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Determination of Integrated Molar Extinction Coefficients for Infrared Absorption Bands of Pyridine Adsorbed on Solid Acid Catalysts

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Integrated molar extinction coefficients were determined for infrared absorption bands of pyridine adsorbed on acid sites in Si/Al-based catalysts. The infrared spectra of five zeolites and two amorphous silica–aluminas were recorded during quantitative dosing of pyridine gas at 150°C. The integrated molar extinction coefficients were calculated assuming that they did not depend on the catalyst or the strength of the acid site. The resulting values were 1.67 cm/μmol for the 1545-cm^{-1} band characteristic of pyridine on a Brønsted acid site and 2.22 cm/μmol for the 1455-cm^{-1} band of pyridine on a Lewis acid site. The 95% confidence limits were estimated at ±15%. Subsequent analysis of the data provided no evidence for a dependence of the integrated coefficients on the catalyst or the strength of the site. The measurements gave indications for differences between the rates of reaction of Brønsted and Lewis acid sites with pyridine.

INTRODUCTION

Infrared (IR) spectroscopic monitoring of adsorbed pyridine is an established tool for investigating the acidity of solid acid catalysts (*1*). Advantages of this technique are: Brønsted acid (B) and Lewis acid (L) sites can be distinguished because the IR spectra of adsorbed pyridine show characteristic differences; *in situ* pretreatments can be given to the catalyst; and the acid strength distribution of sites can be investigated by monitoring the thermodesorption of pyridine. However, the literature data on the integrated molar extinction coefficients (IMEC, defined by Eq. (1) and Beer's law, Eq. (2)) of the IR bands of adsorbed pyridine vary by a factor of about 4 (*2–4*), which hampers the quantitative determination of the number of sites. This unsatisfactory situation prompted us to redetermine the IMEC of bands characteristic of pyridine adsorbed on B sites (1545-cm^{-1} band of pyridinium ion, B band) and L sites (1455-cm^{-1}, L band). The investigation was performed using Si/Al-based catalysts: five zeolites and two amorphous silica–aluminas (ASA). The measurements also yielded the IMEC of the O–H stretch vibration of the acid OH groups. Furthermore, the relative rates of reaction of pyridine with B and L sites are discussed and a comparison is made between the Al content and the concentration of acid sites calculated with the newly determined IMEC values.

$$\mathrm{IMEC} = \int \varepsilon \, d\sigma \qquad \sigma = \text{wavenumber (cm}^{-1}) \qquad (1)$$

$$A = \varepsilon \, c \, D \qquad (2)$$

where

A = absorbance, $\log_{10}(I_0/I)$, where I_0 and I are the intensities of incident and transmitted radiation;

ε = molar extinction coefficient (dm^3/(mol cm));

c = concentration (mol/dm^3);

D = path length (cm).

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METHODS

Samples

The samples are given in Table 1. Solid-state Al NMR data available for zeolite Y indicated that approximately 50% of the Al was present in the framework. Sample MOR2 was prepared by heating MOR1 for 2 h in air at 550°C. The zeolites were in the H form. Pyridine (p.a., Merck) was stored on molecular sieves in a glass container attached to the vacuum system and was degassed by freeze/thaw cycles.

Equipment

A Mattson Cygnus 100 Fourier-transform IR spectrometer equipped with a HgCdTe detector was used. The iris was set at 1%. The spectra were obtained at a spectral resolution of 1 cm^{-1}, using a scan speed of 1.26 cm/s and triangular apodization. The integrated absorbances (IA, cm^{-1}) of bands in the spectrum of a test sample agreed within 3% with the values obtained using other instruments (Mattson Galaxy, Bomem MB, Nicolet 20SXB and Perkin–Elmer 983G).

TABLE 1

Si/Al-Based Catalyst Samples

Catalyst	Code	Si/Al (mol/mol)	(1)[a] (%)	(2)[b]
Mordenite (Union Carbide)	MOR1	8.3	−5.8	0.41
Mordenite	MOR2	8.3	+2.8	0.36
Mordenite (Laporte)	MOR3	20	+4.9	0.93
Zeolite Y (Conteka)	Y	9.5	+4.4	0.24
Zeolite ZSM-5 (Conteka)	ZSM-5	21	−4.2	0.47
ASA[c] (Ketjen)	ASA1	3	−6.9	—
ASA[c] (Ketjen)	ASA2	6.7	+2.5	—

[a] (1) 100 × (left-hand side of Eq. (4) − 1).

