Direct Measurement of the Interaction Energy between Solids and Gases. VIII. A High-temperature Calorimeter for the Determination of Heats of Adsorption from Room Temperature to 700 K

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A high-temperature calorimeter of the twin conduction type was designed with the capability of measuring heats of adsorption of gases on solids in the temperature range RT to 700 K. A chromel-alumel thermopile was used as the detector and a volumetric adsorption apparatus was equipped. Its calibration and preliminary experiments on heats of adsorption of ammonia on zeolites are described.

Adsorption of gases on solids at higher temperature occurs, in many cases, by specific interaction of gases with solid surfaces. The energetical analysis of the interaction provides informations on activity and reactivity of solids, and permits effective use of catalysts, adsorbents, fillers and so on. Calorimetric studies on high temperature adsorption have been made mainly by means of dynamic methods such as DTA, TGA, DSC, or TPD. However, these methods are less satisfactory from the standpoint of quantitative analysis and difficult to examine active sites of surfaces in detail. Measurements of isosteric heats of adsorption from temperature change of adsorption are not adequate in view of the possibility that the characteristics of active sites vary with temperature. In particular, as chemisorption depends to a great extent on temperature and is often characterized by hysteresis, its mechanism and capacity cannot be estimated from equilibrium theory.[1] The temperature change of heats of chemisorption is often different from that expected from heat capacity.[2]

The present authors have already designed the adsorption calorimeter available near room temperature[3] and measured heats of adsorption of ammonia on solid acids.[4-9] However, evaluation of active sites must be the most useful when made at the same temperature as the working one. Therefore, direct measurement of heats of adsorption at higher temperature is indispensable.

This paper reports a newly designed microcalorimeter available from room temperature to 700 K for measurements of interaction energy between solids and gases. Heats of adsorption of ammonia on zeolites are measured as a preliminary experiment to illustrate the applications of this calorimeter.

Experimental

Apparatus. The calorimeter of the twin-conduction type; the detector part and cell are schematically illustrated in Fig. 1. Thermal effects were detected by use of a chromel-alumel thermopile (D) made of 128 thermocouples, amplified and recorded. The thermocouples are connected in series, placed in 8 directions and in 16 steps, insulated by alumina, and attached to the stainless-steel cell container (C). Two detectors are arranged in a differential and similar way in order to eliminate thermal effects other than the intended ones. Detectors and cell containers are set in a heat sink (E) made of

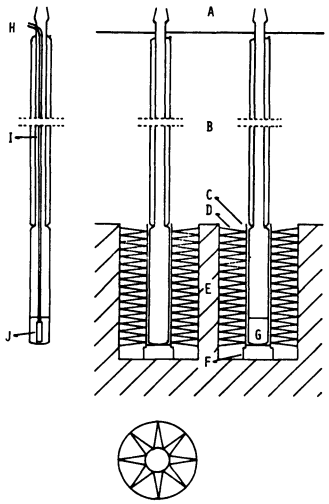

Fig. 1. Schematics of the calorimeter cell and detector. A: Volumetric adsorption line and manometer, B: thermal insulator, C: stainless-steel container, D: thermopile, E: heat sink, F: thermal insulator, G: sample, H: constant voltage circuit, I: platinum lead wire, J: platinum heater.

stainless-steel, the temperature of which is controlled to within $\pm 10^{-3}$K by monitering temperatures and operating noninductively wound Kanthal heaters at three different positions, bottom, side, and top regions. These parts are thermally insulated from the surroundings by bricks and ceramic fibers (B).

Sample and reference cells are made of pyrex or quartz glass, the upper part of which is of dewar-type for thermal insulation. They are symmetrically placed in the stainless-steel container (C) and the thermal insulator (F) in such a way that a good thermal contact is established between them. Both cells are joined together at the top and connected to the volumetric adsorption apparatus (A) outside the calorimeter through vacuum joints and stopcocks, then the dose of gases is introduced simultaneously into both cells. The pressure can be maintained below 1 mPa. Samples (G) in the cell can be heated under vacuum outside the calorimeter and reset in the calorimeter without being exposed to air.

