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Raman Spectra from Several Molybdena–Alumina Preparations

For reasons outlined earlier (*1–3*) we were led to conclude that the support surfaces of preparations made by the usual incipient wetness method are usually not uniformly covered with a molybdena monolayer as pictured by models advanced by several authors (*4–6*). An equilibrium adsorption method was therefore devised (*1*) by which preparations could be made where all parts of the surface have equal access to the same solution concentration. The structural characteristics of these surfaces were then deduced. It was concluded that an epitaxial monolayer formation did not occur, rather, at pH ≤ 8 where monolayer formation was possible, small clusters or islands containing seven or so Mo^{+6} became bound to the support leaving uncovered areas of alumina in between. Evidence was also presented (*2*), however, for the presence of a small fraction of tetrahedrally coordinated monomeric species in catalysts containing approximately 8% Mo, and it was also deduced that this was the dominant species in catalysts made at high pH and consequently having loadings $\leq 2\%$ Mo.

It is the purpose of the present communication to point out how preparation and pretreatment variables may affect the structure of the resulting catalysts, the extent of segregation and/or aggregation and hence the Raman spectra obtained. All spectroscopic methods produce envelopes which are integrals of absorption from all species present. It therefore seems obvious that care must be taken in deriving conclusions from data from such systems and that complicating effects should be avoided or minimized whenever possible when the work is intended to lead to basic understanding of the system.

Spectra from three preparations are shown in Fig. 1. A catalyst containing 8% Mo on Ketjen CK-300 alumina made by the incipient wetness technique (Fig. 1a) is compared with one made by our equilibrium adsorption method (Fig. 1b). The former is the catalyst which has been used in most of the studies reported from this laboratory during the past decade whereas the latter has been used only in studies reported by the present two authors and referenced herein. The same alumina base was, however, used for all preparations. Interestingly, Fig. 1b is a fairly simple spec-

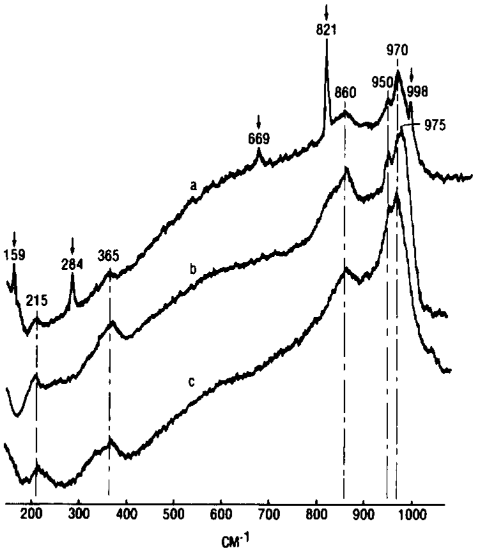

FIG. 1. Spectrum a was obtained from a preparation (8% Mo) made by the incipient wetness method. Arrows indicate bands assignable to MoO_3. Spectrum b is for a similar preparation made with the same alumina by the equilibrium adsorption method. Spectrum c was obtained from a preparation made by adsorption of $Mo(CO)_6$ after calcining.

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trum containing essentially the same bands which are present in solutions of $(NH_4)_6Mo_7O_{24}$. Thus, the principal bands stem mainly from polyanions bound to the support by partial replacement of the surface hydroxyl groups. The band at 950 cm^{-1} may, however, result from a small amount of a tetrahedral monomeric species (*1*). The impregnated catalyst (Fig. 1a) contains a number of bands not present in the more carefully prepared catalyst. Most of these can be attributed to segregated MoO_3. These are indexed with arrows to distinguish them from the others. The remaining bands are those shown in Fig. 1b. Interestingly, the MoO_3 bands disappeared gradually on going through several reduction-oxidation cycles.

The final spectrum (Fig. 1c) was obtained from a preparation made by the adsorption of $Mo(CO)_6$ by vacuum transfer onto the surface of the freshly pretreated alumina (after evacuation at 525°C). About 20 g of alumina were placed in a Pyrex glass reactor to which a side arm containing $Mo(CO)_6$ was connected. The side arm containing the frozen carbonyl was evacuated and isolated from the reactor by a Teflon stopcock. The alumina contained in the reactor was then pretreated by flowing O_2 overnight at 525°C followed by evacuation at this temperature for 30 min. After cooling to room temperature, the stopcock was opened and $Mo(CO)_6$ vapor was allowed to diffuse into the reactor and adsorb onto the alumina. The color of γ-alumina changed from white to bright yellow during this process indicating reaction with the surface. After the adsorption was completed, (overnight) the reactor was flushed with He at 100°C to remove excess $Mo(CO)_6$. This was followed by treatment with flowing O_2 as the temperature was gradually raised to 500°C where it was kept constant overnight. Interestingly, the spectrum from this preparation (Fig. 1c) was indistinguishable from that obtained from that made by the equilibrium adsorption method. Thus, the monomeric carbonyl species following decomposition and oxidation must aggregate into the same kind of bound clusters which result from the adsorption of $Mo_7O_{24}^{-6}$. The same result was obtained from a preparation made by multiple impregnation of the alumina with a solution of $Mo(CO)_6$ in dry pentane. This ability to migrate and form small clusters is of interest for a couple of reasons. The cluster size deduced from our earlier studies (*1*, *2*) suggests the presence of 7 or 8 Mo per cluster. A similar deduction was made from EXAFS measurements by Topsøe and co-workers (*7*). In addition, we have presented evidence that although this cluster is the dominant species, a small amount of tetrahedrally coordinated Mo is also present, possibly on some particular surface plane or site (*2*). Given this information, it is interesting to conjecture that the surface structure and consequently the resulting catalytic properties may be affected by the details of the preparation and pretreatment precedures used. This notion is supported by the existing literature, where many times the Raman bands were not, or could not be assigned. For example, in the pioneering work of Brown *et al.* (*8*), bulk MoO_3 was reported for loadings higher than 18% as MoO_3, but it was not recognized that lines from $Al_2(MoO_4)_3$ were also present. Their work also showed differences in the composition of the molybdena phases from the external surfaces of preformed pellets from those on the surface of the internal volume, and these varied with loading. Cheng and Schrader (*9*) and Jeziorowski and Knözinger (*10*) studied catalysts of varying loadings on aluminas from different sources and having different surface areas. Bulk MoO_3 was present, as in Fig. 1a, in preparations of loadings higher than about 8% MoO_3 when the incipient wetness method was used. Most recently Zingg *et al.* (*11*) made a thorough study of a series of catalysts of varying loading (1–30% MoO_3) on the Harshaw alumina used by Brown *et al.* (*8*). Bulk MoO_3 was found when the loading was 20% or more and $Al_2(MoO_4)_3$ was found at loadings above

14%. Moreover, prolonged calcination at 500°C or above appeared to convert the former into the latter. Many of these complications can be avoided by using an equilibrium adsorption method, thus simplifying interpretation of the data. No evidence exists, however, that this careful preparation technique provides a superior catalyst.

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L. WANG[1]
W. KEITH HALL[2]

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

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[1] Present address: U.O.P., Process Division, Riverside, Illinois 60546.

[2] To whom all correspondence should be addressed.