

Infrared and Gravimetric Study of the Surface Hydration of γ -Alumina

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Infrared and gravimetric studies have yielded new information on the surface hydration of γ -alumina. Dry γ -alumina was found to "chemisorb" one molecule of water per 11–16 \AA^2 of surface at 100°, depending on rehydration procedure. Desorption of chemisorbed water on subsequent heating under vacuum was studied at temperatures between 100 and 900°. Characteristic dehydration isotherms showed that a rapid initial weight loss was followed by a slow continuing loss. Because of these characteristics, the extent of surface hydration is governed primarily by the drying temperature. In addition to the three major isolated hydroxyl bands previously noted in infrared spectra of dry alumina (3800, 3744, and 3700 cm^{-1}), two additional bands are often observed at 3733 and 3780 cm^{-1} . Changes in the bands were studied as a function of temperature. Rehydration of the surface between 400 and 800° was also studied by direct spectroscopic observation of the hot alumina. Results show that hydroxyl groups, although apparently mobile, persist as such on the surface at high temperatures on distinct types of sites rather than in a completely random state. Readsorption of water cannot alone explain the difficulty in removing residual hydroxyl groups at high temperatures. Free energy of activation for desorption of water apparently increases continuously as the surface concentration of hydroxyl groups decreases. Although "strain" sites are undoubtedly created by dehydration, characterization of such sites as strained Al–O–Al linkages seems inadequate.

Introduction

Strongly dried aluminas chemisorb at least a monolayer of water when exposed to moisture at room temperature. Although several crystallographic forms of high-area alumina exist, available information suggests that their surface hydration is similar. The forms most often investigated are usually characterized as either γ - or η -alumina, but mixtures of these two rather similar forms are probably common.

The hydrated surface of γ -alumina retains 13 molecules of water per 100 \AA^2 of surface after evacuation at 25° for 100 hr.,¹ and even after drying at 120°, it may still retain 8.25 molecules per 100 \AA^2 .² Although much of this water is held as hydroxyl groups on the surface, infrared studies show that some of the water strongly adsorbed at 25° remains molecular.³

When wet γ -alumina is heated above 100°, some of the adsorbed water is desorbed while some reacts to form hydroxyl groups. At higher temperatures these, as well as pre-existing hydroxyl groups, gradually condense to eliminate water. Surface hydroxyl groups are

not completely eliminated, however, even by drying under vacuum at 800–1000°.³

Important catalytic properties of γ -alumina are associated with "acid" sites created on the surface during removal of hydroxyl groups at temperatures above 400°. Hydroxyl groups of at least three chemically distinct types remain on the surface after the alumina has been dried under vacuum above 650°,³ but none of these types appears catalytically active, *per se*, for the isomerization of 1-butene.⁴ Instead, the active sites appear to involve abnormal exposure of aluminum ions⁴ or creation of strained Al–O–Al linkages⁵ on the surface

- (1) J. J. Kipling and D. B. Peakall, *J. Chem. Soc.*, 834 (1957).
- (2) J. H. de Boer, J. M. H. Fortuin, B. C. Lippens, and W. H. Meijs, *J. Catalysis*, 2, 1 (1963).
- (3) J. B. Peri and R. B. Hannan, *J. Phys. Chem.*, 64, 1526 (1960).
- (4) J. B. Peri, *Actes Congr. Intern. de Catalyse*, 2^e, Paris, 1960, 1, 1333 (1961).
- (5) E. B. Cornelius, T. H. Milliken, G. A. Mills, and A. G. Oblad, *J. Phys. Chem.*, 59, 809 (1955).

when hydroxyl groups are removed. Some degree of strain is known to characterize crystal surfaces.⁶

Although much progress has been made toward explaining the surface hydration of aluminas, present knowledge remains meager. Because the crucial importance of surface hydration has often been overlooked, much of the literature on catalytic properties of aluminas is of questionable significance. Further understanding of the details of surface hydration is clearly needed.

The present work was undertaken to obtain additional information on the surface hydration of γ -alumina by infrared and gravimetric techniques. Alumina aerogel plates were studied.

Experimental

Materials. Because minor differences in procedure may lead to unsatisfactory plates or may otherwise influence the properties of the alumina, the preparative procedure is described in detail. Unless otherwise noted, reagent grade chemicals were used.

Alumina sol was typically prepared from 80 g. of aluminum metal pellets (0.3 to 0.6 cm., 99.99 + % pure), 60 ml. of glacial acetic acid, 3 l. of distilled water, and 0.1 g. of red mercuric oxide. These materials were combined in a three-necked Pyrex flask equipped with a reflux condenser, a stirrer, and a thermocouple. The flask was warmed with a heating mantle to initiate the reaction. Then the mantle was dropped, and the reaction was allowed to proceed at 65–70° for 24 to 48 hr. The sol was decanted from any unreacted aluminum or coarse precipitate and, if it showed more than a slight milky opalescence, was centrifuged for 15 min. at 30,000 *g* in an angle-head centrifuge.

The clear sol ($\sim 5\%$ Al_2O_3) was floated as a 0.3- to 0.6-cm. layer on clean mercury or carbon tetrachloride in a 20.3-cm. crystallization dish. Open weighing bottles of 10% aqueous ammonia solution were suspended inside the dish, which was covered with a large watch glass. Gelation normally required about 2 hr., but the time varied with the thickness of the sol layer and the amount and concentration of the ammonia solution. (Excessive exposure to ammonia gave opaque plates, whereas correct exposure gave clear, firm plates.)

