Heat of Adsorption from Solution. II. The Heat of Adsorption of Pyridine on Silica-Alumina from the Hexane Solution

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The amounts of physisorbed and chemisorbed pyridine on silica–alumina in the hexane solution were measured at 30 °C, and found to be 1.25 and 0.25 molecules/100 Å^2 respectively. The number of strong acid sites determined by Benesi's method are in good agreement with the chemisorbed molecules, which indicates that the ratio of the number of chemisorbed pyridine molecules to that of the strong acid sites on the surface of silica–alumina is equal. The adsorption calorimetry was carried out on the same system by means of a flow microcalorimeter which permits us to differentiate the heats of physisorption and chemisorption: the results showed that the heats of physisorption and chemisorption of pyridine are 11.3 ± 0.3 and 22 ± 4 kcal/mol respectively.

It is well known that silica–alumina is a typical solid acid; a number of efforts have been devoted to clarify the interaction between the silica–alumina surface and basic molecules.[1] The infrared spectroscopic studies using ammonia, butylamine, and pyridine as adsorbates have made it possible to distinguish the acid sites on silica–alumina into two types, *i.e.*, those of Brönsted and Lewis acid.[2,3] On the other hand, no exact measurements of the interaction energy between the acid surface and basic molecules have satisfactorily been carried out.[4-7]

The present work was undertaken in order to determine precisely the heat of adsorption of pyridine on silica–alumina from the hexane solution. For the calorimetric measurements, a flow microcalorimeter is used; it was found in the preceding paper to be suitable for the exact measurement of a small heat evolved in a solid–liquid system.[8] The present paper will also show the advantage of using flow calorimetry in order to differentiate the heat of the chemisorption of an adsorbate from that of the physisorption; this can be done by combining the heat of adsorption data with the chemisorbed and physisorbed amounts of the adsorbate.

Experimental

Materials. Silica–alumina powder (13 wt % alumina) presented by the Shokubaikasei Co., Ltd., was washed forty times by hot distilled water (*ca.* 80 °C) until the conductivity of the supernatant liquid was brought to a limiting value, 5×10^{-6} Ω^{-1}cm^{-1}. The powder was then dried at 100 °C in the atmosphere, and finally degassed at room temperature for 4 h at a reduced pressure of 10^{-3} Torr. The guaranteed-grade reagents of hexane, benzene, and pyridine were purified by passing them through a silica gel column. On the other hand, the guaranteed-grade reagent of butylamine and such indicators as anthraquinone, benzylideneacetophenone, 4-(phenylazo)diphenylamine, and *p*-dimethylaminoazobenzene were used without further purification.

Surface Area and Porosity of Silica–Alumina. The adsorption and desorption isotherms of nitrogen on silica–alumina were measured at −196 °C by the volumetric method. The surface area was calculated by the BET method, where the adsorbed area of a nitrogen molecule was assumed to be 16.2 Å^2. The pore volume of silica–alumina was estimated from the adsorbed amount of nitrogen at the saturated pressure. The pore-size distribution was calculated from the desorption branch of the isotherms by the method reported by Barret *et al.*, where the shape of pores was assumed to be cylindrical.[9]

Water Content of Silica–Alumina. The surface water content of silica–alumina was determined by the successive-ignition-loss method reported previously.[10]

Acidity of Silica–Alumina. The measurement of the surface acidity of silica–alumina was carried out by Benesi's method by using the indicators mentioned above.[11] Ten milliliters of a 4—12% solution of butylamine dissolved in benzene were mixed with 0.15—0.27 g of silica–alumina which had been pretreated *in vacuo* at room temperature. The mixture was shaken for 10 h at 30 °C. A few drops of a 0.1% indicator solution were then added to the mixture, and the color change of the silica–alumina was observed. The acidity was determined from the minimum amount of butylamine which did not bring about a color change.

Adsorption of Pyridine on Silica–Alumina from the Hexane Solution. The amounts of pyridine adsorbed on silica–alumina from the hexane solution were determined from the difference between the concentrations of the solution before and after the adsorption. Ten milliliters of the pyridine solution were poured into a 15 ϕ centrifugal tube with a cap, containing 0.35—0.65 g of silica–alumina. The tube was then shaken for 10 h at 30 °C. The equilibrium concentration of the pyridine was determined by means of absorption spectroscopy at the wavelength of 220 nm. In this experiment, the adsorption measurement of pyridine was carried out on the fresh and pyridine-chemisorbed surfaces. The latter surface was prepared by immersing the silica–alumina into a 0.1 M pyridine solution and by then washing the sample in a column with a sufficiently large quantity of hexane until no pyridine was detected in the hexane. The wet sample was then transferred to the centrifugal cell. After the residual hexane in the cell had been pipetted out, the pyridine solution of a known concentration was again poured into the cell. The effect of dilution due to the residual hexane was within an experimental error of adsorption (2%).