The calibration cell is designed in the same way as for the sample or reference cell, in which a platinum heater (J) (176.7 Ω at 473 K) sealed in a glass tube was inserted, joined to a platinum lead wire (I) and connected to a constant voltage supply (H).

Calibration. In order to ascertain the reliability of the calorimeter, a known amount of electric voltage was fed to the heater and the saturation electromotive force obtained was plotted against the power. The calibration was carried out by feeding a Joule heat and measuring the area under the thermogram, *i.e.* time (t) *vs.* recorder response due to the temperature difference between the calibration cell and the reference cell (ΔT).

Heats of Adsorption. The adsorbent was NH_4–$Y_{4.7}$ zeolite, $0.93(NH_4)_2O \cdot 0.07Na_2O \cdot 4.7SiO_2 \cdot Al_2O_3$, which was obtained by conventional ion-exchange of Na-type zeolite. One gram (dehydrated and decationated basis) of the zeolite was placed in a sample cell and pretreated at 673 K under a pressure of 1 mPa for 10 h. The sample cell was set in a calorimeter and connected to a volumetric line. After the thermal equilibrium was established, a small quantity of adsorbate gas, ammonia, was admitted. The heat evolution was recorded and when the thermal equilibrium was reestablished, another dose of gas was admitted. The adsorption amount was determined by the pressure change before and after adsorption. Since the temperature gradient existed between the thermostated lower part and the top part of the cell, the dead volume of the system was determined by helium under the same conditions as those of calorimetric measurement. The minor temperature change at the gas reservoir which is placed outside the calorimeter was corrected for. The amount of heat evolved was determined by comparison of the area with the area under a calibration curve obtained as mentioned above.

Infrared Spectra. Infrared spectra of adsorbed ammonia which were obtained by the *in situ* method described elsewhere[7] were analyzed in order to interprete the calorimetric data.

Results and Discussion

Calibration of the Calorimeter. The calibration was carried out at 313, 373, 473, 573, and 673 K and the results are shown in Fig. 2. The test at 473 K was carried out under several conditions in order to examine influences of the heat capacity and the heat transfer: the heater was buried in different quantities of inert quartz powder and/or different amount of helium was maintained in the cell.

A linear correlation was obtained between the electrical power and the saturated electromotive force irrespective of calibration conditions; therefore the calibration can be separately carried out by use of the calibration cell. A quantitative determination of the heat by means of a conduction calorimeter is based on Tian's equation,[10]

$$dQ/dt = C \cdot d(\Delta T)/dt + \sigma \cdot \Delta T,$$

where dQ/dt refers to the heat evolved or absorbed in a unit time within the cell, C the heat capacity of the cell and detector, ΔT the temperature difference between the cell and the heat sink, and σ the apparent heat transfer coefficient. Therefore, the calorimeter cell should be devised in such a way that the heat evolved in the cell flows only through the detector to the heat sink. A linear relation of Fig. 2 implies that thermal leak along the wall of the cell could be neglected and that Tian's equation can be considered to hold in this system.

After the saturation, the electric current was turned off and then the cooling curve was obtained from which the time constant was calculated. The time constants with 6.5 g of quartz under 6.67 kPa of helium were 28.0, 22.7, 16.2, 12.2, and 9.0 min at 313, 373, 473, 573, and 673 K, respectively. The decrease with temperature may be explained on the basis of the possibility that, as temperature rises, the thermal fiux becomes liable to transfer from the cell to the heat sink by means of radiation, convection or conduction through the thermopile, resulting in an increase in the value of σ.

