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Intraframework potential energy function of zeolites

Molecular mechanical studies of the structure determination of Cs_xNa_{12-x}-A type zeolite and the transmission of H_2 molecules

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Potential energy functions suitable for the $(Cs_{1-x}Na_xT_2O_4)$-A type zeolite family were obtained from the known crystal structure of Cs_7Na_5-A zeolite. Using these potential functions, several other crystal structures in these family were obtained by molecular mechanical calculations. The activation energy α- to α-cage transmission of the H_2 molecule and the void volume of Cs_3Na_9-A zeolite were calculated.

Key words: Molecular mechanics — Activation energy — Zeolites

1. Introduction

Zeolitic encapsulation of non-polar molecules is a very interesting phenomenon which has been widely investigated [1-5]. Hydrogen encapsulation is particularly important for industrial applications and is also interesting from a theoretical point of view. It was reported that zeolite A type, especially forms containing combinations of Cs and Na as exchangeable cations, is most efficient for trapping hydrogen.

The diffusion parameters D_0 and E of several A type zeolites were obtained by Fraenkel [5], the crystal structure of the Cs_7Na_5-A zeolite was found by Vance and Seff [6], and the potential experienced by the Cs ion located at the center of the eight-membered ring has been investigated by Takaishi and Hosoi [7]. For the theoretical investigation of encapsulation or diffusion in a zeolite framework, both the crystal structure and the inter- and intra-framework potential energy functions of a zeolite are necessary. The dependence of the diffusion parameter E on the pressure of H_2, on the temperature, and on the composition of the cations may be calculated from the structures and potential energy functions.

Therefore in this study, potential energy functions suitable for the (Cs_xNa_{12-x})-A type zeolite will be obtained from the X-ray structure of the (Cs_7Na_5)-A zeolite using a constraint method. Next, the crystal structures of several (Cs_xNa_{12-x})-A zeolites, which have not been investigated by X-ray crystallography, will be obtained by a molecular mechanical calculation with these potential energy functions. The minimum energy path for the transmission of a H_2 molecule in the (Cs_3Na_9)-A zeolite, the most effective H_2 encapsulating zeolite, will also be calculated.

2. Methods of calculation

2.7. *Determination of the potential energy functions and crystal structure of* (Cs_xNa_{12-x})-A *type zeolites*

The potential energy functions of the (T_2O_4Na)-A type framework have been obtained by No et al. [8] using the constraint method, and the stabilities, net forces, and force constants of each atom have been calculated from the potential functions. For the $(SiAlO_4Na)$-A type zeolite, the potential energy functions are described in the preceding paper [9]. Since the dynamical properties of the molecules, bound to or encapsulated by the zeolite framework, are mostly influenced by the oxygen atoms and the bound ions, the $(T_2O_4Cs_xNa_{12-x})$-A type model may be used for dynamical studies without serious error and the results should be comparable to those of the $(SiAlO_4Cs_xNa_{12-x})$-A type model. In this study, the $(T_2O_4Cs_7Na_5)$-A zeolite structure obtained by Vance and Seff [6] was used for the determination of potential function parameters. The structure had been solved in the cubic space group *Pm*3*m* with a cell edge of 12.158 Å. Three Cs ions, Cs(1), are located at the centers of the eight-membered ring, and the remaining Cs ions, Cs(2) and Cs(3), and four Na ions, Na(1) lie on the three-fold axis of the six-membered rings. The Cs(3), one Cs ion per unit cell, is located in the β-cage which reduces the electrostatic repulsion between the ions in the α-cage. Thus, the coodinates of the nine atoms, T1, T2, O(1), O(2), O(3), Na(1), Cs(1), Cs(2) and Cs(3), which are all located in different potential fields, can be used as constraints in the determination of the parameters of the potential. Since the number of total constraints is 27, the number of potential parameters must be less than or equal to 27. The potential parameters to be determined are the six harmonic potential parameters of the T—O(1), T—O(2), T—O(3) bonds, and six nonbonding potential parameters for the Lennard-Jones potential of O---O, O---Na, O---Cs interacting pairs. The parameters and the method of applied constraints are described in preceding papers [8].

The electrostatic field produced by the framework, the Madelung potential, plays an important role in the determination of crystal structures. The average net atomic charge of Na ions (δ_{Na}) bound to the (T_2O_4Na)-A type zeolite was obtained as 0.625 from theoretical work [8]. Since the electronegativities of Na and Cs have similar magnitudes and these atoms touch the framework, which is a large electron reservoir since the charge coefficient of the oxygen atom is large, the net atomic charge of Cs(δ_{Cs}) in the zeolite framework may be similar to that of Na. Thus, in this study, the potential parameters have been determined for $\delta_{Na} = \delta_{Cs} = 0.625$. The positional parameters and occupancy factors for (Cs_7Na_5)-A type zeolite are listed in Table 1. The crystal structures of other (Cs_xNa_{12-x})-A type zeolites are obtained by molecular mechanical calculations utilizing the equilibrium condition of the crystal in the potential energy surfaces.

