A Study on a New Method of Measurement of Pore Volume Distribution in Porous Materials by Adsorption of Gases

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A new method of measurement of pore volume distribution in a porous material by adsorption of gases is proposed. In the newly proposed method the use of spherical molecules with relatively large molecular weight as adsorbates is strongly recommended to eliminate the troubles caused by stereospecificity and low boiling point of widely used N_2. It is also claimed that the universal t-curves that have been widely used since proposed by de Boer et al. must be replaced by the flat-surface isotherms that can be derived from the theory proposed by Chang et al. The results of analysis of pore volume distribution based on the method described in this paper are found to be reasonable and satisfactory.

Introduction

Measurements of adsorption isotherms of gases are generally believed to provide the most reliable informations about the pore volume distribution in porous materials and nitrogen has been the most popular adsorbate used for this purpose due to its nonspecificity. Use of nitrogen as adsorbate, however, gives some problems in two respects. First, nitrogen isotherms are usually obtained at as low a temperature as the boiling point of liquid nitrogen and at such a low temperature it is very difficult to maintain constant temperature necessary for the adsorption experiment. Especially when the relative pressure is close to unity, slight fluctuations of temperature can cause large variations in the adsorbed amount of nitrogen and thus make it difficult to obtain the accurate adsorption isotherm. Second, the adsorption behavior of nitrogen is not so nonspecific as generally believed. For example, there are a few reports[1-3] that molecular area for an adsorbed nitrogen molecule greatly depends on the kinds of adsorbent.

For these reasons there have been several attempts to use some other gases as adsorbates. In these attempts several gases such as nitrogen, oxygen[4], argon[5], water[6], and various organic vapors[7] have been adsorbed on porous silica. From these experiments informations regarding pore size distribution as well as data for cumulative surface area have been obtained and thus obtained results have been compared with one another. The results have been quite diverse and have shown no consistency among adsorbates. In particular, for water and organic vapors, results have shown wide variations depending on specificity of adsorbates and molecular sizes.

From the above discussion we see that two major difficulties arising from specificity and temperature problem should be alleviated in order to get more reliable and consistent results in the analysis of pore volume distribution. It is not difficult to suppose that use of nonpolar and spherical molecules as adsorbates will eliminate the specificity problems while the low boiling temperature problem should be eliminated by the use of gases with molecular weight larger than that of nitrogen. Two best examples among such gases are tetramethylsilane and carbon tetrachloride.

In this paper we describe the results obtained by use of such nonpolar and spherical molecules in the adsorption experiment. In our experiment adsorption-desorption isotherms for TMS, CCl_4, cyclohexane, n-hexane, and benzene as well as N_2 adsorbed on porous alumina have been obtained and thus obtained data have been analyzed on the basis of the method proposed by Ahn et al[8]. In the process of such analysis we need the knowledge of thickness of adsorbed phase on flat surface as a function of relative pressure. De Boer et al.[9] have claimed the existence of so-called "universal t-curve" for each adsorbate and have recommended the use of such t-curve for estimating thickness of adsorbed phase on flat surface as a function of relative pressure. There have, however, been some controversies over the use of universal t-curves[10]. To make the matter worse, such t-curves have been reported only for very few numbers of adsorbates. Therefore, instead of using such controversial t-curves, we have decided to use the theoretical adsorption isotherms for flat surface that can be derived from the theory proposed by Chang et al.[11] The results of pore volume analysis based on the method proposed in this paper are found to be quite satisfactory.

Theory

Since our observed isotherms for TMS, CCl_4, cyclohexane, benzene, n-hexane, and N_2 all show the A-type hysteresis loops, we expect that the adsorbent employed in our experiment, a porous alumina, has open-ended cylindrical pores. Therefore, in the discussion that follows we restrict our attention to the case of open-ended cylindrical pores only.