Adsorption Calorimetry of Pyridine on Silica–Alumina. A flow microcalorimeter was used for the adsorption calorimetry.[8] Silica–alumina (0.10—0.12 g) was set into the calorimeter. Hexane was forced to flow through at the flow rate of 0.21 ml/min by means of the pump. After a stable base line with no slope had been recorded, the hexane was replaced by a 0.1 M pyridine solution. A solution of the same concentration was then allowed to flow through until no heat evolved by the adsorption was detected; the temperature went

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down to the same level as the original base line (Fig. 6). In this stage, the adsorption equilibrium was established. In this calorimetry, the measurement was carried out at 30 °C; the two surfaces mentioned above were also used.

Results and Discussion

Characterization of Silica–Alumina Powder. Prior to the measurement of the interaction energy between the silica–alumina surface and the pyridine molecules, such properties of silica–alumina as the surface area, the pore volume, the pore-size distribution, the water content, and the surface acidity were examined.

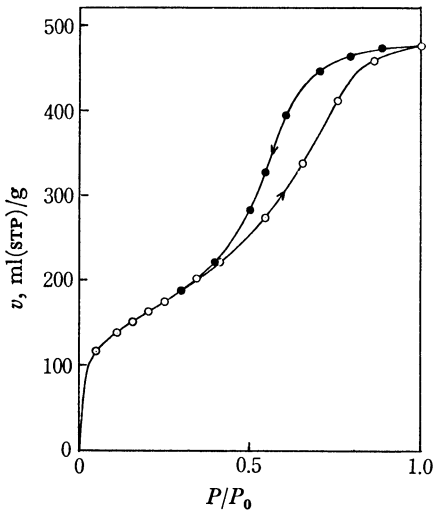

Fig. 1. Adsorption isotherm of nitrogen on silica–alumina at −196 °C. Pretreatment at 25 °C. ○: adsorption, ●: desorption.

Figure 1 shows the adsorption isotherm of nitrogen gas on silica–alumina. The facts that a distinct hysteresis appears in the isotherm and that the isotherm is of Type IV[12] reveal the sample used to be porous. From the isotherm, the BET surface area and the pore volume were estimated to be 596 m^2/g and 0.74 ml/g respectively. Assuming that the pores are cylindrical, we can calculate the average radius of the pores, $\bar{r}_p$, from the $\bar{r}_p=2v_p/S$ relation, where v_p is the pore volume, and S, the surface area. The calculated value of $\bar{r}_p$ is found to be 25 Å. The pore-size distribution curve given in Fig. 2 shows a peak at 21 Å, representing an asymmetric distribution extending to larger pores. It should be noted that most pores in silica–alumina are remarkably larger than the molecular size of butylamine or pyridine; this suggests that these molecules can easily diffuse into pores.

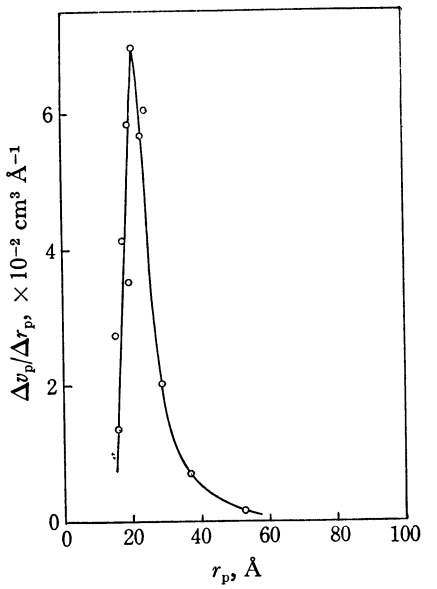

Fig. 2. Pore size distribution of silica–alumina.

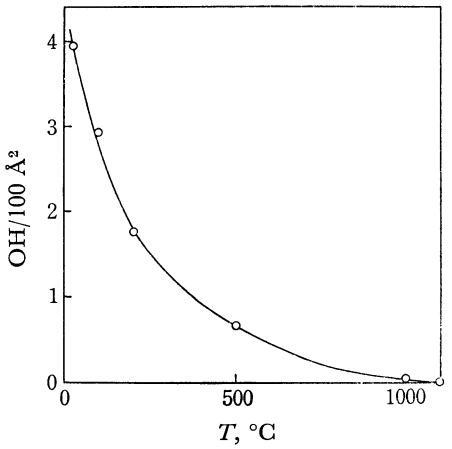

Fig. 3. Water content of silica–alumina.

