Curvature and Parametric Sensitivity in Models for Adsorption in Micropores

A. Saito and H. C. Foley
Center for Catalytic Science and Technology, Dept. of Chemical Engineering, University of Delaware, Newark, DE 19716

The sensitivity of the calculated micropore size of zeolite Y in a fluidized cracking catalyst based on empirical models for argon adsorption has been tested by examining the effect of curvature and by systematically verifying the magnitude of physical constants in the model equations. With a consistent set of physical parameters the slit model provided a pore size value of 0.45 nm, while the new cylindrical models provided values of 0.69 and 0.74 nm. The latter values are found to correspond well with the known aperture size of zeolite Y, 0.74 nm. By separately varying the magnitudes of five of the physical constants in the model over a range of ±30%, it was concluded that the diameter of the oxide ion at the surface had a large effect on the calculated pore size, while the other parameters had only moderate to small effects. Preliminary application of the cylindrical pore model to isotherms of argon on other zeolites and molecular sieves leads to promising results, especially for medium to large pore zeolites. These results suggest that the cylindrical pore model is a useful means for the transformation of argon adsorption data on a zeolite into a micropore size distribution.

Introduction

Quantitative evaluation of microstructure in porous solids is a crucial aspect of the processes involved in the design and application of materials for adsorption and catalysis. The evaluation typically consists of a careful acquisition of an adsorptive isotherm for a selected adsorbate on the solid, followed by an analysis and transformation of the isotherm into structural information on the basis of a model. The structural data usually take the form of surface area, pore volume, and pore size distribution. Each of these data can then be used as parameters in other models used to predict the adsorptive or diffusional behavior of the solid in a given application.

In the case of meso- and macroporous solids (defined in the IUPAC classification as 2 to 50 nm and > 50 nm, respectively), the Kelvin equation, Eq. 1, provides a useful model for the transformation of adsorption data into a pore size distribution (Brunauer et al., 1967; Defay et al., 1966).

$$\ln \frac{P}{P_o} = -\frac{2\gamma V_L}{RT}\left(\frac{1}{r_m}\right) \tag{1}$$

The basis for this model is thermomechanical equilibrium across the hemispherical meniscus of a capillary condensate within a cylindrical pore. This model is widely applied but is limited to pores greater than 2 nm dia. Below this pore size the liquid cannot be considered a fluid with bulk properties because of the forces exerted by the wall. Theoretical calculations suggest that properties of fluids in microporous structures are highly sensitive to the size of the pore.

Many technologically important solids, such as zeolites and ultramicroporous carbon, have micropore structures that are well below the lower limit of pore size at which the Kelvin equation is applicable. Yet the need for relatively simple, Kelvin-like methods to quantitatively describe these micropore structures has driven considerable research to this end. Useful information about micropore structures can be derived from nitrogen or argon isotherm data in terms of the c constant from the BET equation, t or alpha plots, and the Dubinin-Radushkevich model (Brunauer et al., 1940; Lippens and de Boer, 1965; Sing, 1970; Dubinin and Radushkevich, 1947). While quite useful, these methods do not provide Kelvin-equation type pore size information, or more specifically, straight-

---

Correspondence concerning this article should be addressed to H. C. Foley.

forward relationships between the logarithm of relative pressure and the pore size.

Ultramicroporous carbons are considered to have slit-shaped pores based on the accumulated evidence from carefully conducted molecular probe adsorption experiments. The origin of this so-called turbostratic structure is still the subject of considerable research and debate. However, on the basis of adsorption experimental results it is apparent that the lateral dimensions of the slitlike pores are considerably larger than the slit dimensions. The slit dimensions may be 0.4 to 0.6 nm, while the lateral dimensions may range from 2.5 to 6.0 nm. In the limit one can consider the walls of the pores to be two graphitic planes that extend laterally to infinity separated by a fixed distance. Two important papers have treated adsorption in microporous carbon on this basis (Everett and Powl, 1976; Horvath and Kawazoe, 1983). Because of the conceptual and mathematical simplicity of these models, recently they have been used to describe adsorption in zeolitic and clay structures (Davis et al., 1988; Venero and Chiou, 1988; Davis et al. 1989; Vaughan, 1988). This provides an easy analysis of the micropore structure in terms of the argon adsorption isotherm. Although the slit or slab geometry may be a reasonable description for a layered clay, it is at best a crude approximation to the actual structure of a zeolite since it does not allow for any effect of curvature on adsorption within a zeolite. Yet curvature effects on micropore adsorption have long been recognized as important (Gregg and Sing, 1982, ch. 4), and most recently curvature effects in zeolite adsorption have come under careful scrutiny (Derouane et al., 1987; Derouane and Nagy, 1987; Schmeits and Lucas, 1976). A particularly cogent and thorough report by Peterson et al. (1990) has recently appeared, which provides an analysis of Lennard-Jones fluids in cylindrical pores utilizing mean field density function theory. In addition to the issue of curvature, a number of physical parameters that are characteristic of the surface properties of either a zeolite or clay must be considered in order to accurately model the adsorption. The objectives of this research have been first to develop a cylindrical pore model as a better approximation to the zeolite microstructure and then to assess the parametric sensitivity of the apparent pore size calculated on the basis of the model for argon adsorption.

