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Direct Measurement of the Interaction Energy between Solids and Gases. X. Acidic Properties of Hydroxyl Sites of H–Y Zeolite Determined by High-temperature Calorimetry

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Differential heats of adsorption of bases on H–Y zeolite were measured at 473 K and separated into those evolved at 3640 and 3550 cm^{-1}-OH sites respectively by a combined use of calorimetric and IR measurements, and then the acid strength of two OH sites was compared each other. In case of pyridine, heats of adsorption were larger on OH sites at 3640 cm^{-1} than 3550 cm^{-1}, which was in agreement with the results obtained by many authors by IR measurements. However, heats of adsorption on 3640 cm^{-1}-OH sites were only slightly higher than those on 3550 cm^{-1}-OH sites in case of ammonia, and almost the same in case of piperidine. The difference in heats of adsorption between the OH sites was explained by positional difference between the two OH sites, molecular size of the titrated bases and proton mobility induced by a strong base. The order of the strength of bases was determined by replacing a base molecule with another one on H–Y zeolite as follows; piperidine>pyridine>ammonia. This differs from the order expected from their pK_a values in solution.

Infrared measurements have revealed that 3640 cm^{-1}-OH sites were stronger in their acidity than 3550 cm^{-1}-OH sites.[1,2] However, heats of adsorption of bases have not yet been measured on the respective OH sites until now. In the present work, bases were adsorbed on original and poisoned H–Y zeolites at 473 K and heats of adsorption were then measured. Since the selective adsorption on the acid sites occurred at 473 K in each case of pyridine and ammonia as was confirmed previously,[3] heats of adsorption could be separated into those resulted from 3640 and 3550 cm^{-1}-OH sites respectively by a combined use of calorimetric and IR measurements.

Experimental

NH_4–Y zeolite was prepared by treating Y-type zeolite, SK-40, which was supplied by Linde Co. in the sodium form, several times with 1 mol dm^{-3} NH_4Cl solution at *ca.* 323 K. The chemical composition of the sample was analyzed as follows; $0.72(NH_4)_2O \cdot 0.15Na_2O \cdot Al_2O_3 \cdot 5.0SiO_2$. It could be converted to H–Y zeolite by the pretreatment before measurements. The sample was used in granular form of 28—60 mesh for calorimetric measurements. Ammonia was obtained from Matheson Co., and pyridine and piperidine from Wako Pure Chemicals Co. They were purified by the freeze-thaw method.

Differential heats of adsorption were measured at 473 K by a twin-conduction type microcalorimeter as described in a previous paper.[4] IR measurements were carried out by the *in situ* method described elsewhere.[3] Samples were outgassed for 5 h under a pressure of 10^{-3} Pa at 673 K before calorimetric and IR measurements.

Results

Heats of Adsorption and IR Spectra. Heats of adsorption of bases on H–Y were measured at 473 K and shown in Fig. 1. The H–Y was estimated to possess 4.73 mmol g^{-1} of positively charged sites from the view point of chemical composition. Heats of adsorption could be measured over a wide range in case of ammonia, but only below *ca.* 3 mmol g^{-1} in cases of pyridine and piperidine. This can be attributed to pore structure of the zeolite and molecular size of a base. In fact, the amount of adsorption at relative pressure of 0.25 was measured as 3.65 and 3.47 mmol g^{-1} at 293 K for pyridine and piperidine respectively, and as 9.3 mmol g^{-1} at 252 K for ammonia.

Figure 2 shows changes of hydroxyl bands with adsorption or desorption of bases. Since no Lewis acid site on H–Y was detected on the spectra between 1800—1200 cm^{-1} after adsorption of bases, only OH sites (Brønsted acid sites) were taken into account hereafter. In adsorption and desorption processes, only 3640 cm^{-1}-OH band was preferentially perturbed by pyridine (Fig. 2-D,E), while both of the 3640 and 3550 cm^{-1}-OH bands were simultaneously perturbed by ammonia (Fig. 2-B,C) and the behavior of perturbation by piperidine was intermediate between the former two cases (Fig. 2-F,G,H).

