Phase Transition and Structural Heterogeneity; Benzene Adsorption on Silicalite

Adsorption equilibria have been gravimetrically measured at 10, 20, 30, 50, and 70°C for benzene on pure crystalline silicalite. Isotherms change from type I to type IV with decreasing temperature, indicating heterogeneous behavior. The transition temperature is determined to be 38 ± 1°C by isobaric experiments. Silicalite is energetically homogeneous since there are no cations present. The observed structural heterogeneity is due to the comparable sizes of benzene molecules and the silicalite pore system. Silicalite is modeled as two types of homogeneous pores where a van der Waals model describes local equilibrium. Model parameters are calculated via nonlinear regressions with prescribed pore distribution determined from crystallographic considerations. Data and model predictions are in good agreement with highly significant parameters.

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Introduction

The adsorption isotherm data of pure components are important to classify adsorbents and to predict multicomponent equilibrium behavior. Adsorption on molecular sieve zeolites usually shows type I isotherm shape, where the amount adsorbed increases continuously with pressure, asymptotically approaching a limit. This limit, commonly referred to as monolayer capacity or ultimate capacity, corresponds to complete filling of pores with gas molecules. Although zeolites are not usually homogeneous, the overall behavior observed as a type I isotherm fits the formulations of homogeneous models.

Variation of the adsorption potential from point to point on the zeolite surface can cause energetic heterogeneity. The existence of ions on the surface with their associated potential island is known to cause heterogeneous behavior, especially if the dimensions of the adsorbed molecule are comparable to those of the potential island. If the adsorbed molecule is large enough to be exposed to more than one ion, the overall potential is averaged and the system can usually be modeled as homogeneous.

Heterogeneity can also be caused by the structure of the micropores even if the surface does not contain any variation in potential. An extreme example is steric exclusion, where a molecule cannot fit into a specific type of pore in the structure. This idea was used by Valenzuela and Myers (1987) to satisfactorily explain high nonidealities observed for propane-hydrogen sulfide and propane-carbon dioxide binary mixtures on H-mordenite (Talu and Zwiebel, 1986). Their approach was to model competitive adsorption between the large (propane) and the small (hydrogen sulfide or carbon dioxide) molecules in the large pores while completely excluding propane from entering the smaller pores. On the other hand, there is no indication of heterogeneity in the pure-component isotherms of the mentioned system; they are all type I. It is not readily apparent from only pure-component isotherms that a heterogeneous model should be used to predict binary mixture behavior.

The size of micropores can play an important role in determining the heterogeneity of the surface even when there is no clear-cut rejection of a molecule due to steric exclusion. Assuming a uniform potential distribution, as the curvature of the surface increases the total potential on a molecule located close to the surface increases. The total potential goes through a minimum as the diameter of the surface approaches the diameter of the molecule. For even smaller pores, the total potential is not defined because the molecule simply cannot enter the pore, resulting in steric exclusion. The total potential can be depicted as an exponential decay up to the molecular diameter, where a strong transition from attractive to repulsive forces takes place and potential rapidly goes to infinite repulsion, Figure 1.

An indication of this behavior is reported in the literature with respect to the catalytic behavior of ZSM-5 for benzene by Olson et al. (1980, 1981). They showed that the similarity of the

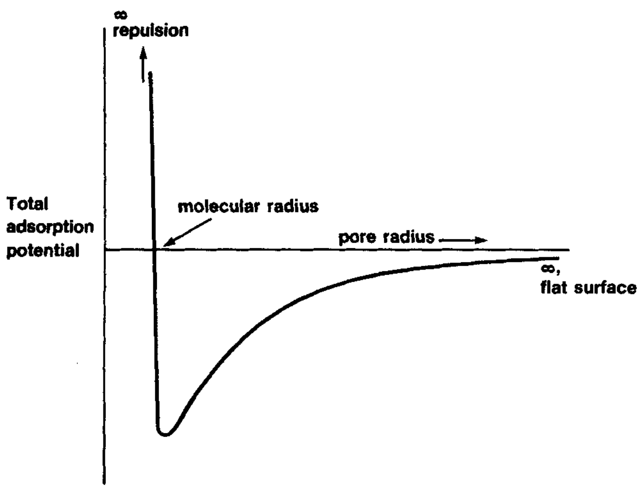

Figure 1. Effect of pore radius on total adsorption potential.