If the vapor pressure of adsorbed phase on the inside wall of an open-ended cylindrical pore with radius r is denoted by p_a and the thickness of adsorbed phase by t, it can be shown that[8]

$$\ln(p_a/p_0) - \ln(p_\infty/p_0) = -\frac{\gamma V_m}{RT(r-t)} \quad (1)$$

where p_0 is the saturation vapor pressure, p_∞ the vapor

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pressure of adsorbed phase of thickness t on the flat surface, and V_m is the molar liquid volume of adsorbed phase. It is obvious that γ in Eq. (1) is the surface tension for the curved surface of adsorbed phase. Broekhoff and de Boer[12] have shown that the equilibrium condition $(dG)_{p,T}=0$, where G is the Gibbs free energy for the system, leads to an equation of the following form:

$$\ln(p_a/p_0)+F(t)/RT=-\frac{\gamma V_m}{RT(r-t)} \tag{2}$$

where the function $F(t)$ is defined as the difference between μ_a, the chemical potential for adsorbed phase, and μ_L, the chemical potential of the bulk condensed phase: that is,

$$F(t)=\mu_L-\mu_a \tag{3}$$

By comparing Eq. (2) with Eq. (1) we can easily confirm that $F(t)$ is identical to $-RT\ln(p_\infty/p_0)$.

The surface tension of a liquid is known to depend on the curvature of its surface and such curvature dependency of the surface tension has thermodynamically been derived by Tolman[13]. His result has later been rederived by Kirkwood[14] based on the statistical thermodynamical arguments. On the other hand Ahn et al.[15] have shown that the transition state theory of liquids also leads to the similar result. According to these theories, for an open-ended cylindrical pore γ/γ_∞ is expressed as follows:

$$\gamma/\gamma_\infty=(r-t)/(r-t-\delta) \tag{4}$$

where γ_∞ is the surface tension of the flat surface. The parameter δ, in Tolman and Kirkwood theory, is the distance between the surface of tension and the surface of boundary. Ahn et al. have interpreted this parameter as the monolayer thickness. Thus for the closest packing structure of adsorbed phase δ may be given as follows:

$$\delta=0.9165\,(V_s/N_0)^{1/3} \tag{5}$$

where V_s is the molar volume of solid phase and N_0 is the Avogadro number.

Substitution of Eq. (4) into Eq. (1) leads to

$$\ln(p_a/p_0)-\ln(p_\infty/p_0)=-\frac{\gamma_\infty V_m}{(r-t-\delta)RT} \tag{6}$$

Broekhoff and de Boer have also shown that the stability condition for equilibrium $(d^2G)_{p,T}\geq 0$ leads to

$$-dF(t)/dt\geq\gamma V_m/(r-t)^2 \quad \text{for } t=t_e \tag{7}$$

where t_e is the thickness of adsorbed phase at equilibrium. Relation (7) is always satisfied for sufficiently small values of t_e, but there is a value of t_e, the critical thickness t_{cr}, given by

$$-\left(\frac{dF(t)}{dt}\right)_{t=t_{cr}}=\gamma V_m/(r-t_{cr})^2 \tag{8}$$

at which the adsorbed phase in a cylindrical pore just becomes unstable. At this point capillary condensation takes place and the pore fills spontaneously.

If the curvature dependency of surface tension is taken into consideration as before and the function $F(t)$ is set equal to $-RT\ln(p_\infty/p_0)$, Eq. (8) may be rewritten as follows.

$$\left(\frac{d\ln(p_\infty/p_0)}{dt}\right)_{t=t_{cr}}=\frac{\gamma_\infty V_m}{RT(r-t_{cr}-\delta)^2} \tag{9}$$

Because of difficulty of expressing $\ln(p_\infty/p_0)$ as a single analytical function of t, de Boer et al.[16] have divided the whole pressure region into two and have used different expression for $\ln(p_\infty/p_0)$ as a function of t for each region. However, it can be easily seen that this kind of approximation violates the stability condition $(d^2G)_{p,T}\geq 0$; that is, at a certain value of p_∞/p_0 the derivative $d\ln(p_\infty/p_0)/dt$ does not exist and Eq. (9) fails to hold. In order to avoid this kind of difficulty we have calculated $\ln(p_\infty/p_0)$ as a function of t on the basis of the theory proposed by Chang et al[11].