The plates were broken into suitable pieces and carefully transferred to a crystallization dish containing methanol. (The plates never occupied more than 20% of the volume of methanol in the dish.) The dish was gently swirled once or twice a day, and the methanol was replaced at 2- to 4-day intervals; it was changed at least four times over a 2-week period.

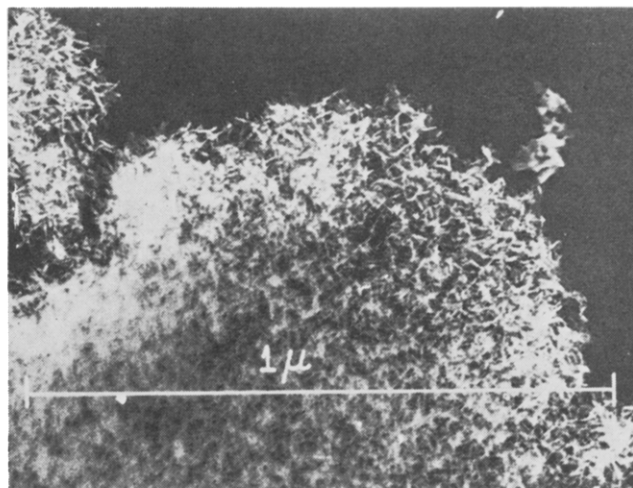


Figure 1. Electron micrograph of calcined alumina aerogel.

After alcohol exchange, the plates were packed loosely in a glass autoclave liner (3.2 cm. i.d. and 26.7 cm. in length) filled with pure methanol. The liner was placed in a stainless steel autoclave, and methanol was added to fill the autoclave completely, which was then sealed and heated slowly to 260° while the methanol was bled off slowly, as necessary, to keep the pressure below 1500 p.s.i. Between 260 and 280° bleeding was continued for about 2 hr. to maintain the pressure as long as possible in the range from 1200 to 1500 p.s.i. Ultimately, the pressure was slowly lowered, and the autoclave was evacuated for about 0.5 hr. while still hot ($\sim 300^\circ$). The clear aerogel was removed from the autoclave and calcined in air or oxygen at 600° before use.

X-Ray analysis showed that the original sol, which had been dried in air at 130°, was mainly amorphous with some microcrystalline Boehmite; the calcined aerogel was γ -alumina.

For electron micrographs, the calcined aerogel was ground in ethanol, and a thin film of the suspension was dried onto a carbon supporting film. Figure 1 illustrates the typical rod- or lath-like appearance of the alumina particles. Some samples also contained sheet-like structures.

Spectroscopic analysis of a typical plate showed <0.035% impurities, mostly silicon (0.019%).

Because small amounts of carbon dioxide are strongly held by γ -alumina, the water used in this work was distilled into the vacuum system from a solution containing a few per cent of barium hydroxide and was further

(6) W. A. Weyl, *Trans. N. Y. Acad. Sci.*, **12**, 245 (1950); "A New Approach to Surface Chemistry and Heterogeneous Catalysis," Mineral Industries Experiment Station Bulletin 57, State College, Pa., 1951; "Structure and Properties of Solid Surfaces," R. Gomer and C. S. Smith, Ed., University of Chicago Press, Chicago, Ill., 1953, p. 147.

degassed by vacuum distillation before admission to the cell.

Equipment and Techniques. Most of the equipment and techniques used in this work have been described.^{3,4} However, in some of the infrared work, a Beckman IR-9, double-beam, grating spectrometer was used to re-examine hydroxyl stretching bands at a higher resolution than was possible in previous studies. Desorbed gases were, in some instances, analyzed by mass spectrometry.

Gravimetric Study

Rehydration at 100°. Three aerogel plates were used in the gravimetric study. All had surface areas, as measured by nitrogen adsorption, in the range of 310–350 m.²/g. Infrared spectra were recorded at intervals during the gravimetric studies.

Plate I (dry weight, 0.210 g.) was evacuated in the cell for 2 hr. at 800°, and its nitrogen adsorption at –195.6° was measured. Then it was held at 100° for 9 days while water vapor was admitted in small doses. The weight changes showed that the initial doses were rapidly and irreversibly adsorbed. However, above a total adsorption approximating 53% of a filled monolayer (6.25 molecules of water/100 Å.² assumed as 100%), a significant fraction of the water held after 0.5- to 1-hr. equilibration could be desorbed by evacuation for 30 min. through a trap cooled with liquid

