

Direct Measurement of Interaction Energy between Solids and Gases. II. Microcalorimetric Studies on the Surface Acidity and Acid Strength Distribution of Solid Acid Catalysts

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(Received January 10, 1978)

The differential heats of adsorption of ammonia on several solid acids were measured by means of a twin conduction type microcalorimeter, and surface acid strength distribution and acidity were evaluated. Silica-alumina showed very high initial heats which were not observed in decationated zeolite and silica-magnesia. The acidity of zeolite was about 6 times as high as that of silica-alumina, showing very characteristic acid site distribution at 100 kJ/mol of adsorption energy, and suggesting the existence of homogeneous acid sites. The surface water modified surface acidic nature transforming strong acid sites into weaker ones. The poisoning of acid sites of silica-alumina with alkali occurred preferentially at sites on which adsorption energy of ammonia was 96–105 kJ/mol.

The measurement of the acidity and acid strength distribution of solid acid surfaces has been the subject of many researches, different methods being employed. The most common method is titration with amine in nonaqueous systems using various indicators. A number of reports have appeared on the adsorption of basic gases on solid acids.¹⁾ Attempts were made to use a calorimeter for measurements of a surface acidic nature. Kevorkian and Steiner²⁾ measured heats of ammonia gas adsorption on alumina specimens from bayerite as a function of coverage. Hsieh³⁾ obtained the adsorption isotherms and heats of adsorption of ammonia at 0 °C on a series of commercial silica-alumina cracking catalysts and concluded that about one-tenth of the surface is heterogeneous with respect to ammonia adsorption. Similar measurements for alumina, silica-alumina, and X-type zeolite were carried out by Stone and Whalley.⁴⁾ None of these were satisfactory to account for the surface acidity and acid strength distribution of solid acids quantitatively. Tsutsumi *et al.*⁵⁾ have measured the differential heats of ammonia adsorption on several cation exchanged zeolites, obtaining a good correlation between the differential heats of adsorption and cumene-cracking activities.

In this work, the surface acidity and acid strength distribution were studied in detail with a twin conduction type microcalorimeter for several solid acids. The effects of surface water contents and sodium poisoning of silica-alumina were examined.

Experimental

Materials. Two types of silica-alumina catalyst (Al₂O₃ contents, 13 and 28%, SA-13 and SA-28, respectively) supplied by Shokubai Kasei Co., Ltd. were calcined at 500 °C for 3 h in the air. Sodium poisoned silica-alumina was obtained by impregnation with 0.1 M aqueous sodium acetate solution at 50 °C for 24 h, followed by washing with distilled water, drying at 110 °C and heating at 550 °C in the air (Na-1). Na-2 was obtained by repeated impregnation and washing 3 times under the same conditions as those of Na-1, followed by drying at 110 °C and heating at 550 °C in the air. Sodium contents were 0.38, 0.64 mmol/g in Na-1 and Na-2, respectively.

Y-type zeolite was supplied by Linde Co. in the sodium

form. NH₄-Y zeolite was prepared by the conventional cation exchange procedure with NH₄NO₃ solution. The degree of ion-exchange determined by flame photometry was 69.78%.

Silica-magnesia and silica were supplied by Fuji Chem. Co. and Degussa Co., respectively. The magnesia content of silica-magnesia was 20.5 wt% on dry base.

All the substance were used as granules of 28–60 mesh in the calorimeter. The surface areas of these samples determined by N₂ adsorption at 77 K are given in Table 1. Ammonia was obtained from Matheson Co., and purified by the freezing and thawing method.

TABLE 1. SURFACE AREA OF SOLID ACIDS

	m ² /g		m ² /g
SA-13	557	H-Y _{5.0}	614
SA-28	511	Si-Mg ^{a)}	450
Na-1,2	473	SiO ₂	380

a) Silica-magnesia.

Apparatus and Procedure. The calorimeter and the procedure of measurement have been described.⁶⁾ In order to measure differential heats of adsorption, ca. 0.5 g of adsorbent was weighed into the sample cell and outgassed at several temperatures, mainly at 400 °C, under a pressure of 10⁻⁵ Torr for 5 h and set in the calorimeter. The calorimeter was maintained at 25±0.01 °C. The amount adsorbed was calculated from the pressure change before and after adsorption measured by a MKS capacitance manometer (below ≈10 Torr) and a mercury manometer (above ≈10 Torr). The amount of gas admitted was ca. 5 × 10⁻⁶ mol at low surface coverages, while at higher coverages some larger doses were admitted. The fraction of surface coverage was calculated by taking the cross-sectional area of the ammonia molecules as 16 Å² at 25 °C.

