# Measurement of Bronsted Acid Sites on Aluminum Oxide Surfaces Using Deuterated Pyridine and Wide Line Nuclear Magnetic Resonance

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The concentration of Bronsted acid sites on aluminum oxide surfaces has been measured using a deuterated pyridine, wide line nuclear magnetic resonance technique. The wide line nmr spectrum of a transition alumina consists of a narrow line, due to physically adsorbed water, superimposed on a broad line, due to water chemically bound to the lattice. The physically adsorbed water and therefore the narrow line in the nmr spectrum can be removed by mild heating under vacuum. If deuterated pyridine is then added to the surface, it will react with Bronsted acid sites according to the following:
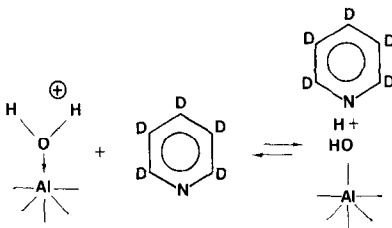
Under proper experimental conditions the proton associated with the pyridinium ion appears as the only narrow line in the nmr spectrum and can be quantitatively measured.

INTRODUCTION

Commercially available transition aluminum oxides have surface areas ranging up to about 350 m²/g. The reactive properties of aluminum oxides are in large part determined by species such as hydroxyl groups and certain types of acid sites found on their surfaces. Nuclear magnetic resonance has been used to measure the total proton content of oxides including alumina (1). The present writer was able to show how nmr line widths can be combined with intensity measurements to determine the concentration of surface hydroxyl groups (2). Gravimetric methods have been com-

bined with nmr spectra to show that the latter measures proton content to an accuracy of a few percent (3).

Our present understanding of the acidic properties of the alumina surface stems as much from explanations of the reactions which occur on the oxide surface as it does from direct spectroscopic and adsorption studies of the surface as such.

Pines and Haag (4) used the isomerization of neohexene (3,3-dimethyl 1-butene) to study the acidic properties of the alumina surface. They suggested that the alumina surface contains "weak" acid sites capable of isomerizing neohexene to 2,3-
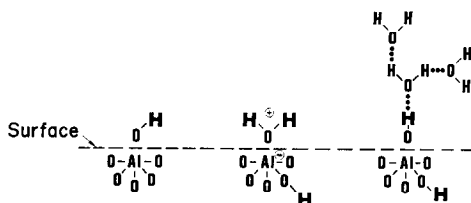
Fig. 1. Proton sites in a transition alumina.

dimethyl butenes and "strong" acid sites capable of isomerizing neohexene to methyl pentenes and *n*-hexenes. Walling (5) and later Benesi (6) used adsorption indicators to measure the strengths of the acid sites on the oxide surface. A recent review (7) compares the various methods for determining the acidity of solid surfaces, and a book (8) has recently been published on the subject.

The measurement of surface acidity is both a quantitative and a qualitative problem. The total amount of acidity can be relatively easily measured with an amine titration or adsorption (9, 10) combined with gravimetric measurement. Neither of these methods distinguishes between Bronsted and Lewis acidity. That distinction can be made by spectroscopic methods, and these methods have been dominated by infrared spectroscopy. Parry (11) first proposed the use of infrared spectroscopy to measure the spectrum of pyridine adsorbed on acidic surfaces. He showed how this technique can be used to distinguish between Bronsted and Lewis type acid sites. Many authors have used this technique over the last several years, but it has two serious limitations. It is difficult to quantitate, and the technique can be used only after rigid sample handling conditions have been met.

Most workers would agree that the alumina surface acidity is principally Lewis type. Although Bronsted acid sites have not been detected on the alumina surface by the infrared-pyridine method, their existence cannot be ruled out. Ward and Hansford (12) investigated a series of silica–aluminas with the infrared-pyridine adsorption technique. They showed that Bronsted acidity could be detected down to the equivalent of 0.25% alumina in the silica–alumina catalyst. They demonstrated a direct correlation between Bronsted acidity and *o*-xylene isomerization and showed that carbonium ion reactions were found on oxides where Bronsted acidity could not be detected by the infrared-pyridine method.

THEORY

The method proposed here is based on the reaction of deuterated pyridine with the alumina surface. It was shown that under certain conditions the pyridinium ion formed when a deuterated pyridine molecule reacts with a Bronsted acid site can be quantitatively measured with proton nmr. In order to explain the method, we must first discuss the relationship between the proton nmr spectrum and the proton content of an alumina.