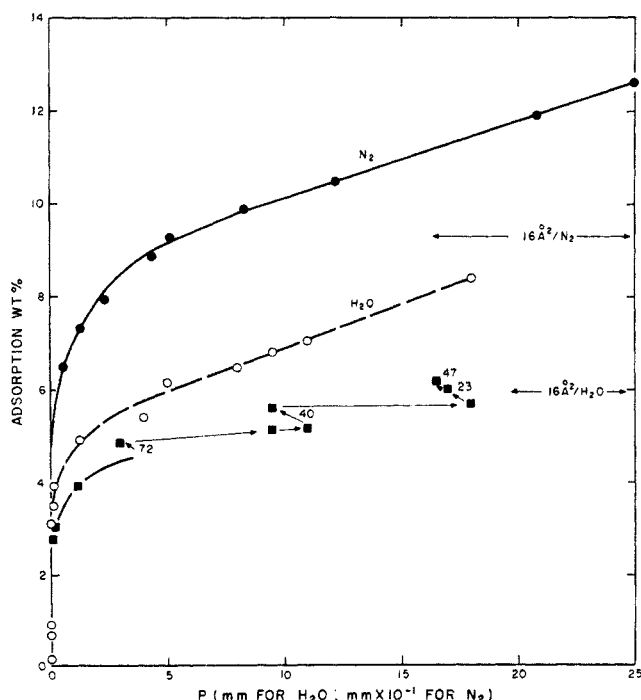


Figure 2. Adsorption of water (100°) and nitrogen (–195.6°) on alumina aerogel.

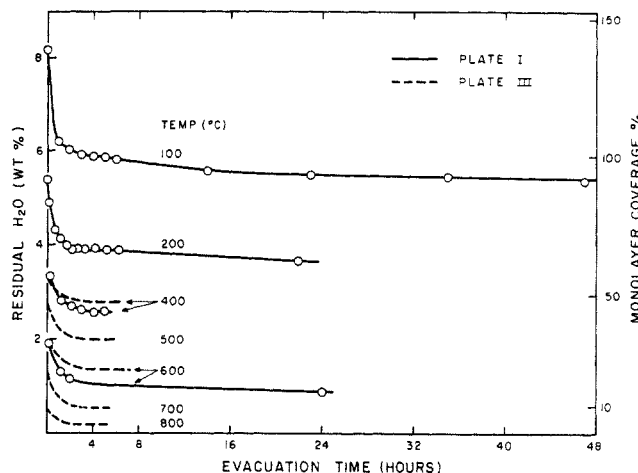


Figure 3. Dehydration of alumina aerogel.

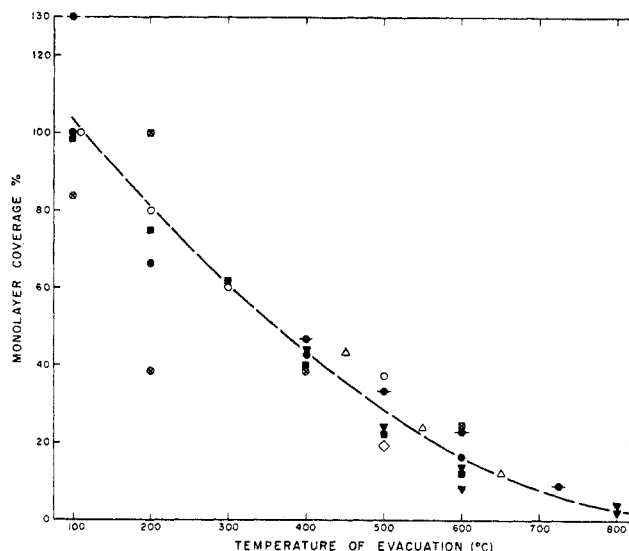


Figure 4. Dehydration of alumina (drying times normally 1–25 hr.): O, Haldeman and Emmett⁸; Δ, Hindin and Weller⁹; ⊗, Whalley and Winter¹⁰; Δ, Kloosterziel¹¹; ⊠, Boreskov, *et al.*, 100 hr.¹²; ●, plate I; ■, plate II; -●-, plate III; ▼, deuterium exchange.

nitrogen. Further additions of water were incompletely adsorbed, but adsorption increased slowly with time—due mainly to an increase in the irreversible adsorption. The results are summarized in Figure 2.

Open points on the water isotherm represent measurements made 0.5 to 1 hr. after each addition of water. The set of solid points below this isotherm represents irreversible adsorption measured after evacuation through the cold trap for 0.5 hr. from an initial pressure represented by the ordinate. Numbers on arrows between points represent the elapsed time (in hours) between measurements. Following each evacuation the cell was closed off, and the water in the cold trap

was allowed to revaporize. All other time intervals represented by arrows between points are between 0.5 and 1 hr.

Maximum total adsorption at the highest pressure studied (18 mm.) was approximately 9.3 molecules/100 Å.². Subsequent evacuation at 100° reduced this to 6.4/100 Å.² after 2 hr. and to 5.7/100 Å.² after 71 hr.

Rehydration of plate II under similar conditions produced similar results. The isotherm obtained after 0.5- to 1-hr. equilibration again gave a B point corresponding to approximately 6.25 molecules/100 Å.². Slowly increasing irreversible adsorption in a closed cell (at an initial pressure of 5 mm.) gave 8.7 molecules/100 Å.² (final pressure, 1.5 mm.) after 2 days' equilibration. This was reduced to approximately 6.2/100 Å.² after 1-hr. evacuation.

Plate III was rehydrated by exposure to water vapor at saturation pressure (~200 mm.) and at room temperature for 16 hr. and then was held at 100° for 2 hr. at the same pressure. Despite the much shorter equilibration time at 100°, maximum adsorption was appreciably greater than that obtained with plates I and II. Increasing the period of heating at 100° to 16 hr. did not increase the adsorption. Total adsorption at 100° and 20 mm. never exceeded 12.5 molecules/100 Å.². After evacuation for 2 hr. at 100°, 8.3 molecules/100 Å.² (or one hydroxyl group/6 Å.²) remained.

