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# Argon Sorption in ZSM-5

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A new physisorption device collects accurate isotherm data at low pressures and low adsorptions. Thus, physisorption isotherms of microporous materials can be determined in fine detail in the region where the first sorbing atoms enter the unit cell of the solid. For argon physisorption in ZSM-5 at 87 K, a complex isotherm is observed. It is reproducible for several different crystal size samples. Simple molecular mechanics calculations for the ZSM-5/argon system allow interpretation of the observed isotherms. We found that:

- We can identify the individual sorption features for argon in ZSM-5.
- The first argon atom sorbing in the ZSM-5 unit cell can be discerned.
- Initial argon sorption in ZSM-5 occurs in the 10-ring structures.

The calculations employed are able to describe the main features of the observed isotherms but are not sufficiently refined to deal with the fine structure. 

## INTRODUCTION

We have previously reported some of the capabilities of our physisorption unit (*1*). In particular, the isotherm of a gas sorbing in microporous materials can be determined with great accuracy. The methodology employed is strictly an equilibrium one, and the isotherms so determined are therefore independent of sample diffusivities, gas flows in the apparatus, etc. We have found that the best representation of these data is the first derivative of the adsorption isotherm plotted against the log of the relative pressure. This derivative shows peaks that represent adsorption into various physical locations. The location of the peak can be translated from the log of the relative pressure to "pore size" by the Horváth–Kawazoe method (*1, 2*). In some cases, the derivative shows many peaks or shoulders. This occurs reproducibly for argon sorption into ZSM-5. In order to obtain a better understanding of the structure of the isotherms, we employed energy minimization calculations to determine where the argon atoms were sorbing. The physisorption data for argon in ZSM-5 and its interpretation based on our energy calculations are described herein.

## EXPERIMENTAL

The physisorption unit has been described previously (*1*). The ZSM-5 samples examined in this work are listed in Table 1. Argon physisorption isotherms were determined by the method described in Ref. (*1*). Briefly, the sample is dried under vacuum at 575 K for 3 hr, cooled to ambient in vacuum, and stored under 760 Torr of argon (1 Torr = 133.3 N m $^{-2}$) in a glass tube. After the sample tube is placed on the adsorption unit, the argon is removed at 575 K for 3 hr under vacuum. Then, the sample is cooled and held at 87 K with liquid argon. Gaseous argon is dosed into the sample tube from a reservoir in a step-wise fashion. At each step the pressure of the sample as well as the change in pressure of the reservoir is recorded. From these data an isotherm is constructed. Derivatives are taken with a B-spline smoothing routine.

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TABLE 1

ZSM-5 Samples Examined

| Sample no. | Crystal size ($\mu$m) | Si/Al |
|---|---|---|
| 1 | 0.04 | 50 : 1 |
| 2 | 0.4 | 70 : 1 |
| 3 | 1 | 70 : 1 |
| 4 | 10 | 50000 : 1 |

We performed simple energy calculations using the molecular mechanics program PCK6 (*3*, *4*). PCK6 does a pairwise summation of intermolecular nonbonded energies, $E$, using the equation

$$E = 0.5 \sum_j \sum_k [B_{\alpha\beta}\exp(-C_{\alpha\beta}r_{jk}) - A_{\alpha\beta}r_{jk}^{-6} + q_\alpha q_\beta r_{jk}^{-1}], \quad (1)$$

where $r$ is the interatomic distance, $A$, $B$, and $C$ are the potential energy parameters, and $q$ is the electrostatic charge. In this work, only van der Waals interactions were calculated; the coulombic term was set to zero. For most energy minimization calculations, the argon atoms were free to move in any direction. The only exception was when we mapped the zeolite channels. Then, movement was not permitted along the channel. The zeolite was treated as a rigid body in all calculations. The potential energy parameters used in these calculations are listed in Table 2. The oxygen and argon parameters were determined by Williams and co-workers (*5*, *6*). The silicon parameters are discussed in Ref. (*3*). Bulk phases of the sorbate (liquid and solid argon) were neglected since they are not encountered in the range of the experimental conditions. The zeolite structure used in these calculations was obtained from the work of Olson *et al.* (*7*).