An electrical energy was supplied through this heater during an appropriate length of time and areas obtained under the thermogram were plotted against the Joule heat in Fig. 3. In this temperature range, the area is proportional to the generated heat, which fact suggests that this calibration is applicable to determine quantitatively the heat evolved in the adsorption cell. A change of the time constant calculated from a change of the area by use of Tian's equation was consistent with that

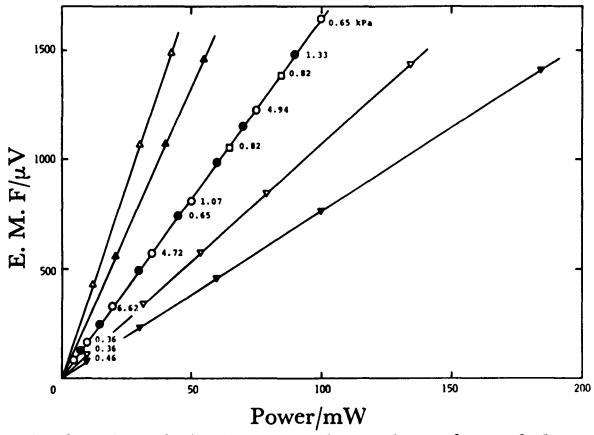

Fig. 2. Correlation between thermal powder and electromotive force.
△: At 313 K with 6.5 g of quartz and 6.67 kPa of He, ▲: at 373 K with 6.5 g of quartz and 6.67 kPa of He, ▽: at 573 K with 6.5 g of quartz and 6.67 kPa of He, ▼: at 673 K with 6.5 g of quartz and 6.67 kPa of He, ○: at 473 K with 21.5 g of quartz, □: at 473 K with 10.8 g of quartz, ●: at 473 K without quartz. The figures represent He pressure in the measurements at 473 K.

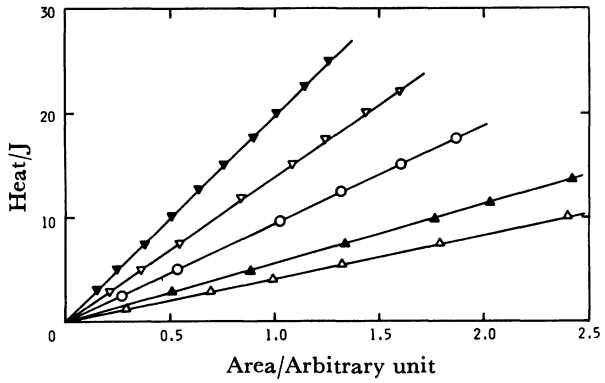

Fig. 3. Electrical calibration of the calorimeter.
△: 313 K, ▲: 373 K, ○: 473 K, ▽: 573 K, ▼: 673 K.

obtained from the cooling curve as mentioned above. When this calorimeter was used at lower temperature, calibration became more reliable, whereas an increase in the time constant resulted in the tailing phenomenon in the recorder response.

The sensitivity of this calorimeter at 473 K was 300 μJ/s within the error of 1% and the fluctuation below 0.25 μW/h. In favor of the twin system, the calorimeter response was not disturbed by thermal effects other than the intended reaction or adsorption. Such thermal effects were brought about by a temperature change of the surrounding or by a dose of gas. Two kinds of errors must result from the latter effect: the first is due to the work delivered to the cell by dosed gas and the second due to the temperature difference between dosed gas and the adsorbent. The simultaneous introduction of helium into adsorption and reference cells, the former of which contained one gram of zeolite, gave no appreciable thermal response, then the work delivered by dosed gas could be considered to be energetically cancelled. As to the second, although the upper part of the cell served to preheat an adsorbate, its temperature should be still different from that of the adsorbent. However, when the gas was preheated outside the calorimeter before being introduced, the heat value obtained was not different from the corresponding one obtained by the measurement without preheating. Therefore, the gas temperature effect was not corrected.

Heats of Adsorption of Ammonia on Decationated Zeolite. Acidic properties of decationated zeolites have been extensively studied by means of IR spectroscopy, amine titration and so on.[11,12] Calorimetric studies on acidities have also been made by many workers including the present authors.[1,3,7,13–15] The measurement of heats of adsorption of ammonia on zeolites can, therefore, be considered to be a good example to illustrate the application of the calorimeter.

