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Studies of the Hydrogen Held by Solids IV. Deuterium Exchange and NMR Investigations of Silica, Alumina, and Silica-Alumina Catalysts

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Rising temperature D_2 exchange experiments were used to characterize the several kinds of hydrogen held by solids. Results are presented which demonstrate that the temperature region (activation energy) for exchange increases in the order: alumina, silica-alumina, and silica. All of these substances have about the same surface density of terminal hydroxyl groups following overnight evacuation at 500°C; these values fell between 1.5 and 4.5×10^{14} OH/cm². Within the ±20% experimental error, identical values were obtained for a particular silica or silica-alumina catalyst from integrated intensities of proton magnetic resonance absorption spectra. The spectra from silica-alumina were qualitatively indistinguishable from those of silica gel. Both sets of data led to the conclusion that silica-alumina is not an intimate mixture of microcrystals of silica and alumina grown together at contact areas, but a more nearly homogeneous substance. This information, together with infrared absorption data taken from the literature, is used to show that the largest fraction, and perhaps all, of the hydrogen of dehydrated silica-alumina closely resembles that of silica gel, i.e., it is chemically similar to alcoholic hydrogen. There is no evidence that any portion should be classified as acidic. The possibility that up to 20% of the total hydrogen exists as acidic AlOH could not be excluded, however, as this is the accuracy of the NMR data. Therefore, an upper limit for Bronsted acidity of $< 3 \times 10^{13}$ H^+/cm^2 is suggested. The hydrogen studied was identified with that involved in well-known exchange reactions with hydrocarbons.

INTRODUCTION

Carbonium ions are thought to be involved in the mechanisms of the acid-catalyzed reactions of hydrocarbons (*1–4*). With solid catalysts, uncertainty exists concerning the nature of the acid sites responsible for carbonium ion formation. Silica gel lacks these acid properties; alumina is thought to contain Lewis acid sites or dual sites created by dehydration. Silica-alumina is frequently said to contain a Bronsted acid, which is either intrinsic or is formed by reaction of H_2O with the Lewis acid. One school of thought holds that hydride ions are directly abstracted from paraffin molecules by the silica-alumina surface. This latter concept recently received considerable support from proof that the corresponding carbonium ions were generated from triphenylmethane, 1,1-diphenylethane, and cumene by a process in which hydride ions were, in some way, transferred to the catalyst (*5*a). That silica-alumina contains strongly electrophilic centers is also evident from the observation that polynuclear hydrocarbons are readily oxidized to their radical ions (*6–8*) on contact with the surface *in vacuo*. Recently, the almost axiomatic assumption that olefins form carbonium ions by the addition of surface protons was questioned (*5*b, *9*, *10*) and the suggestion was advanced that olefins form carbonium ions as Lewis acid adducts. The present work was undertaken to test these ideas further by examining alumina, silica, and silica-alumina catalysts in a search for a form of hydrogen that might be termed acidic. The results obtained were negative, but studies of the covalently bound hydrogen atoms have served to restrict severely the choice of possible models for a silica-alumina catalyst.

Earlier studies of the hydrogen contents of these materials have been made by exchange with D_2O (*11, 12*), by exchange with D_2 (*13, 14*), and with H_2O^{18} or O_2^{18} (*12, 15, 16*). In the present work, the hydrogen was classified according to its chemical reactivity as well as the amounts present. The same hydrogen was measured by NMR, supplementing and confirming earlier work (*17–19*); a quantitative relationship between the hydrogen responsible for the resonance and the total hydrogen present in samples evacuated at 525° was established for silica and silica-alumina. Mention should also be made of the work of Zimmerman *et al.* (*20–22*), who studied the NMR spectra of H_2O adsorbed on silica gel.

EXPERIMENTAL

Catalysts. Aside from several special preparations which are numerically designated, three series of catalysts were used in this work: one of alumina, one of silica-alumina, and one of silica gels. The surface area of each of these was varied by suitable treatment of aliquots of high area, parent materials. The parent silica gel and alumina β-trihydrate were Davison preparations. The untreated silica gel had a surface area of 560 m^2/g; spark spectra analysis indicated that the sum of all metallic impurities was less than 500 ppm, the principal impurities being Fe, Ti, Zr, and Mg at less than 100 ppm each; the alkali metal content was less than 1 ppm. The manufacturer's analysis of the untreated alumina (*23*) indicated that its total metallic impurities amounted to about 800 ppm with Si and Sn being 500 and 200 ppm, respectively. The silica-alumina series was prepared from the familiar Houdry M-65 catalyst, the surface area of which was 425 m^2/g.

TABLE 1

PREPARATION PROCEDURES FOR SILICA SERIES[a]

NH$_4$OH solutions			
Normality	Temperature (°C)	Time (hr)	Surface area (m^2/g)
0[b]	30	4	560
1	30	48	324
0.1	30	24	267
1	30	24	214
1	85	23	129
1	85	48	116
3.6	85	65	100
1.3	85	65	98
6.0	85	65	85
			13[c]

[a] 150 cc batches of 30–60 mesh Davison silica gel were soaked in 250 ml of solution made from Anal. Reagent Grade NH_4OH with distilled and ion-exchanged H_2O.