Proton nmr Spectra of Transition Aluminas

Saito and Hagewara (13) showed that the nmr spectrum of partially dehydrated gibbsite consists of a narrow line about 0.3 G wide due to physically adsorbed water superimposed on a broad line about 5 G wide due to protons chemically bound to the oxide lattice.

When an nmr spectrum consists of a compound line, we know that the sample contains two different populations of protons and that exchange between these populations is slower than the line width of the broad line in cycles per second. For a transition alumina this amounts to about 10^4 Hz.

The wide line in the nmr spectrum, due to chemically bound water, will go undetected if a narrow field sweep and a low amplitude modulation are used. Under these conditions the proton nmr spectrum is that of the physically adsorbed water in the

sample. The amount of physically adsorbed water can be measured by comparing the intensity of this narrow line to the intensity of the nmr line from a suitable standard (2). It was also shown in Ref. (2) that the width of the nmr line due to physically adsorbed water is an inverse function of the amount of water adsorbed on the surface.

The physically adsorbed water can be removed by gentle heating ($\sim 100\,°C$) under vacuum. The nmr spectrum of the resulting sample consists of one broad band due to chemically bound water. The width of this band is an inverse function of the surface area of the alumina (2).

A model for an alumina consistent with its proton nmr spectrum is shown in Fig. 1. The proton sites shown in this model can be divided into two fundamentally different populations. These are (a) protons on oxygen atoms bound to the oxide lattice, and (b) protons in physically adsorbed water molecules. Protons within each population are exchanging rapidly within that population, but a much slower rate of exchange occurs between protons in the different populations. The rapid proton exchange within each population produces an averaged nmr spectrum of the protons in that group.

The width of these nmr lines can be qualitatively understood by introducing the concept of correlation time, τ_c, which is a measure of the time scale of the random motion of the protons. The correlation time is the amount of time it takes a proton to rotate through an angle of a radian or to move a distance comparable to its dimensions. If the motion in the system is rapid enough, only the average of the local field will be seen by a given spin, and the line width will be narrowed. Abragam (14) pointed out that motional narrowing occurs when the product of the rigid lattice line width and the correlation time are small,
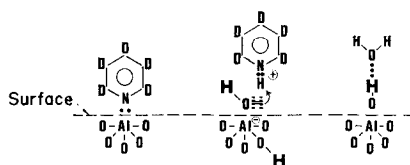

FIG. 2. Deuterated pyridine on alumina surface.

i.e., $(\Delta H_2{}^2)^{\frac{1}{2}}\tau_c \ll 1$ where $\Delta H_2{}^2$ is the rigid lattice second moment expressed in Hz.

One would expect that the first water physically adsorbed to the surface would be more firmly bound than subsequent layers, and as the concentration of physically adsorbed water increased, the nmr line width would decrease. The rapid exchange of protons between water molecules would average the width of the nmr line due to physically adsorbed water.

The mobility of the protons chemically bound to the oxide surface will be greater than those bound to an interior lattice site. Thus, surface protons will produce a narrow nmr line, while the nmr line associated with protons on interior sites will be broad. The rapid exchange of protons between surface and interior sites results in an nmr line whose width is a weighted average of the concentration of protons in each type of site.

It is important to remember that when an alumina contains both physically adsorbed water and protons chemically bound to the lattice, the width of each line is a measure of the average mobility of the protons in each population. A narrow line exists in the nmr spectrum of an alumina when the proton causing the narrow line exchanges only slowly or not at all with the protons bonded to the alumina lattice.