Separation of Heats of Adsorption into Heats Evolved at 3640 and 3550 cm^{-1}-OH Sites. Since the 3640 cm^{-1}-OH band was preferentially poisoned by pyridine,

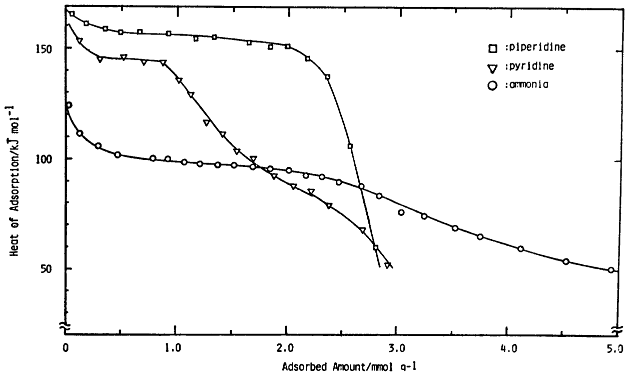

Fig. 1. Differential heats of adsorption of bases measured at 473 K.

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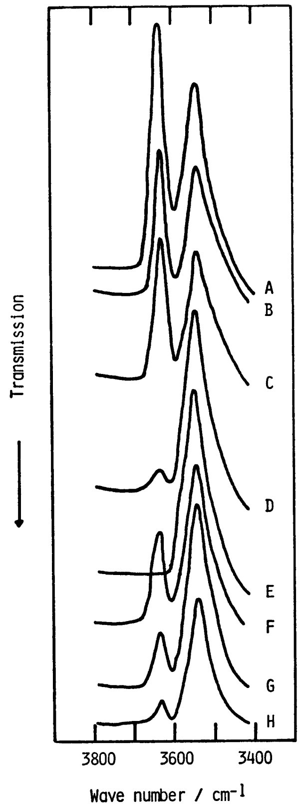

Fig. 2. Hydroxyl bands on H–Y after adsorption or desorption of bases. A: Original H–Y evacuated at 673 K then cooled to 473 K, B: 1 mmol g^{-1} of ammonia added to A, C: evacuated at 473 K after ammonia addition, D: 1 mmol g^{-1} of pyridine added to A, E: evacuated at 473 K after pyridine addition, F: 1 mmol g^{-1} of piperidine added to A, G: evacuated at 673 K after piperidine addition, H: evacuated at 573 K after piperidine addition.

one could easily obtain the H–Y which posessed only 3550 cm^{-1}-OH sites (Fig. 2-E). Heats of adsorption of pyridine were measured on the original and poisoned H–Y as shown in Fig. 3. The heat curve of the poisoned H–Y was almost superimposed on the original H–Y in the coverage above 1.6 mmol g^{-1}. Therefore, heats of adsorption of pyridine on the 3640 cm^{-1}-OH sites proved to correspond to a region above 105 kJ mol^{-1} involving the plateau leveling at *ca.* 145 kJ mol^{-1} and those on the 3550 cm^{-1}-OH sites, to a region below 105 kJ mol^{-1}.

Figure 4 shows heats of adsorption of ammonia on the original and pyridine-poisoned H–Y. On the original H–Y, the heat should result from the simultaneous adsorption on both 3640 and 3550 cm^{-1}-OH sites (Fig. 2-B). In addition, the acid strength of the 3550 cm^{-1}-OH sites must be weakened by poisoning the 3640 cm^{-1}-OH sites with pyridine. In fact, the band near 3550 cm^{-1} shifted by about 8 cm^{-1} to a lower frequency by pyridine adsorption. Moreover, a semi-quantitative IR analysis revealed that the amount of ammonia irreversibly adsorbed on the 3550 cm^{-1}-OH sites of the poisoned H–Y after addition of excess ammonia and subsequent evacuation at 473 K was one-third of that of the original H–Y. For these reasons, the difference between two curves does not necessarily correspond to actual difference in heats of adsorption between two types of OH sites. However, it seems likely that the difference would not be negligible but remarkably smaller than that obtained in case of pyridine.