[b] Control—no NH_4OH added.

[c] Part of 116 m^2/g sample was heated in Pt dish to 1100° for 20 hr.

The surface area of the parent silica was reduced by leaching 30- to 60-mesh aliquots with solutions of NH_4OH under conditions given in Table 1. The treated gels were washed with distilled water until free of base as judged by litmus. These samples were then dried overnight at 110° before calcining at 600° for 6 hr. The calcined samples were rehydrated in water for 4 hr and again dried overnight at 110° before storing for further work.

The treatments used in preparing the silica-alumina series are outlined in Table 2; the series included the parent Houdry S-65. These preparations were rehydrated by soaking in deionized water for 4 hr at room temperature and then oven-dried at 110° before storing.

TABLE 2

PREPARATION PROCEDURES FOR SILICA-ALUMINA SERIES[a]

Treatment conditions			
Temperature (°C)	Time (hr)	Vapor pressure of H_2O at, °C	Surface area (m^2/g)
600	24	30	390
600	23	78	327
700	20	78	270
750	10	78	210
850	8	78	147
850	16	100	48
950[b]	16	100	4.7

[a] 30–60 mesh samples of Houdry S-65 were treated with flowing O_2 saturated with H_2O at its indicated vapor pressure.

[b] X-ray patterns revealed that this sample contained mullite.

The alumina series was prepared to duplicate, in so far as possible, the series made by Bailey, Holm, and Blackburn (*23*). This involved treatment of aliquots of Davison beta alumina trihydrate with air or steam as indicated in their Table 1. Based on their X-ray study, the samples as tested were mainly *eta* alumina (air-treated) or mixtures of *eta* and *gamma* alumina (steam-treated).

Two samples of high purity silica gels were prepared. Redistilled ethylorthosilicate was hydrolyzed with deionized water and calcined at 600°; this preparation (S-6-2) had a surface area of 565 m^2/g. A portion of this material was soaked in a solution of transistor grade NH_4OH for 24 hr, washed with deionized water, and recalcined at 600°. This preparation (S-14-M) was found to have a surface area of 285 m^2/g. Spark spectra analysis of these samples revealed a total metallic impurity level less than 50 ppm.

A sample of highly pure gamma alumina (DA-9) was made in a similar way. Harshaw aluminum isopropoxide was twice vacuum-transferred before hydrolyzing with deionized water. After calcining at 600°, the resulting alumina was found to have a total metallic impurity level of less than 100 ppm and a surface area of 190 m^2/g.

An equally pure silica-alumina catalyst (DSA-13) was prepared by dissolving aluminum isopropoxide in ethylorthosilicate before hydrolyzing. The resulting catalyst (12% Al_2O_3) was quite similar in properties to catalyst DSA-1, used in our studies of the electronic spectra of adsorbed molecules (*5, 10, 24*) and of cracking activity (*25*).

Catalyst pretreatment. Except where otherwise noted, the catalysts were all treated in a standard way before being used in the experiments. A catalyst was evacuated overnight at room temperature; evacuation was continued while the temperature was raised to 525° during a period of several hours. It was then treated with oxygen for 2 hr at this temperature to remove adsorbed hydrocarbons. This was followed by a final evacuation of from 16 to 24 hr at 525°. The treatments were carried out either in small glass reactors fitted with stopcocks (used for the D_2 exchange experiments) or in 15-mm OD Pyrex tubes used in the NMR probe; the latter were sealed off *in vacuo*. Generally about 5 g of catalyst was used, although larger amounts were taken for D_2 exchange experiments where the surface area was exceptionally low.

For the dehydration study, samples of the (rehydrated) silica-alumina series were sealed in NMR tubes, which were fitted with stopcocks. These were evacuated to constant weight at successively higher temperatures, between room temperature and 500°. Spectra were taken after each treatment. After the 500° treatment, H_2O was "added-back" to the samples by cooling in water vapor (20 mm Hg) from 500° to 150° at a rate of about 1°/min followed by evacuation at 150° for 1 hr. This duplicates a procedure used by Haldeman and Emmett (*11*).

Equipment and procedures. Varian Associates 12-inch electromagnet, V-4200A, V-4300A spectrometers, and a calibration circuit similar to that described by Redfield (*26*) were used in the measurement of hydrogen nuclei concentration. "Slow passage" signals were observed from the commercial samples of silica gel and silica-alumina. For purposes of quantitative intensity measurements, the sweep modulation amplitude and radiofrequency level were sufficiently small so that appreciable overmodulation and saturation, respectively, did not occur. "Fast passage" signals were observed at high rf levels from the very pure preparations of silica gel and silica-alumina described above. Corresponding spin-lattice relaxation times for these samples have been reported previously (*18*) and were as long as 30 sec and as short as 30 msec.

Absolute intensities of the resonances of commercial samples were determined by comparison with a sample of a known amount of water doped with manganous chloride. The weight of water and amount of doping were selected to yield a peak derivative intensity and line width comparable to the proton resonances under study. Comparisons of doubly integrated absorption derivatives were made with the corresponding quantity of the reference solution.

