[January, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 1—4 (1985)

Adsorption Properties of Pillar Interlayered Montmorillonite

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(Received March 31, 1984)

From analyses of Langmuir-type isotherms and α_s-plots for nitrogen adsorption, both the micropore volume and the external surface area have been determined for pillar interlayered montmorillonite (abbreviated as PILM) prepared by intercalating the polynuclear Al cation into the montmorillonite interlayer. The applicability of the Gurvitsch rule to microporous PILM samples was confirmed for adsorption of heptane, whereas the adsorbed amounts of polar adsorbates were dependent on dehydrated states of the alumina pillar. High density of benzene in the micropore independent of calcination temperature suggests some peculiar orientation of benzene in the adsorbed state due to its molecular shape. The interaction of a water molecule with the adsorption site is weak and dependent on the calcination temperature of PILM samples. On this basis, the inhibition of rehydration of the alumina pillar has been discussed.

The pore structure of a solid is essentially important for its adsorption properties. For example, the diffusion characteristics of benzene molecules adsorbed on pillar interlayered montmorillonite (abbreviated as PILM) are in contrast with those on faujasite-type zeolite, although both the adsorbents are similar in micropore size;[1] irreversible dehydration of the alumina pillar has been correlated with surface chemical properties of PILM.[2]

Since Langmuir-type isotherms for nitrogen adsorption on hydroxy-zirconium,[3] hydroxy-chromium,[4] and hydroxy-bismuth[5] montmorillonites were attributed to steric hindrance to the multilayer formation in micropores, elucidation has been expected of the adsorption behavior inside PILM micropores of various adsorbates including nitrogen. Moreover, some new clue to the characterization of surface chemical properties of PILM is necessary, since the generally adopted method of measuring heat of immersion[6] is inapplicable to microporous solids. In this study, we attempt to clarify surface chemical properties by measuring the adsorption enthalpy of water, because the small and polar molecule of water may penetrate with ease through pores of a solid during the adsorption process. An additional purpose is to examine whether or not surface hydroxyl groups can be regenerated, as it is important for the acidic nature of PILM catalysts.

Experimental

Montmorillonite. Otay montmorillonite, supplied from Ward's Natural Science Establishment, Inc., was separated by gravity sedimentation in water dispersion to obtain the fraction less than 2 μm in diameter, and was treated with NaCl (1.0 mol dm^{-3}) to obtain the mother material for PILMs in the Na ion exchanged form (hereafter the material is referred to as Na-Mont).

Preparation of Intercalation Compounds. Preparation of the polynuclear cation $[\mathrm{Al}_{13}\mathrm{O}_4(\mathrm{OH})_{24}(\mathrm{OH}_2)_{12}]^{+7}$[7—9] and its intercalation into montmorillonite were done in the same manner as in previous studies.[1,2] The sample dried in an oven overnight at 393 K is referred to as PILM 120. This sample was calcined in air for 2 h at 473, 673, 873, or 1073 K (hereafter the calcined sample is referred to as PILM 200, PILM 400, PILM 600, or PILM 800, respectively). All these samples were kept in a vessel containing saturated aqueous solution of NH$_4$Cl to provide a constant humidity. A perspective view of PILM 120 is shown in Fig. 1.

Adsorption Analysis. Both volumetrical adsorption measurements with nitrogen at 77 K using an Orr surface-area

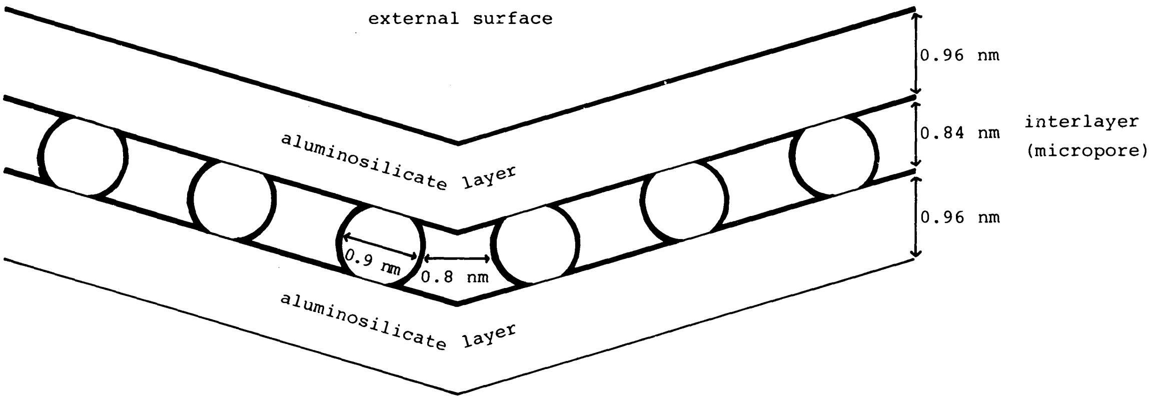

Fig. 1. Perspective view of the pillar interlayered montmorillonite, with the interdistance minimized for the homogeneous arrangement.

