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Mechanism of Adsorption of Methylene Blue on Magnesium Silicate

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The adsorption of Methylene Blue on magnesium silicate prepared by three different methods at 30° and 90° was investigated in order to elucidate the mechanism of adsorption of Methylene Blue on porous magnesium silicate. The adsorption isotherm of Methylene Blue was well described by the Langmuir equation. The amount of Methylene Blue adsorbed on porous magnesium silicate was dominated by its total pore volume. It is suggested that the pores with radius smaller than 14.5 Å are completely filled with Methylene Blue, while the pores with radius larger than 15 Å remain partially unfilled.

Keywords——mechanism of adsorption; porous magnesium silicate; methylene blue; Langmuir equation; total pore volume

In the previous work,[2–4] the amount of Methylene Blue adsorbed on magnesium silicate was found to be mainly determined by pore volume rather than surface polarity factors such as acidity and acid strength.

In the present work, the pore size distribution of magnesium silicate was determined in order to elucidate the adsorption mechanism of Methylene Blue on porous magnesium silicate. The adsorption isotherm of Methylene Blue on magnesium silicate was consistent with the Langmuir equation. The results of the present study suggest that pores with radius smaller than 14.5 Å are completely filled with Methylene Blue and that pores with radius larger than 15 Å remain partially unfilled.

Experimental

Preparation of Magnesium Silicate——Magnesium silicate Nos. 1 and 2 were prepared by adding 10% sodium silicate solution to 10% magnesium sulfate solution at a rate of 10 ml per minute under constant stirring.[2] Magnesium silicate Nos. 3 and 4 were prepared by similarly adding 10% magnesium sulfate to 10% sodium silicate.[2] Magnesium silicate Nos. 5 and 6 were homogeneously coprecipitated[5] with 10% magnesium sulfate and 10% sodium silicate. Nos. 1, 3, and 5, and Nos. 2, 4, and 6 were prepared at 30° and 90°, respectively. The precipitates in each preparation were collected by filtration with suction, washed several times with distilled water to remove impurities, and dried for 10 hr at 110°. Finally, the magnesium silicate was sieved in the range of 100 to 200 mesh. The chemical composition of magnesium silicate was measured by the method described previously.[2] The specific surface areas were measured at liquid nitrogen temperature with a B.E.T. apparatus assembled by us, using argon gas.

Procedure for Adsorption of Methylene Blue——The pH of an aqueous Methylene Blue solution was adjusted to 6.6 to 7.5. It took 15 days at 37° to attain adsorption equilibrium, and after that time, the equilibrium amount of Methylene Blue adsorbed on magnesium silicate was measured at 665 nm with a spectrophotometer (Hitachi model 101).

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1) Location: *a) Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan; b) 380 Nishiyama, Sayama-cho, Minamikawachi-gun, Osaka 589, Japan; c) Yamashiro-cho, Tokushima 770, Japan.*
2) S. Tanada and K. Boki, *Yakuzaigaku*, 33, 146 (1973).
3) S. Tanada, K. Boki, T. Tamura, and K. Matsumoto, *Yakuzaigaku*, **34**, 128 (1974).
4) S. Tanada, K. Boki, T. Tamura, S. Kyotani, Y. Arai, and K. Matsumoto, *Yakuzaigaku*, **35**, 67 (1975).
5) T. Shirasaki, M. Kato, H. Shimizu, I. Nozawa, H. Sakurai, and S. Sakamoto, *Shokubai*, **6**, 37 (1964).

Measurement of Pore Size Distribution——The pore size distribution of magnesium silicate in the range of 7.5 to 300 Å was obtained by the method of Dollimore and Heal,[6] the calculation being performed on a FACOM 203-28S computer (Fujitsu Co., Kawasaki) using a FORTRAN program.[7]

Results and Discussion

Table I shows the pH of the mother liquor, and the chemical composition and the specific surface area of the magnesium silicate. The pH values of the mother liquor are in the range of about pH 8—9, regardless of the preparation method and temperature. The molar ratios of magnesium silicate were larger than the theoretical value ($SiO_2/MgO=1.50$) but were approximately constant ($SiO_2/MgO=2.11$—2.43). The specific surface areas measured by the use of argon gas and Methylene Blue were in the range of about 440 to 620 m^2/g and about 60 to 230 m^2/g, respectively.