The experiments in which the hydrogen

held by the surfaces of these catalysts was exchanged with pure deuterium gas were carried out in an all-glass circulating system described earlier (*27*). Starting with the catalyst tube, the closed loop consisted of a mixing chamber large enough to hold 95% of the gas in the system, a small volume trap filled with glass beads and thermostated at −195°, a set of thermal conductivity gauges, an all-glass circulating pump, and the return to the catalyst. Accurately measured amounts of D_2 were transferred into this loop from a BET system and circulated over the catalyst as the temperature was raised according to a linear program from room temperature, where the exchange was immeasurably slow, to 1040°. This procedure circumvented one of the difficulties encountered in earlier work (*13*), i.e., not knowing what temperature is required to achieve isotopic equilibrium in a reasonably short time. In all cases reported herein, the exchange was substantially complete by the time the final pretreatment temperature was reached. At higher temperatures, the catalyst was nearly completely dehydroxylated. The water so formed was collected in the −195° trap from which it was regenerated and measured volumetrically in the BET system at the end of the experiment. The thermal conductivity data were insufficient to provide individual analyses for H_2 and HD. However, the bridge unbalance was, to a good approximation, a linear function of x, the atom per cent H. As separate experiments showed that the rate of the H_2–D_2 exchange over these materials was much more rapid than the rate of exchange of D_2 with the catalyst hydrogen, the gas phase was always at equilibrium; its composition was continually monitored by plotting the bridge unbalance on a strip chart recorder.

The temperature of the furnace surrounding the catalyst was raised at a linear rate of about 2°/min and was recorded (thermocouple emf) on the same chart as the bridge unbalance. Very little exchange took place until RT approached the magnitude of the activation energy for exchange, E; the exchange rate increased exponentially with time (RT) but fell to zero as equilibrium was approached. Thus, a sigmoid-shaped curve was produced whose inflection point was characteristic of the magnitude of E. In a mathematical treatment developed earlier (*27*), it was shown that

$$E = \frac{RT_i^2(dx/dt)_i}{(x_\infty - x)_i(dT/dt)_i} \qquad (1)$$

where the subscripts, i, indicate that the value of the variable must be selected at the point of inflection. The derivation assumed that the isothermal exchange rate was first order in the distance from equilibrium; implicit in this is the restriction that only one form of hydrogen is being exchanged and that isotope effects are negligible. The former requirement is probably not strictly true for the present systems but Eq. (1) nevertheless leads to a useful treatment of the data. The recorder record is differentiated to obtain values of dx/dt. These are plotted vs. corresponding values of T, taken from the same chart. Such plots have maxima, corresponding to points of inflection, which are characteristic of the type of hydrogen being exchanged. If several forms of hydrogen with different activation energies for exchange are present in the same catalyst, several peaks appear in a manner analogous to differential thermal analysis. It has been convenient, therefore, to dub this procedure a differential hydrogen analysis (DHA).

The amounts of hydrogen initially present in the solids could be accurately calculated from the amount of deuterium measured out at the start of the experiment and the equilibrium composition of the mixture (*27*). Where several forms of hydrogen are present in the same catalyst, the amounts of each are given by the areas under their DHA peaks. The measurement of water from the liquid nitrogen trap afforded an independent check on the total hydrogen content of the material. Values of hydrogen content could also be calculated from the integrated intensities of the proton resonance absorption. The accuracy of the D_2 exchange method was better than ±5% in the most unfavorable cases and generally better than ±2%, i.e., better than the reproducibility of the samples. The accuracy of the H_2O measurements was, at best, ±5%. This error is difficult to estimate because of losses to the glass of the system and because the measurement was the sum of a number of increments evaluated at pressures below the vapor pressure of H_2O. Uncertainty of up to 20% exists in the calibration factor used in connection with the NMR data; random fluctuations in bulk density further reduced the absolute accuracy.

Results

The behavior of alumina, silica, and silica-alumina preparations in rising temperature D_2 exchange experiments is compared in Fig. 1. Curve A was obtained from pure alumina catalyst DA-9. The maximum in the exchange rate near 250° has been observed as the principal peak with all of the alumina preparations which we have examined. The smaller, less well defined peak in the 350° region is evidence for a second kind of hydrogen; this peak is not always observed. With some preparations, a peak occurs near 175°.

Curves B and C correspond to the pure silica gel preparations. The single principal peak in the 600° region is characteristic of silica gels. The low-temperature edges of these curves nearly coincide, indicating that the activation energy is nearly the same in both experiments. Catalyst S-14-M had a much lower surface area (and hence a lower hydrogen content) than catalyst S-6-2. As the area under a curve is proportional to the amount of hydrogen exchanged, the maximum of C occurs at slightly lower temperature than that of B.

Curve D was obtained from a mechanical mixture of DA-9 and S-14-M which had been intimately mixed in a ball mill. This result demonstrates the method. All of the DHA peaks of the separate materials are observed with the mixture.

