Direct Measurement of Interaction Energy between Solids and Gases. I. Heat of Adsorption of Ammonia on Zeolite

Kazuo Tsutsumi, Hong Qui Koh, Seiichi Hagiwara*, and Hiroshi Takahashi
Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106
**Tokyo Riko Co. Ltd., 3-2-16 Kita-machi, Hoya-shi, Tokyo 188*

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The differential heat of adsorption of ammonia on synthetic zeolites was calorimetrically measured and the distribution of the surface acidity was discussed in relation to the catalytic activity for cumene-cracking as a function of zeolite compositions. A newly designed apparatus, a twin-conduction-type calorimeter equipped with a semiconductor thermoelement and an adsorption apparatus, was used for the direct measurement of the differential heat of adsorption. The differential heat of adsorption of ammonia decreased with the increase in surface coverage, the acid site on the surface becoming stronger up to 27 kcal/mol for ammonia-adsorption when the ratio of silica to alumina was higher and the content of exchanged ammonium ions was higher. The cumene-cracking reaction was effectively catalyzed by zeolites having such sites with heat of adsorption of ammonia exceeding 25 kcal/mol.

Calorimetric studies on the interaction between solids and gases or liquids provide significant information on the surface state of the solids. For this purpose, the heats of adsorption of gas and the heats of immersion of solid into liquids are the important quantities to be measured. The heat of immersion of solids into liquids has been extensively measured calorimetrically for the past two decades.[1] It is difficult, however, to measure the heat of adsorption calorimetrically and it was usually calculated from the isotherm of adsorption[2] or from the temperature dependence of the retention volume in gas-chromatography.[3] The calculation of heat of adsorption is based on the assumptions that a reversible adsorption mechanism holds and the surface state is invariable during measurement. However, these assumptions are not necessarily applicable to the practical systems.

The difficulty in the calorimetric measurement of the interaction energy between solids and gases lies in the accurate measurement of the heat evolved. A few authors reported the results on evaporated metal films using metallic thermometers[4-6] and some other dealt with Dewar-type calorimeters.[7-11] Recently, Gravelle measured the heat of adsorption on heterogeneous catalysts by means of a heat-flow calorimeter.[12] Several other studies have also appeared.[13-16]

This paper reports a newly designed calorimeter for the measurements of the interaction energy between solids and gases, and the measurements of differential heat of adsorption of ammonia on zeolites, the results being discussed in relation to the cracking of cumene catalyzed by the zeolites.

Experimental

The calorimeter used is of a twin-conduction-type, the main cell of which is illustrated in Fig. 1. The cell is made of stainless steel and Pyrex glass which are joined by Kovar glass. The calorimeter has a second cell as a reference, which is of the same structure as that of the sample cell and serves to eliminate the effect of external disturbance. The two cells and the gas storage tank are connected to each other by a Pyrex glass tube having a stopcock connected to a vacuum line and a manometer. The sample in the cell was pretreated at various temperatures and pressures. The two cells and the gas storage tank were set in a thermostated bath. After the whole system reached thermal equilibrium, the gas storage tank was opened and the gas was led to the cell. The heat evolved in the sample cell caused the thermoelectromotive force in the thermoelement, which was amplified and recorded as shown in Fig. 2. When the thermal equilibrium was again established after completion of adsorption, the amount of heat was calibrated by flowing a given amount of electrical energy through a standard electric heater which was set in contact to the cell. An example of the cooling curve and the calibration curve is shown in Fig. 2. The ordinate, ΔT, indicates the temperature difference between the sample cell and the thermostated bath. When the heat, q, is generated in a unit of time within the cell, the following equation can be derived for the

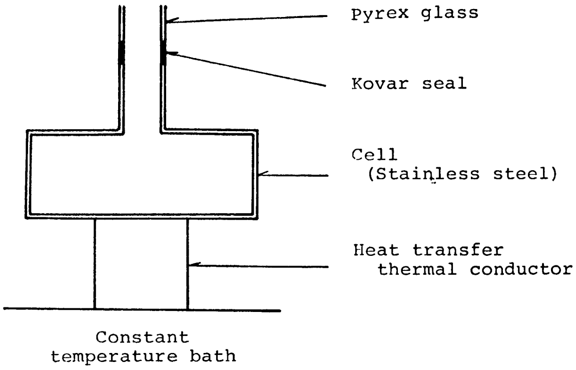

Fig. 1. Calorimetric cell.

