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Wide Line Nuclear Magnetic Resonance Studies on Transition Aluminas—Distribution of Protons Between Surface and Bulk Phases

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Wide line nuclear magnetic resonance (NMR) has been used to study the distribution of protons between the surface and bulk phases in a transition alumina. The width of the proton NMR line in a series of transition aluminas was shown to be a function of the surface area as measured by the nitrogen adsorption method (BET). The NMR method can be used to quantitatively estimate the concentration of total hydroxyl content in a transition alumina. The fraction of hydroxyl groups located on the surface of the sample can be estimated from the width of the proton NMR line. This fraction was shown to be related to the surface area of the sample. Proton line widths were combined with aluminum-27 amplitudes to estimate the concentration of protons in the first two molecular layers of a transition alumina.

INTRODUCTION

The transition aluminas are a class of compounds prepared by partial dehydration of an aluminum trihydrate, monohydrate or gel. They can contain up to 20% water by weight either as physically adsorbed water molecules or as chemically combined water. Surface areas of several hundred square meters per gram give the transition aluminas important industrial applications as desiccants and catalyst supports.

The crystal structures of the transition aluminas have been extensively studied by X-ray diffraction (*1*). This method is, however, insensitive to the proton moiety of the sample, a knowledge of which is essential to any real understanding of the chemical properties of these materials. Infrared techniques have been used to study the hydroxyl and water content of the alumina surface (*2*). This technique has serious limitations. It requires special sample preparation which may alter the surface or limit the kinds of materials which can be studied, and it is difficult to quantitate.

Wide line nuclear magnetic resonance offers a quantitative method of studying the protons in an alumina without special sample preparation. Saito and Hagewara (*3*) showed that the NMR spectrum of partially dehydrated gibbsite consists of a narrow line about 0.3 G wide due to adsorbed water superimposed on a wide line about 5 G wide due to hydroxyl groups. These workers also showed that the adsorbed water can be removed by heating at 100°C under vacuum. The NMR spectrum then consisted of only the broad hydroxyl band.

METHODS

Materials. Two types of transition alumina were studied. A nodular desiccant alumina (Kaiser KA-201)* and a gel derived alumina designed as a catalyst support. The desiccant alumina has a sur-

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* Registered trademark.

face area of about 350 m^2/g; whereas the gel derived material has a surface area of around 250 m^2/g.

Apparatus. Surface area measurements were carried out on a Numinco Model 103 surface area analyzer.

The NMR cells used in this study were prepared from 15 mm o.d. Pyrex test tubes or 15 mm o.d. quartz tubing fitted with O-ring or ground glass joints so that they could be attached to a vacuum rack. The cell could be evacuated and the spectrum determined without exposing the sample to the atmosphere.

The NMR measurements described here were made at 16 MHz using a Varian Model DA-100-15D spectrometer equipped with a 4210 Variable Frequency Oscillator. The magnetic field was modulated at 40 Hz with a modulation amplitude dependent upon the width of the line being measured. The modulation amplitude was 0.125 G for the narrow proton line and 2.0 G for the wider hydroxyl band. A 20-G modulation amplitude was used for the aluminum-27 spectra.

The amplitude of the aluminum-27 spectra was used as a measure of relative concentration. In the proton work all spectra were integrated twice to yield the area under the absorption curve. This was done by feeding the data from the derivative curve into a digital computer which integrated it to yield the absorption curve. The computer then adjusted the base line on the absorption curve until the last point returned to within ±0.05 units of zero. The curve was then integrated a second time yielding the area under the absorption curve. This area is proportional to the concentration of protons in the sample. Or:

$$\text{concentration protons} = K\,(\text{area under absorption curve}). \quad (1)$$

The constant term in Eq. (1) can be divided into the product of two ratios. These are the ratio of proton concentration in the standard to the area under the NMR curve of the standard and the ratio of the bulk density of the standard to the bulk density of the sample. Thus Eq. (1) becomes:

$$H_{\text{sam}} = \left[\frac{\text{H}}{(\text{area})}\right]_{\text{std}} \times \left[\frac{(\text{bulk density})_{\text{std}}}{(\text{bulk density})_{\text{sam}}}\right] (\text{area})_{\text{sam}}, \quad (2)$$

where H = concentration of protons; std = standard; sam = sample; (area) = area under absorption curve.

The derivative presentation of the NMR absorption curve is obtained by modulating the magnetic field. The absolute area under the curve depends on the ratio of the NMR line width to the amplitude of the modulation used to obtain the derivative. One must be certain that, for any given set of samples, the modulation used does not change the ratios of the area between the sample and the standard and, therefore, the relative measure of the proton concentration, i.e., K in Eq. (1).