Curve E demonstrates that silica-alumina is probably not a mixture of microscopic crystallites of silica and alumina grown together at interfaces as has been suggested (*28*). The hydrogen being exchanged appears to be influenced by the propinquity of both silicon and aluminum ions. The absence of the DHA peaks typical of silica and alumina may imply that the hydrogen atoms held by silica-alumina differ in chemical reactivity, or are geometrically distributed in a different manner from those of the pure components.

Data corresponding to the experiments of Fig. 1 are listed in Table 3. In all cases, the amounts of H_2O evolved to 1040° were in fair agreement with, although somewhat smaller than, the hydrogen contents derived

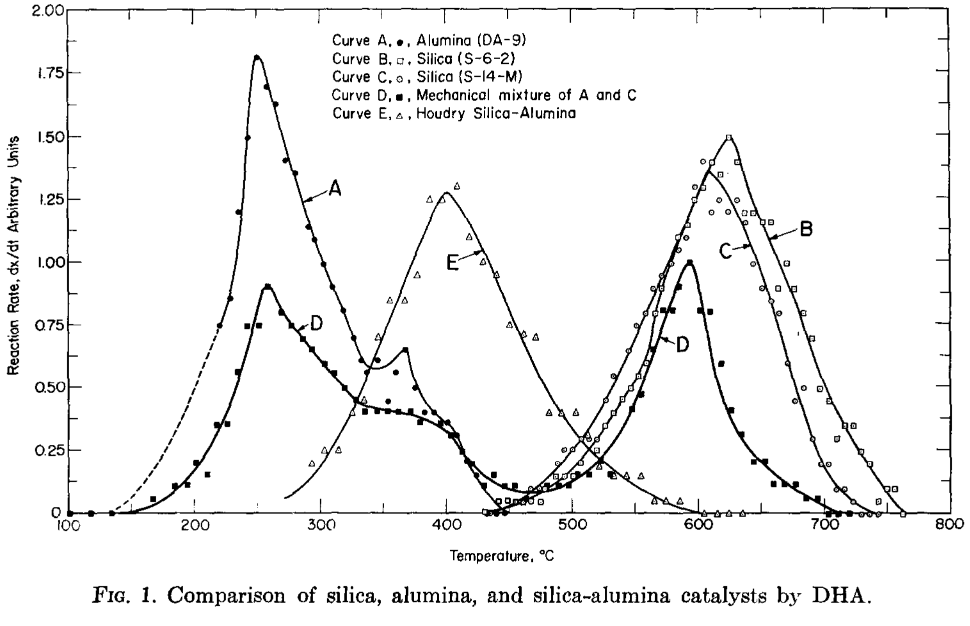

FIG. 1. Comparison of silica, alumina, and silica-alumina catalysts by DHA.

from the D_2 exchange experiments. All of these materials contain about the same number of hydroxyl groups per unit area. The activation energies listed in the last column were calculated from Eq. (1); they reflect the temperature of the exchange maximum.

Summarized in Table 4 are similar data for the silica-alumina series. With the exception of the catalyst with lowest surface area, the amounts of water evolved to 1040° are in fair agreement with the values calculated from deuterium exchange data. Similarly, the integrated intensities of the NMR spectra yield values which cannot be said to differ significantly. It may be concluded, therefore, that most of the hydrogen held by silica-alumina following overnight pumping at 530° contributes to the resonance. The data of Col. 4 are also calculated as weight per cent H_2O so that direct comparison can be made with earlier work (*11–15, 29–33*).

TABLE 3

COMPARISON OF THE HYDROGEN HELD BY SILICA, SILICA-ALUMINA, AND ALUMINA CATALYSTS

Catalyst composition	Area (m^2/g)	Hydrogen content			Temperature of maximum exchange rate (°C)	E_a (kcal/mole)
		H_2O evolution [cc(NTP)/g]	D_2 exchange			
			[cc(NTP)/g]	[H Atoms/cm² × 10^{-14}]		
Silica Gel (S-6-2)	565	16.2	17.0	1.6	625	23
Silica Gel (S-14-M)	285	12.6	13.8	2.6	610	22
γ-Alumina (DA-9)	190	14.1	15.4	4.4	250	6
Mechanical mixture	238	12.2	13.2	3.0	260 & 595	6[a]
Houdry silica-alumina	327	—	9.1	1.5	395	10
Silica-alumina (DSA-13)	374	13.0	13.4	1.9	350	8

[a] For alumina peak.