According to Chang and his coworkers t may be set equal to $\omega\delta$ where ω is the average number of molecular layers adsorbed for a given value of relative pressure p_∞/p_0 and δ, as before, may be regarded as the monolayer thickness. The theory by Chang et al. predicts that ω can be calculated as following:

$$\omega=x+\frac{x^n y}{1-y^n} \tag{10}$$

where x and y are obtained by solving the following equations for a given relative pressure p_∞/p_0.

$$y=\frac{ap_\infty/p_0}{ap_\infty/p_0+f(y)} \tag{11}$$

and

$$x=\frac{ap_\infty/p_0}{ap_\infty/p_0+\frac{q}{q_1}g(x,y)} \tag{12}$$

where

$$f(y)=(1-y)^{\frac{ny^{n-1}}{1+(n-1)y^n}}\exp\left[\frac{cw}{2kT}\left(2y-\frac{ny^{n-1}}{1+(n-1)y^n}y^2\right)\right] \tag{13}$$

and

$$g(x,y)=(1-y)^{\frac{nx^{n-1}}{1+(n-1)y^n}}\exp\left[\frac{cw}{2kT}\left(2x-\frac{nx^{n-1}}{1+(n-1)y^n}y^2\right)\right] \tag{14}$$

The physical meanings of the parameters involved in the above equations have been described elsewhere[11]. In practice, these parameters are determined in the process of theoretical fitting of Eq. (10) into the experimental adsorption isotherms and the mathematical procedure for such parametric optimization has also been described by Chang et al.[17]

For simplicity let us denote the relative pressure p_a/p_0 by ξ from later on. In actual calculations the relative pressure range of 0 to 1 is divided into many sections with each interval being sufficiently small, so that the k-th interval is bounded by ξ_{k-1}, the upper pressure bound, and the ξ_k, the lower pressure bound. When the total length of the pores belonging to the k-th pore group, filling with condensate at a relative pressure between ξ_k and ξ_{k-1}, and their mean pore radius are denoted by L_k and r_k, respectively, it is obvious that the change in volume condensed in the porous system over the k-th interval, ΔV_k^c, is given by

$$\Delta V_k^c=\pi(r_k-t_{r_k,\xi_k})^2L_k+\pi\sum_{i=1}^{k-1}L_i\left[(r_i-t_{r_i,\xi_k})^2-(r_i-t_{r_i,\xi_{k-1}})^2\right] \tag{15}$$

in which t_{r_i,ξ_k} denotes the equilibrium thickness of the adsorbed layer in a cylindrical pore with radius r_i at a relative pressure ξ_k. The first term on the righthand side of Eq. (15) represents the change in the adsorbed volume due to the fill-

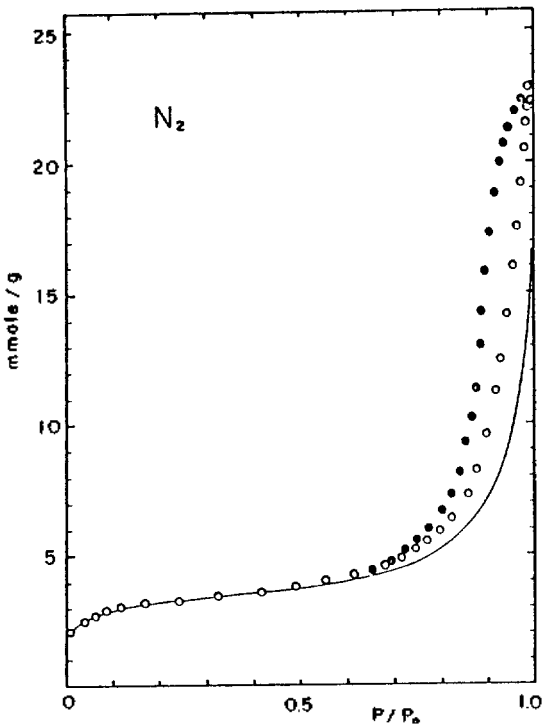

Figure 1. Adsorption-desorption isotherm of nitrogen on alumina at 78°C. o; adsorption, •; desorption, –; calculated flat surface isotherm.

