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Direct Measurement of the Interaction Energy between Solids and Gases. IX. Heats of Adsorption of Ammonia and Pyridine on Several Solids at High Temperature

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Heats of adsorption of ammonia and pyridine on H–Y zeolites and other solids were measured using a microcalorimeter in the temperature range of 313 to 673 K. Infrared spectra of adsorbed ammonia and pyridine were obtained in order to interpret the calorimetric data. There appeared two kinds of the temperature dependence of heats of adsorption. One is that heats of adsorption on H–$Y_{5.0}$ and silica-alumina do change with coverage to a greater extent at high temperature range (above 473 K) than low temperature range. The difference in the shape of the heat curves was found to be attributable to the difference in the selectivity of adsorption at different temperatures, that is, adsorption occurred on stronger acidic sites is preference to weaker or non-acidic sites in the high temperature range, while random adsorption occurred simultaneously on acidic and non-acidic sites in the low temperature range. The other kind of temperature dependence was recognized to appear as a slight decrease in heats of adsorption with a temperature rise, which were observed in cases of ammonia adsorption on H–Y zeolites above 473 K and on Na–Y and silica above 313 K while the shapes of heat curves were similar to one another irrespective of the adsorption temperature. Such decrease may be attributed to the fact that the temperature dependence of the heat of adsorption was thermodynamically defined by the difference in molar heat capacity between adsorbed state and gaseous state.

Heats of adsorption of basic gases on solid acid catalysts have been widely measured using a microcalorimeter near room temperatures in order to estimate their acidic characters.[1–7)]

Since solid acid catalysts are generally used for reactions at high temperatures, it will be interesting to measure heats of adsorption at high temperatures. Auroux *et al.*[8)] measured heats of adsorption of ammonia at 416 K. However, a temperature dependence of heats of adsorption has not extensively been studied in the range of room temperature to high temperature.

In the present work, heats of adsorption of ammonia and pyridine were respectively measured on H–Y zeolites in the temperature range of 313 to 673 K using a twin-conduction type microcalorimeter. Likewise, heats of adsorption of ammonia on silica-alumina, Na–Y zeolite, and silica were measured.

Experimental

NH_4–Y zeolite was prepared by treating repeatedly Na–Y zeolite, SK-40, with 1 mol dm^{-3} NH_4Cl solution at *ca.* 323 K. The zeolite was then washed with distilled water until no chlorine ion was detected. The chemical composition was $0.72(NH_4)_2O\cdot 0.15Na_2O\cdot Al_2O_3\cdot 5.0SiO_2$. It was converted to H–$Y_{5.0}$ zeolite by the pretreatment at 673 K before each measurement. Silica-alumina (Al_2O_3 content, 13%) and Aerosil 380 were supplied by Catalysts and Chemicals Ind. Co., Ltd. and Nippon Aerosil Co., Ltd., respectively. All samples were used in granular form of 28—60 mesh. Ammonia and pyridine were obtained from Matheson Co. and Wako Pure Chemicals Co., respectively. Both were purified by the freeze-thaw method.

Heats of adsorption were measured using a twin-conduction type microcalorimeter. The calorimeter and the procedure of measurements were described in a previous paper.[9)] The sample weighing from 0.25 to 1.0 g in the sample cell was outgassed at 673 K under a pressure of 10^{-3} Pa for 5 h and set in the calorimeter. The adsorbed amount was calculated from the pressure change before and after adsorption.

Infrared spectra were obtained by the *in situ* method. The sample was pressed into wafers of thickness of *ca.* 10 mg cm^{-2} under a pressure of 1.6×10^3 kg cm^{-2} and outgassed for 5 h at 673 K before the measurement. The transmission was converted into the absorbance and the spectrum intensity was determined from its band area. The influence of emission was negligible in the temperature range up to 473 K permitting quantitative analysis, but qualitative analysis of the spectra was possible even up to 673 K.

Results and Discussion

Differential Heats of Adsorption of Pyridine and Ammonia on H–$Y_{5.0}$ at 313 and 473 K. Differential heats of adsorption of pyridine on H–$Y_{5.0}$ were measured at 313 and 473 K as shown in Fig. 1. The curve of heats of adsorption obtained at 473 K had a plateau leveling at *ca.* 145 kJ mol^{-1} in the initial stage, thereafter decreasing sharply. On the other hand, the curve obtained at 313 K showed a more monotonic change with coverage, thereafter intersecting the one obtained at 473 K. Differential heats of adsorption of ammonia were measured at 313, 473, 573, and 673 K as shown in Fig. 2. In cases of ammonia adsorption, the difference between heat curves at 313 and 473 K was less explicit than the case of pyridine adsorption. The temperature dependence above 473 K will be discussed later. In case of both adsorbates, measurable pressures of the adsorbate were present even at lower coverage at 473 K or above, while not at 313 K, therefore the equilibrium proved to be obtained in the former system.

