

Density of He Adsorbed in Micropores at 4.2K

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Abstract. The density of He adsorbed in the cylindrical micropores of zeolites NaY and KL has been determined by He adsorption at 4.2K. He adsorption isotherms were then compared with N₂ adsorption isotherms at 77K. Crystallographic considerations of the micropore volumes gave the density of the He adsorbed layer, which is necessary for assessment of ultramicroporosity of less-crystalline microporous solids, such as activated carbons. The determined density of He adsorbed in the cylindrical micropores of the zeolite was in the range 0.22 to 0.26 gml⁻¹, greater than that of He adsorbed on a flat surface (0.202 gml⁻¹). A value for the density of He between 0.20 to 0.22 gml⁻¹ is recommended for evaluation of ultramicroporosity of a slit-shaped microporous system such as activated carbon.

Keywords: He adsorption, micropore, ultramicroporosity, N₂ adsorption, zeolite

Introduction

There are two types of microporous solids, i.e., intrinsic crystalline microporous solids and ill-crystalline microporous solids. The micropore structure of the crystalline solids can be principally assessed by X-ray crystallographic data. Alternatively, the micropore structures of ill-crystalline solids such as activated carbons can be assessed by molecular probe methods, in particular, N₂ adsorption at 77K (Carrot, Roberts and Sing, 1987, Rodriguez et. al., 1989, Jaroniec, Gilpin, Kaneko and Choma, 1991). The molecular probe method provides information on the specific surface area, micropore volume, and micropore width (Gregg and Sing, 1982). Then, these three parameters have been used for specification of illcrystalline microporous solids. However, IUPAC have concluded that a BET analysis inapplicable to microporous systems and have recommended the use of the micropore volume rather than the surface area (IUPAC, 1985).

It is believed that molecular states in micropores are liquid-like on the basis of the density of an adsorbed layer (Dubinin, 1966, Kaneko, Ishii, Ruike and Kuwabara, 1992). The Gurvitsch rule generally guarantees the assumption of liquid-like state of adsorbed molecules in micropores (Gregg and Sing, pp. 113, 1982). Consequently, the density (0.808 gml⁻¹) of the bulk N₂ liquid at 77K has been used for evaluation of the microporosity using N₂ adsorption. How-

ever, the heats of adsorption of vapors in the sub-monolayer regions on the flat surface and in micropore filling are higher than the heat of vaporization (Wang and Kaneko, in press, Dubinin, 1960, Grillet, Rouquerol and Rouquerol, 1979, Rouquerol et. al., 1988). With micropores, the interaction potentials of an admolecule with the surface are overlapped (Everett and Powl, 1976), which leads to an intermolecular structure different from that of bulk liquid. This is because the strong molecule-surface interaction results in more densely packed admolecules. A recent D-NMR study clearly showed that the molecular motion of benzene is completely different from that of bulk liquid in a slit-shaped micropore regardless of the good agreement of the densities of adsorbed layer and bulk liquid (Fukasawa, Poon and Samulski, 1991). Hence, we must be cautious even on evaluation of micropore volume.

During recent years we have tried to assess the microporosity, in particular, ultramicroporosity of ill-crystalline microporous solids by He adsorption at 4.2K (Kuwabara, Suzuki and Kaneko, 1991, Setoyama, Ruike, Kasu, Suzuki and Kaneko, 1993), as a helium molecule is the smallest inert molecule. The kinetic molecular diameters of He and N₂ are 0.22 and 0.35 nm, respectively. Activated carbon fibers (ACFs) are believed to consist of highly uniform micropores with large pore volumes, and show better adsorption characteristics than granulated activated carbons. The

micropore volumes of ACFs determined by He adsorption at 4.2K do not obey the Gurvitch rule if the bulk liquid density of He (0.125 gml^{-1}) is used for the evaluation of the micropore volumes. The micropore volumes are often two times greater than those obtained from N_2 adsorption. The heat of He adsorption on the flat surface at low temperature is about 1 kJmol^{-1} in the submonolayer region (Steele, 1970, Steele, 1956, Antoniou, 1986), which is 12 times greater than the heat of vaporization. Consequently, even for He adsorption on a flat surface, the interaction of He with the surface should be taken into account in the density evaluation of the adsorbed He. Furthermore, He molecules in the second layer on the flat surface interact strongly with the surface according to theoretical consideration by Steele (1956). Thus, the density of adsorbed He should be completely different from that of the bulk liquid.