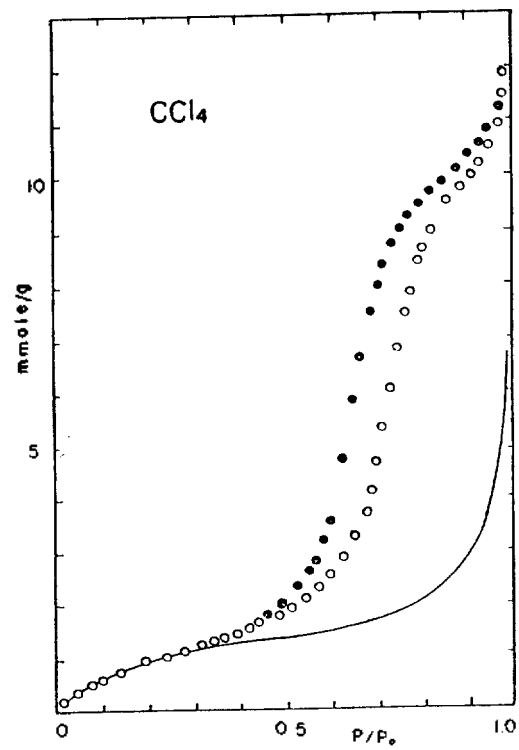

Figure 2. Adsorption-desorption isotherm of carbon-tetrachloride on alumina at 293°K. o; adsorption, •; desorption, –; calculated flat surface isotherm.

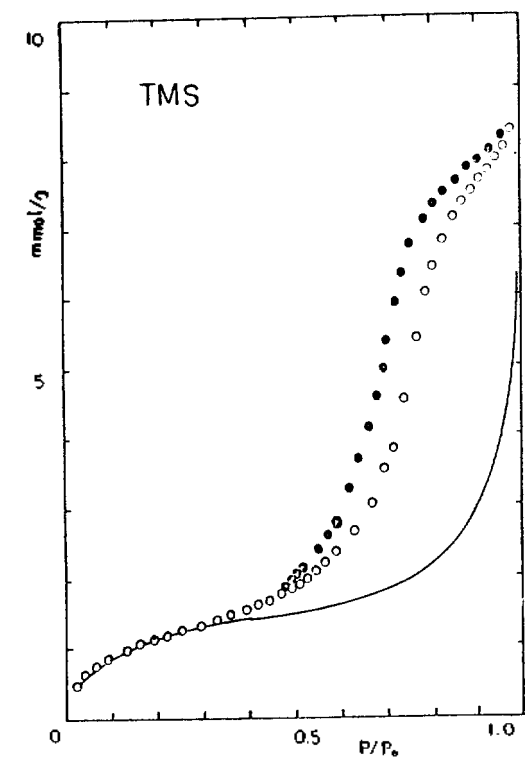

Figure 3. Adsorption-desorption isotherm of tetramethylsilane on alumina at 268°K. o; adsorption, •; desorption, –; calculated flat surface isotherm.

ing of pores of the k-th group and the second term corresponds to that due to the formation of multilayers in larger pores that have not yet been filled up by the capillary condensate.

Since the pores are assumed to have the cylindrical shape, we may write

$$S_k = 2\pi r_k L_k \tag{16}$$

and

$$V_k = \pi r_k^2 L_k \tag{17}$$

where S_k and V_k denote the total surface area and the total pore volume of pores in the k-th group, respectively.

Substitution of Eqs. (16) and (17) into Eq. (15) yields

$$S_k = \frac{2r_k}{(r_k - t_{r_k, \xi_k})^2}\Big[\Delta V_k^c - \sum_{i=1}^{k-1} S_i (t_{r_i, \xi_{k-1}} - t_{r_i, \xi_k}) + \sum_{i=1}^{k-1} (S_i/2r_i)(t_{r_i, \xi_{k-1}}^2 - t_{r_i, \xi_k}^2)\Big]. \tag{18}$$

r_k and t_{r_k, ξ_k} are obtained by solving Eqs. (6), (9), and (10) simultaneously for a given relative pressure ξ_k and t_{r_k, ξ_k} is obtained from Eq. (6) if r_i and ξ_k are given. Thus experimental measurements of adsorption-desorption isotherms can give us informations about S_k and V_k. Also, by performing the calculations from the point $\xi \approx 1$ to that of no capillary condensation, we can obtain the cumulative surface area, ΣS_k, and the cumulative pore volume, ΣV_k.

Experimental

In this work the Nernst-Donau type quartz beam microbalance has been used for the adsorption-desorption measurement and the apparatus used for this experiment has already been described elsewhere[18].