$$F_i^k = -(\partial V/\partial q_i^k) \tag{1}$$

where the crystal energy of the zeolite V is described as follows,

$$V = V(q_1^1, q_1^2, q_1^3, q_2^1, \ldots, q_N^3) \tag{2}$$

q_i^k represents the kth coordinate of the ith atom. In this study, the Cartesian coordinate ($k = x, y, z$) is used and N represents the number of atoms located on different potential energy surfaces. For simplicity, the models will be denoted as Na_{12}, Cs_3Na_9, Cs_5Na_7, Cs_7Na_5, Cs_8Na_4 models for, respectively, the (NaT_2O_4), $(Cs_{3/12}Na_{9/12}T_2O_4)_n$, $(Cs_{5/12}Na_{7/12}T_2O_4)_n$, $(Cs_{7/12}Na_{5/12}T_2O_4)_n$, and $(Cs_{8/12}Na_{4/12}T_2O_4)_n$-A zeolites. The structures of these zeolites will be obtained theoretically. The detail form of V is described in previous papers [8, 9].

In the distribution of the ions among the binding sites in each model, the configurations which give the minimum electrostatic ion-ion repulsion are selected. One pseudo-unit cell of the A type zeolite can be represented by one α-cage and one β-cage. The binding sites in the α-cage are three 8-ring windows, eight 6-rings, and twelve 4-rings. The β-cage can hold only one ion, although the site is eight-fold degenerate. The 4-ring sites are energetically unfavorable compared with the other sites, especially for large ions. If both sides of a six-ring are coordinated by two ions, one from an α-cage and the other from a β-cage, the binding energies of these two ions decrease, so there are only eleven stable binding

Table 1. Positional parameters and occupancy factors used for the potential parameter refinement of dehydrated Cs_7Na_5-A

Atom	Wyckoff position	X	Y	Z	Occupancy factor
T(Al, Si)	24(k)	0.3697	0.0000	0.1814	1
O(1)	12(h)	1/2	0.0000	0.2248	1
O(2)	12(i)	0.3016	0.0000	0.3016	1
O(3)	24(m)	0.3348	0.1124	0.1124	1
Cs(1)	3(c)	1/2	0.0000	1/2	1
Cs(2)	8(g)	0.2825	0.2825	0.2825	3/8
Cs(3)	8(g)	0.0847	0.0847	0.0847	1/8
Na(1)	8(g)	0.1960	0.1960	0.1960	1/2

The space group is *Pm*3*m* and the cubic cell parameter 12.158 Å. The geometries are taken from Vance and Seff [6]

Table 2. Occupancy factors of several models obtained from molecular mechanical calculations

Atom	WP	$Na_{12}A$	Cs_3Na_9A	Cs_5Na_7A	Cs_7Na_5A	Cs_8Na_4A
Na(1)	8(g)	1(1)[a]	1	6/8	4/8 (4/8)[a]	3/8
Na(2)	3(c)	1 (1)[a]				
Cs(1)	3(c)		1	1	1 (1)[a]	1
Cs(2)	8 (g)			2/8	3/8(3/8)[a]	3/8
Cs(3)	8(g)				1/8(1/8)[a]	1/8
Cs(4)	8(g)					1/8

[a] Values in parentheses are the experimentally obtained occupancy factors
WP, Wyckoff position

sites for twelve ions in the Na-A zeolite framework. In order to minimize the influence of twelfth ion, in these calculations, it will be placed at the potential equipoint from the other ions. The center of an α-cage is one such position. In Table 2, the distribution of ions in each model is described.

$$f = \sum_i \sum_i |F_i^k|. \tag{3}$$

The value f, the sum of the absolute value of the net force on each atom, is minimized in order to achieve the equilibrium condition. In this study all the crystal structures are confined to the cubic space group $Pm3m$. In order that the symmetry of the potential field of the crystal does not deviate appreciably from the crystal symmetry, the twelfth ion (Na(3)) is placed at the center of α-cage in each model. For the refinement of potential parameters, the calculations of binding energies, net atomic forces, force constants and for the determination of crystal structure, our computer program ZEOAPOT86 [10] was used.

Table 3. The refined potential energy function parameters at $\delta_{Na} = 0.625$ and $\delta_{Cs} = 0.625$ and the potential parameters of H_2---framework interactions

Parameter	Cs_7Na_5-A	Na_{12}-A	H_2---framework interaction	
$r^0_{T-O(1)}$	1.691	1.659	σ_{O---H}	2.496
$k_{T-O(1)}$	4.125	4.125	ε_{O---H}	0.119
$r^0_{T-O(2)}$	1.695	1.631	σ_{Na---H}	2.142
$k_{T-O(2)}$	4.300	4.300	ε_{Na---H}	0.126
$r^0_{T-O(3)}$	1.680	1.685	σ_{Cs---H}	2.785
$k_{T-O(3)}$	4.035	4.035	ε_{Cs---H}	0.168
σ_{O---O}	2.913	2.702		
ε_{O---O}	0.230	0.230		
σ_{O---Na}	2.501	2.484		
ε_{O---Na}	0.242	0.242		
σ_{O---Cs}	3.251			
ε_{O---Cs}	0.323			

