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칼륨 이온 치환 제올라이트 L 중의 C_1-C_5 알칸 및 벤젠의 열역학적 특성

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Thermodynamic Characteristics of Alkanés C_1-C_5 and Benzene in K^+ Ion Exchanged Zeolite L

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요 약. 칼륨 이온 치환 제올라이트 L과 C_1-C_5 알칸 및 벤젠의 상호작용 퍼텐셜 에너지를 원자-원자 근사를 적용시켜서 계산하였다. 퍼텐셜 에너지 계산에 사용된 벤젠의 구성 원자 전하는 칼륨 이온과 벤젠 사이의 실험적 엔탈피 값으로부터 구했다. 계산된 퍼텐셜 에너지를 기초로하여 흡착분자의 열역학적 특성(흡착분자의 퍼텐셜 지도와 매우 낮은 피복률에서의 등량흡착열 및 내부에너지 변화량)을 계산하였다. C_1-C_5 알칸의 계산된 등량흡착열은 실험데이타와 잘 일치하였지만, 벤젠의 계산값은 실험 값보다 조금 크게 나타났다.

ABSTRACT. The potential energy of interaction of alkanes C_1-C_5 and benzene with K^+ ion exchanged zeolite L was calculated by applying the atom-atom approximation. For benzene molecule, the atomic charges used for the potential energy calculations were derived from the experimental enthalpy of K^+ ion-benzene interaction. The thermodynamic characteristics of the adsorption of the adsorbate molecules (the changes in the internal energy and the isosteric heats at very low coverages) and the potential maps of the adsorbate molecules were determined on basis of the calculated values of potential energy. The calculated values of the isosteric heats agreed fairly well with experimental data for alkanes C_1-C_5, whereas the calculated isosteric heat for benzene was somewhat greater than that for the experimental value.

INTRODUCTION

The theoretical method have been considerably used in the determination and understanding of the cation sites and adsorption characteristics of zeolites. Calculations of the potential energy of interaction and thermodynamic adsorption characteristics of zeolites have been carried out mainly for relative simple adsorbate molecules[1-3] such as noble gas, saturated hydrocabons and some inorganic substances. These calculated values are in satisfactory agreement with corresponding experimental values. Also, the theoretical studies[4,5] of adsorption of polar molecules on zeolites by atom-atom approximation have been reported. A considerable number of these calculations were concerned with A, X, and Y zeolites, which have simpler structures than those of the other zeolites.

Serveral works[6-10] have been reported on properties and structures of zeolite L and its catalytic effects. The structure of zeolite L which has now been accepted was proposed by Barrer and Villger[6].

Zeolite L is hexagonal with unit cell dimension $a = 1.84$ nm and $c = 0.75$ nm[6]. This zeolite is composed of alternating cancrinate cages and hexagonal prisms arranged in connected columns. This gives rise to a large channel, which is circumscribed by oxygen-12 ring having free diameters of 0.71 and 0.78 nm, along the crystallographic *c* axis (*Fig.* 1a). This channel cannot be blocked by simple stacking faults. And selective catalysis of zeolite L is attributed to cylindrical pore structure.

In the fully hydrated form, zeolite L has four different sets of cation sites, *A*, *B*, *C*, and *D* sites[6]. *D* site is near the wall of the main channel and contains those cations which are most likely to be exchangeable. Cations in this site are coordinated to the adsorbate molecules.

In this paper, the potential energy of the adsorbate molecule in the main channel of K^+ ion exchanged zeolite L (K-L) was calculated using the atom-atom approximation. The potential maps were calculated on the basis of the potential energy distribution in the main channel of K-L. Also, the thermodynamic characteristics of the adsorption of several alkanes and benzene (the changes in the internal energy and the isosteric heats) were determined.

Potential Energy Calculation.

