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Apparent Abnormal Adsorption of Nitrogen over NaA Zeolite and Adsorption of Helium

The surface areas of porous solids have frequently been estimated by the Brunauer–Emmett–Teller (BET) method from the adsorption isotherms of gases, especially nitrogen (*1*). But a 100-fold discrepancy was found between the surface areas of some coals estimated from nitrogen adsorption and those of the same coals from water or methanol adsorption (*2*). Maggs suggested that the anomaly may have arisen from a reduced accessibility of nitrogen to the internal surface at liquid nitrogen temperature (*3*).

Some zeolites must show an extraordinarily abnormal phenomenon for adsorption because the sizes of their pores are comparable with the dimensions of adsorbates. We found apparent negative values for the adsorption of nitrogen over a NaA zeolite.

This paper is concerned with the apparent negative values for the adsorbed amounts of nitrogen over a NaA zeolite at liquid nitrogen temperature and the quantitative analysis based on the overestimation of the dead space of the adsorption cell containing the zeolite.

The specially synthesized NaA zeolite was kindly provided to us by Toyo Soda Mfg. Co., Ltd. The particles of the zeolite were crystalline and uniform in size, about 4 μm large (*4*).

Helium and nitrogen from tanks were purified by passing them through tubes filled with copper powder at 773 K and activated carbon at 77 K.

The adsorption of nitrogen was measured by a temperature-compensated differential tensimeter that was symmetrical in design (*5*) as shown in Fig. 1. The apparatus consists of a differential micromanometer whose two arms are connected to a pair of sample and reference burettes of nearly equal volume. Both burettes and adsorption cells are constructed to be as symmetrical as possible. Surface areas as small as 0.03 m^2 can be measured through volumetric measurements of nitrogen uptake at liquid nitrogen temperature with the apparatus described here.

The volume of the reference burette, V_A, that of the sample burette, $V_A + DV_A$, the volume of the reference adsorption cell, V_B, and the difference in volumes between the sample adsorption cell containing the adsorbent and the reference absorption cell containing several glass rods, DV_B, were determined by measuring the initial and final pressures after the expansion of the given quantity of helium on the assumption that the amount of helium adsorbed is negligibly small.

The amount adsorbed was estimated from the difference between the amount of adsorbate, nitrogen, admitted and the amount remaining in the gas phase described previously (*5*). The method of "accumulated introduction" was used in the adsorption run.

Figure 2 shows the apparent adsorbed amount of nitrogen estimated with $V_A + DV_A$ and $V_B + DV_B$ described previously. The adsorbed amounts of nitrogen were apparently negative at high equilibrium pressures. The estimation of values other than DV_B (therefore $V_B + DV_B$) is reliable in the equation for the estimation of the adsorbed amount of nitrogen. Thus, the apparent

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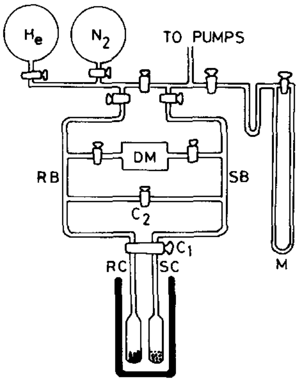

FIG. 1. Scheme of apparatus: DM, differential micromanometer; M, mercury manometer; RB, reference burette; SB, sample burette; RC, reference adsorption cell; SC, sample adsorption cell.

negative values suggest that the value of DV_B (therefore $V_B + DV_B$) was overestimated.

The pore constrictions of the NaA zeolite are comparable with nitrogen dimensions. The abnormal phenomenon may have arisen from a considerably reduced accessibility of adsorbate, nitrogen, to the internal surface of the NaA zeolite at liquid nitrogen temperature in spite of the full accessibility of the dilatometric fluid, helium, to the internal surface.

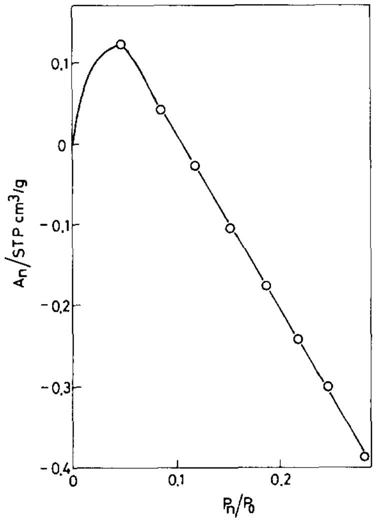

FIG. 2. The apparent adsorption isotherm of nitrogen over the NaA zeolite at liquid nitrogen temperature. A_n and P_n/P_0 are the apparent amount of adsorbed nitrogen and relative pressure of nitrogen, respectively.

