An Infrared Study of Acid Sites on Silica-Alumina Catalysts Poisoned with Sodium Hydroxide[1)]

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We investigated the effect of NaOH impregnation on the acidic properties (the type, strength, and amount of acid sites) of silica–alumina by means of IR spectroscopy of chemisorbed pyridine. Most acid sites on the unpoisoned catalyst were of the Lewis type. Some Lewis-bound pyridine was retained on the surface even at 400 °C, but the pyridinium ion was eliminated at 300 °C, indicating that the strong acid sites were also of the Lewis type. Impregnated NaOH affected both Lewis and Brønsted sites. An increase in the amount of NaOH resulted in the elimination of the Brønsted acid sites of medium strength, and also in a significant reduction in the number of Lewis acid sites over the whole range of acid strength. Weak Brønsted acid sites showed no marked change in number. When the NaOH-impregnated catalysts were exposed to pyridine, a new IR band appeared at about 1445 cm^{-1}; this band is attributable to pyridine associated with the Na ions on the surface.

The infrared spectroscopy of pyridine chemisorbed on solid acids permits the differentiation of Lewis acid sites from Brønsted ones.[2,3)] Since the strength of acid sites should be related to the upper limit of the temperature at which the sites are capable of holding pyridine molecules, a measure of the acid strength may be given in terms of the evacuation temperature of chemisorbed pyridine. Thus, the acid-strength distributions of Brønsted and Lewis acid sites will be determined by means of the IR spectroscopy of chemisorbed pyridine combined with its evacuation temperature, which is successively elevated. Recently, a similar IR technique has been applied to silica–alumina[4)] and Y zeolite[5)] catalysts for the purpose of investigating the influence of aluminium extraction on the surface acid properties.

Previous studies have shown that Na-poisoned silica–alumina catalysts decrease in catalytic activity for cumene cracking,[6)] the isomerization of dialkylbenzenes,[6)] and propene origomerization.[7)] A few brief studies have been reported on the effect of alkali-poisoning on the acidic properties of silica–alumina. Parry[2)] has reported that Na-poisoning (0.8 mg-ion/g) markedly reduced the number of Brønsted acid sites on silica–alumina, and also weakened the Lewis acid sites. The IR spectral data obtained by Bourne, Cannings, and Pitkethly[8)] show a partial and nonselective poisoning of the Brønsted and Lewis acid sites on "aluminium-on-silica" with sodium (0.71 wt%). Basila, Kantner, and Rhee[3)] have reported that the K-poisoning (*ca.* 1 mg-ion/g) of silica–alumina resulted in the elimination of the Brønsted sites and a severe weakening of the Lewis acid sites. The present study was undertaken in order to see, in detail, the effect of NaOH poisoning on the acidic properties of silica–alumina by means of the IR spectroscopy of pyridine, which was retained on the surface after evacuation at successively elevated temperatures.

Experimental

Materials. The Na-poisoned silica–alumina catalysts (SA-1-Na-1, -2, -3, and -4) were prepared by soaking the cracking catalyst (SA-1, 13% Al_2O_3) in an aqueous solution of sodium hydroxide and by then evaporating it to dryness. Some physical properties of these catalysts shown in Table 1 are taken from previous papers.[6,9)] The silica gel (S-3, 600 m^2/g) and γ-alumina (A-1, 170 m^2/g) were prepared by the neutral hydrolysis of ethyl orthosilicate and aluminium isopropoxide, respectively, and by calcination at 550 °C in air for 7 h. The two starting materials were distilled two or three times before use. The pyridine was distilled from a reagent of a GR grade, dried over KOH under a vacuum, and finally vacuum-distilled into a vessel containing a molecular sieve 5A, which had been evacuated *in situ* at 350 °C for 2 h before use.

