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Catalytic Aluminas I. Surface Chemistry of Eta and Gamma Alumina

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Surface properties of well-characterized samples of eta and gamma alumina were studied and compared by means of gas adsorption and immersion calorimetry. From the results obtained, it was concluded that the surface chemistry of an alumina sample may depend to a pronounced degree upon the structure or "type" of alumina being considered. Gamma alumina differed from eta alumina, not only in its pore-size distribution, but also in the fact that the water content of gamma alumina was much greater than that of eta alumina. This "excess" water associated with gamma alumina was regarded as consisting of molecular water strongly adsorbed on the surface of the alumina. Both types of alumina developed surface acidity as they were heated at temperatures up to 900°C, but the strengths of the acid sites were greater in the case of eta alumina.

INTRODUCTION

Because alumina has been widely employed as a catalyst or as a catalyst support, a considerable amount of research has been devoted to elucidating the nature of its catalytic properties. In general, alumina has been regarded as an acid-type catalyst, and, recently, Pines and Haag (*1*) have shown how these acid properties serve as a basis for explaining the role of alumina in a number of catalytic applications. However, despite a general agreement as to the acidic nature of alumina surfaces, an exact chemical description of this acidity has not been achieved, and it seems clear that additional research will be required before a thorough understanding of the catalytic chemistry of alumina can be realized.

It is well known (*2*) that there are two general classes of aluminas, the low surface area, alpha alumina, or corundum, and the highly porous aluminas, which are of catalytic interest. These latter exist in several forms (*2*), of which the so-called "eta" and "gamma" modifications are perhaps the most common. Both eta alumina, which is obtained by the thermal decomposition of bayerite (*2*, *3*, *4*), and gamma alumina, the decomposition product of boehmite (*4*, *5*), have been regarded as having tetragonally deformed spinel lattices, but are structurally dissimilar in that the tetragonal character of eta alumina is considered to be much weaker than that of gamma alumina (*5*). Unfortunately, the X-ray powder diffraction patterns of these two forms are so similar (*3*), that in the case of poorly crystallized alumina samples of ill-defined origin and history, it is often extremely difficult to distinguish one from the other. It has been shown (*5*) that not only the structure, but also the "texture" (i.e., surface area, pore size, etc.) of these two aluminas differ greatly, and the question naturally arises as to whether the catalytic properties and related surface phenomena might not also depend upon the form of the alumina. If such were the case, then it would obviously be necessary to regard structure as an important variable controlling the catalytic chemistry of alumina.

The research reported here represents an attempt to clarify this latter point by means of a comparative study of various properties of well-defined samples of eta and gamma alumina. The present paper reports on certain aspects of the surface chemistry of these two aluminas, and a succeeding paper will describe their catalytic properties.

EXPERIMENTAL

Materials. Gamma alumina was obtained by the thermal decomposition of boehmite at 500°C. The boehmite was prepared by slowly adding an aqueous solution of aluminum nitrate to a solution of ammonium hydroxide, with constant stirring. The resulting precipitate was immediately filtered, washed, and dried at 120°C for 50 hr. X-ray diffraction showed that this dried precipitate consisted entirely of a gelatinous boehmite, which, when calcined for 24 hr at 500°C, yielded a white solid having an X-ray diffraction pattern characteristic of gamma alumina.

Eta alumina was obtained by the thermal decomposition of bayerite at 500°C. The bayerite was prepared by slowly adding a water solution of aluminum nitrate to a solution of ammonium hydroxide with constant stirring, and with the continuous addition of sufficient ammonium hydroxide so as to maintain the pH above 9. After the precipitation was completed, the mixture was allowed to stand for 4 hr, after which it was filtered. The precipitate was then contacted with water for 12 hr, refiltered, and dried for 72 hr at 120°C. The X-ray diffraction pattern of this material indicated that it was well-crystallized bayerite. This was then dehydrated to eta alumina by heating for 16 hr at 250°C and for 24 hr at 500°C.

The two aluminas, after final calcination, were examined for chemical impurities by emission analysis. Both were quite pure and had total impurity contents of 500–700 ppm, the principal contaminants being Mg(100 ppm), Fe(200 ppm), Na(100 ppm), and Si(100 ppm). The aluminas were ground to 50–140 mesh powders and used in this form for all subsequent experimental purposes.

American Cyanamid Triple A silica-alumina having a surface of 445 m^2/g and Davison silica-magnesia (16 wt % Mg) with an area of 568 m^2/g were ground to 50–140 mesh and then calcined at 500°C for 24 hr.

The sources of the various gases employed in this work, and the techniques by which they were purified, have been described in earlier publications (*6*, *7*). Water and methanol (J. T. Baker Chemical Co., Reagent Grade) were de-aerated, prior to use, by repeatedly freezing and evacuating at −78°C.

Apparatus. Surface areas (BET) and pore-size distributions were obtained with nitrogen as the adsorbate, using an automatic, volumetric adsorption system described by Ballou and Doolen (*8*). The adsorption of H_2O, CH_3OH, and NH_3 was determined gravimetrically on a silica spring balance of the McBain-Bakr type discussed in an earlier publication (*9*).