TABLE 4

RESULTS OF D_2 EXCHANGE EXPERIMENTS WITH SERIES OF HOUDRY SILICA-ALUMINA CATALYSTS

Surface area (m^2/g)	Hydrogen content					Temperature at inflection point (°C)	E_a (kcal/mole)
	H_2O evol. [cc(NTP)/g]	NMR [cc(NTP)/g]	D_2 Exchange				
			[cc(NTP)/g]	(H Atoms/cm² × 10^{-14})	% H_2O		
425	11.2	11.2	11.7	1.5	0.94	395	10
390	10.2	10.4	10.9	1.5	0.88	385	7
327	—	7.3	9.1	1.5	0.73	395	10
270	7.3	5.2	7.5	1.5	0.60	385	11
210	4.9	4.5	5.0	1.3	0.40	345	8
147	4.1	3.2	4.7	1.7	0.38	365	10
48	2.8	1.6	2.8	3.2	0.23	375	10
4.7	0.09	0.52	0.87	10.0	0.07	515	27

All of the catalysts of higher surface area have nearly identical specific hydrogen contents (Col. 5). Similarly, except for the catalyst at lowest area, the temperature for maximum exchange rate lies between 345° and 395°, corresponding to activation energies of from 7 to 10 kcal/mole in good agreement with Hansford *et al.* (*14*). An X-ray pattern revealed that mullite was present in the last catalyst, but was not detectable in any of the others. This suggests that the higher activation energy may have resulted from exchange with the silica left after most of the alumina was consumed in the formation of mullite, a phase which has no hydrogen associated with it.

When the hydrogen contents (Col. 4) are plotted against surface area, a good linear curve results (Fig. 2), having a finite intercept [0.9 cc(NTP)/g of H_2]. Hence, a part of the catalyst hydrogen does not appear to

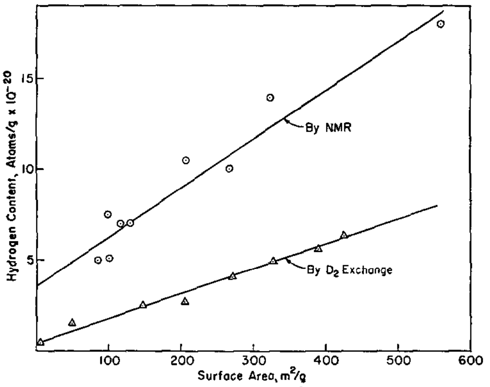

FIG. 2. Variation of hydrogen content with surface area of silica gels, ⊙, and silica-alumina catalysts, △.

be present on the surface. This portion is relatively small when the surface area is high, but becomes a major fraction when the surface area falls below 100 m^2/g. Thus, the high values of surface density of hydroxyl groups listed for the catalysts of low surface area are probably fictitious.

We reported earlier (*17*, *18*) that relatively sharp proton magnetic resonance signals were obtained from a Houdry S-65 catalyst and that the line shape was closely Lorentzian. Plots of integrated intensity vs. surface area are approximately linear (e.g., Fig. 2) and the average surface density of hydroxyl groups may be calculated from their slopes. Figure 3 summarizes results derived in this way from experiments in which the catalysts were evacuated to constant weight at successively higher temperatures. The square, which does not fall on the curve describing the rest of the data, resulted from catalysts rehydrated at 150° following evacuation to 500°. This value is in nearly perfect agreement with the result reported by Haldeman and Emmett (*11*) for Catalyst M-46 ($3.6 \times 10^{14}/cm^2$). The shape of the absorption curves was no longer Lorentzian, when H_2O was added back.

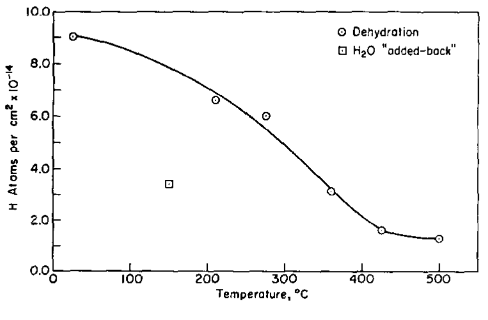

FIG. 3. Dehydration of silica-alumina—integrated intensity of proton resonance vs. temperature of dehydration.

As the catalysts were dehydrated, the surface density of hydroxyl groups diminished. This was accompanied by a narrowing of the resonance signal. Similarly, the signal sharpened and decreased in intensity as the catalysts were deuterated either with D_2 or D_2O. When the catalysts were exhaustively deuterated, the signal was completely eliminated. When such a catalyst was exchanged with i-C_4H_{10} (about 0.1% D_2O was added back), the proton resonance signal reappeared and from its integrated intensity it was concluded that $2.3 \pm 0.3 \times 10^{20}$ protons had entered the catalyst; mass spectrometric analysis of the gas phase showed that $2.9 \pm 0.3 \times 10^{20}$ deuterons had been simultaneously transferred to the gas phase. These experiments served to identify the nuclear resonance absorption with the hydrogen atoms which are measured by exchange with D_2 or D_2O, the exchange of which with various hydrocarbons has been studied by a number of workers (*11*, *29–33*). For a given sample, the line width and shape were found to be independent of temperature over the range from −210° to +280° and the intensity of the signal varied as $1/T$ in this interval.

Members of the Houdry series showed no Al^{27} resonance. Spectra corresponding to resonance of the Al^{27} nuclei residing several layers below the surface of pure alumina phases have been reported (*18*, *34*). In this case, the energy absorption is possible because the symmetry around these nuclei is nearly cubic. Evidently, this condition is not fulfilled with silica-alumina, even with the catalysts of lowest area. Aluminum resonance was found in silica-alumina catalysts containing more than 40% Al_2O_3, but in these cases the intensities were lower than expected on the basis of composition. It was concluded, therefore, that in these cases segregation of separate alumina phases had occurred. These data support the view that silica-alumina is not a mechanical mixture of microcrystallites of silica and alumina.