Review of Slit Model

Adsorption in ultramicroporous carbon was treated in terms of a slit-potential model by Everett and Powl (1976) and was later extended by Horvath and Kawazoe (1983). Horvath and Kawazoe assumed a slab geometry with the slit walls comprised of two infinite graphitic planes; adsorption occurs on the two parallel surfaces, as shown in Figure 1. The potential energy of interaction, ϵ, for one adsorbate molecule at a distance z from an atom in the surface layer can be expressed as

$$\epsilon(z) = K\epsilon^*\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10}\right] \tag{2}$$

where ϵ^* is the potential energy minimum. Everett and Powl (1976) provided relationships for K and σ.

$$K = \left(\frac{n}{n-m}\right)\left(\frac{n}{m}\right)^{\frac{m}{(n-m)}} \tag{3}$$

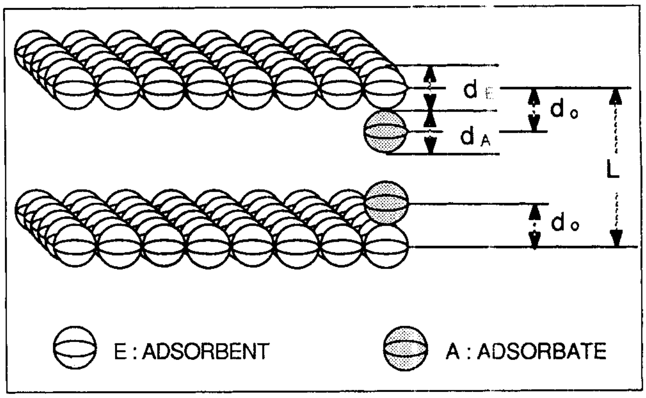

Figure 1. Slab geometry.

$$\sigma = \left(\frac{m}{n}\right)^{\frac{1}{(n-m)}} d_o \tag{4}$$

The parameters n and m are the order of the dispersion and repulsion terms in Eq. 2, respectively, and d_o is taken as the arithmetic mean of the diameters of the adsorbent atoms in the wall, d_E, and the adsorbate atoms, d_A, as shown in Figure 1, and following the earlier work of Horvath and Kawazoe (1983). With $n = 10$ and $m = 4$, $K = 3.07$ and $\sigma = 0.858\ d_o$.

If the distance between the nuclei of the two parallel layers is L, then the potential function of one adsorbate molecule between the two layers is:

$$\epsilon(z) = K\epsilon^*\left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4 + \left(\frac{\sigma}{L-z}\right)^{10}\right] \tag{5}$$

In the case of the pore filled with adsorbate molecules one must account for adsorbate–adsorbent, and adsorbate–adsorbate–adsorbent interactions. Walker (1966) expressed the potential energy minimum, ϵ^*, corresponding to these two respective interactions in terms of two dispersion constants, A_{E-A}, and A_{A-A}, as well as the number density of adsorbate and adsorbent atoms per unit area. This potential minimum takes the form:

$$\epsilon^* = \frac{3}{10}\,\frac{N_A A_{A-A} + N_E A_{EA}}{d_0^4} \tag{6}$$

where the dispersion constants can be expressed according to the Kirkwood-Müller formalism as:

$$A_{E-A} = \frac{6Mc^2\alpha_E\alpha_A}{\left(\frac{\alpha_E}{\chi_E}\right) + \left(\frac{\alpha_A}{\chi_A}\right)} \tag{7}$$

$$A_{A-A} = \frac{3Mc^2\alpha_A\chi_A}{2} \tag{8}$$

Using Eq. 4 to reexpress d_o in terms of σ and by replacing ϵ^* in Eq. 5 by the expression in Eq. 6, one obtains:

$$\epsilon(z) = \frac{N_A A_{A-A} + N_E A_{E-A}}{2\sigma^4} \times \left[-\left(\frac{\sigma}{z}\right)^4 + \left(\frac{\sigma}{z}\right)^{10} - \left(\frac{\sigma}{L-z}\right)^4 + \left(\frac{\sigma}{L-z}\right)^{10}\right] \tag{9}$$

If the free energy of adsorption is taken as equal to the net energy of interaction between the layers, then the energy balance yields:

$$RT\ln\left(\frac{P}{P_o}\right) \cong N_{AV}\frac{\int_{d_o}^{L-d_o}\epsilon(z)dz}{(L-d_o)-d_o} \tag{10}$$

With substitution of Eq. 9 into Eq. 10 and integration this yields the Horvath and Kavazoe (1983) result for slitlike geometry:

$$RT\ln\left(\frac{P}{P_o}\right) = N_{AV}\frac{N_A A_{A-A}+N_E A_{E-A}}{\sigma^4(L-2d_o)} \times\left[-\frac{\sigma^4}{3(L-d_o)^3}-\frac{\sigma^{10}}{9(L-d_o)^9}-\frac{\sigma^4}{3d_o^3}+\frac{\sigma^{10}}{9d_o^9}\right] \tag{11}$$

This has Kelvin-like simplicity in that it relates the relative pressure, P/P_o, to the relevant pore size, L, in terms of the physical properties of the adsorbate-adsorbent couple.