r^0 in Å, ε in kcal/mole, σ in Å and k in mdyne/Å

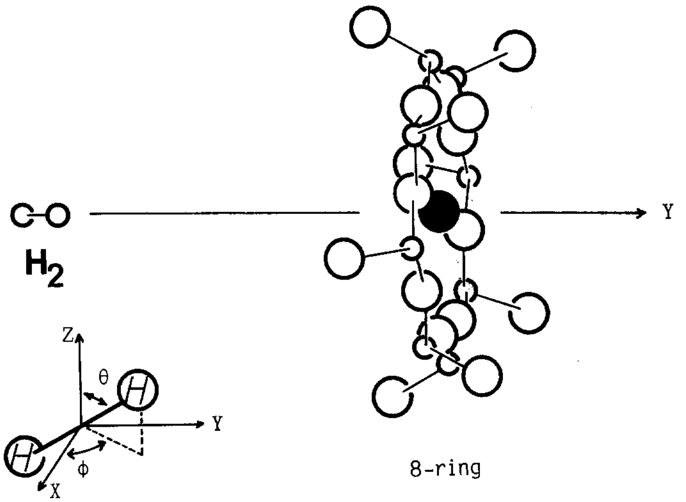

Fig. 1. The internal coordinates, 5 degrees of freedom for H_2 and 3 degrees of freedom for Cs ion, used for the calculation of the minimum energy path of H_2 transmission. ○: T; ◯: O; ●: Cs

2.2. *Calculation of the minimum energy path of α- to α-cage transmission of a hydrogen molecule*

Figure 1 shows the internal coordinates used for the calculation of the minimum energy path. The hydrogen molecule is assumed to be rigid and has five degrees of freedom, center of mass coordinate r_{H_2}, and two angular parameters θ and ϕ, and the Cs ion has three degrees of freedom, the position r_{Cs}. It is assumed that the conformation of the framework does not change during the transmission of a hydrogen molecule. The pair potential parameters of Cs---H_2, Cs---O, H_2---Na are listed in Table 3. The minimum energy configurations of H_2 and Cs are calculated as one component of the center of mass coordinate r_{H_2} approaches an eight-membered ring.

3. Results and discussion

The potential parameters obtained from the crystal structure of the Cs_7Na_5-A type zeolite, using the constraint method described in a previous paper [8a] are listed in Table 3. The sum of net forces remaining at each atom, f, calculated at the X-ray geometry is 0.0021 mdyne. This net force is relatively small compared with those calculated for (T_2O_4Na)-A and $(SiAlO_4Na)$-A type zeolites [8, 9]. In Table 4, the geometrical parameters of each atom obtained from molecular mechanical calculations are listed in Cartesian coordinates, and are also described in internal coordinates (Table 5). The cell parameters decrease as the content of Cs is increased ($\chi < 0.6$) because the dispersion interaction of Cs---framework is larger than that of Na---framework. The dispersion interaction and repulsion play an important role in determining the crystal structure because its first derivatives, the forces, are steep compared with those of the electrostatic interaction although the contribution of the electrostatic interaction to stabilization energy is predominant.

The calculated geometry of Na$_{12}$-A deviates greatly from the X-ray structure. Since the potential parameters are determined at high Cs content, the potential functions may not give reliable structures for zeolites without Cs. The local geometry of the oxygen atoms is greatly influenced by the Cs ion bound to 6-ring. The geometrical parameters vary very much from Cs$_3$Na$_9$-A to Cs$_8$Na$_4$-A zeolites.

Table 4. The positional parameters and occupancy factors of several models obtained from molecular mechanical calculations

Atom	WP		Na$_{12}$A^a (Exp.^{b})	Cs$_3$Na$_9$A	Cs$_5$NA$_7$A	Cs$_7$Na$_5$A	Cs$_8$Na$_4$A
	CP		12.2644 (12.2640)	12.2364	12.1901	12.1581	12.1574
T(Si, Al)	24(k)	x	0.3721 (0.3720)	0.3715	0.3683	0.3698	0.3698
		y	0.0000 (0.0000)	0.0000	0.0000	0.0000	0.0000
		z	0.1812 (0.1850)	0.1809	0.1809	0.1815	0.1815
		OF	1 (1)	1	1	1	1
O(1)	12(h)	x	0.2286 (0.2250)	0.2267	0.2190	0.2248	0.2248
		y	0.0000 (0.0000)	0.0000	0.0000	0.0000	0.0000
		z	0.5000 (0.5000)	0.5000	0.5000	0.5000	0.5000
		OF	1 (1)	1	1	1	1
O(2)	12(i)	x	0.2948 (0.2882)	0.2955	0.3024	0.3016	0.3016
		y	0.0000 (0.0000)	0.0000	0.0000	0.0000	0.0000
		z	0.2946 (0.2882)	0.2955	0.3024	0.3016	0.3016
		OF	1 (1)	1	1	1	1
O(3)	24(m)	x	0.3383 (0.3443)	0.3367	0.3325	0.3348	0.3348
		y	0.1120 (0.1137)	0.1118	0.1119	0.1124	0.1124
		z	0.1120 (0.1137)	0.1118	0.1119	0.1124	0.1124
		OF	1 (1)	1	1	1	1
Na(1)	8(g)	x	0.1985 (0.2000)	0.1981	0.1963	0.1961	0.1961
		y	0.1985 (0.2000)	0.1981	0.1963	0.1961	0.1961
		z	0.1985 (0.2000)	0.1981	0.1963	0.1961	0.1961
		OF	1 (1)	1	6/8	4/8	3/8
Na(2)	3(c)	x	0.5000^c (0.429)				
		y	0.0000 (0.000)				
		z	0.5000 (0.429)				
		OF	1 (1)				
Cs(1)	3(c)	x		0.5000	0.5000	0.5000	0.5000
		y		0.0000	0.0000	0.0000	0.0000
		z		0.5000	0.5000	0.5000	0.5000
		OF		1	1	1	1
Cs(2)	8(g)	x			0.2808	0.2826	0.2826
		y			0.2808	0.2826	0.2826
		z			0.2808	0.2826	0.2826
		OF			3/8	3/8	3/8

