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The Detection of Acidity on Silica-Alumina Catalysts by Infrared Spectroscopy–Pyridine Chemisorption

Relationships between Catalyst Acidity and Activity

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The Brönsted acidity and catalytic activity of two series of silica-alumina catalysts have been measured. The Brönsted acidity was measured by means of the infrared spectrum of chemisorbed pyridine. Brönsted acid sites can be detected in silica-alumina containing 0.25% alumina. For a constant degree of cross-linking, the Brönsted acidity is proportional to the alumina content of the silica-alumina. For two series of silica-alumina catalysts, containing up to 14% alumina, there is a linear relationship between the Brönsted acidity and the catalytic activity for *o*-xylene isomerization. It is possible for catalysts to possess carbonium ion type activity while exhibiting no Brönsted acidity detectable by infrared spectroscopy.

INTRODUCTION

Spectroscopic studies of the chemisorption of nitrogen bases, such as ammonia, pyridine, and piperidine, have become well established for detecting and estimating the acidity of catalysts (*1–10*). It is now relatively straightforward to determine the type (Lewis and/or Brönsted) and relative amounts of acid sites. More recently, Hughes and White (*6*) and Watanabe and Habgood (*11*) have obtained quantitative estimates of the acid site concentrations on zeolites.

Most acidity studies have been made on commercial silica-alumina cracking catalysts, alumina, and on the highly acidic synthetic zeolites. Except in the case of alumina, Brönsted as well as Lewis acid sites are detected. With alumina, only Lewis acid sites are detected. Since no absorption band in the spectrum of chemisorbed base is observed which could be attributed to adsorption on Brönsted acid sites, it has been concluded that Brönsted acidity was absent. However, no study has been reported in which the limits of detection of Brönsted acidity have been investigated. The acidity of a series of silica-alumina catalysts, containing various amounts of alumina, by observation of the infrared spectra of chemisorbed pyridine is reported in this study.

Although catalyst acidity has been investigated by many techniques (*12*), few of these methods distinguish between Lewis and Brönsted acidity (*3*). Furthermore, few attempts have been made to simultaneously measure catalyst acidity and catalyst activity so as to obtain the relationship between the two. Tamele (*13*) measured total catalyst acid sites by *n*-butylamine titration and related the concentration to cumene cracking and propylene polymerization and Milliken, Mills, and Oblad (*14*) have correlated acidity concentrations measured by various techniques with cumene cracking activity. Holm, Bailey, and Clark (*15*) measured protonic acidity and total acidity of a series of silica-alumina catalysts. They found that the protonic acidity related better to the propylene polymerization activity than total acidity.

In this study parallel protonic acidity and catalysts acidity measurements are reported. The isomerization of *o*-xylene was investigated as a reaction catalyzed by

TABLE 1
COMPOSITION OF THE SILICA-ALUMINA CATALYSTS USED

Sample	Synthetic catalysts			Commercial catalysts		
	% Alumina	% Na_2O	Surface area (m^2/g)	% Alumina	% Na_2O	Surface area (m^2/g)
A	1.15	0.015	598	0.02	0.07	497
B	3.08	0.015	555	3.45	0.06	460
C	5.34	0.009	517	6.81	0.04	434
D	7.13	0.011	478	9.85	0.03	380
E	—	—	—	11.67	0 03	361
F	—	—	—	14.43	0.01	350

Brönsted acid sites (16–18). Ion-exchange capacities were also measured on the same samples.

EXPERIMENTAL

Materials. The silica-alumina samples were prepared in two different ways:

(1). Commercial silica-alumina (Davison 13% Al_2O_3) was ground to a fine powder and mixed with various amounts of silica (Davison Code 62) so as to yield samples with several different alumina contents. After thorough mixing, portions of the samples were analyzed for alumina; the alumina contents are given in Table 1. Other portions were treated as described below to put them in a suitable form for spectroscopic and reactor measurements. For the purpose of this paper, these samples will be referred to as the commercial catalysts.