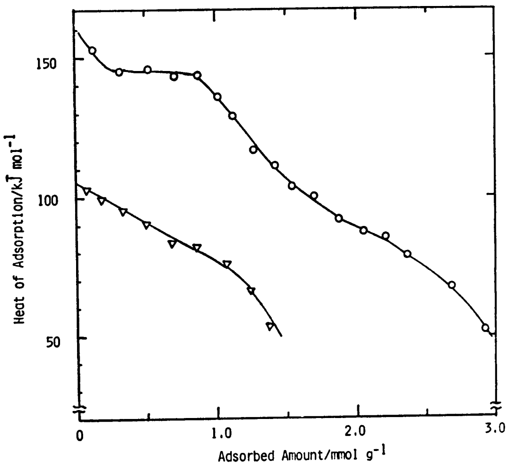

Fig. 3. Differential heats of adsorption of pyridine measured at 473 K. ○: On original H–Y, ▽: on the H–Y after pyridine addition followed by evacuation at 473 K, only 3640 cm^{-1}-OH sites were thus poisoned (see Fig. 2-E)

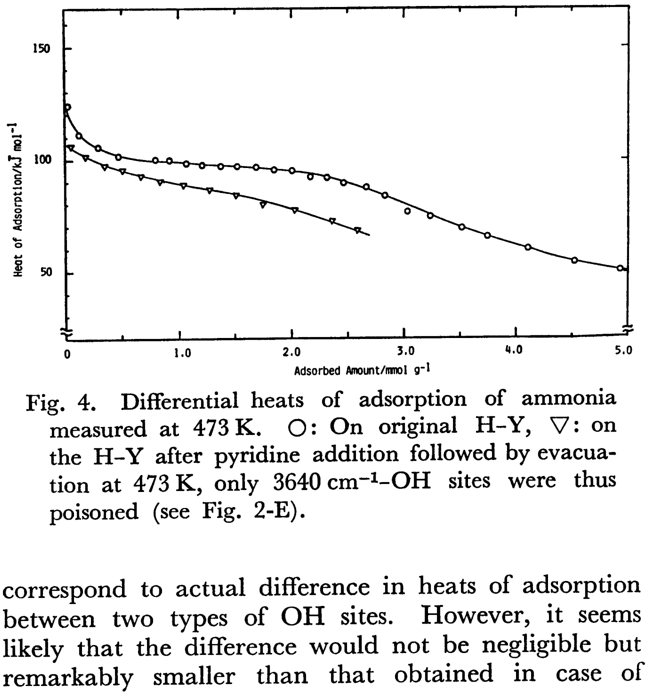

Fig. 4. Differential heats of adsorption of ammonia measured at 473 K. ○: On original H–Y, ▽: on the H–Y after pyridine addition followed by evacuation at 473 K, only 3640 cm^{-1}-OH sites were thus poisoned (see Fig. 2-E).

In case of piperidine adsorption, the pyridine-poisoned H–Y was not available, because pyridine was easily replaced by piperidine on the surface as discussed later. The H–Y was, therefore, poisoned by piperidine, and heats of adsorption of piperidine were measured on it (Fig. 5). Although the poisoning by piperidine was not necessarily selective as shown in Fig. 2-G,H, the result obtained on the poisoned H–Y by piperidine addition and subsequent evacuation at 673 K could be considered to reflect the heat evolved by adsorption mainly on the 3640 cm^{-1}-OH sites. From the fact that heats of adsorption on this sample and on the original H–Y were almost equivalent, it is suggested that both OH sites were energetically same for piperidine adsorption. A decrease in heats at higher coverage which was more explicit in samples evacuated at lower temperatures after piperidine poi-

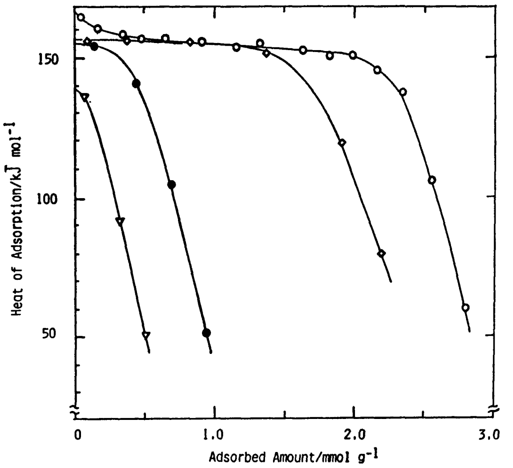

Fig. 5. Differential heats of adsorption of piperidine measured at 473 K. ○: On original H-Y, ◇: on the H-Y after piperidine addition followed by evacuation at 673 K (see Fig. 2-G), ●: On the H-Y after piperidine addition followed by evacuation at 573 K (see Fig. 2-H), ▽: on the H-Y after piperidine addition followed by evacuation at 473 K, both OH bands of this sample were found to be poisoned.

soning can best be explained by a decrease in the number of specific adsorption sites.

