

## LETTER TO THE EDITORS

## On the Genesis of Molybdena-Alumina Catalyst

Molybdena-alumina catalysts are usually prepared by the incipient wetness impregnation method. Recently Jeziorowski and Knözinger (1) published Raman and uv spectra taken during the preparation of such catalysts and reviewed nicely the earlier literature in this area. Loadings of 3 and 8% Mo were made using aqueous  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ . It was suggested that during impregnation the surface hydroxyl groups of alumina were replaced by base exchange with tetrahedral  $\text{MoO}_4^{2-}$  ions, the degradation of the polyanions being brought about by an increased local pH close to the surface due to the exchange reaction. Although this idea is in agreement with a surface model which we favored previously (2), we now have evidence that the species initially removed from solution is not  $\text{MoO}_4^{2-}$ , except possibly when the *final* pH  $\geq 8.5$ .

The spectra of Jeziorowski and Knözinger were taken from preparations made using solutions having an *initial* pH of 6 or 11; they contained bands which could be attributed to both monomeric and polymeric anions, and indeed to  $\text{MoO}_3$  crystallites as well. Thus, the distribution of molybdena was heterogeneous even though the loadings were well below those required for monolayer coverage and the spectra necessarily reflected this difficulty. The *final* pH of the solutions in the filled pores was in all cases greater than 8.5 because of the fairly large buffer capacity of the alumina support (3, 4) which altered the pH toward its isoelectric point (5) near this value. An example of this phenomenon is seen in the work of Sonnemans and Mars (6) who passed a solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$

of pH 2 through an alumina bed; the initial effluent had pH  $\geq 8$ . A change in pH was thus unavoidable in the small volume of solution used in the incipient wetness method. Consequently, even though the equilibrium



is far to the left at pH 11 and far to the right at pH 6, the pH values in the catalyst pores during impregnation were much closer to the isoelectric point. Moreover, the same results (6) showed that at this high pH the equilibrium loading was quite low. Thus, the conditions for adsorption of anions probably were unfavorable in the preparations of Jeziorowski and Knözinger (1) and with the wet catalyst a part, or a majority, of the molybdate species remained in solution in the pores during the preparation of the 3 and 8% loaded catalysts, respectively. On drying and calcining, bonding must then have occurred as molybdate species replaced some of the surface OH groups (7), but it cannot be concluded that  $\text{MoO}_4^{2-}$  ions were preferentially adsorbed and later formed polymeric species during drying and calcining. Instead, a proper description is that the content of the solution precipitated nonuniformly onto the surface of the support as the solvent was removed, as evidenced by Raman lines from  $\text{MoO}_3$ . The aggregates thus formed could be responsible for the generation of polymolybdate species during drying, as the pH decreased as  $\text{NH}_3$  was expelled.

To avoid these complications and the resulting ambiguities of molybdate interpretation, several catalysts were prepared by

TABLE 1  
Effect of Preparation Variables on Catalyst Loading<sup>a</sup>

Solution		Major molybdate (8, 9) species	Catalyst	
pH value			Specific Mo loading (atoms/g × 10 <sup>-20</sup> )	Surface area (m <sup>2</sup> /g cat.)
Initial	Final			
0.8	1.0	[Mo <sub>8</sub> O <sub>26</sub> ] <sup>4-</sup>	7.4	151
2.0	3.9	[Mo <sub>7</sub> O <sub>24</sub> ] <sup>6-</sup>	4.0	170
8.6	8.6	[MoO <sub>4</sub> ] <sup>2-</sup>	1.0	184

<sup>a</sup> Ketjen CK-300 alumina was used having a surface area of 188 m<sup>2</sup>/g.