Cylindrical Model

To test the geometric sensitivity of the calculated pore size for a zeolitic material, a cylindrical potential was utilized along with the following assumptions:

1. The pore is a perfect cylinder of infinite length but finite radius, r_p.
2. The inside wall of the cylinder is a single layer of atoms, oxide ions in the case of a zeolite, which is taken as a continuum of potential interaction. The interaction with the pore wall is taken to be due only to the dispersion forces, just as has been assumed previously (Horvath and Kawazoe, 1983; Everett and Powl, 1976).
3. Adsorption occurs only on the inside wall of a cylinder in the micropore region.
4. The interaction of adsorption is taken to be due only to that between the adsorbate and the adsorbent, with the latter considered to be the oxide ion of the zeolite.

Based on these assumptions, the potential energy for the cylindrical pore displayed in Figure 2 is a function of r, the distance from the central axis. A general expression for a cylindrical potential was provided by Everett and Powl (1976).

$$\epsilon(r)=\frac{5}{2}\pi\epsilon^*\left[\frac{21}{32}\left(\frac{d_o}{r_p}\right)^{10}\sum_{k=0}^{\infty}\alpha_k\left(\frac{r}{r_p}\right)^{2k}-\left(\frac{d_o}{r_p}\right)^4\sum_{k=0}^{\infty}\beta_k\left(\frac{r}{r_p}\right)^{2k}\right] \tag{12}$$

where the constants α_k and β_k are given by:

$$\alpha_k^{0.5}=\frac{\Gamma(-4.5)}{\Gamma(-4.5-k)\Gamma(k+1)} \tag{13}$$

$$\beta_k^{0.5}=\frac{\Gamma(-1.5)}{\Gamma(-1.5-k)\Gamma(k+1)} \tag{14}$$

The potential energy minimum, ϵ^*, can be expressed in terms of Eq. 6 using the dispersion constants from Eqs. 7 and 8.

Once again, if one assumes that the free energy of adsorption is given by the average of the intermolecular potential in the cylindrical pore, then one can take either a line average or an area average. In the latter, one can envision the molecules as having two degrees of freedom to move across the pore, while in the former they may have only one degree of freedom, along the diameter of the pore. This could correspond to the physically real case in which a portion of the pore is blocked by foreign atoms such as carbon.

For the line-averaged case, the potential for the cylindrical model becomes:

$$\bar{\epsilon}_{LA}=\frac{\int_0^{r_p-d_o}\epsilon(r)dr}{r_p-d_o} \tag{15}$$

and the model equation that results is:

$$\ln\left(\frac{P}{P_o}\right)=\frac{3}{4}\frac{\pi N_{AV}}{RT}\frac{(N_A A_{A-A}+N_E A_{E-A})}{d_o^4} \times\sum_{k=o}^{\infty}\left[\frac{1}{2k+1}\left(1-\frac{d_o}{r_p}\right)^{2k}\left\{\frac{21}{32}\alpha_k\left(\frac{d_o}{r_p}\right)^{10}-\beta_k\left(\frac{d_o}{r_p}\right)^4\right\}\right] \tag{16}$$

For the case of the area-averaged cylindrical potential:

$$\bar{\epsilon}_{LA}=\frac{\int_0^{r_p-d_o}\epsilon(r)2\pi r dr}{\int_0^{r_p-d_o}2\pi r dr} \tag{17}$$

and the model equation that results is:

$$\ln\left(\frac{P}{P_o}\right)=\frac{3}{4}\frac{\pi N_{AV}}{RT}\frac{(N_A A_{A-A}+N_E A_{E-A})}{d_o^4} \times\sum_{k=o}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{d_o}{r_p}\right)^{2k}\left\{\frac{21}{32}\alpha_k\left(\frac{d_o}{r_p}\right)^{10}-\beta_k\left(\frac{d_o}{r_p}\right)^4\right\}\right] \tag{18}$$

Estimation of Physical Parameters

Having derived two new model equations relating the free energy of adsorption to the average interaction potential in a cylindrical pore, the next step is estimation of the constants in the model equations that correspond to the physical properties of the adsorbate and adsorbent. Aside from the geometric problem in applying the slit-pore model to zeolites, the next major source of inaccuracy and discrepancy is the variation in the values of these physical parameters, especially for surface oxide ions in zeolites. In contrast, physical property data of this kind are more readily available for carbon. In this work, values derived from the literature were utilized for the physical parameters, including the diameters of oxide ion and argon, as well as the polarizability of oxide ion and argon, and the magnetic susceptibility of argons (Derouane et al., 1987; Derouane and Nagy, 1987; Taniguchi and Takaishi, 1986; Tatewaki and Nakamura, 1981). The density per unit area of

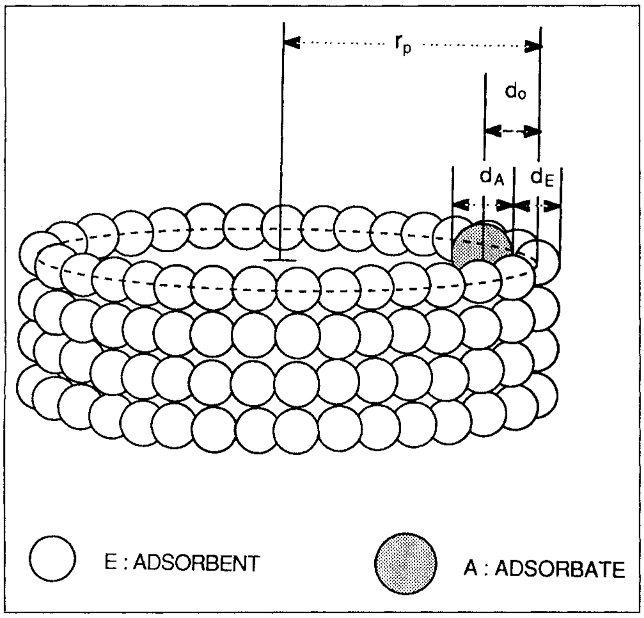

Figure 2. Cylindrical geometry.