Potential energy calculations were carried out using a simplified structural model of dehydrated K-L lattice. The unit cell formula of dehydrated K-L is $K_9Al_9\,Si_{27}O_{72}$. The bond angles and lengths were obtained from X-ray data[6]. A total of 12 unit cells was used in calculating the interaction energy. The radius of the model compound of zeolite L was 1.84 nm. The coordinates orgin was taken as the center of the main channel. For simplicity of calculations the occupancies of sites were adjusted as shown in *Table* 1. Zero charge was ascribed to Si and Al atoms. A charge equal to +1 was attributed to each K^+ ion so that the total positive charge on each unit cell was +9. The compensating negative charge was assumed to be distributed uniformly overall oxygen atoms. Consequently a charge of $-9/72 = -0.125$ was attributed to each oxygen atom. The charges of the boundary oxygen atoms and cations of the model compound were determined by the electroneutrality of lattice as a whole. The Si and Al ions were not directly included in the calculations. This approximation[11] seems justified because Si and Al ion are completely screened by oxygen ions, and their polarizabilities are very small, and correspondingly their contribution to the energy of dispersion interaction is negligible. The hydrocarbon molecules were assumed to be rigid. For alkanes, all bond angles were assumed to be tetrahedral, and all C-C bond lengths and all C-H bond lengths were assumed to be equal to 0.154 nm and 0.109 nm, respectively.

Table 1. Site occupancy factors in ref. 6(column A) and adjusted occupancy factors used for the present study (column B)

	A		B	
Site	Cation	Fractional occupancy factor	Cation	Fractional occupancy factor
A	Na, K	0.7	K	0.5
B	K	1.0	K	1.0
C	K	0.9	K	1.0
D	Na	0.6	K	0.5

We calculated the optimum positions of K^+ ion in the main channel because the X-ray data for dehydrated K-L have not been reported yet. In order to obtain optimum values for the positions of three K^+ ions of D site, we used a minimization computer program[12]. In this program, the nine Cartesian coordinates of three K^+ ions of D site were adopted as the variables in the interaction energy calculation zeolite lattice. The Cartesian coordinates of three K^+ ions in previous paper[2] were used as the initial values of these variables in energy minimization. Further details of minimization method applied in this study are given elsewhere[13].

The Cartesian coordinates (in nm unit) of the optimized positions of three K^+ ions of D site, $K^+(1)$, $K^+(2)$, and $K^+(3)$ were (0.501, 0.285, 0.000), (−0.497, −0.292, 0.000) and (−0.003, −0.576, 0.000), respectively, and show that K^+ ions of D site in dehydrated K-L are bound to the four membered ring of hexagonal prism on the wall of the main channel. $K^+(2)$ and $K^+(3)$ ions were located by the rotation of $K^+(1)$ ion about z axis through an angle of 120° and 240°, respectively. These results seem to be reasonable because $K^+(1)$, $K^+(2)$, and $K^+(3)$ ions have to be circumscribed by the same circumstances according to the symmetry of the model compound.

The potential energy (ϕ) of interaction of the adsorbate molecule with the lattice of K-L was compound of four types of contributions: electrostatic energy (ϕ_e), polarization energy (ϕ_p), dispersion energy (ϕ_d), and repulsion energy (ϕ_r).

Electrostatic energy can be obtained using the Coulombic formura:

$$\phi_e=\sum_k\sum_i\rho_k\rho_i\gamma_{ki}^{-1} \qquad (1)$$

In Equation (1), ρ_i and ρ_k are the net charges of i th ion of zeolite lattice and the k th atom of the adsorbate molecule, respectively, and r_{ki} is the distance between the i th ion and the k th atom.

The values of net atomic charges for benzene can be obtained from the quadrupole moment (Q). For benzene Q is given by the quardrupole moment along z axis of the molecule[14].

$$Q=Q_{zz}=-0.5\sum_k\rho_k\gamma_k^2 \qquad (2)$$

where γ_k is the distance from the center of benzene molecule to the k th constituent atom of benzene molecule. But the literature[14] presents a wide spread of possible values for the quadrupole moment of benzene $(-10$ to $-40)\times10^{-40}$ C m[2]). Due to the uncertainty in the quadrupole moment, we calculated the net charges of atoms in benzene by equating our potential function for $K^+(C_6H_6)_{0,1}$ to experimental enthalpy[15], $\Delta H_{0,1}$ and $\partial\Delta H_{0,1}/\partial R_o=0$. Here R_o is the equilibrium distance. The calculated ρ_C and ρ_H were −0.075 and 0.075, respectively. The ϕ_e, ϕ_p, ϕ_d, ϕ_r and ϕ of $K^+-C_6H_6$ interaction at $\partial\Delta H_{0,1}/\partial R_0=0$ were −36.7, −60.2, −16.8, 34.2 and −79.5 kJ mol^{-1}, respectively. The equilibrium distance R_o of $K^+-C_6H_6$ was 0.265 nm. The Q of benzene calculated from Eq. (2) using these ρ_C and ρ_H was $-15.2\times10^{-40}C.m^2$.