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pore-volume analyzer (2100 D, Micromeritics Instrument Corp.) and gravimetrical measurements at 298 K using a spring balance for heptane, benzene, 1-chlorobutane, and 1-nitropropane were conducted after a standard pretreatment of overnight evacuation ($<10^{-3}$ Pa) at 393 K.

Calorimetric Measurements of Water Adsorption. A twin conduction type calorimeter (Tokyo Riko Co., Ltd.) equipped with a vacuum system was used to detect the heat evolved during the adsorption process. Before measurement at 298 K, all samples were heat-treated at 393 K for 6 h under vacuum ($<10^{-3}$ Pa).

Results and Discussion

Estimation of the External Surface Area of Montmorillonite Samples with and without Interlayered Pillar. Figure 2 shows adsorption and desorption isotherms for nitrogen. The Langmuir-type adsorption, observed for all the samples except PILM 800, indicates the predominance of adsorption to fill up the micropore. The adsorption behavior in the middle pressure region will correspond to the adsorption on external surface, which may be ignored in the case of zeolite.[10] Abrupt change is noticed with the desorption isotherms at $p/p_0 \simeq 0.5$, resulting from the tensile strength effect.[11]

The α_s-method is useful for discriminating the monolayer capacity of external surface from the micropore capacity.[12,13] As for nonporous adsorbents, the external surface area, S_{ex}, is deduced from the slope of its α_s-plot, a straight line passing through the origin. In the case of microporous adsorbents, however, both the external surface and the micropore provide adsorption sites as far as the micropore is unfilled with adsorbate. Adsorption behavior different from that of nonporous solids would be expected; the α_s-plot provides a linear portion in the region of high coverage, whose slope gives the S_{ex} value for microporous solids.

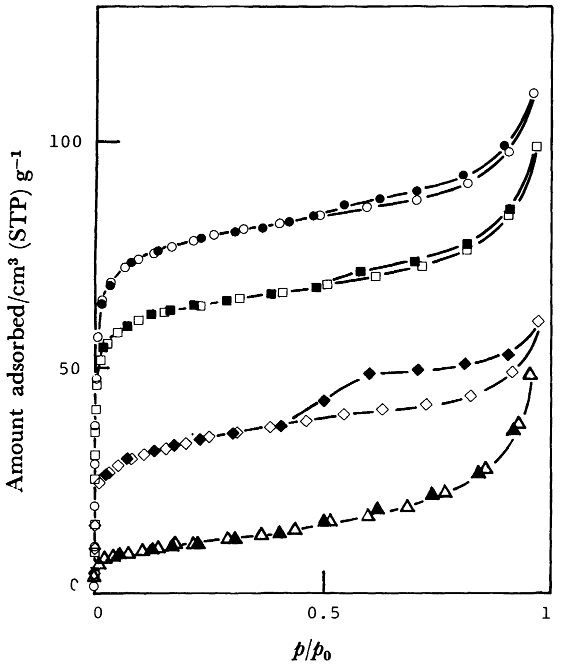

Fig. 2. Nitrogen adsorption and desorption isotherms of montmorillonite samples with and without the interlayered pillar at 77 K.
Open symbols: adsorption points, solid symbols: desorption polints. ○,●: PILM 120, □,■: PILM 400, △,▲: PILM 800, ◇,◆: Na-Mont.

Representative α_s-plots are shown in Fig. 3. Table 1 summarizes the S_{ex} values thus obtained from the slope of linear portion. The coincidence of the S_{ex} values among all the PILM samples except PILM 800 in Table 1 is remarkable. The α_s-plot for PILM 800 gives a straight line passing through the origin; thermal collapse of montmorillonite layer structure was previously observed in an X-ray diffraction pattern.[2]

Surface Areas of Montmorillonite Samples with and without Interlayered Pillar. The surface area, S, of adsorbent is generally evaluated by

$$S = v_a s N / M, \tag{1}$$

where v_a is the apparent monolayer capacity, s the cross-sectional area of adsorbate,[14] N Avogadro's number, and M the molar weight of adsorbate. Table 2 summarizes physical properties of adsorptives necessary for the adsorption analysis described later.

