6. Gaylord, N. G. *Reduction with Complex Metal Hydride*; Interscience publisher Inc.: New York 1956.
7. Nystron, R. F.; Brown, W. G. *J. Am. Chem. Soc.* **1947**, *69*, 1197.
8. Chaikin, S. W.; Brown, W. G. *J. Am. Chem. Soc.* **1949**, *71*, 122.
9. Yoon, M. N.; Cha, J. S. *J. Korean Chem. Soc.* **1977**, *21*, 108.
10. Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765.
11. Zweifel, G.; Brown, H. C. *Org. Reactions* **1963**, *13*, 1.
12. Brown, H. C; Cha, J. S.; Nazer, B.; Kim, S. C.; Krishnamurthy, S.; Brown, C. A. *J. Org. Chem.* **1984**, *49*, 885.
13. Brown, H. C.; Kim, S. C.; Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 1.
14. Banus, M. D.; Bragdon, R. W.; Hinckley, A. A. *J. Am. Chem. Soc.* **1954**, *76*, 3848.
15. Brown, H. C.; Krishnamurthy, S. *Tetrahedron* **1979**, *35*, 567.
16. Kim, S.; Moon, Y. C.; Ahn, K. H. *J. Org. Chem.* **1982**, *87*, 5614.
17. Borch, R. F.; Durst, H. D. *J. Am. Chem. Soc.* **1969**, *91*, 3996.
18. Zakharkin, L. I.; Gavrilenko, V. V.; Maslin, D. N.; Khorlina, I. M. *Tetrahedron Lett.* **1963**, 2087.
19. Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.
20. Yoon, N. M.; Gyoung, Y. S. *J. Org. Chem.* **1985**, *50*, 2443.
21. Brown, H. C.; Heim, P.; Yoon, N. M. *J. Am. Chem. Soc.* **1970**, *92*, 1637.
22. Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464.
23. Brown, H. C.; Murray, K. J.; Murray, L. J.; Snover, J. A.; Zweifel, G. *J. Am. Chem. Soc.* **1760**, *82*, 4233.
24. Ashby, E. *J. Am. Chem. Soc.* **1959**, *81*, 4791.
25. Burg, A. B.; Schlesinger, H. I. *J. Am. Chem. Soc.* **1966**, *55*, 420.
26. Brown, H. C.; Heim, P.; Yoon, N. M. *J. Am. Chem. Soc.* **1977**, *92*, 1639.
27. Marlett, E. M.; Park, W. S. *J. Org. Chem.* **1990**, *55*, 2968
28. Cha, J. S.; Brown, H. C. *J. Org. Chem.* **1993**, *52*, 5564
29. Shirk, A. E.; Shriver, D. F. *Inorganic Synthesis* **1977**, *17*, 48.
30. Choi, J. H.; Chung, D. W. *Bull. Korean Chem. Soc.* **1995**, *16*, 419.
31. Greenwood, N. N.; Storr, A.; Wallbridge, M. G. H. *Inorganic Chemistry* **1963**, *2*, 1036.
32. Shriver, D. F.; Parry, R. W. *Inorganic Chemistry* **1963**, *2*, 1039.

Activation Energy for the Decapsulation of Small Molecules from A-Type Zeolites

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Received May 20, 1996

Potential energy function sets for some ion-exchanged A-type zeolites, K-A and $Rb_{11}Na_1$-A, were determined by introducing the X-ray crystal structures as constraints. The potential functions reproduced well the X-ray crystal structures of the monovalent ion-exchanged zeolites. The activation energies for the en- or decapsulation of small molecules (H_2, O_2, N_2, and CH_4) and inert gases from the α-cage of model zeolites (Na-A, K-A, $Rb_{11}Na_1$-A, and Cs_3Na_9-A) were obtained by the molecular mechanical calculations. The calculated activation energies agreed well with experimental results.

Introduction

Zeolites are well known for their industrial applications as catalysts, adsorbents, and molecular sieves. One of the practical applications of zeolites is to use those as a storage vessel for small gas molecules.[1-11] A small molecule whose kinetic diameter is a little larger than the opened window of a zeolite can be encapsulated by being compelled into the

pores at high pressure and elevated temperature and then by cooling the system to room temperature and by depressurizing. This kind of phenomena, zeolitic encapsulation, was reported by Sesny and Shaffer.[8] They found that K-A zeolites can efficiently trap large amounts of small nonpolar molecules. Fraenkel *et al.*[4] showed experimentally that the diffusion parameters depend on both of the radius of alkali cation, M, which blocks the eight-ring window and the kinetic diameter of the encapsulated molecule.

Dehydrated A type zeolite ($M_xNa_{12-x}Si_{12}Al_{12}O_{48}$) has one large cavity, α-cage, per pseudo unit cell. This α-cage is

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roughly spherical with the diameter of 11.4 Å, and is sur-rounded by six eight-membered oxygen rings which lie on the surfaces of the pseudo-unit cell cube. Each eight-ring roles as a window to its neighboring α-cage. Therefore, for the capsulation of gas molecules to the α-cages, the win-dows must be blocked with monovalent cations of moderate size. The ions locate on the eight-ring window planes can be easily displaced to make a path for the en- or de-capsulation of the molecules, α- to α-cage transmission. The activation energy, E_a, for the decapsulation of the molecule from the α-cage corresponds to the energy dif-ference between the minimum and the maximum on the min-imum energy transmission path (METP). The E_a strongly de-pends on the physical properties of both the blocking cation and the capsulated molecule.[5]

Recently, several computational methods have been in-troduced for the investigation of the properties of zeolites. Molecular Mechanics,[12-17] Monte Carlo simulation,[18-24] Molecular Dynamics simulation,[25-39] and Molecular Orbital calculation[40-44] are such.