Calibration of hydroxyl spectra. Gibbsite was used as a standard for calibration of the broad hydroxyl spectra. Table 1 shows the effect of modulation on relative proton concentration for a typical transition alumina with a 5.0-G line width (ΔH) and the gibbsite standard ($\Delta H = 12.75$ G) used in this study.

The data in Table 1 indicate that, for this range of line widths and this range of modulation amplitude, precision of at least ±5% can be achieved.

Calibration of narrow adsorbed water band. The weight of water adsorbed by a transition alumina is not always a measure of water physically adsorbed on the sample; some of the water being converted to chemically bound hydroxyl groups. Gibbsite ($\Delta H = 12.75$ G) is not suitable standard for physically adsorbed water with 0.3-G line width.

The physically adsorbed water line was calibrated by adsorbing water on a transition alumina at two levels of relative humidity (10 and 60% RH). Both weight gain and NMR signal area of adsorbed water were determined for both samples. Table 2 summarizes the data.

The effect of chemisorbed water on weight is canceled out by using the difference in response between the two samples. Thus, the unit response for unit gain in

TABLE 1
EFFECT OF MODULATION AMPLITUDE ON RELATIVE HYDROXYL CONCENTRATION

Sample	Modulation amp. (G)	Area (cm^2) (abs. curve)	Ratio	Δ
Trans. alumina	1.00	2.65	0.224	0.006
Gibbsite	1.00	11.81		
Trans. alumina	1.25	3.02	0.209	0.009
Gibbsite	1.25	14.44		
Trans. alumina	1.60	4.05	0.216	0.002
Gibbsite	1.60	18.75		
Trans. alumina	2.00	5.18	0.222	0.004
Gibbsite	2.00	23.3		
Trans. alumina	2.50	6.51	0.218	—0—
Gibbsite	2.50	29.8		

weight of physically adsorbed water can be measured. The two samples showed a differential response.

$$\frac{\Delta R}{\Delta \text{wt}} \text{ of } \frac{93.5}{0.0334} = 2800 \text{ cm}^2/\text{g of H}_2\text{O/g of alumina.}$$

Another transition alumina sample which gave a response of 165 cm^2 under identical instrumental conditions would contain $^{165}/_{2800} = 0.0590$ g of physically adsorbed water/g of alumina. This sample had gained 6.39% by weight on treatment with water. The chemisorbed water, by difference, was 0.49%. This sample was used as an adsorbed water standard for the remainder of the study. It has recently been recalibrated and after 1 year had not changed.

RESULTS

A typical transition alumina can contain several different types of protons. These include water hydrogen bonded to the surface and hydroxyl groups and coordinated water molecules either on the surface or internally bound in a crystal.

The width of the NMR signal is proportional to how firmly held the proton is in the solid. For example, hydroxyl groups and coordinated water bound inside a crystal should produce broad NMR signals; whereas physically adsorbed water would yield a relative narrow signal. Thus, the hydroxyl band in gibbsite is 12.75 G wide, the hydrated water band in aluminum fluoride trihydrate is 19.3 G wide, but the adsorbed water band in a transition alumina is on the order of a few tenths of a gauss wide. A transition alumina which contains both chemically bound and physically adsorbed water would produce a compound NMR line consisting of a narrow line superimposed on a broad line. Figure 1 shows such a spectrum.

TABLE 2
CALIBRATION OF NARROW NMR LINE

Relative humidity (%)	Wt gained (g of H_2O/g of alumina)	Δ	NMR response (cm^2)	Δ
10	0.0095		30.9	
60	0.0429	0.0334	124.4	93.5

Narrow NMR line due to adsorbed water. We stated earlier that the signal intensity depended upon the ratio of line width to modulation amplitude. In a compound line such as that shown in Fig. 1, the broad band can be suppressed by using a narrow modulation. Under these conditions, the spectrum is a function of the physically adsorbed water only and can be used to measure the concentration of water adsorbed on the sample.

One would expect the first water physically adsorbed to the surface would be more firmly bound than subsequent layers;

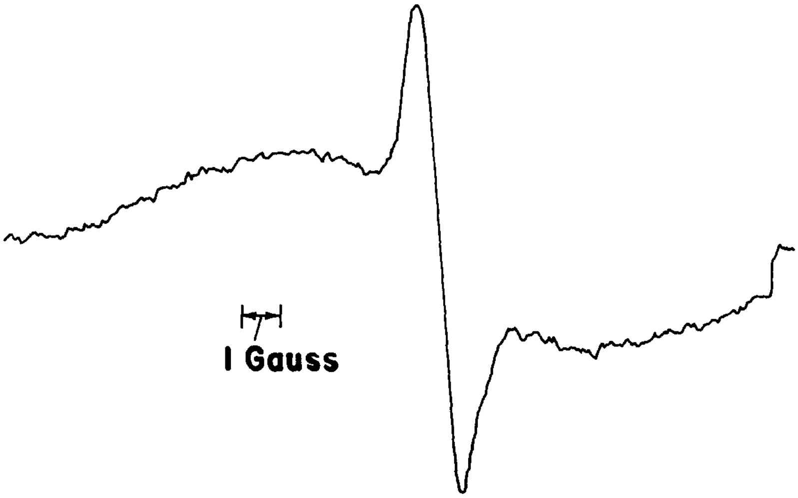

FIG. 1. Typical NMR derivative absorption curve.

