Estimating the Relative Acid Site Density of Silica-Alumina by Infrared Spectroscopy Using a Selective Reactant Poison

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Introduction

Infrared (IR) spectroscopy of molecules chemisorbed on heterogeneous catalysts has enjoyed success as a qualitative probe of catalyst surface states (Mapes and Eischens, 1954; Benesi and Winquist, 1978). The position and number of vibrational bands have been used to infer the type of bonding between the surface and adsorbate molecules (Parry, 1963). However, attempts to determine the number density of chemisorbed species have met with less success due to the difficulty of determining the IR absorption coefficients at each relaxation for the adsorbed species.

We show here a promising new technique to determine relative acid site densities of a silica-alumina using IR spectroscopy of chemisorbed pyridine. The novelty of the procedure is the specific elimination of Bronsted sites by the reaction of surface hydroxyls with gaseous hexamethyldisilazane (HMDS) (Hertl and Hair, 1971). Unlike neutralization by alkali, the gaseous base will not form multiple layers of another solid phase that could absorb infrared radiation (Rosenthal, 1985). Bronsted activity measurements using cumene cracking confirm the effectiveness of HMDS to selectively poison Bronsted sites.

Experimental

A Perkin-Elmer 580-B infrared spectrometer and computer data station were used to collect infared data. The amorphous silica-alumina catalysts (Nalco, silicon/aluminum atomic ratio = 2.54 ± 0.15) were pressed at a force of 10,000 lb (4,540 kg) into thin, self-supporting wafers of 25 mm dia. The wafers were treated inside a large-volume Pyrex gas-sample cell equipped with 25 mm calcium fluoride windows. Pressures were measured to the nearest 13.3 Pa (0.1 torr) with a Heise gauge; the temperatures were measured to the nearest 1 K with a type K thermocouple placed near the wafer inside the cell.

Activities of the catalysts for cumene cracking were determined in a microreactor of standard design containing between 0.05 and 1.35 g of catalyst. Catalyst temperature was measured to the nearest 1 K with an axially mounted thermocouple. The fixed flow rate (90 STP mL/min, 1 mL = 10^{-6} m^3) of helium carrier gas transported small doses of cumene (0.19 μmol) from a room-temperature gas saturator loop to the microreactor. The effluent lines were traced with electrical heating tape to ensure that no products condensed on these lines. A Perkin-Elmer gas chromatograph with thermal conductivity and flame ionization detectors was used for analysis. Products were separated on a 1.52 m (5 ft) long × 6 mm (¼ in.) dia. column of 10% OV-101 on 80/100 mesh Chromosorb P. BET surface areas were determined by nitrogen sorption using a Micromeretics 2600 analyzer.

Cumene (99% purity) obtained from the Fischer Scientific Co. was purified over activated alumina prior to use. Pyridine (99+% purity) and HMDS (98%) from Aldrich were purified by the freeze/pump/thaw technique. For infrared measurements, samples were evacuated (1.33 mPa) in the infrared cell at 673 K for 1 h and cooled to room temperature before spectra were taken. Samples were exposed to pyridine at pressures of 667 Pa or 1.33 kPa at room temperature and evacuated (1.33 mPa for 30 min) before the infrared spectra were recorded. Rehydrations at 5 torr (667 Pa) and 10 torr (1.33 kPa) were completed at 298 K for 30 min, followed by room temperature evacuation for 30 min. HMDS treatments in the infrared cells were performed with 667 Pa of HMDS at 523 K for 3 h, followed by evacuation (1.33 mPa) at 673 for 1 h. The absence of any vibrational bands in the OH stretching region (3,750–3,400 cm^{-1}) indicated that the reaction with HMDS under these conditions was complete.

