Direct Measurement of the Interaction Energy between Solids and Gases. XI. Calorimetric Measurements of Acidities of Aluminum Deficient H-Y Zeolites

Yoshio Mitani,[††] Kazuo Tsutsumi,*,[†] and Hiroshi Takahashi
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
[†]*Toyohashi University of Technology, Tempaku-cho, Toyohashi 440*

(Received December 2, 1982)

Heats of adsorption of pyridine and ammonia were respectively measured on aluminum deficient H–Y zeolites using a microcalorimeter at 473 K. The calorimetrically determined acidity was discussed in relation to the positional difference between 3640 and 3550 cm^{-1}-OH acidic sites and compared with the catalytic activity. Dealumination generally brings about a decrease in the acid site concentration. However, the extent of the decrease varied with the kind of titrated base and a significant change was observed in the ratio of acid site concentration when titrated with pyridine. This may be explained by the fact that the pore size of the zeolite becomes widely distributed as dealumination proceeds; 3550 cm^{-1}-OH sites in supercages must become accessible to such a large molecule as pyridine. Also observed with dealumination was a slight increase in the heat of adsorption from initial to the middle stage of adsorption, which reflected the enhancement in acid strength of each OH site. The catalytic activity for cumene cracking increased with dealumination, which agreed with the acidity determined by the adsorption of pyridine rather than ammonia.

The acid strength of catalysts has widely been studied in relation to catalytic activity by use of butylamine and coloured indicators.[1–3] However, since it was not certain whether adsorption of butylamine selectively occurred on strong sites in preference to weak sites and whether the molecular size of butylamine was same with that that of reactant, the concentration obtained often deviated from the true value.[4]

In our previous papers,[5,6] the selective adsorption of bases was confirmed to occur onto strong sites in high temperature range above *ca.* 473 K and acid strength was determined as heats of adsorption by calorimetry. In addition, the relative acid strength changed with the kind of titrated base. Thus, the acid strength of solid surfaces should be investiated with respect to basic properties of adsorbate in high temperature range.

In the present work, the acid strength of Al-deficient H–Y zeolites was measured by pyridine and ammonia adsorption. The difference in acid strength between 3640 and 3550 cm^{-1}-OH sites will be discussed in correlation to the positional difference, which is useful for correlating calorimetric acid strength with catalytic activity.

Experimental

NH_4–Y zeolite was obtained by repeated ion exchange of Na-form zeolite (Linde SK 40) in 1 mol/dm^3 NH_4Cl solution at *ca.* 323 K. Al-deficient zeolites were prepared by means of a slow addition of ethylenediaminetetraacetic acid (H_4EDTA) as described by Kerr.[7] Table 1 shows chemical compositions of zeolites determined by chemical analysis. Ammonia and pyridine were purified by the freeze-thaw method before use.

Table 1. Zeolite compositions

Sample	Composition
H-$Y_{5.0}$	$0.72(NH_4)_2O\cdot0.15Na_2O\cdot Al_2O_3\cdot5.0SiO_2$
H-$Y_{7.4}$	$0.68(NH_4)_2O\cdot0.19Na_2O\cdot Al_2O_3\cdot7.4SiO_2$
H-$Y_{10.3}$	$0.67(NH_4)_2O\cdot0.16Na_2O\cdot Al_2O_3\cdot10.3SiO_2$

After the sample (0.25—0.50 g) was outgassed for 5 h at 673 K under a pressure of 1 mPa, differential heats of adsorption of bases were measured at 473 K using a twin-conduction type microcalorimeter as described previously.[8] IR spectra were obtained at 473 K by the *in situ* method as described eleswhere.[5]

Catalytic activity for cumene cracking reaction was tested in a microreactor made of stainless steel of 0.3 cm in inner diameter, connected to a conventional gas chromatography assembly with a product trap. The catalyst (0.25 g) was pretreated in a stream of helium at 673 K for 3 h. The cracking activity was determined at 543 K by injecting cumene (10^{-2} cm^3 as liquid) into the carrier gas, He, stream (60 cm^3/min). The gas chromatographic separation of the products was carried out with a column of 20 wt% dioctyl sebacate on 100—120 mesh Uniport B at 473 K. Catalytic activity was given in terms of the conversion of cumene to propylene and benzene during the first pulse reaction.