In Fig. 3, the water content of silica–alumina, expressed by the number of surface hydroxyl groups per 100 $Å^2$, is given as a function of the pretreatment temperature. It may be seen from Fig. 3 that the water content of the silica–alumina used in the present experiment approximates that of pure silica,[13–15] but the dehydration behavior is greatly different from that in silica; that is, the surface water content of silica–alumina decreases rapidly with an increase in the pretreatment temperature.

In Fig. 4, the acidity is given as a function of the acid strength (H_0), expressed by the number of acid sites per 100 $Å^2$. The fact that the acidity goes nearly parallel to the abscissa leads to the conclusion that all the acid sites on silica–alumina are strongly acidic. Benesi reported a similar result for silica–alumina calcined at 550 °C.[11] On the other hand, the average

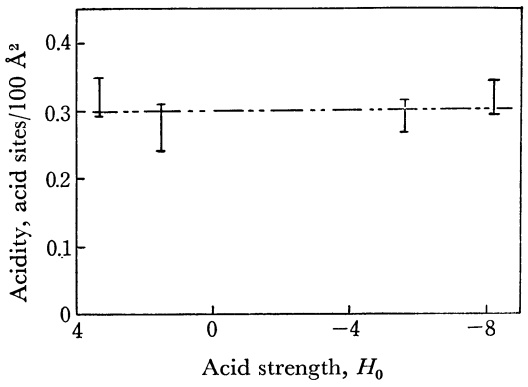

Fig. 4. Acidity *vs.* acid strength for silica–alumina.

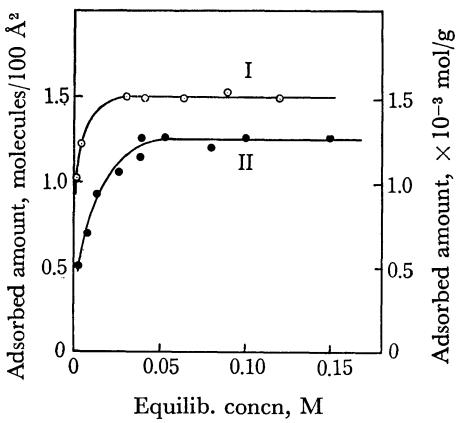

Fig. 5. Adsorption isotherm of pyridine on silica–alumina from *n*-hexane solution at 30 °C. I: fresh surface, II: pyridine-chemisorbed surface.

surface population of acid sites is only 0.3 sites/100 Å² (Fig. 4), indicating that the acid sites are very sparse on silica–alumina.

Adsorption of Pyridine on Silica–Alumina from the Hexane Solution. The adsorption isotherm of pyridine measured on silica–alumina from the hexane solution is shown in Fig. 5. Curves I and II correspond to the adsorption of pyridine on fresh and pyridine-chemisorbed surfaces of silica–alumina respectively; both curves are found to be of the Langmuir type. The difference between the two curves at saturation is read to be 0.25 molecules/100 Å² from Fig. 5, which indicates the amount of strongly adsorbed pyridine which could not be removed by washing the pyridine-preadsorbed surface with a large quantity of hexane, while the II isotherm represents the physisorption of pyridine, 1.25 molecules/100 Å² as a maximum (Fig. 5). Taking account of the magnitude of the heat of adsorption to be given later, these pyridine molecules may be considered to be chemisorbed on the surface of silica–alumina. Here, it is interesting to note that the acidity mentioned above is in fairly good agreement with the quantity of chemisorbed pyridine; this enables us to conclude that one molecule of chemisorbed pyridine interacts with one acid site.

One further question remains to be solved, whether pyridine molecules are chemisorbed on the Brönsted or Lewis acid sites. Shiba *et al.* determined both Brönsted and Lewis acid on silica-alumina as a function of the silica content.[16] On silica–alumina containing 13 wt % alumina, the amounts of Brönsted and Lewis acid were found to be *ca.* 80 and 20% respectively when treated at 500 °C. In our sample, the pretreatment temperature is 25 °C. As may be seen from Fig. 3, the water content decreases remarkably with the increase in the temperature from 25 to 500 °C. It is expected that, in the present silica–alumina, the greater part of the acid sites are of the Brönsted type, because the Brönsted acid sites increase with the water content. Thus, it may reasonably be considered that, in the present investigation, pyridine molecules react with the Brönsted sites to form pyridinium ions.[3]