1. Adsorption Isotherm of Methylene Blue on Magnesium Silicate

The Langmuir plots of C/V *vs.* C were linear, as shown in Fig. 1. The Langmuir equation was applicable at equilibrium concentrations up to 15000 ppm.

Table I. pH of the Mother Liquor, and Chemical Composition and Specific Surface Area of Magnesium Silicate

No.	pH of mother liquor	Molar ratio SiO_2/MgO	Surface area (m^2/g) argon	Surface area (m^2/g) Methylene Blue
1	6.35→8.9	2.29	501.0	226.1
2	6.35→8.10	2.37	480.8	80.4
3	12.32→8.94	2.93	619.1	99.8
4	12.32→8.03	2.29	620.9	179.5
5	9.15	2.11	443.5	197.0
6	8.13	2.17	522.1	59.4

The cross-sectional areas of argon and Methylene Blue are 14.6[a] and 162 $Å^2$,[b] respectively.
a) H.K. Livingston, *J. Colloid Sci.*, **4**, 447 (1949).
b) D. Graham, *J. Phys. Chem.*, **59**, 896 (1955).

2. Pore Size Distribution of Magnesium Silicate and Amount of Methylene Blue Adsorbed

The pore size distribution was determined in order to elucidate the adsorption mechanism of Methylene Blue. Figure 2 shows the pore size distribution curves for pore radii from 7.5 to 300 Å. Although the curves for magnesium silicate Nos. 1, 3, and 5 (upper part of the figure) prepared at 30° showed different shapes, the curves for magnesium silicate Nos. 2, 4, and 6 (lower part) prepared at 90° showed similar shapes. On the other hand, the curves of Nos. 2—4 and 6 were concave towards the pore radius axis and they approached constant pore volume at a radius of about 20—30 Å. Thus, these results indicate that magnesium silicate Nos. 2—4 and 6 mainly have pores with radius less than about 20—30 Å. Figure 2 also shows that the pore volume of magnesium silicate No. 1 increased markedly as the pore radius increased in two ranges of radius, from 7.5 to 20 Å and from 150 to 200 Å. Furthermore, magnesium silicate No. 5 increased its pore volume markedly in the range of 7.5 to 20 Å, and it then increased monotonically with increasing pore radius. Dubinin[8] pointed out that the pore structure of an adsorbent can be divided into three classes, micropores (radius<15—16 Å), transitional pores (15—16<radius<1000—2000 Å), and macropores (radius<1000—2000 Å). Table II shows the values of pore volume of magnesium silicate and the amount of Meth-

6) D. Dollimore and G.R. Heal, *J. Appl. Chem.*, **14**, 109 (1964).
7) K. Boki, *Nippon Eiseigaku Zasshi*, **32**, 482 (1977).
8) M.M. Dubinin, "Chemistry and Physics of Carbon," ed. by P.L. Walker, Jr., Vol. 2, Marcel Dekker, Inc., New York, 1966, pp. 51—120.

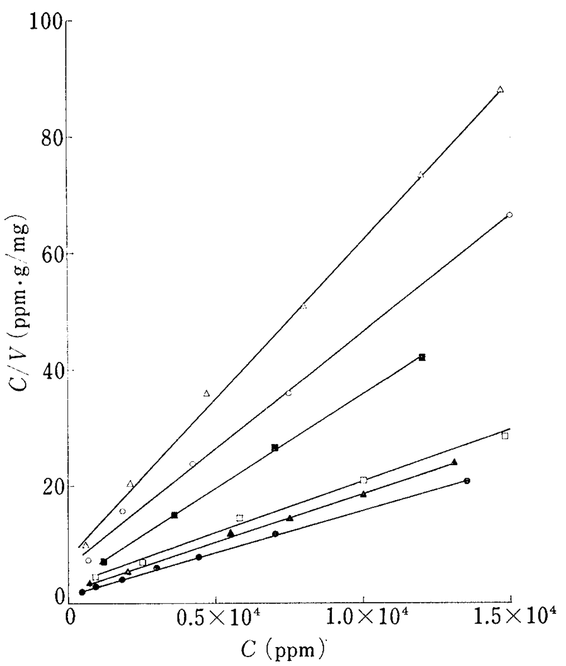

Fig. 1. Langmuir Plots of Adsorption Isotherms of Methylene Blue on Magnesium Silicate at 37°

—●—: No. 1, —○—: No. 2, —■—: No. 3, —□—: No. 4, —▲—: No. 5, —△—: No. 6.
C: equilibrium concentration, V: amount adsorbed.