adsorption of molybdate from relatively dilute aqueous solutions (250 ml of 0.007 M) of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub> onto 5-g aliquots of  $\gamma$ -alumina (Ketjen CK-300, 188 m<sup>2</sup>/g). The loading was controlled (6) by varying the pH (with HNO<sub>3</sub> or NH<sub>4</sub>OH). This also dictated the majority species in solution (8, 9) as shown in Table 1. The preparations in Erlenmeyer flasks were agitated on a mechanical shaker for periods of up to 100 h before filtering and determining the *final* values of pH. The resulting loadings, deter-

mined by chemical analysis of the catalysts, are given in Table 1. If no adsorption occurred, a loading of about 1.5 × 10<sup>19</sup> Mo/g should result from the solution left in the pore volume. Significant Raman signals were not produced from these solutions; the concentrations were too low. A useful Raman spectrum could not be obtained from a catalyst prepared at pH 9.5 (0.3 × 10<sup>20</sup> Mo/g) because the signal was too weak. In all cases the filtrates contained more than half the initial reagent. Conse-

TABLE 2  
Summary of Raman Spectroscopic Observations<sup>a</sup>

pH 8.6				pH 3.9				pH 1.0			
Solution	Wet	Dried	Calcined	Solution	Wet	Dried	Calcined	Solution	Wet	Dried	Calcined
				215 (w)	217 (w)	216 (w)	215 (w)	215 (w)	218 (w)	216 (w)	215 (w)
318 (m)	326 (w)	326 (w)		365 (w)	364 (w)	365 (w)	365 (w)	368 (w)	366 (w)	365 (w)	365 (w)
	547 (w)	545 (w)									
846 (w.br.)							860 (m.br.)				860 (m.br.)
896 (st.sh.)	905 (w)	908 (w)		895 (m)	906 (m)	905 (m)		905 (m)	903 (m)	895 (m)	
					928 (w.shl.)	928 (w.shl.)			930 (w.shl.)	930 (w.shl.)	
	945 (w)	945 (w)	950 (w)	940 (st.sh.)	951 (st.sh.)	950 (st.sh.)	950 (shl.)	965 (st.sh.)	956 (st.sh.)	955 (st.sh.)	950 (shl.)
			965 (w.shl.)				970 (st.sh.)	980 <sup>b</sup> (shl.)			975 (st.sh.)

<sup>a</sup> The frequencies are in cm<sup>-1</sup>; the error is about ± 2 cm<sup>-1</sup>.

<sup>b</sup> This band was suggested (10) to be the protonated form of [Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup>.

quently the distributions of molybdena species over the surface area should have been fairly uniform.

The Raman data are summarized in Table 2 where the frequencies observed with the wet, dried (at 373 K), and calcined (at 773 K) catalysts may be compared with those from solutions (0.07 M) having the same (final) pH values as in the preparations. Spectra from the wet and calcined states, respectively, are shown in Figs. 1 and 2. The frequencies recorded from the wet catalyst prepared at pH 8.6 resembled closely those from  $\text{MoO}_4^{2-}$  in solution. The slight shift of the  $\text{Mo}=\text{O}$  band from 896 to  $905\text{ cm}^{-1}$  may be due to the bonding interaction with the alumina surface as suggested by Jezirowski and Knözinger (1). The weak band at  $945\text{ cm}^{-1}$  (Fig. 1a) may be indicative of a small amount of adsorbed polymolybdate, i.e., corresponding to the strong 950-to  $955\text{-cm}^{-1}$  bands shown in

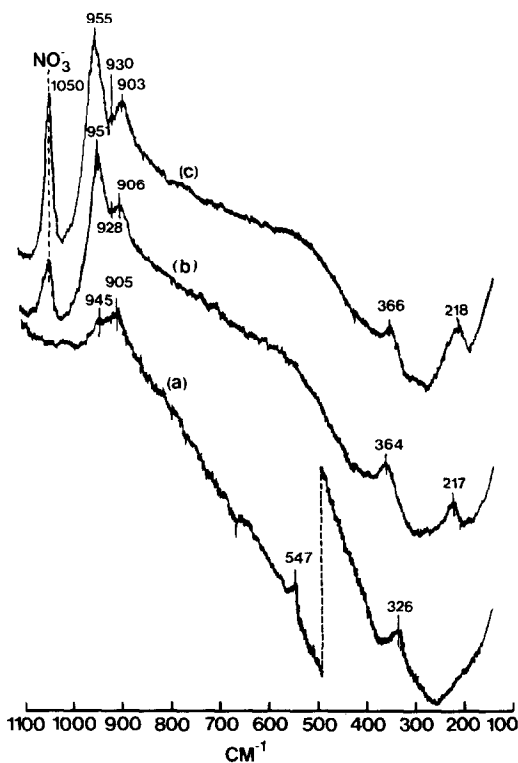


FIG. 1. Raman spectra of wet catalysts prepared at (a) pH 8.6, (b) pH 3.9, and (c) pH 1.0.