Table 4 (continued)

Atom	WP		$Na_{12}A^{a}$ (Exp.^{b})	Cs_3Na_9A	Cs_5NA_7A	Cs_7Na_5A	Cs_8Na_4A
	CP		12.2644 (12.2640)	12.2364	12.1901	12.1581	12.1574
Cs(3)	8(g)	*x*				0.0847	0.0847
		y				0.0847	0.0847
		z				0.0847	0.0847
		OF				1/8	1/8
Cs(4)	8(g)	*x*					0.2780
		y					0.2780
		z					0.2780
		OF					1/8
f			0.1566 (1.3970)	0.2934	0.1637	0.1481	2.2306

[a] For $(SiAlO_4Na)_n$-A type zeolite

[b] The experimental data of $Na_{12}A$ zeolite are taken from [11a]. The difference of the positions in [11a] and in this table are arise when the framework is constructed using translational and point symmetric operations

[c] For the symmetric electrostatic fields, Na(2)s are put in the center of 8-rings

WP, Wyckoff position; CP, cell parameter, in Å; OF, occupancy factor; *f*, sum of net atomic forces (in mdyne × 10^{-4})

Table 5. The positional parameters of each model are represented by internal coordinates

	$Na_{12}A^{a}$ (Exp.)	Cs_3Na_9A	Cs_5NA_7A	Cs_7Na_5A	Cs_8NA_4A
(Si, Al)—O(1)	1.673 (1.650)	1.669	1.671	1.669	1.668
(Si, Al)—O(2)	1.685 (1.630)	1.683	1.685	1.679	1.679
(Si, Al)—O(3)	1.667 (1.681)	1.664	1.661	1.660	1.659
Na(1)—O(3)	2.278 (2.318)	2.260	2.208	2.217	2.217
Na(1)—O(2)	2.951 (2.890)	2.952	3.012	2.996	2.996
Na(2)—O(1)	3.328 (3.355)				
Na(2)—O(2)	3.562 (3.674)				
Cs(1)—O(1)		3.344	3.426	3.346	3.345
Cs(1)—O(2)		3.539	3.406	3.411	3.411
Cs(2)—O(3)			2.979	2.994	2.994
Cs(2)—O(2)			3.443	3.451	3.451
O(1)—T—O(2)	104.2 (111.2)	103.9	102.3	101.2	101.2
O(1)—T—O(3)	114.2 (110.6)	114.3	113.1	113.8	113.8
O(2)—T—O(3)	106.2 (106.1)	106.4	108.6	108.3	108.3
O(3)—T—O(3)	111.0 (112.1)	110.6	110.4	110.9	110.9
T—O(1)—T	139.3 (144.1)	140.8	147.7	143.2	143.2
T—O(2)—T	158.7 (168.2)	157.1	146.9	149.1	149.1
T—O(3)—T	141.0 (145.4)	140.4	139.7	140.2	140.2
O(3)—Na(1)—O(3)	118.9 (119.2)	118.8	118.9	119.2	119.2
O(3)—Cs(2)—O(3)			79.3	79.4	79.4

Interatomic distances and angles are listed in Å and degrees, respectively

[a] The bond lengths and angles are calculated from the fractional coordinates of the atoms in [11a]