Results and Discussion

Differential Heats of Silica-Alumina and Silica.

Differential heats of adsorption of ammonia on SA-13, SA-28, and silica are given in Fig. 1 as a function of surface coverage. The samples were pretreated at 400 °C *in vacuo*. Curve (c) shows the results of re-adsorption of ammonia on SA-13 which was NH₃-pre-adsorbed and evacuated at 25 °C for 6 h. In silica-alumina, the differential heats fall abruptly from

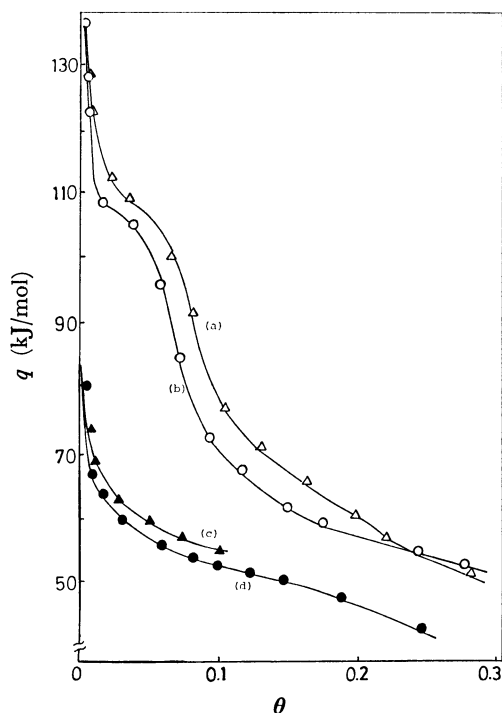


Fig. 1. Heats of adsorption of ammonia on silica-alumina and silica at 25 °C.

(a); SA-28, (b): SA-13, (c): NH_3 -preadsorbed SA-13, (d): silica.

initial heat value of *ca.* 140 to 109 kJ/mol. The abrupt decrease in the differential heats indicates that the adsorption of ammonia molecules occurs on the strongest acid sites successively. Details of the q - θ curve in these regions were given previously.⁶⁾ After the abrupt decrease, the q - θ curve shows a stepped curve, differential heats decreasing gradually to 54.4 kJ/mol at 0.3 of θ . The stepped region in q - θ curve indicates that considerably homogeneous acid sites exist. The behavior of the q - θ curve is very similar in the two silica-alumina, but SA-28 has larger number of strong adsorption sites as compared with SA-13, especially over 105 kJ/mol. Clark and co-workers⁷⁾ studied the differential molar entropy for ammonia adsorbed on silica-alumina of various composition and reported that their values in the region of adsorbed amount smaller than 0.4 molecules/100 Å² are smaller than that of perfect two dimensional gas. This corresponds to the region of adsorption energy larger than about 96 kJ/mol, where no residual gas above 10⁻³ Torr was observed. This suggests that the mobilities of adsorbed ammonia are fairly restricted in this region.

Silica does not exhibit high initial heats of adsorption, the differential heats falling very slightly to *ca.* 41.8 kJ/mol at 0.25 of θ . From the fact that ammonia adsorbed on silica is easily desorbed by evacuation at 25 °C, the heat evolved during the course of adsorption is considered to be due to mainly hydrogen bonding and van der Waals interaction. The ammonia preadsorbed SA-13 shows a q - θ curve very similar to that of silica. However the former exhibits somewhat higher differential heat probably due to the interaction of ammonia molecules with the NH_4^+ ions. The

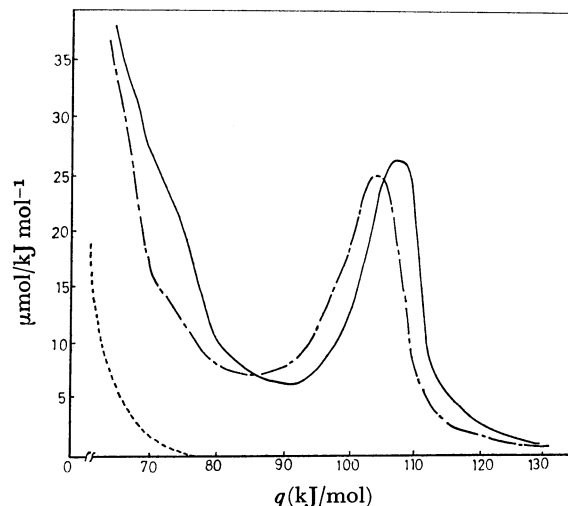


Fig. 2. Acid site distributions of silica-alumina and silica.