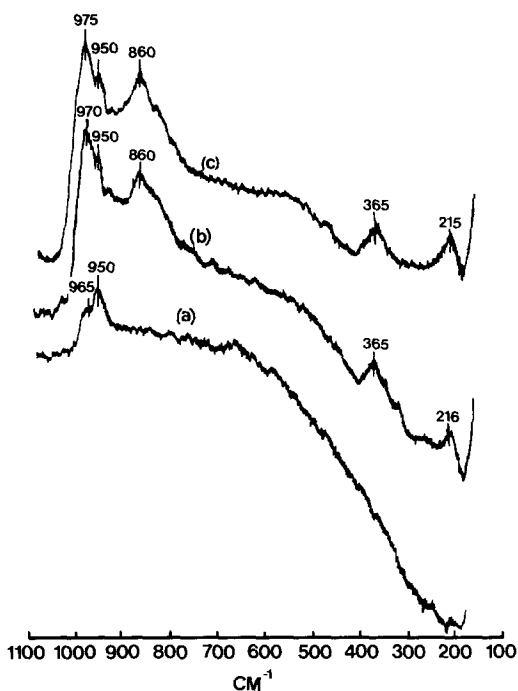


FIG. 2. Raman spectra of calcined catalysts (773 K) prepared at (a) pH 8.6, (b) pH 3.9, and (c) pH 1.0.

spectra 1b and 1c. This species could have reformed as  $\text{NH}_3$  was evaporated from the solutions (compare Figs. 1a and 2a).

The spectral bands at about 215 and  $365\text{ cm}^{-1}$  obtained from the wet preparations made at pH 3.9 or 1.0 clearly identify the adsorbed species as polymolybdate. The low-frequency bands obtained from the solutions remained virtually unchanged on drying and calcining. The bands at higher frequencies did not undergo significant change on drying. Note that the solution at pH 1.0 produced a band at  $980\text{ cm}^{-1}$  thought to stem (10) from a protonated form of  $\text{Mo}_8\text{O}_{26}^{4-}$ . Bands in this region were also observed with the calcined catalysts, viz., at 965, 970, and  $975\text{ cm}^{-1}$  for catalysts produced from solutions at pH 8.6, 3.9, and 1.0, respectively. Very likely these correspond to an  $\text{Mo}=\text{O}$  vibration of a polymolybdate species bonded to the alumina surface (7), this bonding affecting the bond order as does protonation. The degree of aggregation may also be a factor. It is

known that this terminal stretching frequency increases with the Mo/O ratio (11).

Iannibello *et al.* (12) suggested that the band at  $950\text{ cm}^{-1}$  corresponded to the Mo = O frequency of a tetrahedral molybdate group bonded to the surface. This interaction was supposed to increase the bond order from that in the aqueous free ion, and hence the frequency (from about  $900$  to  $950\text{ cm}^{-1}$ ). The frequency shifts observed on calcination of the pH 8.6 preparation (compare Figs. 1a and 2a) could be taken in support of this idea. On the basis of this assignment, all preparations contained the tetrahedral monomeric species as this band appeared in the spectra of all preparations, regardless of pH. The ratio of intensities of the  $950$  and  $970\text{ cm}^{-1}$  bands can then be taken as a measure of the ratio of tetrahedral monomeric to octahedrally coordinated polymolybdate species. Note that this ratio decreases with increasing loading, in agreement with the findings of Giordano *et al.* (13). However, an alternative interpretation cannot be ruled out on the basis of the present data. This is that the  $950\text{-cm}^{-1}$  absorption corresponds to polymolybdate clusters of small size (say seven Mo) and the higher frequency bands to clusters of larger size. All preparations exhibited the latter after calcination, whereas none of these contained the  $900\text{-}$  to  $905\text{-cm}^{-1}$  band, which would now correspond to the monomeric species. Either this species is rare after calcining or its Raman band is broadening beyond detection by distortion as it becomes bonded to the surface. We think the former explanation (12) is the more likely.