ZSM-5 channel size and the size of the benzene molecule has a very significant influence on the performance of the catalyst in several potentially important processes. Benzene adsorption in the structurally identical silicalite must also be significantly different from adsorption on flat surfaces or in large pores. The objective of this paper is to develop the necessary concepts and mathematical models for analyzing structural heterogeneity and to validate the model with experimental data.

Silicalite rather than ZSM-5 is used in this study. Its pore structure is identical to that of ZSM-5; however, calcined silicalite is essentially devoid of cations. The use of silicalite singles out the effect of pore sizes on heterogeneity. The term "structural heterogeneity" is used to distinguish this effect from others caused by potential variations. Benzene is used as the probe molecule. The results of isothermal and isobaric experiments and the mathematical model used to represent the system are presented and discussed in this paper.

Experimental Method

The silicalite crystals were produced in our laboratories using the protocol outlined by Hayhurst and Lee (1986). Crystals were measured to be 270 × 70 × 70 μm in size and twinned along the longest axis. Prior to adsorption testing, the silicalite was calcined at 550°C for 3 h. Some test samples were calcined for longer periods. Longer calcinations did not change the adsorption of benzene. X-ray diffraction and scanning electron microscopy analysis performed on the silicalite crystals indicated that the test materials were well crystallized and essentially uniform in size.

Adsorption measurements were performed in a high-vacuum Cahn 1000 microbalance. Silicalite samples were activated *in situ* at 450°C under vacuum (1.33×10^{-3} Pa) for 12 h prior to testing. Benzene vapor was dosed into the adsorption chamber. Changes in sample weight and vapor phase pressure were recorded until equilibrium was reached. Equilibrium was assumed when the sample weight changed less than ±0.01 mg in a 1 h period. By sequentially increasing and then decreasing the pressure of benzene, a complete isotherm was constructed. The sample was then reactivated and other adsorption temperatures were tested.

Table 1. Experimental Data of Benzene Adsorption on Silicalite

T = 10°C		T = 20°C		T = 30°C		T = 50°C		T = 70°C	
P	n	P	n	P	n	P	n	P	n
0.13	0.648	0.17	0.573	0.04	0.156	0.10	0.193	0.11	0.068
0.36	0.684	0.70	0.659	0.12	0.339	0.35	0.329	0.27	0.130
1.31	0.743	1.57	0.701	0.20	0.447	0.95	0.468	1.10	0.317
3.15	0.855	3.92	0.753	0.71	0.579	2.09	0.561	2.02	0.415
6.35	1.097	8.06	0.839	1.79	0.628	4.02	0.612	4.19	0.502
10.49	1.187	13.33	1.014	3.74	0.658	9.60	0.642	7.43	0.551
14.81	1.198	17.45	1.080	6.80	0.687	16.22	0.664	13.04	0.579
24.53	1.202	21.54	1.120	13.67	0.738	24.26	0.682	20.61	0.598
34.06	1.206	26.90	1.127	24.13	0.857	34.19	0.703	34.99	0.614
45.72	1.208	40.63	1.137	33.22	0.959	43.12	0.716	55.45	0.630
56.25	1.214	53.85	1.139	41.66	1.020	51.96	0.725	76.25	0.637
—	—	64.65	1.139	57.85	1.052	66.37	0.744	91.98	0.639
—	—	77.45	1.142	71.18	1.066	73.78	0.750	—	—
—	—	91.31	1.142	78.91	1.069	80.09	0.757	—	—
—	—	—	—	—	—	85.45	0.762	—	—

P, pressure, kPa; *n*, amount adsorbed, gmol/kg

The adsorption temperature was controlled to within 0.5 K. The accuracy of pressure measurements was ±0.13 Pa and the sample weight was determined to within 5×10^{-6} g. The benzene used was research grade (Fisher Scientific Co.).