Heats of immersion in water were measured using a calorimeter that was, except for several minor details, identical with that described by Zettlemoyer *et al.* (*10*), and which employed a thermistor, a Mueller bridge, and a ballistic galvanometer as a temperature-sensing system. The sensitivity of this latter was such that a resistance change of 10^{-4} ohm could be measured, corresponding to a temperature change of 2×10^{-5}°C. Uniform sample bulbs were prepared from thin-walled Pyrex tubing. The necessary correction for the heat-of-bulb-breaking was obtained by measuring the heats of solution of samples of sodium chloride, sealed in bulbs, in water at 25°C and by actually breaking empty bulbs in the calorimeter. The heats-of-bulb-breaking so obtained were 0.6 and 0.8 joules, respectively.

The X-ray data were obtained using nickel-filtered CuK_α radiation, a Norelco diffractometer, and a xenon-filled, gas proportional counter.

Procedure. The adsorptions of H_2O and CH_3OH were determined gravimetrically in the usual fashion on samples of alumina which had been pretreated by evacuation at 25°C for 24 hr, followed, in some cases, by 24 hr evacuation at a selected elevated temperature. In calculating the surface area covered by the two adsorbates, molecular cross sectional areas of 11 $Å^2$ and 21 $Å^2$ were taken for physically adsorbed H_2O and CH_3OH (*11*), respectively. The adsorption of NH_3 was studied, gravimetrically, on alumina samples, pretreated as above, by determining an adsorption isotherm at 25°C. Following this, the samples were evacuated for 24 hr at 25°C and the weight loss measured; the temperature was then raised to 100°C, the sample evacuated for another 2 hr, and the weight loss again measured. This latter procedure was repeated at 100°C intervals up to the pretreatment temperature of the particular sample being studied, a fresh sample being used for each pretreatment temperature. It may be noted that at each evacuation temperature, the sample, containing adsorbed ammonia, reached a constant weight within a few minutes. In general, the ammonia adsorption technique just described was quite similar to that employed by Webb (*12*).

Heats of immersion in water at 25°C were measured on 2 g samples of the aluminas employing calorimetric procedures common to this type of experimentation (*10*, *13*). The alumina was placed in a thin-walled Pyrex bulb attached to the vacuum system via a standard taper joint and evacuated at the desired pretreatment temperature for 24 hr. The bulb was then sealed off under vacuum and placed in the calorimeter. When thermal equilibrium had been attained, as indicated by a rating curve of 0.0001 to 0.0003 ohm/min, the heat capacity of the calorimeter was determined in the usual fashion by means of an internal resistance heater. The bulb was then broken and the temperature recorded as a function of time until a slope equal to that of the original rating curve was obtained. The heat capacity was then redetermined. As a rule, the evolution of heat upon immersion was complete with 5 min. The results, in all cases, were corrected for the heat-of-bulb-breaking.

RESULTS

Since the object of the present research was to compare surface properties of two different types of catalytic alumina, it was obviously necessary that these be obtained in relatively pure form and this, in turn, required the preparation of well-characterized precursor alumina hydrates. As indicated earlier, the gamma alumina was prepared from a sample of boehmite whose X-ray diffraction pattern was that of a gelatinous boehmite. This boehmite was composed of relatively small crystallites and contained a slight excess of water, relative to pure boehmite, as evidenced by a small displacement of the (020) line to a larger "*d*" spacing than is characteristic of pure boehmite. Upon heating this material at 500°C, an X-ray pattern (*2*) characteristic of relatively poorly crystallized gamma alumina was obtained. The absence of any trihydrate diffraction lines in the pattern of the precursor boehmite suggested that the gamma alumina obtained therefrom was relatively free from other crystalline alumina phases. The preparation of eta alumina from bayerite was somewhat more complicated in that it was necessary to insure that the bayerite did not transform to boehmite upon dehydration since this latter hydrate would have converted to gamma alumina at higher temperatures. The X-ray pattern of the original hydrate indicated a well-crystallized bayerite with a minor amount of gibbsite also present. When this material was heated at 250°C overnight, an X-ray diffraction pattern was obtained which was that of eta alumina, possibly containing a trace of boehmite. Upon final calcination at 500°C an X-ray pattern of rather well ordered eta alumina resulted. Presumably this was a nearly pure eta alumina with perhaps a very small amount of gamma alumina originating from traces of a boehmite dehydration intermediate. In summary, the X-ray data indicated that the two aluminas obtained upon calcination at 500°C were distinctly different and could be considered as fairly representative samples of eta and gamma alumina.

The two materials differed considerably in physical appearance. The gamma alumina was a hard, translucent solid while the eta alumina was a soft, chalky-white material. The aluminas also differed in their "texture," as indicated by the data of Table 1. From this it can be noted that the gamma alumina was characterized by a rather uniform pore size with about 95% of the pore volume being in pores of 20 to 40 Å radius. Eta alumina, on the other hand, exhibited a somewhat bimodal pore distribution with 66% of the pore volume in pores less than 30 Å radius and the remainder distributed in larger pores. These two types of pore-size distributions appear to be typical of the

TABLE 1
SURFACE PROPERTIES OF ALUMINA DRIED AT 500°C

	η-Al_2O_3	γ-Al_2O_3
Surface area (m^2/g)	240	204
Average pore radius (Å)	21.6	29.4
Total pore volume (cm^3/g)	0.33	0.35
Pore radius (Å)	% Pore volume	
<20	37.4	0.0
20–30	29.2	54.1
30–40	5.6	41.4
40–50	4.4	2.0
50–100	6.8	1.0
100–200	9.2	0.7
>200	7.4	0.8

respective aluminas and have been noted and discussed by Lippins (*5*).

