Direct Measurement of the Interaction Energy between Solids and Gases. V. Change of the Differential Heats of Adsorption of Ammonia with Specific Poisoning on Silica–Alumina

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Heats of adsorption of ammonia on specifically poisoned silica–alumina were measured by use of a twin-conduction-type calorimeter in order to elucidate the adsorption energy and acid strength distributions for both Brönsted (hereafter referred to as B) and Lewis (L) acid sites. Infrared spectra of adsorbed pyridine and cumene cracking activity for the poisoned sample were also examined. Sodium alcoholate–alcohol solution was used as the reagent poisoning only B sites. The use of sodium 2-propanolate–2-propanole dilute solution of which sodium contents was approximately equal to the expected amount of proton on silica–alumina surface caused a large portion of B sites to be poisoned without the decrease in the number of L sites. The following conclusions could be drawn from the experimental results that i) above 115 kJ/mol of the differential heat of adsorption of ammonia no B acid sites were present but only L acid sites, and ii) B acid sites existed chiefly in the vicinity of the adsorption energy distribution of 110 kJ/mol.

The acid strength distribution of dehydrated silica–alumina was determined by amine titration using Hammett indicators[1)] or by gas adsorption calorimetric titration[2)] and the relation between these two methods was clarified.[3)] However, bases such as butylamine and ammonia are adsorbed on both L and B acid sites so that the acid strength distribution of one kind of acid sites has been still uncertain.

On the basis of the inference that B acid sites are generated by the addition of water to L acid sites,[4,5)] heats of adsorption of ammonia on the latter may be higher than that on the former. However, a number of other models of acid sites of silica–alumina have been proposed[4–7)] and the real silica–alumina surface seems to be more complex.

In this study, heats of adsorption of ammonia on specifically poisoned sample were calorimetrically determined in order to evaluate the acid strength distribution of only L acid sites or B sites. An ion exchange method has been mainly adopted so as to poison B acid sites. Since the exchange technique using aqueous solution such as aq sodium acetate is unsuitable for the specific poisoning of B sites because of the new generation of B sites accompanied by the addition of water molecules to L sites, sodium alcoholate–alcohol solution was used as exchange reagent of proton. Sodium alcoholate reacts easily with the hydroxyl group and has been known as the reagent for the determination of active hydrogen content on the surface. Triphenylchloromethane–hexane solution was used as the reagent poisoning L acid sites.[8,9)]

Experimental

Materials. Commercial FCC silica–alumina (Catalysts & Chemicals Ind. Co., Ltd.: alumina 13 wt%) was used as a starting material. Sodium exchanged silica–aluminas (NaSA series) were obtained by impregnation of a starting material into sodium alcoholate–alcohol solutions after pretreatment at 400 °C under 10^{-3} Pa for 5 h. Silica–alumina of which L acid sites were poisoned (TSA) was prepared by impregnation of pretreated original silica–alumina into triphenylchloromethane–hexane solution. The poisoned samples were washed with corresponding alcohol or hexane and subsequently freed from the solvent by the evacuation at 400 °C.

Apparatus and Procedure. Heats of adsorption were determined by a twin-conduction-type microcalorimeter (Tokyo Riko Co., Ltd.) with a conventional vacuum system.[10)] In order to measure the differential heat of adsorption, about 0.5 g of the sample was weighed into the sample cell which was evacuated at 400 °C under 10^{-3} Pa for 5 h and placed in the calorimeter. The heat of adsorption of ammonia was measured at 25 °C.

Cumene cracking activity tests were performed by use of a micro pulsereactor connected to a conventional gas chromatography assembly. One hundred and fifty milligrams of the sample was packed in a stainless steel tube and pretreated at 400 °C for 3 h in a stream of helium gas as a carrier. The helium flow rate was 30 cm^3/min. Catalytic activity was given in terms of the conversion ratio of cumene to propylene and benzene during the first pulse reaction.

Infrared spectra of the adsorbed pyridine were measured in an *in situ* quartz cell connected to a vacuum system. Twenty milligrams of sample was pressed to a thin wafer and set in the cell. After evacuation at 400 °C under 10^{-3} Pa for 3 h, pyridine was adsorbed with an equilibrium pressure of 1.3 kPa at room temperature. Then the sample was evacuated at 150 °C for 1 h in order to remove physisorbed pyridine. The spectral measurement was carried out at room temperature.

Specific surface area was determined by the BET nitrogen adsorption method.