argon was calculated on the basis of its solid density, 1.65 g/cm^3 (*Handbook of Chemistry and Physics*). The density per unit area of oxide ion was calculated based on an ionic diameter of 0.276 nm (Derouane, 1987; Derouane et al., 1987; Derouane and Nagy, 1987). Finally, the magnetic susceptibility of the oxide ion was calculated on the basis of the Kirkwood-Müller constant for argon and zeolite A equal to 11.9×10^{-43} cal•cm^6/mol, as reported by Soto and coworkers (1981). These parameter values for the physical properties of the surface oxide ion and argon are collected in Table 1.

Calculation of Micropore Size Variation with P/P_o for Cylindrical and Slit Geometry

Utilizing the parameters for the physical properties of the surface oxide ion and argon, the slit and cylindrical model equations can be compared. The slit model equation becomes:

$$\ln\left(\frac{P}{P_o}\right) = \frac{28.57}{(L-0.612)}\left[\frac{1.584\times 10^{-3}}{(L-0.306)^3} - \frac{1.729\times 10^{-7}}{(L-0.306)^9} - 4.793\times 10^{-2}\right] \tag{19}$$

Table 1. Physical Parameters for Micropore Size Calculation

Parameter	Adsorbent Oxide Ion	Adsorbate Argon
	Subscript	
	E	*A*
Diameter, *d*, nm	0.276^a	0.336^b
Polarizability, α, cm^3	2.5×10^{-24}^{b}	1.63×10^{-24}^{c}
Magnetic susceptibility, χ, cm^3	1.3×10^{-29}*	3.25×10^{-29}^{c}
Density, *N*, molecules/cm^2	1.31×10^{15}*	$8.52\times$ ^{14}*

^{a}Derouane (1987)
^{b}Taniguchi and Takaishi (1986)
^{c}Tatewaki and Nakamura (1981)
*Estimated in this work

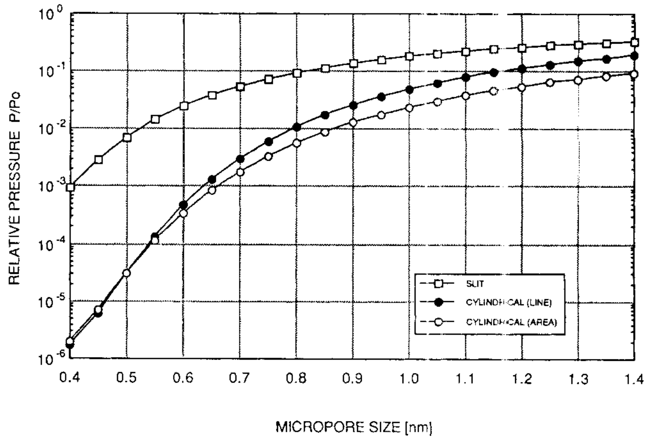

Figure 3. Relationship of pore size to relative pressure for each model.

The effective pore width becomes $(L-0.276)$ nm. The corresponding line-averaged and area-averaged model equations become:

$$\ln\left(\frac{P}{P_o}\right) = 36.48 \sum_{k=o}^{\infty}\left[\frac{1}{2k+1}\left(1-\frac{0.306}{r_p}\right)^{2k} \times \left\{\frac{21}{32}\alpha_k\left(\frac{0.306}{r_p}\right)^{10} - \beta_k\left(\frac{0.306}{r_p}\right)^4\right\}\right] \tag{20}$$

and

$$\ln\left(\frac{P}{P_o}\right) = 36.48 \sum_{k=o}^{\infty}\left[\frac{1}{k+1}\left(1-\frac{0.306}{r_p}\right)^{2k} \times \left\{\frac{21}{32}\alpha_k\left(\frac{0.306}{r_p}\right)^{10} - \beta_k\left(\frac{0.306}{r_p}\right)^4\right\}\right] \tag{21}$$

where the effective pore diameters become $(2r_p-0.276)$ nm.

The expansion coefficients α_k and β_k in Eqs. 20 and 21 are expressed as:

$$\alpha_k = \left(\frac{-4.5-k}{k}\right)^2 \alpha_{k-1} \tag{22}$$

$$\beta_k = \left(\frac{-1.5-k}{k}\right)^2 \beta_{k-1} \tag{23}$$

with α_o and β_o both equal to one.

These equations can provide the relationships between the micropore size and the relative pressure. These results are displayed for the three model equations in Figure 3. The cylindrical pore model equations display consistently larger pore sizes at equivalent relative pressures. The cylindrical models also indicate a steeper drop-off in the relative pressure as the pore size decreases, especially at pore sizes smaller than approximately 0.8 nm.

These model results can be used to transform isotherm data from the volume adsorbed in terms of relative pressure to the volume adsorbed in terms of the pore size. This requires that an adsorption isotherm of argon in a zeolite be carefully obtained by experimental methods.

