

Acidity of Silica-Alumina Catalysts By Amine Titration Using Hammett Indicators and FT-IR Study of Pyridine Adsorption

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In this study, characterization and surface acidity of Siral ($\text{SiO}_2\text{-Al}_2\text{O}_3$) compounds were investigated with Hammett acidity functions, the n-butylamine titration method and FTIR analysis of the spectra of pyridine adsorption. All the samples had an acid strength of $H_0 \leq +2.8$. The calculated total amount of acid of the samples increased with the increase in SiO_2 content up to Siral 40 and then decreased sharply in the case of Siral 80. Maximum amount of acidity was observed in the case of Siral 40 as 1.37mmole/g. No evidence was found for a band at 1540 cm^{-1} on Pural indicating that there were no Bronsted sites on the surface strong enough to react with pyridine. As a result, we can say that the Lewis sites predominate in all the silica-aluminas.

Introduction

Solid acid catalysts such as silica and alumina are widely used in many kinds of chemical reactions. The catalytic activity and selectivity of these reactions are closely related to both the amount and the strength of the acid sites distributed over the surface of the catalyst.

Theory¹⁻³

The acid strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral base into its conjugate acid. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is quantitatively expressed by Hammett and Deyrup's H_0 acidity function¹,

$$H_0 = pK_a + \log[B]/[BH^+] \quad (1)$$

Where $[B]$ and $[BH^+]$ are the concentrations of the neutral base and its conjugate acid respectively, and pK_a is pK_{BH^+} . If the reaction takes place by means of the electron pair transfer from the adsorbate to the surface, H_0 is expressed by

$$H_0 = pK_a + \log[B]/[AB] \quad (2)$$

Where [AB] is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor, A.

The amount of acid on a solid is usually expressed as the number or mmol of acid sites per unit weight or per unit surface area of the solid. There are two main methods for the determination of strength and amount of a solid acid. These are an amine titration method (n-butylamine titration) using Hammett indicators and a gaseous base adsorption method (ammonia and pyridine adsorption).

In the amine titration method using indicators, the color of suitable indicators adsorbed on the surface will give a measure of its acid strength. If the color is that of the acid form of the indicator, then the value of the H_0 function of the solid is equal to or lower than the pK_a of the conjugate acid of the indicator.

The Hammett indicators used in the present study are listed in Table 1, together with color changes and pK_a 's. To give some idea of the acid strength range, corresponding sulfuric acid compositions are also listed.

Table 1. Basic indicators used for the measurement of acid strength³

Indicator	Color Base Form	Color Acid Form	pK_a	[H ₂ SO ₄] %
Neutral red	yellow	red	+6.8	8.10 ⁻⁸
Methyl red	yellow	red	+4.8	-
Phenylazonaphthylamine	yellow	red	+4.0	5.10 ⁻⁵
p-Dimethylaminoazobenzene	yellow	red	+3.3	3.10 ⁻⁴
2-Amino-5-azotoluene	yellow	red	+2.0	5.10 ⁻³
Benzeneazodiphenylamine	yellow	purple	+1.5	2.10 ⁻²
Crystal violet	blue	yellow	+0.8	0.1
p-Nitrobenzeneazo-(p'-nitro-diphenylamine)	orange	purple	+0.43	-
Dicinnamalacetone	yellow	red	-3.0	48
Benzalacetophenone	colorless	yellow	-5.6	71
Anthraquinone	colorless	yellow	-8.2	90
2,4,6-Trinitroaniline	colorless	yellow	-10.10	98
p-Nitrotoluene	colorless	yellow	-11.35	*
m-Nitrotoluene	colorless	yellow	-11.99	*
p-Nitrofluorobenzene	colorless	yellow	-12.44	*
p-Nitrochlorobenzene	colorless	yellow	-12.70	*
m-Nitrochlorobenzene	colorless	yellow	-13.16	*
2,4-Dinitrotoluene	colorless	yellow	-13.75	*
2,4-Dinitrofluorobenzene	colorless	yellow	-14.52	*
1,3,5-Trinitrotoluene	colorless	yellow	-16.04	*

* The indicator is liquid at room temperature and acid strength corresponding to the indicator is higher than the acid strength of 100 percent H₂SO₄.

The amount of acid sites on a solid surface can be measured by amine titration immediately after determination of acid strength by the above method. The method consists of titration a solid acid suspended in benzene with n-butylamine, using an indicator. This method gives the sum of the amounts of both Bronsted and Lewis acid, and is rarely applied to colored or dark samples where the usual color change is difficult to observe. On the other hand, the infrared spectroscopic method using pyridine as an adsorbate is

extensively used and considered to be a most reliable method, although there are many other methods to distinguish between Bronsted and Lewis acid sites.