In previous work we have used the calculated density (0.202 gml^{-1}) of He adsorbed on the flat surface on the basis of Steele's theoretical study (Kuwabara, Suzuki and Kaneko, 1991). Steele has shown that the surface molecule interaction of He at the flat surface is greater than the He-He interaction even in the second adsorbed layer, which is the reason why He molecules are adsorbed in a bilayer-like fashion below $P/P_0 = 0.1$. He adsorption on a flat surface has an apparent resemblance to micropore filling of N_2 due to the fact that bilayer adsorption of N_2 is accelerated by the strong micropore field. Although the micropore filling of He has never been studied theoretically, we can predict that the interaction of He with the surface must be enhanced in micropores. The density of He adsorbed in micropores should vary as the difference of the molecular potential with the micropore geometry. In this study, we chose zeolites with a well-known micropore structure in order to determine the density of adsorbed He in the micropores, although the molecular potential field is different from that of the slit-shaped pore in activated carbon.

Experimental

Samples

Two types of zeolite were used for He adsorption at 4.2K, namely NaY (Tosoh Co. HSZ-320NAA) and KL (Tosoh Co. HSZ-500KOA) types. The crystal structures are schematically shown in Fig. 1. The crystal structure of NaY is the same as that of Faujasite with three dimensional cavities linked tetrahedrally. The minimum diameter of aperture in NaY is 0.74 nm and

the maximum diameter of void is 1.3 nm. The micropore structure of the KL-type can be presumed to be a one dimensional cylinder, which is parallel to the c-axis of the unit cell. The minimum diameter of aperture is 0.70 nm. Chemical compositions of NaY and KL are $\text{Na}_{51.2}(\text{AlO}_2)_{51.2}(\text{SiO}_2)_{140.8} \cdot x\text{H}_2\text{O}$ and $\text{K}_{8.79}\text{Na}_{0.21}(\text{AlO}_2)_{8.96}(\text{SiO}_2)_{27.04} \cdot x\text{H}_2\text{O}$, respectively.

Adsorption Experiment

The He adsorption isotherms at 4.2K were measured gravimetrically using a quartz spring. Pressures were measured by capacitance pressure transducers (MKS Baratron) over the range 1×10^{-1} to $1 \times 10^5 \text{ Pa}$ (Kuwabara, Suzuki and Kaneko, 1991). The double Dewar type cryostat was used to maintain the adsorption conditions at 4.2K for 4 hrs. Equilibrium was obtained within 10 minutes. The samples were evacuated at 623K and 1 mPa for 2 hrs after the preheating (573K, 1 mPa for 5 hrs).

Nitrogen adsorption isotherms of the zeolites were measured at 77K in order to compare the results from He adsorption. The measurements were carried out using a computer-aided automatic gravimetric adsorption apparatus. The samples were evacuated using the same conditions as for He adsorption.

Results and Discussion

Adsorption Isotherms of He and N_2

The adsorption isotherms of He at 4.2K and N_2 at 77K on NaY are shown in Fig. 2. Adsorption is represented as the number of adsorbed molecules per unit cell. The amount of He adsorbed is about two times greater than that of N_2 adsorbed because of mutual molecular size differences. Although NaY has the micropores inherent to the crystal structure, defects produce not only mesopores but macropores. Mesopores or macropores should cause adsorption in the middle or high pressure regions. The observed adsorption isotherm shows no such evidence, and hence this NaY sample is less-defective and has a good crystallinity.

Figure 3 shows adsorption isotherms of He at 4.2K and N_2 at 77K on KL. The amount of He adsorbed on KL is also two times greater than that of N_2 . The limiting adsorption ratio of He and N_2 , $W_{\text{He}}/W_{\text{N}_2}$, is greater than that of NaY, due to micropore structural differences. NaY has a large void in comparison with

