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The Preparation and Properties of Rhenia–Alumina Catalysts

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A series of rhenia–alumina catalysts were made using an equilibrium adsorption technique. These were characterized by laser Raman, infrared, and visible reflectance spectroscopy. Only a monomeric rhenia species was found bound to the alumina of the resulting catalysts. The visible reflectance spectra showed, however, that the symmetry around the Re was lower than tetrahedral, possibly C_{2v} or C_{3v}, i.e., distorted tetrahedral. The laser Raman spectra were sensitive to moisture; the alumina-bound rhenia could be readily hydrolyzed to $HReO_4$. The extremely broad band (hump) between about 300 and 800 cm^{-1} decreased with increase in loading and nearly disappeared from spectra of samples evacuated at temperatures above 350°C. It may therefore be attributed to fluorescence from the surface hydroxyl groups on the alumina support. A brief temperature programmed reduction (TPR) study revealed that most of the rhenia could be reduced to Re^0 at 275°C, but a very small amount appeared to resist reduction up to 500°C.

INTRODUCTION

Molybdena–alumina, tungsta–alumina, and rhenia–alumina are all metathesis catalysts after induction with olefin at room temperature (*1–3*), or following a very mild reduction in H_2 (*4*). Superior bimetallic reforming catalysts have been prepared by the addition of rhenium to the usual Pt-alumina preparations (*5, 6*) and there has been much discussion (*7–10*) concerning the origin of this synergisms. The present work contributes to the understanding of the nature of the rhenia–alumina portion of these catalysts prior to reduction. Previous closely related work (*11–14*), because of varying preparation procedures and rhenia loadings, has produced somewhat contradictory results and an incomplete picture of the raw catalyst. Olsthoorn and Boelhouwer (*11*) sublimed Re_2O_7 onto the surface of a dehydroxylated alumina (200 m^2/g). The loading was varied from about 20 to 26% Re_2O_7 by changing the temperature of the alumina support. These loadings ($>5 \times 10^{20}$ Re/g) were close to the epitaxial monolayer capacity of the alumina as judged by related results for the molybdena–alumina system (*15, 16*). Yao and Shelef (*12*) prepared rhenia–alumina catalysts containing 1.2 to 5.5% Re_2O_7 by the incipient wetness technique. These authors reported that two different aggregation states of rhenia were present: a two-dimensional phase together with three-dimensional crystallites. Kerkhof *et al.* (*13*) prepared catalysts containing 6 to 18% Re_2O_7 by the incipient wetness method. Their Raman spectroscopic studies suggested that tetrahedral ReO_4^- ion was the only species present. On the other hand, the ir results of Nakamura *et al.* (*14*) indicated that only ReO_4^- was present in catalysts containing less than 13% Re_2O_7, but at higher loadings (~17%) excess Re_2O_7 was found.

A problem with all spectroscopic techniques is that they integrate over all species present. The incipient wetness method is not well designed to prepare catalysts uniformly covered with the catalytically active transition metal ion species. Moreover, it is more likely that segregation of a portion of the active component into three-dimensional crystallites will occur at higher load-

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ings than at low. Recently we devised an equilibrium adsorption method (*15, 16*) to circumvent these difficulties. Anions of the active component are adsorbed from solutions having pH values below the isoelectric point of the support. The like charge of the adsorbed anions prevents clustering although polyanions may be present in, and be adsorbed from, the solutions. This occurs with molybdena and tungsta preparations but should not occur with rhenia where only the monomeric anion is present over the entire pH range (*17*). Because of this difference, it seemed worthwhile to extend these earlier studies to the rhenia–alumina system.

EXPERIMENTAL

Catalyst Preparation

The preparation method has been described in detail elsewhere (*15, 16*). Typically 5 g of the support (Ketjen CK-300 high purity γ-alumina having a BET surface area of 192 m^2/g) were added to 250 ml of a 0.05 *M* solution of ammonium perrhenate (supplied by Research Organic/Inorganic Chemical Co. with nominal purity of 99.9%) and the pH was adjusted to the desired value by either adding HNO_3 or NH_4OH. These mixtures were agitated for up to 100 h on an automatic shaker. Initial and final pH values were recorded before the supernatant liquid was filtered away. The wet catalysts were dried in air at 150°C for 6 h without any further washing and finally calcined at 500°C under a stream of dry air. Spectra were recorded at the various steps. The rationale behind these procedures has been given previously (*15*).