The IR measurements were performed to ascertain the temperature dependence of the shape of heat curves. In these experiments, the spectra measured at room temperature were used for contrasting them

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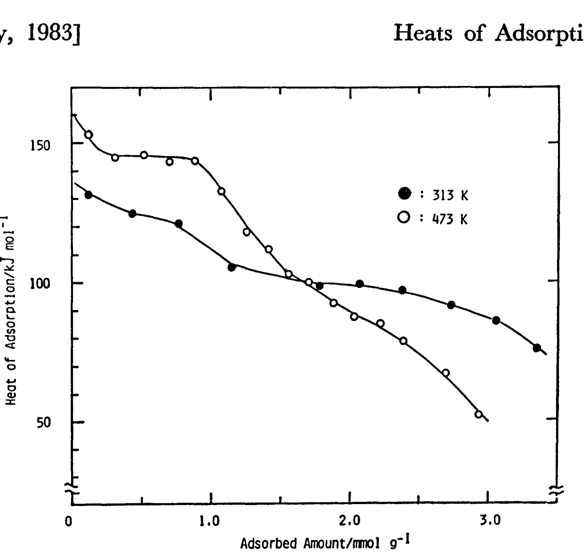

Fig. 1. Differential heats of adsorption of pyridine on H-$Y_{5.0}$. The indicated temperatures represent adsorption temperature.

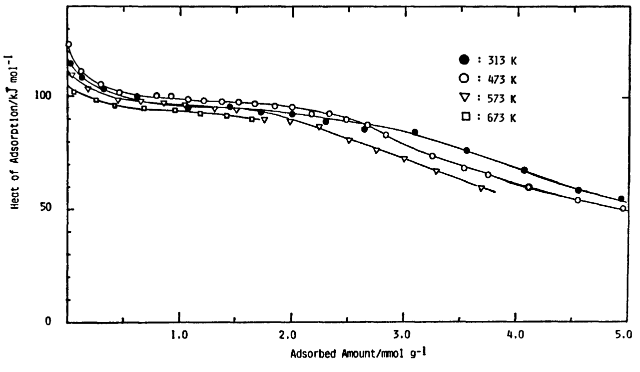

Fig. 2. Differential heats of adsorption of ammonia on H-$Y_{5.0}$.

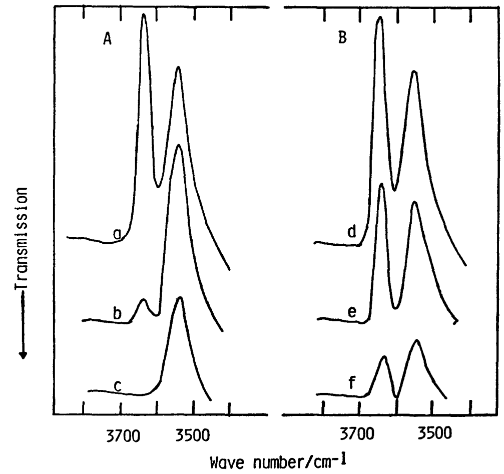

Fig. 3. Changes of bands on H-$Y_{5.0}$ after adsorption of pyridine (A) at 473 K and (B) at room temperature. (a): Evacuated at 673 K then cooled to 473 K; (b): after addition of 1 mmol g^{-1} of pyridine to (a); (c): after addition of 2 mmol g^{-1} of pyridine to (a); (d): evacuated at 673 K then cooled to room temperature; (e): after 1 mmol g^{-1} of pyridine added to (d); (f): after 2 mmol g^{-1} of pyridine added to (d).