—: SA-28, ----: SA-13, ----: silica.

remaining amount of ammonia after evacuation at 25 °C on SA-13 measured by gravimetric methods is 0.6 mmol/g, corresponding to 0.1 of surface coverage. In comparison with the q - θ curve of SA-13 it can be concluded that the adsorbed ammonia with heat of adsorption lower than 70.0 kJ/mol can be desorbed by evacuation at 25 °C. The value nearly coincides with the initial heat of ammonia on preadsorbed SA-13.

The surface acid site distributions of silica-alumina and silica are given in Fig. 2. The maximum distributions are observed at 105 and 109 kJ/mol in SA-13 and SA-28, respectively. The region with a heat of adsorption between 75 and 92 kJ/mol shows relatively low distribution values, indicating that only a small amount of acid sites exists in these regions. Rouxhet and Sempl⁸⁾ observed two hydroxyl groups in silica-alumina; type 1, Si-OH groups identical with those present on the surface of silica; type 2, the sites responsible for the protonation of adsorbed ammonia whose acidity corresponds to the $\text{p}K_a$ range from -4 to -8. The latter OH groups seem to be responsible for the maximum site energy distribution.

The distribution curve of silica has neither maximum nor minimum.

Effects of Outgassing Temperature on q - θ Curve of SA-13. The q - θ curves of SA-13 outgassed at various temperatures between 25 and 400 °C for 5 h are shown in Fig. 3. The initial heat obtained on the sample outgassed at 150 °C (curve b) is 159 kJ/mol, almost the same as that obtained on the sample outgassed at 400 °C (curve a). The sample outgassed at 25 °C exhibits no stronger adsorption energy than 110 kJ/mol. No apparent difference could be observed among all samples in the region below 70 kJ/mol. Similar results were also obtained in SA-28.

Figure 4 shows the acid strength distribution of the samples. The maximum at 105 kJ/mol in curve (a) shifted towards lower strength along with the lowering of outgassing temperature. The results indicate that the surface water modified the acidic nature and the strong acid sites were transformed into weak ones.

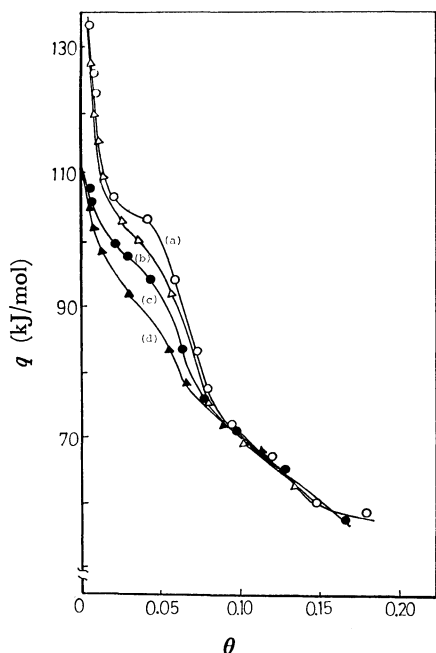


Fig. 3. Effects of outgassing temperature on q - θ curve of SA-13.

(a): 400 °C under 10^{-5} Torr, (b): 150 °C under 10^{-5} Torr, (c): 25 °C under 10^{-5} Torr, (d): 25 °C under 10^{-3} Torr.

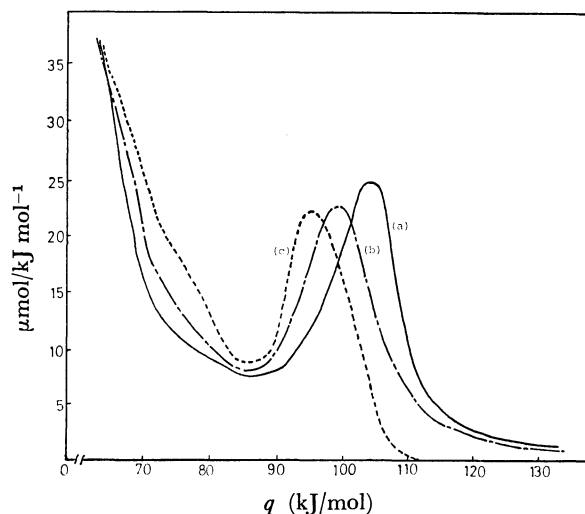


Fig. 4. Effects of outgassing temperature on acid site distributions of SA-13.