Spectroscopic Techniques

These also have been discussed previously. The uv-visible spectra were taken with a Cary 17 spectrometer fitted with a Model 1711 diffuse reflectance attachment. Samples were pretreated in a vacuum Cuvette cell where they were first calcined in flowing O_2 at 500°C before examination. An identical cell filled with the support material was used as a reference when recording the spectra.

The ir spectra were recorded using a Nicolet MX-1 Fourier transform spectrometer using signal averaging over a 10-min period with 32 scans per minute. Self-supporting wafers were used in a vacuum tight cell where high temperature pretreatments could be carried out *in situ*.

The laser Raman spectra were obtained using a Spex-Ramalog Model 1401 spectrometer equipped with a Spectra-Physics Model 164 Ar^+ laser. The 488-nm line was used as the exciting source. Estimated accuracy was ± 2 cm^{-1} with a slit setting of 4 cm^{-1}. Two methods were used. Pressed, self-supporting wafers 0.5 mm thick were calcined overnight at 500°C in a stream of dry air and then mounted on a rotation device and spun in air at about 1000 rpm. A special cell was constructed which allowed spectra to be recorded in controlled atmospheres following *in situ* treatments with O_2 at 500°C, vacuum, and other subsequent treatments as required. This is shown in Fig. 1. The catalyst wafer was mounted against the flat face of the cold finger. The latter was kept filled with liquid nitrogen while the spectra were being recorded to minimize effects of heating by the laser beam. Where cross-comparison was meaningful, identical spectra were obtained by the two methods.

The TPR apparatus was conventional. The disappearance of H_2 (*17*) from a N_2 carrying stream was measured as the temperature was increased linearly from room temperature to 600°C at 5°/min, where it was maintained constant for an additional hour. The catalyst weight was varied inversely with Re loading so that a constant amount of Re^{7+} was available for reduction in all experiments. Thus, the ease of reduction may be judged by the sharpness of the peaks. The catalyst was contained as a column in a 10-mm i.d. tube; weights used were 1.44, 0.36, and 0.15 g for catalysts ReA-0.3, ReA-1.2, and ReA-2.9, respec-

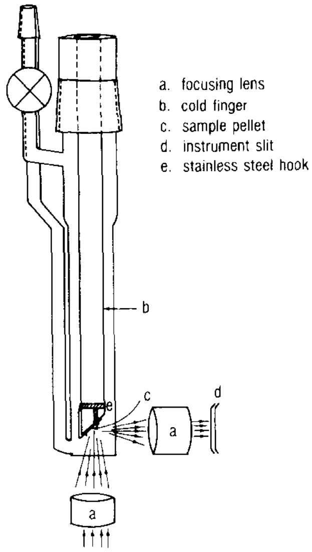

FIG. 1. Schematic drawing of controlled atmosphere Raman cell. Note provision for cooling platelet to about 78 K.

TABLE 1

Equilibrium Loadings of Rhenia on γ-Alumina at Various pH[a]

Initial pH	Final pH	Final loading (Re/gcat) × 10^{-20}	Surface area m^2/g
1.00	1.40	1.3	—
1.50	2.20	1.4	—
1.80	4.40	1.2	1.97
3.20	4.90	0.6	—
9.10	9.00	0.3	1.88
1.70[b]	4.20	2.9	1.96

[a] Gamma-alumina (5 g Ketjen CK-300) was mixed with 250 ml of 0.05 *M* ReO_4^- solution and shaken for about 100 h for each preparation.

[b] Solution concentration was 0.5 *M*. The increase in loading was entirely due to excess reagent in the solution held in pore volume.

tively; the column lengths filled were about 19, 5.0, and 2.0 mm. The flow rate was 60 cc/min.

Various calibration standards were used as outlined in the text.

RESULTS

Catalyst Preparation

The effect of pH on catalyst loading is shown in Table 1. As observed previously, the pH drifted during the preparation in the direction of the isoelectric point of alumina, i.e., toward pH ≈ 8.7. Moreover, the loading fell by a factor of about 6 as the final pH was increased from 1.4 to 9.0 as expected (*15*). Surface areas are shown for the preparations discussed further herein. In the following text the loading is indicated in the catalyst designation, e.g., ReA-1.2 represents 1.2 × 10^{20} Re/g mounted on alumina.