Results and Discussion

Silica–alumina was treated with sodium methanolate, sodium 2-propanolate and sodium 2-methyl-2-propanolate in order to clarify the effect of the chain length and the steric conformation of the alkyl group on the amount of sodium exchange. The properties of NaSA series samples were shown in Table 1. NaSA(I), (III), and (IV) were obtained by the impregnation of pretreated silica–alumina into the concentrated sodium alcoholate–alcohol solutions in which sodium contents were in large excess in relation to the expected proton contents of silica–alumina surfaces. On the other hand, NaSA(II) was obtained by treatment with sodium 2-propanolate–2-propanole dilute solution in which

Table 1. Samples

Sample	Specific surface area, $S/\mathrm{m^2\,g^{-1}}$	Na content / mmol $\mathrm{g^{-1}}$	Treatment[b]
SA-13[a]	410	0	none
NaSA(I)	374	0.25	$(CH_3)_3CONa$–$(CH_3)_3COH$, concn
NaSA(II)	404	0.52	$(CH_3)_2CHONa$–$(CH_3)_2CHOH$, dilute
NaSA(III)	361	0.97	$(CH_3)_2CHONa$–$(CH_3)_2CHOH$, concn
NaSA(IV)	390	1.64	CH_3ONa–CH_3OH, concn

a) Commercial FCC silica–alumina. b) Each poisoned sample was obtained by impregnation with sodium alcoholate–alcohol solution at room temperature.

sodium content was nearly equal to the expected proton content. The amount of sodium exchange was maximum in case of NaSA(IV) which was treated with sodium methanolate and decrease with an increase in the steric hindrance of the alkyl group. Since no remarkable reduction of specific surface area with the treatment of sodium alcoholate was observed for each sample, the surface structure of the original silica–alumina remained unchanged after the treatment.

Figure 2 shows the differential heats of adsorption of ammonia on sodium exchanged samples. With an increase in sodium content, the heat of adsorption of ammonia decreased. The initial heats of adsorption of ammonia on NaSA(I) and (II) were approximately equal to that on original silica–alumina, however, those on NaSA(III) and (IV) were remarkably reduced. Ammonia gas adsorption energy distributions are shown in Fig. 3. In cases of NaSA(I) and (II), the distribution around 110 kJ/mol of the heat of adsorption became markedly lower with an increase in sodium content, while that above 115 kJ/mol remained unchanged compared with original silica–alumina. In cases of NaSA(III) and (IV), however, the adsorption sites distribution became lower in a whole range above 80 kJ/mol. It is noteworthy that this range for original silica–alumina was also influenced by the heat treatment as shown in Fig. 1. The effect of the treatment with sodium 2-methyl-2-propanolate–2-methyl-2-propanol solution or sodium 2-propanolate–2-propanol dilute solution differed from that with sodium methanolate–methanol solution or sodium 2-propanolate–2-propanol concentrated solution.

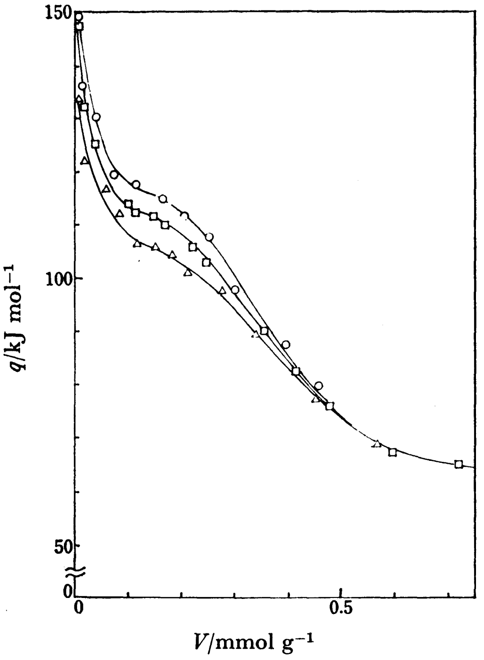

Fig. 1. Effect of pretreatment temperature on differential heat of adsorption of ammonia on silica–alumina. ○ 600, □ 400, △ 150 C.

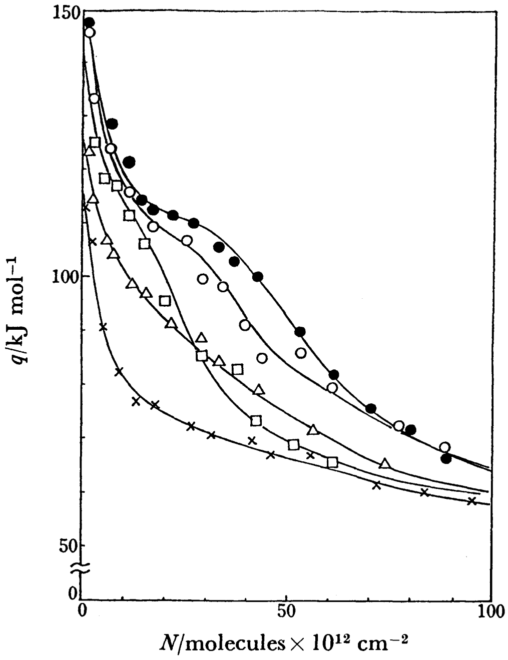

Fig. 2. Differential heat of adsorption of ammonia on silica–alumina poisoned with sodium alcoholate.
● SA-13, ○ NaSA(I), □ NaSA(II), △ NaSA(III), × NaSA(IV).