(a): 400 °C, (b): 150 °C, (c): 25 °C under 10^{-5} Torr.

Gravimetric experiments showed that water released from SA-13 with an increase of evacuation temperature from 25 to 400 °C is *ca.* 3.1 mmol/g. The value is greater than the number of acid sites which were calculated to be *ca.* 0.6 mmol/g. This suggests that the surface water does not interact in a 1:1 molar ratio with acid sites. It should be pointed out that the infrared spectrum of pyridine adsorbed on SA-13 outgassed at 25 °C showed only pyridinium ion absorption band, suggesting the absence of Lewis acid sites. If protonic acid sites are formed by the interaction of water with Lewis acid sites, the adsorption energies

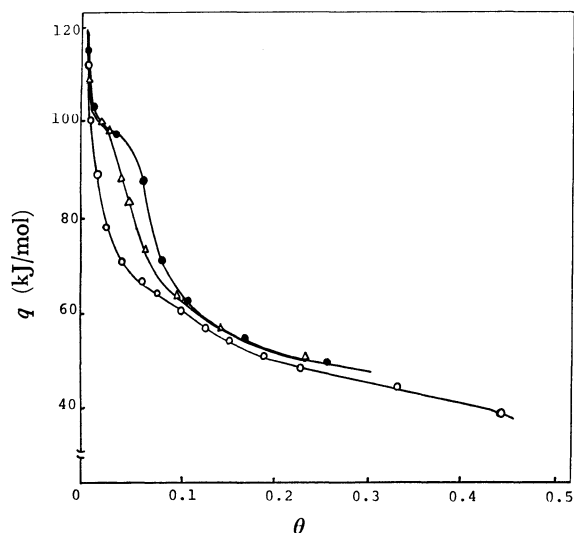


Fig. 5. Heats of adsorption of ammonia on sodium ion-exchanged silica-alumina at 25 °C.

—△—: Na-1, —○—: Na-2, —●—: SA-13.

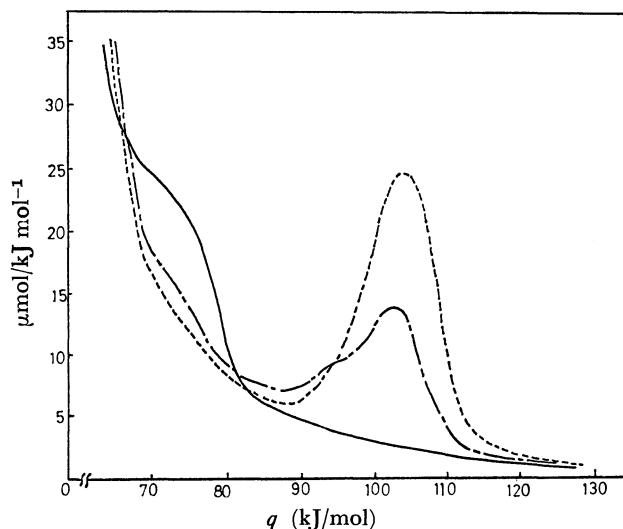


Fig. 6. Acid site distributions of sodium ion-exchanged silica-alumina.

—: Na-2, ---: Na-1, ----: SA-13.

of the resulting sites are probably lower than those of the original Lewis acid sites. The acid strength of the hydrated surface proton becomes less. The results given in Figs. 3 and 4 probably imply the circumstances of silica-alumina surface. It is noteworthy that the differential heats of the sample outgassed at 25 °C is greater than the heat of solution of ammonia in water, 35.6 kJ/mol.