The Brønsted acidity is formed on heating NH_4-type zeolites and originates from the hydroxyl groups. Heating the decationated zeolites to higher temperature results in a decrease in the concentration of Brønsted acid sites, accompanied by the formation of Lewis acid sites.[12]

In this study, NH_4–$Y_{4.7}$ zeolite was evacuated at 673 K and heats of adsorption of ammonia were measured at 473 K. An example of the thermogram of the heat evolved on adsorption of 0.071 mmol of ammonia is shown in Fig. 4 with the calibration thermogram. This adsorption amount corresponds to about one-three hundredth of the total adsorption capacity and about one-sixtieth of acid sites. Therefore, this calorimeter can provide information on fine structure of about one-several hundredth of active sites by considering the precision. The time required for one measurement depended on the adsorption amount as well as the temperature. The measurement at 473 K required from 100 to 150 min.

Differential heats of adsorption are given in Fig. 5. A lower curve shows the results of readsorption of ammonia on the same sample which was evacuated overnight at 473 K at 1 mPa after the first run of the adsorption measurement. Since the number of total

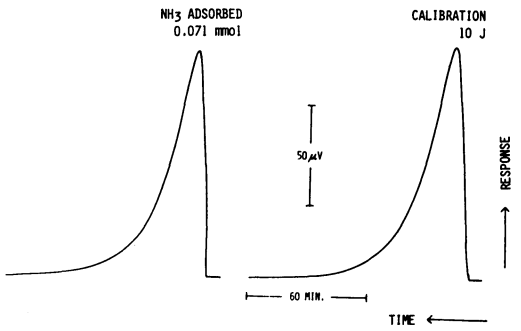

Fig. 4. An example of the recorder response of ammonia adsorption.
Initial pressure of ammonia: 1.098 kPa, equilibrium pressure: 0.007 kPa.

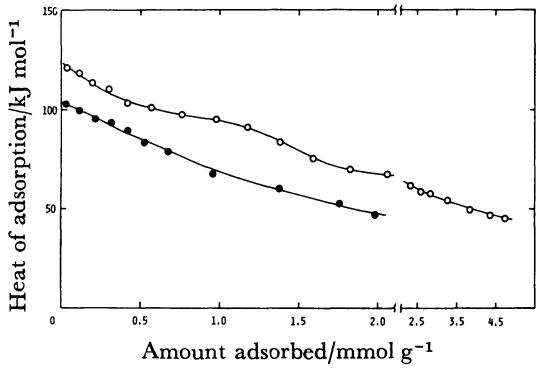

Fig. 5. Differential heats of adsorption of ammonia on decationated zeolites.
○: Original zeolite, ●: ammonia-preadsorbed zeplite

protons contained in the zeolite is 4.6 mmol/g which was calculated under the assumption that ammonium ions were converted into protons during the course of heat treatment at 673 K, the mutual interactions of adsorbed ammonia can be neglected and the heat should be evolved by the interaction of ammonia with the proton in this experimental condition. In the original sample, heats decrease from the initial value of about 120 kJ/mol, attain a plateau region of about 100 kJ/mol and decrease again. The presence of the plateau region is also observed in the measurement at room temperature.[3,4] The differential heats on the ammonia-preadsorbed sample are lower even in the initial region and decrease in monotonic way. The amount of ammonia which was irreversibly adsorbed after evacuation at 473 K was determined volumetrically to be 0.45 mmol/g, which agrees with the value obtained by comparison of two heat curves. Then relatively strong acid sites can be considered to evolve heats with ammonia adsorption higher than 105 kJ/mol.