Having obtained well-characterized specimens of both eta and gamma alumina, the first variable to be investigated was their hydration–dehydration behavior. As was to be expected in the case of highly porous solids, the two aluminas lost considerable quantities of water when evacuated, even at relatively low evacuation temperatures. Since a large portion of this water was obviously physically adsorbed, it was necessary to remove as much of this as possible before any study could be made of the chemisorbed or "bound" water. It was found that evacuation of an alumina sample at 25°C removed appreciable amounts of water over an 8 to 10 hr period, after which no further water loss took place over periods as long as 48 hr. Subsequent readsorption of water vapor at relative pressures of 0.1 to 0.2 took place rapidly and reversibly as would be expected if only physical adsorption were involved. When the evacuation temperature was raised to 100°C more water was lost than at 25°C, and upon re-exposure to water vapor at 25°C a rapid readsorption took place to approximately the same extent as that observed after the 25°C evacuation, followed by a slower adsorption process which eventually accounted for the difference in water loss at the two temperatures. It seemed reasonable to assume that this slow process involved some chemisorption of water desorbed in heating from 25° to 100°C. From the foregoing, itwas concluded that evacuation at 25°C for 24 hr was sufficient to remove most of the physically bound water from the alumina surfaces. Although the above definition of physically adsorbed water was somewhat arbitrary, it was consistent with that used by other workers (*14*), and it was an operational definition sufficient for the purposes of the present paper. On this basis, all subsequent experiments were carried out on samples of alumina pretreated by evacuation for 24 hr at 25°C, and it was assumed that after such a treatment the alumina was essentially free of weakly physically adsorbed water.

The amounts of chemisorbed or "bound" water associated with the two aluminas were determined by heating samples of alumina, pretreated as described above, for 24 hr periods at temperatures from 25° to 1100°C, a fresh sample of alumina being used for each temperature. It was found that, at any specified temperature, a constant sample weight was obtained after 8 to 10 hr of evacuation. The results of this dehydration study, presented in Fig. 1, show that the water content of gamma alumina was considerably greater than that of eta alumina, and that this "excess" water in gamma alumina was evolved below 500°C. Above this temperature both aluminas behaved quite similarly and, in both cases, the water loss was essentially complete at 900°C with only small (~ 1 mg H_2O/g alumina) amounts of water lost from 900–1100°C. Accompanying the water loss above 600°C there was a gradual decrease in the surface areas of the two aluminas with increasing temperature.

X-ray diffraction patterns of the dehydrated aluminas demonstrated a general decrease in broadness of the diffraction lines as the temperature was increased above 600°C, indicative of a growth in crystallite size and consistent with the observed decline in surface area at these temperatures. As far as could be determined by X-ray diffraction, no major phase transformations took place with either alumina *in vacuo* between 500° and 900°C; above this latter temperature the usual transformation to alpha alumina was found (*2*).

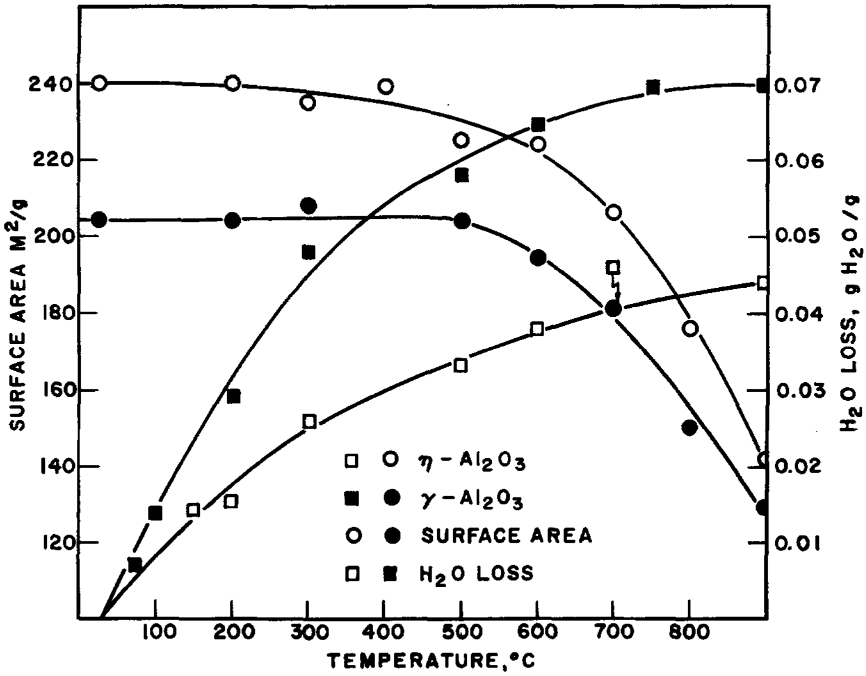

FIG. 1. Surface area and water loss of eta and gamma alumina.