Results

Isothermal data at 10, 20, 30, 50, and 70°C for the benzene-silicalite system are listed in Table 1 and shown in Figure 2. Adsorption and desorption data are essentially coincident, indicating no hysteresis for this system.

Surface critical temperature

Type IV isotherms are observed at temperatures of 10, 20, and 30°C, while the isotherms at 50 and 70°C are type I. The transition from type I to type IV isotherm is experimentally determined to occur at 38 ± 1°C by isobaric experiments, as shown in Figure 3. The existence of a convex region in the low-temperature isotherms indicate that surface transition occurs below a certain surface critical temperature.

The bulk critical temperature of benzene is 289°C. The surface critical temperature approximated from gas phase van der Waals constants as described by Ross and Olivier (1964) is 8°C. This value corresponds to an ideal surface critical temperature, which is not affected by the solid substrate. The regression results indicate that the surface critical temperature is −113.7°C as calculated by $T_c = 2\alpha/k\beta/6.75$. Due to the very low vapor pressure of benzene at or below the regressed critical temperature, we could not substantiate this finding by measuring the isotherms to show the vertical increase associated with a first-order phase change.

Structural heterogeneity of the surface

The silicalite-benzene system clearly displays heterogeneous behavior. The concave region of type IV isotherms at low pressure cannot be explained by the phase transition. A type IV isotherm can, however, be generated as the sum of type I and type V isotherms, as shown in Figure 4. If the type I and V isotherms are considered to characterize two homogeneous patches of the

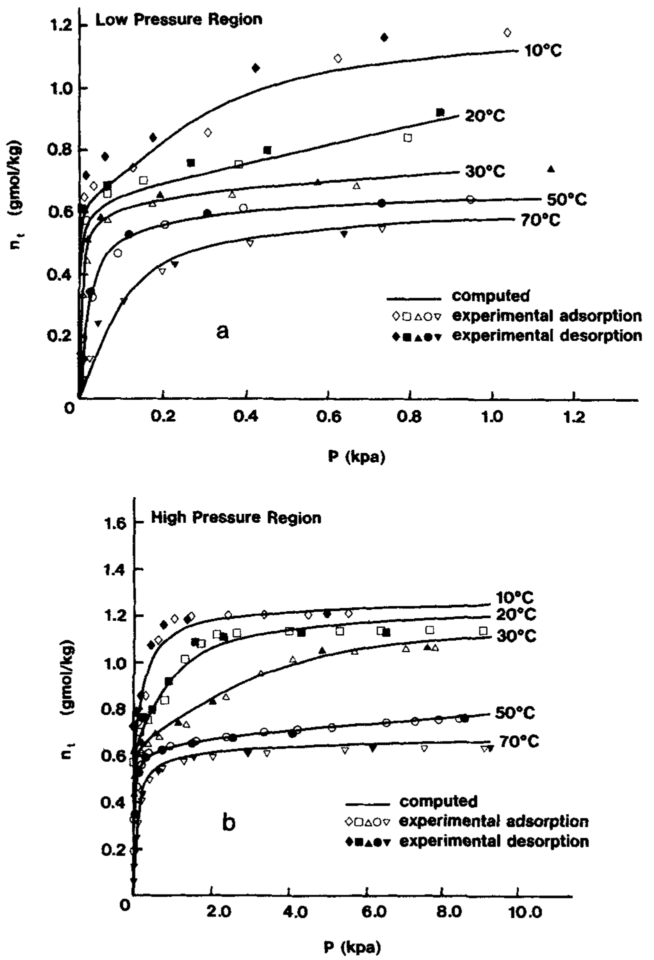

Figure 2. Experimental and calculated adsorption isotherms for benzene on silicalite.

a. Low-pressure region
b. High-pressure region

surface with the type V being responsible for phase transition, the resultant type IV isotherm corresponds to a composite (heterogeneous) surface. The observed type IV isotherm can then be reconstructed as the sum of the two component isotherms weighted according to the fraction of each homogeneous patch. Not surprisingly, the silicalite channel system contains two types of pores: large, straight pores and smaller, zigzag side channels.