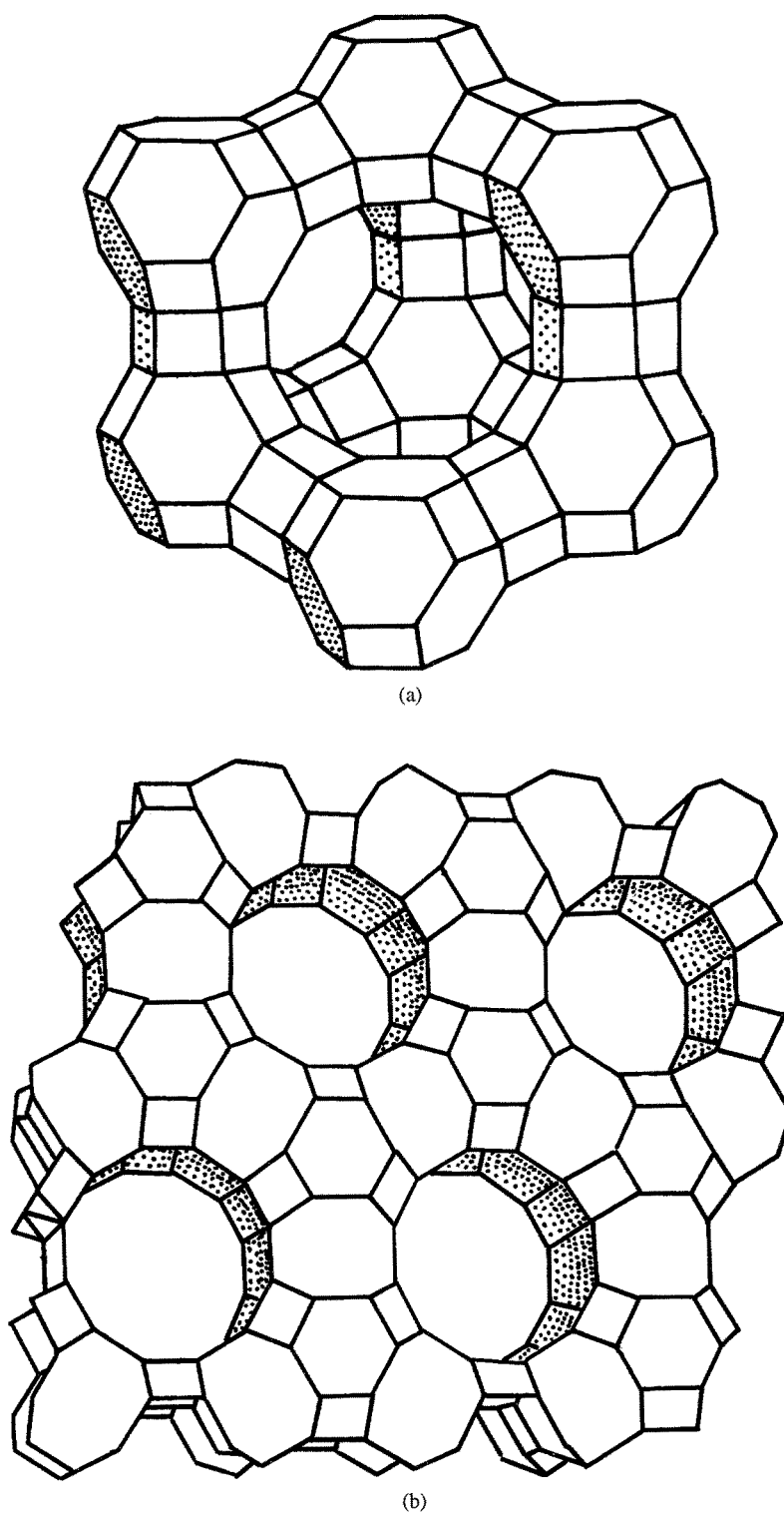


Fig. 1. Schematic crystal structures of zeolites (a; NaY, b; KL).

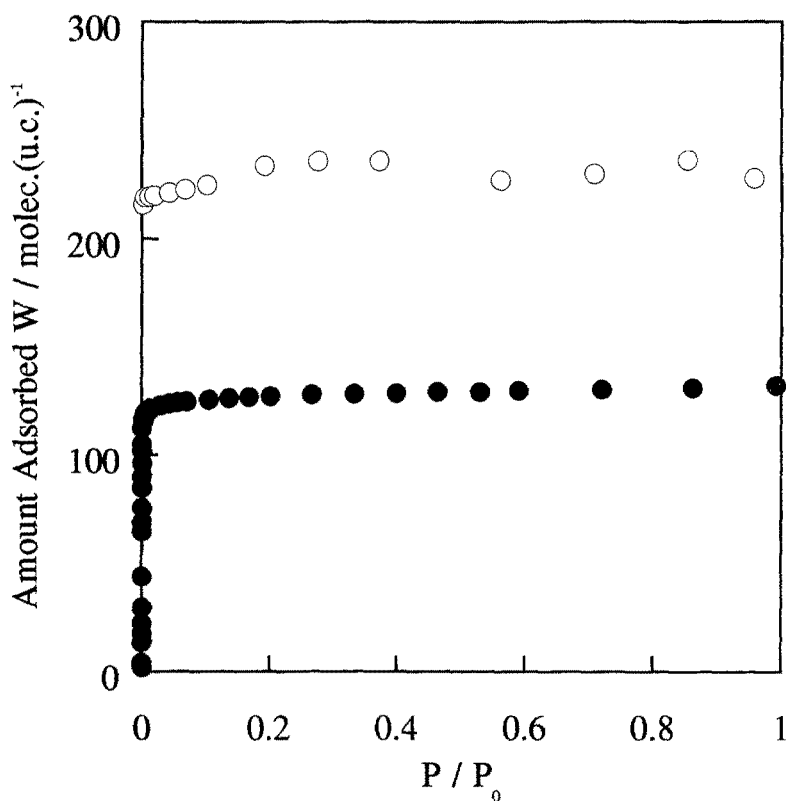


Fig. 2. Adsorption isotherms of He and N_2 on NaY (open symbols: He, solid symbols: N_2).