TABLE 1. CATALYSTS

Symbol	Surface area m^2/g	Na$^+$ content mg-ion/g
SA-1	540	0.003
SA-1-Na-1	450	0.048
SA-1-Na-2	480	0.087
SA-1-Na-3	480	0.168
SA-1-Na-4	452	0.807

Sample Preparation and IR Cell. Self-supporting 20-mm diameter wafers of the catalysts were formed by pressing about 50 mg of the samples at 3200 kg/cm^2 in a conventional KBr die. The cell was described in detail in a previous paper.[10)]

Procedures. The wafer mounted in a sample holder was pretreated first in a dry oxygen stream at 550 °C for 2 h and then in a wet oxygen stream at 150 °C for 0.5 h. Afterwards, it was activated in the cell by evacuation at 10^{-4}—10^{-5} mmHg and at 450 °C for 2 h, and then cooled to room temperature. Pyridine vapor (about 16 mmHg) was allowed to equilibrate with the wafer at 150 °C for 1 h after the background spectrum had been recorded. The wafer was evacuated at 150 °C for 1 h and then successively at the desired temperatures for 1 h. After each evacuation, the spectra were recorded on a model DS-401G grating spectrometer (Nihon Bunko) at room temperature. The spectra were scanned at a rate of 1/6 cm^{-1}/s on an expanded wave-number scale (*ca.* 3.3 mm/cm^{-1}). The spectral slit width was approximately 3 cm^{-1} in the 1300—1600 cm^{-1} region.

The band area (or integrated absorbance) was used for the quantitative measurements. The backgrounds for the integration of the bands of adsorbed pyridine were constructed in the same manner as that used by Hughes and White.[11)] The integrated absorbances were normalized so as to indicate the absorbance per unit of "optical thickness" of the wafer. This normalized absorbance, AS/W (cm/g), corresponds to the $\varepsilon M/W$ quantity, where A and ε are, respectively, the integrated absorbance and the apparent integrated molar absorption coefficient of a band, where M is the amount (mmol) of the responsible species, and where S and W are the cross section (cm^2) and weight (g) of the wafer, respectively.

Results and Discussion

Spectra of Adsorbed Pyridine. The absorption spectrum of pyridine adsorbed on S-3 showed that the adsorbate was hydrogen-bonded (HPY) after evacuation for 1 h at room temperature. The characteristic bands appeared at around 1440 and 1600 cm^{-1}, in accordance with Parry's results.[2] The bands disappeared completely upon evacuation at 120 °C for 1 h.

The A-1 catalyst produced Lewis-bound pyridine (LPY) which gave rise to characteristic bands at 1450 and 1492 cm^{-1} when the adsorbed pyridine was evacuated at 150 °C for 1 h. The peak of the 19*b* mode of LPY was slightly shifted from 1450 to 1458 cm^{-1} as the evacuation temperature was raised from 150 to 300 °C. After evacuation at 300 °C, a weak shoulder remained at around 1452 cm^{-1}; the 19*a* mode (1492 cm^{-1}) also split into two bands at 1500 and 1492 cm^{-1}. A similar shift of the 19*b* mode has been reported for η-alumina.[2] No conversion occurred from LPY into the pyridinium ion (BPY) exhibiting characteristic bands at around 1540 and 1490 cm^{-1}, on dosing water vapor, as has been reported in the literature.[2,3,11]

The spectra of pyridine adsorbed on SA-1 and Na-poisoned SA-1 are illustrated in Fig. 1. After evacuation at 150 °C for 1 h, the pyridine adsorbed on SA-1 displayed three bands, at 1455, 1493, and 1540 cm^{-1}, indicating the coexistence of Lewis and Brønsted acid sites on the surface. The 19*b* mode (1540 cm^{-1}) of BPY disappeared upon evacuation at 300 °C for 1 h (Spectrum b). It has already been shown that this disappearance is accompanied by a partial loss of the Brønsted acid sites.[10]

The splitting of the bands at 1455 and 1493 cm^{-1} took place after evacuation at 300 °C, as was also observed for A-1. The original bands remained with reduced intensities, and additional bands appeared at 1462 and 1497 cm^{-1} (Spectrum b). The 1462 cm^{-1} band, as well as the 1458 cm^{-1} band for A-1, is probably due to another kind of pyridine bound to a Lewis acid site stronger than that characterized by the 1455 cm^{-1} band. Other researchers have reached the same conclusion.[2,4,8] The appearance of the 1497 cm^{-1} band is probably related to the same Lewis acid site as that for the band at 1462 cm^{-1}. The 19*b* mode (1455 and 1462 cm^{-1}) of LPY still remained even after evacuation at 400 °C (Spectrum c), in contrast with that of BPY. This fact implies that the strong acid sites on SA-1 are of the Lewis type. The addition of water vapor converted LPY into BPY, as is well known.