Alumina (manufactured by Conoco, BET surface area for N_2 = 360m^2/g) calcined at 250°C has been outgassed at 10^{-5}

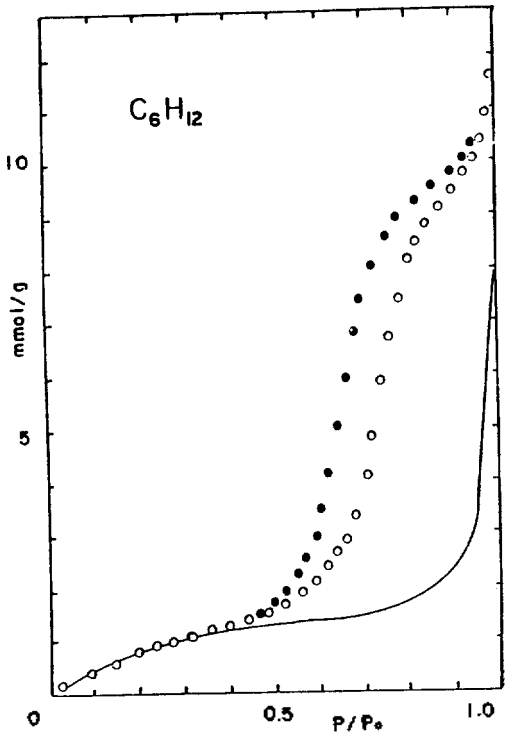

Figure 4. Adsorption-desorption isotherm of cyclohexane on alumina at 293°K. o; adsorption, •; desorption, –; calculated flat surface isotherm.

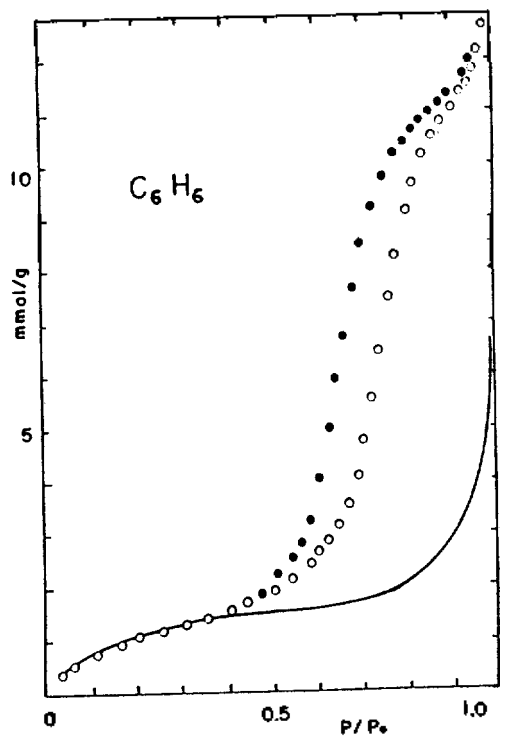

Figure 5. Adsorption-desorption isotherm of benzene on alumina at 293°K. o; adsorption, •; desorption, –; calculated flat surface isotherm.

torr and 300°C for 24 hours before being used as the adsorbent for our experiment. As adsorbates, Merck spectroquality CCl_4 and n-hexane and Matheson & Coleman chromatoquality TMS, cyclohexane, and benzene have been used

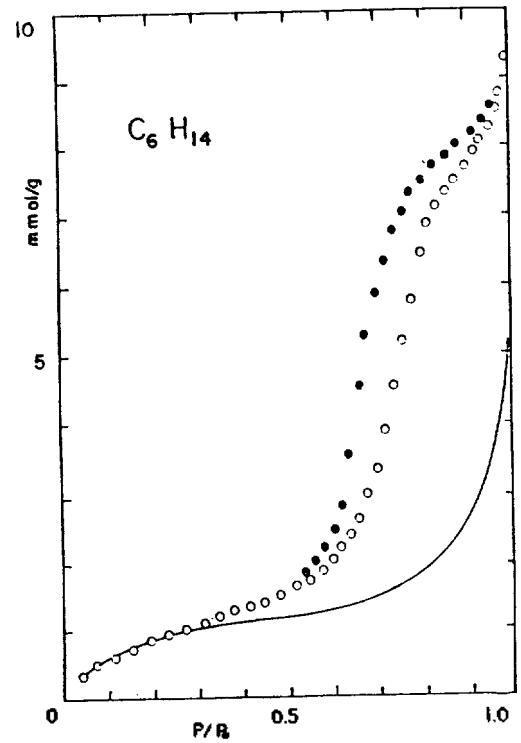

Figure 6. Adsorption-desorption isotherm of n-hexane on alumina at 283°K. o; adsorption, •; desorption, –; calculated flat surface isotherm.