To obtain additional information on the hydration of the two aluminas, heats of immersion in water at 25°C were determined as a function of dehydration temperature from 25° to 500°C as shown in Table 2. For purposes of comparison, these heats are plotted in Fig. 2 as a function of the amount of water removed during dehydration. It must be recognized that these are integral heats and, as such, may represent a summation of several energetic processes. Further, it has been shown by other workers (*15*) that when alumina is immersed in water there may be, in addition to the rapid initial heat effect, a slow evolution of heat which can be appreciable over a period of several hours. The nature of the calorimeter employed in the present work did not permit detection of this later thermal process. The values reported in Table 2 and Fig. 2 are, therefore, those for the rapid initial process alone. In general, they agree quite well with the data reported by Wade and Hackerman (*16*). As can be seen from Fig. 2 the heat of immersion of eta alumina in water was approximately proportional to the amount of water removed at elevated temperatures. In the case of gamma alumina, however, the initial stages of dehydration did not cause as large an increase in the heat of immersion, and it was not until some 3 to 4 wt % of water had been removed that the rate of heat increase with water loss approached that of eta alumina. It might be noted that the fact that the heats of immersion of eta

TABLE 2

HEATS-OF-IMMERSION OF ALUMINA IN WATER AT 25°C

Evacuation temp. (°C)	Heat-of-Immersion (Ergs/cm²)	
	η-Al_2O_3	γ-Al_2O_3
25	199	270
75	310	328
100	—	354
150	406	412
250	470	530
350	548	635
450	648	761
500	698	787

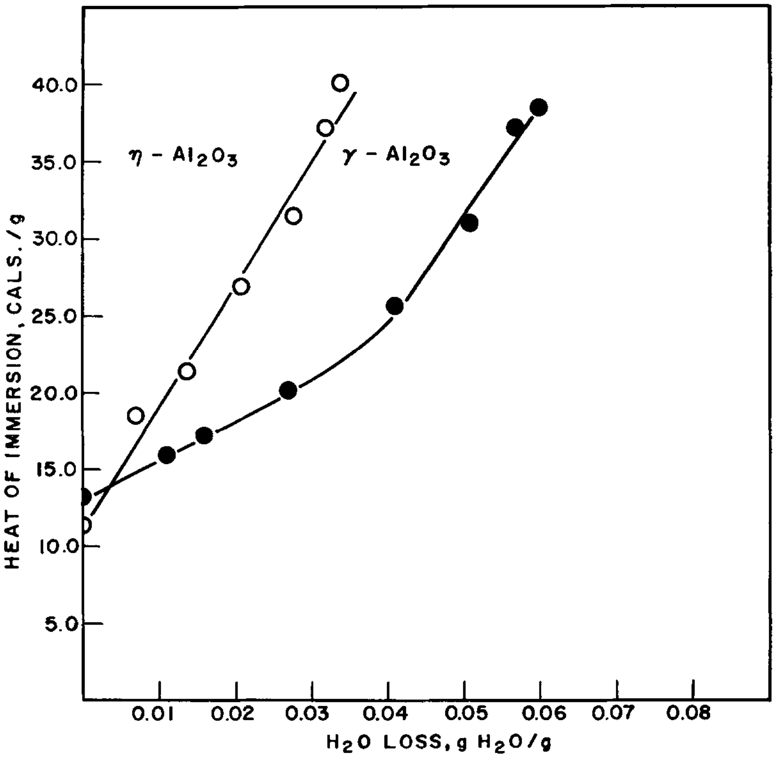

FIG. 2. Heat of immersion of alumina in water at 25°C.

alumina are fairly linear in water content over dehydration temperatures ranging from 25° to 500°C is additional evidence that the surface was relatively free of weakly held, physically adsorbed water after evacuation at 25°C; if this were not so, one would expect some discontinuity or change in slope of the plot in Fig. 2 at the point at which the physically adsorbed water was removed.

The adsorptions of H_2O, CH_3OH, and NH_3 were studied on the two aluminas after pretreatment by evacuation for 24 hr at 25°C. The resulting isotherms, were reversible in the sense that, below the region of capillary condensation, decreasing pressures gave the same isotherms as increasing pressures and, in all three cases, the adsorbates could be removed from the surface at 25°C by evacuation. BET plots of the water and methanol isotherms were linear over the usual range of relative pressures, which permitted calculation of the monolayer volume, V_m, and the BET "C" value. Using molecular cross-sectional areas of 11 Å^2 for water and 21 Å^2 for methanol (*11*), it was possible to estimate the fractions (θ) of the surface covered by the two adsorbates. These values are summarized in Table 3. A number of experiments were carried out in which, after measuring the original water isotherm, the alumina was dehydrated at temperatures up to 500°C, exposed to water vapor at 25°C for 24 hr, evacuated for 24 hr, and a second isotherm measured. In all cases, the water

TABLE 3
ADSORPTION OF H_2O AND CH_3OH ON ALUMINA SURFACES AT 25°C[a]

Alumina	Adsorbate	V_m [cc(STP)/m^2]	C	θ
Eta	H_2O	0.198	26	0.59
Eta	CH_3OH	0.122	157	0.68
Gamma	H_2O	0.226	25	0.67
Gamma	CH_3OH	0.133	177	0.75

[a] V_m = BET monolayer volume;
C = BET "C" value;
θ = fraction of total surface covered by V_m.

lost at elevated temperatures was regained by the sample at 25°C within a few hours, and, in each instance, the second isotherm was identical with the first. As can be seen from Table 3, the physical adsorption of water and methanol took place on only a limited (60–80%) portion of the surface, a situation somewhat analogous to that observed in the case of silica by Young (*17*), who attributed the restricted adsorption to the existence of hydrophobic surface regions. Several experiments were also performed in which the alumina was evacuated at elevated temperatures and a methanol isotherm determined at 25°C. It was found that such dehydration caused a decrease in the adsorption of methanol. A similar observation has been made by Every, Wade, and Hackerman (*11*), and is perhaps due to a decrease in the number of the surface hydroxyl groups with which methanol interacts.