It has been defined that the solid acid sites on commercial silica-alumina surfaces in terms of the infrared spectra of adsorbed pyridine in the region $1660\text{-}1400\text{cm}^{-1}$ ^{4,5}. From the obtained spectra, the types of site affecting adsorption were classified as Lewis (LPY), Bronsted (BPY) and surface hydroxyl (HPY). Table 2 lists the assignments of the different bands; the 19b modes were used to distinguish between different types of adsorbed pyridine ^{6,7}.

Table 2. Pyridine Assignments ^{6,7} in the Range $1660\text{-}1400\text{ cm}^{-1}$

Type	PY cm^{-1}	HPY cm^{-1}	BPY cm^{-1}	LPY cm^{-1}
Mode 8a	1582	1614	1639	1617
8b	—	1593	1613	—
19a	1483	1490	1489	1495
19b	1440	1438	1539	1451

It can be seen that the pyridinium ion alone produced a band in the vicinity of 1540 cm^{-1} and the appearance of this band in the spectrum is taken as indication of Bronsted acidity. Coordinately bonded or Lewis pyridine generated a unique band at 1451 cm^{-1} where the pyridinium ion did not absorb. Pyridine itself gave a band at 1440 cm^{-1} .

In this study, characterization and surface acidity of Siral compounds were investigated with Hammett acidity functions, the n-butylamine titration method and FTIR analysis of the spectra of pyridine adsorption.

Experimental

Materials: The silica-alumina (SIRAL) samples used in this work were the obtained from CONDEA AG-Germany. The compositions, surface areas and the pore size distribution of the samples are given in Table 3. Other chemicals i.e. the Hammett indicators, benzene, n-butylamine and pyridine were Merck and Fluka reagent grades, respectively. They were used directly without further purification.

Table 3. Samples used in this study

Sample	Pural	Siral 5	Siral 20	Siral 30	Siral 40	Siral 80
SiO ₂ content, %	—	4.5	21.8	28.1	39.7	78.3
Al ₂ O ₃ content, %	75.6	95.5	78.2	71.9	60.3	21.7
BET area, m ² /g	250	380	428	467	406	224
density, gmL ⁻¹	0.70	0.53	0.38	0.34	0.33	0.54
particle size distribution, %						
<25 μ	25.3	20.7	36.5	26.9	26.3	73.3
<45 μ	50.6	49.1	69.9	52.1	52.2	96.2
<90 μ	93.3	90.0	99.9	94.0	99.1	98.7

Techniques:

Acid Strength Measurements:

Color tests were made by transferring 0.1g of dried, powdered solid to a test tube, adding a 0.1% solution of indicator in benzene (three drops in the case of all indicators). From the results of such tests, it

was easy to decide whether the solid under study was basic to all indicators, acid to all indicators, or had an H_0 lying between two adjacent indicator pKa's.

Samples were freshly dried at 393K before carrying out the indicator tests, and were subjected to color immediately after drying, or if this was not convenient, were stored in screw cap test tubes in a desiccator until color tests were performed. Since water is a base, the effect of water adsorption changed the color intensities of the adsorbed indicators or caused a shift to lower acid strengths.

Acid Amount Determination:

The amount of acid sites on the samples can be measured by amine titration immediately after determination of acid strength by above method. The method consists of titration of the sample suspended in benzene with n-butylamine, using an indicator. The 0.1N n-butylamine solution was prepared by weighing 1.0mL of n-butylamine in a 100mL volumetric flask and making up the volume using dried benzene. The procedure was as follows: 0.2g of dried sample was transferred to a 50mL screw-cap Erlenmeyer flask. Nine milliliters of dry benzene and 3mL of indicator solution in benzene were added to the sample suspension. Then, enough 0.1N n-butylamine in benzene was added from a 2mL burette to the sample so as to bracket the expected titer by the appropriate number of millimoles of n-butylamine per gram of sample. Silica-alumina catalyst having a surface area of $500\text{m}^2/\text{g}$ has an anticipated titer of 0.4mmole/g^8 . The amounts added should thus be less than this amount. The tightly capped sample was then equilibrated in a rotator at least four hours (or overnight) at room temperature. The titration was then continued using smaller stepwise increases in n-butylamine content until the end point.

