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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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;

Table 1. Cartesian Coordinates (Å) and Bond Angles (°) of $AlPO_4$-5

atom	x	y	z	atom	x	y	z
P	5.358	1.475	0.662	Al	5.459	1.426	3.818
O(1)	4.260	2.578	4.462	O(2)	5.399	1.478	2.121
O(3)	5.004	-0.044	4.479	O(4)	6.732	1.852	0.119

bond	angle	bond	angle
P-O(1)-Al	150.2	P-O(2)-Al	178.1
P-O(3)-Al	148.8	P-O(4)-Al	151.0
O(1)-P-O(2)	108.1	O(1)-Al-O(2)	109.8
O(3)	110.9	O(3)	104.2
O(4)	110.1	O(4)	108.6
O(2)-P-O(3)	107.9	O(2)-Al-O(3)	112.8
O(4)	109.3	O(4)	110.3
O(3)-P-O(4)	110.5	O(3)-Al-O(4)	111.0

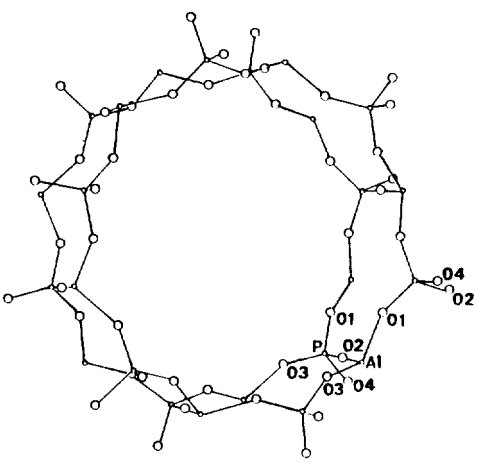

Figure 1. Aluminophosphate-5($AlPO_4$-5) Model($AlPO_4$ basic unit).

$$\delta_P+\delta_{Al}+\delta_{O(1)}+\delta_{O(2)}+\delta_{O(3)}+\delta_{O(4)}=0 \quad (1)$$

$$\begin{aligned} a_P+b_P\delta_P &= a_{O(1)}+b_{O(1)}\delta_{O(1)} \\ &= a_{O(2)}+b_{O(2)}\delta_{O(2)} \\ &= a_{O(3)}+b_{O(3)}\delta_{O(3)} \\ &= a_{O(4)}+b_{O(4)}\delta_{O(4)} \\ &= a_{Al}+b_{Al}\delta_{Al} \end{aligned} \quad (2)$$

where a and b are the inherent electronegativity and the charge coefficient.[8] From equations (1) and (2), the net atomic charges are obtained as follows; $\delta_p = 0.29683$, $\delta_{Al} = 1.23133$, $\delta_{O(1)} = -0.37497$, $\delta_{O(2)} = -0.40466$, $\delta_{O(3)} = -0.37189$, $\delta_{O(4)} = -0.37665$. P atom which is more electronegative than Al atom shows less positive charge. O(2) having the largest s-character has the largest negative charge.

The stabilization energy(V) of the model is expressed as a sum of several terms[7];

$$V=V_{el}+V_{d-r}+V_{ha} \quad (3)$$

Electrostatic energy (V_{el}) is obtained by using the Coulombic formula. The charges of the atoms are considered as point charges. The difficulty in calculating the electrostatic energy in $AlPO_4$-5 is the slow convergency of the electric field along with the c-axis in the lattice sums due to the structure of $AlPO_4$-5.[5,9]

$$V_{el}=\sum_m \sum_{n>m} \delta_m \delta_n / \gamma_{mn} \quad (4)$$

Lennard-Jones 6-12 potential function is used for describing dispersion and repulsion energy (V_{d-r}) which is a nonbonding interaction of O-O atomic pairs.

$$V_{d-r}=4\varepsilon_{ij}[(\sigma_{ij}/\gamma_{ij})^{12}-(\sigma_{ij}/\gamma_{ij})^{6}] \quad (5)$$

Harmonic energy (V_{ha}) is obtained by using the harmonic function for P(Al)-O bonds.

$$V_{ha}=\frac{1}{2}\sum_i \sum_{j>i}' k_{ij}(\gamma_{ij}-\gamma_{ij}^0)^2 \quad (6)$$

ε_{ij} and σ_{ij} in V_{d-r} term and k_{ij} and r_{ij}^0 in V_{ha} term are potential parameters. They are refined by the constraint method. Since the energy of each atom in a crystal must correspond to a minimum in potential energy surface, the potential parameters are obtained by the minimization of the following function;

$$\sum_{l=1}^{k} \sum_{i=1}^{N} \sum_{j=1}^{3} \frac{\partial}{\partial a_l} \frac{\partial V^0}{\partial q_j^{0i}}=f, \quad j=1,\ 2,\ 3 \quad (7)$$

where

$$\begin{aligned} V &= V(a_1, a_2, \cdots, a_n, q_1^1, q_2^1, q_3^1, \cdots, q_3^N) \\ V^0 &= V(a_1, a_2, \cdots, a_n, q_1^{01}, q_2^{01}, q_3^{01}, \cdots, q_3^{0N}) \end{aligned} \quad (8)$$

where a_l is ith potential parameter, q_j^i and q_j^{0i} represent the jth coordinate of 1th atom and that of the equilibrium structure, respectively. V and V^0 are the stabilization energies at (q_1^1, q_2^1, q_3^1, ..., q_3^N) and (q_1^{01}, q_2^{01}, q_3^{01},..., q_3^{0N}), respectively.