without further purification. These adsorbates have been dehydrated by making use of the 4X molecular sieve (Linde Co.) and degassed by repeating the freeze-pump-thaw cycles. The nitrogen gas used in our experiment was a 99.999% product.

Results and Discussion

Adsorption-desorption isotherms of CCl_4, cyclohexane, and benzene on porous alumina at 293°K, n-hexane at 283°K, and TMS at 268°K obtained in our experiment are shown in Figure 1 through Figure 6 and all of these isotherms show typical A-type hysteresis loops. This justifies our assumption that the porous alumina sample we have used for our experiment has open-ended cylindrical pores.

The parameters q/q_1 and $cw/2kT$ are determined in such a way that the calculated ω in Eq. (10) can best fit into experimental adsorption isotherms up to $\xi = 0.30$ for each adsorbate, while the parameters n and a are, respectively, assumed equal to 3 and 0.95 from the outset. Thus determined values of parameters are listed in Table 1. Also listed in Table 1 are other relevant data such as γ_∞, the surface tension of adsorbate, V_m, molar liquid volume of adsorbate, and δ, monolayer thickness calculated from Eq. (5). In Table 2 the calculated cumulative surface area data are listed for each adsorbate and these data are also compared with those calculated by other methods. Calculated pore volume distribution curves are shown in Figure 7. In Figures 8 and 9 pore volume distribution curves calculated by de Boer's method with and without correction due to the curvature dependency of surface tension are shown.

From the results listed in Table 2 we see that the cumulative surface areas for spherical molecules such as

Table 1. Physical Constants and Parameters.

	N_2	CCl_4	TMS	C_6H_{12}	C_6H_6	C_6H_{14}
$\frac{cw}{2\,kT}$	-0.001	-0.01	-0.01	-0.01	-0.01	-0.01
$\frac{q}{q_1}$	0.005	0.085	0.038	0.131	0.035	0.070
m(A)	3.54	4.73	5.40	5.04	4.62	5.24
(dyne/cm)	8.72	27.00	17.81	25.30	28.02	18.40
V_m(cm^3/mole)	34.68	96.51	130.86	108.04	88.06	130.76
T(°K)	78	293	268	293	293	283

Table 2. Cumulative Surface Area. (m^2/g)

	N_2	CCl_4	C_6H_{12}	C_6H_6	C_6H_{14}	TMS
I	224.1	425.8	429.3	243.6	237.9	424.1
II	300.4	587.9	546.4	604.0		
III	258.8	536.4	500.4	546.3		

Method I: New method. II: Broekhoff-de Boer's method. III: Ahn et al's method.

CCl_4, cyclohexane, and TMS are strikingly close to one another while those for nonspherical molecules are much smaller than the former. This can be understood if we assume that actual monolayer thickness in adsorbed layers of nonspherical molecules would be smaller than δ values calculated from Eq. (5). Cumulative surface area data calculated by other methods are larger than those obtained by our method as can be seen from Table 2. Such differences can be expected since the universal t-curves used by de Boer et al. predict larger amount of adsorption than the real flat-surface isotherms calculated from the theory of Chang et al. This is not surprising because use of the universal t-curves usually does not exclude the possiblity of pendular ring condensation and/or adsorption due to the presence of micropores. Furthermore, cumulative surface area data calculated by the method of de Boer et al., even if the correction due to curvature dependency of surface tension is made, do not show as much consistency as those obtained by our method. Thus we may conclude that in order to obtain more reliable informations about the cumulative surface area for meso-pore systems the employment of real flat-surface isotherms is as important as the use of spherical adsorbates such as CCl_4, TMS, and cyclohexane.