No *et al.*[5,45] developed the potential energy function (PEF) sets which are suitable for the description of the structural stability and the dynamical properties of Na-A and Cs,Na-A zeolites. Those PEFs can be used for the investigation of the zeolitic encapsulation phenomena. In this work, the PEFs of some monovalent cation exchanged A-type zeolites which are the candidates for capsulation vessels will be de-veloped. Those will be determined by using the X-ray cry-stal structures of some M_xNa_{12-x}-A type zeolites as con-straints. The metal ion, M can be Na, K, Rb, Cs, or their bi-nary combinations. With the developed PEF sets, the min-imum energy paths (MEP) for the α- to α-cage transmis-sion (METP) of some small gas molecules (H_2, O_2, N_2, CH_4, Ne, Ar, Kr, and Xe) over the four zeolites will be in-vestigated.

Computations

Determination of the PEF. In our previous works,[5,45] the PEFs of some A-type zeolites were determined by in-troducing the X-ray crystal structures as constraints. In this work, for simplicity, the $(M_xNa_{12-x}T_{24}O_{48})_n$ model was used instead of the $(M_xNa_{12-x}Si_{12}Al_{12}O_{48})_n$ framework. The struc-tural informations of model zeolites, $(K_{12}T_{24}O_{48})_n$ and $(Rb_{11}Na_1T_{24}O_{48})_n$, were taken from X-ray diffraction results.[46-49] It was assumed that the unit cells of all the model zeolites have Pm3m space group symmetry. Chemically equivalent ion binding sites are designated by same index number of m, M(m). For each model zeolite, the positions and oc-cupancy factors of the atoms which are located at chem-ically nonequivalent sites are summarized in Table 1 for $(K_{12}T_{24}O_{48})_n$, and in Table 2 for $(Rb_{11}Na_1T_{24}O_{48})_n$. The struc-tures of $(Na_{12}T_{24}O_{48})_n$ and $(Cs_3Na_9T_{24}O_{48})_n$ were taken from our previous works.[5,45]

The atomic positions which are chemically nonequivalent each other can be used as the constraints for the de-termination of the parameters of the PEFs. These atoms are T(Si,Al), O(1), O(2), O(3), M(1), M(2), M(3), M(4), M(5), and some of the Na ions in $(M_xNa_{12-x}T_{24}O_{48})_n$ zeolites. Since each atom has three degrees of freedom, the number of po-tential parameters must be less than 3N; N is the number of

the chemically non-equivalent atoms. However, some of the atoms are located on the symmetric potential energy surface, the number of independent informations is reduced to around 20.

The potential energy, the stabilization energy of the zeol-ite framework, can be described as a function of both the atomic positions, q's, and the potential parameters, αs.

$$V = V(\alpha_1, \alpha_2, ..., \alpha_n, q_1^o, q_2^o, ..., q_{3N}^o) \quad (1)$$

Since the atoms in a crystal are located at the minimum en-ergy positions, $(q_1^o, q_2^o, q_3^o,...,q_3N^o)$, on the potential energy surface of the crystal, the potential energy at the crystal geometry, V^o, can be described as a function of the po-tential parameters only,

$$V(\alpha_1, \alpha_2, ..., \alpha_n, q_1^o, q_2^o, ..., q_{3N}^o) = V^o(\alpha_1, \alpha_2, ..., \alpha_n) \quad (2)$$

Since the net force on each atom must be zero to satisfy the equilibrium conditions of the crystal, the potential paramet-ers, αs, were determined so that the following function f could reach to minimum.

$$f = \sum_{i=1}^{n} \sum_{l=1}^{3N} \left| \frac{\partial}{\partial \alpha_i} \left(\frac{\partial V''}{\partial q_l} \right) \right| \quad (3)$$

The total energy of a system, the stabilization energy, was described as a sum of atom-atom pair interactions. The stabilization energy of the model, V, was expressed as the sum of several terms as follows:

$$V = V_{el} + V_{pol} + V_{d-r} + V_{bond} \quad (4)$$

where V_{el}, V_{pol}, V_{dr}, and V_{bond} represent electrostatic, po-larization, dispersion-repulsion, and bond stretching po-tential energy. Instead of O-T-O bending potential function, 6-12 type function of 1-3 positioned O-O was used. Details of the PEFs are described well in our previous work.[45]

The electrostatic interaction energy was calculated from the following equation.

$$V_{el} = \sum_{m} \sum_{n>m} \delta_m \delta_n / r_{mn} \quad (5)$$

where δ_m and δ_n are the net atomic charges of mth and nth atom, respectively, and r_{mn} represents the distance between the mth and nth atom. The net atomic charge on each atom, δ_i was calculated by using Sanderson's electronegativity equalization conditions[50] with Huheey's atomic elec-tronegativity sets, $\{a_i, b_i\}$.[51] It was assumed that the elec-tronegativity of the cation does not equalized with those of the framework atoms whereas the framework atoms have same electronegativity. The average net atomic charge of the Na, δ_{Na}, in A-type zeolite was determined as +0.625 e by No *et al.*[5,45]

$$\sum_{i \neq Na} \delta_i = -\delta_{Na} \quad (6)$$

$$a_i + b_i \delta_i = a_j + b_j \delta_j \quad (7)$$

If the Madelung sum of the electrostatic potential energy is made for all the *atoms* within cube $(R \times R \times R)$, the elec-trostatic potential is very sensitive to the value of the R and fluctuates as a function of the R. To overcome the slow con-

vergence and the fluctuation, the summation was carried out for all the (NaT$_2$O$_4$) *units* instead of all the *atoms* within the cube and fast convergence was obtained. In this calculation, R was used as $7a$. a is the length of the pseudo-unit cell of A zeolite. Details of the electrostatic potential summation method is described in our previous work.[45]