Some adsorption data of the silicalite-benzene system have been reported in the literature (Flanigan et al., 1978; Wu et al., 1983; Zikanova et al., 1987; Pope, 1986). All studies were above the critical temperature determined in this study; therefore, no phase transition was reported. Very recently, the heat of adsorption data reported by Thamm (1987) indicate phase transition (referred to as surface phase reorientation) at 0.75 mmol/g coverage. Although isotherms at several temperatures were not measured and no mathematical formulation of this anomalous behavior was attempted, the *reported phase transition is in* agreement with our results.

Model for Heterogeneous Phase Transition

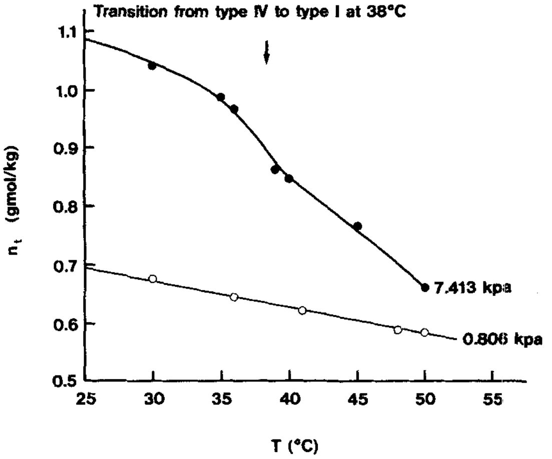

Figure 3. Results of isobaric experiments.

To date, type IV isotherm behavior has never been modeled using molecular arguments. It is a challenging task since both heterogeneity and phase transition must be included. As with any heterogeneous system, assumptions must be made with respect to the local isotherm model and the energy distribution function. These cannot be determined independently from isotherm data, which are the sum of the two effects. This summation is given by the equation:

$$n_t(T, P) = \int_0^\infty n(T, P, \epsilon) \cdot \lambda(\epsilon) \cdot d\epsilon \qquad (1)$$

where n_t is the overall observed isotherm, n is the local model that applies at a patch having a characteristic energy of ϵ, and λ is the fraction of the surface with ϵ energy.

For some simple local isotherm equations and distribution functions, Eq. 1 has been integrated. The final equation for the total amount adsorbed contains the local isotherm parameters and distribution function parameters. Such an integral equation can be used to fit the isothermal data directly. However, use of an integral equation is not possible for the system under consideration since local isotherm equations with phase transition were never integrated. In addition, the number of parameters in these integrated isotherms is so large that they are statistically ill defined if all are determined from regressions. Because of these difficulties, we chose to use a surface distribution function

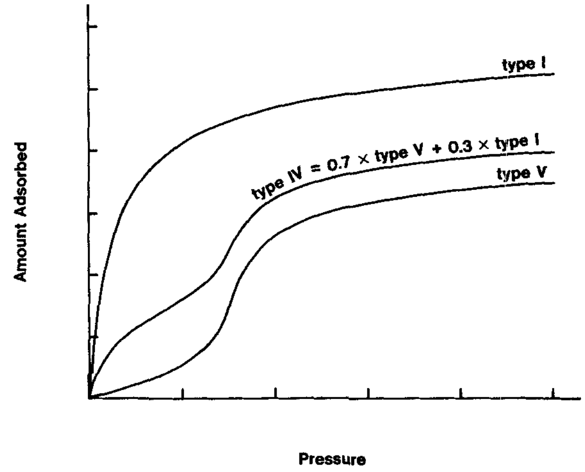

Figure 4. Construction of composite type IV isotherm from two-patch model with types I and V.

determined by crystallographic arguments, independent of adsorption data.