Determination of the Order of Basic Strength. The order of basic strength has often been taken as piperidine>ammonia>pyridine, considering their pK_a values in aqueous solutions (piperidine, 11.1; ammonia, 9.3; pyridine, 5.2).[1,5] However, in the present work, the order was examined directly by means of replacing basic molecules with another one on H-Y surface. First, in order to compare basic strength of piperidine with that of pyridine, the poisoned H-Y with pyridine (Fig. 2-E or Fig. 6-A) was exposed to excess piperidine under a pressure of *ca.* 1 kPa, and followed by evacuation at 473 K. A band at 1545 cm^{-1} for pyridinium ions almost disappeared, and that at 1610 cm^{-1} for piperidinium ions newly appeared as shown in Fig. 6-B.[6] The spectra obtained after completion of the replacement (Fig. 6-B) were almost the same as those obtained by piperidine adsorption on the original H-Y. On the other hand, no piperidine molecule held on H-Y was replaced upon exposure to pyridine vapour. Moreover, ammonia molecules were also easily replaced by piperidine, while no piperidine molecule was replaced by ammonia. Thus, piperidine proved to be the strongest of the three.

Similar treatments were performed on H-Y zeolite-pyridine-ammonia system. The poisoned H-Y with pyridine (Fig. 6-A) was exposed to excess ammonia under a pressure of *ca.* 1 kPa, and followed by evacuation at 473 K. Bands at 1475 and 1435 cm^{-1} for ammonium ions newly appeared, while that of pyridinium ions at 1545 cm^{-1} was unchanged as shown in Fig. 6-C.[6] Ammonium ions must be formed on 3550 cm^{-1}-OH sites, because 3550 cm^{-1}-OH band was slightly perturbed. They could not be removed by successive addition of pyridine followed by evacuation at 473 K. In addition, these spectra agreed with those obtained on exposure of ammonia-loaded H-Y to pyridine vapor.

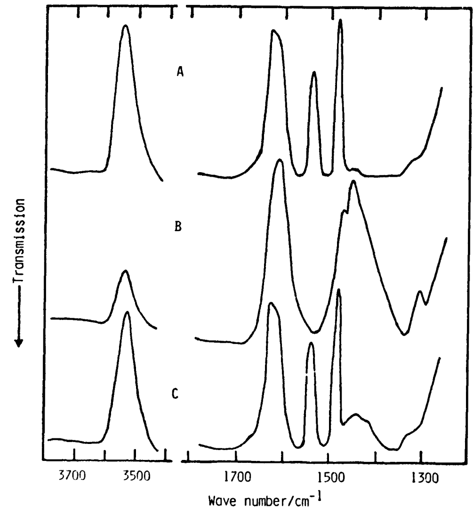

Fig. 6. IR spectra of adsorbed pyridine, piperidine, and ammonia on H-Y at 473 K. (A): Addition of pyridine followed by evacuation at 473 K, (B): addition of piperidine (1 kPa) to (A) followed by evacuation at 473 K, (C): addition of ammonia (1 kPa) to (A) followed by evacuation at 473 K.

In consequence, apparent order of the basic strength seemed to depend on whether acidic sites are 3640 or 3550 cm^{-1}-OH sites. The order at 3640 cm^{-1} was determined as piperidine>pyridine>ammonia, and that at 3550 cm^{-1} as piperidine>ammonia>pyridine. However, since all bases are considered to be accessible to the 3640 cm^{-1}-OH sites as described later, the basic strength should be judged on the 3640 cm^{-1}-OH sites; the order obtained here was in good agreement with the finding of Kebarle *et al.* who determined proton exchange equilibria of bases in vapor phase by mass spectrometer.[7]

Discussion

The positional assignments of hydroxyl sites in H-Y have been widely studied. Eberly[8] assigned the positions on the basis of the interaction of OH groups with olefins. He considered that 3640 cm^{-1}-OH sites existed in supercages having maximum entrance diameter of *ca.* 9 Å and that 3550 cm^{-1}-OH sites existed in hexagonal prisms having maximum entrance diameter of 2.2—2.5 Å (Fig. 7). In contradiction to this, Hughes and White[1] suggested that both OH sites were located on O_1, or O_4 oxygen atoms and accessible to large molecules. Olson and Dempsey[9] assigned 3640 cm^{-1} band to O_1-H groups and 3550 cm^{-1} band to O_3-H groups, using single crystal X-ray techniques. This model was in analogy with Eberly's first observations[8] and agreed with his positional assignments. Additional confirmation was obtained by Ward from exchange of cesium ions into NH_4-Y.[10] Hence, we take Eberly's assignments in order to explain heats of adsorption hereafter.

