

The Preparation and Genesis of Molybdena-Alumina and Related Catalyst Systems

LI WANG AND W. KEITH HALL¹

Department of Chemistry, Laboratory for Surface Studies, University of Wisconsin, Milwaukee, Wisconsin 53201

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Molybdena-, tungsta-, chromia-, and vanadia-alumina preparations were made using an equilibrium adsorption technique. The Na⁺ cation was also tested and other supports (titania, magnesia, and silica gel) were employed. The loading of the support was not very dependent on the solution concentration, but for anions was a strong inverse function of the pH. It is shown that this (and the opposite dependence for cations) reflected the isoelectric point of the support surface. Reflectance spectra of the wet, dried (150°C), and calcined (500°C) catalysts are reported for molybdena-alumina preparations made at several pH values. In agreement with our previously published Raman data, the catalyst prepared at pH = 8.6 yielded spectra of a monomeric tetrahedral species while those made at lower pH yielded spectra characteristic of octahedral (polymeric) molybdena. Thus, better defined catalysts could be prepared for further study. The data support a model for the ordinary raw catalyst made by incipient wetness from solutions of ammonium paramolybdate in which the surface of the support becomes populated with randomly distributed small clusters (or islands) of polymolybdate species.

INTRODUCTION

A number of studies have been made of the surface chemistry of molybdena-alumina catalysts. An objective has been to establish a model describing the surface of the raw catalyst and the changes it undergoes during reduction and/or sulfiding. Two general pictures have emerged. In the first, monomeric molybdate ions are supposed to form an epitaxial monolayer by replacement of the alumina surface OH groups. The latter are supposed to be removed as H₂O by reaction with molybdic acid on calcining (1-3). The changes in structure on reduction have been described by considering the reaction of the oxygen atoms of the capping layer with hydrogen to form Mo-OH and/or anion vacancies as H₂O is removed (4, 5). The second model starts in a similar way with molybdena bound to the surface, but it is supposed that microcrystalline MoO₂ is formed on reduc-

tion and that this may be intercalated with Co²⁺ when present (6, 7). The present work corrects the notion that the raw catalyst ordinarily contains bound monomer and suggests instead that the reduced catalysts usually contain MoO₂ in the form of small clusters of seven or so ions. This "patch model" is also consistent with the published Raman data (8-12) which show clearly the Mo-O-Mo bending vibrations in the 220-cm⁻¹ region. Because the clusters remain partially bound to the alumina surface they are stabilized and contain Mo⁵⁺ as well as Mo⁴⁺ and very likely have sites of high coordinative unsaturation (CUS). These may be Mo³⁺ at edges or corners; thus they would permit the chemisorption of NO as a dimeric or dinitrosyl species in very limited amounts (13, 14) and they could also chemisorb O₂ or H₂, i.e., they could be the center of the hydrogenation activity (15). Clearly, at high pH preparations corresponding to the earlier monomeric model can be made.

Recently we have studied the surface hy-

¹ To whom all correspondence should be sent.

droxyl groups of the parent alumina (as well as raw and reduced molybdena-alumina catalysts made from it) by chemical and spectroscopic means. Several significant results have emerged. First it was determined (5) that between one and two alumina OH groups disappeared for every Mo^{6+} loaded onto the surface, confirming this aspect of the picture. Some of these reappeared, however, as the catalyst was reduced and ir determinations showed that alumina OH groups were regenerated, suggesting that reduction (partially) reversed the process of formation. Other data (4, 16, 17) suggested that much more Mo^{5+} could be present than determined from the integrated intensities of the EPR signals. Proton resonance measurements (18) then revealed that a large portion (50–70%) of the hydroxyl groups actually present on reduced molybdena-alumina could be detected by proton resonance, in spite of the large amount of surface paramagnetism present. If only those paramagnetic centers actually determined from the integrated intensities of the EPR spectra were counted, the proton resonance signal should have been broadened beyond detectability provided that the paramagnetic centers and the hydroxyl groups were uniformly intermingled on the catalyst surface. The experimental result obtained indicated that the molybdena must be present in patches leaving large areas of the alumina surface uncovered. Second-moment calculations were in agreement with this interpretation. We were concerned that this finding might have resulted from the method of preparation of our catalyst, viz., the incipient wetness method.