The acidic properties of the two aluminas were determined by studies of ammonia adsorption as a function of dehydration. Ammonia was adsorbed on the dried alumina at 25°C and the amount of ammonia remaining adsorbed after evacuation at elevated temperatures measured as described in the preceding section. A similar method has been used by Webb (*12*) who attempted to relate acid strength to the temperature required for desorption of the ammonia, the desorption temperature increasing with increasing acid strength. The data obtained in the present study are plotted in Figs. 3 and 4, where the ordinates indicate the amount of ammonia remaining adsorbed after evacuation for 24 hr at the temperatures specified on the figures; the abscissae are the temperatures at which the alumina was dehydrated, prior to the initial adsorption of ammonia. Thus, the line labeled (25°C) indicates the amount of ammonia remaining adsorbed on the alumina after evacuation for 24 hr at 25°C as a function of dehydration temperature. The difference between this and the similar line labeled (100°C) may be taken, after the manner of Webb

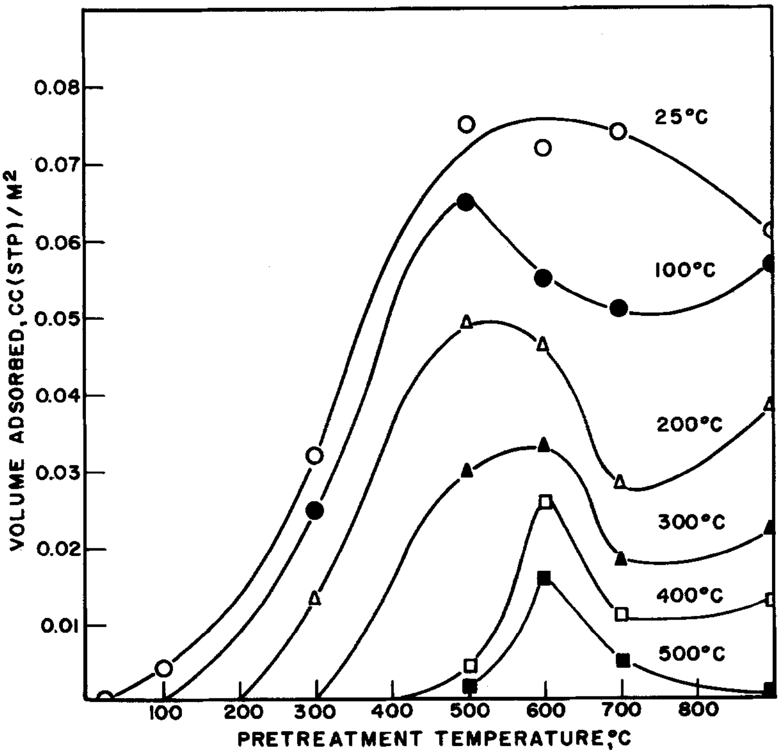

FIG. 3. Ammonia chemisorbed on eta alumina.

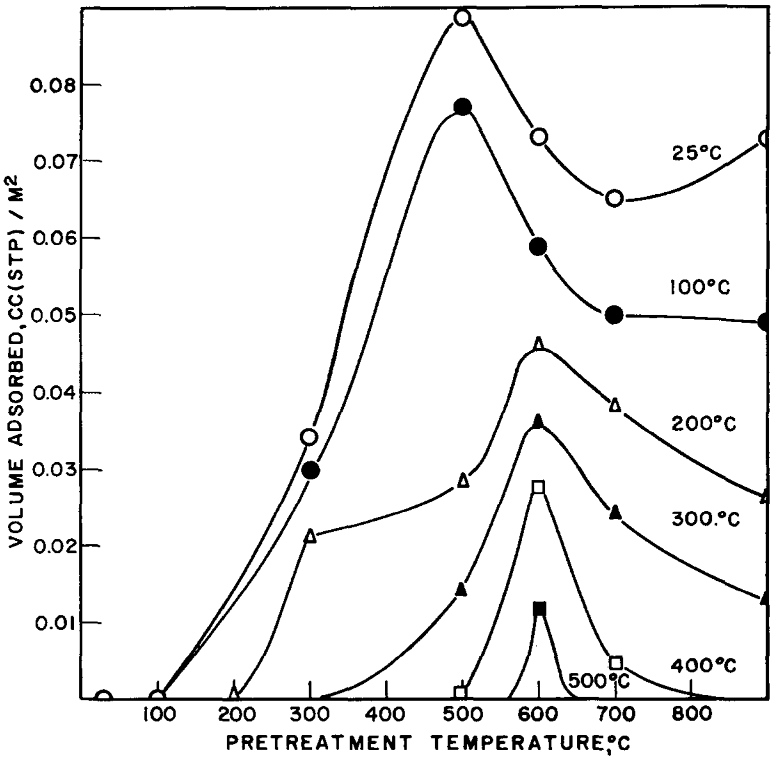

Fig. 4. Ammonia chemisorbed on gamma alumina.