Pore size distribution of silicalite

The crystal structure of silicalite was first reported by Flanigen et al. (1978); the framework is formed by two groups of intersecting channels defined by 10-ring members. One half of a unit cell is shown in Figure 5. One group of pores comprises the small, zigzag channels along the *a* direction with a circular cross section of about 5.4 ± 0.2 Å. The other group comprises the large elliptical straight channels along the *b* direction with a cross section of about 5.75 × 5.15 Å. These large pores intersect the small pores. As shown by Wu et al. (1983), the total channel length in each unit cell ($a = 20.02$, $b = 19.80$, $c = 13.36$ Å) is 66 Å. There are two large pores (including the four intersections) each of length 19.80 Å, and four small pores each of length 6.6 Å.

The benzene molecule has a kinetic diameter of 5.85 Å and a width of 6.6 Å (Breck, 1974). Based on these reported dimensions, benzene should not enter silicalite's pore system at all. Conversely, the size of the benzene molecule calculated from the bond lengths is 4.962 Å, which corresponds to the static diameter at 0 K. Benzene, therefore, can adsorb in silicalite, fitting very tightly in either type of pore. Such a tight fit indicates that benzene molecules in the pores cannot overlap, while they may be situated either perpendicular or parallel to the pore axis. As benzene molecules cannot overlap in the pores of silicalite, the fraction of pores of the two types must be calculated with respect to pore lengths rather than pore volumes.

In a silicalite unit cell, the length fraction of the small pores is 0.4, and that of large pores (including the intersections) is 0.6. Although the intersections have a different characteristic potential than the large pores, they are not treated separately in this study. Equation 1 can then be reduced to a simple summation for the two types of pores:

$$n_t(T, P) = \phi_s(\epsilon_s) \cdot n(T, P, \epsilon_s) + \phi_l(\epsilon_l) \cdot n(T, P, \epsilon_l) \quad (2)$$

where $\phi_s(\epsilon_s)$ is the fraction of small pores fixed at 0.4 and $\phi_l(\epsilon_l)$ is the fraction of large pores fixed at 0.6.

Local isotherm equation

A physical model is needed to describe the local equilibrium between a given type of pore (a homogeneous patch) and the vapor phase, $n(T, P, \epsilon)$ in Eq. 2. The local model must be able to accommodate phase transition as discussed earlier. Two concave type I isotherm equations (such as Langmuir) cannot produce the shape of a type IV isotherm, irrespective of how they are weighted by the distribution function in Eq. 1.

The choice of a local equilibrium model is somewhat arbitrary. In this study the Hill-de Boer (two-dimensional van der Waals) equation was used since the physical meaning of the parameters is well understood. This equation is

$$P = K \frac{\Theta}{1 - \Theta} \exp\left(\frac{\Theta}{1 - \Theta} - \frac{2\alpha}{k\beta} \frac{\Theta}{T}\right) \quad (3)$$

where Θ is the fractional coverage and K is the Henry's law constant. The parameters α and β are the two-dimensional van der Waals constants related to adsorbate-adsorbate interactions and to molecular size.

The Hill-de Boer equation can exhibit either type I or type V behavior, depending on the value of $2\alpha/k\beta$. At low temperatures, Eq. 3 exhibits an inflection (type V isotherm) within the coverage range of zero to unity. The inflection point moves with changing temperature as shown in Figure 6. Above a certain temperature the inflection point completely disappears and the isotherm assumes type I shape.

The local isotherm equation, Eq. 3, must be valid for the two homogeneous patches in the silicalite crystal. The van der Waals constants, α and β, depend only on the characteristics of the adsorbed molecule (benzene) and should be the same for all types of pores. (This, however, assumes that the surfaces do not perturb the lateral interactions between adsorbed molecules.) Conversely, K and Θ are dependent on the pore type. They are defined as

$$\Theta_i = n(T, P, \epsilon_i)/n_i^\infty \quad (4)$$

and

$$K_i = A_i^\circ \exp\left(-\frac{U_i^\circ(\epsilon_i)}{RT}\right) \quad (5)$$

where i is a patch index. Clearly, the ultimate capacity n_i^∞ and adsorption energy $U_i^\circ(\epsilon_i)$ must be functions of the pore size. The intrinsic affinity of a patch as temperature approaches infinity, A_i°, is also dependent on the characteristics of the specific pore. A_i° is related to the entropy change in moving a molecule from