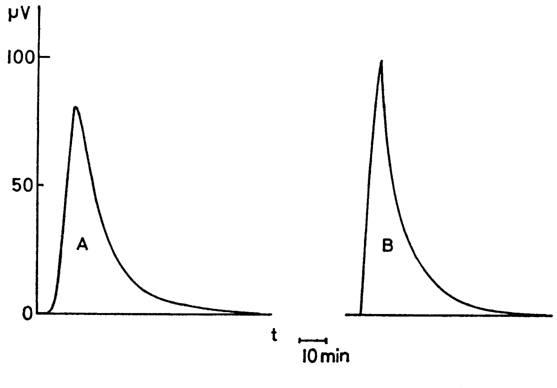

Fig. 2. Representation of $\Delta T-t$ curve (500 mcal)
A: curve recorded at the measurement
B: calibration curve by a standard electric heater

Table 1. Chemical composition and extent of exchange of zeolites

Zeolite	Composition	Extent of exchange (%)
NH_4-$Y_{10.29}$	$0.67(NH_4)_2O \cdot 0.15Na_2O \cdot 10.29SiO_2 \cdot Al_2O_3$	80.7
NH_4-$Y_{7.38}$	$0.67(NH_4)_2O \cdot 0.16Na_2O \cdot 7.38SiO_2 \cdot Al_2O_3$	78.1
NH_4-$Y_{4.8}$	$0.78(NH_4)_2O \cdot 0.15Na_2O \cdot 4.8SiO_2 \cdot Al_2O_3$	83.9
NH_4-$Y_{3.47}$	$0.70(NH_4)_2O \cdot 0.10Na_2O \cdot 3.47SiO_2 \cdot Al_2O_3$	87.5
NH_4-$X_{2.5}$	$0.41(NH_4)_2O \cdot 0.36Na_2O \cdot 2.5SiO_2 \cdot Al_2O_3$	53.3
La-$Y_{4.71}$	$0.66La_2O_3 \cdot 0.27Na_2O \cdot 4.71SiO_2 \cdot Al_2O_3$	71.0
Ca-$Y_{5.0}$	$0.80CaO \cdot 0.10Na_2O \cdot 5.0SiO_2 \cdot Al_2O_3$	88.9

relation between the amount of q and the temperature change of the cell by assuming a uniform temperature distribution in the cell.

$$q = C \cdot \mathrm{d}(\Delta T)/\mathrm{d}t + \sigma \Delta T \qquad (1)$$

where C is the heat capacity of the cell with the sample and the thermoelement, and σ the heat transfer coefficient. The total heat released, Q, can be obtained by integrating q with respect to time t:

$$Q = \int_{-\infty}^{+\infty} q \cdot \mathrm{d}t = C(\Delta T)_{-\infty}^{+\infty} + \sigma \int_{-\infty}^{+\infty} \Delta T \cdot \mathrm{d}t \qquad (2)$$

Since the thermal equilibrium is established in the cell before and after the adsorption, the first term on the right side of Eq. 2 is reduced to zero. Thus the total heat should be proportional to the area under the ΔT–t curve.

The amount of adsorbed gas was determined as the difference between the amount introduced to the adsorption vessel and that of the residual gas. In most initial doses, no gas remained in the gas phase. In these runs, the relation between the heat of adsorption and the adsorbed amount of gas gave the differential heat of adsorption. After the adsorption of the first dose had been accomplished, the second dose of gas was introduced; the same procedure was repeated until the differential heat of adsorption became constant.