[b] (2) (conc. of acid sites determined by IR)/(aluminium conc.).

[c] Amorphous silica–alumina.

The IR *in situ* cell consisted of a stainless-steel housing onto which ZnSe windows were sealed. The pressure in the cell was measured by means of Pirani and hot cathode ionisation pressure meters. The cell contained a quartz-clad heating device in which a disk of compressed solid sample was placed. The pump section consisted of a turbomolecular pump connected to a rotary pump. Copper O-rings were used in all flange connections. Pyridine vapour was added from a gas admission compartment with a volume of 3.63 cm^3. The pressure in this compartment was determined with the aid of an MKS instruments capacitance-type pressure meter.

Procedures

The samples were pressed into disks with a radius (R) of 0.9 cm and a weight of 30 mg. The disks were heated in the *in situ* cell for 30 minutes *in vacuo* at 450°C. The sample was cooled to 150°C and a spectrum was recorded. All measurements were performed at this temperature in order to prevent physisorption of pyridine. The IR radiation emitted by the sample, not modulated by the interferometer, did not influence the absorption spectrum. After closing the valve between cell and pump system, pyridine gas was added stepwise in amounts of approximately 2 μmol. The amount of added pyridine was calculated from the ideal gas law. A spectrum was recorded 5 min after each addition. Spectra recorded after longer time intervals showed no significant changes. After a number of additions, the sample was contacted for 15 min with 2 Torr pyridine (1 Torr = 133.3 N m^{-2}). The pyridine was pumped off for 15 min and a spectrum was recorded. The sample was then heated for 15 min at 350°C, cooled to 150°C and a spectrum was recorded in order to assess the amount of strongly acidic sites. Difference spectra were obtained by subtracting the spectrum of the dehydrated catalyst from the spectra obtained after pyridine adsorption. The difference spectra were used to obtain IA values of the B and

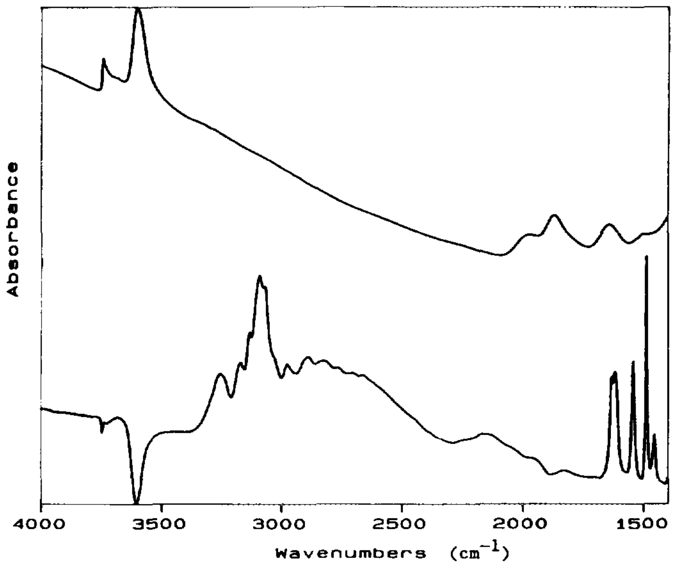

FIG. 1. Infrared spectra of mordenite MOR3. Top: after dehydration. Bottom: difference spectrum obtained during addition of pyridine, before saturation occurred.

L bands (integration regions approximately 1515–1565 cm^{-1} and 1435–1470 cm^{-1}, respectively) and of the acid OH difference bands. The IA values of the latter bands, which are negative, are, for convenience, reported as positive.