Results and Discussion

Heats of adsorption of ammonia and pyridine were measured on H–$Y_{5.0}$, H–$Y_{7.4}$, and H–$Y_{10.3}$ as shown in Figs. 1 and 2. The change of acid site strength with dealumination could be compared each other in both

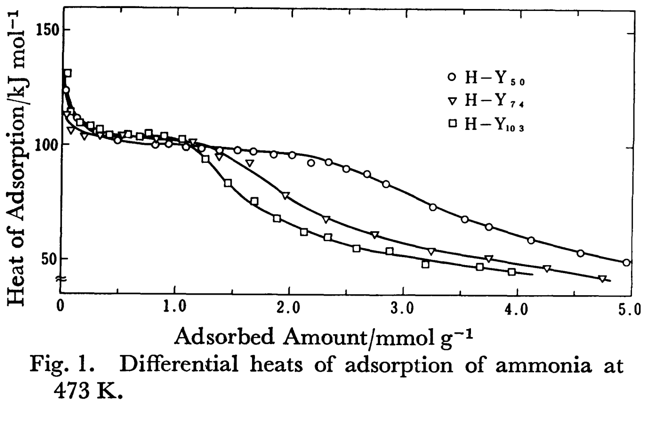

Fig. 1. Differential heats of adsorption of ammonia at 473 K.

[††] Present address: Tokuyama Soda Co., Ltd., Mikage-cho, Tokuyama, Yamaguchi 745.

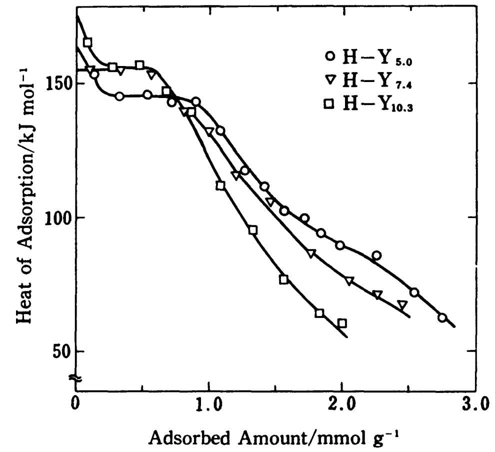

Fig. 2. Differential heats of adsorption of pyridine at 473 K.

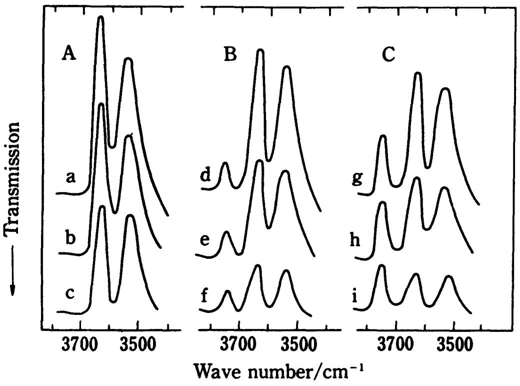

Fig. 3. Infrared spectra of hydroxyl bands measured at 473 K.

(A): On H-Y$_{5.0}$, (B): on H-Y$_{7.4}$, (C): on H-Y$_{10.3}$; (a), (d), and (h): evacuated at 673 K then cooled to 473 K; (b), (e), and (i): 0.5 mmol/g of ammonia added to (a), (d), and (h); (c), (f), and (j): 1 mmol/g of ammonia added to (a), (d), and (h)

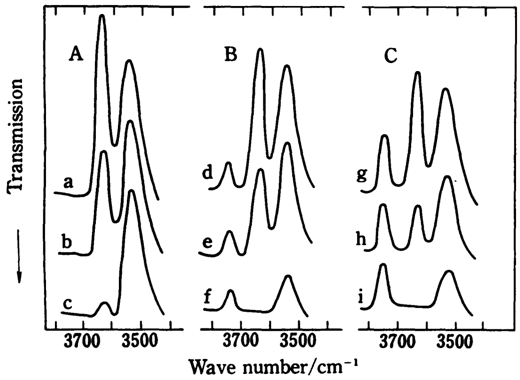

Fig. 4. Infrared spectra of hydroxyl bands measured at 473 K.