IR Measurements:

IR measurements were performed with self-supporting pressed discs contained in a cell with NaCl windows, which allowed discs to be heated under vacuum or in the presence of pyridine. IR spectra were recorded in situ at room or elevated temperatures by a Mattson 1000 FTIR instrument, equipped with a conventional evacuation-gas manipulation ramp (10^{-3} Pa).

The FTIR instrument was typically operated at a resolution of 2cm^{-1} , collecting 50 scans per spectrum. All the samples were subjected to a standard pretreatment involving heat treatment at 673K in vacuo for 8h. After adsorption studies, desorption experiments were also done at elevated temperatures for 10min.

The quantitative analysis was carried out after 3h pyridine adsorption and followed by evacuation at 298 K for 10 min. at a pressure of 10^{-3} Pa. The bands at 1490 and 1450 cm^{-1} were employed for the determination of Bronsted and Lewis acid sites respectively in the case of pyridine adsorption. The extinction coefficients (ϵ) of these bands are available in the literature⁹⁻¹⁷. The concentration of Bronsted and Lewis acid sites referenced to unit weight of dry sample [q_H ($\mu\text{equiv.g}^{-1}$)] was obtained according to the equation below¹⁵

$$q_H = (A\pi R^2)/w\epsilon \quad (3)$$

Where $R(\text{cm})$ is the radius of the catalyst wafer and $w(\text{g})$ is the weight of the dry sample. Values were evaluated from the difference spectra relative to all samples after baseline correction. ϵ values relative to the absorption bands at 1490 cm^{-1} (Bronsted sites, ϵ_B and at 1450 cm^{-1} (Lewis sites, ϵ_L) were used as 1.67 and $2.22\text{ cm}^2\mu\text{mol}^{-1}$ which were reported in the literature¹⁰. The calculated values according to the equation above are given in Table 6.

Results and Discussion

Acidic strength and the amount of acid in the samples are given in Tables 4 and 5, respectively. The limits of the H_0 of samples were established by observing the color of the adsorbed form of the Hammett indicators. As can be seen from Table 4, all the samples had an acid strength of $H_0 \leq +2.8$ which means that the sample with an $H_0 < +1.1$ gave acid colors with all Hammett indicators. It can also be seen from Table 5 that the calculated total amounts of acids in the samples with the increase in SiO_2 content up to Siral 40 and then decreased sharply in the case of Siral 80 with approximately 80% of SiO_2 . The maximum amount of acidity was observed in the case of Siral 40 as 1.37mmole/g. We assumed that 20\AA^2 is the area of an acid site in the case of the silica-alumina catalysts⁸. We calculated that the acid centers on Siral 40 catalyst occupy 32.6% of the surface. This value is 8.23, 23.34, 24.23 and 36.55% of the surfaces of the catalysts Siral 5, Siral 20, Siral 30 and Siral 80, respectively.

Table 4. Distribution of the acidic strength with Hammett indicators

Indicator	Pural	Siral 5	Siral 20	Siral 30	Siral 40	Siral 80
Neutral red pKa=+6.8	-	+	+	+	+	+
Methyl red pKa=+4.8	-	+	+	+	+	+
4-Aminoazobenzene pKa=+2.8	-	+	+	+	+	+
4-Nitroanilin pKa=+1.1	-	-	-	-	-	-
Crystal violet pKa=+0.8	-	-	-	-	-	-
Chalcone pKa=-5.6	-	-	-	-	-	-
Anthraquinone pKa=-8.2	-	-	-	-	-	-

Table 5. The amount of acids as mmole g^{-1} which was calculated from the n-butylamine titration

Indicator	Siral 5	Siral 20	Siral 30	Siral 40	Siral 80
Neutral red pKa=+6.8	0.11	0.37	0.42	0.68	0.29
Methyl red pKa=+4.8	0.10	0.30	0.35	0.49	0.24
4-Aminoazobenzene pKa=+2.8	0.05	0.16	0.17	0.20	0.15

The binary oxide of $SiO_2-Al_2O_3$ develops much stronger acids than those of individual oxides upon the evacuation under heating. Their acid strength is higher at smaller contents of Al_2O_3 . Without the evacuation, the presence has been reported of 0.25mmole/g of acids of $H_0 \leq 1.5$ on the catalyst which contained 15wt% of Al_2O_3 , and 0.57mmole g^{-1} of acid ($H_0 \leq 3.3$)¹⁹.