When the Na-poisoned catalysts were exposed to pyridine vapor and then evacuated at 150 °C for 1 h, the adsorbed pyridine produced the same spectra as those obtained for SA-1, except for the appearance of a new band. The new absorption occurred at 1445 cm^{-1} without the appearance of the 1600 cm^{-1} band characteristic of HPY; it was especially pronounced for SA-1-Na-4 (Fig. 1B). This band disappeared upon evacuation at 200 °C for SA-1-Na-1 or -2, but it remained even after evacuation at 300 °C for SA-1-Na-4. Additionally, the band is very similar in frequency to a band at 1438—1445 cm^{-1} due to pyridine adsorbed on the Na ion in Na-exchanged X or Y zeolites.[12] Therefore, the new band is attributable to pyridine associated with the Na ion on the surface, rather than to hydrogen-bonded pyridine. A similar band has also been found on Na-exchanged "aluminium-on-silica."[8] The three

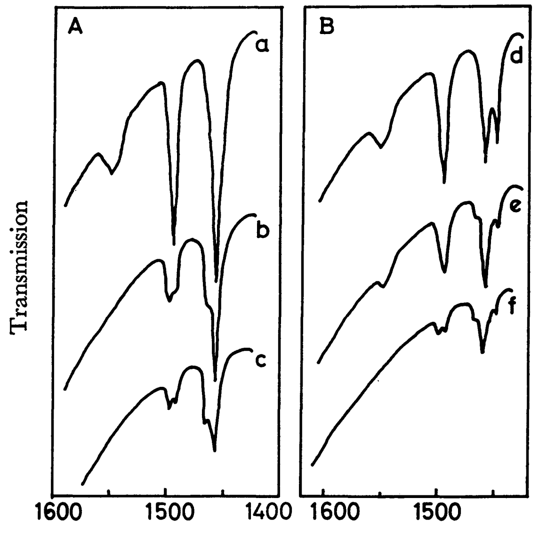

Fig. 1. Infrared spectra of pyridine chemisorbed on slica-alumina catalysts. Spectra A with SA-1 were recorded after evacuation at 150 (a), 300 (b), and 400 °C (c); spectra B with SA-1-Na-4 were obtained after evacuation at 150 (d), 200 (e), and 300 °C (f).

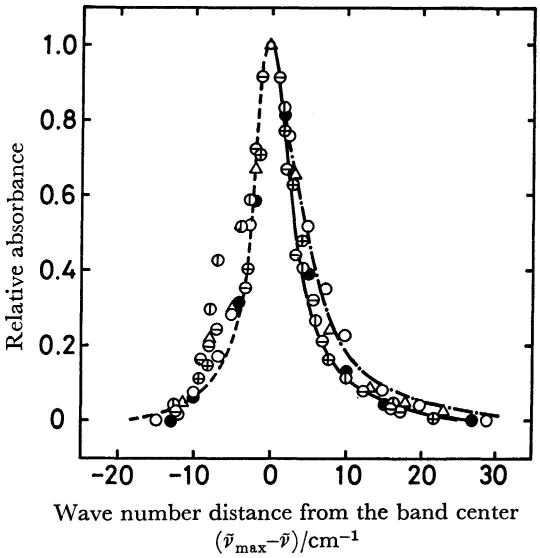

Fig. 2. Band shapes of the 19*b* mode (1455 cm^{-1}) due to Lewis-bound pyridine on various catalysts.
△, ○: SA-1 (150 °C evac.); ●: SA-1 (200 °C evac.); ⦶: SA-1 (300 °C evac.); ⊖: SA-1-Na-1 (200 °C evac.); ⊕: SA-1-Na-2 (200 °C evac.).

other bands at 1455, 1490, and 1540 cm^{-1} behaved in essentially the same way as SA-1 when the evacuation temperature was raised or when water vapor was dosed. Since the 1455 cm^{-1} band overlapped to a considerable extent with the 1445 cm^{-1} band (Fig. 1B), the deconvolution of the observed band into these two components was necessary for quantitative measurements of the Lewis acid sites on the Na-poisoned catalysts. The deconvolution was carried out in the manner described below.