The 3640 cm^{-1}-OH groups form pyridinium ions in the presence of pyridine while 3550 cm^{-1}-OH groups

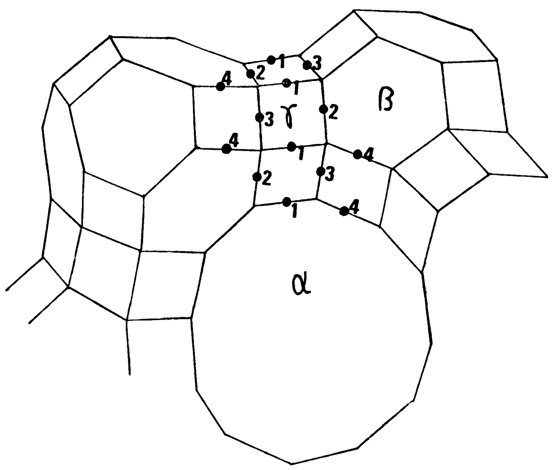

Fig. 7. Framework indication of H–Y zeolite. α: Supercage cavity having maximum entrance diameter of about 9 Å, β: sodalite cavity having maximum entrance diameter of 2.2—2.5 Å, γ: hexagonal prism having maximum entrance diameter 2.2—2.5 Å. The figures 1 through 4 represent oxygen atoms.

form only hydrogen bonds as shown in the formation of 1440 cm^{-1} band. These facts observed by Hughes and White,$^{1)}$ and other authors$^{2,11)}$ were confirmed also in the present work. The large molecular size of pyridine prevents it from approaching 3550 cm^{-1}-OH sites and thus it cannot be protonated. Higher heats of adsorption on OH sites at 3640 cm^{-1} must reflect such a situation. Although piperidine is also too large in size to approach the 3550 cm^{-1}-OH sites, it could be actually protonated by these sites as well as the 3640 cm^{-1}-OH sites, which may be rationalized in terms of proton mobility. Strong bases such as piperidine are known to be able to induce proton movement even at lower temperatures.$^{9,10)}$ The protonation must result in the evolution of similar heats of adsorption on both OH sites at 3550 and 3650 cm^{-1}.

Ammonia was found to be the weakest base of the three, however, it was protonated on the 3550 cm^{-1}-OH sites,$^{12)}$ then heats of adsorption were not much different on the 3550 and the 3640 cm^{-1}-OH sites. This might originate from the fact that ammonia was small enough to access to the 3550 cm^{-1}-OH sites and to be protonated in spite of its weaker basicity than pyridine. In order to confirm the interaction of ammonia with the 3550 cm^{-1}-OH sites, the following adsorption and/or poisoning measurements of pyridine and ammonia were carried out. The original H–Y (referred to A) was evacuated at 673 K and its weight was taken as reference. Two kinds of poisoned samples were prepared from the evacuated H–Y; one was poisoned with pyridine followed by evacuation at 473 K (B) and the other was further poisoned with ammonia followed by evacuation at 293 K (C). In B, the 3640 cm^{-1}-OH sites were poisoned by pyridine, and in C, the 3550 cm^{-1}-OH sites were also poisoned but by ammonia. All samples were exposed to pyridine vapor at 298 K and their weight change was measured. A weight increase in A coincided with that in B, which reflects the reproducibility in pyridine adsorption. On the other hand, a weight increase in C was higher than that in A by a corresponding value of 1.2 mmol g^{-1} of ammonia. This finding indicates that ammonia interacts with the 3550 cm^{-1}-OH sites, not in supercages but by entering hexagonal prisms or being adsorbed to the 3550 cm^{-1}-OH sites which are inaccessible for pyridine.

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