The present research was initiated with the objective of preparing catalysts with each unit area of surface the same as every other. Another objective was to further study the surface chemistry of the raw catalyst by following its genesis using spectroscopic and chemical techniques. A question to be answered was how closely does the epitaxial monolayer model (1–4) represent

the actual situation? It was also hoped that this investigation would shed light on the question of why Mo^{5+} is missing from the EPR signal. A preliminary account of this work has already been made (8). The present paper presents the experimental details of the catalyst preparation and correlates the results obtained from Raman spectroscopy with those from optical reflectance spectroscopy.

Sonnemans and Mars (19) prepared catalysts by passing large volumes of molybdate solutions over columns of the support. It was presumed that the catalysts were uniformly covered when the composition of the effluent solution became identical to that flowing onto the top of the column. It was found that the loading obtained was fairly independent of the concentration of the solution used, but was an inverse function of the pH. It was further suggested that the increased loading at low pH was caused by the formation of polymeric anions as the pH was lowered. From some preliminary experiments we concluded that while there was considerable merit in these ideas, the method would not achieve our objectives. Similarly, Iannibello *et al.* (20) devised a method similar to the one used herein but followed pH changes as a criterion of approach to equilibrium. As a result, they concluded that the loading was concentration dependent; the effect of pH was not investigated, but it was suggested that monomeric molybdate species were bound to the alumina surface in accordance with the existing epitaxial monolayer models. This criterion we have found to be of inadequate accuracy.

Recently, D'Aniello (21) studied the adsorption of $\text{Co}(\text{CN})_6^{3-}$ ions from aqueous solutions onto alumina. Again the loading of the catalyst was found to be nearly independent of the initial concentrations of the solutions used, but was pH dependent. Moreover, the adsorption was reversible and desorption could be effected by increasing the pH of the solution. These processes were fast, equilibrium being ob-

tained in the order of 10 min. D'Aniello suggested that the adsorption was an electrostatic process, the $\text{Co}(\text{CN})_6^{3-}$ ions being adsorbed on a positively charged surface. These ideas are in substantial agreement with the picture which we recently presented (8) for the genesis of molybdena-alumina catalysts.

Parfitt (22) showed how ideas from colloid chemistry can sometimes be carried over to the surface chemistry of oxides. In particular, he recalled that each oxide has an isoelectric point (IEP) and that the surface can become either positively or negatively charged when in contact with an aqueous solution of pH lower or higher than the IEP, respectively. The fact that the charge on the surface can be adjusted by varying the pH provided an explanation for the variations in loading with pH and the reversibility of the adsorption process noted above. It is the anions that are present in the solution (23–25, 30) which are adsorbed on positively charged surfaces of oxides at low pH as established by our recently published Raman study (8). Further support for this picture is contained herein.

EXPERIMENTAL

Catalyst Preparation

An equilibrium adsorption method was devised to overcome the shortcomings of the incipient wetness technique. The supports were contacted with relatively large volumes of aqueous solutions containing the transition metal anions (TMI). These solutions were shaken mechanically at room temperature for periods of about 100 hr. The excess solution was then separated by filtration and analyzed. Provided that the remaining TMI concentration was at least half its initial value, it was deemed that this time was sufficient to ensure that all parts of the surface area had been in contact with the same solution concentration. In addition, the solutions were suffi-

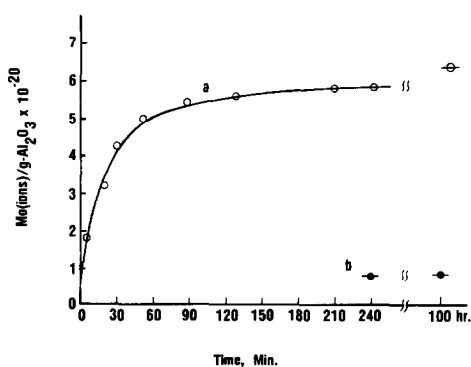


FIG. 1. Molybdena uptakes vs adsorption time. Five-gram aliquots of γ -alumina were suspended in 250 ml of an aqueous solution of 0.007 M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$; pH values of the solutions were adjusted by adding either HNO_3 or NH_4OH . (a) pH = 1.0; (b) pH = 8.6. The pH values specified are the initial values.