Reaction of Deuterated Pyridine with Alumina Surface

The reaction which takes place when isotopically pure deuterated pyridine is added to a hydrated alumina surface is shown in Fig. 2. Here a deuterated pyridine molecule has been added to both a Lewis
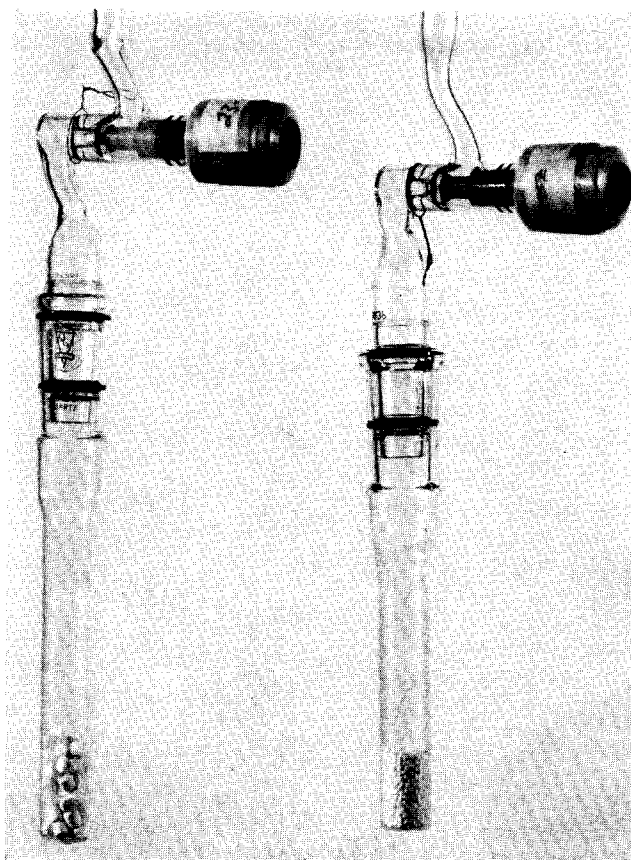
FIG. 3. nmr tubes.

acid site and a Bronsted acid site. The Bronsted site has donated a proton, which was rapidly exchanging among the lattice sites, to the deuterated pyridine molecule. This proton will now exchange rapidly with the protons of the physically adsorbed water molecules on the oxide and contribute to the narrow line in the nmr spectrum. If the physically adsorbed water is removed from the sample before the deuterated pyridine is added, the only narrow line in the proton nmr spectrum of the oxide is due to the proton from the Bronsted acid site. The area under the absorption curve of this narrow line is directly related to the concentration of sites capable of furnishing a proton to the deuterated pyridine molecule. The deuterium nmr spectrum can be used to

measure the total concentration of deuterated pyridine on the surface and thus the concentration of both Lewis and Bronsted acid sites. The concentration of Lewis sites can be found by difference.

Proton Impurity in Commercial Deuterated Pyridine

The deuterated pyridine used in this study was purchased from Merck and Co. About 1% of the possible deuterium sites on this material was occupied by protons. These proton impurities can interfere with the analysis under certain conditions. High resolution nmr spectra of both new deuterated pyridine and deuterated pyridine which had been adsorbed onto an alumina surface showed that each contained proton concentrations equivalent to 0.86% of their
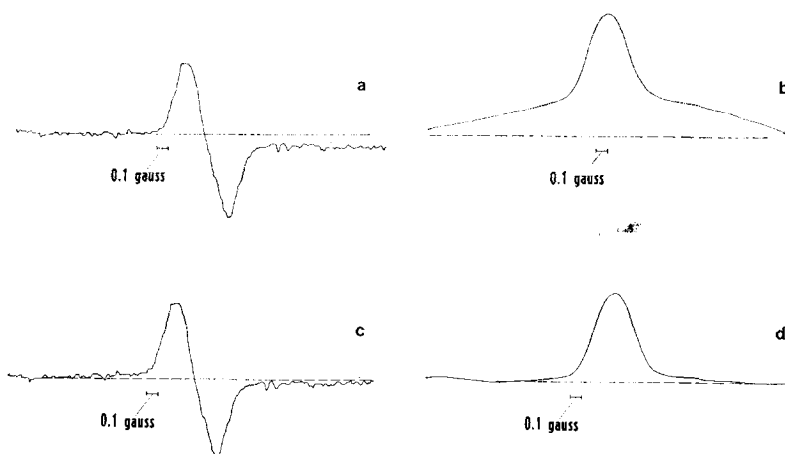
Fig. 4. Proton nmr spectrum of deuterated pyridine on alumina surface: (a) original derivative curve, (b) integral of a, (c) base line adjusted derivative curve, (d) integral of c.

ring positions. This illustrates that there is no exchange between protons in the oxide sample and deuterium on the pyridine ring when the deuterated pyridine is adsorbed on the oxide surface. The relative intensities of the three proton bands in the high resolution nmr spectrum of deuterated pyridine are about the same as those of ordinary pyridine. This shows that the proton impurities in the deuterated pyridine are randomly distributed around the aromatic ring.

Kiviat and Petrakis (15) used both infrared and nmr spectroscopy to study the adsorption of pyridine on the alumina surface. They were able to show that, under certain conditions, a transition alumina will contain both physically adsorbed and chemically bound pyridine. Just as with the water discussed above, the physically adsorbed pyridine produces a narrow nmr signal ($\Delta H \sim 0.1$ G), whereas chemically bound pyridine produces a nmr signal several gauss wide.