Adsorption Calorimetry of Pyridine on Silica–Alumina. Figure 6 shows the response of the flow microcalorimeter to the adsorption of pyridine on silica–alumina from the hexane solution. Peaks I and II were obtained by the adsorption of pyridine on the fresh and pyridine-chemisorbed surfaces respectively. After Peak I was measured, the flowing liquid was converted from the solution to the solvent. In order to wash away the physisorbed pyridine, the solvent was forced to flow through the calorimeter for a prolonged period (15—20 h), until no pyridine was detected in the solvent flowing out of the calorimeter. Again, a pyridine solution of the same concentration was introduced into the calorimeter. Peak II was thus obtained. Pyridine molecules adsorbed on silica–alumina are composed of two part, *i.e.*, reversible and irreversible parts, as has been stated above; the corresponding heats of adsorption can be analyzed from the areas of the two peaks. As a matter of course, Peak II arises from the reversible or physical adsorption of pyridine, while Peak I should involve both kinds of adsorption. First, the reliability of adsorption calorimetry was confirmed by the measurements of twelve runs at the concentration of a 0.1 M pyridine solution; the data were calibrated by using electrical energy. The results obtained are listed in Table 1, giving the average values of 19.6 ± 0.2 and 14.1 ± 0.2 cal/g for Peaks I and II respectively.

Table 1. Calorimetric results on the pyridine adsorption on silica–alumina from 0.1 M solution at 30 °C

Run no.	Fresh surface (cal/g)	Pyridine-chemisorbed surface (cal/g)
1	18.3	13.5
2	19.0	12.6
3	19.8	14.2
4	20.2	15.7
5	20.2	14.6
6	19.6	13.7
7	18.7	12.3
8	19.9	14.9
9	20.5	15.8
10	19.8	14.3
11	18.8	13.0
12	20.1	14.4
av.	$19.5_8\pm0.2_1$	$14.0_8\pm0.2_0$

Next, on the basis of the calorimetric data (Table 1) and the adsorption isotherms (Fig. 5), the heat of adsorption of pyridine can be computed to be 11.3 ± 0.3 and 22 ± 4 kcal/mol for the physisorbed and chemisorbed pyridine respectively. In the present calorimetric measurements, the heat of dilution should be a factor in addition to the heat evolved by adsorption. The heat of dilution can be estimated from the dependence of the heat-of-mixing, ΔH_{mix}, on the concentration of the solution. The calorimetric measurement of ΔH_{mix} was carried out at 30 °C in a pyridine–hexane system by means of an adiabatic calorimeter. In the concentration range from 0.03 to 0.1 M pyridine, ΔH_{mix} was found to be 2.10 ± 0.02 kcal/mol. The fact that ΔH_{mix} is independent of the concentration indicates that the heat of dilution is less than the limits of experimental

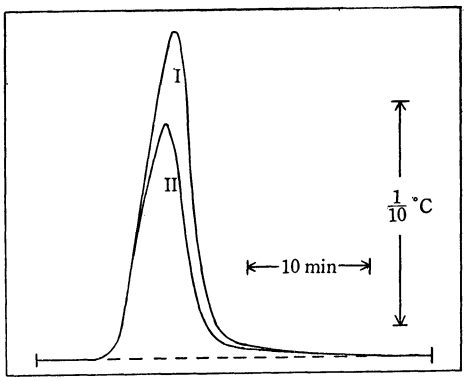

Fig. 6. Adsorption peaks of pyridine on silica–alumina from 0.1 M solution at 30 °C. I: fresh surface, II: pyridine-chemisorbed surface.

error, *i.e.*, ±0.02 kcal/mol. Accordingly, the heat of dilution is neglected compared with the heats of adsorption mentioned above.

The larger heat of chemisorption may be attributed to the strong interaction of strong Brönsted acid sites with pyridine molecules through the relation of 1 : 1 between the site and molecule. In other words, the heat of chemisorption is considered to be the heat of the formation of pyridinium ions on the silica–alumina surface. On the other hand, the heat of the physisorption of pyridine is probably due to the interaction of the physisorbed molecules with possible surface sites other than the strong acid sites, *i.e.*, with surface silanol groups.

So far, several investigators have reported on the heat of adsorption in systems of basic molecules silica–alumina.[4–7] However, the direct calorimetric heats of physisorption and chemisorption in the system of pyridine–silica–alumina have not been measured. Roca *et al.* estimated indirectly the heats of physisorption and chemisorption of pyridine on silica–alumina by utilizing the adsorption isosters and the temperature-programmed desorption technique;[17] they obtained 8 kcal/mol for the heat of physisorption and 33 and 39 kcal/mol for the heat of chemisorption on two different sites. Their heat of physisorption is slightly lower than ours, while their heat of chemisorption is fairly larger than ours.

In considering the discrepancy between the two sets of data, it is necessary to compare the pretreatment conditions. In our sample degassed at 25 °C, there is a great possibility that the surface includes physisorbed water molecules, because of the remarkable decrease in water content with the temperature (Fig. 3), while in Roca's sample degassed at 400 °C, physisorbed water molecules are considered to be almost entirely removed from the surface. It may, therefore, be considered that the heat of chemisorption of pyridine may be greatly reduced by the existence of physisorbed water, while the heat of physisorption may not be influenced significantly by the existence of physisorbed water.

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