The heat of adsorption of ammonia was measured at 25 °C. Ammonia was condensed in a liquid nitrogen trap and then allowed to evaporate into the vacuum system. The pretreatment of zeolites was carried out at 400 °C and 10^{-5} Torr for 8 hr. The catalytic activity for the cumene-cracking reaction was measured in a microreactor, the details of which were described in a previous paper.[17)]

Materials. The original zeolites were the commercial Linde Molecular Sieve 13X, SX-40 and Na-$Y_{3.47}$ synthesized from silica-alumina gel and sodium hydroxide. The calcium-, lanthanum- and ammonium-form zeolites were prepared by treating Na-form zeolite with an 0.1 M solution of the corresponding chloride (guaranteed-grade reagents of Wako Pure Chemicals Industries, Ltd.). The treatment was repeated several times in order to obtain a high extent of exchange. The remaining salts were removed by washing the samples with distilled water until no chloride ions detected in washing solutions with silver nitrate. The samples were then dried and stored over the saturated sodium chloride solution. Zeolites with silica-to-alumina ratios greater than 5 were prepared by extracting aluminum atoms in NH_4-$Y_{4.8}$ zeolite with EDTA.[18)] Decationated zeolites were obtained by heat treatment of the ammonium-form zeolite at 400 °C. The compositions of zeolites were measured by chemical analysis and flame photometry. The results are summarized in Table 1.

Results and Discussion

The accuracy of the calorimeter was confirmed by comparing the areas under the ΔT–t curve for the standard electric heater. The constant current supplied to the heater buried in the solid yielded a typical ΔT–t curve as shown in Fig. 2A. The ΔT–t curve for the calibration heat is also shown in Fig. 2B The ratio of the integrated area of the former ($S_{\mathrm{samp.}}$) to that of the latter ($S_{\mathrm{calib.}}$) is given in Table 2. We see that the ratio is equal to unity. The integrated area changes linearly with the amount of the supplied heat, the lower limit of the detected heat being a few milli-calories. The results on the heat of adsorption of ammonia on the ammonium-form zeolites with various ratios of silica-to-alumina (H-$Y_{10.29}$, H-$Y_{7.38}$, H-$Y_{4.8}$, H-$Y_{3.47}$ and H-$X_{2.5}$) are shown in Fig. 3. Since the initial stages of adsorption below 2 mmol/g are considered to be important for the catalytic activity, the results in these ranges are shown in Fig. 4 in a larger scale. Except the case of H-$X_{2.5}$, the initial heats of adsorption of ammonia on the

Table 2. Calibration of a standard electric heater

Heat supplied	$S_{\mathrm{samp.}}/S_{\mathrm{calib.}}$
7.0 mcal	0.96
41.6 mcal	0.98
62.5 mcal	1.01
83.2 mcal	0.99
250.0 mcal	1.01
500.0 mcal	1.01
1.0 cal	1.00
2.0 cal	1.01
5.0 cal	1.00

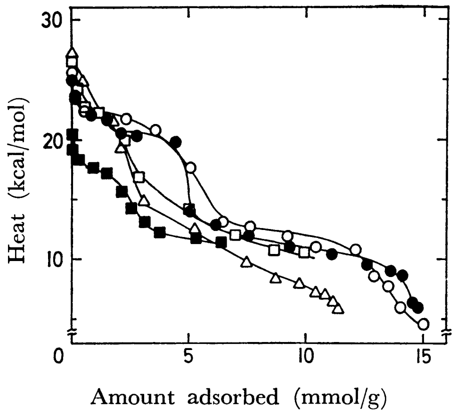

Fig. 3. Variation of differential heat of adsorption of ammonia with amount adsorbed on zeolites.
△: H-$Y_{10.29}$ □: H-$Y_{7.38}$ ○: H-$Y_{4.8}$ ●: H-$Y_{3.47}$
■: H-$X_{2.5}$