ciently dilute so that the loading could not be changed appreciably when the solvent was evaporated from the solution held within the pore system. Thus, in a typical preparation, molybdate ions were adsorbed onto 5-g aliquots of γ -alumina from 250 ml of 0.007 M solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ in H_2O . The loading was controlled by varying the pH (with HNO_3 or NH_4OH). This also dictated the majority species in solutions (23, 24). After shaking the preparation in an Erlenmeyer flask for about 100 hr, the final value of the pH was determined. In these circumstances if no adsorption occurred a loading of about 1.5×10^{19} Mo/g would result from the solution left within the pore volume. Similar preparations were made with chromia, tungsta, and vanadia on alumina, silica, titania, and magnesium. Loadings were determined from aliquots of the final calcined catalysts using an atomic absorption method. In the experiments concerning the rate of adsorption (Fig. 1), the uptakes were calculated by monitoring the changes of the solution concentration at pH \approx 1.0. For pH \approx 8.6, since the uptakes were small, in order to obtain sufficient accuracy, aliquots of catalysts were withdrawn from the solution and analyzed.

Support Materials and Reagents

The Ketjen CK-300 high-purity γ - Al_2O_3 had a surface area of $192 \text{ m}^2/\text{g}$ and a pore volume of $0.5 \text{ cm}^3/\text{g}$. A 20- to 40-mesh fraction was used in the experiments. Its main impurities were Cl, Ca, Mg, and Si, but with a total impurity content of less than 100 ppm. Other support materials used were Davison grade 62 SiO_2 gel (60–200 mesh, surface area $340 \text{ m}^2/\text{g}$) and MK Research and Development high-purity MgO powder (surface area $10 \text{ m}^2/\text{g}$). A hydrated TiO_2 was prepared by hydrolyzing tetraisopropyl titanate in water. Its surface area after calcining at 500°C was $57 \text{ m}^2/\text{g}$. ACS grade $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was obtained from Fisher Scientific Company. Its major impurities were Cl^- , NO_3^- , SO_4^{2+} , Mg^{2+} , and other metals in trace amounts (total impurities were less than 200 ppm). Tungstic acid (major impurities were 60 ppm Mo, 77 ppm Na, and 10 ppm Pb) and ammonium metavanadate (impurities included Fe, Si, Cl, and sulfate; less than 0.15% in total) were Alfa-Ventron products. Ammonium dichromate was analytical reagent grade and was purchased from Mallinckrodt (main impurities were Cl, alkalis, and SO_4 ; total was less than 0.15%). Fisher-certified NaHCO_3 was used to load the alumina by the incipient wetness method. It contained no more than 200 ppm total impurities including Ca, Mg, K, and Fe. Distilled water, further purified by passing through a Corning demineralizer, was used in the preparation. The specific conductance of the final purified water ranged from 0.12 to $0.25 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$.

Spectroscopy

Diffuse optical reflectance spectroscopy was used to characterize catalysts in the wet condition, after drying at 150°C , and after calcining in air at 500°C . Spectra were recorded with a Cary-17 spectrometer equipped with a model 1711 diffuse reflectance accessory.

Wafers of the catalysts were made and

loaded into cuvette cells. Spectra were recorded against identical cells containing an alumina blank (the support material) dehydroxylated at 500°C . Automatic slit control was applied when recording the spectra. These data may be compared directly with the Raman data reported earlier (8).

RESULTS

The rate of approach to equilibrium and the effect of pH on the final equilibrium loading may be assessed from the data of Fig. 1. Usually the loading reached about 85% of its final value within the first hour. After 100 hr further change in either direction was within the experimental error (<5%). The final loadings could be varied by nearly an order of magnitude by changing the pH and this equilibrium adsorption appeared to be reversible. The alumina was not soluble over the pH range studied as evidenced by the minor changes between the initial and final values (Table 1). (A simple calculation revealed that a pH change from 1 to 7 would occur if 1.7% of the alumina used was dissolved.)