TABLE 1. ENHANCEMENT OF PYRIDINIUM ION FORMATION AFTER HEATING H-$Y_{5.0}$-PYRIDINE SYSTEM

	Amount of pyridinium ions/Arb. unit			
	Pyridine adsorbed/mmol g^{-1}			
Temperature/K	0.5	1.0	2.0	3.0
Room temp	0.24	0.47	1.00	1.00
373	—	0.60	—	—
423	—	0.68	—	—
473	0.56	0.85	1.00	1.00
573	—	0.85	—	—
673	—	0.85	—	—

with the data of heats of adsorption at 313 K because analogous IR data were obtained at these two temperatures. First, the experiment was performed on H-$Y_{5.0}$-pyridine system. Since no Lewis acid site existed judging from the absence of 1450 cm^{-1} band[10] for pyridine, most active sites on H-$Y_{5.0}$ proved to be limited to Brønsted acid sites. Figure 3 shows the spectra of OH bands after pyridine adsorption on H-$Y_{5.0}$ measured at room temperature and 473 K. The spectra measured at 573 and 673 K were analogous to those measured at 473 K. In the temperature range of 473 to 673 K, the 3640 cm^{-1} band was preferentially perturbed, indicating that the selective adsorption occurred on the 3650 cm^{-1}-OH sites in preference to the 3550 cm^{-1}-OH sites. On the other hand, both of the 3640 and 3550 cm^{-1} bands decreased simultaneously in their intensity at room temperature, indicating that random adsorption occurred. The results presented here are in good agreement with the observations of Hughes and White[11] and others[12,13] on the difference in the interaction of two types of hydroxyl groups with pyridine.

In addition to above, temperature dependence of the formation of pyridinium ions was investigated by heating H-$Y_{5.0}$-pyridine system as shown in Table 1. The experimental procedures employed were as follows. After addition of a certain amount of pyridine on H-$Y_{5.0}$ at room temperature, the zeolite was heated for 1 h at a desired temperature, then, the relative amount of pyridinium ions formed was determined from the integrated intensities of 1545 cm^{-1} band which is known to be characteristic of pyridinium ions[10] before and after the heat-treatment. The amount at room temperature after pyridine adsorption of 3 mmol g^{-1} was referred to 1.00. At lower coverage, the amount of pyridinium ions increased with a temperature rise below 473 K, then, remained constant up to 673 K. Moreover, spectra in Fig. 4 showed that pyridine molecules adsorbed on the 3550 cm^{-1}-OH sites at room temperature did migrate to the 3640 cm^{-1}-OH sites on heating in agreement with the results in Table 1. It was indicated that the adsorption occurred simultaneously on the 3650 cm^{-1}-OH sites and on other sites at room temperature, but that the adsorbed base on the latter sites migrated to the former sites on heating and was protonated. At higher coverage region, however, the amount remained unchanged on heating, which would tell that the 3650 cm^{-1}-OH sites are wholly saturated at room temperature so that no migration occurred.

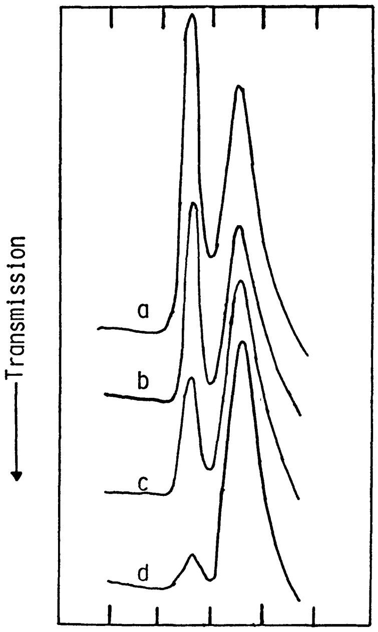

Fig. 4. Redistribution of pyridine on H–$Y_{5.0}$. Spectra were taken at room temperature. (a): Evacuated at 673 K then cooled to room temperature; (b): after adsorption of 1 mmol g^{-1} of pyridine to (a); (c): after heat-treatment of (b) at 423 K for 1 h; (d): after heat-treatment of (c) at 473 K for 1 h.