(*12*), as a measure of acid sites so weak that ammonia may be desorbed from them over this temperature range. Similar considerations apply to the other lines in these figures. It should be kept in mind that a fresh sample of alumina was used for study at each dehydration temperature. For purposes of future discussion it will be assumed that the amount of ammonia retained at 25°C represents the total chemisorption of ammonia. It is apparent from Figs. 3 and 4 that ammonia chemisorption on alumina is a rather complex phenomenon and depends both on the type of alumina and its temperature of dehydration. Both aluminas are essentially nonacidic after evacuation at 25°C; upon evacuation at 100°C acidity develops in eta alumina, but it is necessary to heat gamma alumina to somewhat higher temperatures before appreciable acidity is observed. Beyond this point both aluminas increase rapidly in acidity as the temperature is raised. Over this range, while the acidity of gamma alumina equals or exceeds that of eta alumina, the latter possesses acid sites of greater strength. As the temperature is raised above 500°C there is a slight decline in total acidity; the strong acidity seems to pass through a maximum at around 600°C and then fall off up to 900°C.

For orientational purposes, similar ammonia adsorption experiments were carried out on samples of silica-alumina and silica-magnesia pretreated at 500°C. These data were compared with the alumina data by arbitrarily defining three classes of acid sites in terms of the amount of chemisorbed ammonia desorbed within certain temperature ranges, viz., weak (25–200°C), medium (200–400°C), and strong (>400°C). The comparative data are presented in Table 4. It can be seen that the acidities of the two modifications of alumina are similar in some respects to the silica-alumina and silica-magnesia acidities. Thus, after evacuation at 500°C, gamma alumina resembles silica-magnesia in having a majority of weak acid sites, while eta alumina, like silica-alumina,

TABLE 4

SURFACE ACIDITIES

Adsorbent	Evacuation temp., (°C)	Acidity ($meq/M^2 \times 10^4$) Strong	Medium	Weak	Total
SiO_2-Al_2O_3	500	3.7	3.8	3.4	10.9
SiO_2-MgO	500	0.5	6.3	9.0	15.8
γ-Al_2O_3	500	0.4	11.8	27.2	39.4
η-Al_2O_3	500	1.3	20.5	11.7	33.5
γ-Al_2O_3	700	2.9	19.4	15.9	38.2
η-Al_3O_2	700	6.5	10.0	27.0	43.5
γ-Al_2O_3	900	0	15.3	27.6	32.9
η-Al_2O_3	900	7.6	14.7	13.5	35.8

contains a relatively large amount of medium and strong acidity. However, it should not be inferred from this that there is necessarily any chemical or catalytic similarity between the "acidic" sites on, say, gamma alumina and silica-magnesia. This comparison is used simply to demonstrate the large differences in surface acidity between eta and gamma alumina. Upon raising the dehydration temperature to 700°C, there is a general increase in acid site strength for both aluminas; above this temperature, the strong acidity of gamma alumina decreases and that of eta alumina increases. As will be shown in a succeeding paper, these differences in acidity between eta and gamma alumina apparently give rise to large differences in catalytic activity. It should be pointed out in this connection that, while small amounts of chemical impurities, especially alkali metals, may severely influence the acidity of catalytic aluminas (*1*), the differences in properties of the two aluminas reported here do not seem attributable to such an effect because, first, the total chemical impurity level was quite low (i.e., 600 ppm), and, second, both aluminas had almost identical chemical compositions.

DISCUSSION

As indicated earlier, the object of the present work was to compare certain aspects of the surface chemistry of eta and gamma alumina. In order to do this it was necessary to assume that the two aluminas being investigated were representative samples of the eta and gamma modifications having properties typical of the two forms. The X-ray evidence cited above seems to support such an assumption, although it is not to be inferred that all "eta" aluminas or all "gamma" aluminas are necessarily the same in all respects, nor have precisely the same properties. What does seem justified is the assertion that the present research was carried out on two different forms of alumina, which could be classified as an eta and a gamma alumina, respectively.

Apart from physical appearance and texture, the most obvious difference between the two aluminas was that, after removal of any weakly bound, physically adsorbed water by evacuation at 25°C, gamma alumina contained 7 wt % water as compared to 4.5 wt % in the case of eta alumina. This "excess" 3.5% water appeared to be desorbed, for the most part, below 300°C, and coinciding with its removal was a change in the surface properties of the gamma alumina. Thus, while the acidity of eta alumina, as measured by ammonia adsorption, increased continuously with dehydration temperature up to 500°C, gamma alumina did not develop appreciable acidity until 200–300°C (i.e., until elimination of the "excess" water). Similarly, the heat of immersion versus water loss plot for gamma alumina in Fig. 2 shows a distinct change in slope above the point corresponding to the removal of about 3.5 wt % water (i.e., 200–300°C). These latter data suggest a considerable difference between the energetics of desorption of the "excess" water and that of the water removed from gamma alumina at higher temperatures, and this appears to justify separate consideration of the chemical nature of this "excess" water.