(2). Experimental silica-aluminas, containing 1–7% alumina, were prepared from a common silica hydrogel source by impregnation with aluminum nitrate, followed by precipitation with ammonia. The silica hydrogel was prepared by pouring a cold (8°C) solution of 1310 ml of 40° Baumé sodium silicate (Baker and Adamson Code No. 2289) plus 1690 ml of water into a solution of 142 ml of concentrated (96%) sulfuric acid in 2858 ml of water cooled to 8°C. After stirring for approximately 7 min, the solution set to a firm hydrogel. The hydrogel, having a pH of about 5, was allowed to synerize overnight and then broken into lumps for washing. Washing was done on a large Büchner funnel by soaking for 1 hr in 7 liters of 0.1 N H_2SO_4, draining, and resoaking in fresh acid solution for a total of eight washes. Then the hydrogel was washed with distilled water by soaking and draining for a total of ten washes to remove all soluble salt. The residual sodium content was 0.033% as Na_2O (calcined basis). The washed hydrogel was then divided into four parts, each containing 105 g of anhydrous SiO_2. Each portion of hydrogel was then slurried with 1000 ml of a solution containing the appropriate amount of $Al(NO_3)_3 \cdot 9H_2O$ to give the desired amount of alumina. After stirring the slurry for 1 hr, aqueous ammonia (approximately 1.5 N) to give a pH of 8–9 was added slowly with stirring. The product was then filtered, and washed three times with an equal volume of water on the filter. The washed gel was then dried at 110°C and calcined for 12 hr at 600°C.

The surface area, and sodium and alumina contents ar given in Table 1.

Apparatus, sample preparation, and technique. For spectroscopic studies, the samples were ground to a fine powder with an agate mortar and pestle. Thin wafers, 1 inch in diameter, were prepared by compacting approximately 0.05 g of the sample in a metallurgical die under 20 000 psi. The thickness ranged from 5 to 10 mg cm^{-2}. Infrared spectra were recorded using a Cary-White 90 spectrophotometer. The spectral resolution was about 3 cm^{-1} and the scan speed 1 cm^{-1} sec^{-1}. The infrared cell was the same as used previously (7). Sample calcinations and dosings with pyridine and water were carried out with the cell attached to a vacuum system capable of achieving a dynamic vacuum of 10^{-5} to 10^{-6} torr. The cell could be inserted on a carriage in the spectrophotometer reproducibly. A simple evacu-

ated gas cell was placed in the reference beam.

The sample was placed in the furnace end of the cell and evacuated. The temperature was then raised to 500°C during 1 hr and maintained at this temperature overnight while evacuating. The sample was cooled to room temperature and its spectrum recorded. Excess pyridine was adsorbed on the catalyst (i.e., sufficient to leave a small residual pressure of pyridine in the gas phase) and allowed to equilibrate during 2 hr. The excess pyridine was desorbed by evacuation at 125°C for 2 hr, and the spectrum of the chemisorbed pyridine recorded. Water (6 μmole) at a pressure of 10 torr, was added to the sample, and, after equilibrating for 1 hr, the excess was removed by evacuation for 1 hr at 125°C. The spectrum of the adsorbed species was again recorded.

Catalytic activity measurements were made in a flow microreactor at atmospheric pressure. A helium carrier gas was used at a flow rate of 50 ml min^{-1}. The helium passed through a saturator containing *o*-xylene thermostated at 20°C. The reactor consisted of a stainless steel tube and contained 1 g of catalyst in the form of 20–40 mesh granules supported on quartz wool. The feed passed through a preheat section before entering the reactor. Analysis of feed and product streams was made by gas chromatography using a 5-ft column filled with a 20% mixture of 60% Silicone Fluid 96 and 40% Carbowax 20M supported on 60–80 mesh Chromosorb W. The column was maintained at 150°C. The catalyst, precalcined at 600°C, was dried by heating in the reactor in flowing helium for 1 hr at 500°C. The catalyst was then cooled to about 315°C and the helium diverted through *o*-xylene saturator. The catalyst activity was measured by observing the isomerization of the *o*-xylene to *m*- and *p*-xylene. After steady state had been obtained, the conversion was measured by determing the concentration of *o*-xylene and and *m*- plus *p*-xylene in the product. The conversion was measured at several temperatures. Temperatures were adjusted so that the conversions were sufficiently low that diffusion effects were minimized.

The ion-exchange capacity of the laboratory-prepared silica-alumina was measured in the following way: Five grams of the catalyst was stirred with 10 g of sodium chloride in 50 ml of distilled water overnight. The liberated acid was titrated potentiometrically with 0.1 *N* caustic soda solution.