Deconvolution of the Overlapped Bands Near 1450 cm^{-1}. In Fig. 2, representative absorption bands at 1455 cm^{-1} are plotted in a normalized form for the catalysts which exhibit no absorption band at 1445 cm^{-1}. The solid and chain lines in Fig. 2 represent two types of Lorentz curves, whose respective half-widths are 7 and 10 cm^{-1}. Apparently, the right half of an absorption curve is fitted approximately by a Lorentz curve with a half-width of 10 cm^{-1} for the bands recorded after evacuation at 150 °C, or by one with a half-width of 7 cm^{-1} for the bands obtained after evacuation at 200 or 300 °C. A Lorentz curve (broken line) with a half-width of 5 cm^{-1} fits the left half of an absorption curve for all the bands, except for a shoulder at around 1460 cm^{-1}.

The procedure for resolving the 1455 cm^{-1} band from the 1445 cm^{-1} band is based on these findings, as illustrated in Fig. 3. First, the shape of the right half of the 1455 cm^{-1} band was determined by drawing a Lorentz curve (broken line) with a half-width of 7 or 10 cm^{-1} from the peak onto the lower-frequency side. Secondly, the absorption curve (dotted line) of the 1445 cm^{-1} band was determined by subtracting the absorption curve of the 1455 cm^{-1} band from the observed curve (solid line).

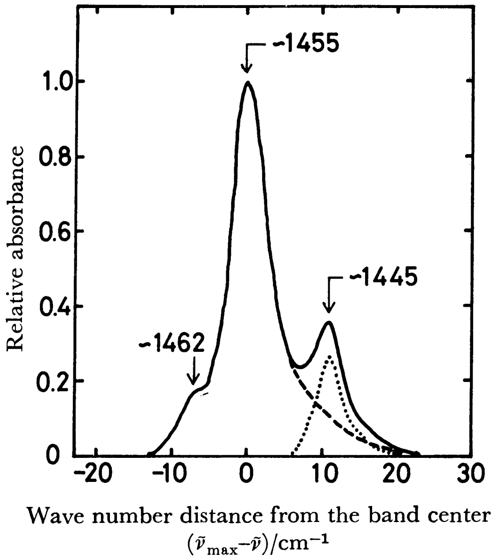

Fig. 3. Illustration of deconvolution of the observed band into the 1455 and 1445 cm^{-1} bands. Original spectrum was recorded after evacuation of pyridine chemisorbed on SA-1-Na-2 at 200 °C.

Changes in Acidic Properties. The two bands at 1455 and 1540 cm^{-1} were chosen to measure the numbers of the Lewis and Brønsted acid sites, respectively. Figure 4 shows the integrated absorbances of the two bands recorded after evacuation at the indicated temperatures for all the catalysts. These absorbances are related quantitatively to the numbers of acid sites capable of retaining the pyridine at the respective temperatures. Since the apparent integrated molar absorption coefficient is approximately the same for the two bands.[11,13] The results shown in Fig. 4 also permit a direct comparison between the Lewis and Brønsted acidities. The acid-strength distributions of the Lewis and Bronsted acids are given in Table 2, in which the number of acid sites is represented as the ratio relative to the total amount of the corresponding type of acid for each catalyst. In Table 3, the integrated absorb-

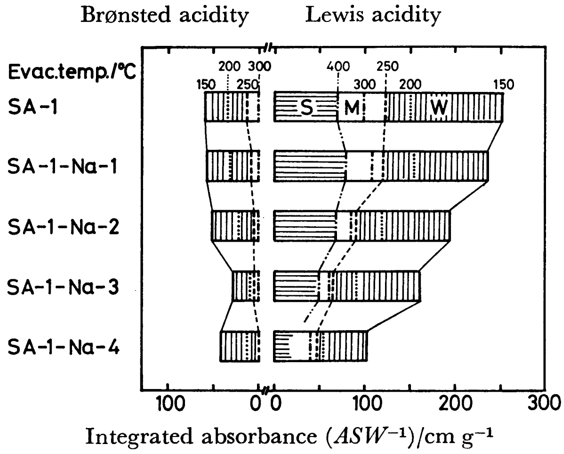

Fig. 4. Acidic properties of catalysts.
S: Strong, M: medium, W: weak.