RESULTS

Quantitative Addition of Pyridine

An example of a reference spectrum and a difference spectrum is shown in Fig. 1 (zeolite MOR3). The 1700–1400 cm^{-1} part of the difference plots of all samples is shown in Fig. 2. The IA values of the B, L, and acid OH difference bands were plotted against the amount of added pyridine. Figure 3 shows the result for MOR3. The IA values of the B and acid OH difference bands increased linearly until approximately 14 μmol pyridine had been added. When more pyridine was added, the increase of the B and acid OH difference bands levelled off due to saturation of the B sites. The L-band intensity increased linearly until approximately 18 μmol had been added. The spectrum recorded after pump-

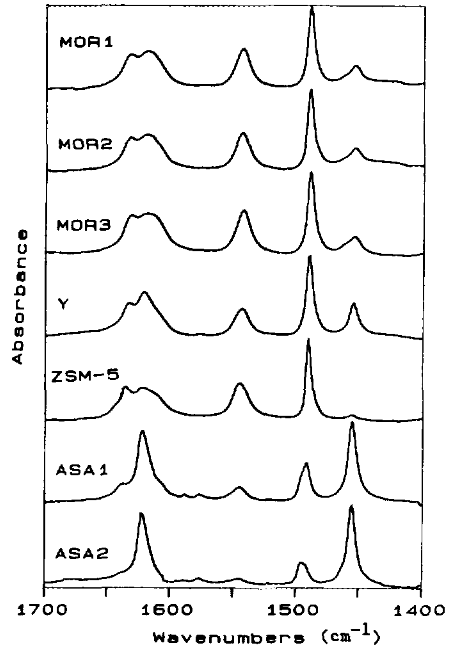

FIG. 2. Difference spectra obtained during addition of pyridine, before saturation occurred.

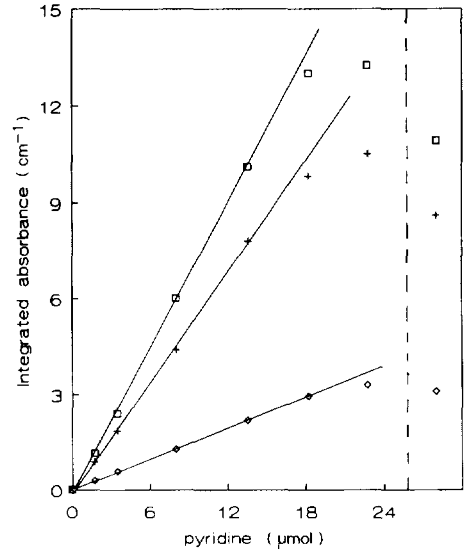

FIG. 3. Integrated absorbances determined for pyridine adsorption by mordenite MOR3. The horizontal axis gives the amount of added pyridine. The integrated absorbances after pumping off excess pyridine at 150°C are shown to the right of the dashed line. □ = 0.5 × acid OH difference band, + = B band, and ◇ = L band.

ing off excess pyridine showed that part of the acid OH groups had not adsorbed pyridine, due to inaccessibility or too low an acid strength. The B, L, and acid OH difference band intensities were then approximately at the level where the linear region ended.

The other zeolites showed a behaviour similar to MOR3. Levelling off occurred for the B and acid OH differences band intensities at 10–30% lower amounts of added pyridine than for the L-band intensity. In the case of the amorphous silica-aluminas (ASAs) the L-band intensity levelled off before the B-band intensity. Acid OH groups could not be distinguished for the ASAs.

Straight lines were drawn by a least-squares fit through the data points in the linear region (see, e.g., Fig. 3). The slopes were determined with a repeatability of approximately 10% (95% confidence). The pyridine pressure in this region was below 10^{-3} Torr and the band intensities did not decrease noticeably when the cell was pumped. This indicates that the added pyridine had been quantitatively adsorbed. To a good approximation, the lines passed through the origin. The amount of pyridine adsorbed by the cell walls is estimated from the intercept to be smaller than 0.1 μmol. The change in cell wall coverage in the linear region is expected to be even smaller. For these reasons, the amount of added pyridine was set equal to the amount adsorbed by the sample, which gives

$$\text{slope}(X) = \Delta \text{IA}(X)/\Delta \text{ (amount of adsorbed pyridine)}, \quad \text{cm}^{-1}/\mu\text{mol} \qquad (3)$$

where

$$X = \text{B, L, acid OH difference bands.}$$

The slopes and the IA values, measured before pyridine addition and after pumping off excess pyridine, are given in Table 2.