The Effects of Alkali Metal Poisoning. The q - θ curves of sodium ion-exchanged SA-13 are shown in Fig. 5. These samples were pretreated at 400 °C *in vacuo*. The initial heat is almost the same as that of original SA-13. A remarkable difference from original SA-13 is a decrease of the number of the acid sites between 95 and 110 kJ/mol of adsorption heats. This is evident from the disappearance of a maximum in acid strength distribution of Na-2 shown in Fig. 6. In the region of adsorption heat lower than

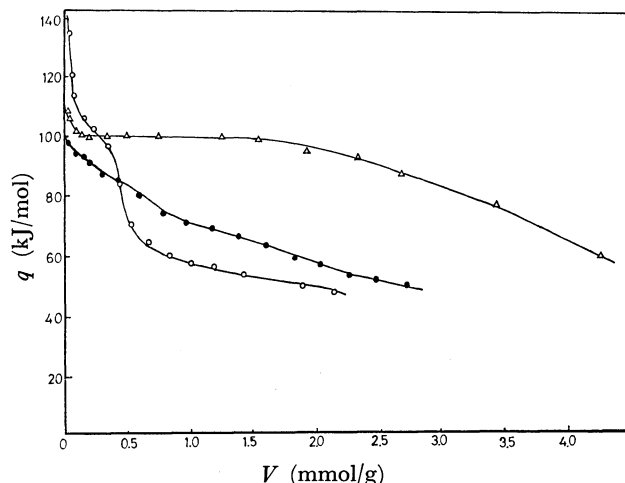


Fig. 7. Heats of adsorption of ammonia on H-Y_{5.0} and silica-magnesia at 25 °C.
 \triangle —: H-Y_{5.0}, \bullet —: silica-magnesia, \circ —: SA-13.

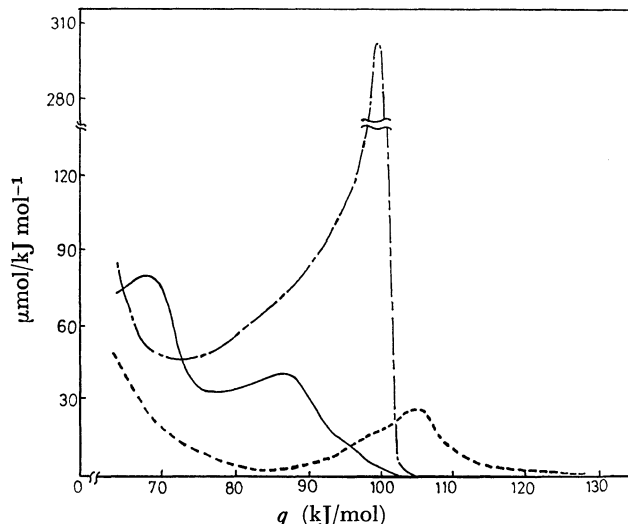


Fig. 8. Acid site distributions of H-Y_{5.0} and silica-magnesia.
 —: Silica-magnesia, ----: H-Y_{5.0}, ----: SA-13.

68 kJ/mol, however, the q - θ curve and acid strength distribution curve are little affected by sodium ion-exchange. This suggests that ammonia molecules probably interact physically with adsorption sites in this region. An increase in the number of the acid sites between 68 and 80 kJ/mol implies that an exchanged Na⁺ ion transforms a part of strong acid sites to weaker ones in line with the results of Hirshler.⁹⁾

Flockhart and Pink¹⁰⁾ have reported that single base exchange-dehydration cycle can not poison all of the acid sites, especially Lewis acid sites. The infrared spectrum of ammonia adsorbed on Na-2 showed the presence of a very small amount of ammonium ions. This suggests that at low surface coverage, *i.e.*, in the region of high adsorption energy, ammonia molecules interact with Lewis acid sites on Na-2.

Differential Heats of H-Y_{5.0} and Silica-Magnesia.

The differential heats of H-Y_{5.0} and silica-magnesia are shown in Fig. 7 together with the results of SA-13. Both samples were pretreated at 400 °C *in vacuo*. In H-Y_{5.0}, there are no acid sites with a value greater than 111 kJ/mol which can be seen in silica-alumina surface. The differential heats remain *ca.* 100 kJ/mol up to 1.5 mmol/g of the amount adsorbed and then smoothly decrease to 65 kJ/mol at 4.0 mmol/g. Those homogeneous acid sites giving about 100 kJ/mol of adsorption heats are probably protonic acid sites. The same results have been obtained in a series of H-Y zeolite with a different silica-alumina ratio.⁵⁾ The calculated number of protons which generated during the course of heat treatment of ammonium form zeolite at 400 °C is 2.27 mmol/g. This corresponds to the number of acid sites over 94 kJ/mol of adsorption heats.