The rehydration experiments indicate that the area per water molecule retained after evacuation for 1 hr. at 100° may range from 11 to 16 Å.², depending on the method and extent of rehydration. Clearly, equilibrium was not reached either during readsorption of water vapor at 100° or during the period of evacuation arbitrarily used to define irreversible adsorption. Although rehydration at room temperature (under conditions where physically adsorbed water is held to a considerable extent by the alumina) yields higher values for the chemisorbed water retained after evacuation at 100°, it is not obvious that such chemisorption represents only water or hydroxyl ions held on the same surface measured by nitrogen adsorption.

Dehydration of the Hydrated Surface. After rehydration as described, the plates were dried by evacuation at progressively higher temperatures. Figure 3 shows the data obtained for plates I and III. Correction was made for a small difference in specific surface areas. Plate II, which was dried by evacuation for about 2 hr. at several temperatures from 100 to 600°, showed a similar behavior.

The existence of the sloping plateaus in the dehydration curves suggests that, despite variations in drying procedures, some uniformity should exist in literature data on surface hydration of alumina. Abundant

data are available, but they are usually complicated by variations in drying conditions and, in the case of older data, by unknown surface area. Data reported by Gregg and Wheatley,⁷ for example, indicate that drying in air above 600° caused loss of surface area at almost the same rate as loss of water, the surface remaining about 33% covered with hydroxyl groups. Figure 4 presents data, recalculated to show surface coverage with hydroxyl groups, from published studies of high-area alumina⁸⁻¹² in which samples were dehydrated under reasonably good vacuum and surface areas were given. Points representing work by Haldeman and Emmett⁸ were calculated from a curve representing maximum hydration. Points obtained from study of the aerogel plates discussed above and from equilibrium deuterium exchange on other similar plates in this laboratory are also included. For data of the present study, surface coverage after 5-hr. evacuation is plotted for plates I and II. Considering the wide variations in alumina preparation, rehydration, and drying procedures, agreement is fairly remarkable. The only data located which appear to be in major disagreement¹³ have been acknowledged as irreproducible.¹⁴ Thus, a reasonable estimate for surface hydroxyl coverage can probably be made if the temperature of dehydration under vacuum is known.

Infrared Study

Spectra of Hydroxyl Groups on Dry Alumina. The major characteristics of spectra obtained during vacuum dehydration of γ -alumina at elevated temperatures have been described.³ Further information on detailed changes in the isolated hydroxyl bands on "dry" alumina has been obtained. In addition to the three major bands due to isolated, chemically distinct, hydroxyl groups, two other bands are sometimes evident in the region from 3700 to 3800 cm.⁻¹: one lies near 3780 cm.⁻¹ and is normally most apparent after the alumina has been dried under vacuum at 600-650°; the other occurs near 3733 cm.⁻¹ and is typically observed as a shoulder on a stronger band at 3744 cm.⁻¹.

(7) S. J. Gregg and K. H. Wheatley, *J. Chem. Soc.*, 3804 (1955).

(8) R. G. Haldeman and P. H. Emmett, *J. Am. Chem. Soc.*, **78**, 2917 (1956).

(9) S. G. Hindin and S. W. Weller, *Advan. Catalysis*, **9**, 70 (1957).

(10) E. Whalley and E. R. S. Winter, *J. Chem. Soc.*, 1175 (1950).

(11) H. Kloosterziel, "Chemisorption," W. E. Garner, Ed., Butterworth and Co., Ltd., London, 1957, p. 76.

(12) G. K. Boreskov, V. B. Dzisko, and M. S. Borisova, *Zh. Fiz. Khim.*, **27**, 1176 (1953).

(13) J. H. de Boer and G. M. M. Houben, *Proc. Intern. Symp. Reactivity Solids, Gothenburg, 1952*, **1**, 237 (1954).

(14) J. H. de Boer, "Chemisorption," W. E. Garner, Ed., Butterworth and Co., Ltd., London, 1957, p. 85.

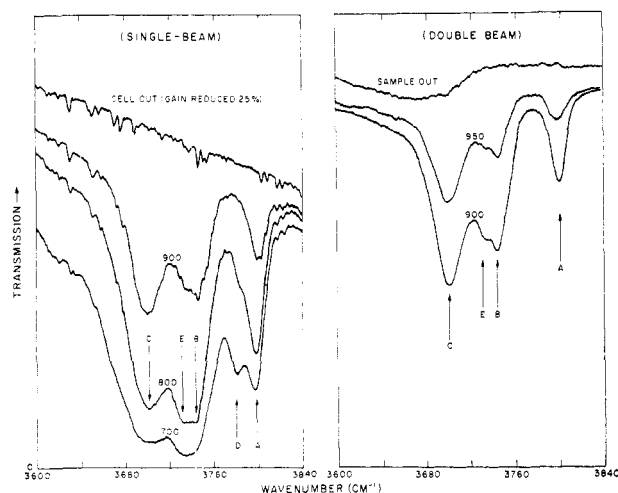


Figure 5. Spectra of alumina dried at indicated temperatures, °C.

Except on very dry alumina these bands are typically difficult or impossible to locate because of overlapping.