In the Cs_3Na_9-A zeolite, all three Cs ions are bound to an 8-ring window Cs(1), and in the Cs_5NA_7-A zeolite, three Cs ions are bound to an 8-ring window and two Cs ions are distributed to a 6-ring Cs(2) with a maximum separation in α-cage. In the Cs_7Na_5-A zeolite, three Cs ions are bound to 8-ring windows, three Cs ions are located at three corners of a tetrahedron formed with the 6-ring, and the remaining Cs ion is bound to the 6-ring in the sodalite cage, Cs(3). Therefore, one corner, a Cs(1) site, of the tetrahedron is not occupied by Cs. The Cs_8Na_4-A zeolite may be prepared by exchanging the Na(1) located on the diagonal line connecting the Cs(3) and the center of the α-cage with a Cs ion, Cs(4). The Cs(4) is moved, compared with Cs(2), to the center of β-cage in order to minimize the electrostatic repulsion. Since the size of the 8-ring is suitable for the inclusion of a Cs ion, there are no significant differences between Na_{12}-A and Cs_3Na_9-A zeolites in the theoretically obtained geometrical parameters. The geometry of the Cs_3Na_9-A zeolite is greatly changed upon further exchange of Na ions by Cs ions. Since the symmetries of the frameworks are cubic, the net atomic force remaining at each atom increases at high Cs content, because the potential fields of exchanged Cs crystals, except Cs_3Na_9-A, have symmetry lower than cubic. The stabilization energy and the force constants in Cartesian coordinates of each atom located in the framework have been calculated and are listed in Table 6. The cell parameters are plotted as a function of Cs contents in Fig. 2. Although the structure of fully Cs exchanged A type zeolite has been reported recently [11c], the molecular mechanical calculation of high content Cs-A zeolites involves some difficulties because the energy minima corresponding to these crystal structures may be metastable states. The calculation of the crystal structures corresponding to these metastable states was performed using some additional constaints necessary for locating local minima. Since the binding energy and the force constant of Na(1) are large compared with those for other ions, Na(1) does not easily exchange with other ions. Therefore the replacement in a solution of a large Cs ion excess of Na(1) by Cs ion needs a long time. On the other hand, Na(2) may easily exchange with relatively large ions because it has small force constants. Since Cs(1) has a larger force constant than Na(2), and their binding energies are comparable, Na(2) may be easily replaced by Cs(1). Cs(3) is more loosely bound than Cs(2), although the binding energy of Cs(3) is larger than Cs(2). Replacing a Na(1) for the Cs_7Na_5-A zeolite by a Cs ion, Cs(4), causes an increase of electrostatic repulsion between ions in the α-cage. The destabilization energy of the other ions by Cs(4) is nearly 55 kcal/unit cell. The ion selectivity coefficient, K_{Cs}^{Na}, may be predicted from the binding energies and the force constants of the ions. The selectivity of each position is, $Na(1) \gg Cs(2) \simeq Cs(3)$, and $Na(2) < Cs(1)$.

The stabilization energy of the zeolite crystal decreases as the content of Cs ion increases, except for the Cs_3Na_9-A zeolite. Cs_3Na_9-A may be the most stable crystal in Cs_xVa_{12-x}-A family. The stabilization energies of the ions and of the framework, (T_2O_4), of the Cs_3NA_9-A zeolite are large. The stability of the T atom does not change as the amount of Cs ion is varied because the T atoms are tetrahedrally surrounded by oxygen atoms. The stability of the oxygen atom is

Table 6. The Cartesian coordinates, force constants and binding energy of each atom calculated at minimum energy positions (*k* in mdyne/Å and SE in kcal/mole)

Atom		N_{12}-A	Cs_3Na_9-A	Cs_5Na_7-A	Cs_7NA_5-A	Cs_8Na_4-A
T(Si, Al)	k_x	5.420	5.408	5.227	5.170	5.165
	k_y	5.398	5.352	5.358	5.358	5.361
	k_z	5.405	5.400	5.569	5.570	5.569
	El	−162.93	−162.19	−163.77	−166.32	−164.64
	D-R	0.24	0.36	0.37	0.48	0.49
	SE	−162.69	−162.84	−163.39	−165.84	−164.15
O(3)	k_x	0.957	0.994	0.785	0.734	0.736
	k_y	4.323	4.330	4.302	4.313	4.312
	k_z	4.323	4.330	4.301	4.313	4.312
	El	−20.67	−20.86	−15.40	−14.47	−15.82
	D-R	3.57	3.84	3.47	3.21	3.16
	SE	−20.79	−20.74	−12.83	−12.47	−13.76
O(2)	k_x	4.975	4.999	4.992	5.072	5.074
	k_y	0.323	0.311	0.277	0.255	0.252
	k_z	4.975	4.998	4.993	5.073	5.073
	El	−18.87	−18.91	−19.60	−17.45	−19.34
	D-R	5.12	5.04	4.49	5.41	5.39
	SE	−15.85	−15.96	−16.08	−13.06	−14.82
O(1)	k_x	1.178	1.168	0.931	1.107	1.105
	k_y	0.184	0.164	0.169	0.143	0.141
	k_z	7.924	8.006	8.412	8.372	8.374
	El	−14.60	−14.60	−16.08	−13.69	−16.28
	D-R	2.50	2.57	3.10	3.75	3.74
	SE	−13.48	−13.33	−14.31	−14.40	−13.93
Na(1)	k_x	0.460	0.516	0.730	0.680	0.680
	k_y	0.460	0.516	0.721	0.680	0.680
	k_z	0.460	0.516	0.730	0.692	0.694
	El	−124.41	−124.96	−123.34	−126.17	−125.25
	D-R	2.26	3.22	5.60	5.11	5.12
	SE	−121.82	−121.76	−117.76	−121.07	−120.14
Na(2)	k_x	−0.048				
	k_y	0.085				
	k_z	−0.048				
	El	−102.68				
	D-R	−3.40				
	SE	−106.07				
Na(3)	k_x	0.000	0.000	0.000	0.000	0.000
	k_y	0.000	0.000	0.000	0.000	0.000
	k_z	0.000	0.000	0.000	0.000	0.000
	El	−64.73	−64.69	−45.98	−53.76	−47.03
	D-R	−0.17	−0.17	−0.18	−0.18	−0.18
	SE	−64.91	−68.86	−46.16	−53.95	−47.24
Cs(1)	k_x		0.109	0.100	0.135	0.131
	k_y		0.055	0.065	0.062	0.065
	k_z		0.109	0.100	0.138	0.132
	El		−102.59	−93.74	−99.55	−94.56
	D-R		−1.23	−3.56	−3.29	3.29