TABLE 2. ACID-STRENGTH DISTRIBUTION

	Lewis acid			Brønsted acid		
	Weak[a]	Medium[a]	Strong[a]	Weak	Medium	Strong
SA-1	0.51	0.14	0.35	0.77	0.23	0
SA-1-Na-1	0.48	0.19	0.33	0.87	0.13	0
SA-1-Na-2	0.53	0.11	0.35	0.91	0.09	0
SA-1-Na-3	0.60	0.10	0.30	0.88	0.12	0
SA-1-Na-4	0.54	0.46		1.0	0	0

a) Weak and medium sites are incapable of retaining the pyridine in the evacuation temperature (T_e) ranges of $150 < T_e/°\mathrm{C} \leqslant 250$ and $250 < T_e/°\mathrm{C} \leqslant 400$, respectively; strong sites are capable of retaining the pyridine at $T_e/°\mathrm{C} = 400$; their amounts are given as ratios relative to the total amount of the corresponding type of acid for each catalyst.

Table 3. Integrated absorbances^a) of the 1445 cm^{-1} band on Na-poisoned catalysts

Catalyst	Evacuation temperature/°C		
	150	200	300
SA-1-Na-1	17	0	0
SA-1-Na-2	27	0	0
SA-1-Na-3	35	7	0
SA-1-Na-4	38	13	3

a) ASW^{-1}/cm g^{-1}.

ances of the 1445 cm^{-1} band are listed for the Na-poisoned catalysts.

Figure 4 indicates that most (*ca.* 80%) of the acid sites on unpoisoned SA-1 are of the Lewis type. Of the Lewis acid sites, about 35% are so strong as to be capable of holding the pyridine even at 400 °C; about a half are weak, so the pyridine is evolved at 250 °C; the remainder are medium in acid strength. The Brønsted acid sites are not so strong as the Lewis acid sites, since they are incapable of retaining the pyridine even at 300 °C. A similar trend is also found in the results of Ballivet, Barthomeuf, and Pichat.4) Therefore, such a trend seems general in the acidic properties of dehydroxylated silica–alumina.

The poisoning effect of the impregnated NaOH is apparent on both Lewis and Brønsted acidities, as may be seen in Fig. 4. The Lewis acid sites are markedly decreased in number as the Na^+ content is increased. However, the acid-strength distribution of Lewis acid sites shows no significant change, as is shown in Table 2. This implies that the poisoning action is exerted to an almost equal extent on the sites over the whole range of acid strength; hence, it does not mean that the impregnated NaOH weakens the Lewis acid sites, in contrast with the results of the previous researchers.3) Of the Brønsted acid, a considerable change in the acid-strength distribution is noticed (Table 2). The Brønsted acid sites of medium strength are decreased in number with an increase in the Na^+ contents, and finally are eliminated (Fig. 4 and Table 2). The weak Bronsted acid sites show no significant change in number. Consequently, the Brønsted acid sites on the poisoned catalysts are weakened and also reduced in number with the impregnated NaOH.

Therefore, the present data confirm the general agreement in the literature2,3,8) that alkali ions affect both Lewis and Brønsted acid sites over silica–alumina. Such behavior of alkali ions cannot be expected only as a result of their exchange with the protons of Brønsted acid sites. Many other complex chemical processes are probably involved in alkali poisoning. For example, our poisoned catalysts are probably partially hydrolyzed during the course of preparation. There are some differences in the poisoning effect between the present results and those in the literature,2,3) as has been mentioned above. This strongly suggests that the poisoning effect of alkali ions also considerably varies depending on the preparation of poisoned catalysts. Thus, one must be careful about interpreting the results of alkali ion poisoning unless the effect of poisoning has been well characterized.

Table 3 indicates that, in the range of low Na^+ content (SA-1-Na-1 and -2), the absorbance of the 1445 cm^{-1} band after evacuation at 150 °C increases almost proportionally to the increase of Na^+ content, but its increase becomes slight more and more as the Na^+ content is additionally increased (SA-1-Na-3 and -4). This finding implies that, in the range of high Na^+ content, the number of pyridine molecules interacting with the Na ions is limited. However, the interaction is strengthened more and more with an increase in the Na^+ contents. Therefore, these findings suggest that, when the Na ions are increased in amount, they may be distributed in groups over the surface. This type of distribution may restrict sterically the number of pyridine molecules interacting with the Na ions, but may enhance electrostatically the interacting power of the Na ions.

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