and, as the concentration of physically adsorbed water increased, the proton NMR line would be expected to decrease. That this is so is shown in Fig. 2. In this experiment, the transition alumina was placed in a quartz tube and adsorbed water driven off by passing dry nitrogen gas over the sample while heating in a muffle furnace to 250°C. Nitrogen gas was then saturated with water and flowed at a constant rate of 2 ft^3/hr through the sample tube at room temperature. The proton NMR spectra of the adsorbed water was taken as a function of the time the sample was treated with moist nitrogen, i.e., the concentration of physically adsorbed water.

Broad NMR line due to chemisorbed water. The physically adsorbed water can be removed by gentle heating (100°C) under vacuum. The resulting NMR signal consists of one broad band such as is shown in Fig. 3.

The physically adsorbed water was removed from a series of transition aluminas and the NMR spectra of each was determined. It was found that the width of the proton signal was an inverse function of the surface area of the sample as measured by the BET method, see Fig. 4. In these samples the more mobile surface proton must be exchanging with the less mobile interior protons to yield a NMR spectrum

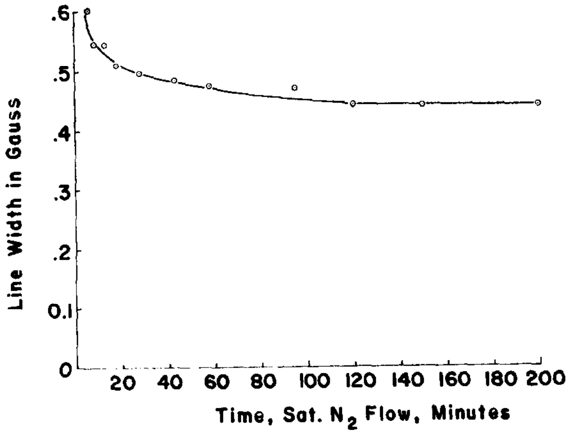

FIG. 2. NMR line width as a function of adsorbed water concentration.

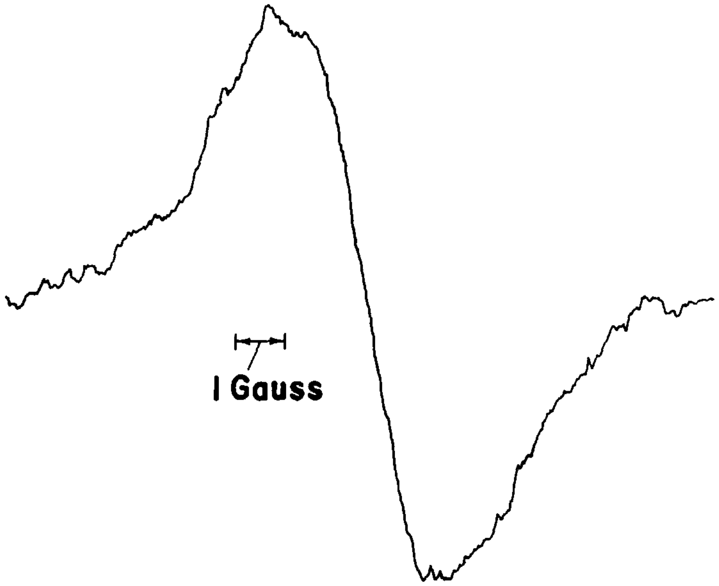

FIG. 3. Typical NMR derivative curve of hydroxyl groups in Kaiser KA-201.

which is a weighted average of the protons in the sample. Thus, the NMR line width of the samples can be calculated from the measured surface according to:

$$\Delta H = 13.20 - 0.0243 \text{ (BET surface area).} \quad (3)$$

Concentration of protons near the surface. O'Reilly (*4*) has shown that the aluminum-27 spectral amplitude of the transition aluminas is also a function of BET surface. He found that aluminum atoms located within two molecular layers of the surface did not contribute to the NMR signal, thus the proton signal from a sample with zero aluminum amplitude would represent protons located within two layers of the surface.