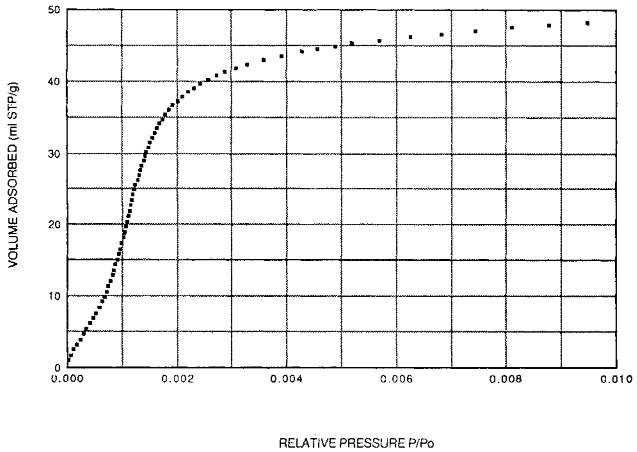

Figure 4. Static adsorption isotherm of argon on fresh zeolite Y containing fluidized cracking catalyst.

Results

Experimental measurement of argon adsorption isotherm on zeolite Y

A fresh sample of a commercial fluidized cracking catalyst (Engelhard Co.) containing zeolite Y was used as the control sample in this work. Argon adsorption was conducted in a Omnisorp-100 porosimeter supplied by Omicron Corporation. After outgassing 0.150 g of the catalyst sample for 2 h at 100°C, 1 h at 200°C, 1 h at 300°C, and 1 h at 400°C, at a pressure of 10^{-5} torr, the sample was cooled and transferred under vacuum to the adsorption port.

Adsorption was conducted in the so-called static mode. This was done to insure that sample and gaseous adsorbate could come to equilibrium. Argon was flowed into the sample cell held at 87 K in liquid argon for 30 sec at 0.19 sccm, and then the system was allowed to equilibrate for 5 min before the next plug of argon was admitted. This was repeated from an initial pressure of 10^{-5} torr to a final pressure of 20 torr. Data on the pressure in the cell, and mass of argon admitted were continuously stored in a dedicated personal computer during the course of the experiment. The adsorption of argon was computed by comparison of the mass flow and pressure rise obtained with nonadsorbing helium over the same sample at 87 K.

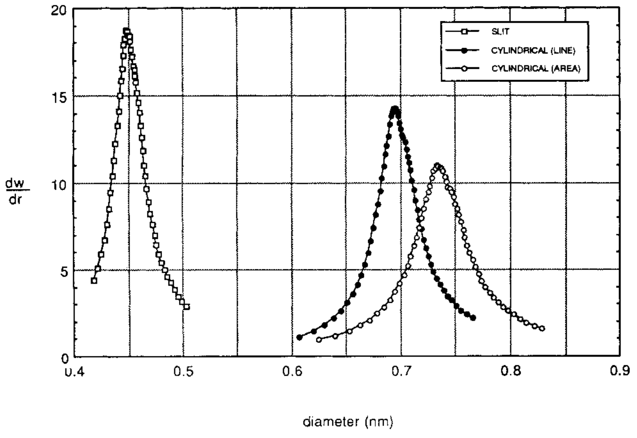

Figure 5. Micropore size distribution of fresh FCC catalyst for each model.

The results of the argon adsorption experiment on the zeolite Y containing FCC sample are displayed in Figure 4 as the volume adsorbed vs. the relative pressure up to 0.0025.

Geometric sensitivity of the calculated pore size of zeolite Y in a fluidized cracking catalyst

The isotherm data displayed in Figure 4 can be transformed into pore size distribution data for each of the models. Micropore size distributions of the fresh FCC material for each of the models are displayed in Figure 5 as the differential volume adsorbed with respect to the differential pore size, vs. pore size. The results indicate that for the slit model, the calculated average pore size is approximately 0.45 nm, while for the line-averaged and area-averaged cylindrical models it is 0.69 and 0.74 nm, respectively.

Parametric sensitivity in the area-averaged cylindrical model

Since there is uncertainty in the physical parameters used in the model equations both for the oxide ion and argon, tests of the parametric sensitivity of the calculated pore size from the area-averaged cylindrical model were conducted. In order to readily ascertain the effects of parameter uncertainty, a range of ±30% variation was separately applied to each of the parameters in Table 1 and the pore size distribution for zeolite Y was recalculated. The results on the calculated pore size are compiled in Table 2. Based on these results it is clear that the diameter of the oxide ion has a large effect on the calculated pore size because of the higher powers to which it is raised in the model equations. The variations in the density per unit area of argon and the oxide ion, as well as the magnetic susceptibility of argon, have only moderate effects on the result. Finally, variation in the polarizability of the oxide ion has only a small effect on the calculated pore size.