KL. The structural difference of micropores affects the packing form of adsorbed molecules, especially for N_2 due to its nonspherical shape. A gradual increase in adsorption above $P/P_0 = 0.5$ is observed in the N_2 adsorption isotherm. The crystal structure of KL should be slightly imperfect, producing mesopores. However, adsorption by the mesopores is quite small and can be corrected on evaluation of adsorption by micropores.

Adsorption Capacity in a Zeolite Cavity

A Dubinin-Radushkevich (DR) analysis was used to determine the adsorption capacity in the zeolite micropores. The DR equation is expressed as follows (Dubinin, 1966);

$$\ln W = \ln W_0 - (A/\beta E_0)^2$$

Here, W_0 is the micropore volume, E_0 is a structural constant for a micropore structure and A is Polanyi's adsorption potential defined as $A = RT \ln(P_0/P)$. β is an affinity coefficient related to the adsorbate-adsorbent interaction. The β value of N_2 is 0.33

(Dubinin, 1966). Previous work by us showed that β of He is 0.04 (Kaneko, Setoyama, Suzuki and Kuwabara, 1993). These β values were used for the DR analysis. The DR plots of NaY and KL are shown in Figs. 4 and 5, respectively. The abscissa region of the DR plot for He is narrow due to the small A values caused by the adsorption at low temperature compared with that of N_2 . All DR plots show good linearity except for those near the ordinate; the deviation in the high pressure region arises from adsorption by non-microporous surfaces originating from partial destruction of the crystal structure. The extent of the deviation can be easily evaluated by separation from the linear region of the DR plot. The micropore volume was precisely determined from the intercept of the extrapolated DR plot. In Table 1, the micropore volume expressed by the adsorption molecules per unit cell is shown.

Density of He Adsorbed in Zeolitic Micropores

It is possible to determine the He adsorption capacity by micropores of NaY and KL zeolites, as

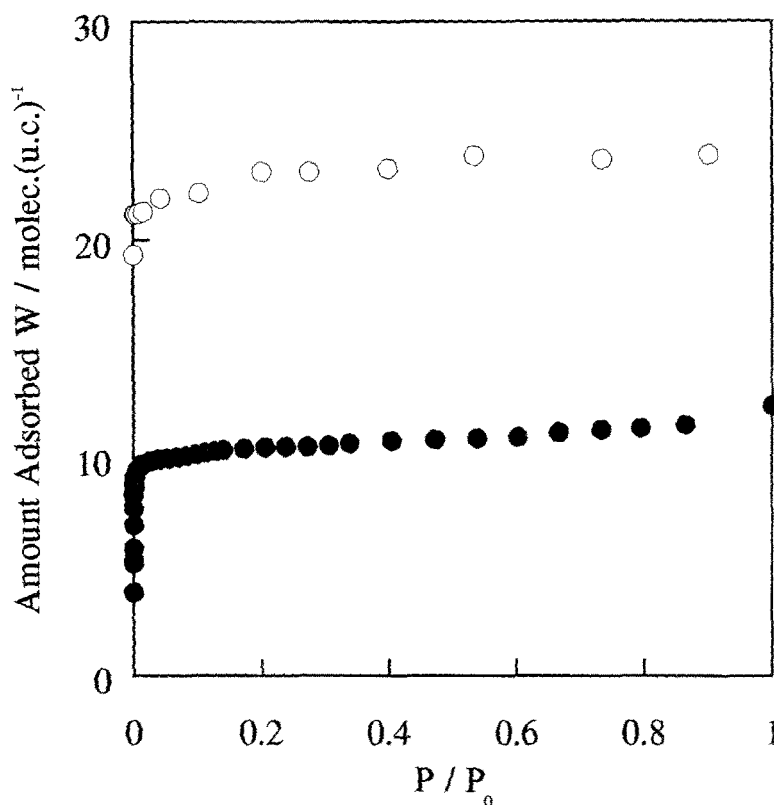


Fig. 3. Adsorption isotherms of He and N₂ on KL (open symbols: He, solid symbols: N₂).

Table 1. Micropore volumes of zeolites.

	W_0 / molec. per unit cell	
	He	N ₂
NaY	223	126
KL	21.8	10

mentioned above. If we can evaluate the micropore volume available for He adsorption using the crystallographic data, the density of adsorbed He in micropores is obtained. Hence we can calculate the micropore volume from the crystal structure.