It has already been pointed out that a narrow line would be expected when the product of the nmr line width and the correlation time is small. The correlation time for the proton impurity in the deuterated pyridine would be the same as the correlation time for the deuterium in the same molecule. The line width of the deuterium nmr spectrum of chemically bound deuterated pyridine is similar to the line width of the proton nmr spectrum of ordinary pyridine. Because of this, we can expect the two spectra to behave in a similar manner. That is, if the proton impurity on the aromatic ring produces a narrow line in the proton nmr spectrum, the deuterium will also produce a narrow line in the deuterium nmr spectrum. If there is no narrow line in the deuterium nmr spectrum of the adsorbed deuterated pyridine, there will be no narrow line in the proton nmr spectrum which will interfere with the measurement of the narrow proton signal from the Bronsted acid site. Thus, by running the deuterium nmr spectrum of the adsorbed deuterated pyridine, we can tell when an interference will occur.

METHODS

Apparatus

All nmr spectra described in this paper were made at 15 MHz using a Varian Model DA-100-15D nmr spectrometer equipped with a Model 4210 Variable Frequency RF unit. At this nmr frequency

TABLE 1

Data for Adsorption of Deuterated Pyridine on Transition Alumina

Conc OH		Conc H+ 0°C Py	g Py/g Al$_2$O$_3$	
Total	Surface		by wt	NMR
9.74×10^{20}	5.63×10^{20}	6.87×10^{19}	0.1294	0.1503
9.77×10^{20}	5.79×10^{20}	5.12×10^{19}	0.1557	0.1547

the proton signal is obtained at a magnetic field strength of about 3.5 kG and the deuterium signal at about 23 kG. The method described in this paper depends on quantitatively measuring the intensity of a narrow line in the presence of a broad nmr signal. The intensity of the broad nmr signal is also measured. The instrumental techniques used to quantitate these two signals have been previously discussed (2). All nmr signals were fed directly from the spectrometer into a Nicolet Model 1074 instrument computer for signal averaging and data reduction.

Samples

A sample of commercially available gel-derived transition alumina was activated at 600°C for 2 hr in air. The sample was then equilibrated at 100% relative humidity for 48 hr. This sample was used for all subsequent experiments. Its measured BET surface area was 280 m²/g.

Portions of the sample were placed in 15 mm quartz nmr tubes which had been fitted with 19/38 O-ring vacuum joints, see Fig. 3. The sample tubes were attached to a vacuum system capable of maintaining a pressure of 10^{-4} to 10^{-5} Torr. Vacuum grease was eliminated by use of EPR rubber O-ring joints. After overnight evacuation at an appropriate temperature, the samples were placed in the spectrometer and the nmr spectrum was determined. The samples were then returned to the vacuum rack, the pressure was reduced to less than 10^{-4} Torr, deuterated pyridine

was introduced into the rack and the sample was equilibrated overnight.

nmr Spectrum of Adsorbed Deuterated Pyridine

An alumina sample (activated at 300°C) was equilibrated with deuterated pyridine. The pressure of deuterated pyridine in the vacuum system was set equal to the vapor pressure of deuterated pyridine at 0°C. (The reason for this choice of pressure of deuterated pyridine is discussed below.) The sample was placed in the spectrometer and the proton nmr spectrum was determined using instrumental conditions such that only the narrow proton signal is obtained. This spectrum, which is a composite of one thousand twenty-four 1-min scans, is shown in Fig. 4A. Energy absorbed by the chemically bound protons in the sample causes the base line in Fig. 4A to fall off toward the high field side. The integral of this spectrum, Fig. 4B, shows severe base line distortion. This problem can be overcome by correcting the base line of the original derivative spectrum by adding a straight line. The corrected spectrum then appears as shown in Fig. 4C and gives a properly shaped integral as in Fig. 4D. Base line corrections done in this laboratory were all carried out on the Nicolet instrument computer used to time average the spectra.

RESULTS

The deuterium adsorption method and the resulting nmr spectrum at each step in

the process will now be illustrated. The numerical data calculated from all the spectra plus that of a duplicate sample are summarized in Table 1.