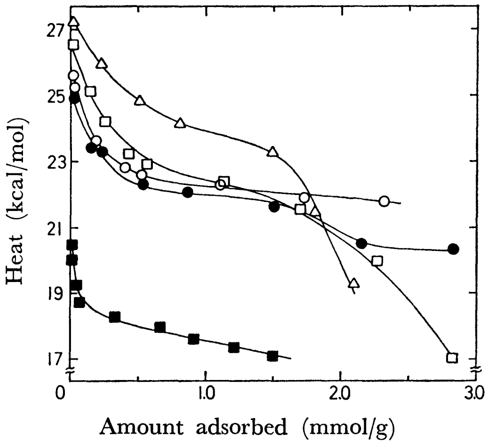

Fig. 4. Variation of differential heat of adsorption of ammonia with amount adsorbed on zeolites.
△: H-$Y_{10.29}$ □: H-$Y_{7.38}$ ○: H-$Y_{4.8}$ ●: H-$Y_{3.47}$ ■: H-$X_{2.5}$

zeolites were larger than 24 kcal/mol in the coverage range less than 3×10^{-2} mmol/g. The heats, then, decrease sharply to about 21.5 kcal/mol, where the four curves intersect at 1.75 mmol/g. The abrupt decrease of the heat of adsorption at the coverage of 3×10^{-2} mmol/g suggests that the selective adsorption of ammonia molecules on the strongest acid sites takes place at a lower coverage.

It is interesting to note that the number of sites with the heat of adsorption of ammonia above 23 kcal/mol on the surface of H-$Y_{10.29}$ is larger than those of other specimens (Fig. 4). As the adsorbed amount increases to about 1.7 mmol/g, the heats of adsorption H-$Y_{10.29}$ and on H-$Y_{7.38}$ fall off steeply to about 15 kcal/mol, whereas the heats of adsorption on H-$Y_{4.8}$ and H-$Y_{3.47}$ decrease gradually to about 19.5 kcal/mol in the coverage range up to 4.5 and 5.0 mmol/g, respectively.

It is known that the thermal treatment of ammonium-form zeolites at 400 °C generates Brönsted acid sites. The initial heats of adsorption of ammonia on H-$Y_{7.38}$ and H-$Y_{10.29}$ are larger than those on H-$Y_{4.8}$ and H-$Y_{3.47}$ (Fig. 3 and 4). However, the total number of acidic sites with heats of adsorption larger than 20 kcal/mol on H-$Y_{4.8}$ and H-$Y_{3.47}$ is greater than those on H-$Y_{10.29}$ and H-$Y_{7.38}$. Since H-$Y_{10.29}$ and H-$Y_{7.38}$ were prepared by extracting aluminum atoms from the alumino-silicate frame-work with EDTA, the treatment would bring about a decrease in the total number of sites to which protons could combine. On the other hand a decrease in the aluminum content reduces the number of negative sites and lowers the electric shielding for the cations in the zeolitic cavity. Thus, the protons with weaker electrostatic shielding should be more mobile and form stronger acidic sites.

The total number of protons contained in the zeolites could be calculated by assuming that ammonium ions were converted into protons during the course of heat treatment at 400 °C. The numbers of protons thus calculated for H-$Y_{10.29}$, H-$Y_{7.38}$, H-$Y_{4.8}$ and H-$Y_{3.47}$ are 1.76, 2.26, 3.79 and 4.76 mmol/g, respectively. If one ammonia molecule is chemisorbed on one acidic site, the chemisorption of ammonia on H-$Y_{10.29}$ would amount to 1.76 mmol/g. The heat of adsorption of ammonia on H-$Y_{10.29}$ falls steeply from 22 kcal/mol to 14 kcal/mol at the coverage of 1.76 mmol/g, in accordance with the prediction (Fig. 3). A similar coincidence occurs also in the other cases. The heats of adsorption of ammonia on H-$Y_{7.38}$, H-$Y_{4.8}$ and H-$Y_{3.47}$ steeply decrease at the adsorbed amounts of 2.3, 3.4, 4.5 mmol/g, respectively, which are also consistent with the values calculated above. The heat values at these amounts are about 19.5 kcal/mol in all three cases. We can conclude that the minimum value of the chemical interaction energy between ammonia molecules and Brönsted acid sites is greater than 19.5 kcal/mol. It is likely that the acidic sites of H-$Y_{10.29}$ and H-$Y_{7.38}$ are more homogeneous in energetic character than those of H-$Y_{4.8}$ and H-$Y_{3.47}$.