The polarization energy was calculated as

$$V_{pol} = -\frac{1}{2} \sum_{n}^{x,y,z} \sum_{j} \alpha_n [(\sum_{m \neq n} \varepsilon_{jm})^2] \qquad (8)$$

where α_n is the atomic polarizability of nth atom and ε_{jm} is the j-directional electric field at nth atomic position due to mth atom.

Lennard-Jones (6-12) type potential function was used to describe the interactions of 1-3 positioned intraframework oxygen-oxygen, of the framework oxygen-cation, and of the framework oxygen-encapsulated molecule pairs.

$$V_{d-r} = 4\varepsilon_{ij} [(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^6] \qquad (9)$$

where ε_{ij} and σ_{ij} are the L-J potential parameters and r_{ij} is the interatomic distance of atomic pair i-j.

For T-O covalent bonds, harmonic type potential function was used as follows:

$$V_{bond} = \frac{1}{2} \sum_{i} \sum_{j>i} k_{ij} (r_{ij} - r_{ij}^o)^2 \qquad (10)$$

where k_{ij} and r_{ij}^o are harmonic function parameters.

The potential function parameters to be determined are the σ_{O-O}, σ_{O-M}, ε_{O-O}, and ε_{O-M} in V_{d-r} and the $k_{T-O(1)}$, $k_{T-O(2)}$, $k_{T-O(3)}$, $r^o_{T-O(1)}$, $r^o_{T-O(2)}$, and $r^o_{T-O(3)}$ in V_{bond}.

Crystal Data used as the Constraints for the PEF Determination. In the distribution of ions among the binding sites of each model zeolite, the configuration which has minimum electrostatic ion-ion repulsion was taken. One pseudo-unit cell of A type zeolite can be represented by one α-cage and one β-cage. The binding sites in the α-cage are three eight-ring windows, eight six-rings, and twelve four-rings. The β-cage can hold only one ion though the β-cage has eight equivalent binding sites. The four-ring bonding sites are energetically unfavorable compared with the other binding sites, especially for large cations. If both sides of one six-ring are occupied by two ions, one from the α-cage and the other from the β-cage, the binding energies of the these two ions decrease. Consequently, there are only eleven stable binding sites are available per pseudo-unit cell whereas twelve monovalent cations must be accommodated. In order to minimize the influence of the twelfth cation, it was placed at the potentially equipoint of the framework, the center of the β-cage. In Table 1 and 2, the location of the cations and the atomic coordinates of each model which were used as the constraints for the PEF parameters determination are summarized.

Determination of the Crystal Structure of the Model Zeolites. The crystal structures of the model zeolites were determined from molecular mechanical calculations utilizing the equilibrium conditions of the crystal. In the potential energy surfaces, the net atomic forces of all the atoms in the crystal must be zero.

$$F_i^k = -(\partial V / \partial q_i^k) = 0 \quad \text{for all } k \text{ and } i \qquad (11)$$

where F_i^k represents the net atomic force in k-direction of

ith atom. In the calculation, the forces were calculated in the cartesian coordinate system. Details of the calculation were described in elsewhere of our previous works.[5,45]

Minimum Energy Path Calculation for the α- to α-cage Transmission of the Encapsulated Molecule.

The activation energy of the zeolitic de/encapsulation strongly depends on the size of the molecule and the cation and their interaction energy with the framework. Especially the cation bound to the eight-ring window plays dominant role. In this work, the de/encapsulation process was assumed a pure single jump of a molecule from one α-cage to its neighbor or to the outward of the zeolite. Based on this assumption, the E_a for the de/encapsulation of the molecule in the α-cage can be approximated to the transmission energy of a molecule from one α-cage to its neighbor α-cage.

Figure 1 shows the internal coordinate system which was used for the MEPs calculation of the transmission of the molecules. Diatomic molecule was assumed rigid and allowed five degrees of freedom: three for the center of mass coordinate (r, θ, ϕ) and two angles for describing the relative orientation of the molecule (θ_r, ϕ_r). For the inert gases, they were allowed three degrees of freedom for the position. All the cations have three degrees of freedom. The framework of the zeolite was assumed rigid. The MEPs were obtained from molecular mechanical calculations. The minimum energy conformations were obtained along the y-coordinate in Figure 1. The y was increased by Δy step by step from the center of the α-cage. At each step, while y (y component of the $\vec{r}$) was fixed, the minimum energy conformation was obtained. This procedure was repeated until the molecule pass through the eight-ring window.