There is a spherical void, the so called α -cage or supercage, in the crystal structure of NaY. It is recognized that the α -cage plays the role of adsorption sites for most molecules. NaY has another spherical void, the β -cage which is smaller than the α -cage. The β -cage is the intercrystalline void of sodalite units of truncated octahedra; the aperture of the β -cage (about 0.22 nm) is too small to be accessible to an adsorbate molecule. As the molecular diameter of He from

viscosity measurements is 0.22 nm, it is difficult to examine the accessibility of He to the β -cage. In the case of He adsorption at 4.2K, we assume that He cannot diffuse into the β -cage through the aperture. As the activation energy of diffusion for He into the β -cage is not known, we must estimate it from H₂ diffusion in the KA zeolite. The activation energy of H₂ diffusion (molecular size: 0.24 nm \times 0.32 nm) in the KA zeolite having an effective aperture of 0.3 nm is 41 kJmol⁻¹ at 293K, thus H₂ diffusion at 4.2K is impossible (Walker, Austin and Nandi, 1966). Accordingly, it is presumed that even He cannot diffuse at 4.2K in the β -cage having an entrance of similar size to the He atom. Only α -cages are regarded as the adsorption spaces for He in the NaY sample.

There are 8 α -cages in the unit cell of NaY, which are tetrahedrally linked to each other (Breck, 1964). The α -cage is presumed to be spherical in evaluation of the total volume of the α -cages. As the α -cage diameter is 1.3 nm from X-ray diffraction, the diameter of the effective space of the α -cage was obtained as 1.15 nm by subtraction of the contributions of oxygen atoms (the

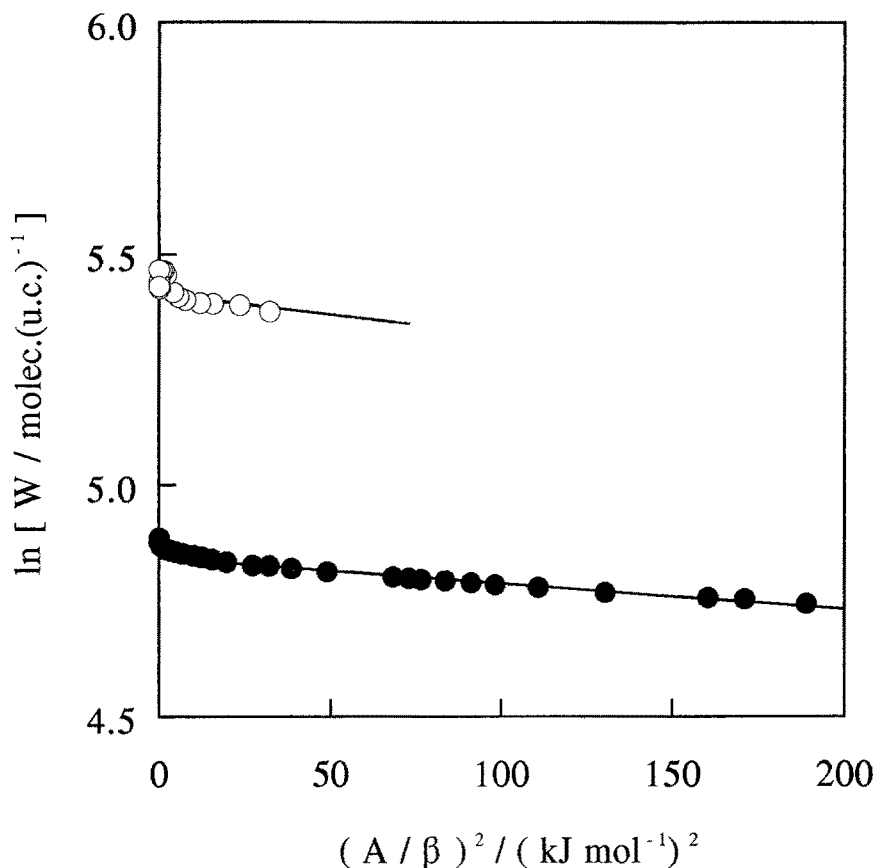


Fig. 4. DR plots of the He and N₂ adsorption isotherms on NaY (open symbols: He, solid symbols: N₂).

bonding radius: 0.07 nm). Then the effective volume of an α -cage for adsorption is *ca.* $8.0 \times 10^{-1} \text{ nm}^3$; the total effective pore volume of the unit cell is 6.4 nm^3 . The DR analysis provided 223 He molecules per unit cell, which leads to a density of 0.231 gml^{-1} . This density value is larger than the density of He adsorbed on the flat surface (0.202 gml^{-1}).