## RESULTS AND DISCUSSION

Figure 1 shows the argon physisorption isotherms for the four ZSM-5 samples. The derivatives of the isotherms are presented in Fig. 2. This sorption regime does not represent the conventional multilayer adsorption that occurs on relatively open surfaces (pores > 50 Å) at pressures greater than $P/P_0 = 0.4$. Rather, it is the low-pressure sorption of argon into the channels of ZSM-5. There are two major peaks in the derivative along with small peaks or shoulders on the low-pressure side of the larger peak. Since this fine structure occurs for all samples of ZSM-5 but has never appeared for any other microporous material whose sorption isotherm we have determined, we conclude that it is related to the crystal structure. All of the figures show an upward trend at high $P/P_0$. This is attributable to extra-crystalline (macroporous) sorption of the type commonly seen for samples of packed powders.

There are consistently two minor features on the leading edge of the lower pressure peak. The first at about $1 \times 10^{-6}$ $P/P_0$ is a small peak. The second is a shoulder at about $3 \times 10^{-6}$ $P/P_0$. The cumulative adsorptions associated with these features as well as the Dubinin–Radushkevitch micropore adsorption are listed in Table 3. These data are listed as both $\mu$mol/g and atoms/unit cell (atoms/uc). The latter value is calculated using $1.04 \times 10^{20}$ unit cells/gram of ZSM-5. Note that for the first minor feature, the sorption is about 1 atom/uc. Therefore, it appears that the sorption data have enough resolution to show the first argon atom sorbing into ZSM-5. The calculated global minimum energy for this first atom in

TABLE 2

Potential Energy Parameters Used in PCK6

| Atomic interaction | Potential energy coefficients | | |
|---|---|---|---|
| | $A$ (kJ · A) | $B$ (kJ) | $C$ (A$^{-1}$) |
| Ar–Ar | 5410 | 675,524 | 3.58 |
| Ar–O | 2443 | 440,712 | 3.77 |
| Ar–Si | 5697 | 405,157 | 3.20 |
| O–O | 1103 | 287,520 | 3.96 |
| O–Si | 2573 | 264,324 | 3.39 |
| Si–Si | 6000 | 243,000 | 2.82 |

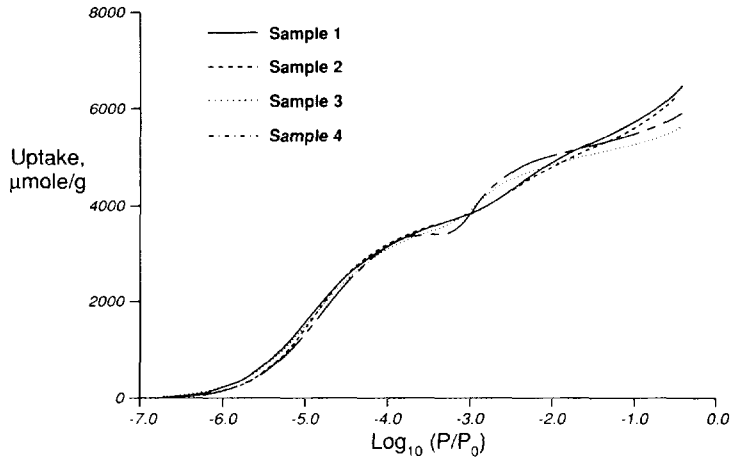


FIG. 1. Comparison of argon isotherms for ZSM-5 samples.

ZSM-5 is about −17 kJ/mol, and it is sited in the sinusoidal channel ring system. The second minor feature (the shoulder) represents 3–4 cumulative argon atoms/uc.