The picture which has emerged is as follows. The alumina surface becomes positively charged at low pH and readily adsorbs the molybdena polyanions which are present in solution under these circumstances. The binding in the wet and dried catalysts is primarily electrostatic. At high pH, the surface takes on a net negative charge and tends not to adsorb the monomeric  $\text{MoO}_4^{2-}$  ions present in these solu-

tions although, as with the incipient wetness technique, molybdena compounds are deposited on the surface as  $\text{H}_2\text{O}$  and  $\text{NH}_3$  are removed. On calcination, bonding to the surface will occur as molybdena species replace the surface OH groups of the alumina (7). At low pH, the wet surface should be uniformly covered by polyanions and on calcination these should result in patches or islands of bound polymolybdate clusters perhaps two layers deep. This model is in accordance with the recent finding (14) that large areas of alumina surface remain uncovered at the 8% Mo loading level so that the proton resonance is unaffected by paramagnetic centers introduced into the molybdena clusters by reduction.

#### ACKNOWLEDGMENT

This work was supported by NSF Grant CHE77-07772 for which we are grateful.

#### REFERENCES

1. Jeziorowski, H., and Knözinger, H., *J. Phys. Chem.* **83**, 1166 (1979).
2. Hall, W. K., and Massoth, F. E., *J. Catal.* **34**, 41 (1974); Hall, W. K., and LoJacono, M., *Proc. Sixth Int. Congr. Catal. (London)* **1**, 246 (1977).
3. Parfitt, G. D., *Pure Appl. Chem.* **48**, 415 (1976).
4. Murrell, L. L., and Yates, D. J. C., in "Preparation of Catalysts. II. Scientific Bases for the Preparation of Heterogeneous Catalysts," Proceedings of the Second International Symposium, Louvain-la-Neuve, September 4-7, 1978 (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 307. Elsevier.
5. Parks, G. A., *Chem. Rev.* **65**, 177 (1965).
6. Sonnemans, J., and Mars, P., *J. Catal.* **31**, 209 (1973).
7. Millman, W. S., Crespin, M., Cirillo, A. C., Jr., Abdo, S., and Hall, W. K., *J. Catal.* **60**, 404 (1979).
8. Aveston, J., Anacker, E. W., and Johnson, J. S., *Inorg. Chem.* **3**, 735 (1964).
9. Honig, D. S., and Kustin, K., *Inorg. Chem.* **11**, 65 (1972).
10. Griffith, W. P., and Lesniak, P. J. B., *J. Chem. Soc. A*, 1066 (1969).
11. Cheng, C. P., and Schrader, G. L., Jr., *J. Catal.* **60**, 276 (1979).
12. Iannibello, A., Marengo, S., Trifiro, F., and Villa,

- P. L., in "Preparation of Catalysts. II. Scientific Bases for the Preparation of Heterogeneous Catalysts," Proceedings of the Second International Symposium, Louvain-la-Neuve, September 4-7, 1978 (B. Delmon, P. Grange, P. Jacobs, and G. Poncelet, Eds.), p. 65. Elsevier.
13. Giordano, N., Bart, J. C. J., Vaghi, A., Castellan, A., and Martinotti, G., *J. Catal.* **36**, 81 (1975).
  14. Cirillo, A. C., Jr., Dereppe, J. M., and Hall, W. K., *J. Catal.* **61**, 170 (1980).

LI WANG  
W. KEITH HALL

*Department of Chemistry and Laboratory  
for Surface Studies  
University of Wisconsin-Milwaukee  
P.O. Box 413  
Milwaukee, Wisconsin 53201*

*Received March 5, 1980*