Laser Raman Studies

Reference spectra from solid perrhenates and from ReO_4^- in solution are compared with that from ReA-1.2 in Fig. 2. The bands from the solids are quite sharp compared with those from solutions and from the catalyst when taken in air. Thus, the same bands appear in all spectra, but the resolution is better with the solids. Moreover, the spectrum from the catalyst resembles most

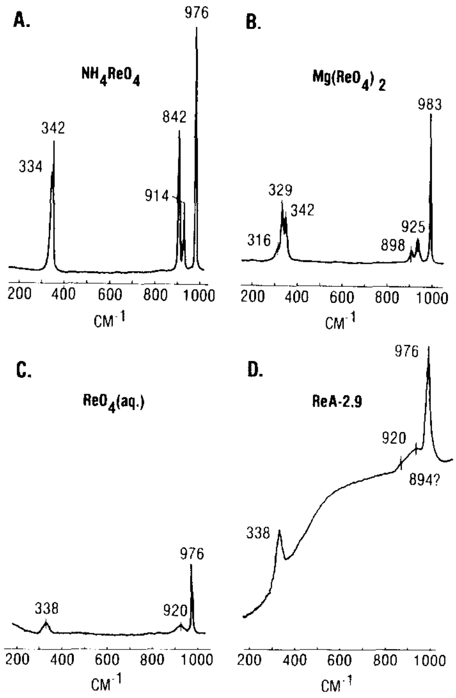

FIG. 2. Comparison of the spectrum from the oxidized form of a rhenia–alumina catalyst (D) with various reference spectra.

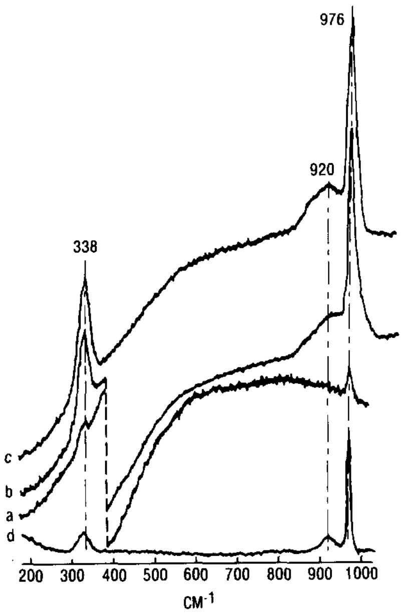

FIG. 3. Raman spectra taken in air of calcined (500°C): (a) ReA-0.3; (b) ReA-1.2; (c) ReA-2.9 made at pH = 9.0, 4.4, and 4.2, respectively. Spectrum (d) was from a 0.1 M solution of ammonium perrhenate (NH_4ReO_4). Note that ReA-2.9 was prepared from a 0.5 M solution. Its higher loading can be accounted for solely on the basis of the excess solute held in the pore system.

closely that from the solution for reasons that will become apparent later.

The laser Raman spectra from catalysts of increasing loadings are shown in Fig. 3 where they are compared with (d), the solution spectrum of Fig. 2C. These data leave little doubt that ReO_4^- is present on the alumina surface. Note the broad hump in the region between 400 and 800 cm^{-1} which became more pronounced as the loading was lowered, i.e., as the surface hydroxyl concentration was increased. It may be supposed therefore that its origin is from fluorescence. Similar results have been reported earlier for molybdena–alumina and tungsta–alumina catalysts (*15, 16*).

The above spectra were taken in air and thus the calcined catalysts were in contact with atmospheric moisture. The previous ir studies of Olsthoorn and Boelhouwer (*11*) suggested that the rhenia species bound to the alumina surface underwent partial hydrolysis on brief exposure to water vapor, thus regenerating surface hydroxyl groups. This phenomenon was studied in more detail using the controlled atmosphere cell. The corresponding spectra are presented in Fig. 4. Catalyst ReA-1.2 was first oxidized at 500°C overnight, and then resaturated with doubly distilled water vapor at room temperature. When the spectrum was taken after evacuation for one hour at room temperature (Fig. 4a), it was found to be identical with that obtained for the same catalyst in air (Fig. 3b). The catalyst was then evacuated at successively higher temperatures for periods of 1 h. The 338-cm^{-1} band remained unaffected, but the 925-cm^{-1} band was shifted to 894 cm^{-1} and the band at 976 cm^{-1} was gradually replaced by a band at 991 cm^{-1} which shifted continually upward as the catalyst was evacuated at higher and higher temperatures. This band was finally replaced by two bands at 1004 and 1015 cm^{-1} on evacuation at 350°C where a splitting of the 338-cm^{-1} band also occurred. This later splitting suggested that a species