Results and Discussion

The potential parameter sets for the model zeolites, Na-A, K-A, Rb$_{11}$Na$_1$-A, and Cs$_3$Na$_9$-A, are summarized in Table 3.
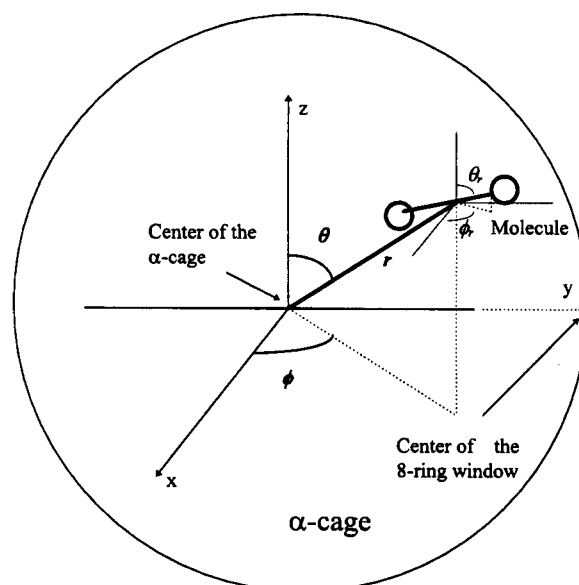

Figure 1. The internal coordinates which are necessary to describe the position of encapsulated atom, (r, θ, ϕ), and of encapsulated diatomic molecule, (r, θ, ϕ, θ_r, ϕ_r).

Table 1. Positional parameters and occupancy factors of the dehydrated K-A model zeolite were taken from X-ray structure[47] and obtained by the molecular mechanical calculation (in parentheses)

Atom	Wycoff position	x	y	z	Occupancy factor
T(Si,Al)	24(k)	0.3774(0.3773)	0.	0.1886(0.1887)	1
O(1)	12(h)	0.5	0.	0.2457(0.2458)	1
O(2)	12(i)	0.2833(0.2834)	0.	0.2833(0.2834)	1
O(3)	24(m)	0.3597(0.3598)	0.1111(0.1111)	0.1111(0.1111)	1
K(1)	8(g)	0.2311(0.2311)	0.2311(0.2311)	0.2311(0.2311)	3/4
K(2)	12(i)	0.4770(0.4779)	0.	0.4770(0.4779)	1/4
K(3)	8(g)	0.3557(0.3557)	0.3557(0.3557)	0.3557(0.3557)	1/8
K(4)	8(g)	0.1306(0.1306)	0.1306(0.1306)	0.1306(0.1306)	1/8
K(5)	8(g)	0.1849(0.1847)	0.1849(0.1847)	0.1849(0.1847)	1/8

Space group is Pm3m and cubic cell parameter, a, is 12.3092 Å. The sum of net atomic forces, $\sum_i |F_i|$, was 6.24×10^{-4} mdyne at the minimum energy crystal structure and the cell parameter was obtained as 12.3091 Å.

Table 2. Positional parameters and occupancy factors of the dehydrated $Rb_{11}Na_1$-A model zeolite were taken from X-ray structure[48] and obtained by the molecular mechanical calculation (in parentheses)

Atom	Wycoff position	x	y	z	Occupancy factor
T(Si,Al)	24(k)	0.3753(0.3790)	0.	0.1852(0.1890)	1
O(1)	12(h)	0.5	0.	0.2405(0.2529)	1
O(2)	12(i)	0.2871(0.2529)	0.	0.2871(0.2899)	1
O(3)	24(m)	0.3530(0.3561)	0.1122(0.1057)	0.1122(0.1057)	1
Rb(1)	8(g)	0.2514(0.2299)	0.2514(0.2299)	0.2514(0.2299)	5/8
Rb(2)	3(c)	0.5000(0.4954)	0.	0.5000(0.4954)	1
Rb(3)	8(g)	0.3929(0.3801)	0.3929(0.3801)	0.3929(0.3801)	1/8
Rb(4)	8(g)	0.1125(0.1352)	0.1125(0.1352)	0.1125(0.1352)	1/8
Rb(5)	8(g)	0.1456(0.1454)	0.1456(0.1454)	0.1456(0.1454)	1/8
Na(1)	8(g)	0.1904(0.1898)	0.1904(0.1898)	0.1904(0.1898)	1/8

Space group is Pm3m and cubic cell parameter, a, is 12.2610 Å. The sum of net atomic forces, $\sum_i |F_i|$, was 4.48×10^{-4} mdyne at the minium energy crystal structure and the cell parameter was obtained as 12.2650 Å.

The nonbonding potential parameters for the interaction between the zeolite and the encapsulated molecules are also listed. The L-J potential parameters for the interaction between the ions and the atoms in the encapsulated molecules were taken from mean values, geometric means for the ε's and arithmetic means for the σ's. During the optimization of the potential parameter sets, it was assumed that the net atomic charges of the cations does not change and have the same value, $\delta_M = +0.625e$, because the electronegativity of the alkali cations are not much different. For Na-A and Cs_3Na_9-A zeolites, the PEFs were taken from our previous works[5,45] in which the net atomic charges of Na and Cs were fixed to +0.625e. In the works, when the cationic charge was equal to +0.625e, both experimental spectroscopic and structural properties of the model zeolites were well reproduced. For this reason, for K-A and $Rb_{11}Na_1$-A models, the PEF parameter sets were determined with the same cationic charge.