The v_a values of PILMs 120—600 were obtained from their Langmuir plots (for nitrogen $0.05<p/p_0<0.30$ and for the other adsorbates $0.10<p/p_0<0.35$). Since the adsorption isotherms of PILM 800 obeyed the BET equation, its S values were determined from BET

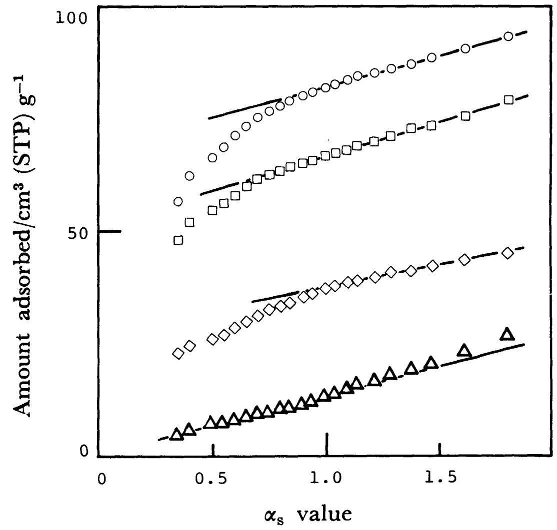

Fig. 3. The α_s-plot of montmorillonite sample with and without the interlayered pillar.
○: PILM 120, □: PILM 400, △: PILM 800, ◇: Na-Mont.

TABLE 1. EXTERNAL SURFACE AREAS OF MONTMORILLONITE SAMPLES WITH AND WITHOUT INTERLAYERED PILLAR AS CALCULATED FROM α_s-PLOTS

Adsorbent	PILM 120	PILM 200	PILM 400	PILM 600	PILM 800	Na-Mont
S_{ex}/m² g⁻¹	38.7	42.8	40.7	46.8	38.7	28.6

Table 2. Physical properties of adsorptives necessary for adsorption analyses

Adsorptive	Nitrogen	Heptane	Benzene	1-Chlorobutane	1-Nitropropane
Molar weight (M/g mol^{-1})	28.01	100.21	78.12	92.57	89.09
Density of liquid (ρ/g cm^{-3})	0.808$^{a)}$	0.6796$^{b)}$	0.8737$^{b)}$	0.8866$^{c)}$	1.0009$^{c)}$
Cross-sectional area$^{d)}$ (s/nm^2)	0.162	0.631	0.436	0.446	0.305$^{e)}$

a) At 77 K. b) At 298 K. c) At 293 K. d) Quoted from Ref. 14. e) Calculated with the equation: $s=1.091\times 10^{14}\ (M/\rho N)^{2/3}$.

Table 3. Surface area (S/m^2 g^{-1}) determined with various adsorbates

Adsorbate$^{a)}$	Nitrogen	Heptane	Benzene	1-Chlorobutane	1-Nitropropane
PILM 120	348.5	330.4	461.2	411.0	401.7
PILM 200	294.5	292.6	383.6	333.9	353.6
PILM 400	293.2	288.8	383.8	358.9	309.5
PILM 600	286.2	286.0	364.9	286.8	260.0
PILM 800$^{b)}$	37.9	43.4	—$^{c)}$	30.7	32.1

a) Nitrogen was adsorbed at 77 K and the other adsorbates at 298 K. Unless otherwise noted, adsorption obeyed the Langmuir equation. b) Adsorption obeyed the BET equation. c) Adsorption obeyed neither the BET nor the Langmuir equation.

plots (the p/p_0 range was the same as above) except the case of benzene. Table 3 shows surface area values of PILM samples thus derived from Eq. 1 with various adsorbates. The coincidence between the BET surface area, S (37.9 m^2 g^{-1}), and the α_s-plot external surface, S_{ex} (38.7 m^2 g^{-1}), for PILM 800 strongly supports the applicability of the α_s-method to the present system.

Applicability of the Gurvitsch Rule to Pillar Interlayered Montmorillonite. According to Breck and Grose,[15] the Gurvitsch rule on the amount of adsorbate taken up at saturation holds good for various types of zeolites, *i.e.*, a given adsorbent adsorbs different adsorbates up to the same amount as expressed in volume of liquid. This rule was applied to obtain the micropore volume of PILM samples as follows.

From the monolayer capacity, v_{ex}, of external surface obtainable from

$$S_{ex} = v_{ex}sN/M, \tag{2}$$

micropore capacity, v_{in}, is obtained as

$$v_{in} = v_a - v_{ex} \tag{3}$$

and is used to evaluate micropore volume, v, according to

$$v = v_{in}/\rho, \tag{4}$$

where ρ is the density of liquid.

Comparison of micropore volumes obtained with various adsorbates is useful for elucidating adsorption properties of PILM micropore. Figure 4 shows the relationship between the micropore volume for a polar or nonpolar adsorbate relative to that of nitrogen, v_{N_2}, and the calcination temperature. The dipole moment of each adsorbate is given in parentheses.