We have another way to evaluate the void space unoccupied by constituent atoms using crystallographic data following work by Breck. His estimated values for NaX and KL were 0.30 and 0.15 mlg^{-1} , respectively (Breck, and Grose, 1973). Although NaX has the same crystal structure as NaY, the chemical composition is slightly different. We have calculated the volume of the void space for NaY. As Breck has not described the composition of NaX, we assume that the chemical composition of NaX is $\text{Na}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106} \cdot x\text{H}_2\text{O}$; the void volume per unit cell of NaX being $6.576 \times 10^{-3} \text{ nm}^3$. This void volume gives the adsorbed He density

as 0.225 gml^{-1} which is slightly smaller than that determined from the above-mentioned geometrical consideration of pores. The chemical composition of NaY is not the same as NaX; the difference originates mainly from the content of the sodium ions. If we presume that the difference of the cation content varies the void volume due to the different cation occupancy, the void volume of NaY will deviate from that of NaX. The void volume of NaY evaluated using the volume of a sodium ion as $3.82 \times 10^{-3} \text{ nm}^3$ is $6.71 \times 10^{-3} \text{ nm}^3$ and the density is calculated as 0.221 gml^{-1} . The true density of He adsorbed in cylindrical micropores should be in the range 0.221 to 0.231 gml^{-1} . The reason for the greater density than that of a flat surface is attributed to enhanced interactions in the micropores.

The density of He adsorbed in the micropores of KL zeolite was also determined in a similar way. The KL zeolite consists of one dimensional cylindrical pores. The maximum diameter of void is about 1.3 nm ,

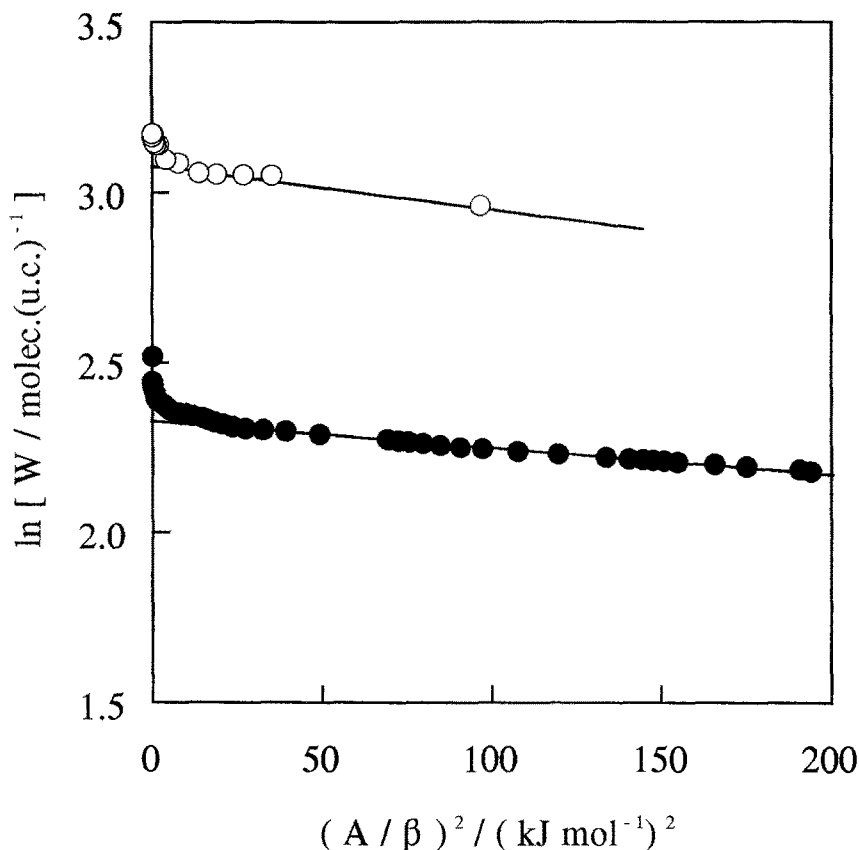


Fig. 5. DR plots of the He and N₂ adsorption isotherms on KL (open symbols: He, solid symbols: N₂).

while the aperture is 0.71 nm (Kato, Ishioh, Wada, Ito and Watanabe, 1987). The effective pore space was approximately determined by assuming KL has one dimensional smooth cylindrical pores. We estimated the dimensions of the cylinder whose diameter and height were 1.15 nm and 0.75 nm, respectively. The contributions of the oxygen atoms to the aperture must be corrected for in the calculation of the void volume. The schematic model of the micropore geometry of KL is shown in Fig. 6. The obtained pore volume was $6.28 \times 10^{-1} \text{ nm}^3$. As the He adsorption capacity was 21.8 molecules per unit cell, the density was calculated as 0.231 gml^{-1} . The density of He adsorbed in KL is 0.236 gml^{-1} from Breck's estimation of the void volume (0.15 mlg^{-1}). Moreover, the KL sample used by Breck is the proton-exchanged form, while our KL sample is the potassium type. It is quite difficult to evaluate the void volume of our KL sample from the amount of potassium. This is because the position of K ions is not definite. We determined the smallest limit

of the void volume using plausible cation contents, and obtained a maximum density of 0.263 gml^{-1} for He adsorbed in micropores. This density value should be overestimated.