The effect of the solution concentration on the equilibrium loading was found to be small. As depicted in Fig. 2, at concentrations greater than 0.007 M the curve was virtually flat at high pH and had only a slight slope at low pH. The crossed points (\otimes), are from experiments where virtually

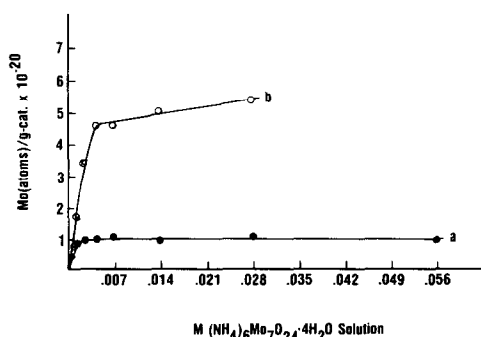


FIG. 2. Molybdena adsorbed on γ -alumina after 100 hr of equilibration for different initial solution concentrations and at final values of (a) pH = 8.1 and (b) pH = 2.1.

TABLE I
Equilibrium Loadings of Anions Adsorbed on γ -Alumina at Various pH Values

Mo			W			V			Cr ^a						
Initial pH	Final pH	Prin. ion spec. ^b	Mo/g cat. $\times 10^{-20}$	Initial pH	Final pH	Prin. ion spec. ^c	W/g cat. $\times 10^{-20}$	Initial pH	Final pH	Prin. ion spec. ^c	V/g cat. $\times 10^{-20}$	Initial pH	Final pH	Prin. ion spec. ^c	Cr/g cat. $\times 10^{-20}$
0.85	1.00	Mo ₉ O ₂₆ ⁴⁻	7.3	1.45	3.2	W ₁₂ O ₃₉ ⁶⁻	4.5 ^d	1.20	1.55	V ₁₀ O ₂₇ (OH) ⁵⁻	5.1 ^d	1.90	3.50	HCrO ₄ ⁻ ≠ Cr ₂ O ₇ ²⁻	1.5
0.95	1.15	Mo ₉ O ₂₆ ⁴⁻	6.2	1.91	4.00	W ₁₂ O ₃₉ ⁶⁻	4.8 ^d	1.95	3.85	V ₁₀ O ₂₇ (OH) ⁵⁻	6.2	4.00	5.55	HCrO ₄ ⁻ ≠ Cr ₂ O ₇ ²⁻	1.3
1.30	1.75	Mo ₉ O ₂₆ ⁴⁻	5.0	2.54	4.50	W ₁₂ O ₃₉ ⁶⁻	5.6	2.40	4.25	V ₁₀ O ₂₇ (OH) ⁵⁻	6.0	9.70	9.20	CrO ₄ ²⁻	0.3
2.00	3.90	Mo ₇ O ₂₄ ⁴⁻	4.0	3.60	5.80	W ₆ O ₂₀ (OH) ⁵⁻	4.8	3.70	6.05	V ₃ O ₉ ³⁻	5.0	10.80	9.80	CrO ₄ ²⁻	0.3
2.80	5.50	Mo ₇ O ₂₄ ⁴⁻	3.6	5.40	6.65	WO ₄ ²⁻	4.6	4.65	6.30	V ₅ O ₁₃ ³⁻	4.7				
4.00	5.80	Mo ₇ O ₂₄ ⁴⁻	3.5	6.65	7.10	WO ₄ ²⁻	4.2	5.30	6.85	V ₃ O ₉ ³⁻	4.6				
4.95	6.10	Mo ₇ O ₂₄ ⁴⁻	3.3	7.60	8.20	WO ₄ ²⁻	2.0	6.90	8.40	VO ₄ ³⁻	2.5				
5.50	6.35	Mo ₇ O ₂₄ ⁴⁻ > MoO ₄ ²⁻	3.1	8.30	8.80	WO ₄ ²⁻	1.4	8.90	9.25	VO ₄ ³⁻	2.0				
6.10	7.40	Mo ₇ O ₂₄ ⁴⁻ ≈ MoO ₄ ²⁻	1.5	9.75	9.30	WO ₄ ²⁻	1.0	10.50	10.00	VO ₄ ³⁻	2.0				
7.20	7.50	Mo ₇ O ₂₄ ⁴⁻ ≈ MoO ₄ ²⁻	1.3	11.00	10.00	WO ₄ ²⁻	0.5								
8.55	7.8	MoO ₄ ²⁻ > Mo ₇ O ₂₄ ⁴⁻	1.1												
9.00	8.90	MoO ₄ ²⁻	0.5												
10.00	9.50	MoO ₄ ²⁻	0.4												

^a Chromate solutions with initial pH ranging from 4 to 8 were not obtainable.