The alumina sample previously described was evacuated overnight at 300°C. Figure 5 shows the proton nmr spectrum of the sample under these conditions. Analysis of this spectrum shows the sample contains 1.45% chemically bound water, no physically adsorbed water, and by methods previously described (2), it can be shown that the sample contains 5.63 × 10^{20} surface protons/g of Al$_2$O$_3$. Proton and deuterium nmr spectra of the sample after overnight equilibrium with deuterated pyridine at room temperature are shown in Fig. 6A and B. Analysis of the narrow line proton spectrum (Fig. 6A) shows the sample contains 1.83 × 10^{20} protons/g of Al$_2$O$_3$ contributing to the narrow line proton spectrum. The presence of the narrow line deuterium spectrum (6B) shows that the sample contains physically adsorbed deuterated pyridine. The proton impurity in this physically adsorbed deuterated pyridine will contribute to the narrow line proton spectrum. We know from the high resolution spectrum of the deuterated pyridine that it contains 3.09 × 10^{20} protons/g. We could calculate the amount of physically adsorbed deuterated pyridine on the sample from the deuterium spectrum and correct the proton spectrum for this impurity, but it can be shown that a 10% error in our deuterium spectrum would produce a 50% error in our final value for Bronsted acid sites.

This large error source can be circumvented by eliminating the physically adsorbed deuterated pyridine on the alumina
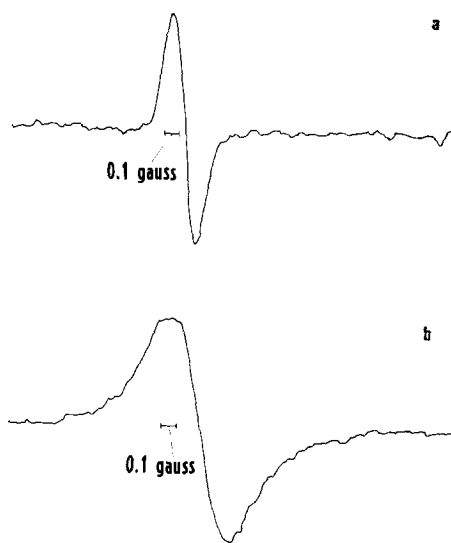

FIG. 6. nmr spectrum of deuterated pyridine on alumina surface: (a) proton, (b) deuterium.

sample. This is done by reducing the pressure of deuterated pyridine in the vacuum rack by placing the deuterated pyridine in an ice bath at 0°C. The deuterium nmr spectra of the above sample equilibrated with deuterated pyridine under these conditions is shown in Fig. 7A and B. The lack of an absorption band in Fig. 7A shows that the sample contains no physically adsorbed deuterated pyridine. The spectrum in Fig. 7B consists of one broad band with a width of 6.82 G. The signal intensity of the pyridine spectrum shows a quantitative response when compared to gravimetric measurements. The data for this comparison is given in Table 1. The narrow line proton spectrum of the sample is shown in Fig. 8.

This spectrum is a composite of eighty-one 1-min scans and can be used as a quantitative measure of the Bronsted acid sites on the alumina surface.

Water Content and Bronsted Acidity as a Function of Evacuation Temperature

Previous workers have shown that activation temperature affects the surface

FIG. 5. Proton nmr spectrum of chemically bound water in a transition alumina.
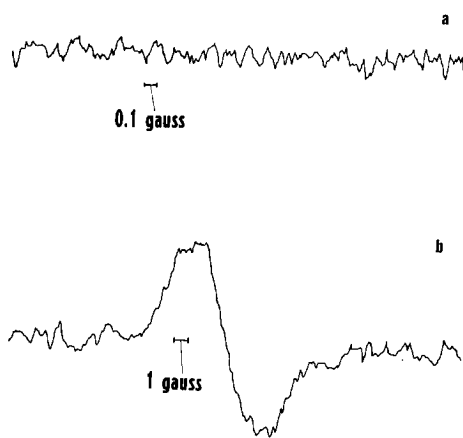
0.1 gauss

b

1 gauss

FIG. 7. Deuterium nmr spectrum of deuterated pyridine (0°C) on alumina surface: (a) physically adsorbed, (b) chemically bound.

acidity of an alumina (16). Therefore, the effect of evacuation temperature on the water content and Bronsted acidity was studied in the range of 100–700°C. The results are listed in Table 2. A fresh sample was used at each temperature, and the sample was evacuated overnight ($\sim$18 hr). Total and surface proton contents were determined by previously described methods (2).

DISCUSSION

Infrared spectroscopy of pyridine adsorbed on pure alumina surfaces has consistently failed to detect protonic acidity. This appears inconsistent with the work described here. This apparent inconsistency can probably be explained by the inherent weakness of the protonic acidity on the alumina surface and differences in technique between the infrared and nmr methods.