The surface adsorption site distribution which was obtained by graphical differentiation of Fig. 5 is given in Fig. 6. The maximum of the distribution is observed at about 100 kJ/mol in the original sample, indicating the existence of considerably homogeneous active sites. About one-fifth of the total protons corresponded to adsorption sites contained in the maximum. However, this distribution was less significant than that observed at 298 K.[4] On the other hand, no maximum is observed

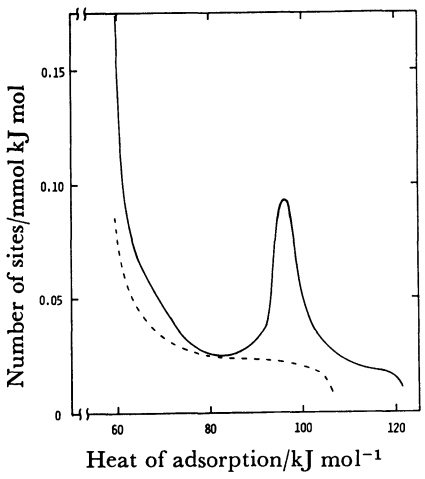

Fig. 6. Adsorption energy distribution on decationated zeolites.
——: Original zeolite, ------: ammonia-preadsorbed zeolite

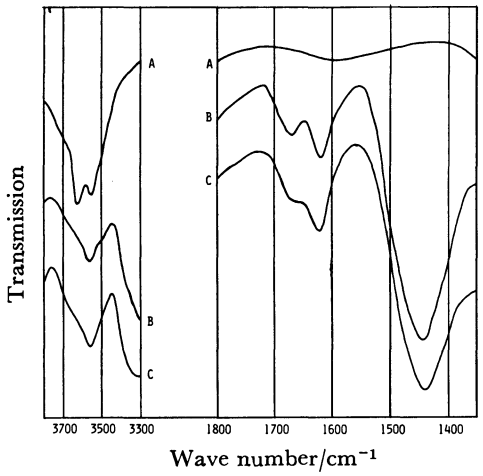

Fig. 7. Infrared spectra of OH and NH bands.
A: Decationated zeolite evacuated at 673 K, B: after ammonia adsorption and evacuation at 298 K, C: after ammonia adsorption and evacuation at 473 K.

in the ammonia-preadsorbed sample and more active sites having heats of adsorption above 105 kJ/mol are completely poisoned.

Infrared spectra of hydroxyl groups of the zeolite and adsorbed ammonia are shown in Fig. 7. The elimination of NH bands was completed by evacuation of the NH_4–$Y_{4.7}$ zeolite at 673 K, accompanied by the appearance of OH bands as shown in Fig. 7A, which is consistent with many previous results.[12] Ammonia was adsorbed at 298 K on this sample at the equilibrium pressure of 4 kPa and evacuated at the same temperature, then the spectrum was recorded (Fig. 7B). The reformation of bands from ammonium ion vibrations (1440 and 1670 cm^{-1}) was observed and also Lewis acid-bonded ammonia was detected at 1670 cm^{-1}. The hydroxyl band at 3650 cm^{-1} simultaneously disappeared, which fact indicates that ammonia interacted with these hydroxyl groups. The spectrum in Fig. 7C was taken after the treatment as follows; ammonia was adsorbed at 473 K at the equilibrium pressure of 40 kPa, which corresponded to the adsorbed amount of 4.83 mmol/g and desorbed overnight at the same temperature at 1 mPa. The intensities of bands at 1440 and 1670 cm^{-1} became weaker, whereas the intensity at 1620 cm^{-1} remained constant. This observation suggests that the irreversibly adsorbed ammonia on Brønsted acid sites decreases at higher temperature. In comparison with calorimetric data, the adsorption with heats higher than 105 kJ/mol can be suggested to occur mainly on Lewis acid sites.

In conclusion, this type of adsorption calorimeter is available at higher temperature and capable of providing information on fine structure of active sites of solid surfaces near their working temperature. The results of heats of adsorption of several bases on solids in the temperature range up to 673 K will be presented in another paper.

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