^b References (23, 24).

^c Reference (30).

^d Precipitation occurred.

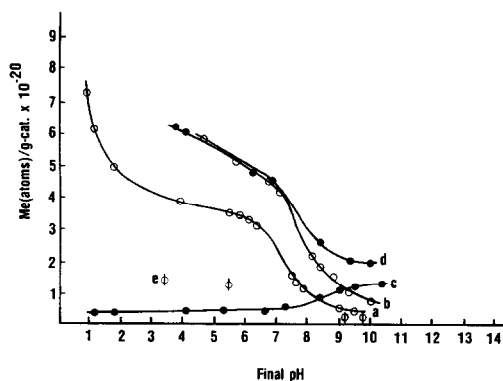


FIG. 3. Equilibrium loadings of a variety of metal ions adsorbed on γ -alumina as a function of the final pH of the adsorbate solutions: (a) molybdena; (b) tungsta; (c) Na^+ ; (d) vanadia; and (e) chromia.

all of the reagent was removed from the solutions. In these cases all of the surface could not participate in the equilibrium.

Figure 3 shows how the loading of alumina with (1) molybdena, (b) tungsta, (c) Na^+ , (d) vanadia, and (e) chromia is controlled by pH. The loadings were obtained from chemical analysis of the calcined catalysts; they are plotted versus the final pH reached by the several solutions at equilibrium. Note that the response for the cationic Na^+ is just the opposite of that for the anionic TMI, but that the break comes at about the same value of the pH. The initial concentrations of the solutions used were in all cases 0.05 M in TMI.

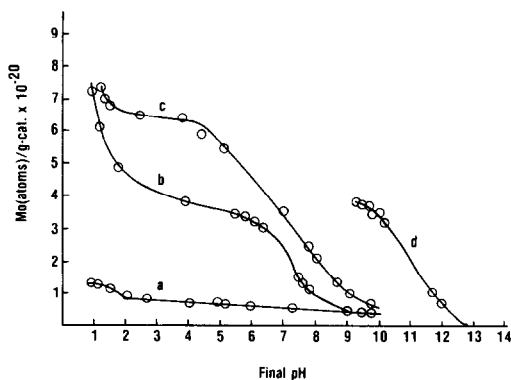


FIG. 4. Equilibrium loadings of molybdena adsorbed on a variety of supports: (a) silica gel; (b) γ -alumina; (c) titania; and (d) magnesia.

The results of similar experiments where molybdena was loaded on (a) silica gel, (b) γ -alumina, (c) titania, and (d) magnesia are presented in Fig. 4. Now the pH regions where the loading dropped sharply varied from less than 1 for silica gel to around 7 for alumina and titania to about 11 for magnesia. With the latter, experiments could not be made at $\text{pH} \leq 9$ where the oxide became soluble. A second upward break appeared near $\text{pH} = 1.5$ on both curves b and c. [The origin of this second increase is not known. It may be that the different exposed crystal planes of the support have different IEPs; it also could be due to cooperative effects which could occur as the coverage becomes high, e.g., the formation of higher polymeric molybdate species on the surface.]

The species present in the molybdate solutions varied with pH. At $\text{pH} = 8.6$ the monomeric MoO_4^{2-} was the dominant ion present (Fig. 8A). Figure 5 shows reflectance spectra taken from this catalyst in the

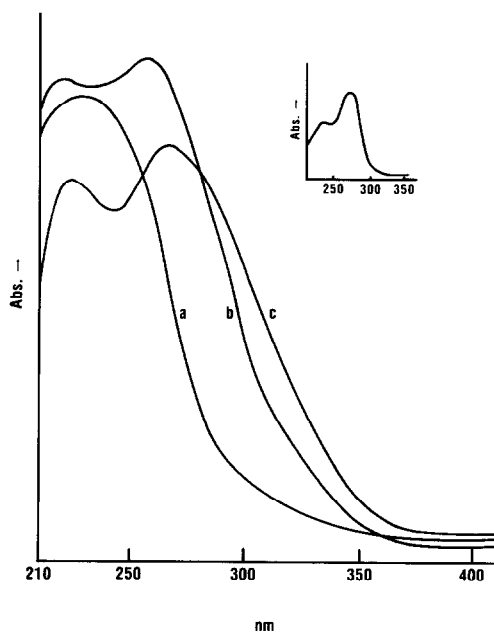


FIG. 5. Ultraviolet-visible reflectance spectra of molybdena-alumina prepared at $\text{pH} = 8.6$: (a) in the wet state; (b) dried at 150°C ; and (c) calcined at 500°C . Inset spectrum is from solid Na_2MoO_4 which contains only tetrahedrally coordinated Mo.