Nitrogen adsorbs only on the external surface of the NaA zeolite at liquid nitrogen temperature because nitrogen molecules scarcely diffuse into the pores through the intercrystalline channels. Thus, the corrected adsorption isotherm of nitrogen should obey a BET equation.

If the value of DV_B changes, the corrected adsorbed amount with the corrected value of DV_B changes. Then the linearity obtained from the corrected BET plot changes if the value of DV_B changes.

The linearity was estimated from the root mean square, Δ, of the difference between the corrected experimental value and the calculated value with a BET equation. The root mean square changed with a function of dV_B as shown in Fig. 3. The least value of the root mean square corresponds to the best linearity of the BET plot. The best linearity of the BET plot was obtained if the volume of the sample adsorption cell, $V_B + DV_B$, was reduced by $dV_B = 2.95\ \mathrm{cm^3/g}$ from Fig. 3. The BET plot obtained on the assumption that the $V_B + DV_B$ was reduced by $dV_B = 2.95\ \mathrm{cm^3/g}$ was a straight line. The BET plots with the other values of dV_B showed convex or concave lines.

The surface area (the external surface area) estimated from the monolayer volume

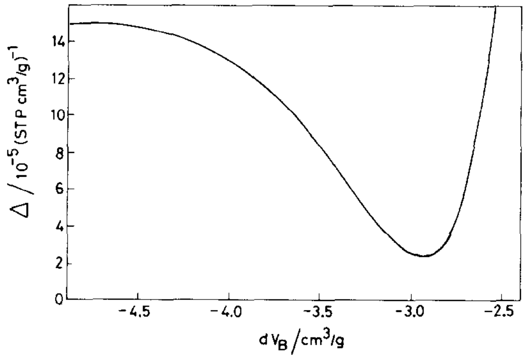

FIG. 3. The root mean square, Δ, of the difference between the corrected experimental values and the calculated values with a BET equation with a function of dV_B.

of nitrogen obtained from the corrected linear BET plot was 0.90 m^2/g, which was in agreement with the external surface area of the NaA zeolite obtained by the filled pore method or with the geometrical surface area estimated from its scanning electron micrograph (*4*).

The overestimated dead space of the sample adsorption cell, dV, is attributed to two facts. One was caused by the difference, DV_1, between the exclusion volume obtained with the dilatometric fluid, helium, and that obtained with the adsorbate, nitrogen. This may be estimated from the pore volume of the NaA zeolite. The pore volume of NaA zeolite had been determined from the amount of adsorbed water at saturation, and it was 0.29 cm^3/g (*6*). Then DV_1 was estimated at $0.29 \times (300/77) = 1.13$ cm^3/g, where 300 and 77 are the temperatures at the burette and at the adsorption cell, respectively.

The other was caused by the adsorption of the dilatometric fluid, helium, which was used for the estimation of the dead space of the adsorption cell containing the zeolite described above. Helium is known to be the least adsorptive gas onto solids. It has been frequently used as a dilatometric fluid for the determination of the dead space of the vessels of the volumetric measurements (*7*).

The external surface area of the NaA zeolite was about 0.9 m^2/g, and it was much smaller than the total surface area (*4*). Helium can diffuse into the internal pores whereas nitrogen scarcely diffuses into the internal pores at liquid nitrogen temperature. Thus, the adsorbed amounts of helium on the internal surface of the NaA zeolite may be comparable with those of nitrogen over the external surface.

On the assumption that the amount of adsorption of the dilatometric fluid, helium, is not considered, the volume of the sample adsorption cell containing the zeolite is overestimated and the overestimated volume caused by the adsorption of helium, dV_2 (in cm^3), is described as

$$dV_2 = \frac{KRT}{22414}, \tag{1}$$

where K and T are the adsorption equilibrium constant of helium and the temperature at the burette, respectively.

Recently we developed a method for the volumetric determination of the amount of adsorption of helium with the apparatus used in this experiment (*8*). The amount of adsorption of helium was determined by measuring an increase in the apparent dead space between the sample adsorption cell containing the adsorbent and the reference adsorption cell containing several glass rods on the assumption that the adsorbed amount of helium at 673 K was small, the temperature of the adsorption cells being changed after each determination.

The adsorption equilibrium constant over the NaA zeolite at 77 K was 2.011×10^{-5} STP $cm^3/Pa\ g$ (*8*) and it was nearly equal to that on a chabazite on 77.3 K obtained by Ignatov and Jachel (*9*). The dV_2 was estimated at 2.21 cm^3/g from Eq. (1).

The total overestimated volume, dV, is described with the addition of dV_1 and dV_2 as

$$dV = dV_1 + dV_2 = 3.34\ cm^3/g. \tag{2}$$

The value of dV, 3.34 cm^3/g, is in agreement with the value of dV_B, 2.95 cm^3/g, obtained in Fig. 2.

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