Samples in the microreactor were pretreated in flowing He (90 STP mL/min) at 673 K for 18 h. Silylation was performed using the same temperatures and durations used in the IR cell. HMDS was introduced by flowing He through a room-temperature saturator (vapor pressure 2.67–4.00 kPa). The space-time of the reactor was changed by varying the weight of catalyst at constant He carrier flow rate. Blank tests for noncatalytic conversion of cumene were run using a reactor containing only quartz chips. All of the microreactor tests were conducted at 673 K. At complete conversion of the 0.19 μmol pulse of cumene over the smallest loading of catalyst (0.05 g), only 1% of the surface would be covered by the reactant; therefore, deactivation by coke deposition should not disguise the catalyst activity. It was observed that the activity of a fresh catalyst (0.05 g) did not change with 10 pulses passed over the catalyst. Usually, 5–10 pulses were used to establish the average conversion over a particular weight of catalyst. The same catalyst particles were used to determine the cumene cracking activity before and after silylation with HMDS at each loading in the reactor. For the cases of the oxidized HMDS experiments, the catalyst was tested for cumene activity before and after the silylation and oxidation.

Theory

The infrared spectrum of pyridine coordinatively bound to a Lewis acid site (LPy) differs significantly from that of protonated pyridine absorbed on a Bronsted site (BPy) (Parry, 1963). Pyridine sorbed to Bronsted sites shows a characteristic band at approximately 1,540 cm^{-1}, whereas coordinatively bound pyridine has a distinctive band at 1,450 cm^{-1}. Both species have a band near 1,490 cm^{-1}. The intensities of these peaks can be used to calculate the relative concentrations of each site if the IR absorption coefficients are known at each frequency.

Rather than calculate the exact number of sites, most researchers have calculated the relative concentrations of acid sites (Lewis to Bronsted ratio) using the Beer-Lambert law, which relates the intensity of an infrared absorption band to the concentration of the absorbing species. The three characteristic absorbances (1,452, 1,492, and 1,545 cm^{-1}) can be related to the Lewis and Bronsted acid concentrations as follows:

$$A(1{,}452) = e^{\ddagger}(1{,}452)C^{\ddagger}d \qquad (1)$$

$$A(1{,}492) = [e^{\ddagger}(1{,}492)C^{\ddagger} + e^{*}(1{,}492)C^{*}]d \qquad (2)$$

$$A(1{,}545) = e^{*}(1{,}545)C^{*}d \qquad (3)$$

where the superscripts ‡ and * refer to pyridine bound to Lewis and Bronsted sites, respectively. A and e are the integrated absorbance and extinction coefficients, respectively; d is the sample thickness. Combining Eqs. 1 and 2 gives the following expression for the concentration ratio of Lewis to Bronsted sites:

$$(C^{\ddagger}/C^{*}) = \boldsymbol{ab}A(1{,}452)/[A(1{,}492) - \boldsymbol{b}A(1{,}452)] \qquad (4)$$

where $\boldsymbol{a}$ is $(e^{*}/e^{\ddagger})$ at 1,492 cm^{-1} and $\boldsymbol{b}$ is $e^{\ddagger}(1{,}492)/e^{\ddagger}(1{,}452)$. The integrated absorbances for each peak may be calculated directly from the IR data of each sample. This technique does not require IR data from different wafers.

Calculating *a* and *b*

Basila and Kantner (1966) have derived an expression for $\boldsymbol{a}$ in terms of $\boldsymbol{b}$ as follows:

$$\boldsymbol{a} = \frac{\boldsymbol{b}[A'(1{,}450) - A''(1{,}450)] - [A'(1{,}490) - A''(1{,}490)]}{\boldsymbol{b}[A'(1{,}450) - A''(1{,}450)]} \qquad (5)$$

where ′ and ″ refer to the absorbances before and after addition of water. For this derivation they assumed that any increase in the number of Bronsted sites upon addition of water equaled the decrease in Lewis sites. We evaluate $\boldsymbol{a}$ and $\boldsymbol{b}$ in separate experiments by examining a catalyst wafer before and after treatment with HMDS. This procedure should alter the optical density of the catalyst wafer only very slightly. Treatment with HMDS has been shown to completely eliminate Bronsted IR absorbance of pyridine adsorbed on a catalyst (Rosenthal, 1985). Thus, by measuring the IR absorbances of pyridine adsorbed on a catalyst before and after treating with HMDS, we should be able to determine $\boldsymbol{b}$ directly.