Table 6 (continued)

Atom		N_{12}-A	Cs_3Na_9-A	Cs_5Na_7-A	Cs_7NA_5-A	Cs_8Na_4-A
	SE		−103.82	−97.32	−102.92	−98.01
Cs	k_x			0.360	0.337	0.340
	k_y			0.360	0.334	0.333
	k_z			0.360	0.334	0.333
	El			−90.14	−91.19	−85.87
	D-R			1.38	0.89	0.89
	SE			−92.71	−94.14	−89.69
Cs(3)	k_x				0.204	0.205
	k_y				0.204	0.205
	k_z				0.204	0.205
	El				−98.19	−95.52
	D-R				−2.76	−2.76
	SE				−102.04	−99.19
Cs(4)	k_x					0.460
	k_y					0.460
	k_z					0.460
	El					−103.48
	D-R					3.170
	SE					−106.83
SE of ions		−1357.68	−1354.40	−1230.10	−1231.45	−1176.78
SE of framework		−4755.48	−4757.28	−4698.60	−4647.84	−4680.60
Total SE		−6113.16	−6111.68	−5928.70	−5879.29	−5857.38

SE, the SE is well defined in [8a] as *V*. This includes electrostatic, polarization, dispersion-repulsion, and bond potential

Total SE = SE of ions + SE of framework. Total SE is defined as the same quantity decribed in Eq. (2) and of this table is SE of the $M_{12}T_{24}O_{48}$ unit

sensitive to the location of the Cs(2) ions. The O(1) and O(3) atoms are significantly influenced by the Cs(2) ions. As Na(1)'s are exchanged by Cs(1)'s, the shape of the potential surface at the remaining Na(1) sites will be sharpened and the potential depths become smaller. Cs(2) is bound more tightly to the 6-ring than the Cs(1) is bound to the 8-ring, although the binding energy of Cs(2) is smaller. Cs(3) is more loosely bound than Cs(2), because there are eight degenerate binding sites in the β-cage and these sites are connected by low energy barriers. Since Cs(4) is moved from the center of the α-cage, it has large force constants due to the electrostatic repulsions.

The potential experienced by the Cs ion located at the center of the eight-membered oxygen ring was investigated by Takaishi and Hosoi [7]. They pointed out that the Cs ion is floating at the center of the 8-ring in the direction perpendicular to the 8-ring plane. This means that the force constant of the Cs ion motion perpendicular to the 8-ring must be negative. In the present work, it

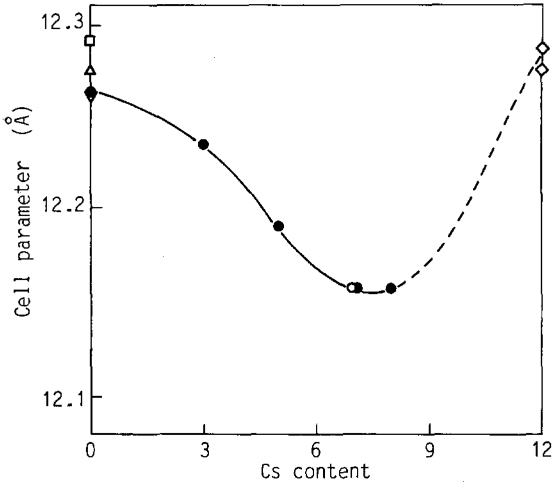

Fig. 2. The cell parameters are plotted as a function of the Cs contents. △: Pluth and Smith [11d]; ▽: Yanagida and Seff [11a]; □: Subramanian and Seff [11b]; ○: Vance and Seff [6]; ◇: Heo et al. [11c]; ●: this work

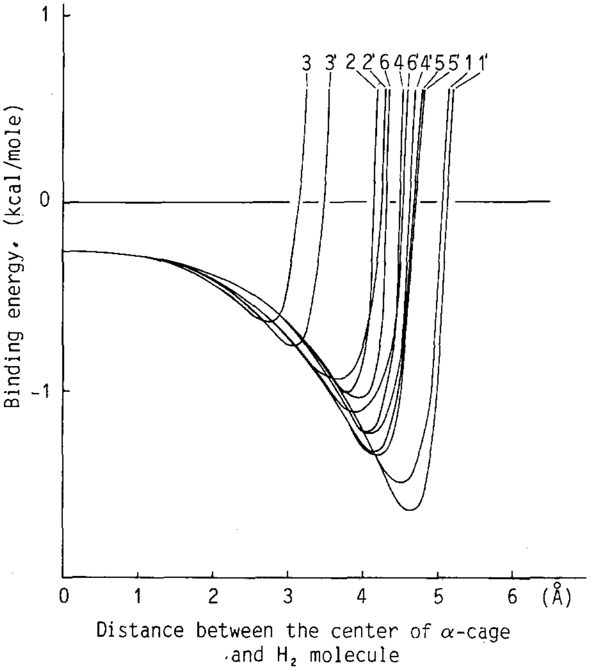

Fig. 3. The binding energies of H_2 are plotted along the six axes at two different angles