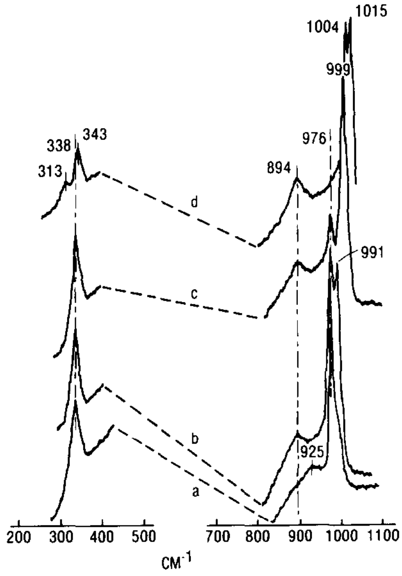

FIG. 4. Raman spectra of ReA-1.2 (made at pH = 4.4) at various degrees of surface hydroxylation taken in the controlled atmosphere cell. (a) Exposed to H_2O and then evacuated at 25°C; (b) at 150°C; (c) at 250°C, and (d) at 350°C.

on the catalyst remained tetrahedral but became strongly distorted on binding to the surface. It is possible that the bands at 925 and 894 cm^{-1} coexist in all these spectra and simply vary in intensity, although this is not clearly demonstrated by our observations (see also Fig. 2D). On cooling to room temperature and reexposure to H_2O the system was returned to its initial condition (Fig. 4a). The cycle could be reproduced; all changes were reversible. The fact that the unspun sample in the controlled atmosphere cell gave the same spectrum as the sample spun in air, as well as the reproducibility of the cycle, indicated that the spectral changes were not caused by heating in the laser beam.

Spectra for catalysts of several different loadings after evacuation at 500°C are compared in Fig. 5. The catalyst of lowest loading (ReA-0.3) showed only one peak at 1013 cm^{-1}. The higher loading ReA-1.2 preparation showed bands at 313, 343, 894, 1004, and 1015 cm^{-1}. The spectrum from ReA-2.9 contained the same bands except that an additional weak peak was observed at about 800 cm^{-1} which might be attributed to an Al–O–Re vibration. Note that the broad fluorescent hump is much less pronounced in these spectra.

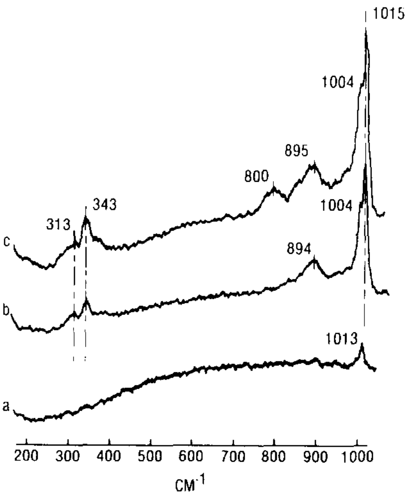

FIG. 5. Raman spectra from several catalysts taken in the controlled atmosphere cell after evacuation at 500°C: (a) ReA-0.3; (b) ReA-1.2; (c) ReA-2.9.

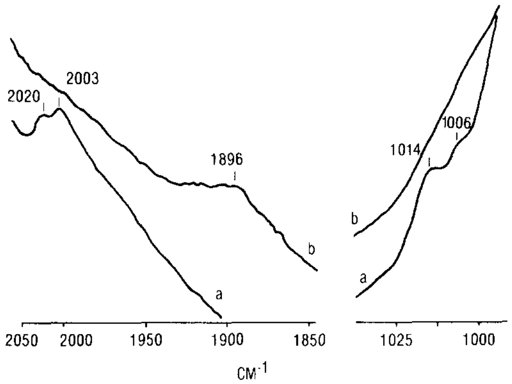

FIG. 6. Infrared spectra from the fundamental and first overtone stretching modes of the Re═O vibration. Spectrum (a) is for ^{16}O and spectrum (b) for ^{18}O substituted ReO_4^-.