Figure 5 illustrates spectra obtained during dehydration of an aerogel plate by evacuation for 0.5 hr. at progressively higher temperatures. The frequencies (at 40°) of the five bands found are given in Table I.

Table I

Band	Wave number, cm. ⁻¹	
	Current	Previous ^a
A	3800	3795
B	3744	3737
C	3700	3698
D	3780	..
E	3733	..

Corresponding deuterioxy bands fall between 2730 and 2805 cm.⁻¹. Bands A, B, and C are the most prominent after the usual (1-2 hr.) dehydration under vacuum above 650°, but the other two bands persist to some extent. Three isolated hydroxyl bands, corresponding approximately to the A, B, and C bands described above, have been reported for other aluminas.^{15,16}

The frequencies depend on temperature as well as extent of surface hydration. In view of the difficulty of resolving these overlapping bands, some difference in the frequencies reported should be expected, even had the aluminas studied all been identical. Additional bands are found on alumina dried below 600°, apparently reflecting hydrogen-bonded hydroxyl, but little further information was obtained from studies of "wetter" alumina. Some isolated hydroxyl groups

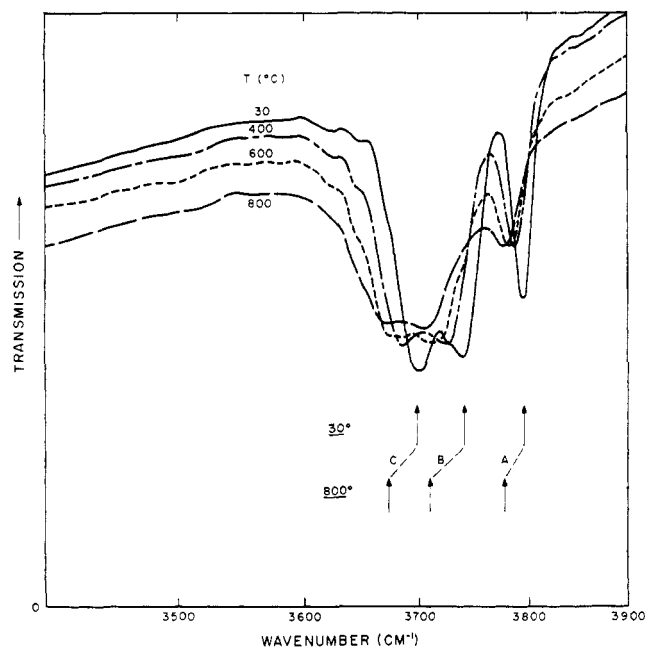


Figure 6. Spectra of alumina showing changes in hydroxyl bands with temperature.

appear to exist, however, even on extensively hydrated alumina.¹⁷

Additional evidence was obtained by direct infrared study of alumina at elevated temperatures. The aerogel plates were dried by evacuation at 800-1000°, and spectra were recorded at the drying temperature and at various lower temperatures, the number of surface hydroxyl groups remaining constant (Perkin-Elmer 12C spectrometer, LiF prism). Figure 6 illustrates typical changes in frequency and configuration as the temperature was decreased after initial drying at 800°. All changes were reversible on reheating. The major hydroxyl bands shift to lower frequencies and broaden with increasing temperature. Frequency shifts appear to differ for the individual bands, ranging from ~20 cm.⁻¹ for the A band to ~35 cm.⁻¹ for the B band, as the temperature is changed between 30 and 800°. Nevertheless, the bands appear to persist as distinct entities, indicating that even at 800° hydroxyl groups exist on distinct surface sites and are not in completely random motion.

The possibility that the hydroxyl groups observed at lower temperatures do not actually exist on alumina at high temperatures but are formed by readsorption of water only on cooling is excluded by these experi-

(15) R. H. Lindquist and D. G. Rea, presented at 136th National Meeting, American Chemical Society, Atlantic City, N. J., Sept. 1959.

(16) D. J. C. Yates and P. J. Lucchesi, *J. Chem. Phys.*, **35**, 243 (1961).

(17) A. V. Uvarov, *Zh. Fiz. Khim.*, **36**, 1346 (1962).

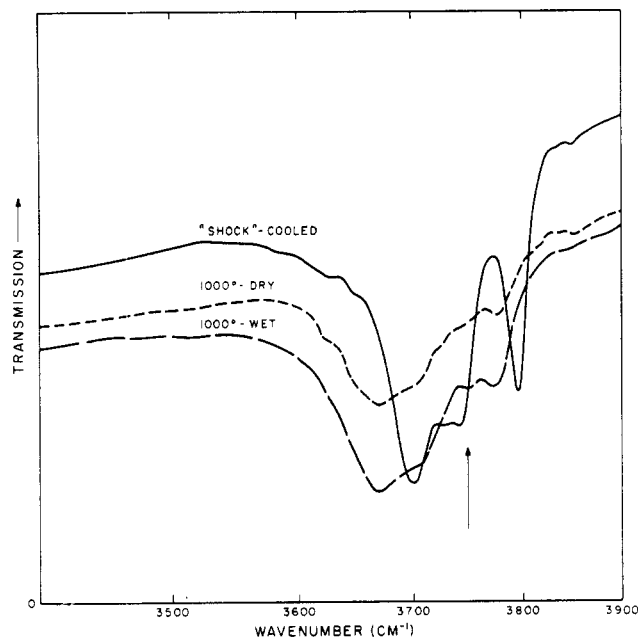


Figure 7. Spectra of alumina showing hydroxyl-stretching bands after readdition of water at 1000°.

ments. The observed frequency shifts probably reflect changes due to increased vibration of the hydroxyl groups perpendicular to the surface, as well as possible increased lateral interaction with neighboring oxide ions.