Preliminary application to other zeolites and molecular sieves

To date, argon adsorption isotherms for other zeolites have not been determined in our laboratories. However, application of the cylindrical pore model can be tested against argon isotherm data available in the literature. Isotherms determined by the continuous adsorption method (Venero and Chiou, 1988) for a number of zeolites and VPI-5 have been reported (Venero and Chiou, 1988; Davis et al., 1988; 1989). On the

Table 2. Calculated Pore Size with Variation in Physical Parameters in Area-Averaged Cylindrical Pore Model

	Calculated Pore Size, nm		
	Variation in Parameters		
Physical Parameter	−30%	0	+30%
Argon			
Density, 8.52×10^{14} mol/cm^2	0.68	0.74	0.78
Oxide Ion			
Diameter, 0.276 nm	0.99	0.74	0.55
Polarizability, 2.5×10^{-24} cm^3	0.71	0.74	0.75
Magnetic suscept., 1.3×10^{-29} cm^3	0.65	0.74	0.81
Density, 1.31×10^{15} mol/cm^2	0.63	0.74	0.83

Table 3. Preliminary Results from Application of Cylindrical Pore Model to Argon Isotherms of Other Zeolites and Molecular Sieves

Molecular Sieve	Area Avg. Cylind. Pore Dia. nm	Source of Argon Isotherm	Expected Based on X-ray nm	Source of X-ray Pore Size
Ca-A	0.58	a	~0.49	d
Na-Y	0.71	a	0.47	e
ZSM-5	0.56	a	0.56×0.53	e
Na-X	0.65	b	0.74	e
VPI-5	0.81	b	~1.20	b,c
VPI-5	0.79, 1.04	c	-	-
$AlPO_4$-11	0.54	c	0.63×0.39	e
$AlPO^4$-5	0.60	c	0.73	e

[a] Venero and Chiou (1988)
[b] Davis et al. (1988)
[c] Davis et al. (1989)
[d] Dyer (1988)
[e] Meier and Olson (1987)

basis of these argon isotherms a pore size calculation was made with the area-averaged cylindrical pore model equation and the parameter values given in Table 1. The results for Ca-A, Na-Y, ZSM-5, Na-X, $AlPO_4$-5, $AlPO_4$-11, and VPI-5 are provided in Table 3.

Discussion

In Figure 3, a comparison of the slit model with either of the cylindrical model results indicates that for any given pore size the predicted relative pressure is always lower for the cylindrical than for the slit geometry. The departure becomes quite dramatic at effective pore sizes less than approximately 1.1 nm. Conversely, at any given relative pressure the slit model predicts a smaller pore size than the cylindrical model. This is particularly noticeable in the region of critical interest between 10^{-5} and 10^{-1}. This is the pressure regime in which zeolites are typically analyzed by gas adsorption methods. As an example, a relative pressure of 10^{-3} corresponds to an effective pore size under 0.5 nm in the slit model, while in the cylindrical model it corresponds to an effective pore size between 0.7 and 0.8 nm. These differences between the two model results are particularly interesting in the context of curvature effects in adsorption within zeolites, as established by Derouane (Derouane et al., 1987; Derouane and Nagy, 1987; and Derouane, 1987). It seems as though the enhanced interaction due to curvature is captured better in the cylindrical model presented here than in the earlier slit model.

The results of the models pictured in Figure 3 can be applied to the low-pressure end of the argon adsorption isotherm for the FCC material. Recalling that zeolite Y, present in the fresh and unsteamed FCC material, has a pore mouth of approximately 0.74 nm, determined by X-ray diffraction studies, it is apparent that the cylindrical pore models, either line- or area-averaged, provide a better result than the slit-pore model that has been applied previously to zeolites. Apparently, reasonable values for the pore size can be obtained even with the slit-pore model, but presumably only with adjustment of the values of the physical parameters (Venero and Chiou, 1988). However, when physically realistic values for these parameters are used, such as those displayed in Table 1, then the slit model underpredicts the pore size of the zeolite.

The deviation between the line-averaged and area-averaged cylindrical pore models is, as expected from the model equations, quite small. The results of the systematic variation in the physical parameters shows that the results of the calculation can be quite sensitive to certain of these physical constants, especially the diameter of the oxide ion at the zeolite surface, because of the power law dependency of the potential on this parameter. Other physical parameters had only moderate to small effects on the final calculated pore size. These results can serve to focus attention on where further efforts toward physical characterization of zeolites may be placed, especially if adsorptive characterization is to become a more rigorous technique.

It is curious that the cylindrical model result provides a pore size that corresponds closely to the size of the aperture in zeolite Y rather than the approximately 1.15 nm of the supercage dimension or even some weighted average of the two. Rather than being a coincidental result of the values that were used for the physical parameters in the model equations, it is reasonable to consider it to be a reflection of the real physics of adsorption in the system. That is, at very low relative pressures the pore mouths may be expected to be sites of lowest energy for the adsorption of argon. This would be especially true after one argon atom has adsorbed into the pore mouth, thus further restricting access to the inner supercage. On the basis of either the model developed here or the Kelvin model, used for the calculation of P/P_0 at pore sizes just below its useful lower limit, the relative pressure for equilibration in a 1.0–1.5 nm pore would be at least 10^{-2} to 10^{-1} if not higher. Thus it may be physically reasonable to expect argon to adsorb initially into the pore mouths at 87 K and not in the supercages of zeolite Y. However, computer simulation of xenon at high occupancies and low temperatures in zeolite suggest that the supercage is preferentially occupied (Woods and Rowlinson, 1989).