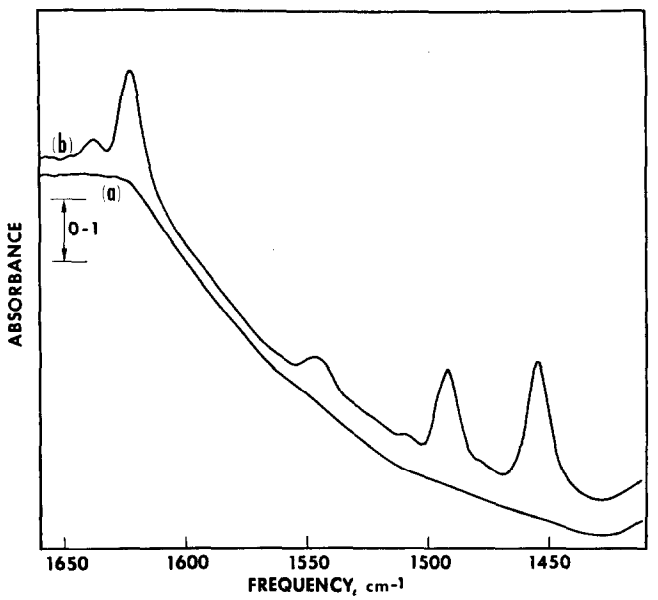

FIG. 1. Infrared spectra of a typical silica-alumina before and after pyridine chemisorption.

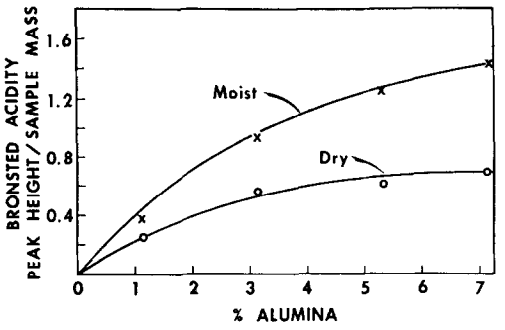

FIG. 2. Brönsted acidity of synthetic (laboratory) silica-alumina catalysts.

RESULTS

A measure of the catalyst Brönsted acidity was obtained from the intensity of the 1545-cm^{-1} absorption band in the spectrum of chemisorbed pyridine. Typical spectra are shown in Fig. 1. The peak heights of the 1545-cm^{-1} band divided by the sample mass are plotted in Figs. 2 and 3 for the two sets of samples. The band intensity is plotted for both the anhydrous and hydrated samples, the latter always being considerably larger than the former, in agreement with previous studies of silica-alumina acidity (*3*, *4*).

The isomerization of *o*-xylene is a clean reaction believed to be promoted by Brönsted acid sites. Mostly *m*- and *p*-xylenes were formed but small amounts of toluene and the isomeric trimethylbenzenes were also detected. From the plots of log conversion versus reciprocal temperature, the conversions at several temperatures were obtained. These values are plotted against

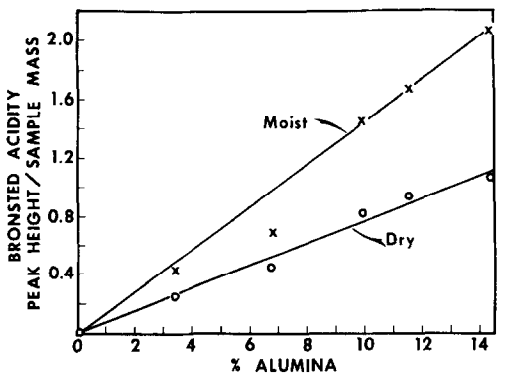

FIG. 3. Brönsted acidity of commercial silica-alumina catalysts.

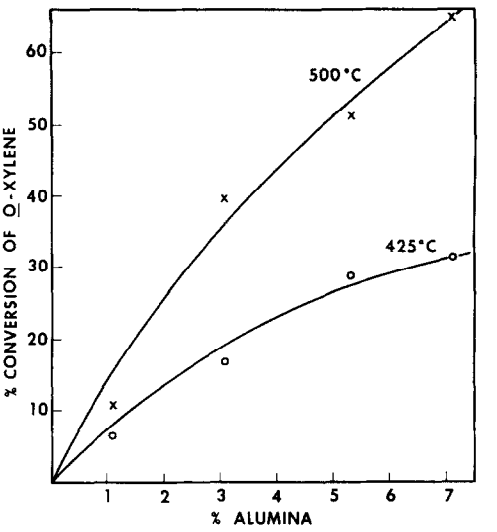

FIG. 4. Catalytic activities of synthetic silica-alumina catalysts.

the alumina contents of the two series of catalysts in Figs. 4 and 5.