Results

Cumene cracking

The BET surface areas for these catalysts were different:
Fresh catalyst (A) = 333 m^2/g
HMDS-treated catalyst (B) = 282 m^2/g
Oxidized, HMDS-treated catalyst (C) = 247 m^2/g

The cumene conversion for all three catalysts are plotted vs the sample weight times the specific surface area of the sample in Figure 1. The zero conversion of the HMDS-treated sample for catalyst weights up to 1.35 g (Rosenthal, 1985) shows the efficiency of HMDS to poison Bronsted sites required for cumene

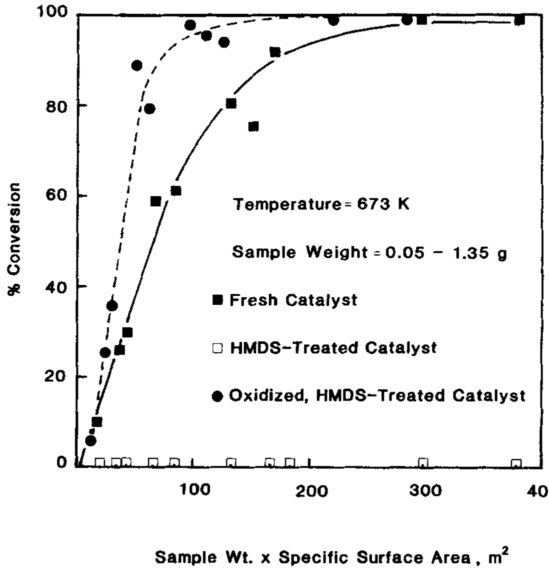

Figure 1. Cumene cracking activity.

cracking (Ward, 1967). In addition to silylating the catalyst, reaction with HMDS produces ammonia as a by-product (Hertl and Hair, 1971) that can deactivate the catalyst (Rosenthal, 1985). Therefore, a fresh catalyst was exposed to ammonia at 523 K and carried through the normal pretreatment. The conversion of cumene was the same as the unpoisoned catalyst. This experiment showed that ammonia will not poison the catalyst under the conditions used for our experiments. Therefore, the poisoning of these catalysts for cumene cracking is due to the elimination of Bronsted sites by attachment of silyl ether fragments. When samples were oxidized in an attempt to recover their original activity, they were more active than the untreated catalysts. This treatment apparently increased the Bronsted site density per unit surface area. When relative activities are estimated by comparing initial slopes of the data in Figure 1, sample *C* shows about twice (2.1) the activity of sample *A*. These two catalysts were used to evaluate the feasibility of the IR technique for determining the relative numbers of Lewis and Bronsted sites.

Infrared calibration

The theory suggestd that two experiments were necessary to determine the parameters a and b. Having established that HMDS quantitatively reacts with all the cumene-active Bronsted sites, the parameter b is simply the ratio of the integrated absorbances at 1,492 and 1,452 cm^{-1} of those samples treated with HMDS and exposed to pyridine. Notice the absence of BPy (1,545 cm^{-1}) in the spectra of the HMDS-treated catalysts, Figures 2b and 2d, as compared to the fresh catalysts, Figures 2a and 2c. We determined values of b for two catalysts that showed different degrees of hydration prior to the HMDS treatment (Figure 2 a, b, rehydrated at a pressure of 1.33 kPa water and room temperature; Figure 2 c, d, not rehydrated). The values of b were 0.203 and 0.211.