was found to be positive (k_y of Cs(1) in Table 6 has values between 0.055 and 0.065 mdyne/Å). This force constant was very sensitive to the ionicity of the crystal in Takaishi and Hosoi's calculation and the average net atomic charge of oxygen was assumed to be 0.75e. If δ_0 is assumed to be 0.5e in his calculation, then this force constant may take a positive value. Whether the Cs ion is floating or has a gentle minimum near the 8-ring window, the large displacement of Cs(1) from the 8-ring window may not need much energy. Therefore α- to α-cage transmission of an H_2 molecule may take place in Cs exchanged zeolites, although the sizes of the 8-ring and the Cs ion are similar.

The binding energies of H_2 are plotted along the six axes at two different angles in the α-cage in Fig. 3. H_2 molecules are placed on and perpendicular (denoted by "′") to these axes. As shown in Fig. 3, the three axes point towards the centers of the 4-ring (curves 1,1′ in Fig. 3), the 6-ring(2,2′), and the 8-ring(3,3′) and the other three axes are toward the edges formed among these rings, i.e. the 4,6-rings(4,4′), the 6,8-rings(5,5′), and the 4,8-rings(6,6′). From these curves, the void

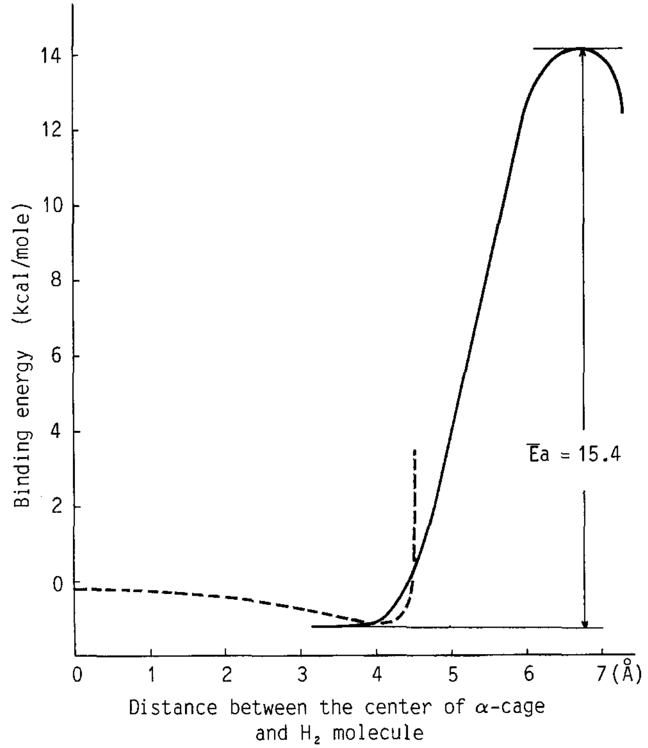

Fig. 4. The minimum energy path for α- to α-cage jump of H_2 is plotted against the distance between the center of α-cage and the H_2 molecule (——). The dashed line (- - -) represents the potential curves when a Cs ion is fixed to the window. The saddle point of the H_2 jump is located outside of the eight ring window, 6.8 Å from the α-cage center. The reference state of the binding energy corresponds to the crystal energy of Cs_3Na_9-A type zeolite

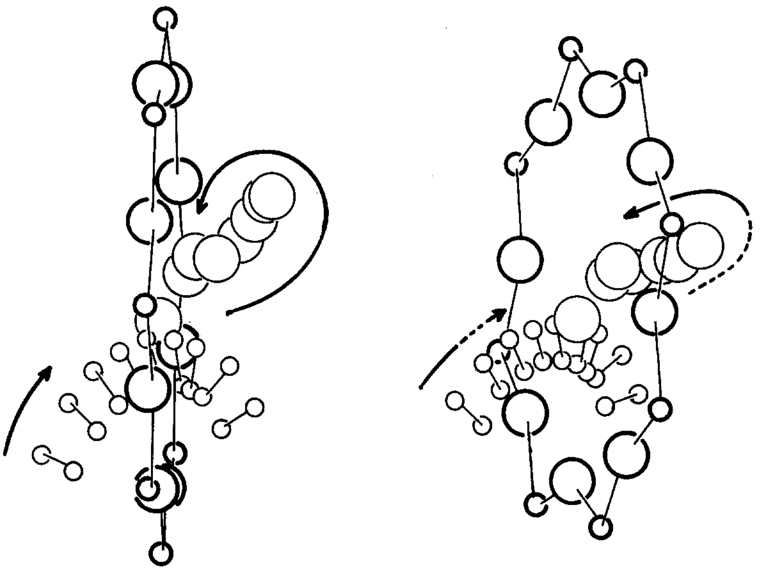

Fig. 5. The configurations of H_2 and Cs(1) during the transmission of H_2 passing through the 8-ring window along the minimum energy path described in Fig. 3. ∘: T; O: O; ○: Cs; ∘—∘: H_2