The proton resonance signals from silica gels and silica-alumina catalysts were qualitatively indistinguishable. The width between the points of maximum slope of the Lorentzian derivatives was 310 milligauss for the silica gel of highest area and 260 milligauss for the corresponding silica-alumina catalyst. The spin-spin relaxation times were 1.8×10^{-4} and 2.1×10^{-4} sec, respectively. This parameter was, however, a function of both surface area and hydrogen content (dehydration temperature). T_2 was constant for areas above about 200 m^2/g and 100 m^2/g for members of the silica-alumina and silica series, respectively, but increased as the surface area was further lowered, e.g., to 3.6×10^{-4} sec for the silica-alumina with a surface of 4.7 m^2/g. On partial deuteration, the line did not narrow as much as expected for completely random substitution. This is demonstrated in Table 5, which includes data for two samples of the 324 m^2/g silica gel following treatment at 150° with D_2O–H_2O mixtures and evacuation to 500°. These results indicate that certain hydrogen atoms are more accessible for exchange than others, i.e., there are regions in the solid where few, and other regions where most, of the H have been replaced by D.

TABLE 5

RATIOS OF NMR PARAMETERS OF PARTIALLY DEUTERATED TO UNDEUTERATED SILICA GEL[a]

Atom fraction $f = H/(H + D)$	Line width ratio		Deflection ratio	
	$(\Delta/\Delta_0)^b_{obs.}$	$(\Delta/\Delta_0)^c_{random}$	$(D/D_0)^b_{obs.}$	$(D/D_0)^c_{random}$
0.33	0.66	0.36	0.74	2.55
0.017	0.30	0.14	0.19	0.92

[a] Line shape was in all cases Lorentzian; samples were evacuated at 500° following exchange with D_2O.

[b] $f = KD\Delta^2 = (D\Delta^2)/(D_0\Delta_0^2)$; subscript zero designates the undeuterated sample for which $f = 1$.

[c] Calculated from Theory of Kittel and Abrahams, ref. (*38*).

The hydrogen contents of the silica and silica-alumina series (outgassed at 525°) are compared in Fig. 2. Because of the favorable agreement between the D_2 exchange and NMR values found with the silica-alumina series, only the latter method was used with the silica gel series. The slopes of these curves indicate surface densities of 2.7 and 1.36×10^{14} H/cm^2 for silica gel and silica-alumina, respectively; the intercepts (3.5 and 0.4×10^{20} H/g) indicate that part of the hydrogen is held internally in the solid, and that this amount is greater with silica gel than with silica-alumina. This is in agreement with the conclusion reached by Basila (*35*) from infrared studies of these systems.

Proton resonance signals from several alumina preparations were examined and found to be considerably wider (~ 4 gauss) than the absorptions for silica and silica-alumina. This broadening is apparently caused by the relatively large magnetic moment of Al^{27}. Hence, Al–OH cannot contribute significantly to the resonance observed from silica-alumina.

When the alumina series was examined by the DHA method, the results were all quite similar. A single maximum occurred at 245 ± 25° and the hydrogen contents did not vary widely, the limits being between 2.5 and 4.5 ± 10^{14}/cm^2. These data are summarized in Fig. 4. The point for the parent material (triangle) falls a little below the curve defined by the steam-sintered samples (open circles), as do the data for the samples which were heated in air to high temperatures (solid circles) to lower their surface areas. These results are in accord with the finding of MacIver *et al.* (*36*), that *gamma* alumina contains more bound water than *eta*, following a given pretreatment. That the hydrogen content can be lowered without affecting the surface area by extending the pretreatment evacuation time at 500° to 72 hr is also indicated (square). The slope of the line suggests an average

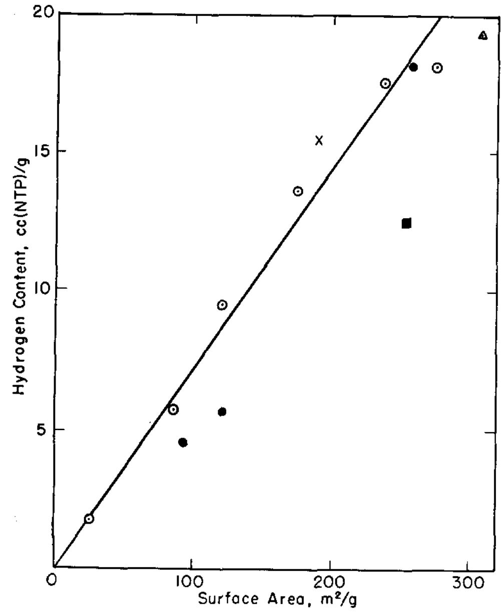

FIG. 4. Relation between hydrogen content and surface area of alumina samples.

hydrogen content of $3.6 \times 10^{14}/\text{cm}^2$. No intercept is evidenced, indicating that most of the residual hydrogen is held on the surface. The point (X) for Catalyst DA-9 (Table 3) is in fair agreement with the remaining data.