The heat of adsorption on silica-magnesia is about 109 kJ/mol at an initial stage and then decreases gradually to 54 kJ/mol at 2.5 mmol/g of the amount adsorbed.

The acid strength distribution of these solid acids is shown in Fig. 8. Richardson¹¹⁾ studied the effects of

faujasite cations on acid sites by means of infrared spectroscopic measurements of several types of OH groups existing in the supercage and observed two kinds of centers with acid strength corresponding to $pK_a = 4.95$ and -4.9 , respectively. Although his model was not well defined, the shape of the distribution curve is very similar to ours. In comparison with the case of silica-alumina, maximum and minimum positions of site energy distribution of silica-magnesia differ greatly. At around 80–92 kJ/mol of the adsorption energy, silica-alumina has minimum distribution, and silica-magnesia a maximum one. Such a tendency is in line with the results of amine titration, *viz.*, silica-magnesia has no stronger acid sites found in silica-alumina, its acid sites being more widely distributed from strong acid sites to weak acid sites as compared with the case of silica-alumina. More heterogeneous distributions observed for acid sites of amorphous silica-alumina and silica-magnesia in comparison with that of H-Y_{5.0} might be probably due to a localization of their acid sites originated from surface Al and Mg, respectively.

Acid Distribution of Solid Acids.

No estimation of the number of surface acid sites of solid from the measurements of differential heats of adsorption of basic molecules seems to have been made. The number and density of acid sites are shown as a function of adsorption energies (Table 2), calculated on the assumption that the effective acid sites are $q \geq 70$ kJ/mol and ammonia molecules interact in a 1:1 molar ratio with acid sites. The definition of the effective acid sites is somewhat arbitrary in this case. The results of acid distribution of silica-alumina measured with a Hammett indicator¹²⁾ show the existence of only very weak acids and very strong acids. However, our results show the existence of a considerable amount of medium strength acid sites between 75 and 95 kJ/mol, which is consistent with the results of H_R indicator¹³⁾ and ammonia desorption method.¹⁴⁾ The discrepancy might have resulted from the adsorption of Hammett

TABLE 2. ACID DISTRIBUTION OF SOLID ACIDS (mmol/g)

	$70 \leq q$	$80 \leq q$	$90 \leq q$	$100 \leq q$	$110 \leq q$	$120 \leq q$
SA-13	0.61 (1.09) ^{a)}	0.47 (0.84)	0.40 (0.70)	0.32 (0.57)	0.10 (0.18)	0.04 (0.07)
SA-28	0.72 (1.41)	0.52 (1.02)	0.44 (0.86)	0.35 (0.68)	0.18 (0.35)	0.06 (0.11)
Na-2	0.31 (0.61)	0.12 (0.25)	0.06 (0.13)	0.04 (0.08)	0.03 (0.06)	0.02 (0.04)
H-Y _{5.0}	3.78 (6.16)	3.23 (5.31)	2.45 (3.99)	1.55 (2.52)	0.01 (0.02)	—
Si-Mg	0.97 (2.16)	0.62 (1.38)	0.22 (0.49)	0.04 (0.09)	—	—
SiO ₂	0.03 (0.08)	0.01 (0.02)	—	—	—	—

a) (mmol/m² × 10³)

indicators on the acidic surfaces.¹⁵⁾ The surface acid density of SA-28 is larger than that of SA-13, its difference becoming greater in the region over 110 kJ/mol of adsorption energy. In comparison with silica-alumina, H-Y_{5.0} possesses about 6 times the number of acid sites with q higher than 70 kJ/mol, which are rather homogeneous. The acidic properties of H-Y_{5.0} probably support its high catalytic activity and selectivity in cracking reaction.

In Na-2, the reduction of the number of acid sites by base exchange is 0.3 mmol/g, which is smaller than the number of Na⁺ ions on Na-2, suggesting that exchanged Na⁺ ions do not correspond in a 1:1 molar ratio to acid sites or that they only decrease the strength of some acids.

The use of adsorption calorimetry and particularly the measurement of differential heats of basic gas molecules on solid acids seems to be useful for the determination of surface acidity and acid strength distribution. The method could be utilized in the measurements of very strong acid sites which can not be measured exactly by the conventional amine titration.

This work was partly supported by a Grant-in-Aid for Science Research from the Ministry of Education.

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