Water that is evolved from alumina upon evacuation at elevated temperatures may be considered as originating from the following sources: (1) the condensation of surface hydroxyl groups, (2) molecular water, bound to the surface by forces strong enough to prevent desorption at 25°C, and (3) chemically bound water incorporated into the bulk lattice as internal hydroxyl groups. While the present data do not permit unambiguous assignment of the "excess" water content of gamma alumina to a single, specified source, they do form the basis for some reasonable speculation on this matter, as follows. The maximum possible number of surface hydroxyl groups on alumina may be estimated by considering an alumina surface to be represented by a cubic close packing of oxide ions. If this surface were fully hydroxylated (i.e., if all the surface oxide ions were converted to surface hydroxyl groups), then, assuming an oxide ion radius of 1.4 Å (*18*), there would be about 12.5 OH/100 Å^2, which, upon heating at elevated temperatures, could evolve 6.2 H_2O molecules/100 Å^2. On this basis, eta alumina, having a surface area of 240 m^2/g, would be expected to contain the equivalent of 4.5 wt % water if all the water were present as surface hydroxyl groups; as can be seen from Fig. 1, this, in fact, corresponds to the observed water content of eta alumina. It is interesting, in this connection, to consider the physical adsorption of water on alumina. It was indicated, in Table 3, that in the case of an alumina evacuated at 25°C, physical adsorption of water, as here defined, took place on only a portion of the surface. Other workers (*19*, *20*) have discussed a similar phenomenon reported by Young (*17*) for the case of a silica surface and have suggested that the physical adsorption of first layer water molecules takes place by hydrogen bonding of each water molecule to two surface hydroxyl groups. If this picture is accepted, the BET monolayer volume, V_m, for water may be taken as a measure of the number of silanol groups on a silica surface. Applying this argument of two hydroxyl groups per adsorbed molecule to the case of an alumina surface, one calculates from the V_m values given in Table 3 that there are approximately 11 OH/100 Å^2, in good agreement with the calculated value. While this close agreement may be fortuitous, it would appear to represent a reasonable indication of an upper limit to the number of surface hydroxyl groups, since it is difficult to see how the bonding of a water molecule to the surface could involve more than two hydroxyl groups. Similar consideration of the methanol adsorption gives a value of about 7 OH/100 Å^2, indicative, perhaps, of some steric hindrance by this relatively large adsorbed molecule. In the case of gamma alumina, therefore, it would appear that, on the basis of the results obtained with eta alumina, only about 3.8 wt % water can possibly be attributed to surface hydroxyl groups. Subtraction of this value from the total water content of gamma alumina gives a value of 3.2 wt %, which corresponds quite well to the observed "excess" water of gamma alumina. In summary, while the water content of eta alumina can be accounted for, if need be, in terms of surface hydroxyl groups, it does not seem possible to attribute all the water in gamma alumina to this single source.

The remaining possible sources are internal water and molecular water adsorbed on the surface. The presence of water, chemically combined with alumina as internal hydroxyl groups, has been claimed by Glemser and Rieck (*21*), although Fortuin (*22*) and Meijs (*23*) concluded from their work that all the hydroxyl groups were actually on the surface. DeBoer and Houben (*24*) suggested, some time ago, that the structure of gamma alumina is analogous to that of the lithium spinel described by Kordes (*25*), with internal protons substituted for lithium ions, but, more recently, deBoer (*26*) has indicated that subsequent work has failed to substantiate this model. Some evidence for the presence of "internal" hydroxyl groups in alumina has been obtained by Urarov (*27*), who concluded from infrared spectra that gamma alumina is partially rehydrated to alumina trihydrate when exposed to water vapor at low temperatures. Thus, while the existence of internal hydroxyl groups in alumina has not yet been convincingly demonstrated, such groups cannot be completely eliminated as the source of the "excess" water of gamma alumina. However, the strong dependency of such surface properties as acidity and heat of immersion on the water content seems to suggest that this water is associated to a large extent with the surface rather than with the bulk lattice. Since, as indicated above, this water is in excess of that water which could possibly be contained as surface hydroxyl groups, it can only be concluded that the "excess" water of gamma alumina may exist as molecular water strongly bonded to the surface. In fact, it can be noted that the amount of "excess" water observed in the case of gamma alumina is of the order of a monolayer. A somewhat related conclusion has been reached by deBoer, Fortuin, Lippens, and Meijs (*31*) who describe a "chemisorbed" water bound to the surface of alumina by strong hydrogen bonds to surface oxide ions.

The foregoing discussion does not demonstrate that there was no molecular water on the eta alumina surface after evacuation at 25°C, but merely indicates that the gamma alumina retained a great deal more molecular water on its surface at 25°C than did eta alumina. If this be granted, then the question naturally arises as to reasons for this difference. Unfortunately, it does not seem possible, at the present time, to offer an explanation, except to suggest that it could reflect a difference in the polarity or arrangement of the surface hydroxyl groups to which the molecular water may be bonded. Peri and Hannon (*28*) have shown that alumina may contain several types of surface hydroxyl groups of varying degrees of polarity, and it is possible that the more polar types predominate on gamma rather than on eta alumina and that these strongly polar groups are responsible for the tenacious adsorption of molecular water on gamma alumina. Furthermore, since one is dealing, in the present case, with two aluminas of different structures, geometric factors may be important. If, as some workers have suggested (*19*, *20*), the adsorption of water preferentially involves two surface hydroxyl groups, then the strength of bonding of water to the surface would presumably be critically dependent upon the average distance between hydroxyl groups, and this latter would, in turn, depend upon the structure of the alumina.