(A): On H-Y$_{5.0}$, (B): on H-Y$_{7.4}$, (C): on H-Y$_{10.3}$; (a), (d), and (h): evacuated at 673 K then cooled to 473 K; (b), (e), and (i): 0.5 mmol/g of pyridine added to (a), (d), and (h); (c), (f), and (j): 1 mmol/g of pyridine added to (a), (d), and (h)

cases of ammonia and pyridine adsorption on the basis of heat curves. Dealumination generally brought about a decrease in the number of OH sites, which corresponded to a decrease in the plateau region on heat curves. The ratio of the adsorbed amount in the plateau region to the total number of OH sites which was calculated from zeolite compositions may be assumed to reflect a relative concentration of effective acid sites. Its value depended on the kind of adsorbates, and the proportions of the value obtained by pyridine adsortipn to that by ammonia were 0.4 for H-Y$_{5.0}$, 0.45 for H-Y$_{7.4}$, and 0.55 for H-Y$_{10.3}$. This suggests that some OH sites become accessible to pyridine in progress of dealumination.

Figures 3 and 4 show changes of IR spectra of hydroxyl bands with adsorption of ammonia and pyridine, respectively. Acid sites of H-Y zeolites are known to originate from 3640 and 3550 cm^{-1}-OH sites, and the 3750 cm^{-1}-OH sites are to be silicious sites. On H-Y$_{5.0}$, the strength of both acidic OH sites was found to be approximately similar for the adsorption of ammonia, however, only 3640 cm^{-1}-OH sites acted as strong acid sites for pyridine because of differences in accessibility.[6] A consideration of these facts must account for observations that both OH sites interacted with ammonia on H-Y$_{5.0}$ and their band intensities decreased simultaneously (Fig. 3-A) while that only the 3640 cm^{-1}-OH sites interacted with pyridine and the intensity of the 3550 cm^{-1}-OH band remained unchanged (Fig. 4-A). However, preferential adsorption of pyridine on the 3640 cm^{-1}-sites became less significant as revealed in the change of intensity ratios of the 3640 cm^{-1} band to the 3550 cm^{-1} one with progress of dealumination (Fig. 4-B, C). This suggests that a part of the 3550 cm^{-1}-OH sites became somewhat accessible to pyridine. On the other hand, intensity ratios remained almost constant in case of ammonia adsorption (Fig. 3-B, C), which suggests that accessibility of both OH sites to ammonia seemed not to change with dealumination.

Structural change with dealumination was also examined in relation to accessibility to bases of both OH sites. A half width and integral intensity of X-ray profiles suggested that the framework structure of H–

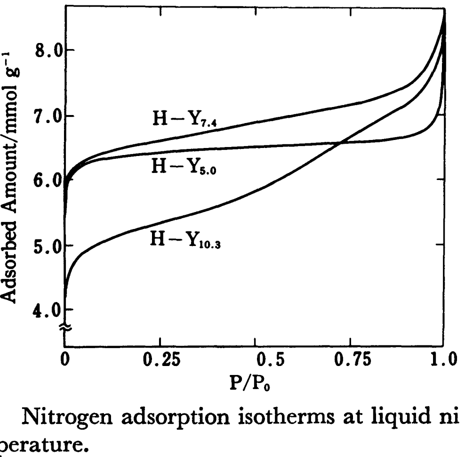

Fig. 5. Nitrogen adsorption isotherms at liquid nitrogen temperature.