To determine a, a fresh catalyst wafer was partially rehydrated before pyridine chemisorption. This rehydration step should (Basilia, 1964) change the relative populations of Lewis and Bronsted sites according to the following equilibrium:

$$\text{Lewis acid site} + \text{water} = \text{Bronsted acid site} \qquad (6)$$

The IR spectra of chemisorbed pyridine on these partially rehydrated fresh samples are shown in Figure 3. Note the changes in the intensities of the bands characteristic of Bronsted-bound pyridine (1,545 cm^{-1}) and Lewis-bound pyridine (1,452 cm^{-1}) as the hydration is affected, Figures 3 a, b, c. Also note that the peak with contributions from both Bronsted- and Lewis-bound pyridine shows very little change (1,491 cm^{-1}). Using Eq. 5 and the average value of b determined earlier (0.207), we calculate a to be 0.99 ± 0.10.

Quantitative IR

Having "calibrated" the IR for the silica-alumina catalysts, the fraction of acid sites may be determined. The ratio of Lewis to Bronsted sites, given by Eq. 4, is determined from the pyridine IR spectra of the fresh catalysts at different states of hydration, Figures 2 and 3, and the oxidized, HMDS-treated catalysts, Figure 4, using $a = 1$ and $b = 0.207$. The fraction of Bronsted sites may be calculated from these ratios as:

$$f^* = (1 - f^\ddagger) = 1 - [(C^*/C^\ddagger + 1)^{-1}] \qquad (7)$$

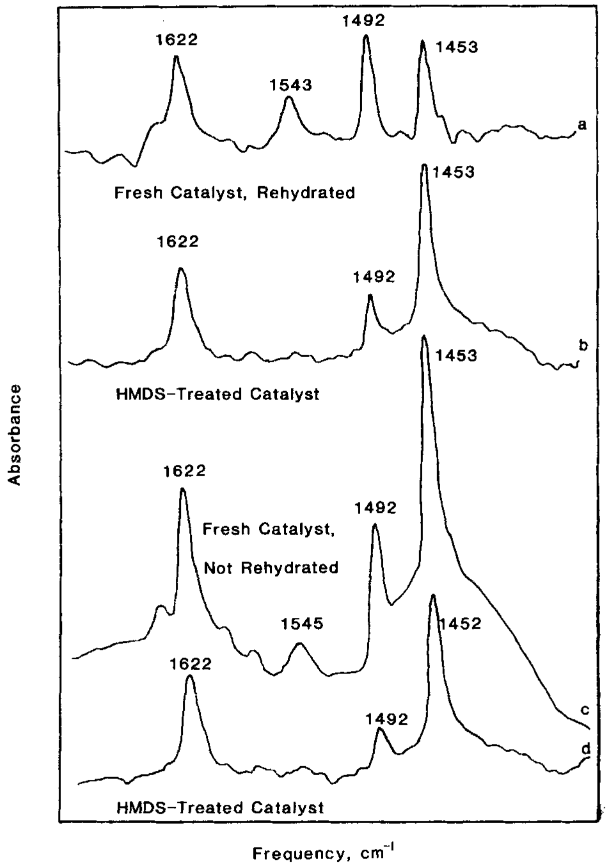

Figure 2. IR spectra of chemisorbed pyridine.
a. Fresh catalyst, rehydrated at 10 torr (1.33 kPa)
b. Catalyst of (a), treated with HMDS
c. Fresh catalyst, not rehydrated
d. Catalyst of (c), treated with HMDS

These values, given in column 2 of Table 1, show the fraction of Bronsted sites to increase with increasing degree of hydration of the sample. Also, the oxidized, HMDS-treated sample (catalyst *C*) showed a fraction of Bronsted sites roughly twice that of the fresh, dehydrated sample (catalyst *A*). The same peak area data were processed using $a = 6$ and $b = 0.25$ to give the fraction of Bronsted sites, column 3 of Table 1. Notice that the fractions of Bronsted sites in column 3 are less than the corresponding values in column 2. Moreover, the ratio of fraction of Bronsted sites for catalysts *C* to *A* in column 3 is 11.3, nearly 5.4 times the ratio of cumene cracking activities.