wet, dry, and calcined conditions. Only one band at about 240 nm was observed with the wet catalyst; bands at this low frequency are attributable to the expected tetrahedral species. On drying at 150°C and calcining at 500°C this band splits into two: one at higher and one at lower frequency. As shown by the inset spectrum from Na_2MoO_4 , these spectra may still be attributed to a tetrahedral species. The splitting may correspond to a change in symmetry around the TMI as NH_3 is removed, forcing a proton back onto the molybdate cation. These data are entirely consistent with the Raman spectra for the same catalyst (8) and indicate that at this low loading the catalyst produced at pH = 8.6 contains mainly the monomeric molybdate bound to the surface as depicted in the earlier models (1-4).

The optical reflectance spectra obtained for catalysts prepared at pH = 3.9 and 1.0 are shown in Figs. 6 and 7, respectively. All of these spectra are similar in that they con-

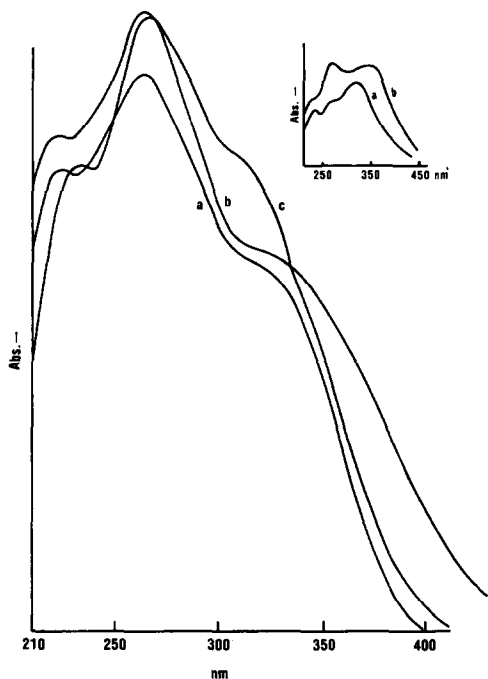


FIG. 6. Ultraviolet-visible reflectance spectra from molybdena-alumina prepared at pH = 3.9; (a) in the wet state; (b) dried at 150°C; and (c) calcined at 500°C. Inset spectra: (a) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$; (b) MoO_3 .

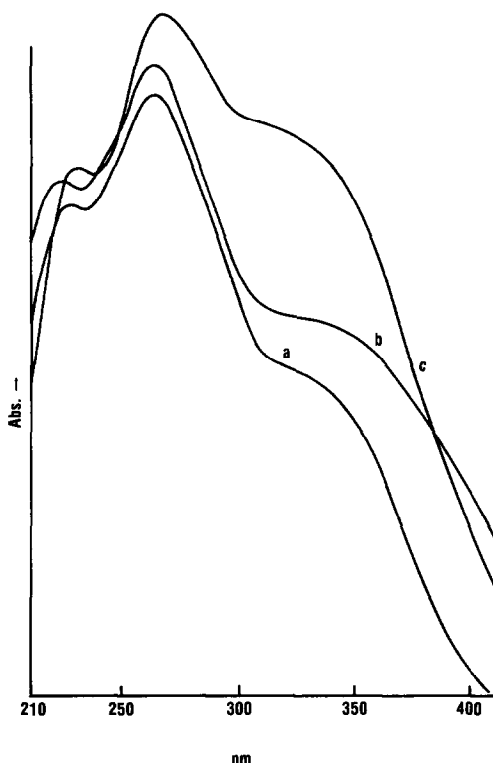


FIG. 7. Ultraviolet-visible reflectance spectra from molybdena-alumina prepared at pH = 1.0: (a) in the wet state; (b) dried at 150°C; and (c) calcined at 500°C.

tain three bands at about 220, 270, and a shoulder above 300 nm. As shown by the inset spectra in Fig. 6 for solid $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ and MoO_3 all three of these bands must be attributable to an octahedral species. Thus, it is not possible to tell from these spectra alone whether or not any monomer is present. In agreement with our previously published Raman data (8), the dominant species on these catalysts appears to be Mo in octahedral coordination, as in the paramolybdate ion. Evidently, the anion which is present in the solution is adsorbed on the support surface in increasing amounts as the pH is lowered. In the pH range usually used (e.g., at pH = 3.9) the solution contains mainly heptamer and probably a small amount of monomer. At pH 1.0 octamer and heptamer are probably both present.