By comparing with the results of infrared spectroscopy, pyridine molecules are supposed to be chemisorbed on the acidic sites of zeolites, where the heat of adsorption is greater than 20 kcal/mol.[18] Since ammonia is chemisorbed on both Brönsted and Lewis acid sites and the steric factor in adsorption of ammonia differs from that of pyridine, no quantitative coincidence was found between the adsorption of pyridine and that of ammonia.

After stepwise decrease, the heats of adsorption attain the nearly plateau region of *ca.* 10 kcal/mol and then decrease to *ca.* 5 kcal/mol. In the cases where the molecules adsorbed exceed the monolayer, the interaction between ammonia molecules and ammonium ions should be considered. According to Hsiesh[14], newly adsorbed ammonia molecules interact with the ammonium ions formed by ammonia molecules adsorbed on Brönsted acid sites. The ammonium ions polarize the ammonia molecule; the ammonia molecules also interact with the catalyst surface by the van der Waals force. In these regions, the differential heat of adsorption continues to decrease gradually until four ammonia molecules "co-ordinate" with each ammonium ion on the surface, which is in accordance with the present observations. The differential heat of adsorption finally drops to *ca.* 6 kcal/mol, which is quite close to the value of the heat of liquefaction of ammonia, 5.2 kcal/mol.

The initial heat of adsorption of H-$X_{2.5}$ is *ca.* 20.5 kcal/mol. The differential heat of adsorption gradually decreases to *ca.* 12 kcal/mol at 4 mmol/g, and then becomes constant at about 11 kcal/mol. The number of the acid sites with heats of adsorption over 19.5 kcal/mol is *ca.* 0.4 mmol/g. The value is very low as compared with that of the zeolites with higher silica-to-alumina molar ratios. Some authors[19,20] reported that the faujasite zeolite with the silica-to-alumina molar ratio of 2.5 is unstable under heat treatment. The remarkable decrease in the heat of adsorption of ammonia on H-$X_{2.5}$ might be due to the destruction of the crystalline structure by the pretreatment at 400 °C.

Figure 5 shows the plots of the heat of adsorption of ammonia *vs.* the adsorbed amount on faujasite Y with various exchange ions (Na-, Ca-, La-, and H-). The heat of adsorption of ammonia on both Ca-$Y_{5.0}$

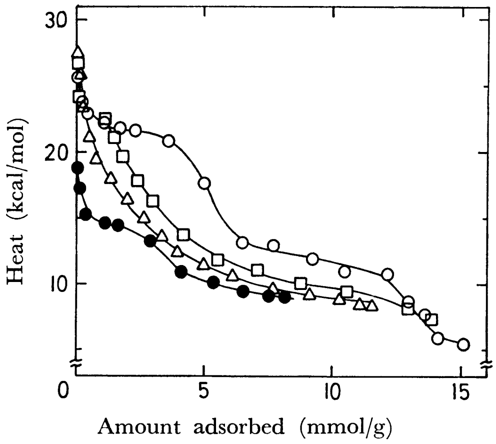

Fig. 5. Variation of differential heat of adsorption of ammonia with amount adsorbed on zeolites.
●: Na-$Y_{5.0}$ □: Ca-$Y_{5.0}$ △: La-$Y_{4.71}$ ○: H-$Y_{4.8}$