Discussion

Questions on the accuracy of a are the major concern when attempting to estimate the relative surface site concentrations using IR spectroscopy. Although the results obtained for b (0.207) appear to be average of those reported by Bassila and Kantner (1966) and by Hughes and White (1967)—0.25 and 0.17, respectively—a values reported in the literature differ significantly. Basila's first reported value (Basila et al., 1964) of $a = 1$ was basd on the fact that both interactions (BPy and LPy) take place at the nitrogen atom, which would presumably lead to the same inductive effect on the absorbance of radiation. Moreover, extinction coefficients at 1,490 cm^{-1} for the homogeneous analogs of BPy and LPy were within 15% of the same value,

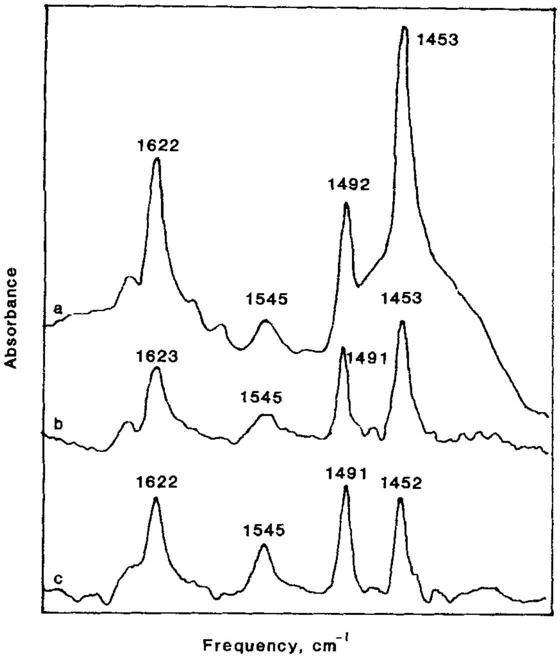

Figure 3. Pyridine IR spectra for partially rehydrated silica-alumina.

a. Fresh catalyst, evacuated at 400°C

b. Fresh catalyst, evacuated at 400°C, rehydrated at 5 torr (667 Pa)

c. Fresh catalyst, evacuated at 400°C, rehydrated at 10 torr (1.33 kPa)

adding validity to their reported value of a. In a later report, Basila and Kanter (1966) described an experiment similar in nature to the present disclosure. Their technique, which involved potassium poisoning to eliminate Bronsted acidity followed by the addition of water to vary the Lewis/Bronsted site populations, led to an a value of 6 ± 0.9. Hughes and White (1967) reported a similar value of a (5.8) using different catalyst samples showing either Lewis acidity alone (alumina) or Bronsted and Lewis acidity (silica-alumina). Lefrancois and Malbois (1971) reported the ratio of extinction coefficients to be 5.2. More recently, Sayed et al. (1984) reported $a = 2.74$ for an H-ZSM5 catalyst in which they changed the site populations by the addition of water. In the present experiment, we return full circle to report $a = 1$. Notice in Figure 3 that the absorbance peak at 1,492 cm^{-1} changes little, if at all, for varying populations of Lewis and Bronsted sites. This is the expected result if $a = 1$, since the area of this peak is described by Eq. 2 and neither the total site density (Lewis + Bronsted sites) nor the path length of the sample should change appreciably. Hence, we feel that $a = 0.99$ represents an adequate approximation for a on this silica-alumina. The relative extinction coefficients of BPy and LPy may vary on different strengths of acid sites, so that a and b are catalyst-dependent.