Analogous spectroscopic results were

obtained for the other catalyst systems. Initial and final values of pH for the solutions used and the principal ionic species they contained are listed in Table 1 together with the final equilibrium loadings obtained. In particular the data for the tungsta-alumina system were quite similar to those for molybdena-alumina. In the other cases, differences were observed which could be attributed to the chemistries of the solutions. These findings will be described in later papers.

DISCUSSION

The concept of the isoelectric point provides a unifying factor for the understanding of the present data. This is a well-understood principle of colloid chemistry. Colloidal solutions are stabilized by the net surface charge (or zeta potential) of the colloidal particles. They tend to flocculate as the net charge is reduced to zero by varying the pH to the isoelectric point. The problem adapted to surfaces is summarized in Fig. 8B. The surfaces of most oxides are terminated by hydroxyl groups which substitute for an extension of the lattice. Partial dehydroxylation is common, but in many cases such as with alumina, rehydroxylation occurs when the oxide is immersed in H_2O . As noted by Parfitt (22) these hydroxyl groups become protonated or deprotonated in acidic or basic solutions, respectively. At low pH anions become adsorbed while in basic solutions cations are favored, e.g., see Fig. 3. The ions adsorbed² from solution were retained unchanged in the wet preparation. Anions are adsorbed at low pH and are held by electrostatic forces. This was particularly clear in the work of D'Aniello (21) with $Co(CN)_6^{3-}$ and was also evident in the present work. When $(NH_4)_6Mo_7O_{24}$ was used as solute and the pH was adjusted by adding HNO_3 , polyanions became the ad-

² Adsorption here is in the Gibbs sense. It includes the excess concentration of ions above that in the bulk solution. These are retained within the pore system as the solution is filtered away and the solvent is evaporated.

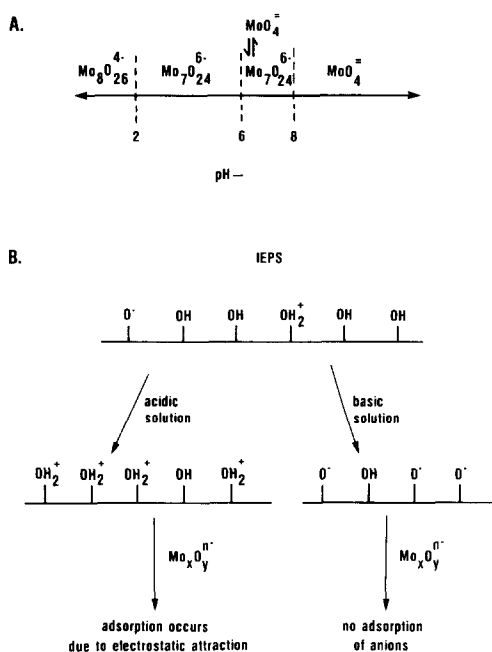


FIG. 8. (A) The dominant molybdenum oxyanions present at various pH regions (Refs. (23, 24)). (B) The proposed adsorption scheme.

sorbed species. On drying, these clusters remained intact as NH_3 was driven off, thus forming a polymolybdic acid. On calcining, reaction with the surface hydroxyl groups of alumina occurred thus binding the clusters to the surface in much the same way as described in earlier models (1-4). It is evident from the available spectroscopic data that these ions remain as bridged clusters as they become bound to the surface. Consequently, the appropriate model for the oxidized form of these catalysts cannot be the epitaxial monolayer, but a surface pimpled with bound polyanions. Some decomposition may occur during calcining and some cluster growth might occur, particularly at the highest loadings, to form islands of bound molybdena several layers deep. Only at the lowest loadings will the monomer exist as the majority species and here its surface concentration will be low. Figure 8A shows the solution composition for the molybdena system. This is evidently a controlling factor in the determination of cluster

size and whether or not much monomeric molybdena is present.