The net force at ith coordinate of nth atom is expressed as,

$$\vec{F}_i^n = -(\partial V/\partial \vec{q}_i^n)q_1^1, q_2^1, q_3^1, \cdots, q_3^N \quad n=1,\ 2,\ 3, \cdots,\ N \quad i=1,\ 2,\ 3 \quad (9)$$

and the force constant is expressed as equation (10).

$$k_{ij}^{m,n}=(\partial^2 V/\partial q_i^m \partial q_j^n)q_1^1, q_2^1, q_3^1, \cdots, q_3^N \quad (10)$$

Table 2. The Refined Potential Parameters and the Standard Deviation of Force

Bond	r^0 (Å)	k (mdyne/Å)
P-O(1)	1.38166	6.40138
O(2)	1.40230	6.40138
O(3)	1.38064	5.89590
O(4)	1.43884	6.15465
Al-O(1)	1.81565	3.33132
O(2)	1.83715	3.42166
O(3)	1.73291	3.52152
O(4)	1.74903	3.70359

$\varepsilon_{O-O} = 0.21429$ (kcal/mole) $\sigma_{O-O} = 2.97438$ (Å)
$\sigma^2_{force} = 0.00258$ (mdyne^2).

Results and Discussion

The refined potential parameters and the standard deviation of force, $\sigma^2_{force} = F_i^2/N$, are listed in Table 2.

In Table 3, the net force of each atom at X-ray position is listed. Although the net force on each atom is still remained,

Table 3. The Net Forces of the Atoms in $AlPO_4$-5 Calculated at the X-ray Positions (mdyne)

atom	F_x	F_y	F_z
P	-0.04937	-0.04709	-0.08953
Al	0.07407	0.08233	-0.09832
O(1)	0.07565	-0.00428	-0.05233
O(2)	0.03091	0.00294	-0.08455
O(3)	-0.02532	0.07046	-0.08106
O(4)	-0.07131	-0.00892	0.02496

Table 4. The Stabilization Energy (E) of the Atoms in $AlPO_4$-5 at the X-ray Positions (kcal / mole)

atom	P	Al	O(1)	O(2)	O(3)	O(4)
-E	29.74	300.51	33.25	60.54	38.42	71.02

The Stabilization Energy (E) of the Atoms in Zeolite A at the X-ray Positions (kcal / mole).

atom	Al	Si	O(1)	O(2)	O(3)
-E	277.34	82.42	25.91	31.68	30.68

Table 5. The Cartesian Coordinate Force Constants of Each atom in $AlPO_4$-5 at the X-ray Positions (mdyne / Å)

atom	k_x	k_y	k_z
P	10.37432	10.65269	10.48700
Al	6.14369	6.65992	5.83486
O(1)	2.51822	8.64479	1.76152
O(2)	0.45421	0.46048	12.14936
O(3)	1.38553	11.65783	2.11389
O(4)	10.14540	1.06594	1.87959

the minimum energy points in potential energy surface are well agreed with the crystal structure. Because of the use of uncalcinated X-ray data,[5] the net force on each atom is not good compared with that of zeolite A.[10] Because the electric field is slowly converged along with the z-axis, the net forces along with the z-axis are fairly large scale.

The stabilization energies of each atom at X-ray position in $AlPO_4$-5 and those of zeolite A[10] are listed in Table 4. Although the structure of $AlPO_4$-5 is different from that of zeolite A, their relative stability is very interesting. In aluminophosphate molecular sieves, it is said that the silicon atoms in aluminosilicate molecular sieves are replaced by the phosphorus atoms and no extra-framework cations. The phosphorus atom in $AlPO_4$-5 framework is less stable than the silicon atom in zeolite A. The phosphorus atom could be partially replaced by the silicon atom, which is already synthesized named silicoaluminophosphate-n (SAPO-n),[11,12] to be a stable molecular sieves. On the other hand, all four kinds of oxygen atoms in $AlPO_4$-5 framework are more stable than those of zeolite A which has three kinds of oxygen atoms. This is consistent with the X-ray data of T_1-O-T_2 bond angles. The angles of P-O-Al bonds in $AlPO_4$-5 framework which are listed in Table 1 are more linear than those of Si-O-Al bonds[13] in zeolite A. The aluminum atom in $AlPO_4$-5 structure is also more stable than that in zeolite A. In Table 5, the second derivatives of the stabilization energy with respect to the cartesian coordinates of each atom are listed.

The parameters obtained in this work can be used to study SAPO-5 molecular sieves in which the phosphorus atoms of $AlPO_4$-5 framework are partially substituted by the silicon atoms. And these parameters are also can be used to study the polar diffusion or adsorption properties.

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