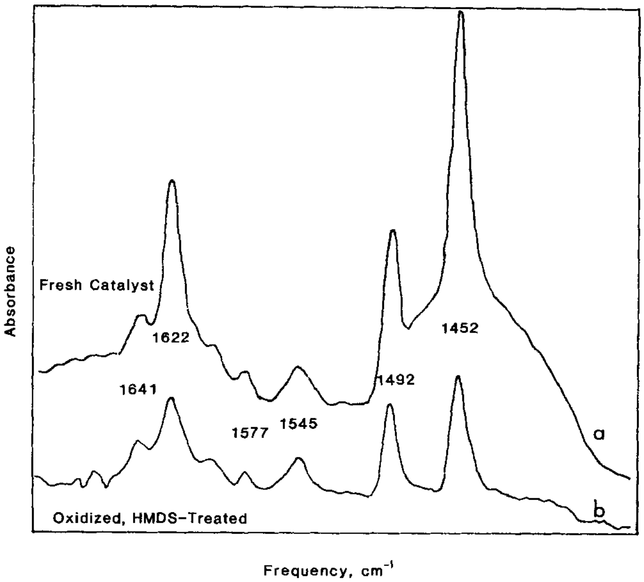

Figure 4. Pyridine IR spectra for fresh and oxidized HMDAS-treated catalyst.

a. Fresh catalyst, not rehydrated

b. Catalyst of (a), treated with HMDS and oxidized

Table 1. Fraction of Bronsted Sites Calculated from IR Absorbance Data of Chemisorbed Pyridine

	Fraction of Bronsted Sites Using	
Catalyst	$a = 1$ $b = 0.207$	$a = 6$ $b = 0.25$
Fresh, dehydrated	0.30	0.015
Fresh, hydrated at 667 Pa	0.64	0.18
Fresh, hydrated at 1.3 kPa	0.82	0.64
Oxidized, HMDS-treated	0.63	0.17

Whereas this IR technique appears similar to others, the chief difference involves the use of a gaseous base (HMDS) to eliminate totally the Bronsted acidity. The question of the efficiency of poisoning by HMDS is answered in a convincing manner by the cumene cracking results. HMDS has been shown to react with surface OH groups to form silyl ethers (van Roosmalen and Mol, 1978). Infrared spectroscopy of the catalysts confirms this by the generation of C-H relaxations and the complete disappearance of O-H relaxations in the spectra of the HMDS-treated catalyst (Rosenthal, 1985). Furthermore, TGA data of the HMDS reactions suggests no extended three-dimensional structures of silyl ethers are formed, since the weight increase upon silylation corresponded to a monolayer of silyl ethers (Rosenthal, 1985). For these reasons, the path length for the IR radiation probably changes very little and consequently, the HMDS technique enhances the accuracy of estimating the two unknowns, a and b. Extending the technique to other catalysts should help to explain the discrepancies between the values of a presented here and those of other investigators.

The changes in the IR spectrum of chemisorbed pyridine when HMDS is reacted with the fresh catalyst are those one would expect. The relaxations due to BPy disappear completely from the 1,545 cm^{-1} peak, and the peak intensities for the BPy/LPy combined peaks decrease. These IR observations are harmonious with the activity decrease to zero for the cumene cracking reaction. Moreover, the return of the BPy relaxations upon oxidizing sample B (i.e., sample C) are expected with the return of the cumene cracking activity. The quantitative results, columns 2 and 3 of Table 1, showing increasing fraction of Bronsted sites with increasing degree of sample hydration agree with the concept that add-back water converts Lewis sites into Bronsted sites. The LPy vibrations are observed to decrease as the BPy vibrations increase: consider Figure 3, 1,453 peak decrease with 1,545 peak increase. However, the best validation of the technique is the agreement between the twofold increase in the fraction of Bronsted sites predicted from the pyridine IR, Table 1, column 2, and the twofold increase in the cumene cracking activity between samples *A* and *C*. When literature values of ***a*** and ***b*** are used to reduce the same IR peak area data, there is no such agreement between IR and cumene cracking results. Based on these results, this IR method appears to predict the results of a model reaction demanding Bronsted acid sites if proper values of ***a*** and ***b*** are used. Considering its ease and the time required (10 h) for the IR experiment, the technique shows promise as a method to estimate relative catalyst activity.

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