Similar conclusions may be drawn from looking into pore volume distribution curves shown in Figures 7, 8, and 9. From Figure 7 we see that the distribution maxima are relatively close to one another as are expected. The distribution curves for spherical molecules such as CCl_4, TMS, and cyclohexane exhibit relatively sharp maxima while those for nonspherical adsorbates show more or less blunt and flattened features. Although the exact reason for this remains to be investigated at this stage, we believe that such phenomena are also caused by stereospecificity of nonspherical molecules. If we take a closer look into Figure 7 we will find that distribution maxima for CCl_4, TMS, and cyclohexane are slightly displaced from one another. This displacement probably arises from incorrect setting of the values of parameter a. We have set a equal to 0.95 for all three adsorbates; however, the values of this parameter for three adsorbates will be slightly different although such differences are small. For more exact determination of this parameter we need the experimental flat-surface adsorption isotherms for these adsorbates which are not available at this stage. Detailed investigations of the effect of parameter a are under way at the author's laboratory and the results will be published elsewhere. Similar trends can be observed both in Figures 8 and 9. Also by comparing Figure 7 and Figures 8 and 9 we see that, in the latter case, distribution maxima are all shifted toward larger pore radius. This can be easily understood if we note the fact that the universal t-curves are used instead of the flat-surface isotherms for the calculation of pore volume distribution shown in Figures 8 and 9. We can also

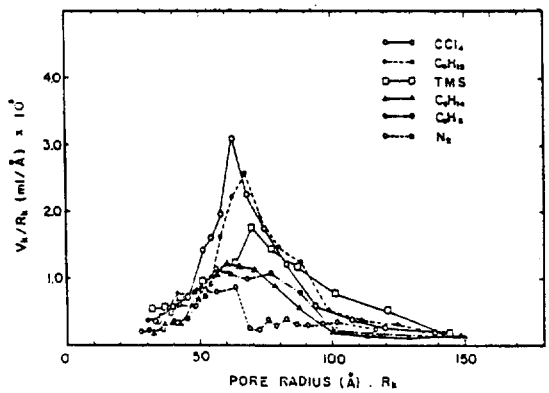

Figure 7. Pore volume distribution curve of alumina sample by a new method.

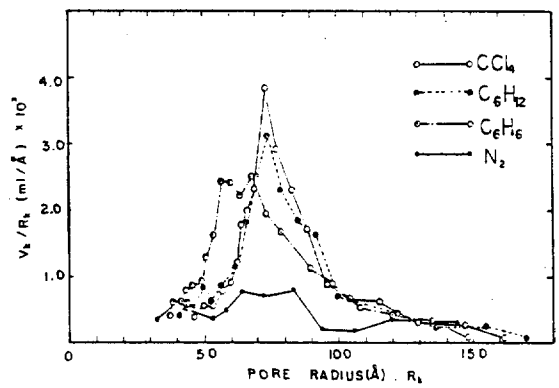

Figure 8. Pore volume distribution curve by Ahn et al's method.

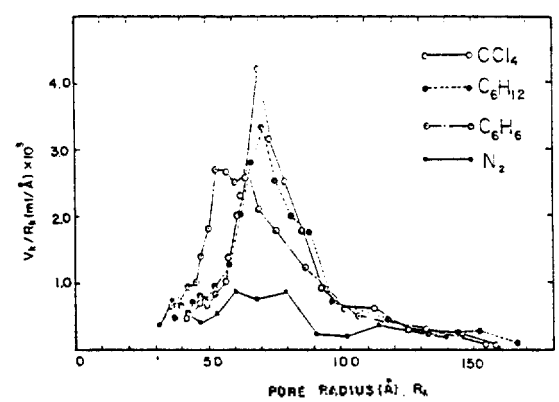

Figure 9. Pore volume distribution curve by Broekhoff-de Boer's method.

confirm that consideration of the curvature dependency of surface tension reduces the cumulative surface area and increases pore radius for distribution maximum. This is in agreement with the conclusion from investigations due to Ahn et al.

In summary we have shown that spherical adsorbates are more suitable for study of pore volume distribution by gas adsorption method and for this purpose the theory of Chang et al. can provide a strong means.