He Density in Slit-Shaped Micropores for Ultramicro-pore Assessment

Table 2 summarizes a variety of He densities. Even the density of He adsorbed on the flat surface is greater than that of liquid He. The adsorbed He density in the cylindrical micropore is in the range 0.23 to 0.24 mlg^{-1} . This range is the middle value of the bulk liquid and solid densities. The adsorbed He density in micropores should change with the micropore field strength and its geometrical restrictions of the adsorbed molecules. As the micropore field of the slit-shaped pore is much less than that of the cylindrical pore, the adsorbed He density in a slit-shaped micropore should range from 0.20

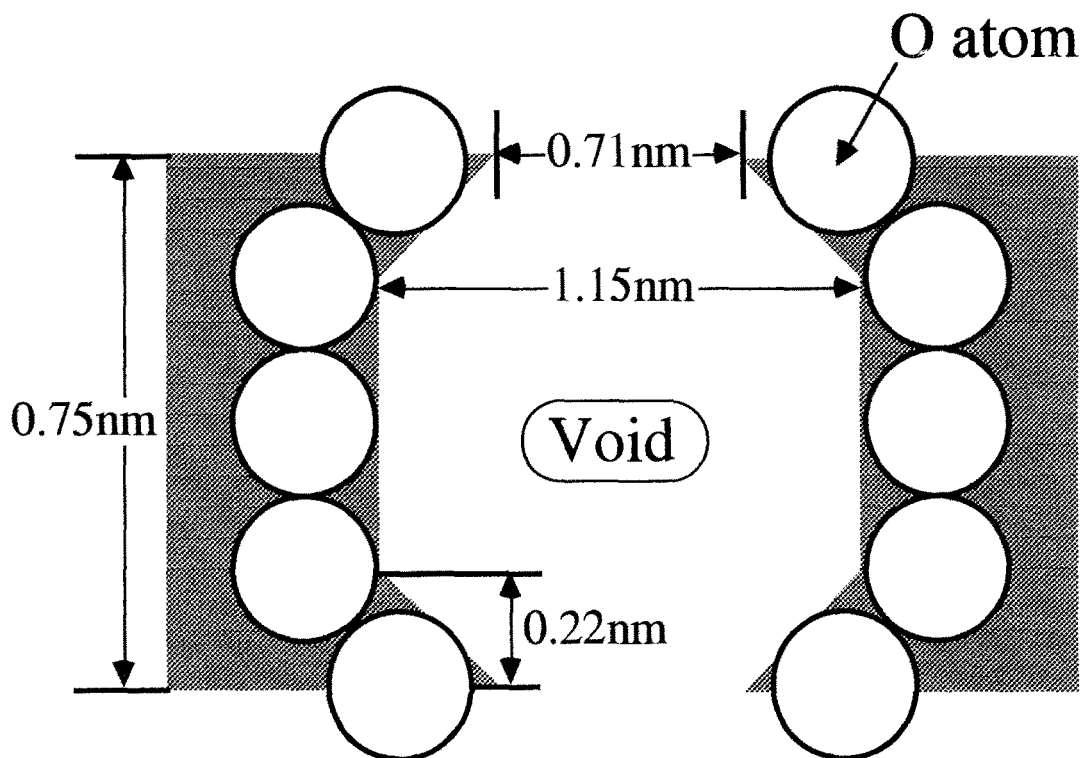


Fig. 6. Micropore geometry of KL zeolite.

Table 2. Densities for He in several states.

	Density gml ⁻¹	Ref.
Solid at 19K (1693 atm)	0.348	a [†]
Liquid at 4.2K	0.125	b
Adsorbed on flat surface at 4.2K	0.202	18
Adsorbed in a slit pore at 4.2K	0.20–0.21?	—
Adsorbed in a cylindrical pore at 4.2K	0.22–0.26	this work

[†]; estimated from X-ray crystallographic data.

a) Chemical Society of Japan (ed.), *Kagaku Binran (in Japanese; the chemistry tables)*, p. 1416, Maruzen, Tokyo, 1975.

b) R. Radebaugh, *NBS Tech. Rep.*, No. 362 (1967).

to 0.23. Although a molecular simulation is necessary for the estimation of the He density in the slit-pore, 0.20 to 0.21 mlg⁻¹ is the most probable density of He in the slit-pore. We compared the micropore volume from N₂ with that from He for activated carbons which are presumed to have only uniform supermicropores. The adsorbed He density of 0.202 gml⁻¹ provided a good agreement with both micropore volumes for such activated carbons. So far the density of He adsorbed on

the flat surface (0.202 mlg⁻¹) is recommended to assess the microporosity of slit-shaped micropores with He adsorption at 4.2K.