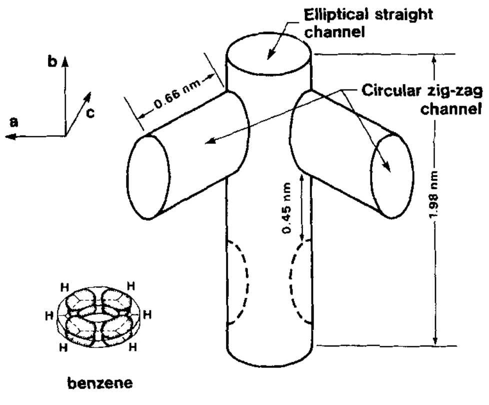

Figure 5. Benzene molecular size in comparison to pore system of silicalite corresponding to 1/2 unit cell.

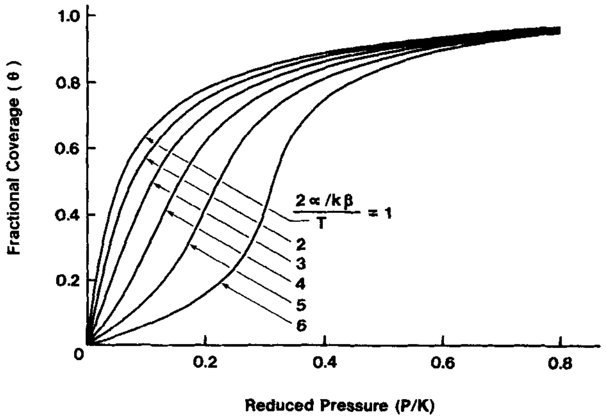

Figure 6. Transition of van der Waals isotherm from type V to type I.

the vapor phase to the adsorbed phase. This change is higher for a smaller pore since there is less freedom for a molecule to move, vibrate, and rotate in a smaller pore.

Results of Model Regressions

The application of the Hill-de Boer equation to the silicalite-benzene system involves two isotherm equations, Eq. 3; that is, separate isotherms for the large and small pores. These equations define the simultaneous equilibrium between each pore type and the vapor phase. There are, therefore, seven parameters to be determined by regressions, namely, A_s°, U_s°, n_s^∞ for the small pores, A_l°, U_l°, n_l^∞ for the large pores, and $2\alpha/k\beta$ for the adsorbed benzene phase. It should be noted that α and β cannot be determined individually.

A nonlinear regression routine utilizing a Gauss-Newton algorithm is used to determine the seven parameters from the data listed in Table 1. The solution of the model for any given set of parameters requested by the regression routine is also nonlinear in nature. The following algorithm is used to generate the objective function value for the regression routine at any given set of parameter values.

1. Values of n_s and n_l are estimated for a specific experimental point.
2. Θ_s and Θ_l are calculated by Eq. 4 according to the n_s^∞ and n_l^∞ values prescribed by the regression routine.
3. Two pressure values corresponding to Θ_s and Θ_l are calculated by Eq. 3.
4. By comparing the two pressure values determined in step 3 with experimental pressure, n_s and n_l values are updated and the algorithm is repeated from step 2.
5. When the roots of Eq. 3 as n_s and n_l values at the given experimental pressure are found, the objective function is calculated as the difference between the experimental amount adsorbed and the total amount adsorbed calculated from Eq. 2. The surface fractions, ϕ_s and ϕ_l in Eq. 2, were externally fixed at 0.4 and 0.6.

