*4, 7*) is in no way contradicted by the findings of the present study, however, since the present work was carried out at pH 4, where the formation of monomeric molybdates, which predominates at about pH 7, is much less likely.

CONCLUSIONS

Two types of interactions between metal oxyanions and alumina have been observed. Permanganate and perrhenate ions appear to adsorb on alumina primarily through electrostatic interactions. The amount of permanganate or perrhenate which adsorbs on alumina is directly proportional to the fraction of perrhenate or permanganate anions present in the solution. Calculated maximum amounts of adsorbable permanganate and perrhenate are in agreement with predictions based on the amount of alumina surface charge determined by potentiometric titration.

Electrostatic interactions between molybdate, tungstate, or chromate and the alumina surface may occur, but these oxyanions appear to adsorb on the alumina surface by some other mechanism, such as acid–base or condensation reaction. Adsorption of molybdate and tungstate occurs on two types of sites to yield tightly and loosely bound surface species. On the basis of EXAFS measurements and ratios of adsorbed molybdate to adsorbed tungstate, both loosely and tightly bound species are most likely formed by the adsorption of polymeric molybdate and tungstate anions. Two types of basic alumina hydroxyl groups are suggested as adsorption sites for loosely and tightly bound molybdate and tungstate species.

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