The minimum energy crystal structures of the model zeolites were determined from molecular mechanical calculations. The total net atomic forces, F_i's, described by the equation 11 were used as the criteria of the equilibrium structure of the model crystal. In Table 1 and 2, the geometrical parameters of each atom at the minimum energy crystal structure are summarized. The geometrical parameters of Na-A and Cs_3Na_9-A model zeolites are taken

Table 3. The calculated PEF parameter sets of model zeolites and the used potential parameters for the encapsulated molecules

Parameter	Na-A[a]	K-A	Rb, Na-A	Cs, Na-A[a]	Encapsulated Gas (M)	
$r^o_{T-O(1)}$	1.691	1.675	1.741	1.691	σ_{H_2}	2.138
$k_{T-O(1)}$	4.125	4.125	4.125	4.125	ε_{H_2}	0.066
$r^o_{T-O(2)}$	1.631	1.647	1.674	1.695	σ_{O_2}	2.673
$k_{T-O(2)}$	4.300	4.300	4.300	4.300	3_{O_2}	0.225
$r^o_{T-O(3)}$	1.685	1.700	1.697	1.680	σ_{N_2}	2.762
$k_{T-O(3)}$	4.035	4.035	4.035	4.035	ε_{N_2}	0.182
σ_{O-O}	2.702	2.655	2.947	2.913	σ_{CH_4}	3.796
σ_{Na-Na}	2.484		2.500	2.501	ε_{CH_4}	0.286
σ_{K-K}		2.900			σ_{Ne}	2.789
σ_{Rb-Rb}			2.904		ε_{Ne}	0.017
σ_{Cs-Cs}				3.251	σ_{Ar}	3.418
ε_{O-O}	0.230	0.230	0.230	0.230	ε_{Ar}	0.246
ε_{Na-Na}	0.242		0.242	0.242	σ_{Kr}	3.610
ε_{K-K}		0.242			ε_{Kr}	0.378
ε_{Rb-Rb}			0.2746		σ_{Xe}	4.055
ε_{Cs-Cs}				0.323	ε_{Xe}	0.455

[a] taken from reference 5 and 45. r^o and σ in Å, ε in kcal/mol, and k in mdyne/Å. In the calculation of σ_{ij} and ε_{ij}, arithmetic and geometric means were used, respectively.

from our previous works.[5,45] The sum of net atomic forces,

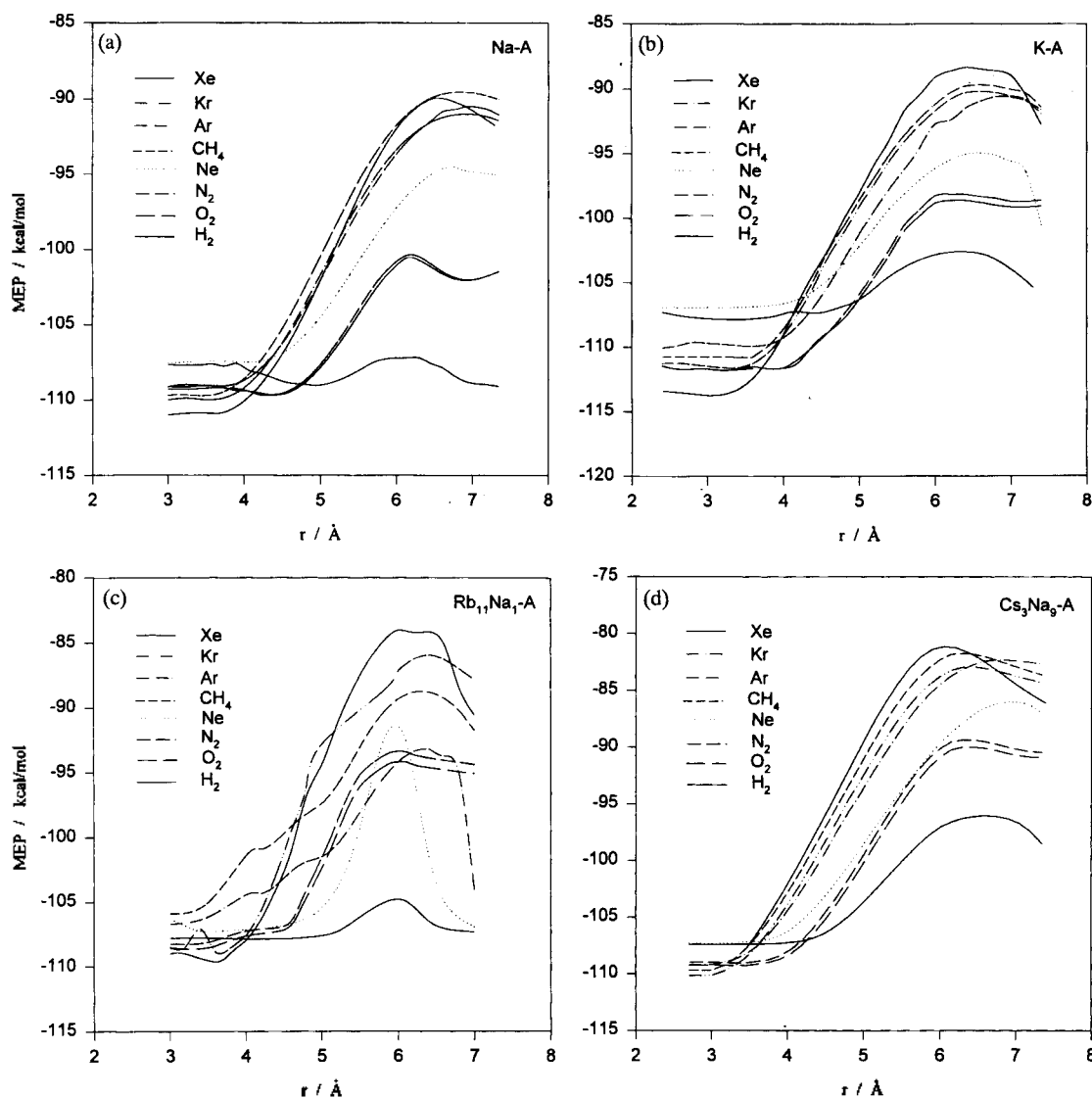**Figure 2.** The decapsulation MEPs of some molecules, H_2, O_2, N_2, CH_4, Ne, Ar, Kr, and Xe, from the α-cage of a) Na-A, b) K-A, c) $Rb_{11}Na_1$-A, and d) Cs_3Na_9-A model zeolite were plotted along the y-axis in Figure 1.