Different sets were used as the initial estimates for the parameters to assure that the results correspond to a global optimum. The regression results for parameter values are listed in Table 2. This table also includes the standard deviations and t-statistics for the parameters and other relevant regression statistics. The F-statistics of the regression indicate that the model is highly effective. Individual parameter t-statistics show that all parameters except A_s° and A_l° are 99.99% significant. Although the t-statistics for A_s° and A_l° are low, they are considered to be important from a theoretical standpoint.

The model is used to generate the curves shown in Figure 2. As can be seen in the figure, the data are well represented by the model. The effect of surface heterogeneity is demonstrated in Figure 7. This figure shows the local isotherms for the large and small pores and their summation at 30°C. It is clear that the phase transition occurs in the small pores.

Physical significance of model parameters

The adsorption potentials, U_s° and U_l°, are the most important parameters for developing a physical interpretation of benzene adsorption in silicalite. The ratio of adsorption potentials obtained from regressions is

$$\frac{U_s^\circ}{U_l^\circ} = 1.427 \tag{6}$$

Table 2. Parameter Values and Regression Statistics for Benzene-Silicalite System

	Value, ±Std. Dev. (t = statistics)	
	Small Pores	Large Pores
Overall Regression F-value = 773.87 R-square = 0.989		
Fraction of pores, ϕ_i, not regressed, dimensionless	0.4	0.6
Adsorption potential (U_i°/R, K)	9,340 ±398 (23.47)	6,494 ±318 (20.42)
Adsorption capacity ($n_i^\infty\phi_i$, gmol/kg)	0.682 ±0.022 (30.45)	0.796 ±0.011 (73.67)
Intrinsic affinity (A_i°, kPa)	2.63 ± 3.46 × 10^{14} (0.76)	4.88 ±4.80 × 10^7 (1.02)
van der Waals constants ($2\alpha/k\beta$, K)	1,076 ±95 (11.32)	

This represents a rather large increase in adsorption potential due to the relatively small difference in pore size. It is noted that both pores have the same anionic oxygen lining their surfaces. A simple molecular thermodynamic argument can, however, be used to substantiate this large increase. Assuming that the attraction potential between the pore surface and a point molecule situated at the center of the pore is proportional to the inverse sixth power of the pore radius ($\Gamma = -A/r^6$), the total potential in an infinitely long cylindrical pore (neglecting the end effects) can be calculated as

$$\Gamma_t = \int_0^{2\pi} \Gamma \cdot r \cdot dQ = -\frac{2\pi A}{r^5} \tag{7}$$

where Q is the angle in cylindrical coordinate system. Applying Eq. 7 to small and large pores of silicalite, the ratio of total potentials can be calculated as if, for simplicity, both type of pores have a circular cross section.

$$\frac{\Gamma_{ts}}{\Gamma_{tl}} = \left(\frac{r_l}{r_s}\right)^5 = (1.065)^5 = 1.369 \tag{8}$$

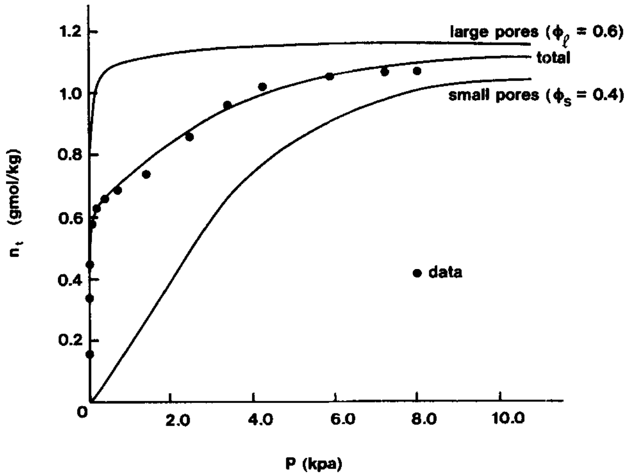

Figure 7. Experimental and composite calculated isotherms for benzene on silicalite at 30°C.