DISCUSSION

The present studies were made on materials which had been evacuated at or above 500° for extended periods of time; the results are representative of the initial condition of surfaces of catalysts used in many investigations. If the catalytic properties of these surfaces stem from intrinsic Bronsted acids, as frequently supposed, one might reasonably expect to find supporting evidence in a difference in properties of the hydrogen held by these acidic materials and that held by nonacidic silica gel.

Two parameters of interest can be determined from simple experiments where the hydrogen held by a solid is exchanged with pure D_2. These are the total amount of hydrogen initially present in the solid, and the temperature interval over which the exchange takes place at an appreciable rate. If the former information is required, the latter accrues as a premium of the rising temperature method. In addition, if several forms of hydrogen are present and these differ substantially in reactivity, they may separate, allowing estimates to be made of the amounts of each. Several examples of this behavior are shown in Fig. 1 and several more are given in a following paper (*37*). Carrying the exchange to increasingly higher temperatures provides a criterion for judging whether equilibrium has been established with all of the kinds of hydrogen in the sample. Our results show that this condition was not met in some of the experiments of Lee and Weller (*13*), where equilibrium obviously was not obtained with silica gels at 500°.

The data of Fig. 1 show that only a small portion of the hydrogen of a silica-alumina catalyst has exchanged at temperatures where alumina may be equilibrated in a few minutes, and that the exchange is nearly complete before temperatures are reached where silica gels react rapidly. Had peaks also been obtained at these higher and lower temperatures, as with the mechanical mixture, it might have been concluded that the central peak, near 400°, corresponded to the acid hydrogen of silica-alumina. As this result was not obtained, it is tempting to suggest that the reactivity of the hydrogen associated with these materials is collectively influenced by both of the underlying positive ions, i.e., that aluminum ions proxy randomly for silicon in the silica gel structure. This interpretation is not unique, however, as it is equally possible to assume the exchange rate is limited by factors other than the strength of the OH bond.

The NMR absorption derivative has four measurable properties: the line shape, width, integrated intensity, and chemical shift. It was shown earlier (*17, 18*) that the line shape for both silica and silica-alumina was Lorentzian and that the signal was unexpectedly narrow. This could conceivably occur in one of two ways, viz., a rapid random motion of the hydrogen, with a jump frequency which is large compared to the reciprocal of the spin-spin relaxation time, or from a dilute, randomly populated, spin lattice of rigidly held hydrogen atoms (*38*). Ordinarily, these situations could be distinguished by observing the temperature dependence of the line width. Thus, if the former situation prevails, the line should broaden when the temperature is lowered to the point where the translational motion is quenched; on the other hand, if the line shape results from rigidly held, noninteracting protons, raising the temperature to the point where translation starts should cause an additional motional narrowing. Over the temperature interval accessible to us (−210° to +280°) the line width was invariant. The upper temperature limit was about 100° lower than that required to effect exchange with D_2 at an appreciable rate, suggesting that motional narrowing may be observed when higher temperatures become accessible. The lowest temperature served to eliminate motional processes having activation energies in excess of about 2 kcal/mole; a lower activation energy is deemed unlikely. Fortunately, the hypothesis that hydrogen is rigidly bonded is supported by a great deal of auxiliary evidence. The chemical shift at 40 mc/sec and at 15.5 mc/sec was found to be -3 ± 2 ppm relative to H_2O (*17, 18*); this result indicates alcoholic-like hydrogen. The saturation behavior and its dependence on paramagnetic impurities also support this view, as does the fact that the average surface density of protons is consistent with theory (*17, 18, 38*). Chemical evidence is also in agreement. H_2 cannot be desorbed at any temperature although H_2O is quantitatively evolved above 900°.

The values derived from the integrated intensities agree with the total hydrogen contents within the experimental error. The uncertainty of the NMR values (ca. 20%) is sufficiently large, however, so that it is not possible to be certain that all of the hydrogen present is contributing to the signal. In a 12.5% Al_2O_3-SiO_2 catalyst, roughly 15% of the metal ions are aluminum. Hydrogen on adjacent sites would not contribute appreciably to the observed resonance. This could account for the somewhat smaller values obtained in the NMR work. However, no real evidence exists for a special kind of hydrogen having different (perhaps acidic) chemical properties. In fact, as noted above, the D_2 exchange data suggest that *all* of the hydrogen of silica-alumina experience the collective effect of the silicon and aluminum ions.