Considering the major features, the first peak in the derivative of the isotherm accounts for 21 argon atoms/uc. The second peak accounts for roughly an additional 9 atoms/uc for a cumulative total of 30 atoms/uc. The data for the Dubinin–Radushkevitch micropore volume (Table 3) are slightly higher than or about equal to the cumulative totals for the second peak. The total sorption, given in the last two columns of the table, shows a correlation with crystal size. Therefore, some of the sorption at higher $P/P_0$ can be attributed to the external surface of the ZSM-5 crystals. This means that the sorption capacity for argon in ZSM-5 at 87 K is around 28 to 30 atoms/uc, since the largest crystal sample has negligible external surface area.

Our calculations indicate that the total energy of the system goes through a minimum

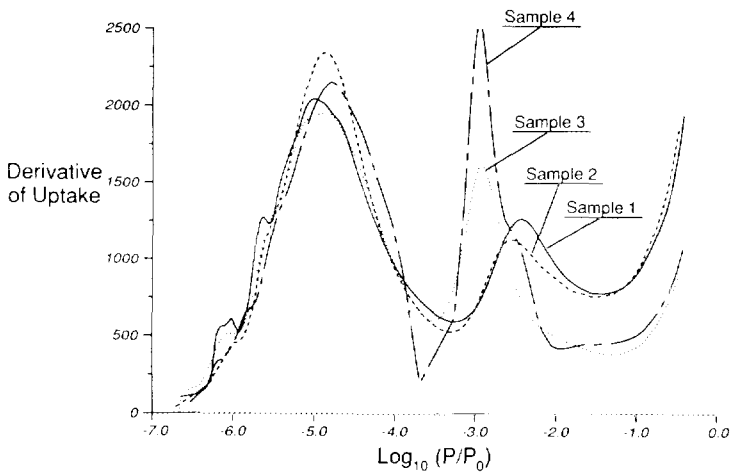


FIG. 2. Comparison of argon isotherm derivatives for ZSM-5 samples.

TABLE 3

Breakdown of Adsorption by the Inflections in the Derivative

| Sample no. | Minor features | | Major features | | D–R[a] |
|---|---|---|---|---|---|
| | 1st | 2nd | 1st | 2nd | |
| | | | As μmol/g | | |
| 1 | 263 | 675 | 3880 | 5384 | 5995 |
| 2 | 195 | 500 | 3639 | 5167 | 5840 |
| 3 | 288 | 782 | 3540 | 5162 | 5273 |
| 4 | 178 | 600 | 3353 | 4906 | 4760 |
| | | | As atoms/uc | | |
| 1 | 1.5 | 3.9 | 21.2 | 31.1 | 34.6 |
| 2 | 1.1 | 2.9 | 21.0 | 29.8 | 33.7 |
| 3 | 1.7 | 4.5 | 20.4 | 29.8 | 30.4 |
| 4 | 1.0 | 3.5 | 19.3 | 28.3 | 27.5 |

[a] Calculated by Dubinin–Radushkevitch method.

near 33 atoms/uc, which indicates the theoretical adsorption capacity for argon in ZSM-5 at 0 K (see Fig. 3). The first 8 atoms/uc go into the sinusoidal channel; the next 8 atoms/uc go into the straight channel. Since the sinusoidal channel ring system is slightly smaller than the straight channel ring system, the former allows for closer argon–zeolite contact and therefore is the site of the deepest energy well (largest heat of adsorption). Argon is small relative to both channels, so repulsion energies in each case are minimal. In fact, two atoms fit comfortably within each double-ring system. However, the calculated adsorption energies for these first 16 atoms/uc are very close. Thus, in the actual measurement (at 87 K), the first 16 sorption sites are probably indistinguishable. Single argon atoms may fill the double 10-rings randomly (8 atoms/uc) and then pair up randomly (8 atoms/uc). For that reason we cannot confidently explain all the minor features (fine structure) of the argon isotherm from our calculations.

The next eight argon atoms fill the channel intersections. Of these, the first four (20 atoms/uc total) have a calculated heat of adsorption which is close to that of the atoms already sorbed in the channel. The additional four atoms/uc (24 atoms/uc total) fill the intersections with little change in incremental energy. After this point in the isotherm, additional sorbed atoms must either increase the packing in the pore space or must sorb onto the sample's external (crystallite) surface. Both of these events involve an energy increment, as seen in Fig. 3 at the 25 atoms/uc point.