This simple molecular thermodynamic argument indicates that a 37% increase in adsorption potential is possible with only a 6.5% decrease in pore radius. The large increase in adsorption potential only occurs when the diameter of the adsorbate molecule is comparable to the pore diameter, so Eq. 7 can be integrated as a uniform potential with respect to Q angle. Although the theoretically calculated ratio of adsorption potentials (1.369) is somewhat lower than the regression value (1.427), the difference is considered reasonable as the elliptically shaped pore was modeled as circular and the end effects were neglected. The significant point is that a very small difference in pore radius results in a substantial difference in adsorption potential if the molecular size is comparable to pore size.

The ultimate adsorption capacity of benzene (in gmol/kg) is calculated as $\phi_s n_s^\infty = 0.682$ for the small pores and $\phi_l n_l^\infty = 0.796$ for the large pores. These values are equivalent to 3.84 molecules per unit cell for small pores and 4.48 molecules per unit cell for the large pores, assuming pure crystals. Considering the silicalite pore structure as shown in Figure 5, it can be deduced that the small pores are almost completely full at saturation while the large pores in the b direction are about half full. Noting that the benzene molecules do not overlap in the pores, it is most likely that the benzene molecules in the large pores are located between intersections, leaving the intersections empty. A benzene molecule is exposed to more of the adsorbent surface if surrounded by pore walls on four sides, which should result in a higher adsorption potential. These results are in contrast to proposed adsorption models for the aluminum-containing ZSM-5. In ZSM-5, adsorption is envisioned to occur at channel intersections where structural aluminum, and the corresponding cation, are located, which substantially increases the surface potential at the intersection. A similar analysis of benzene adsorption data for ZSM-5 should prove interesting.

The total adsorption capacity for benzene in silicalite as determined in this study is 8.32 molecules per unit cell (1.478 gmol/kg). This compares favorably with previously reported data including: 8.7 (Flanigen et al., 1987), 8.4 (Thamm, 1987), and 8.0 (Wu et al., 1983). By comparing these saturation values to a theoretical value based on crystallographic data and the liquid density of benzene, it is concluded that there is significant void space remaining in the silicalite pore system, even at full coverage.

Conclusions

Benzene adsorption in silicalite was measured at temperatures ranging from 10 to 70°C. The system exhibits type IV isotherm behavior, indicating heterogeneity and phase transition. Although silicalite does not contain any cations to cause energetic heterogeneity, differences in pore sizes were shown to result in structural heterogeneity. It was shown that a small difference in pore size can cause pronounced structural heterogeneity, especially if the pore and molecule dimensions are comparable.

Adsorption in silicalite is modeled as occuring on two types of homogeneous surface patches (pores). The first corresponds to silicalite's large elliptical pores and the second to smaller circular pores. The Hill-de Boer model was used to define local equilibrium on each patch. From this, a general model for benzene adsorption was developed. Data were fitted, and model parameters were determined using regression analysis. A good fit was found between the model and experimental results. Surface phase transition is proved to occur in the small pores, as substantiated by model studies and isobaric experiments.

In summary, this report represents a comprehensive study of benzene adsorption on silicalite. The concept of structural heterogeneity is used for the first time to model zeolite adsorption and provides insights into the nature of adsorbate/adsorbent interactions. It is expected that this approach can be extended to many other zeolite/adsorbate systems.

Notation

A_o = potential well depth, constant
A_i^o = temperature independent Henry's law constant
k = Boltzman's constant
n_t = total amount adsorbed
n_i = amount adsorbed in i-type pores
n_i^∞ = ultimate adsorption capacity of i-type pores
P = vapor phase pressure
Q = angle in cylindrical coordinate system
R = universal gas constant
r = pore radius
T = absolute temperature
U_i° = adsorption potential for i-type pores

Greek letters

α = two-dimensional van der Waals interaction parameter
β = two-dimensional van der Waals size parameter
ϵ = surface potential
λ = surface potential distribution function
ϕ_i = fraction of i-type pores
Θ_i = fractional surface coverage in i-type pores
Γ = average interaction potential between a molecule and surface
Γ_t = total average interaction potential between a molecule and surface

Subscripts

s, l = small, large pores

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