Infrared spectra of pyridine adsorbed on sodium exchanged samples were shown in Fig. 4. Both absorption peaks for B acid sites (1540 $\mathrm{cm^{-1}}$) and for L acid sites (1450 $\mathrm{cm^{-1}}$) were observed on original silica–alumina. However, the former was remarkably reduced for NaSA(I) and disappeared for other exchanged samples, which suggests that B acid sites almost or completely disappeared by the treatment with sodium alcoholate. On the other hand, the reduction of the latter peak occurred particularly for NaSA(IV). This fact suggests that sodium methanolate reacted not only with surface active proton but was coordinated with L acid sites. The formation of the coordinative bond must require the small steric hindrance and the strong basicity of the coordinated species. Therefore it is

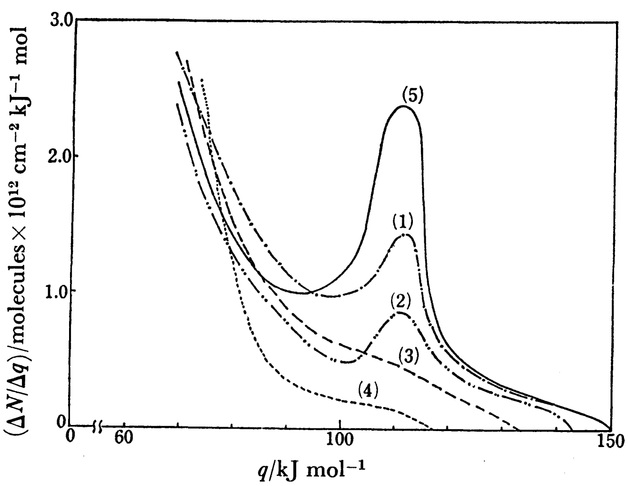

Fig. 3. Adsorption energy distribution on silica–alumina poisoned with sodium alcoholate.
(1) NaSA(I), (2) NaSA(II), (3) NaSA(III), (4) NaSA(IV), (5) SA-13.

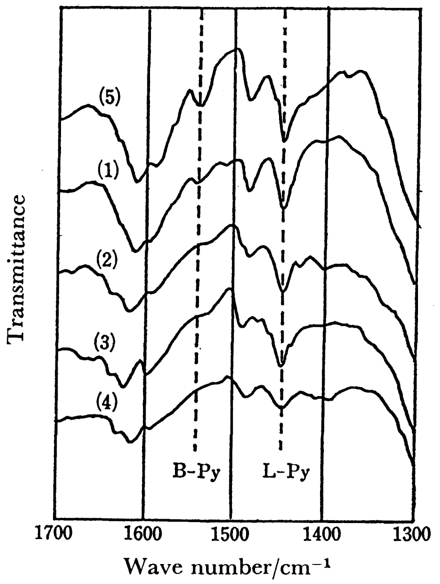

Fig. 4. Infrared spectra of adsorbed pyridine.
(1) NaSA(I), (2) NaSA(II), (3) NaSA(III), (4) NaSA(IV), (5) SA-13.

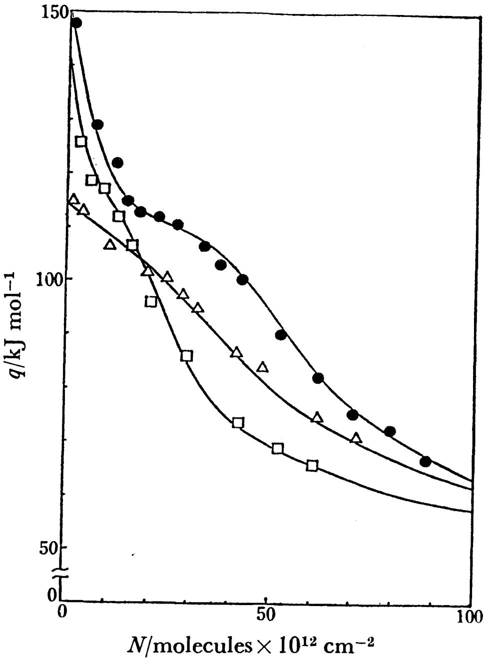

Fig. 5. Comparison of differential heat of adsorption on NaSA(II), (□), with TSA, (△), (poisoned with triphenylchloromethane). SA-13 (●).