The ion-exchange capacities of the laboratory catalysts are shown as a function of alumina content in Fig. 6.

DISCUSSION

Acidity and Ion-Exchange Capacity Measurements

For the laboratory silica-alumina catalysts, a progressive increase in the Brönsted acidity with alumina content is found. It should be noted (Fig. 2) that, both for the anhydrous and hydrous catalysts, the relationship is nonlinear. This is to be expected since it is known that the acidity of silica-alumina catalysts passes through a definite maximum as the alumina content is varied. The nonlinear relationship, even at relatively low alumina contents (up to 7%), probably indicates that the efficiency of cross-linking of the silica and alumina decreases with increasing amounts of alumina, since it is believed that the interaction of the silica and alumina results in the production of Brönsted acid sites.

The variation of the ion-exchange capacity with alumina content (shown in Fig. 6) shows a similar variation with alumina content, again suggesting a fall-off in

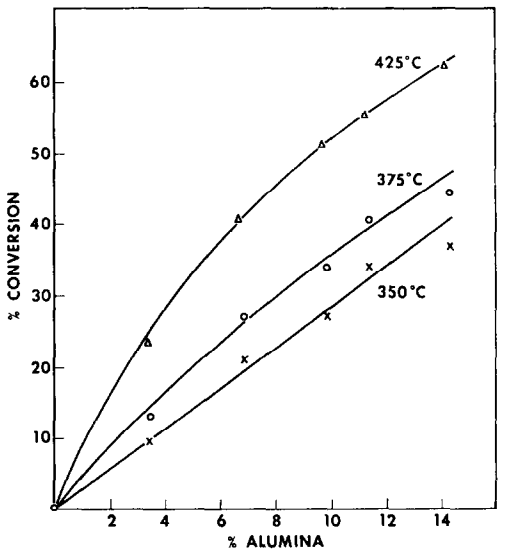

FIG. 5. Catalytic activities of commercial silica-alumina catalysts.

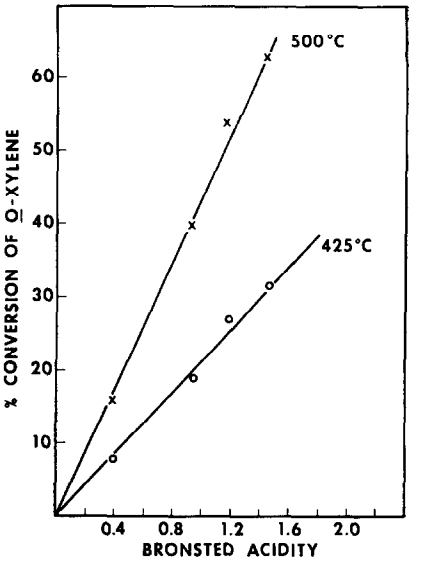

FIG. 7. Conversion of *o*-xylene as a function of catalyst acidity for synthetic catalysts.

cross-linking with increasing alumina content. A linear relationship between ion-exchange capacity and alumina content would be expected if the degree of cross-linking remained constant. From Fig. 2, it can be estimated that if the cross-linking efficiency at 7% alumina content was the same as at 1% alumina, the 7% alumina sample would be 2 to 2.5 times as acidic. As expected, the Brönsted acidity and ion-exchange capacities show similar dependence on the alumina contents of the catalysts.

From the data presented in Fig. 2, the spectroscopic limits of detection can be estimated. Using the experimental technique described above, the measurement of a peak height/sample mass value of 0.1 is perfectly feasible. Hence, it is possible to measure Brönsted acid site concentrations down to the order of 0.5% of alumina in an anhydrous silica-alumina catalyst and to the order of 0.25% of alumina for the hydrated catalyst. Qualitative observations of Brönsted acidity are probably observable down to 0.20% or 0.15% in both cases. When the silica-aluminas were calcined at a lower temperature, for example 400°C, strong absorption bands attributable to Brönsted acidity were observed, thus giving a potential lower limit of detection. However, since most cracking catalysts are calcined and used at 500°C or above, the 500°C calcination temperature was used.