The Raman bands in the high frequency region are thought to be due to Re═O stretching modes. As shown in Fig. 6, these same bands appear in the ir spectra together with their first overtones at 2003 and 2020 cm^{-1}. These assignments were confirmed by substitution of ^{18}O for these oxygens. The catalyst was first reduced with hydrogen and then reoxidized with $^{18}O_2$, the process being repeated six times. The band at 1896 cm^{-1} is in the expected position for the isotopically shifted overtone bands, although the doublet was not resolved. The fundamentals near 1000 cm^{-1} are shifted into the cutoff region covered by the alumina lattice vibrations.

uv-Visible Spectroscopic Studies

Spectra obtained from catalysts with increasing loading (made with decreasing pH) are shown in Fig. 7. In contrast with similar results obtained for molybdena–alumina and tungsta–alumina catalysts, these spectra differed only in intensity. The principal bands appeared near 240 and 305 nm. These data may be compared with those obtained by transmission through solutions which are listed together with their assignments in Table 2 where comparison is also made with the related molybdates and tungstates

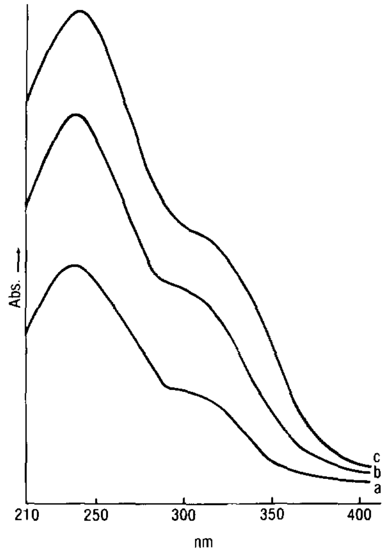

FIG. 7. uv-Visible spectrum taken from catalysts: (a) ReA-0.3; (b) ReA-1.2, and (c) ReA-2.9 after evacuation at 500°C.

(*18*, *26*). Interestingly, the spectra of Fig. 7 indicate the presence of a species having C_{3v} symmetry ($HReO_4$); the absorption band near 300 nm would not appear in the spectra from tetrahedral ReO_4^-. The expected band at about 210 nm could not be detected with our spectrometer.

Temperature Programmed Reduction Studies

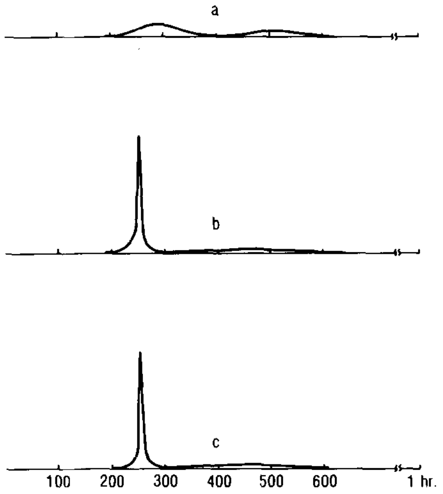

FIG. 8. Temperature programmed reduction (TPR) profiles of (a) ReA-0.3; (b) ReA-1.2, and (c) ReA-2.9. Maximum temperature was 600°C which, when reached, was held constant for 1 h. To maintain the same amount of Re in each experiment the catalyst weight was varied. Therefore, the normalized column lengths were 9.7 to 2.4 to 1.0, respectively.

TABLE 2

uv-Vis. Absorption Band Positions of Some Solution Transition-Metal Oxyanion Species[a]

Ion	Symmetry	$3t_2 \leftarrow t_1$	$2e \leftarrow t_2$	$5e \leftarrow a_2$	$5e \leftarrow 4e$
ReO_4^-	*Td*	205	235		
MoO_4^{2-}	*Td*	205	230		
WO_4^{2-}	*Td*	—	200		
CrO_4^{2-}	*Td*	273	373		
$HReO_4$	C_{3v}	210		230	295
$HMoO_4^-$	C_{3v}	210		230	260
$HCrO_4^-$	C_{3v}	260		350	450

[a] Data taken from Refs. (*18*) and (*26*).