On the other hand, it can be seen from Table 4 that Pural did not give any color change with the indicators listed in Table 1. This means that it has a basic property under these experimental conditions (drying at 393K and treatment with Hammett indicators at 298K). The basic strength of Pural was estimated

with bromothymol blue ($pK_a=7.1$) and phenolphthalein ($pK_a=9.3$) indicators which have acidic characters. It changed phenolphthalein to its red form even when dried at only 393K. The amounts of basic sites on Pural were determined by the benzoic acid titration method, again with bromothymol blue and phenolphthalein as the indicators. The calculated values were 0.325 and 0.35 mmol g^{-1} , respectively. Pural showed strong surface acidity after heating at 673K for 8h in vacuum.

We performed the experiments at room temperature after drying the samples at 393K. It should perhaps be pointed out at this stage that the acidic properties of silica-alumina to a large extent depend upon the method of preparation, the proportion of alumina, the temperature of dehydration, and the method by which the acidity is assessed. Changes in these acidic properties due to both grinding and steam heating have also been reported¹⁹.

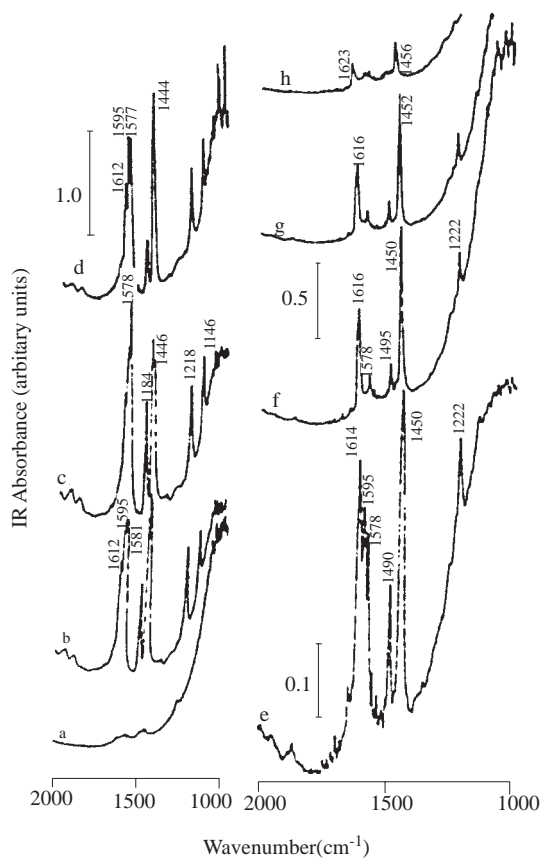


Figure 1. FTIR spectra of pyridine adsorbed on Pural

a) reference b) initial ads. c) 15 min. ads. d) 30 min. ads. e) 373K, des. f) 473K, des. g) 573K, des. h) 673K, des.

The spectra of pyridine adsorbed on a dehydrated Pural, Siral 5 and Siral 40 are shown in figures 1, 2 and 3, respectively. In Figure 1, after evacuation at successively higher temperatures, we observe that the band at 1450 cm^{-1} gradually narrows, its intensity decreases, and an increase in the frequency of the maximum to 1456 cm^{-1} occurs. After evacuation at 373K, a triplet can be observed at 1614, 1595 and 1578 cm^{-1} , the band at 1595 cm^{-1} disappearing first with evacuation at 473K. There may be at least two groups of Lewis sites on the surface of dehydrated alumina differing in acid strength. The retention of pyridine after evacuation at high temperatures, as shown by the 1456 cm^{-1} band, and also the band at

1578 cm^{-1} . The band at 1595 cm^{-1} in the room temperature spectrum (Fig. 1. b, c, and d) represents hydrogen-bonded pyridine and the band at 1578 cm^{-1} represents physically adsorbed pyridine. The band at 1578 cm^{-1} left at 473K (Fig. 1.f) arises from coordinately bonded pyridine.

Table 6. The concentration of Bronsted and Lewis acid sites calculated from the pyridine adsorption data

Sample	$q_H^L + q_H^B / \mu\text{equiv.g}^{-1}$	$q_H^L / \mu\text{equiv.g}^{-1}$
Pural	7.70	13.30
Siral 5	4.64	6.13
Siral 20	4.95	7.50
Siral 30	6.46	13.52
Siral 40	11.68	10.03
Siral 80	0.11	0.28