Experiments were also made to determine approx-

imately how the number and types of hydroxyl groups on the surface at high temperatures depended on the partial pressure of water vapor in the cell. First, an alumina aerogel plate was alternately exposed to flowing dry nitrogen (P_2O_5 -dried) and flowing wet nitrogen (saturated at room temperature) between 500 and 1000° while spectra of the hot alumina were recorded. Typical spectra at 1000° are shown in Figure 7, which also includes a spectrum recorded at room temperature after the quartz cell had been plunged abruptly into an ice bath after brief drying at 1000°. This spectrum does not differ appreciably from spectra obtained for the slowly cooled alumina.

Equilibrium chemisorption of water apparently occurred rapidly under the conditions of the experiments. Spectra recorded after 1 hr. contact with wet nitrogen showed little or no change from those recorded after 5-min. contact. Redrying in flowing dry nitrogen for 1 hr. restored the spectrum obtained after originally drying for 1 hr. The results showed that chemisorption of water increased markedly in the presence of moisture, although certainly not in direct proportion to the increase in water pressure.

At temperatures between 700 and 1000° the additional chemisorbed water appeared to exist mostly as isolated hydroxyl groups, but these were not all identical with pre-existing groups. At least one new band was produced near 3750 cm^{-1} (indicated by the arrow in Figure 7) by chemisorption of water at 800 to 1000°.

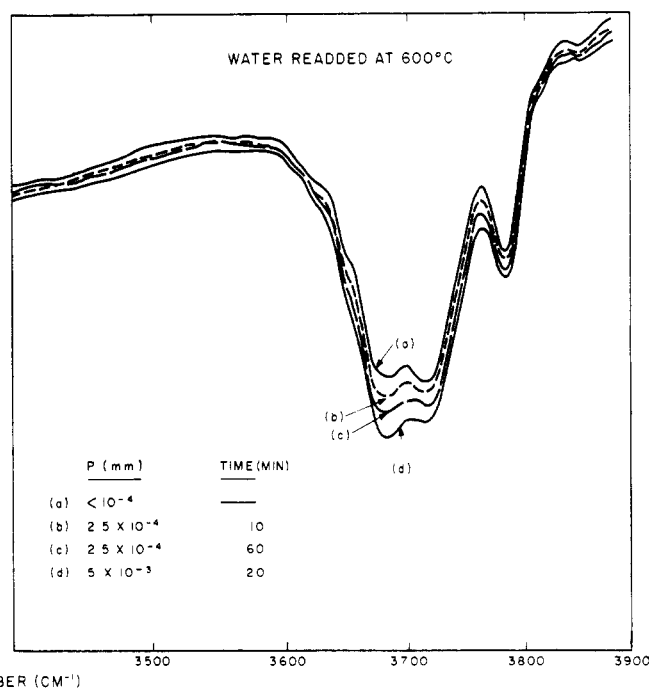
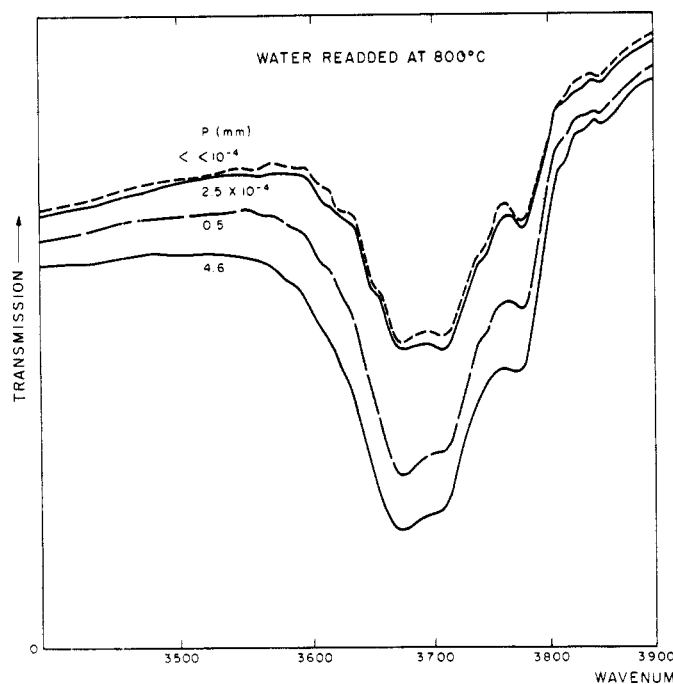


Figure 8. Spectra showing effects of readdition of water to hot alumina predried at 800°.

This band (allowing for the frequency shift due to temperature) apparently corresponds to the D band found at room temperature near 3780 cm^{-1} .

Alumina dried at 500° gained fewer isolated hydroxyl groups when subsequently exposed to flowing wet nitrogen at 500° than did alumina dried at higher temperatures when exposed to wet nitrogen (at the drying temperatures) but showed a greater increase in absorbance due to hydrogen-bonded hydroxyl groups (broad band below 3680 cm^{-1}).