ΣF_i^k, of K-A and $Rb_{11}Na_1$-A models at their minimum energy conformation were obtained as 6.24×10^{-4} and 4.48×10^{-4} mdyne, respectively. Those of Na-A and Cs_3Na_9-A were obtained as 1.57×10^{-5} and 2.93×10^{-5} mdyne,[5,45] respectively. These values are smaller than those of K-A and $Rb_{11}Na_1$-A model because Na-A and Cs_3Na_9-A have higher symmetry compared with K-A and $Rb_{11}Na_1$-A. The optimized minimum energy structure of K-A is almost coincident with X-ray crystal structure whereas that of $Rb_{11}Na_1$-A shows some deviation from X-ray crystal structure.

The MEPs of zeolitic en/decapsulation of some small molecules for each model were calculated with the determined PEFs. The MEPs of the molecules are plotted along the distance from the x-z plane to the molecule in Figure 2. Molecules are usually accommodated within the α-cage not within the β-cage. The activation energy can be calculated with the experimental diffusion data.[3-6,36] In our calculation, the activation energy was confined to the α- to α-cage jump and it corresponded to the energy difference between the minimum binding energy and the maximum on

the MEPs of the α- to α-cage transmission.

The MEPs of the transmission occurred in each model zeolite are plotted in Figure 2a-d. From the observation of the MEP and the position of the molecule along the MEP, it can be concluded that the molecule in the α-cage move around the inner wall surface sites which are energetically favorable. The maximum energy barriers of the MEPs of all kinds of the molecules in this work are located near the eight-ring window plane. During the transmission of the molecule, the cation which blocks the eight-ring window moves out the window surface when the molecule push the cation and it moves back to the eight-ring window plane in order to reduce the repulsion between the cations once the molecule passes the window.

The calculated E_as are summarized in Table 4. For Na-A zeolite, hydrogen has the small E_a, 1.85 kcal/mol. So the hydrogen encapsulated by Na-A zeolite may release out spontaneously at room temperature. The E_as of the H_2 encapsulated in K-A and $Rb_{11}Na_1$-A are 5.0 and 3.0 kcal/mol, respectively. Those E_as are not large enough to store H_2 at

Table 4. The activation energy for the en/decapsulation of small molecules to/from the A-type model zeolites (in kcal/mol)

Molecule	Na-A	K-A	$Rb_{11}Na_1$-A	Cs_3Na_9-A
H_2	1.85	5.0	3.0	11.38(14-20)
O_2	9.18	13.0	15.0	19.27(17-25)
N_2	9.31(6.0)	14.0(15-21)	16.2	19.71(18-22)
CH_4	14.71(7-12)	18.07	19.4	22.75(17-21)
Ne	13.03	13.40	14.1	21.32(18.4)
Ar	17.01	19.0(38-45)	23.0	26.92(22-25)
Kr	18.62	21.0	24.1	27.24
Xe	21.00	25.6	29.0	30.23

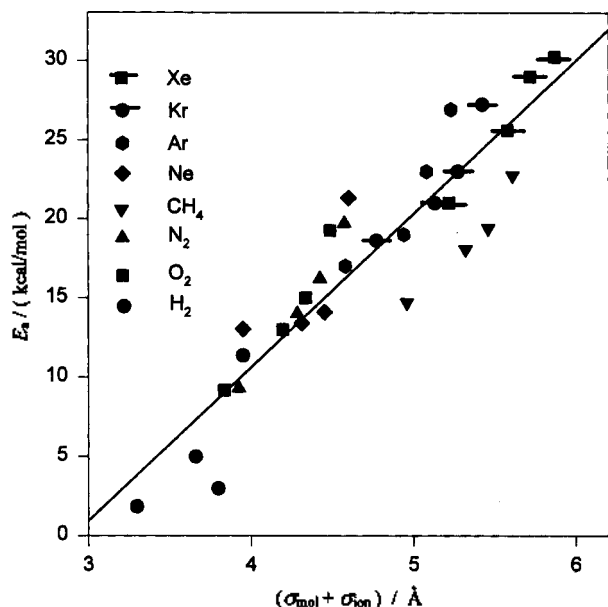The experimental data in parentheses were taken from the references 3, 4, 6, and 26.

Figure 3. The activation energies, E_a, were plotted against the sum of the kinetic diameters of the encapsulated molecule and of the blocking cation, $(\sigma_{mol}+\sigma_{ion})$.

room temperature. Whereas, the H_2 in Cs_3Na_9-A zeolite needs more than 11.38 kcal/mol to escape from the α-cage. The H_2 molecule seldom have kinetic energy larger than 11.38 kcal/mol. Therefore Cs_3Na_9-A zeolite is suitable material for the storage of hydrogen molecule. Experimentally, it was obtained between 14 and 20 kcal/mol.[4]

O_2 and N_2 can be effectively encapsulated by K-A zeolite. E_a of O_2 and N_2, E_a^{O2} and E_a^{N2}, are comparable both in Na-A and in Cs_3Na_9-A zeolite. For K-A and $Rb_{11}Na_1$-A, E_a^{N2} is larger than E_a^{O2} about 1 kcal/mol.