Determination of IMEC(B) and IMEC(L)

For simplicity it was assumed that IMEC(B) and IMEC(L) were the same for all B and L sites, respectively, regardless of the catalyst or the acid strength of the site.

TABLE 2

Infrared Spectroscopic Data for Pyridine Adsorption at 150°C by Catalyst Disks of 30 mg and a Radius of 0.9 cm

	MOR1	MOR2	MOR3	Y[a]	ZSM-5	ASA1	ASA2
1	5.03	4	5.66	4.65	6.03	1.38	0.61
2	1.53	3.65	1.63	2.93	0.34	6.29	8.13
3	12.8	8.4	15.8	5.9/2.7	13.2	0	0
4	38	14	32	5.8/4.9	15	0	0
5	9.8	5.1	8.6	3.8	6.7	0.7	0.3
6	4.9	2.6	4.2	2	5.1	0	0
7	3.4	5.6	3.1	3	0.5	2.2	1.9
8	3.7	3.9	2.8	1.9	0.5	1.4	0.8
9	32.5	10.4	21.8	5.5/2.7	15	—	—
10	23	7.5	14.1	4.3/0.6	13	—	—

Note. 1–3 = 10 × slope (Eq. (3)), cm^{-1}/added μmol pyridine; 1 = B, 2 = L, 3 = acid OH difference. 4–10 = integrated absorbances of IR bands, cm^{-1}. 4 = acid OH of dehydrated catalyst. 5 and 6 = B; 7 and 8 = L; 9 and 10 = acid OH difference. 5, 7, 9 = measured after pumping off pyridine at 150°C. 6, 8, 10 = measured after pumping off pyridine at 350°C.

[a] Properties of 3625/3550 cm^{-1} acid OH bands are given.

In the linear region, the sum of the amounts of pyridine adsorbed by B and L sites was equal to the amount of added pyridine. However, the ratio of the amounts of pyridine on B and L sites was not known. Beer's law gave therefore for each catalyst only one equation for IMEC(B) and IMEC(L) (see the Appendix):

$$3.14\ R^2\ [\text{slope (B)/IMEC(B)} + \text{slope(L)/IMEC(L)}] = 1. \quad (4)$$

The resulting set of equations was solved by a least-squares procedure, giving the values

$$\text{IMEC(B)} = 1.67\ \text{cm}/\mu\text{mol} \quad (5)$$

$$\text{IMEC(L)} = 2.22\ \text{cm}/\mu\text{mol}. \quad (6)$$

Statistical analysis of the data showed that the 95% confidence limits were ±0.12 and ±0.21 cm/μmol, respectively. The systematic error (volume, calibration of the pressure meter, determination of IR absorbances) is estimated to be smaller than 5% (95% confidence). The total 95% confidence limits, due to repeatability and systematic errors, are thus estimated at ±15%. Equations for calculating pyridine concentrations with the aid of these IMEC values are given in the Appendix (Eqs. (14) and (15)).

The slopes of the samples obeyed Eq. (4) within 7% (see Table 1). These deviations are smaller than the repeatability of the slope determinations. There is thus no evidence that any of the samples had deviating IMEC values, although it cannot be ruled out that larger variations of IMEC(B) and IMEC(L) occurred but that their effects cancelled out.

The IMEC of Strongly Acid Sites

The IMEC values of Eqs. (5) and (6) are averages for pyridine adsorbed on sites with a range of acidities. The effect of the acid strength on the IMEC was investigated, for zeolite MOR3 only, by adding pyridine at 350°C so that only the strongest acid sites were probed. After pumping off excess pyridine, spectra were recorded at 350°C and then at 150°C, in order to obtain a correction for the influence of temperature on the extinction coefficients. The slope values, corrected to 150°C, were 0.46 (B) and 0.24 (L) $\text{cm}^{-1}/\mu\text{mol}$. Substitution of these values and of Eqs. (5) and (6) into the left-hand side of Eq. (4) gave 0.98. The deviation from 1 lies within the error limit. There are thus no indications that the IMEC values of pyridine adsorbed on the strongest acid sites of this zeolite deviated from the values of Eqs. (5) and (6).