After the alumina had been dried at 1000° and cooled to produce the spectrum shown in Figure 7, rehydration of the surface was attempted by exposure for 1 hr. to wet nitrogen at 100° . Then the alumina was redried at 500° . A subsequent spectrum indicated that the B and D bands had been only partially restored to their normal relative intensities after 500° drying. All isolated hydroxyl bands had previously been found to be fully restored in the spectrum after more thorough rehydration and redrying, but the B and D bands were typically less easily restored than the A and C bands.

In additional experiments, an aerogel plate was dried at 800° by evacuation for 0.5 hr. through a trap cooled with liquid nitrogen, and then was exposed to water vapor at various low pressures at 600 and 800° . Vapor pressure was controlled by means of suitable cooling mixtures applied to a trap holding ice or water. Typical results are shown in Figure 8. Equilibrium adsorption was not reached in these experiments. Although water at 0.5 mm. or above is chemisorbed fairly rapidly at 800° to form isolated hydroxyl groups, chemisorption occurs only very slowly below 5×10^{-3} mm.

Bands above 4000 cm^{-1} . Bands due to a combination of an OH stretching vibration with other vibrations would be expected to lie above 4000 cm^{-1} and could ultimately provide further information on the characteristics of the hydroxyl groups. In an attempt to locate such bands a very thick ($\sim 250\text{ mg./cm}^2$) sample predried under vacuum at 750° was used. Weak bands were located near 4585 and 4350 cm^{-1} , and possibly at 4107 cm^{-1} . These are evidently combination bands involving the hydroxyl groups. They appear to be relatively much weaker than a corresponding band on microporous glass (4540 cm^{-1}) and were not identified as corresponding to particular OH stretching bands.

Retention of Carbon Oxides. When the aerogel plates (which had been calcined in oxygen and evacuated at 600°) were initially heated from 600 to 800° , the desorbed gases contained small amounts of carbon monoxide, carbon dioxide, and hydrogen, in addition

to the principal product, water. Both carbon dioxide and hydrogen could have been produced from carbon monoxide and water. The amount of carbon monoxide or carbon dioxide could have covered, at most, about 1% of the surface.

Careful study of concurrent spectral changes showed slight decreases in absorption between 1200 and 1700 cm^{-1} , probably reflecting loss of COO^- , CO_3^{2-} , HCO_3^- , or similar groups. On one plate, definite bands near 1380 and $1500\text{--}1600\text{ cm}^{-1}$ persisted after repeated evacuation at 700° and were accompanied by a band near 2350 cm^{-1} , apparently caused by molecular carbon dioxide. Although both carbon dioxide and carbon monoxide are chemisorbed by dry alumina, neither is usually held strongly enough to account for the observations. The presence of a few closed pores in the aerogel plates might explain these findings.

In most subsequent work, plates were calcined at 600° in oxygen, dried at 800° , and then rehydrated to minimize possible complications from chemisorbed carbon oxides. Although possibly a troublesome complication, chemisorbed carbon oxides apparently are not normally involved in the development of active sites and do not significantly affect the characteristics of the isolated hydroxyl bands.

Discussion

The surface chemistry of γ -alumina is complex. Many different crystal planes, edges, or corners may be exposed. Moreover, transition aluminas are commonly believed to possess defect spinel structures wherein various arrangements of the aluminum ions are possible. There is reason to think, however, that γ -alumina may preferentially expose one crystal face. Strong pseudo-morphic relations are known to exist between Boehmite and γ -alumina, and electron and X-ray diffraction evidence suggests that dehydration of gelatinous Boehmite yields γ -alumina in which a considerable part of the surface is formed by the 100 plane of a spinel lattice.¹⁸ Arguments for the preferred exposure of the 111 face¹⁹ based on the greater density of packing of oxide ions on this face of dry alumina are unconvincing because actual exposure may still reflect the relative stabilities of hydrated faces (hydroxyl packing) rather than those of dehydrated faces.

It is reasonable to suppose, as have past workers,^{1,2} that chemisorption of water should be closely related to the spacing of oxide ions on exposed faces of a cubic,

(18) B. C. Lippens, "Structure and Texture of Aluminas," Thesis, Technische Hogeschool of Delft, The Netherlands, 1961.

(19) J. H. de Boer, G. M. M. Houben, B. C. Lippens, W. H. Meijjs, and W. K. A. Walrave, *J. Catalysis*, 1, 1 (1962).

close-packed, oxide lattice. Each oxide ion in a 111 plane occupies 6.74 \AA^2 , whereas on a 100 face the area per oxide is 7.9 \AA^2 . The B points observed in 100° adsorption isotherms suggest exposure of the 100 face. The other evidence indicates, however, that maximum retention of water at 100° (or even at 120°) is somewhat greater than expected, even for the 111 face. Some excess hydration beyond that expected from complete filling of either crystal face with one water molecule for every two oxide ions is apparently possible. How much (and why) is not presently clear.