Table 3. Conversion of cumene-cracking on zeolite catalysts

Zeolite	Conversion %
H-$Y_{10.29}$	91
H-$Y_{7.38}$	95
H-$Y_{4.8}$	62
H-$Y_{3.47}$	44
H-$X_{2.5}$	0
La-$Y_{4.71}$	89
Ca-$Y_{5.0}$	71
Na-$Y_{4.8}$	0

and La-$Y_{4.71}$ falls sharply at first from a high initial value and then gradually to *ca.* 6 kcal/mol, which is nearly equal to the heat of liquefaction of ammonia. As compared with the case of the multi-valent ion-exchange zeolites, the initial heat of adsorption on the original Na-$Y_{4.8}$ is very low (about 19 kcal/mol), and decreases slowly. This indicates that the Na-$Y_{4.8}$ has a rather homogeneous surface. The conversion of the cumene-cracking on the zeolites is listed in Table 3. We see that the conversion of the cumene-cracking on ammonium-form zeolites increases in the order H-$X_{2.5}$<H-$Y_{3.85}$<H-$Y_{4.8}$<H-$Y_{7.38}$; it increases with the increase in the silica-to-alumina molar ratio. The conversion activity of H-$Y_{10.29}$ is somewhat lower than that of H-$Y_{7.38}$. La-$Y_{4.71}$ has a higher activity than Ca-$Y_{5.0}$, while Na-$Y_{4.8}$ has no cracking ability. In the cracking reaction of cumene, the carbonium ion is formed on the Brönsted acid site of the catalyst.[21] A site having stronger acidity will show larger activity of the formation of carbonium ions and consequently a larger cracking ability. Decrease in aluminum content makes the proton active, and increases the catalytic activity.

Morita *et al.*[22] reported that the sites effective for the cracking of cumene have the acid strengths of $H_0 \leq -3.0$, as measured by the butylamine titration with Hammett indicators. By using the same method, we found that the amount of acid sites of H-$Y_{4.8}$ with an acid strength of $H_0 \leq -3.0$ is *ca.* 2 mmol/g.[23] The heat of adsorption of ammonia at this surface coverage is found to be *ca.* 22 kcal/mol (Fig. 4). If sites on which the heat of adsorption is more than 22 kcal/mol were available for the cracking reaction of cumene, the activities of H-$Y_{3.47}$, H-$Y_{4.8}$ and H-$Y_{7.38}$ should be nearly equal to each other and lower than that of H-$Y_{10.38}$. But this is apparently not the case. The H-$Y_{10.29}$ sample has a higher heat of adsorption of ammonia than other samples in the region of coverage 0.2—1.7 mmol/g. However, the cumene-cracking activity of H-$Y_{10.29}$ is lower than that of H-$Y_{7.38}$. Beaumont and Barthomeuf[19] reported that the crystalline structure of zeolite was partially destroyed if the content of aluminum was below 28 atoms per unit cell. The zeolite with 28 atoms per unit cell corresponds to that with a silica-to-alumina molar ratio of 9.8. In fact, the X-ray diffraction pattern of H-$Y_{10.29}$ shows a decrease in intensity.[18] The decrease in activity of cumene-cracking and the high initial heat of adsorption of H-$Y_{10.29}$ might be attributed to the partial destruction of the lattice structure. The H-$Y_{4.8}$ and H-$Y_{3.47}$ samples, which have the same values of the initial heat of adsorption, show a remarkable difference in the activity of cumene-cracking. This is probably owing to the difference in the number of strong sites. The initial heat of adsorption on H-$Y_{3.47}$ is larger than 25.5 kcal/mol. On the other hand, the number of adsorption sites for this energy region on H-$Y_{4.8}$ is three times as much as that of H-$Y_{3.47}$. A possible reason for the difference in the activity of cumene-cracking between the two zeolites may lie in the difference in the degree of change of the Brönsted acid site to the Lewis one. Since the catalyst was treated at 550 °C before activity measurement, its number of Brönsted acid sites should be smaller than that of the sample treated at 400 °C. Dehydration occurs easily at higher temperatures on H-$Y_{3.47}$, since it possesses a larger amount of hydroxyl groups.

The present evidence is not yet conclusive as to which sites are effective in cumene-cracking reaction. However, all the data about the heat of adsorption and the cracking activity seem to be compatible with the suggestion that the sites with the heat of adsorption of ammonia of more than 25 kcal/mol are effective in cumene-cracking reaction and that the sites of stronger acidity show a greater activity. The total number of such strong acid sites also affects the activity.

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