These results are presented in Fig. 8 for ReA-0.3, ReA-1.2, and ReA-2.9. The extents of reduction of these catalysts as determined by integrating the peak areas were 6.6, 7.1, and 6.8 *e*/Re, respectively. The corresponding values determined for the same (reduced) preparations by measuring volumetrically the amounts of oxygen consumed for complete reoxidation were 7.0, 6.9, and 7.0 *e*/Re. It is therefore evident that the rhenia is essentially completely reduced to the metal under these conditions. The TPR data show that most of this reduction occurs below 300°C, but that a small portion resists reduction to nearly 600°C. Moreover, the lowest loading catalyst appeared to be less easily reducible than the other two which produced the sharp peaks near 260°C. The broadening depicted in Fig. 8a may have been due, at least in part, to the much longer column length required to put the same amount of Re in the reaction vessel in this experiment than for the other two. It is also possible, however, that the rhenia at this low loading is bonded to sites on particular lattice planes and that these species are more resistent to reduction. It is well known that molybdena–alumina catalysts become more difficult to reduce as the loading is lowered.

DISCUSSION

For fundamental studies of supported metal oxides, it is highly desirable to make catalysts with all parts of the surface the same as all others. This is particularly important when the research involves spectroscopic measurements where the spectral envelopes are produced, i.e., the integrated data from several related species. Where applicable, equilibrium adsorption techniques afford distinct advantages. The rhenia–alumina system is a particularly simple one. Unlike the molybdena–, tungsta–, and vanadia–alumina preparations previously described (*15*), only one ion, ReO_4^- exists in solution for the entire range of pH. Nevertheless, as shown in Table 1, the loading can be varied by nearly an order of magnitude by control of this factor. The more acidic the solution, the higher is the loading obtained. The data presented herein thus support the previous picture that the alumina surface becomes positively charged (positive zeta potential) at pH values below its isoelectric point.

In contrast with systems which form polyanions as the pH is lowered, only the monomer exists in perrhenate solutions. Bearing this in mind, the loadings shown in Table 1 and their variation with pH are in reasonable agreement with those published earlier (*15, 16*) for molybdena–, tungsta–, and vanadia–alumina catalysts. Interestingly, the Raman spectra of Fig. 3 showed only changes in band intensity as the loading was increased. This is in contrast with the polyanion systems (*15, 16, 22–24*), where the band positions changed with the compositions of the solutions from which they were made (controlled by pH).

The band positions for the rhenia–alumina catalysts were in fair agreement with those expected from the reference spectra (Fig. 2). The bands at 338, 920, and 876 cm^{-1} from aqueous solutions of ReO_4 have been previously interpreted (*19, 20*) as the bending and the antisymmetric and symmetric stretching vibrations of this ion, respectively. Evidently the rhenia monomers are well dispersed; the spectra contain no evidence for dimeric species. Raman spectra of solid Re_2O_7 contain more than 20 sharp bands. In the liquid melt (350°C) major bands appear at 185, 341, 972, and 1009 (*21*). The 185-cm^{-1} band corresponds to the strong Re–O–Re bending mode; it would be diagnostic for this species if present.

The uv-visible spectrum of the undistorted, tetrahedral ReO_4^- ion reportedly has only 2 bands at about 205 and 230 nm (*18*). On distortion, the degeneracy is lifted and 3 bands appear at 205, 230, and 295 nm. The 205-nm band is below the range available to our instrument, but clearly the 2 higher frequency bands are present in Fig. 7. Moreover, these spectra were relatively insensitive to moisture. Consequently, the bound species cannot be distinguished from $HReO_4$ by this technique.

The controlled atmosphere cell afforded a means to study the effects of adsorbed water. As described previously (*25*), a Brönsted acid is produced by the addition of H_2O to unreduced molybdena–alumina catalysts. Olsthoorn and Boelhouwer (*11*) noted that hydrolysis occurred on exposure of rhenia–alumina to H_2O. The acidity of this and related systems can be understood in these terms.