In light of the ability of alumina to retain strongly 13 molecules of water/ 100 \AA^2 at room temperature, some excess hydration at 100° should not be surprising. An alumina trihydrate surface may form,¹ at least to some extent, at low temperatures, and it might be only slowly decomposed at 100° . Rehydration might also extend to underlying layers. Slow penetration of water by diffusion of protons through the solid oxide lattice could lead to the hydration of a surface which is inaccessible to the nitrogen used for surface area measurements (for example, at contact points between primary particles or in closed pores). Thus, quite aside from the uncertainties involved in determining absolute surface areas by nitrogen adsorption, evidence on the maximum extent of hydration cannot easily establish which faces (if any) are preferentially exposed.

The very slow chemisorption of water at 100° , beyond 50% monolayer coverage, apparently reflects some type of reorganization of the surface. This process appears to be facilitated greatly by exposure to water at lower temperatures, suggesting that mobility of surface ions is considerably enhanced by physically absorbed water.

As suggested by Weyl⁶ and others,⁵ strain exists at a crystal surface. To minimize surface energy, metal oxide crystals characteristically chemisorb water, whenever possible, usually to form hydroxyl ions, because two hydroxyl ions can more readily minimize the field irregularities arising at a free surface than can a single oxide ion. Oxide ions, being more polarizable than metal cations, are preferentially exposed after removal of chemisorbed water. Dehydration thus exposes a strained oxide surface which is abnormally reactive. At least, on γ -alumina, however, the strain is not uniformly distributed over the surface but appears to be exceptionally concentrated at relatively few sites. Exactly how such localization of strain occurs is not clear. Some of the surface hydroxyl groups are very difficult to remove, and it is apparently the removal of such groups which creates the high-energy strain sites.

Readsorption of water must seriously limit the extent to which surface hydroxyl groups can be removed from alumina by heating in a humid atmosphere. When a typical powder sample of alumina is dried by calcination in air, slow diffusion of water out of the sample undoubtedly results in "self-steaming" which leaves a fairly high concentration of hydroxyl groups on the surface. Drying by evacuation through a trap cooled with liquid nitrogen is far more efficient for removal of surface hydroxyl groups. Eventually, equilibrium readsorption of water must become important in limiting removal of surface hydroxyl groups, even on vacuum drying. The spectroscopic and gravimetric evidence indicates, however, that the principal cause of the plateaus observed on vacuum dehydration lies not in readsorption of water but in a steady increase of the free energy of activation for desorption as the surface coverage with hydroxyl groups decreases.

The heat of adsorption of water increases with the temperature at which the alumina is predried and may exceed 100 kcal./mole for very low surface coverages on alumina predried at 538° .⁵ Some decrease was noted on alumina predried at 649° .²⁰ Calorimetric data²¹ show heats of adsorption of water vapor at 20 – 25° on alumina predried under vacuum at various temperatures up to 450° which fall between 15 and 22 kcal./mole for complete surface coverage. The very high heats of adsorption observed on partial surface hydration of very dry alumina must reflect relief of a localized surface strain.⁵ Some other type of strain-relieving mechanism apparently becomes operative on the surface of dry alumina above 500 – 600° .²⁰

Cornelius, *et al.*,⁵ have proposed that the high-energy sites on alumina are strained Al–O–Al linkages, formed at high temperatures by condensation of residual hydroxyl groups which are increasingly separated as a result of progressive dehydration of the surface. Although this proposal accounts well for some aspects of the observed behavior, weaknesses are evident. On a regular lattice, hydroxyl ion spacings would fall into distinct groups, only a few of which could apparently permit condensation without disruption of the lattice. Creation of such strained linkages would require virtual immobility of the hydroxyl groups on the surface at high temperatures. The infrared evidence suggests that, although isolated hydroxyl groups are relatively immobile on dry alumina at 250° , migration (possibly through proton transfer) occurs

(20) A. G. Oblad, S. W. Weller, and G. A. Mills, "Second International Congress on Surface Activity," Vol. 2, Academic Press, New York, N. Y., 1957, p. 309.

(21) W. H. Wade and N. Hackerman, *J. Phys. Chem.*, **64**, 1195 (1960).

fairly readily at 400–600°. This, however, is the temperature range wherein highly strained oxide linkages are presumed to be created.

The energy of the sites created during dehydration apparently does not increase indefinitely but passes through a maximum. Results of the present study indicate, however, that the free energy of activation for desorption continues to increase with increasing degree of dehydration up to at least 800°. This suggests that reorganization of the surface involving migration of hydroxyl ions together, rather than the condensation step, may become rate-determining. The increase in free energy of activation for desorption could be largely entropic in origin at very high temperatures.

An explanation for the various types of isolated hydroxyl groups on the surface of dry γ -alumina is presently lacking. Virtually all groups must be on the surface. Although such groups could, for example, be located on different exposed crystal faces, edges, or corners, the detailed changes in relative band intensities

and frequencies on dehydration and in other experiments are difficult to understand on such a basis. The changes are more easily explained in terms of changes in local environment on one crystal face brought about by migration of ions or chemisorption of other molecules.

Conclusion

Much remains to be learned about the details of surface hydration, the creation of high-energy sites, and the significance of the various types of isolated hydroxyl groups on the surface of γ -alumina. Accumulating evidence, however, virtually requires some improvement in present concepts of the alumina surface. With further development, the simple model proposed previously⁴ appears capable of explaining the observations to date. The characteristics of a revised and extended version of this model are discussed in the following paper.

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