The results obtained with the cylindrical pore model for other zeolites and VPI-5 are unexpectedly good, given that a rather unoptimized set of parameters was used for the calculations. In particular, the value for the Na-Y pore, not in a fluid cracking catalyst matrix, is close to the value we obtain from our isotherm. The pore sizes of other medium to large pore zeolites are generally good. In the case of Ca-A the value is somewhat larger than is expected from the X-ray structure. This may arise from the set of parameter values used. However, it seems as likely that part or all of the shift can be explained in terms of a shift of the isotherm to higher relative pressures, as a result of diffusional limitations on the argon adsorption rate in this small pore structure. In our own experimental work with zeolite Y we have noticed that the static adsorption method is required to reach a near-equilibrium state during the uptake of argon.

With VPI-5, a super large pore zeolite, the calculated pore size is unexpectedly low. Here again one could attribute this to the parameter values used in the calculation since they are based on data for silicoaluminates, not aluminophosphates. Although this is justified and needs to be explored, it is also interesting to note that the values in Table 3 are similar to values reported previously on the basis of the argon isotherm (Davis et al., 1988). In the earlier work it was suggested that the small apparent pore size calculated on the basis of argon adsorption might be due to the effects of anomalous argon packing in VPI-5. This may be the case, but there is as yet no sound theoretical basis to either confirm or deny the suggestion. It is also possible that at the larger pore sizes the simplicity of the Howath-Kawazoe model breaks down as the number of argon interactions with themselves begins to outweigh, statistically, the interactions with the wall of the adsorbent. So, it may be that for larger pores, a larger adsorbate like xenon or krypton may be preferred. It is also worth noting that the two argon isotherms reported for VPI-5 are not the same. In the earlier paper the overall shape is roughly sigmoidal (Davis et al., 1988) while in the later paper it displays two inflection points and the whole isotherm is shifted to higher pressure (Davis et al., 1989). Since the value for the pore size of Na-X calculated here (based on the argon isotherm reported in the first paper in VPI-5) is also shifted to lower values, one wonders if a systematic experimental artifact might have shifted the isotherms to lower values of relative pressure, and hence apparently lower pore sizes. This might explain why the more detailed isotherm for VPI-5 in the later paper (Davis et al., 1989) is shifted to higher pressures, more consistent with such a large pore structure. On the basis of the second isotherm for VPI-5, we find one maximum at 0.85 nm, but also a medium intensity, broad shoulder in the apparent pore size distribution, extending from approximately 1.0 to 1.2 nm. This shoulder is in the region expected for the VPI-5 structure. As was noted by Davis earlier (1989), the structure of the argon isotherm in VPI-5 and the underlying adsorbate-adsorbent physics that it conveys are as yet not understood. More recent experimentation has been aimed at investigating adsorbate transitions in VPI-5 and other molecular sieves with high-resolution, quasi-equilibrium sorption studies (Hathaway and Davis, 1990). However, it is also interesting to note that when the area-averaged cylindrical model is applied to the argon isotherms reported for $AlPO_4$-11 and AlPO-5 from the same reference (Davis et al., 1989), the resultant apparent pore sizes are 0.58 and 0.64 nm, respectively, Table 3. As in the case of VPI-5, these values are somewhat lower than expected on the basis of X-ray data. The discrepancy can arise from the parameters used in the calculation, which were not based on aluminophosphates, from the geometry, which is not perfectly cylindrical, or from experimental factors, arising from how the isotherm was measured.

Conclusions

A careful comparison of the slit-pore model with the cylindrical-pore model for zeolites using reasonable values for the physical properties of the oxide ion and argon, indicates that the cylindrical model provides a better result. This is presumably due to the fact that the latter model better incorporates enhanced adsorption in zeolite micropores due to effects of curvature. In addition to geometric sensitivity, the model shows some parametric sensitivity with the variation in the physical constants of the adsorbate-adsorbent pair. Application of the cylindrical pore model using this set of parameters to other zeolites gives promising results, especially for medium and larger pore sieves. This suggests that further research should aim at determining these parameters more accurately in other zeolitic and molecular sieving materials.

Acknowledgment

This research was supported by funds from the Catalysis Center Partners, Mobil Foundation, and the National Science Foundation through a Presidential Young Investigator Award (NSF No. CBT-965714). Nippon Mining Company, Limited is thanked for its support of A. Saito.

Notation

A = dispersion constant, N·m/molecules
c = speed of light, m/s
d = diameter of an atom, nm
d_o = arithmetic mean of diameters of adsorbate and adsorbent atoms, nm
K = coefficient, Eq. (3)
L = distance between nuclei of the two parallel layers, nm
M = mass of an electron, kg
m = order of the repulsion term in Eq. 2; $m=4$
N = density per unit area, molecules/cm^2
N_{AV} = Avogadro's number, molecules/mol
n = order of the dispersion term in Eq. 2; $n=10$
P = pressure of an adsorbate gas, torr
P_o = saturation pressure of an adsorbate gas, torr
R = gas constant, N·m/mol·K
r = diameter from central axis, nm
r_m = radius of inner core, nm
r_p = radius of micropore cylinder, nm
T = temperature, K
V_L = liquid volume of an adsorbate, m^3/mol
z = distance from an atom in the surface layer, nm

Greek Letters

α = polarizability, cm^3
α_k = constant, Eq. 12
β_k = constant, Eq. 12
χ = magnetic susceptibility, cm^3
ϵ = potential energy of interaction, N·m/molecules
ϵ^* = minimum potential energy of interaction, N·m/molecules
γ = surface tension of an adsorbate, N/m
σ = distance from an atom in the surface layer at zero interaction energy, Eq. 4, nm/molecules
Γ = gamma function

Subscripts

A = adsorbate
E = adsorbent
A-A = adsorbate-adsorbate-adsorbent interaction
A-E = adsorbate-adsorbent interaction

Literature Cited

Brunauer, S., L. S. Deming, W. S. Deming, and E. Teller, "On a Theory of the van der Waals Adsorption of Gases," *J. Amer. Chem. Soc.*, **62**, 1723 (1940).