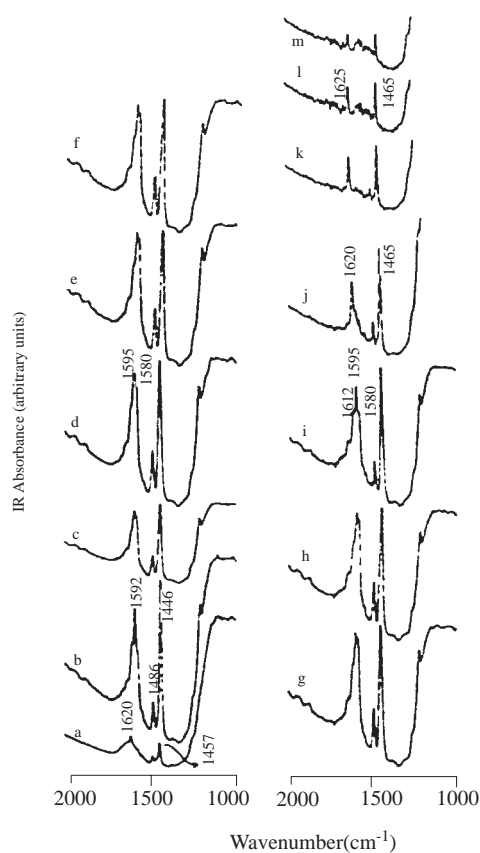


Figure 2. FTIR spectra of pyridine adsorbed on Siral 5

a) reference b) initial ads. c) 15 min. ads. d) 30 min. ads. e) 1h ads. f) 1.5h ads. g) 2h ads. h) 3h ads. i) 298K, des. j) 373K, des k) 473K, des. l) 573K, des. m) 673K, des.

No evidence is found for a band at 1540 cm^{-1} on Pural indicating that there were no Bronsted sites on the surface strong enough to react with pyridine. The band at 1490 cm^{-1} is consistent with both Bronsted and Lewis acid sites, which can be seen in Table 2. Therefore, the calculated values of Bronsted acid sites from the band at 1490 cm^{-1} do not reflect the pure Bronsted acid sites. The presence of physically adsorbed

pyridine apparently held on the surface by hydrogen-bonding interaction with surface OH groups is indicated by the detection of the characteristic 1595 and 1614 cm^{-1} bands. The data also indicate that some molecular water was very strongly adsorbed by the samples, since evacuation at 673K did not completely remove it from the surface.

As can be seen in Figure 2, Siral 5 exhibits similar IR spectra. After evacuation at 373K (Fig. 2j), we observed that the shoulders at 1612 and 1580 cm^{-1} disappeared and the band maximum in Figure 2i shifted to 1620 cm^{-1} . After evacuation at higher temperatures, the intensities of the bands at 1620 and 1457 cm^{-1} decreased and shifted to 1625 and 1465 cm^{-1} . The band at 1580 cm^{-1} disappeared at 473K. On the other hand, the intensity of the band at 1490 cm^{-1} decreased gradually after evacuation at 298K and then largely disappeared at 473K. The IR spectra of Siral 40 in the evacuation processes from 298K to 673K (Fig. 3g-k) were slightly different. A weak band was observed at 1550 cm^{-1} assigned to pyridinium ions. However, this band was very weak and may not be used for quantitative evaluation of the Bronsted acid sites.

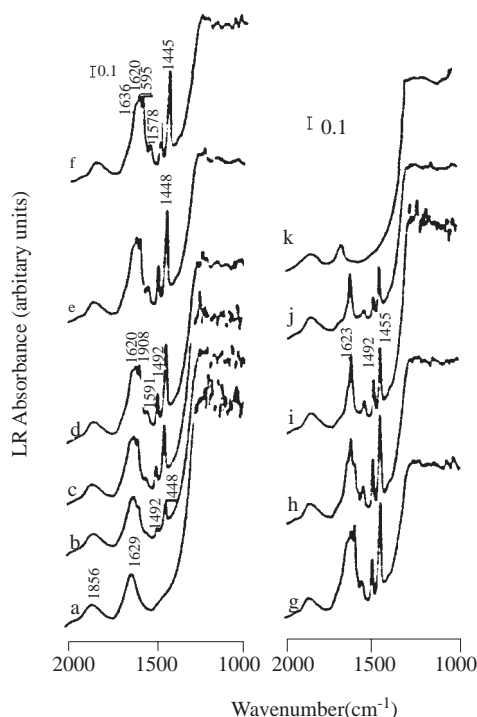


Figure 3. FTIR spectra of pyridine adsorbed on Siral 40

a) reference b) initial ads. c) 30 min. ads. d) 1h ads. e) 2h ads. f) 3h ads. g) 298K, 10 min. des. h) 373K, des. i) 473K, des. j) 573K, des. k) 673K, des.

As a result, we can say that the Lewis sites predominate in all the silica-aluminas, but that a wide range in the ratio of Lewis to Bronsted sites exists.

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