Density of He Adsorbed in Micropores at 4.2K

N. SETOYAMA AND K. KANEKO
Department of Chemistry, Faculty of Science, Chiba University, 1-33 Yayoi, Inage, Chiba 263, Japan

Received May 17, 1994; Revised October 5, 1994; Accepted October 19, 1994

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 g/ml, greater than that of He adsorbed on a flat surface (0.202 g/ml). A value for the density of He between 0.20 to 0.22 g/ml 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 g/ml) of the bulk N2 liquid at 77K has been used for evaluation of the microporosity using N2 adsorption. However, the heats of adsorption of vapors in the submonolayer 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 illcrystalline 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 Na\(_{51.2}\)(Al\(_{2}\)O\(_2\))\(_{51.2}\)(Si\(_2\)O\(_2\))\(_{140.8}\)·\(x\)H\(_2\)O and K\(_{8.79}\)Na\(_{0.21}\)(Al\(_{2}\)O\(_2\))\(_{8.96}\)(Si\(_2\)O\(_2\))\(_{27.04}\)·\(x\)H\(_2\)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 × 10\(^5\) 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