The shifts of the Re═O stretching modes in the region 800–1000 cm^{-1} and the splittings of the 338-cm^{-1} band are of particular interest. Presumably they reflect changes in bond order and symmetry as well as site heterogeneity effected by removal of H_2O. For example, the strong band at 976 cm^{-1} may be assigned to a tetrahedral ReO_4^- species; this band is replaced by one at about 1000 cm^{-1} as dehydroxylation proceeds and the monomer becomes bound to the alumina surface where the symmetry is now C_{3v} and the bond order is increased accordingly. The data of Fig. 7 demonstrate yet another factor which has led to difficulties in interpretation of spectroscopic data in the literature.

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REFERENCES

1. Lin, C. J., Aldag, A. W., and Clark, A., *J. Catal.* **34,** 494 (1974).
2. Lin, C. J., Aldag, A. W., and Clark, A., *J. Catal.* **45,** 287 (1976).
3. Mol, J. C., and Moulijn, J. A., *in* "Advances in Catalysis," Vol. 24, p. 131. Academic Press, New York, 1975.
4. Goldwasser, J., Engelhardt, J., and Hall, W. K., *J. Catal.* **70,** 275 (1981).
5. Kluksdahl, H. E., U.S. Patent 3,415,737 (1968).
6. Robinson, R. C., Frederickson, L. A., and Jacobsen, R. L., *Proc. Div. Refin. Amer. Petr. Inst.* **52,** 163 (1972).
7. Johnson, M. F. L., and LeRoy, V. M., *J. Catal.* **35,** 434 (1974).
8. Bolivar, C., Charcoset, H., Frety, R., Primet, M., and Tournayan, L., *J. Catal.* **39,** 249 (1975).
9. Peri, J. B., *J. Catal.* **52,** 144 (1978).
10. Wagstaff, N., and Prins, R., *J. Catal.* **59,** 434 (1979).
11. Olsthoorn, A. A., and Boelhouwer, C., *J. Catal.* **44,** 197 (1976).
12. Yao, H. C., and Shelef, M., *J. Catal.* **44,** 392 (1976).
13. Kerkhof, F. P. J. M., Moulijn, J. A., and Thomas, R., *J. Catal.* **56,** 279 (1979).
14. Nakamura, R., Abe, F., and Echigoya, E., *Chem. Lett. Japan Chem. Soc.,* 51 (1981).
15. Wang, L., and Hall, W. K., *J. Catal.* **77,** 232 (1982); *J. Catal.* **66,** 251 (1980).
16. Hall, W. K., "Proceedings of the Climax Fourth International Conference on the Chemistry and Uses of Molybdenum" (H. F. Barry and P. C. H. Mitchell, Eds.), pp. 224–234. Climax Molybdenum Company, Ann Arbor, Michigan, 1982.
17. Baes, D. F., and Mesmer, R. E., "The Hydrolysis of Cations," p. 193. Wiley–Interscience, New York, 1979.
18. Bailey, N., Carrington, A., Lott, K. A. K., and Symons, M. C. R., *J. Chem. Soc.,* 290 (1960); Carrington, A., Schonloan, D., and Symons, M. C. R., *J. Chem. Soc.,* 659 (1957).
19. Claasen, H. H., and Zielen, A. J., *J. Chem. Phys.* **22,** 707 (1954).
20. Woodward, L. A., and Roberts, H. L., *Trans. Faraday Soc.* **52,** 615 (1956).
21. Beattie, I. R., and Ozin, G. A., *J. Chem. Soc. A,* 2615 (1969).
22. Jeziorowski, H., and Knozinger, H., *J. Phys. Chem.* **83,** 1166 (1979).
23. Zingg, D. S., Makovsky, L. E., Tischer, R. E., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **84,** 2890 (1980).
24. Salavati, L., Jr., Makovsky, L. E., Stencel, J. M., Brown, F. R., and Hercules, D. M., *J. Phys. Chem.* **85,** 3700 (1981).
25. Segawa, K., and Hall, W. K., *J. Catal.* **77,** 221 (1982).
26. Bartecki, A., and Dembicka, D., *J. Inorg. Nucl. Chem.* **29,** 2907 (1967).
27. Webb, A. N., *J. Catal.* **39,** 485 (1975).
28. Shpiro, E. S., Avaev, V. I., Antoshin, G. V., Ryashentseva, M. A., and Minachev, Kh. M., *J. Catal.* **55,** 402 (1978).