Although the adsorbing species vary in size in different pH solutions (Fig. 8A), the final loading was not controlled by this parameter. In fact, the adsorption was dictated by the extent of surface charging, which in turn was determined by the solution pH and the IEPs of the support. This was demonstrated clearly by the results shown in Fig. 4. In the pH range between 9 and 13 of curve d (MgO support), where the dominant species in the solutions was MoO_4^{2-} , an increase of uptake was observed at pH values lower than the IEPs of MgO (Table 2). Moreover, in the pH range between 10 and 3 of curve a (SiO_2 support), where the dominant species changed from monomer to heptamer, no increase in loading occurred because the pH values in this region were all higher than the IEPs of SiO_2 .

As shown in Table 2, fair agreement was obtained when the break regions of the loading curves were compared with the isoelectric points for the oxide supports as reported in the literature (25). The break regions of the loading curves of Figs. 3 and 4 are well defined but not sharp. This suggests that the different crystal planes may have slightly different isoelectric points. Thus it is possible that at pH = 8.7 the monomeric molybdate species may be

mounted on certain crystal faces and not on others.

The effect of initial solution concentration on the final loading is also unimportant, as shown in Fig. 2, so long as the total molybdena in the available solution is several times the equilibrium adsorption capacity of the support. Otherwise the Mo anions present in the solution will be depleted before they can penetrate completely into the pore system of the support sphere, and consequently, the total uptake will be limited and not homogeneous. This could seriously affect the interpretation of spectroscopic measurements; it was this possibility which instigated the present research.

Because of the method of preparation used, the spectra obtained were well defined. Consequently, it was possible to interpret them fairly and unambiguously. Earlier interpretations (10, 26, 27) have been clouded by impregnation techniques which may have provided mixtures of species.

To date no adequate theory exists for the many bodied problem of the polymeric anions. Consequently, recourse had to be made to comparison with pure compounds. Thus, we have determined spectra for solid MoO_3 and $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, which contain only octahedrally coordinated Mo, and found that three bands are present (inset spectra a, Fig. 6). These are resolved at about 230 and 270 nm and a band in the region 320 to 370 nm, which is seen as a strong shoulder in the catalyst preparations. Similarly, the spectrum for solid Na_2MoO_4 , which contains only tetrahedrally coordinated Mo, contains only two bands (inset of Fig. 5), but at about the same wavelengths as those for the octahedral species. Comparison of these reference spectra with those for our catalysts shows that the catalyst made at pH = 8.6 contains primarily tetrahedral species, in agreement with the Raman data (8). Figures 6 and 7 show two bands below 300 nm with a shoulder above 300 nm. These are indicative of octahedral coordination. However, in these

TABLE 2

Comparison between the Isoelectric Points of the Oxide Supports and the pH Value at the Break Regions of the Molybdena-Oxanyan Adsorption Curves

Oxide supports	Isoelectric point (IEPs) of oxide supports ^a	The break region of the adsorption curve
SiO_2	1.8	1.5-2.0
$\gamma\text{-Al}_2\text{O}_3$	6.0-8.0	7.0-8.0
TiO_2	4.7 (rutile) 6.2 (anatase)	4.0-8.0
MgO	12.4 ± 0.3	10.0-12.5

^a Reference (25).

cases tetrahedral plus octahedral may be present, although this is not a foregone conclusion. The Mo contained in the paramolybdate ion has only octahedral coordination. Nevertheless, regardless of the majority species in solution a small amount of monomeric MoO_4^{2-} will always be present in equilibrium with the heptamer, and this could be adsorbed selectively on particular parts of the surface as a minority species. This is suggested by EPR data (28) as well as by the findings of Hercules and co-workers (12), who studied molybdena-alumina catalysts using ESCA, ISS, and laser Raman spectroscopy. They were led to conclude that monomeric Mo species is always present in the catalyst regardless of the loading level, although the concentration is relatively low. This study, as well as related work with the tungsta-alumina system (29), is in good agreement with the picture presented herein.

In closing it is noted that the features noted herein are rather general and may be applied judiciously to a large number of supported metal oxide systems.

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