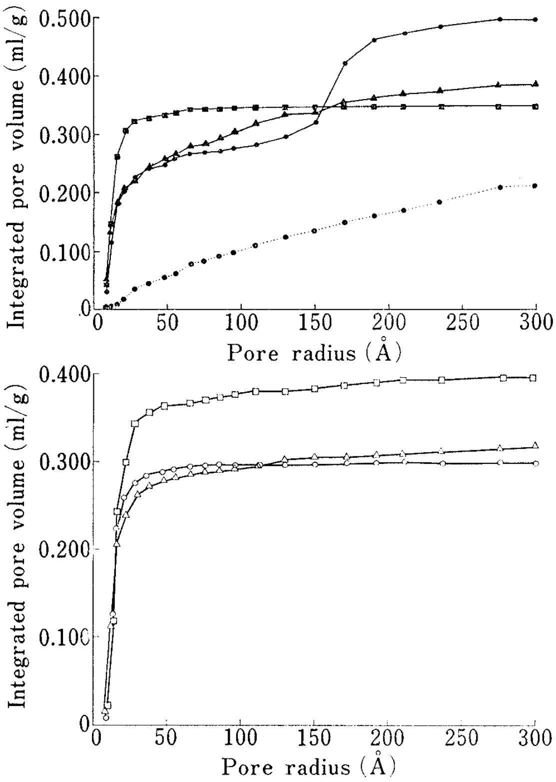

Fig. 2. Pore Size Distribution Curves of Magnesium Silicate

—●—: No. 1, —○—: No. 2, —■—: No. 3, —□—: No. 4, —▲—: No. 5, —△—: No. 6.
---●---: No. 1 with adsorbed Methylene Blue.

Table II. Pore Volume of Magnesium Silicate and Amount of Methylene Blue Absorbed

No.	Micropore volume (ml/g)	Total pore volume (ml/g)	Amount of methylene Blue adsorbed (mg/g)[b]
1	0.1818	0.5167	255.6
2	0.2243	0.2995	103.0
3	0.2656	0.3530	155.8
4	0.2496	0.4454	200.0
5	0.1806	0.4665	236.6
6	0.2038	0.3304	90.4

Micropore volume is the volume at pore radii less than 15.5 Å[8] and total pore volume[c] is the volume at $p_e/p_s=1.0$.
c) K. Urano, H. Mizusawa, and R. Kiyoura, *Kogyo Kagaku Zasshi*, **73**, 1911 (1970).
d) The equilibrium amount was measured at 3000 ppm initial concentration.

ylene Blue adsorbed. Takeda *et al.*[9] reported that the micropores with radius below 15 Å seem to play the most important role in the adsorption of iodine, *p*-nitrophenol, sodium dodecylbenzene sulfonate, and Malachite Green oxalate. If the amount of Methylene Blue adsorbed on magnesium silicate is mainly dominated by its micropore volume (less than 15 Å radius), an approximately linear relationship should exist between the two values. However, no relation between the amount adsorbed and the micropore volume is apparent from the results shown in Table II. On the other hand, a plot of the amount adsorbed *vs.* total pore volume was linear, as shown in Fig. 3. These results also agree with those previously reported

9) T. Takeda, M. Yamanishi, and A. Mori, *Nippon Kagaku Kaishi*, **1976**, 1745.