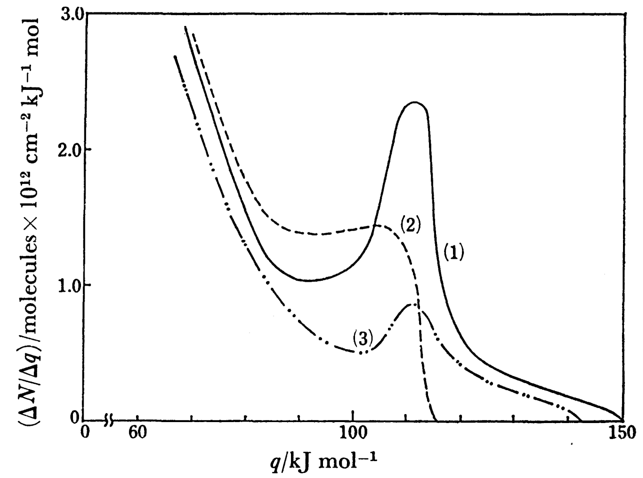

Fig. 6. Adsorption energy distributions on NaSA(II), (3), TSA, (2), and SA-13, (1).

reasonable that the larger the alkyl group of sodium alcoholate is, the more difficult the formation of the coordinative bond with L acid site becomes. On the sample treated with sodium 2-methyl-2-propanolate, even a part of B sites still remained besides L sites.

The adsorbed amount of ammonia having the heat of adsorption below 115 kJ/mol, chiefly in the vicinity of 110 kJ/mol, decreased by sodium exchange. When the coordination of sodium alcoholate with L acid sites occurred besides sodium exchange, even the adsorbed amount of ammonia above 115 kJ/mol decreased together with the reduction of initial heat of adsorption. Hence, B acid sites seem to distribute mainly in the adsorption energy region below 115 kJ/mol.

In Fig. 5 the differential heat of adsorption of ammonia on silica–alumina poisoned with triphenylchloromethane (TSA) is shown together with those on SA-13 and on NaSA(II). The initial heat of adsorption of ammonia on TSA, 115 kJ/mol, was much lower than that on original silica–alumina, while that on NaSA(II) was approximately equal to that on original sample. Furthermore, as shown in Fig. 6, ammonia adsorption sites on TSA existed below 115 kJ/mol of the differential heat of adsorption, which was markedly different from the case of NaSA(II). This supports the above-mentioned suggestion that only L acid sites exist above 115 kJ/mol of the differential heat of adsorption. The number of ammonia adsorption sites above 115 kJ/mol for NaSA(III) or (IV) was smaller than that for NaSA(II) or original silica–alumina, as a result of a decrease in the number of L acid sites.

It is possible to consider that L acid sites are stronger than B sites in silica–alumina from the finding[11] that pyridine adsorbed on B sites was completely removed by evacuation at 300 °C while pyridine on L sites remained after evacuation even at 400 °C. As shown in Fig. 1, the adsorbed amount of ammonia above 115 kJ/mol on silica–alumina pretreated at 600 °C was about twice as much as that on the sample pretreated at 400 °C, which can therefore be ascribed to the increase in the number of L acid sites. The results are similar to those found in Y type zeolites.[12]

TABLE 2. RELATIONS AMONG CUMENE CONVERSION RATIO, SODIUM CONTENT AND CALORIMETRICALLY DETERMINED *acidity*

Sample	*Acidity* / mmol g^{-1}	Na content / mmol g^{-1}	Cumene conversion ratio/%
SA-13	0.35	0	87
NaSA(I)	0.31	0.25	78
NaSA(II)	0.22	0.52	31
NaSA(III)	0.21	0.97	23
NaSA(IV)	0.08	1.64	0

Cumene cracking activity of the catalyst has been known to arise from B acidity and its dependence on the calorimetrically determined surface acidity was reported previously in detail.[13] We now define the adsorbed amount of ammonia between 80 and 115 kJ/mol as *acidity* which seems to be the difference between total acidity and a large portion of L acidity. In Table 2 the relations among *acidity*, sodium content and cumene cracking activity are shown. With an increase in sodium content, both *acidity* and activity decreased. This fact suggests that the treatment with sodium alcoholate reduced B acidity.

The conclusions based on the above experiments are that B acid sites of silica–alumina studied here are distributed below 115 kJ/mol of the differential heat of adsorption of ammonia, mainly in the vicinity of 110 kJ/mol, and above 115 kJ/mol only L acid sites exist. A part of L acid sites may be present below 115 kJ/mol.

Considering a poisoning technique, it was shown that ion exchange in aq solution was unsuitable for the purpose of poisoning only B acid sites. Because the shape of *q-N* curve and the adsorption energy distribution curve of silica–alumina treated with aq sodium acetate solution were close to those of NaSA(IV); the amount of L sites of the latter decreased to about one-third of that of original silica–alumina.

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