The similarity of the infrared spectra of silica and silica-alumina has recently been pointed out by Basila (*35*); the OH stretching vibration of the isolated surface hydroxyls was reported to be 3747 and 3745 cm^{-1}, respectively. This was the only hydrogen vibration observed with silica-alumina dehydrated at 500°; with silica gel, a weak band at 3650 cm^{-1} was also observed, in agreement with the work of McDonald (*39*). Basila attributed this latter band to hydrogen-bonded internal hydroxyl groups. The much higher intercept for silica gels shown in Fig. 2 is consistent with this assignment. The existence of OH vibrations in the hydroxyl region is, perhaps, the most direct evidence that most of the hydrogen is rigidly bonded to oxygen of a silica lattice. Basila observed none of the three vibrations reported by Peri (*40*) for alumina (at 3795, 3737, and 3698 cm^{-1}) even though his silica-alumina contained 25% Al_2O_3. Further evidence that the hydrogen is mainly Si-OH stemmed from the nearly identical hydrogen-bonded frequency shifts of the 3745 cm^{-1} band of silica and silica-alumina when contacted with the same basic molecules (*35*). Finally, there is a considerable body of data (*35, 39–42*) demonstrating that when strong bases, such as ammonia, are chemisorbed on carefully dehydrated catalysts, protons are not transferred. Rather, the infrared spectra and frequency shifts are those expected for the same molecules coordinated with aprotic acids such as $AlCl_3$ (*41, 42*).

One of the conspicuous features of the present work is the close similarity of the surface density of hydrogen of all three materials. As shown in Table 1, these fall between 1.5 and $4.5 \times 10^{14}/cm^2$. This is roughly (within a factor of five) the number of metal atoms adjacent to the surface (or the number of metal atoms that would be in the next layer were the solid continuous). Thus, these hydrogens are held as surface hydroxyl groups required to terminate the lattice, and this requirement is nearly the same with all three materials. If intrinsic Bronsted acidity exists, one may conceive of the following situations: (a) the terminal hydroxyl groups are all acidic in the order alumina > silica-alumina > silica; (b) the active hydrogen required for hydrocarbon catalysis cannot be observed directly, being smaller in amount by at least an order of magnitude; and, (c) silica and alumina do not contain a Bronsted acid while silica-alumina does by virtue of aluminum ions in Si^{4+} sites. The first of these may be discounted on the grounds that both NMR and IR show that there is very little difference in the OH bond of silica-alumina and silica. The second possibility is admissible but, by the same argument, the third possibility is also restricted to about 20% of the hydrogen present. It therefore seems justified to set an upper limit on the Bronsted acidity of silica-alumina, after outgassing at 500°, of not more than $3 \times 10^{12}/cm^2$. It may be noted, however, that where aluminum is substituted for silicon in the surface layer, a hydroxyl may not be required to terminate the lattice and, for this reason, evidence for Al–OH is not found spectroscopically (*17, 18, 35*). The values for surface density of silica-alumina hydrogen, listed in Tables 3 and 4, are consistently lower than those for alumina or silica gel. The present results agree with the picture of Lowen and Broge (*43*) and of Peri and Hannan (*40*) that dehydration occurs by random removal of H_2O among the various adjacent hydroxyl groups. Lowen and Broge report that there are $3 \times 10^{14}/cm^2$ silanol groups left on amorphous silica (170 m^2/g) after dehydration at 620°, in good agreement with the present work.

Weiss, Knight, and Shapiro (*44*) found that 2 to 3 moles of H_2 were liberated for each mole of B_2H_6 consumed by reaction with the hydroxyl groups of silica-gel; the borohydride groups thus formed could be completely exchanged with B^{10}-enriched B_2H_6. On alumina, only 1 mole of H_2 was released per mole of B_2H_6 adsorbed, and only half of this boron was exchangeable. The behavior of a Houdry S-65 silica-alumina catalyst was intermediate. On the basis of these data, it was postulated that the fraction of exchangeable boron was a direct measure of the fraction of hydroxyl groups attached to aluminum or silicon. Thus OBH_2 and O_2BH groups were pictured to form on silica, while with alumina it was presumed that the product was OB_2H_5 and that only one of the two B atoms was exchangeable. On this basis, it was deduced that the fraction of Al–OH groups increased with dehydration temperature. This interpretation is questionable; certainly it is not unique. All that can be ascertained from the available data is that in their work, as in ours, the behavior of silica-alumina was intermediate between that of silica and alumina.

In summary, examination of the hydrogen held by dehydrated silica-alumina and alumina preparations revealed no evidence of a Bronsted acid, whereas when the same preparations were tested for Lewis acidity, evidence for such strongly electrophilic centers was readily obtained (*5, 8, 10, 24*). The possibility that a small fraction of the total hydrogen is acidic cannot be excluded, however, nor can the possibility that protons are generated by interaction of H_2O with Lewis sites. Thus, Hirschler (*45*) finds that about $5 \times 10^{13}/cm^2$ NH_3 or *n*-butylamine molecules must be added to typical silica-alumina catalysts to prevent the generation of carbonium ions from triphenylcarbinol (corresponding to 50% H_2SO_4). While this would seem to be outside the upper admissible limit for Bronsted acidity deduced from our work, it cannot be categorically stated that this much Bronsted acidity could not have been present in Hirschler's experiments, where less stringent dehydrating procedures were used. But, on the other hand, since triphenylcarbinol is as readily ionized by Lewis acids as by protonic acids, the formation of the triphenylcarbonium ion need not be taken as evidence of Bronsted acidity.

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