As far as the Gurvitsch rule is valid for the PILM micropore, all the values of v must be equal to v_{N_2}. Actually, the nonpolar adsorbate heptane gives a value of unity irrespective of calcination temperature, suggesting that the adsorption state in the micropore corresponds closely to liquid nitrogen.

The values for the polar adsorbates, 1-chlorobutane and 1-nitropropane, on the other hand, are larger than unity, especially with the samples for low calcination temperatures. Moreover, the deviation from unity is larger for 1-nitropropane (3.57 D) than for 1-chlorobutane (2.05 D). Since the irreversible dehydration of the alumina pillar proceeds in the calcination pretreatment on PILM samples,[2] water molecules and/or hydroxyl groups on the pillar surface should be responsible for the extraordinarily high density of these

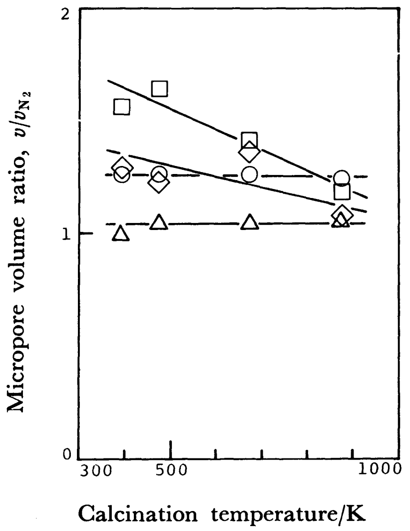

Fig. 4. Micropore volume ratio of PILM samples obtained with polar and nonpolar adsorbates as a function of calcination temperature.
△: heptane (0 D), ○: benzene (0 D), ◇: 1-chlorobutane (2.05 D), □: 1-nitropropane (3.57 D).

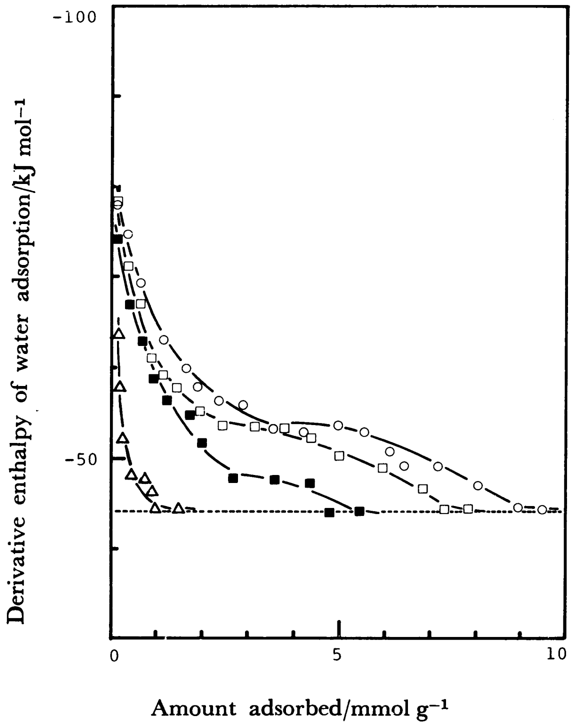

Fig. 5. Derivative enthalpy of water adsorption as a function of the amount adsorbed, with liquefaction enthalpy of water indicated by dashed line. ○: PILM 120, □: PILM 400, ■: PILM 600, △: PILM 800.

polar adsorbates. In addition, it is to be noted that the gradual decrease in the v/v_{N_2} values down to unity with elevating calcination temperature indicates the decisive influence of the alumina pillar on the adsorbate density. The assumption of homogeneous arrangement of the alumina pillars in the montmorillonite interlayer, therefore, is most likely.

The adsorbate density of benzene is high and independent of calcination temperature, which suggests a highly oriented adsorption of benzene due to its molecular shape under restriction of the slit width of PILM micropore.

Derivative Enthalpy of Water Adsorption on Pillar Interlayered Montmorillonite. Derivative enthalpies of water adsorption on PILM samples obtained by calorimetry are given in Fig. 5. In the range of sufficiently large amounts of water adsorbed, all the samples give almost the same values equal to the liquefaction enthalpy of water. The interaction of a water molecule with an adsorption site on a PILM sample is weaker than on zeolite[16] and decreases in degree with elevating calcination temperature.

The heat of immersion of α- and γ-alumina in water was reported to decrease with elevating pretreatment temperature in the relatively high temperature region; this phenomenon was ascribed to irreversible stabilization of dehydrated alumina surface.[17] Inhibition of the rehydration process would as well be responsible in the present PILM system.

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