Turning to the dehydration processes occurring at high temperatures, it has been shown by Peri and Hannon (*28*) that these consist essentially of the condensation of surface hydroxyl groups. The ammonia adsorption data in Figs. 3 and 4 indicate that this dehydration is accompanied by the development of considerable surface acidity and, thereby, demonstrate the second major difference between eta and gamma alumina, namely, the fact that while the total acidity, as measured by ammonia adsorption, was about the same in both cases, the average strength of the acid sites was greatest in the case of eta alumina. In fact, the difference in acid strength distribution between eta and gamma alumina was as distinctive as that between silica-alumina and silica-magnesia. Pines and Haag (*1*) in their discussions of the acid properties of alumina have emphasized the influence of alkaline impurities on these properties; the present work suggests that the structural form of the alumina may also be a significant factor controlling the surface acidity.

The relationships between the amount of water removed from an alumina and the total acidity (i.e., total ammonia chemisorption) are given in Fig. 5, where it can be seen that three general types of behavior can be defined. First, during the initial stages of dehydration, in which it is assumed that strongly bound molecular water is being desorbed from the surface, the acidity of the alumina increases rather slowly, presumably because some of this water is associated with the acid sites. When this process has been completed, the acidity becomes much more sensitive to the water content with about an equal molar correspondence between the amount of water removed and the ammonia chemisorption. Finally, the total acidity reaches a maximum and then decreases as additional water is removed from the alumina. Presumably, these phenomena can be associated with definite chemical processes, although such relationships cannot be established on the basis of present evidence. It is also apparent that as the temperature of dehydration is increased the acid strength distributions of the two aluminas change, relative to each other, a further indication of some basic difference between eta and gamma alumina. Since the surface of eta alumina has been described by Lippens (*5*) as being formed mainly by the (111) plane of the spinel while the surface of gamma alumina is formed by the (110) plane it seems reasonable to attribute some of the observed differences in ammonia adsorption on the two aluminas

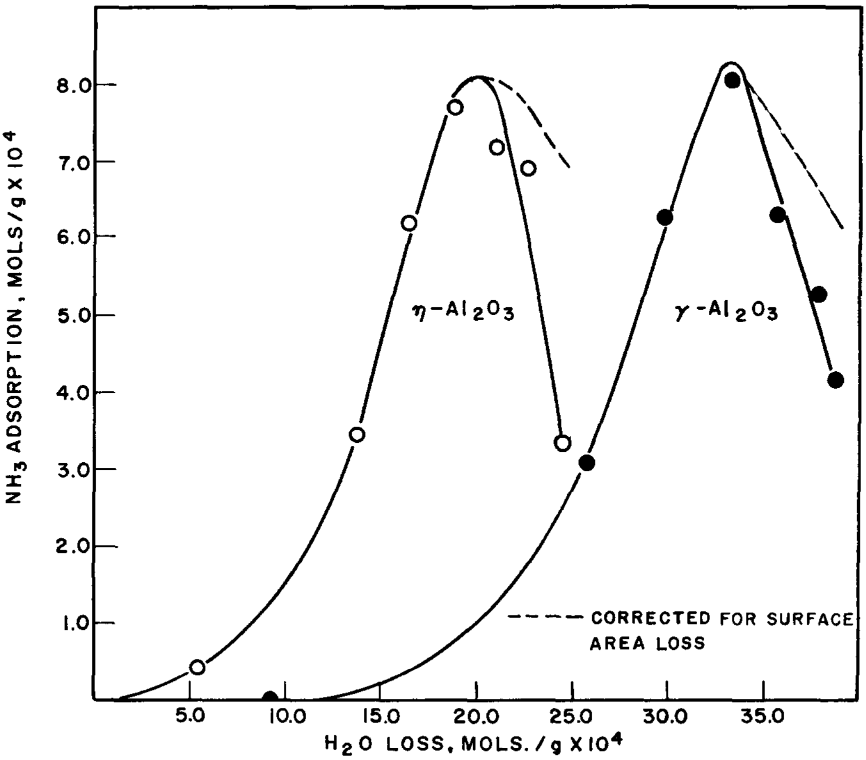

FIG. 5. Effect of water loss on ammonia chemisorption.

as being related to the structures of the two surfaces. Unfortunately, the present data do not permit a more detailed consideration of these differences. It is interesting to note that the total acidity of alumina exceeds by a factor of two or three the total acidity of such strongly acidic materials as silica-alumina and silica-magnesia. In fact, to the extent that ammonia adsorption is a valid measure of catalyst acidity, eta alumina, especially after dehydration above 500°C, has an acidic character that compares very favorably with silica-alumina with respect to both the number and strength of acid sites. The fact that alumina is generally inferior to silica-alumina as a catalyst for such reactions as hydrocarbon cracking is possibly due to the great susceptibility of the acid sites on alumina to poisoning by traces of water (*29*, *30*) and other basic compounds.

The most general conclusion that may be drawn from the foregoing work is that not only the "texture" but also the basic surface chemistry of alumina is, to a significant degree, a function of the structure or "form" of the alumina. Thus, the heat of immersion data presented in Table 2 and Fig. 2 suggest that conclusions drawn from such calorimetric studies may be specific to the particular type of alumina being used and may not be capable of extrapolation to aluminas in general. This observation is in agreement with the data of Every, Wade and Hackerman (*11*) on the heats of immersion of alpha and gamma alumina. Similarly, the observed variations in ammonia adsorption noted above seem to be indicative of a structure-sensitive chemisorption phenomenon which is presumably an inherent feature of alumina surface chemistry. These facts emphasize that close control of preparative procedures, because of their influence on structure, is necessary in order to obtain aluminas of reproducible properties.

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