(A): On H-Y$_{5.0}$, (B): on H-Y$_{7.4}$, (C): on H-Y$_{10.3}$

TABLE 2. CATALYTIC ACTIVITY FOR CUMENE CRACKING REACTION AT 543 K

Catalyst	Conversion/%
H–$Y_{5.0}$	56
H–$Y_{7.4}$	76
H–$Y_{10.3}$	76

$Y_{10.3}$ was partially destroyed, while that of H–$Y_{7.4}$ was almost unchanged. Figure 5 shows nitrogen adsorption isotherms on zeolites. The rectangular shape of the isotherm on H–$Y_{5.0}$ suggested that the zeolite was of a regular pore structure. However, the pore size must become widely-distributed with dealmination as revealed in the shapes of isotherms on H–$Y_{7.4}$ and H–$Y_{10.3}$. The positional assignments were demonstrated by Eberly[9] and others[10,11] that H-atoms contained in 3550 cm^{-1}-OH sites existed in hexagonal prisms with maximum entrance diameter of 2.2—2.5 Å and that those in 3640 cm^{-1}-OH sites in supercages with maximum entrance diameter of *ca.* 9 Å. In consideration of both structural change with dealumination and positional assignments of OH sites, 3550 cm^{-1}-OH sites were concluded to become accessible to large molecule of pyridine in respect of size as dealumination proceeded. Since ammonia was considered to be adsorbed close to 3550 cm^{-1}-OH sites even on H–$Y_{5.0}$,[6] the accessibility of OH sites did not change with dealumination. On the other hand, 3640 cm^{-1}-OH sites on these three zeolites were considered to be equally accessible to both pyridine and ammonia in respect of size. These results in Al-deficient zeolites supported the previous discussion[6] that the difference in the acid strength between two OH sites was explained in terms of positional differences. The acid site strength on Al-deficient zeolites proved to be somewhat larger than that on H–$Y_{5.0}$ as judged by heats of adsorption at plateau region in Figs. 1 and 2.

The catalytic activity for cumene cracking was weaker on H–$Y_{5.0}$ than on Al-deficient H–$Y_{7.4}$ and H–$Y_{10.3}$ as shown in Table 2. A comparison of the result with the acidic properties shown in Figs. 1 and 2 suggested that the activity seemed to correlate with the acidity determined by pyridine rather than by ammonia. In case of pyridine adsorption, it was found that the acid site concentration remained nearly constant and its strength was rather enhanced on dealumination. In case of ammonia adsorption, however, the acid site concentration decreased significantly with dealumination. Ward[12] demonstrated on the basis of IR measurements on H–$Y_{5.0}$ that only 3640 cm^{-1}-OH sites were affected by cumene at 523 K. In a previous paper,[6] piperidine was found to affect simultaneously both 3640 and 3550 cm^{-1}-OH sites. This was considered to be attributable to strong basicity of piperidine, while its molecular size is almost the same as that of pyridine. All the data lead to the notion that the activity for acid-catalyzed reaction should be discussed in relation to the surface acidity only in cases in which the basic molecule used has similar size to that of the reactant and selectively interacts with active sites.

References

1) H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).
2) H. A. Benesi, and B. H. C. Winquist, *Adv. Catal.*, **27**, 97 (1978).
3) W. Klading, *J. Phys. Chem.*, **80**, 262 (1976).
4) M. Deeba and W. K. Hall, *J. Catal.*, **60**, 417 (1979).
5) K. Tsutsumi, Y. Mitani, and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **56**, 1912 (1983).
6) Y. Mitani, K. Tsutsumi, and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **56**, 1917 (1983).
7) G. T. Kerr, *J. Phys. Chem.*, **72**, 2594 (1968).
8) K. Tsutsumi, S. Hagiwara, Y. Mitani, and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **55**, 2572 (1982).
9) P. E. Eberly, Jr., *J. Phys. Chem.*, **71**, 1717 (1967).
10) D. H. Olson and E. Dempsey, *J. Catal.*, **13**, 221 (1969).
11) J. W. Ward, *J. Phys. Chem.*, **73**, 2086 (1969).
12) J. W. Ward, *J. Catal.*, **11**, 259 (1968).