Determination of IMEC(Acid OH)

The assumption that one acid OH group is removed for each pyridinium ion that is formed leads to

$$\text{IMEC(acid OH)} = \text{IMEC(B)} \times \text{slope(acid OH difference)/slope (B)}. \quad (7)$$

Table 3 gives the resulting IMEC(acid OH) values. In the case of zeolite Y, two kinds of acid OH groups were present. The IMEC values could not be determined separately since it was not known in which ratio the two types of OH groups had reacted. The reported value was calculated starting from the assumption that their IMEC values were equal.

TABLE 3

Integrated Molar Extinction Coefficients (IMEC) of Pyridine and Acid OH Groups, Determined at 150°C

Band	Position (cm^{-1})	IMEC (cm/μmol)
Brønsted	1545	1.67
Lewis	1455	2.22
OH/MOR1	3605	4.25
OH/MOR2	3605	3.5
OH/MOR3	3605	4.65
OH/Y	3625	3.1[a]
	3550	3.1[a]
OH/ZSM-5	3605	3.7

[a] Calculated on the assumption that the IMEC values are equal.

DISCUSSION

IMEC Values

The IMEC(B) value obtained in this investigation (1.67 cm/μmol) lies between the value reported in Ref. (*2*) (3.0) and the values of Refs. (*3*) (1.2–1.5) and (*4*) (0.73). The IMEC(L) value (2.22) lies between those of Ref. (*2*) (3.3–3.9) and Ref. *4* (1.11). The catalysts used in Refs. (*2–4*) were similar to those used in the present investigation (Si/Al-based), and the spectroscopic method was the same (transmission measurements on catalyst disks). Differences between the IMEC values are therefore not expected. The origin of the observed differences is not clear but may lie in the experimental procedures and in uncertainties regarding the distribution of pyridine over the B and L sites.

Recently an investigation has been reported in which the concentration of B sites in a ZSM-5 catalyst was determined from elemental analysis, pyridine poisoning of a B-site catalysed reaction and solid-state proton NMR spectroscopy (*5*). The authors concluded that the B-site concentration was 550 μmol/g. The B-site concentration determined from pyridine adsorption/IR measurements, using the IMEC value of Ref. (*2*), was also reported. Recalculating the concentration with the aid of Eq. (5) gives a value of 540 μmol/g. The values agree within the experimental error, which supports the results of the present investigation.

It remains to be investigated whether the IMEC values of Eqs. (5) and (6) also apply to other types of catalysts, e.g., Fe- or Ga-substituted zeolites and Si- or metal-substituted aluminophosphates. In particular IMEC(L) might be different since it belongs in these cases to pyridine directly bonded to an ion other than Al or Si.

The IMEC(acid OH) values lie in a fairly narrow range (3.1–4.7 cm/μmol, see Table 3). In the literature, values between 1 and 20 cm/μmol have been reported (see, e.g., Refs. (*2, 3, 6*)).

Comparison of the Acid Site Concentration with the Al Concentration of Zeolites

The concentration of acid sites, observed by means of IR, was calculated from the spectrum recorded after pumping off excess pyridine at 150°C, by adding the concentrations of occupied B and L sites and remaining acid OH groups. According to the accepted models for acid sites in zeolites, each aluminium ion can give rise to at most one acid site (*7, 8*). The fraction (concentration observed by IR)/(aluminium concentration) is given in Table 1. Fractions greater than 1 were indeed not observed. The deviation from 1 can be due to extralattice aluminium. Also, part of the L sites may not have reacted with pyridine, like part of the acid OH groups.