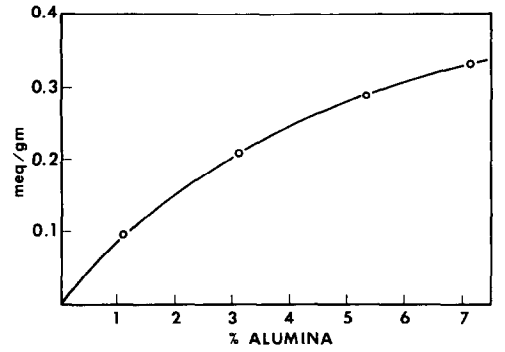

FIG. 6. Ion-exchange capacities of synthetic silica-alumina catalysts.

As shown in Fig. 3, the Brönsted acidities of the commercial silica-alumina catalyst diluted with varying amounts of silica are a linear function of the alumina content. Such a relationship would be expected since, unless some interaction occurs, the degree of cross-linking will be the same for all samples. The limits of detection of acidity for this series are the same as found for the synthetic series. Calculations based on the apparent integrated absorption intensities reported by Hughes and White (*6*) indicate a limit of detection 10^{-2} meq g^{-1}.

The data of Figs. 2 and 3 show that the hydrous catalysts are considerably more acidic than the anhydrous ones. The enhancement of the Brönsted acidity of silica-alumina catalysts has been reported previously (*3*, *4*). Under the conditions of this investigation, the silica-aluminas contain about 2% water during the hydrous measurements. This value was obtained from a thermogravimetric measurement of the weight loss of the catalyst after comparable hydration treatment. Such water levels are probably close to those existing during catalytic cracking reactions.

Catalytic Activity Measurements

The isomerization of *o*-xylene is a very clean reaction believed to be promoted by Brönsted acid sites. From plots of conversion versus the reciprocal of the absolute temperature, the conversion at several temperatures was obtained. This value is plotted against the alumina content in Figs. 4 and 5, for both sets of catalysts. The similarity of the dependence of activity on alumina content to the acidity dependence is readily apparent.

For the commercial catalysts, for conversion at 350°C, the percentage conversion is a linear function of the alumina content just as the Brönsted acidity was shown to be. Such would be expected since the cross-linking is constant and the only difference between the catalysts is the extent of dilution. Hence, under these conditions, there is an excellent relationship between the variation catalyst activity and acidity as the alumina content of the catalyst is changed confirming the validity of the spectroscopic method for determining catalyst acidity and the role of Brönsted acid sites in xylene isomerization. At higher reactor temperatures, for example, 375° and 425°C, the relationship between activity and alumina content becomes nonlinear, suggesting that, at least for the catalysts containing a higher amount of alumina diffusion problems are becoming important. The divergence of the conversion from a linear function of the alumina content increases markedly with the extent of conversion.

For the laboratory catalysts, the conversion was found to be a nonlinear function of the alumina content at all temperatures investigated. This behavior is to be expected since the Brönsted acidity was found to be a nonlinear function. Contrary to expectations for diffusion-limited conditions, as the temperature of reaction is increased, the plot of conversion versus alumina content becomes less nonlinear. These relative changes in activity are probably due to thermal activation of weaker acid sites. As shown in Fig. 7, plots of xylene conversion against Brönsted acidity result in good linear correlations again showing the relationship between Brönsted acidity and catalytic activity.

Although the results of the study show that Brönsted acidity can be detected down to a low concentration in catalysts, the results of the activity study show that appreciable conversion (5–8%) occurs at catalyst alumina contents near the limits of detection of acidity. Hence it is quite possible for catalysts to exhibit no detectable Brönsted acidity and yet be active for carbonium type reactions.

In conclusion, it has been shown that Brönsted acidity in silica-alumina type catalysts can be detected down to the equivalent of 0.25% alumina content. For catalysts containing up to 14% alumina, there is direct correlation between the Brönsted acidity and the catalytic activity for *o*-xylene isomerization. It is also possible for catalysts to possess activity for carbonium ion type reactions altough they exhibit to detectable Brönsted acidity by infrared.

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