E_as of O_2, N_2, CH_4, Ar, Kr, and Xe increase monotonously as the size of the eight-ring blocking cation increases. E_a^{H2} of K-A is 2 kcal/mol larger than that of $Rb_{11}Na_1$-A. For Ne, E_a^{Ne} increases small amount, less than 1 kcal/mol, as the blocking ion changed from Na to Rb. However it increases much, about 7 kcal/mol, if the blocking is changed to Cs. The tendency of the E_a^{H2} and the E_a^{Ne} suggest that if the sum of σ_{mol} and σ_{ion} is less than some critical value, E_a does not much influenced by the size of the blocking ions. In Figure 3, the Eas are plotted against the sum of the kinetic diameters of the encapsulated molecule

and of the blocking cation, $(\sigma_{mol}+\sigma_{ion})$. E_a shows a relatively correlation with the $(\sigma_{mol}+\sigma_{ion})$.

The PEFs for the model zeolites were determined. Those PEFs were used for the estimation of the E_as of the encapsulated molecules for the model zeolites. The calculated E_as reasonably agreed with experimental results. The force field developed in this work can be used for the crystal structures calculation of A-type zeolites and for the simulation of the dynamic properties of the zeolite with encapsulated molecules.

References

1. Cook, G. A. *Argon, Helium, and the Rare Gases*; Interscience: New York, 1961; Vol. 1, p 228.
2. (a) Barrer, R. M. *Zeolites and Clay Minerals as Sorbents and Molecular Sieves*; Academic: New York, 1978. (b) Barrer, R. M.; Vaughan, D. E. W. *Trans. Faraday Soc.* **1967**, *63*, 2275. (c) Barrer, R. M.; Vaughan, D. E. W. *Trans. Faraday Soc.* **1971**, *67*, 2129.
3. Chan, Y. C.; Anderson, R. B. *J. Catal.* **1977**, *50*, 319.
4. (a) Fraenkel, D.; Shabtai, J. *J. Am. Chem. Soc.* **1977**, *99*, 7074. (b) Fraenkel, D.; Shabtai, J. *Alternative Energy Sources* **1987**, *8*, 3771. (c) Fraenkel, D. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2029. (d) Fraenkel, D. *J. Chem. Soc., Faraday Trans. 1* **1981**, *77*, 2041. (e) Fraenkel, D. *CHEMTECH* **1981**, *11*, 60. (f) Fraenkel, D.; Ittah, B.; Levy, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1389. (g) Fraenkel, D.; Levy, A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1817. (h) Fraenkel, D.; Levy, A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 1835.
5. (a) No, K. T.; Kim, J. S.; Jhon, M. S. *Theor. Chim. Acta* **1989**, *75*, 461. (b) Kim, J. S.; Jeong, Y. H.; Park, S. H.; Ahn, B. J.; No, K. T. *J. Phys. Chem.* **1996**, *100*, 7586.
6. (a) Yucel, H.; Ruthven, D. M. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 60. (b) Yucel, H.; Ruthven, D. M. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 71.
7. (a) Yoon, J. H.; Heo, N. H. *J. Phys. Chem.* **1992**, *96*, 4997. (b) Yoon, J. H. *J. Phys. Chem.* **1993**, *97*, 6066. (c) Heo, N. H.; Cho, K. H.; Kim, J. T.; Seff, K. *J. Phys. Chem.* **1994**, *98*, 13328.
8. Sesny, W. J.; Shaffer, L. H. *U.S. Patent* 3316691, 1967.
9. Samant, M. G.; De Menorval, L. C.; Dalla Betta, R. A.; Boudart, M. *J. Phys. Chem.* **1988**, *92*, 3937.
10. McCormick, A. V.; Chmelka, B. F. *Molec. Phys.* **1991**, *73*, 603.
11. Ripmeester, J. A.; Ratcliffe, C. I. *J. Phys. Chem.* **1990**, *94*, 7652.
12. Takaishi, T.; Hosoi, H. *J. Phys. Chem.* **1982**, *86*, 2089.
13. No, K. T.; Chon, H.; Ree, T.; Jhon, M. S. *J. Phys. Chem.* **1981**, *85*, 2065.
14. (a) Blackwell, C. S. *J. Phys. Chem.* **1979**, *83*, 3251. (b) Blackwell, C. S. *J. Phys. Chem.* **1979**, *83*, 3257.
15. Creighton, J. A.; Deckman, H. W.; Newsam, J. M. *J. Phys. Chem.* **1994**, *98*, 448.