Rate of Adsorption of Pyridine

The B sites of the zeolites had a lower proportion of strongly acid sites (retaining pyridine at 350°C) than the L sites (see Table 2). If the distribution of pyridine over the sites during addition was thermodynamically controlled, the rate of coverage of B sites compared to that of L sites would at the start of pyridine adsorption have been lower than the ratio of B to L sites finally covered by pyridine. A higher rate of coverage of B sites would be expected near saturation. However, a constant ratio of coverage of B and L sites was observed, indicating kinetic control. Apparently pyridine, once adsorbed by an acid site, is held so strongly that equilibrium cannot be established. Slope(B)/slope(L) was higher than the ratio of B to L sites finally covered by pyridine, which shows that the B sites reacted faster than the L sites. In agreement with this, saturation of the B sites occurred earlier than for the L sites. The adsorption of pyridine by zeolites may be diffusion controlled (*9*). The mobility of the protons may therefore have contributed to the higher reactivity of the B sites.

It appeared that the distribution of pyridine over the B and L sites of the ASAs was kinetically controlled, too. This follows from arguments analogous to those given for the zeolites. The saturation behaviour and a comparison of the ratio of slopes to the ratio of acid sites shows that the L sites of the ASAs reacted faster than the B sites.

CONCLUSIONS

The integrated molar extinction coefficient of the band at 1545 cm^{-1} due to pyridine on a Brønsted acid site is 1.67 cm/μmol and that of the band at 1455 cm^{-1} due to pyridine on a Lewis acid site is 2.22 cm/μmol. These values apply to Si/Al-based catalysts and a measurement temperature of 150°C. The 95% confidence limits are estimated at ±15%. No evidence was found for a dependence of the integrated coefficients on the structure of the catalyst or the strength of the acid site.

APPENDIX

Derivation of Eq. (4)

Integration of Eq. (2) over absorption band X of species Y gives

$$\mathrm{IA(X)} = \mathrm{IMEC(X)}\, c(\mathrm{Y})\, D \qquad (8)$$

$c(\mathrm{Y})$ = concentration of Y in catalyst disk ($\mathrm{mol/dm^3}$)

D = thickness of disk (cm).

The amount of Y per cm^2 catalyst disk (ϕ) is

$$\phi(\mathrm{Y}) = \mathrm{c(Y)\ D},\ \mathrm{millimol/cm^2}. \qquad (9)$$

Combination of Eqs. (8) and (9) gives

$$\phi(\mathrm{Y}) = \mathrm{IA(X)/IMEC(X)}. \qquad (10)$$

The ϕ values of pyridine on B and L sites were not known separately, but their sum was equal to ϕ(pyridine), given by Eq. 12:

$$\phi(\text{pyridine on B sites}) + \phi(\text{pyridine on L sites}) = \phi(\text{pyridine}) \qquad (11)$$

$$\phi(\text{pyridine}) = (\text{amount of adsorbed pyridine})/(3.14\, R^2). \qquad (12)$$

Substituting expressions for ϕ(pyridine on B sites) and ϕ(pyridine on L sites) (Eq. (10)) and ϕ(pyridine) (Eq. (12)) in Eq. (11) gives

$$[\mathrm{IA(B)/IMEC(B)} + \mathrm{IA(L)/IMEC(L)}] = (\text{amount of adsorbed pyridine})/(3.14\, R^2). \qquad (13)$$

Differentiation of Eq. (13) with respect to the amount of adsorbed pyridine and substitution of slope(B) and slope(L) (Eq. (3)) in the resulting equation gives Eq. (4):

$$3.14\, R^2\, [\mathrm{slope(B)/IMEC(B)} + \mathrm{slope(L)/IMEC(L)}] = 1. \qquad (4)$$

Calculation of Pyridine Concentrations

The amount of pyridine per gram catalyst (C) is obtained by dividing ϕ by the weight per cm^2 disk. Using Eq. (10) and the IMEC values of Eqs. (5) and (6), one obtains the following equations:

$$C(\text{pyridine on B sites}) = 1.88\ \mathrm{IA(B)}\, R^2/W; \qquad (14)$$

$$C(\text{pyridine on L sites}) = 1.42\ \mathrm{IA(L)}\, R^2/W. \qquad (15)$$

C = concentration (mmol/g catalyst);

IA(B,L) = integrated absorbance of B or L band (cm^{-1});

R = radius of catalyst disk (cm);

W = weight of disk (mg).

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