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References

1. J.D. Carruthers, D.A. Payne, K.S.W. Sing and L.J. Stryker, *J. Colloid Interface Sci.*, **36**, 205 (1971).
2. C. Pierce and B. Ewing, *J. Phys. Chem.*, **68**, 2562 (1964).
3. S.J. Gregg and K.S.W. Sing, Adsorption Surface Area and Porosity, p67-72, Academic Press, 1982.
4. K.M. Hanna, I. Older, S. Brunauer, J. Hagymassy, Jr., and E.E. Boder, *J. Colloid Interface Sci.*, **45**, 27 (1973); **45**, 38 (1973).
5. D.A. Payne, K.S.W. Sing and D.H. Turk, *J. Colloid Interface Sci.*, **43**, 287 (1973).
6. J. Hagymassy, Jr. and S. Brunauer, *J. Colloid Interface Sci.*, **33**, 317 (1970).
7. R.S. Mikhail and F.H. Shebl, *J. Colloid Interface Sci.*, **32**, 505 (1970); **34**, 65 (1970); **38**, 35 (1972).
8. W. Ahn, K. Shin and S. Chang, *J. Colloid Interface Sci.*, **51**, 232 (1975).
9. J.H. de Boer, B.G. Linsen and Th. J. Osinga, *J. Catalysis*, **4**, 643 (1965).
10. R.S. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces, p57-66, John Wiley & Sons, 1983.
11. S. Han, J.W. Lee, H. Pak and S. Chang, *Bull. Korean Chem. Soc.*, **1**, 117 (1980).
12. J.C.P. Broekhoff and J.H. de Boer, *J. Catalysis*, **9**, 8 (1967).
13. R.C. Tolman, *J. Chem. Phys.*, **17**, 333 (1949).
14. J.G. Kirkwood and F.P. Buff, *J. Chem. Phys.*, **17**, 338 (1949).
15. W. Ahn, M. John, H. Pak and S. Chang, *J. Colloid Interface Sci.*, **38**, 605 (1972).
16. J.C.P. Broekhoff and J.H. de Boer, *J. Catalysis*, **9**, 15 (1967).
17. S. Chang, H. Pak, J.W. Lee and S. Park, *J. Kor. Chem. Soc.*, **21**, 353 (1977).
18. Y. Kim, Y. Ahn, H. Pak and S. Chang, *J. Kor. Chem. Soc.*, **18**, 79 (1974).

Theoretical Studies on Aluminophosphate-5 ($AlPO_4$-5)

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Parameters of intraframework potential function suitable for aluminophosphate-5($AlPO_4$-5) are obtained by the constraint method. Using these parameters, we calculated the stabilization energies and their second derivatives of framework atoms and these values are compared with those of zeolite A. It is found that the oxygen atoms in $AlPO_4$-5 framework are more stable than those of zeolite A and that the aluminum atom is also more stable than that of zeolite A. On the other hand, the phosphorus atom in $AlPO_4$-5 framework, in which the silicon atoms of aluminosilicate are replaced by the phosphorus atom, is less stable than the silicon atom of aluminosilicate framework of dehydrated zeolite A.

Introduction

The aluminophosphate molecular sieves represent a new class of microporous inorganic solids. They represent the first family of framework oxide molecular sieves synthesized without silica.[1,2] The most widely known molecular sieves are the aluminosilicate zeolites[3] and the microporous silica polymorphs.[4] The aluminophosphate molecular sieves are similar to the zeolite in some properties and have the potentials as adsorbents for separations of molecular species and as catalysts or catalyst supports.

A study was made to obtain the parameters of intraframework potential function, which have been obtained in case of zeolite A,[7,10] suitable for $AlPO_4$-5. Using these parameters, the stabilities of the $AlPO_4$-5 framework atoms were investigated and these values were compared with those of zeolite A.

Method of Calculation

In this study, the bond angles and bond lengths are obtained from X-ray data[5] which are listed in Table 1. $AlPO_4$-5 framework has the topology of hypothetical net no. 81 proposed by Smith.[6] It's basic unit is $AlPO_4$ which is shown in Figure 1 and have four kinds of oxygens.

The coordinate origin was taken as the origin of unit cell. Bacause of the slow convergency of electric field along with the c-axis, the total 300 unit cell were used in calculating the interactions of framework atoms.

The net charges of framework atoms are calculated by the electronegativity equalization method.[8] Because of the neutrality of $AlPO_4$ network and Al(P) atom bonded tetrahedrally by four oxygen atoms, the following equation can be written;