Figure 5 shows the line width of the previous samples plotted as a function of the aluminum-27 spectral amplitude. Extrapolation of the line to zero aluminum-27 amplitude shows the average NMR line width of the protons in the first two molecular layers is 2.50 G.

Assume a model which treats the proton line width as a straight-line function of the fraction of protons found in the first two molecular layers. This fraction would be given by:

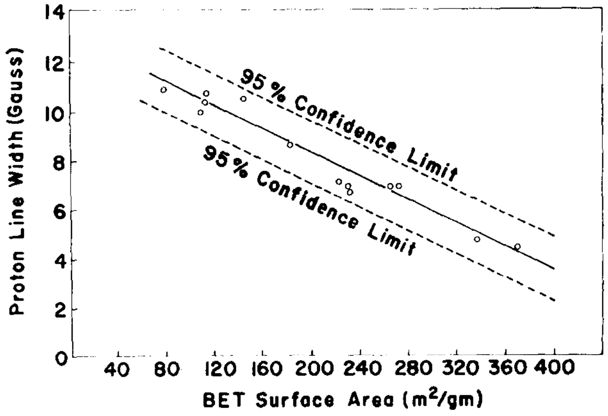

FIG. 4. Proton line width as a function of BET surface area.

$$F_2 = (12.75 - \Delta H)/10.25, \qquad (4)$$

where F_2 = the fraction of proton found within two molecular layers of the surface.

The fraction of the protons found in the first molecular layer can be calculated if an estimate of the surface line width can be made. O'Reilly (*4*) showed that commercially available silica gel with a BET surface area of 687 m^2/g dehydrated at 500°C contained only surface protons and gave a NMR line width of 0.310 G.

By the same reasoning as used before we can derive Eq. (5).

$$F_1 = (12.75 - \Delta H)/12.44, \qquad (5)$$

where F_1 is the fraction of protons found in the surface molecular layer.

Combining Eqs. (4) and (5) with Eq. (3) shows that the fraction of the protons found on or near the surface is a function of the surface area of the material. Thus:

$$F_1 = [0.0243\ (\text{BET}) - 0.95]/12.44, \qquad (6)$$

and

$$F_2 = [0.0243\ (\text{BET}) - 0.45]/10.25, \qquad (7)$$

where F_1 and F_2 are defined as before and BET is the surface area as measured by the BET method.

An alumina with a 350-m^2/g surface area would have 61% of its protons on the surface layer and 75% of its protons in the first two molecular layers.

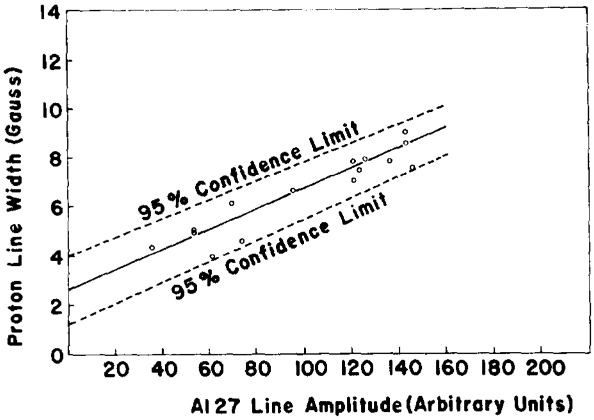

FIG. 5. Proton line width as a function of aluminum-27 amplitude.

DISCUSSION

We can now calculate the concentration of hydroxyl groups on the surface of a transition alumina made by the partial dehydration of gibbsite. For example, the NMR spectrum of the transition alumina shown in Fig. 3 had a line width of 4.88 G and the integrated intensity when compared to gibbsite showed the sample contained 0.00888 g of protons/g of alumina. Substituting the line width into Eq. (5) shows that 0.632 of these protons are on the surface for a concentration of 0.00561 g of surface protons/g of alumina. The adsorbed water had been removed from this sample by heating it to 100°C under a vacuum of 10^{-5} mm Hg. Peri (*2*) showed that under these conditions this type of alumina should contain about a monolayer of hydroxyl groups. If one assumes that all the protons were present on the surface as hydroxyl groups and that each hydroxyl group had a cross sectional area of 10.6 Å^2 (*5*) this would yield a surface area of 358 m^2/g of alumina. The BET area of the sample was 342 m^2/g.

The above calculation does not hold for a gel derived transition alumina. For example, a gel prepared by neutralizing an aluminum sulfate solution with ammonia gave a BET surface area of 275 m^2/g after removal of adsorbed water at 100°C. A NMR calculation similar to the above would have postulated a surface area of over 1000 m^2/g. This is probably due to a different mechanism of bonding water between a gel derived material and transition alumina made from the partial dehydration of gibbsite. This problem is currently under investigation.

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