volume of the (Cs_3Na_9)-A type zeolite may be estimated roughly as

$$V_{\mathrm{void}} = \sum_{i=1} f_i(4\pi/3)(r_i^0 + \sigma_{H_2/2})^3 \tag{4}$$

where f_i, is the fractional factors for the ith binding energy curve, $V_i(r_i)$, r_i^0 is the distance where $V_i(r_i)$ becomes zero, and σ_{H_2} is the L-J potential parameter of H_2 (2.959 Å). Since the binding energy between H_2 and the framework is mainly due to the van der Waals interaction, f_i may be taken as 1/12 without serious error. The V_{void} of the α-cage was determined to be 783 $Å^3$ in this calculation and was experimentally found to be 775 $Å^3$ by Breck [5, 12]. The spherical symmetrical binding energy function was obtained by the least squares fitting of the $V_i(r_i)$'s in Fig. 3. The potential depth and average value of r_i^0, r_0, were determined to be 1.2 kcal/mole and 4.485 Å, respectively. The void volume calculated from $r_0 = 4.485$ Å is 888.8 $Å^3$. If the close packing of H_2 molecules of spheres with $\sigma = 2.959$ Å is assumed, the maximum number of H_2 molecules which could be encapsulated by the α-cage is 31 from accurate void volume calculation and 35 from a crude calculation.

The minimum energy path of the α- to α-cage jump of H_2 is shown in Fig. 4. The displacement of Cs(1) during the transmission of H_2 is large as shown in Fig. 5. The activation energy, $\bar{E}_a$, needed for the H_2 jump was obtained as 15.4 kcal/mole at 0 K, and may be a function of both temperature and the number of H_2 in the α-cage. An activation energy of 19.6 kcal/mole [13a] for H_2 diffusion in the ($Cs_{3.4}NA_{8.6}$)-A zeolite was obtained by Fraenke [5]. More recent experimental results of Fraenkel et al. [13b] gave a value of 17.4+2.9 kcal/mole. Since the net atomic charge of a Cs ion is assumed to be equal to that of an Na ion and the interaction between H_2 molecules is neglected, the theoretically determined activation energy may deviate from the experimental activation energy. The activation energy, the minimum energy needed for the α- to α-cage transmission of H_2, is very sensitive to the net atomic charge of the Cs ion because the Cs ion must move into the α-cage so that the H_2 molecule can pass the 8-ring. The binding energy difference between the molecules in contact with the framework and those located at the center of the α-cage is calculated to be −0.9 kcal/mole.

The potential energy functions obtained from the X-ray structures using the constraint method may be useful for the investigation of those crystal structures which have not been experimentally obtained, for the study of stabilities of the atoms in crystals, and for dynamical studies of zeolite systems [14].

References

1. Sesny WJ, Shaffer LH, US patent 3316691/1967
2. Cook GA (1961) Argoen, helium and rare gases, vol. 1. Wiley, New York, pp 228–230
3. (a) Barrer RM, Vaughan DEW (1967) Trans Faraday Soc 63:2275; (b) Barrer RM, Vaughan DEW (1969) Surf Sci 14:77; (c) Barrer RM, Vaughan DEW (1971) J Phys Chem Solid 32:731; (d) Barrer RM, Vaughan DEW (1971) Trans Faraday Soc 67:2129
4. Chan YC, Anderson RB (1977) J Catal 50:319
5. (a) Fraenkel D, Shabtai J (1977) J Am Chem Soc 99:7074; (b) Fraenkel D (1981) J Chem Soc Faraday Trans I 77:2029; (c) Fraenkel D (1981) J Chem Soc Faraday Trans I 77;2041
6. Vance TB Jr, Seff K (1975) J Phys Chem 79:2163
7. Takaishi T, Hosoi J (1982) J Phys Chem 86:2089
8. (a) No KT, Kim JS, Huh YY, Kim WK, Jhon MS (1987) J Phys Chem 91:740; (b) No KT, Chon H, Ree T, Jhon MS (1981) J Phys Chem 85:2065; (c) Choi KJ, No KT, Jhon MS (1987) Bull Korean Soc 8:158
9. No KT, Huh YY, Jhon MS, J Phys Chem, in press
10. This program is designed for calculation of several physical properties of A-typd zeolites
11. (a) Yanagida RY, Amaro AA, Seff K (1973) J Phys Chem 77:805; (b) Subramanian V, Seff K (1979) J Phys Chem 83:2166; (c) Heo NH, Dejsupa C, Seff K (1987) J Phys Chem 91:3943; (d) Pluth JJ, Smith JV (1980) J Am Chem Soc 102:4704
12. Breck DW (1974) Zeolite molecular sieves. Wiley, New York
13. (a) The activation energy of $Cs_{3.4}$ Na_{86}-A may be estimated from Fraenkel's work of [5] as 19.6 kcal/mole; (b) Fraenkel D, Ittah B, Levy M: J Chem Soc Faraday Trans 1, in press
14. Shin JM, No KT, Jhon MS (1988) J Phys Chem 92:4533