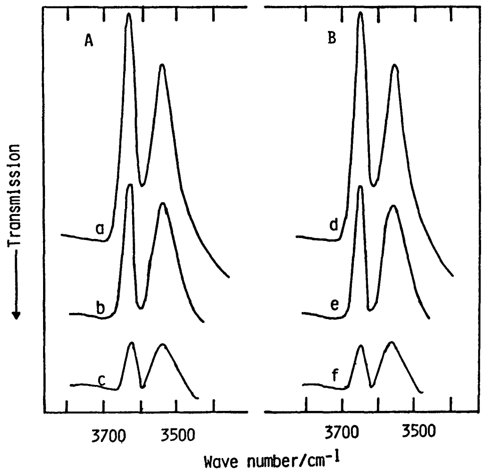

Fig. 5. Changes of bands on H–$Y_{5.0}$ after adsorption of ammonia (A) at 473 K and (B) at room temperature. (a): Evacuated at 673 K then cooled to 473 K; (b): after addition of 1 mmol g^{-1} of ammonia to (a); (c): after addition of 2 mmol g^{-1} of ammonia to (a); (d): evacuated at 673 K then cooled to room temperature; (e): after addition of 1 mmol g^{-1} of ammonia to (d); (f): after addition of 2 mmol g^{-1} of ammonia to (d).

TABLE 2. ENHANCEMENT OF AMMONIUM ION FORMATION AFTER HEATING H–$Y_{5.0}$–AMMONIA SYSTEM

	Amount of ammonium ions/Arb. unit				
	Ammonia adsorbed/mmol g^{-1}				
Temperature/K	0.5	1.0	2.0	3.0	4.0
Room temp	0.20	0.38	0.70	0.98	1.00
373	—	0.40	—	—	—
423	—	0.45	—	—	—
473	0.25	0.46	0.74	0.98	1.00
573	—	0.46	—	—	—
673	—	0.46	—	—	—

By direct comparison with IR spectral results, it seems likely that heats of adsorption of pyridine at 473 K reflect the selective adsorption on the 3640 cm^{-1}-OH sites at lower coverages. At 313 K, however, heats were evolved by rather non-selective adsorption either on the 3640 cm^{-1}-OH sites or other sites, then a monotonic heat curve was obtained.

In case of ammonia adsorption on H–$Y_{5.0}$, both of the 3640 and 3550 cm^{-1}-OH bands were effective for the formation of ammonium ions[14] and were almost simultaneously perturbed at 473 K as well as at room temperature as shown in Fig. 5. However, the amount of ammonium ions increased on heating H–$Y_{5.0}$–ammonia system as shown in Table 2, suggesting that migration of adsorbed ammonia occurred at higher temperature. The experimental procedure employed was the same as that employed in case of H–$Y_{5.0}$–pyridine system and the amount of ammonium ions was calculated from integrated intensities of characteristic bands at 1475 and 1435 cm^{-1}.[10] The results obtained by IR measurements imply that some difference should also be observed in the shape of heat curves obtained by ammonia adsorption and that the extent of the difference should be smaller than the case of pyridine adsorption, which was well confirmed by comparing the heat curves in Figs. 1 and 2. In addition, it is also concluded that the strength of acid sites should preferably be determined by the heat curve obtained at 473 K rather than at 313 K because of more selective adsorption.

The temperature dependence of the selective adsorption on the strongest sites observed in our results will not be reasonably explained on the basis of chemical equilibrium, but chemical kinetics should be introduced to explain the behavior of such an irreversible adsorption. The theoretical analysis of selective adsorption on different sites is now in progress and will be published later.

Differential Heats of Adsorption of Ammonia on H–Y Zeolites at 473, 573, and 673 K. The shapes of heat curves of ammonia adsorption on H–$Y_{5.0}$ obtained were almost similar to one another as shown in Fig. 2. However, the heats decreased slightly as a whole with a temperature rise. Provided that the selectivity of adsorption varies in this temperature range as is predicted by chemical equilibrium, the shape of the heat curve should change with temperature. Therefore, analogous shapes of these three heat curves suggest that the effect expected from the aspect of chemical equilibrium may not be so significant as to influence the shape of the heat curves.

A slight decrease of heats should be explained by the following thermodynamic equation representing

Table 3. Temperature dependence of the enthalpy of the reaction; $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

Reaction temperature/K	$-\Delta H$/kJ mol^{-1}
313	177
473	171
573	166
673	160

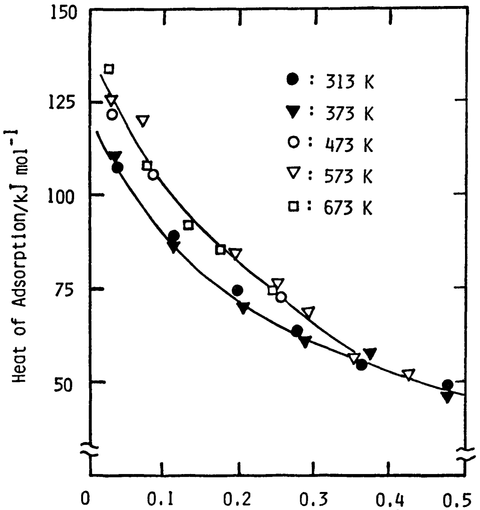

Fig. 6. Differential heats of adsorption of ammonia on silica-alumina.