The correlation between theoretical calculations and the major features of the argon

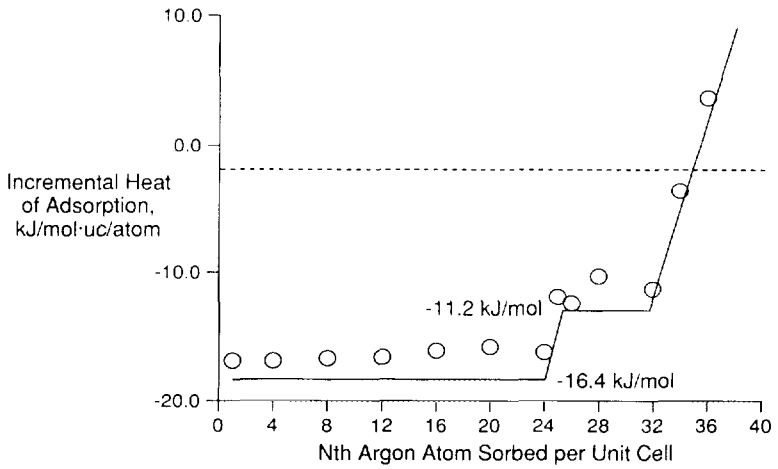


FIG. 3. Calculated sorption energies for argon in ZSM-5.

physisorption isotherm is remarkably good. The first major peak ends at 21 atoms/uc, which compares favorably with our theoretical calculations which indicate a change at 24 atoms/uc. The differences between the theoretical and experimental data can be attributed to thermal effects. That is, a Boltzmann distribution will prevent complete filling of the lower energy states at nonzero temperatures. Further, the empirically determined total sorption of about 28 to 30 atoms/uc is very close to where calculated heats of adsorption predict a second change in the isotherm (33 atoms/uc). Again, thermal arguments can be used to account for the difference.

Although the parameters employed for the theoretical calculations in this study are approximate, the correctness of the trends is verified by comparison with the experimental data. Indeed, by comparison with experiment, the parameters can be refined with an eye toward their application to other systems.

## CONCLUSIONS

There is enough resolution in the physisorption isotherm data that fine structure in its derivative can be discerned. The various features in the isotherm of the ZSM-5/argon system can be related to distinct sorption regimes.

For argon sorbing into ZSM-5 at 87 K, two major features as well as two minor ones can be seen in the derivative. The two minor features are attributed to one and three argon atoms sorbed per unit cell. The first major feature is adsorption into the lowest energy states which are at the double 10-rings plus the initial sorption in the intersections. This accounts for about 75% of the micropore adsorption. The second major feature is the remaining adsorption into the intersections plus a contribution from adsorption on the external surface of the crystals.

Data of this type can be used to characterize unknown materials by identification of prominent features in their physisorption isotherms. Further, these data can be used to refine the atomic interaction parameters used for modelling sorption experiments.

## REFERENCES

1. Borghard, W. S., Sheppard, E. W., and Schoennagel, H. J., *Rev. Sci. Instrum.* **62,** 2801 (1991).
2. Horváth, G., and Kawazoe, K., *J. Chem. Eng. Jpn.* **16,** 470 (1983).
3. Reischman, P. T., Schmitt, K. D., and Olson, D. H., *J. Phys. Chem.* **92,** 5165 (1988).
4. Williams, D. E., *Acta Crystallogr. Sect. A* **28,** 629 (1972).
5. Cox, S. R., Hsu, L., and Williams, D. E., *Acta Crystallogr. Sect. A* **37,** 293 (1981).
6. Williams, D. E., *Acta Crystallogr. Sect. A* **28,** 84 (1972).
7. Olson, D. H., Kokotailo, G. T., Lawton, S. L., and Meier, W. M., *J. Phys. Chem.* **85,** 2238 (1981).