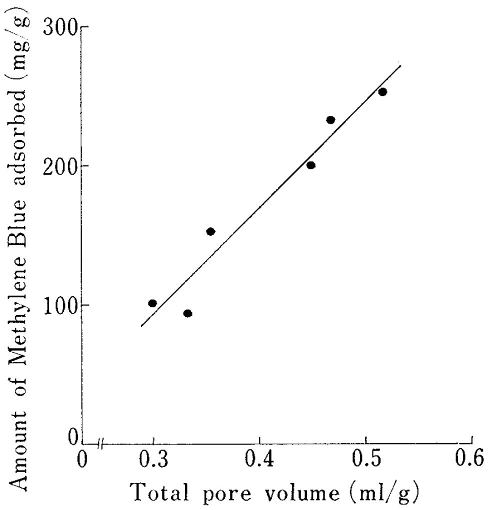

Fig. 3. Amount of Methylene Blue Adsorbed *vs.* Total Pore Volume of Magnesium Silicate

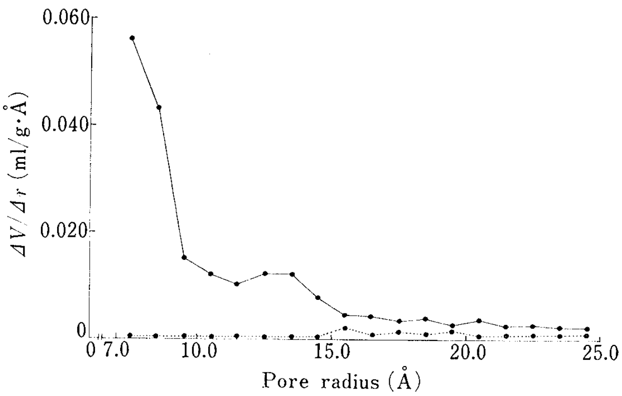

Fig. 4. Differential Pore Size Distribution of MS-1 and MS-1-MB

—●—: MS-1 (magnesium silicate No. 1), ---●---: MS-1-MB (magnesium silicate No. 1 with adsorbed Methylene Blue).

from this laboratory.[4] The results demonstrate that Methylene Blue is adsorbed in micropores, transitional pores, and macropores of magnesium silicate.

The pore size distributions of magnesium silicate No. 1 (MS-1) and magnesium silicate No. 1 with adsorbed Methylene Blue (MS-1-MB) were determined in order to elucidate the nature of the adsorption of Methylene Blue by comparing the two. Figures 2 (upper part) and 4 show the integral pore size distribution for pore radii up to 300 Å and the differential pore size distribution up to 25 Å, respectively. When the equilibrium amount of Methylene Blue was adsorbed on MS-1, the resulting MS-1-MB was collected by filtration, dried *in vacuo* at 37°, and outgassed under a vacuum of 1×10^{-3} Torr for 3 hr at room temperature. The amount of Methylene Blue adsorbed in MS-1-MB was 255.6 mg/g and was larger than the monolayer capacity of 69.9 mg/g. The decrease in pore volume of MS-1-MB due to adsorption was clear at pore radii up to 300 Å. Although the pore volume of MS-1 increased markedly as the pore radius increased in two ranges of radius, the pore volume of MS-1-MB increased monotonically with increasing pore radius, as shown in Fig. 2. On the other hand, at pore radii up to 14.5 Å the value of the differential pore volume of MS-1-MB was zero and then, at pore radii larger than 15 A it was roughly a constant value smaller than that of MS-1, as shown in Fig. 4. These results (Fig. 4) suggest that the micropores with radius smaller than 14.5 Å are completely filled with Methylene Blue and that the pores with radius larger than 15 Å still retain some empty regions. Kawazoe *et al.*[10] found that the pores of activated carbon with radius larger than about 20 Å had empty regions after the amount of adsorbed sodium dodecylbenzene sulfonate reached equilibrium. The difference of values (15 Å for Methylene Blue and 20 Å for sodium dodecylbenzene sulfonate) can best be explained by the difference in their molecular diameters, the diameters of Methylene Blue and sodium dodecylbenzene sulfonate being 9.3 Å and 11.3 Å, respectively.[11] The relationship between the amount adsorbed and the total pore volume, and the pore size distributions of MS-1 and MS-1-MB suggest that Methylene Blue is adsorbed in micropores, transitional pores, and macropores, and that the pores with radius smaller than 14.5 Å are completely filled with Methylene Blue while pores with radius larger than 15 Å remain partially unfilled.

10) K. Kawazoe, Y. Suzuki, and I. Sugiyama, *Seisan Kenkyu*, **27**, 104 (1975).
11) H. Kitagawa, *Nippon Kagaku Kaishi*, **1972**, 1144.