temperature dependence of a heat evolved from a certain site,

$$(q_{ad})_{T_2} - (q_{ad})_{T_1} = \int_{T_1}^{T_2} \Delta C_v dT, \qquad (1)$$

where $(q_{ad})_{T_1}$ and $(q_{ad})_{T_2}$ represent heats of adsorption at temperatures T_1 and T_2, respectively, and ΔC_v, the difference of the molar heat capacity between the gaseous state and the adsorbed state at a constant volume. Since C_v in the adsorption system is difficult to be calculated, the change of the enthalpy in the following reaction in Eq. 2 was calculated as a function of temperature from the tabulated values of molar heat capacities[15] as one of typical instances of the acid-base reactions as shown in Table 3.

$$HCl\ (gas) + NH_3(gas) \longrightarrow NH_4Cl\ (solid) \qquad (2)$$

A decrease of the exothermic heats with a temperature rise in Table 4 probably corresponds to that observed in case of ammonia adsorption on the H–Y zeolites.

Differential Heats of Adsorption of Ammonia on Other Solids. Heats of adsorption of ammonia on silica-alumina were measured at 313, 373, 473, 573, and 673 K as shown in Fig. 6. Heats of adsorption at the former two temperatures were smaller than those at the latter three temperatures in the low coverage region. Moreover, the heat-treatment of silica-alumina–ammonia system resulted in the enhancement of the amount of protonated ammonia likewise observed in case of H–$Y_{5.0}$–ammonia system. Accordingly, the relatively low values of heats in the low coverage region measured at 313 and 373 K are considered to be an average of the heats from stronger and weaker or non-acidic sites.

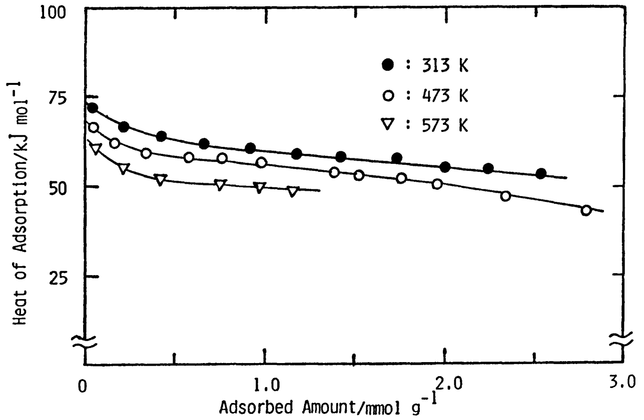

Fig. 7. Differential heats of adsorption of ammonia on Na-$Y_{5.0}$.

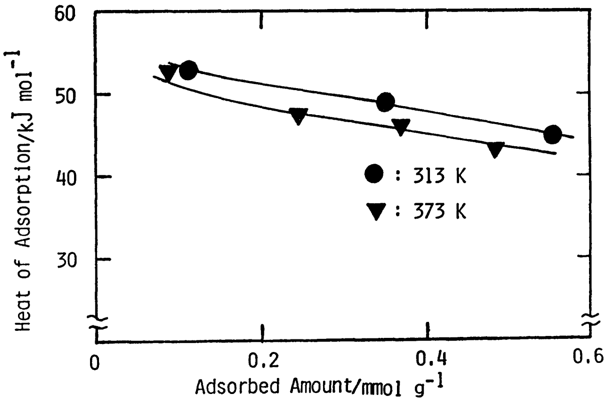

Fig. 8. Differential heats of adsorption of ammonia on silica.

Heats of adsorption of ammonia on Na–Y zeolite resulting from ion-dipole interactions were measured at 313, 473, and 573 K as shown in Fig. 7. Heats on silica resulting from hydrogen bonding were also measured at 313 and 373 K as shown in Fig. 8. In these cases, heats of adsorption showed the same behavior as the case of H–Y zeolites in the temperature range of 473 to 673 K, suggesting similar type of the temperature dependence. In cases of ammonia adsorption on Na–Y and silica, no specific phenomenon was observed on the heat curve because of the weak interaction between ammonia molecule and adsorption site.

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