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16. Iyer, K. A.; Singer, S. J. *J. Phys. Chem.* **1994**, *98*, 12679.
17. (a) No, K. T.; Bae, D. H.; Jhon, M. S. *J. Phys. Chem.* **1986**, *90*, 1772. (b) No, K. T.; Seo, B. H.; Park, J. M.; Jhon, M. S. *J. Phys. Chem.* **1988**, *92*, 6783. (c) No, K. T.; Seo, B. H.; Jhon, M. S. *Theor. Chim. Acta.* **1989**, *75*, 307.
18. Smit, B.; Den Ouden, C. J. J. *J. Phys. Chem.* **1988**, *92*, 7169.
19. (a) Woods, G. B.; Rowlinson, J. S. *J. Chem. Soc.* **1989**, *85*, 765. (b) Woods, G. B.; Panagiotopoulos, A. L.; Rowlinson, J. S. *Molec. Phys.* **1988**, *63*, 49.
20. Soto, J. L.; Myers, A. L. *Molec. Phys.* **1981**, *42*, 971.
21. (a) Van Tassel, P. R.; Davis, H. T.; McCormick, A. V. *Molec. Phys.* **1991**, *73*, 1107. (b) Van Tassel, P. R.; Davis, H. T.; McCormick, A. V. *Molec. Phys.* **1992**, *76*, 411.
22. Razmus, D. M.; Hall, C. K. *J. Am. Inst. Chem. Engrs.* **1991**, *37*, 769.
23. Karavias, F.; Myers, A. L. *Molec. Simul.* **1991**, *8*, 51.
24. Smit, B.; Siepmann, J. I. *J. Phys. Chem.* **1994**, *98*, 8442.
25. Anderson, H. C. *J. Chem. Phys.* **1980**, *72*, 2384.
26. (a) Cohen de Lara, E.; Kahn, R.; Goulay, A. M. *J. Chem. Phys.* **1989**, *90*, 7482. (b) Kahn, R.; Cohen de Lara, E.; Viennet, E. *J. Chem. Phys.* **1989**, *91*, 5097.
27. Song, M. K.; Chon, H. *Bull. Korean Chem. Soc.* **1993**, *14*, 255.
28. El Amrani, S.; Vigne-Maeder, F.; Bigot, B. *J. Phys. Chem.* **1992**, *96*, 9417.
29. (a) Yashonath, S.; Demontis, P.; Klein, M. L. *Chem. Phys. Letters* **1988**, *153*, 551. (b) Santikary, P.; Yashonath, S.; Ananthakrishna, G. *J. Phys. Chem.* **1992**, *96*, 10469. (c) Yashonath, S.; Santikary, P. *J. Phys. Chem.* **1993**, *97*, 3849, 13778.
30. (a) Demontis, P.; Suffriti, G. B.; Quartieri, S.; Fois, E. S.; Gamba, A. *J. Phys. Chem.* **1988**, *92*, 867. (b) Demontis, P.; Suffriti, G. B.; Quartieri, S.; Fois, E. S.; Gamba, A. *Zeolites* **1987**, *7*, 552.
31. June, R. L.; Bell, A. T.; Theodorou, D. N. *J. Phys.*

Chem. **1990**, *94*, 8232.
32. Den Ouden, C. J. J.; Smith, B.; Wielers, A. F.; Jackson, R. A.; Nowak, A. K. *Molec. Simul.* **1989**, *4*, 121.
33. Pickett, S. D.; Nowak, A. K.; Thomas, J. M.; Peterson, B. K.; Swift, J. F.; Cheetham, A. K.; Den Ouden, C. J. J.; Smith, B.; Post, M. *J. Phys. Chem.* **1990**, *94*, 1233.
34. Titiloye, J. O.; Parker, S. C.; Stone, F. S.; Catlow, C. R. A. *J. Phys. Chem.* **1991**, *95*, 4038.
35. Catlow, C. R. A.; Freeman, C. M.; Vessal, B.; Tomlinson, S. M.; Leslie, M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 1947.
36. Nicol, J. M.; Eckert, J.; Howard, J. *J. Phys. Chem.* **1988**, *92*, 7117.
37. Shin, J. M.; No, K. T.; Jhon, M. S. *J. Phys. Chem.* **1988**, *92*, 4533.
38. Lee, S. H.; Moon, G. K.; Chi, S. G.; Kim, H. S. *J. Phys. Chem.* **1994**, *98*, 1561.
39. Smirnov, K. S.; Bougeard, D. *Zeolites* **1994**, *14*, 203.
40. Sauer, J. *Chem. Rev.* **1989**, *89*, 199.
41. Haase, F.; Sauer, J. *J. Am. Chem. Soc.* **1995**, *117*, 3780.
42. Nicholas, J. B.; Winans, R. E.; Harrison, R. J.; Iton, L. E.; Curtiss, L. A.; Hopfinger, A. J. *J. Phys. Chem.* **1992**, *96*, 10247.
43. Hill, J.-R.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 1238.
44. Nicholas, J. B.; Hopfinger, A. J.; Trouw, F. R.; Iton, L. E. *J. Am. Chem. Soc.* **1991**, *113*, 4792.
45. (a) No, K. T.; Kim, J. S.; Huh, Y. Y.; Kim, W. K. *J. Phys. Chem.* **1987**, *91*, 740. (b) No, K. T.; Huh, Y. Y.; Jhon, M. S. *J. Phys. Chem.* **1989**, *93*, 6413.
46. Yanagida, R. Y.; Amaro, A. A.; Seff, K. *J. Phys. Chem.* **1973**, *77*, 805.
47. Leung, P. C. W.; Kunz, K. B.; Seff, K.; Maxwell, I. E. *J. Phys. Chem.* **1975**, *79*, 2157.
48. Firor, R. L.; Seff, K. *J. Am. Chem. Soc.* **1977**, *99*, 1112.
49. Park, C. S.; Yoon, M. S.; Lim, W. T.; Kim, M. C.; Suh, S. H.; Heo, N. H. *Bull. Korean Chem. Soc.* **1995**, *16*, 923
50. Sanderson, R. T. *J. Chem. Educ.* **1945**, *31*, 2.
51. Huheey, E. *J. Phys. Chem.* **1965**, *69*, 3284.