The nmr method described here is undoubtedly more sensitive than the infrared method. However, the concentration of Bronsted acid sites given in Tables 1 and 2 should be detectable by the infrared method. Unfortunately, most infrared workers have measured the infrared spectrum of adsorbed pyridine after evacuation

at an elevated temperature [for recent examples, see the work of Knozinger and Kaerlein (17) and Schwartz (18)] which can remove the pyridine adsorbed on the Bronsted acid sites. That is why in this work the pyridine pressure in the vacuum rack was not reduced to less than the vapor pressure of deuterated pyridine at 0°C. In fact, the strength of the Bronsted acid sites on the alumina surface could probably be studied by measuring the concentration of acidic protons as a function of deuterated pyridine pressure.

The increase in Bronsted acidity as a function of activation temperature shown in Table 2 is in agreement with the work of Peri and Hannon (16). These workers measured the infrared spectrum of surface hydroxyl groups on alumina. They showed that the hydroxyl groups associated with the 3698 cm^{-1} ir bands exchanged with deuterium more rapidly than did the other types of hydroxyl groups on the alumina surface. In subsequent work, Peri (19) was able to show that the hydroxyl groups associated with the 3698 cm^{-1} ir bands were more tenaciously held to the surface on evacuation at elevated temperature. A concise review of Peri's work on this subject is given by Little (20). An alternate to Peri's interpretation of the infrared spectrum of hydroxyl groups on alumina surfaces has recently been given by Tsyganenko and Filimonov (21).

The early nmr studies (1, 22) were interpreted on the basis of protons fixed to particular oxygen atoms. Recent nmr studies, especially on zeolites, (23–26) have shown that the protons are migrating from
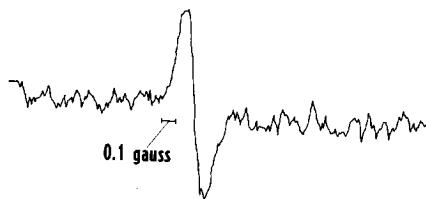
0.1 gauss

FIG. 8. Proton nmr spectrum of deuterated pyridine (0°C) on alumina surface.

TABLE 2

Proton Content and Bronsted Acid Sites as a Function of Evacuation Temperature

Evac temp (0°C)	H^1/g Al$_2$O$_3$		Bronsted sites/ g Al$_2$O$_3$ × 10^{19}	H^1 Acidic	
	Total × 10^{20}	Surface × 10^{20}		% Total	% Surface
100	19.20	11.1	3.48	1.81	3.14
200	11.32	6.56	5.32	4.71	7.18
300	9.76	5.71	6.00	6.12	10.6
400	5.94	3.99	5.89	9.98	14.8
500	6.18	3.86	7.18	11.6	18.6
600	2.11	1.47	7.32	34.9	49.8
700	0.58	0.41	3.28	56.6	80.0

oxygen to oxygen even at room temperature. Fripiat (24) has suggested that increased mobility at higher temperatures would result in increased proton acidity for these materials. The increased acidity as a function of activation temperature shown in Table 2 is probably not related to this theory since our measurements of acidity were all made at room temperature.

In the present work the proton nmr spectrum of a transition alumina is explained with a model which locates protons not only on the surface but also in the interior of the oxide lattice. This model is not new, having been proposed in the 1950's by DeBoer and Houben (27) and Glemser and Rieck (28). More recently DeBoer and coworkers (29) and Peri (30) have proposed models which locate all of the protons on the alumina surface. The problem with these latter models is that an unacceptably small surface area per proton has to be used in order to account for the known proton content of the alumina. DeBoer's model can account for a proton content equivalent to 7.22% chemically bound water on an alumina with 300 m^2/g of surface. Transition aluminas can be prepared (31, 32) with higher chemically bound water contents than that which either of the above models can accommodate. Recently, a model structure for pseudoboehmite has been proposed (31). This model, which distributes the protons through the oxide lattice, can account for the measured proton content, proton nmr spectrum and XRD pattern of these gel-like transition aluminas.

Additional Proof

After the final draft of this paper had been prepared, an article by Dewing, Monks and Youll appeared in this Journal [44, 226 (1976)]. These authors used the infrared spectrum of adsorbed pyridine and 2,6-ditertiary-butyl pyridine to postulate the existence of four types of acid sites on the aluminum oxide surface. Three of these were coordinated sites and one was a weak protonic site which had characteristics similar to the Bronsted sites seen by the deuterated pyridine–nmr method.

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