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References

- Antoniou, A.A., Adsorption of ^4He on Spheron and Grafoil between 2 and 30 K, *J. Chem. Soc., Faraday Trans. 1*, **82**, 483(1986).
- Breck, D.W., Crystalline Molecular Sieves, *J. Chem. Ed.*, **48**, 678(1964).
- Breck, D.W. and R.W. Grose, Correlation of the Calculated Intracrystalline Void Volumes and Limiting Adsorption Volumes in Zeolites, *Advan. Chem. Ser.*, **121**, 319(1973).
- Carrot, P.J.M., R.M. Roberts, and K.S.W. Sing, "Adsorption of Nitrogen by porous and Non-Porous Carbons," *Carbon*, **25**, 59 (1987).
- Dubinin, M.M., The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Nonuniform Surfaces, *Chem. Rev.*, **60**, 235(1960).
- Dubinin, M.M., "Porous Structures and Adsorption Properties of Active Carbons," *Chemistry and Physics of Carbon*, **2**, 51 (1966).
- Everett, D.H. and J.C. Powl, Adsorption in Slit-like and Cylindrical Micropores in the Henry's Law Region, *J. Chem. Soc., Faraday Trans. 1*, **72**, 619(1976).
- Fukasawa, J., C.D. Poon and E.T. Samulski, Deuterium NMR Investigation of Benzene Adsorbed on Boehmite Glasses, *Langmuir*, **7**, 1727(1991).
- Grillet, Y., F. Rouquerol and J. Rouquerol, Two-Dimensional Freezing of Nitrogen or Argon on Differently Graphitized Carbons, *J. Colloid Interface Sci.*, **70**, 239(1979).
- Gregg, S.J. and K.S.W. Sing, *Adsorption, Surface Area and Porosity*, Chap. 4, Academic Press, London, 1982.
- IUPAC, "Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity," *Pure & Appl. Chem.*, **57**, 603 (1985).
- Jaroniec, M., R.K. Gilpin, K. Kaneko, and J. Choma, "Evaluation of Energetic Heterogeneity and Microporosity of Activated Carbon Fibers on the Basis of Gas Adsorption Isotherms," *Langmuir*, **7**, 2719 (1991).
- Kaneko, K., C. Ishii, M. Ruike, and H. Kuwabara, "Origin of Superhigh Surface Area and Microcrystalline Graphitic Structures of Activated Carbons," *Carbon*, **30**, 1075 (1992).
- Kaneko, K., N. Setoyama, T. Suzuki and H. Kuwabara, Ultramicroporosimetry of Porous Solids by He Adsorption, *Fundam. of Adsorption 2*, M. Suzuki(Eds.), pp. 315, Kodansya, Tokyo, 1993.
- Kato, H., K. Ishioh, N. Wada, T. Ito and T. Watanabe, Motional States of ^3He and ^4He in the One-Dimensional Channels of K-L Zeolite, *J. Low Temp. Phys.*, **68**, 321(1987).
- Kuwabara, H., T. Suzuki and K. Kaneko, Microporous Carbon Fibers evidenced by Helium Adsorption at 4.2 K., *J. Chem. Soc., Faraday Trans.*, **87**, 1915(1991).
- Rodriguez-Reinoso, F. et. al, "The Combined Use of Different Approaches in the Characterization of Microporous Carbons," *Carbon*, **27**, 23 (1989).
- Rouquerol, J. et. al, "A Critical Assessment of Quasi-Equilibrium Gas Adsorption Techniques in Volumetry, Gravimetry or Calorimetry", *Characterization of Porous Solids*, K.K. Unger et. al., (Eds.) pp. 67, Elsevier, Amsterdam, 1988.
- Setoyama, N., M. Ruike, T. Kasu, T. Suzuki and K. Kaneko, Surface Characterization of Microporous Solids with He adsorption and Small Angle X-ray Scattering, *Langmuir*, **9**, 2612(1993).
- Steele, W.A., Concerning a Theory of Multilayer Adsorption with particular Reference to Adsorbed Helium, *J. Chem. Phys.*, **25**, 819(1956).
- Steele, W.A., Thermodynamic Properties of Adsorbed Helium, *J. Low Temp. Phys.*, **3**, 257(1970).
- Walker, Jr., P.L., L.G. Austin and S.P. Nandi, Activated Diffusion of Gases in Molecular-Sieve Materials, *Chemistry and Physics of Carbon*, **2**, 257(1966).
- Wang, Z.M. and K. Kaneko, "Oriented Molecular States of SO_2 Confined in a Slit-shaped Graphitic Subnanospace from Calorimetry," *J. Phys. Chem.*, in press.