Brunauer, S., R. Sh. Mikhail, and E. E. Bodor, "Pore Structure Analysis without a Pore Shape Model," *J. Colloid Sci.*, **24**, 451 (1967).

Davis, M. E., C. Saldarriaga, C. Montes, J. Garces, and C. Crowder, "VPI-5: The First Molecular Sieve with Pores Larger than 10 Ångstroms," *Zeolites*, **8**, 362 (1988).

Davis, M. E., C. Montes, P. E. Hathaway, J. P. Arhancet, D. L. Hasha, and J. E. Garces, "Physiochemical Properties of VPI-5," *J. Am. Chem. Soc.*, **111**, 3919 (1989).

Defay, R., I. Prigogine, A. Bellemans, and D. H. Everett, *Surface Tension and Adsorption*, Longmans, London (1966).

Derouane, E. G., and J. B. Nagy, "Surface Curvature Effects on the NMR Chemical Shift for Molecules Trapped in Porous Solids," *Chem. Phys. Lett.*, **137**, 341 (1987).

Derouane, E. G., "The Energetics of Sorption by Molecular Sieves: Surface Curvature Effects," *Chem. Phys. Lett.*, **142**, 200 (1987).

Derouane, E. G., J. M. André, and A. A. Lucas, "A Simple van der Waals Model for Molecule-Curved Surface Interactions in Molecular-Sized Microporous Solids," *Chem. Phys. Lett.*, **137**, 336 (1987).

Dubinin, M. M., and L. V. Radushkevich, "The Equations of the Characteristic Curve of Activated Charcoal," *Doklady Akad. Nauk. S.S.S.R.*, **55**, 327 (1947).

Dyer, A., *An Introduction to Zeolite Molecular Sieves*, Wiley, New York (1988).

Everett, D. H., and J. C. Powl, "Adsorption in Slit-like Cylindrical Micropores in the Henry's Law Region," *J. Chem. Soc., Faraday Trans. 1*, 72, 619 (1976).

Gregg, S. J., and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, London (1982). *Handbook of Chemistry and Physics*, Chemical Rubber Pub. Co. (1974).

Hathaway, P. E., and M. E. Davis, "High Resolution, Quasi-Equilibrium Sorption Studies of Molecular Sieves," *Catal. Lett.*, **5**, 333 (1990).

Horvath, G., and K. Kawazoe, "Method for Calculation of Effective Pore Site Distribution in Molecular Sieve Carbon," *J. Chem. Eng. Japan*, **16**, 470 (1983).

Lippens, B. C., and J. H. de Boer, "Studies on Pore Systems in Catalysts, V: The *t* Method," *J. Catal.*, **4**, 319 (1965).

Meier, W. M., and D. H. Olson, *Atlas of Zeolite Structure Types*, Butterworth, London (1987).

Peterson, B. K., K. E. Gubbins, G. S. Heffelfinger, V. Marini, B. Marconi, and F. van Swol, "Lennard-Jones Fluids in Cylindrical Pores: Nonlocal Theory and Computer Simulation," *J. Chem. Phys.*, **88**, 6487 (1990).

Schmeits, M., and A. A. Lucas, "Physical Adsorption on Small Spherical Particles and Spherical Pores," *J. Chem. Phys.*, **65**, 2901 (1976).

Sing, K. S. W., "Surface Area Determination," *Proc Int. Symp. on Surface Area Determination*, D. H. Everett, R. H. Ottewill, eds., Butterworth, London, 25 (1970).

Soto, J. L., P. W. Fisher, A. J. Glessner, and A. L. Myers, "Sorption of Gases in Molecular Sieves: Theory for Henry's Constant," *J. Chem. Soc. Faraday Trans. 1*, **77**, 157 (1981).

Taniguchi, K., and T. Takaishi, "Polarizability of Zeolite Crystals Determined by XPS Techniques," *7th Int. Zeolite Conf.*, no. 4A-10, 155 (1986).

Tatewaki, H., and T. Nakamura, "The Importance of the Quadrupole Polarizability of Rare Gases on Ionic Crystals," *Surf. Sci.*, **108**, L447 (1981).

Vaughan, D. E. W., "Recent Developments in Pillared Interlayered Clays," *ACS Symp. Series*, **368**, W. H. Flank, T. E. Whyle, Jr., eds., 308 (1988).

Venero, A. F., and J. N. Chiou, "Characterization of Zeolites by Gas Adsorption at Low Pressures," *MRS Symp. Proc.*, **111**, 235 (1988).

Walker, P. L., *Chemistry and Physics of Carbon*, **2**, Dekker, New York (1966).

Woods, G. B., and J. S. Rowlinson, "Computer Simulation of Fluids in Zeolites X and Y," *J. Chem. Soc., Faraday Trans. 2*, **85**, 765 (1989).

Manuscript received Aug. 6, 1990, and revision received Jan. 7, 1991.