Polarization energy of the adsorbate molecule in an elecrostatic field is given by[11]

$$\Phi_p=-0.5\sum_k\alpha_k[(E_x^k)^2+(E_y^k)^2+(E_z^k)^2] \qquad (3)$$

where α_k is the polarizability of the k th atom of the adsorbate molecule; $E_x{}^k$, $E_y{}^k$ and $E_z{}^k$ are the electrostatic field in the x, y, and z direction at the position of the k th atom of the adsorbate molecule, respectively.

Sum of dispersion energy and repulsion energy were calculated using the Lennard-Jones equation:

$$\phi_d+\phi_r=\sum_k\sum_i(B_{ki}\cdot\gamma_{ki}^{-12}-C_{ki}\cdot\gamma_{ki}^{-6}) \qquad (4)$$

Here the constants C_{k1} and B_{k1} were determined for each type of the pair interaction of the k th atom of the adsorbate molecule with the i th ion in the lattice. The constants C_{ki} were calculated by the Slater-Kirkwood formula[1]. The repulsion con-

Table 2. Parameters of atoms and zeolitic ions (r: van der Waals radii, α: polalizabilities, and N_{eff}: effective number of outer subshell electrons)

Atom or Ion	r(nm)	$\alpha \cdot 10^{24}$ (cm^3)	N_{eff}^{a}
C	0.18^b	0.96^b	4.7
H	0.135^b	0.43^b	0.9
$O^{\sigma-}$	0.166^c	0.85^d	8.8
K^+	0.133^e	0.84^f	17.3

^{a}from ref. 17, ^{b}from ref. 18, ^{c}from ref. 19, ^{d}from ref. 20, ^{e}ionic radius, ^{f}from ref. 21

stants[16] B_{ki} were calculated from the condition of the energy minimum of the pair interactions between the corresponding force centers at the equilibrium distance:

$$B_{ki} = 0.5\, \gamma_o^6 \,[C_{ki} + 1/3 \alpha_k \rho_i^2 \gamma_o^2] \tag{5}$$

where equilibrium distance r_o was estimated as a sum of the van der Waals radii of the corresponding atoms (*Table* 2).

Thermodynamic Characteristics. The calculations of the potential energy in many points of the main channel enabled us to determine the thermodynamic characteristics of adsorption at zero coverage. The differential change in the internal energy $\Delta\bar{U}_1$ due to the adsorption and the initial isosteric heat of adsorption $q_{st,1}$ were calculated by the following equations[20]:

$$\Delta\bar{U}_1 = \int \phi \exp(-\phi/RT)\, dq dH / \int \exp(-\phi/RT)\, dq dH \tag{6}$$

$$q_{st,1} = -\Delta\bar{U}_1 + RT \tag{7}$$

where q designates the coordinates of the center of the adsorbate molecule and H represents the totality of Euler's angles by which the orientation of the molecule is specified. Due to the high degree of symmetry of the zeolite model it was possible to restrict the potential energy calculation to the 1/12th part of the volume of the main channel (*Fig.* 1b).

The calculations were performed only in the nodes of the network built up by spacing the coordinates ρ, θ' and z of the cylindrical coordinate system. The limits of integration corresponding to the region ABCDEO in *Fig.* 1b were $0 \le \rho \le 0.6$ nm, $0 \le \theta' \le 1/3\ \pi$ and $0 \le z \le 0.376$ nm. At each node of the network the potential energy was calculated for different orientations of molecule defined by Euler's angles θ, ϕ and Ψ. To reduce the calculation time calculations were carried out using a rather rough net of integration. The numbers of steps along the coordinates ρ, θ', z, θ, ϕ and Ψ were 20, 8, 8, 3, 3, and 3, respectively. The intervals in ρ, θ', z, θ, ϕ and Ψ were equal (for each coordinate separately).

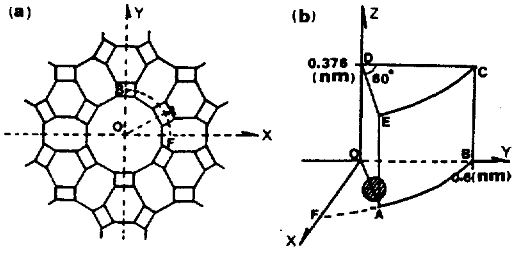

Fig. 1. (a) A projection of the framework of zeolite L parallel to z axis. (b) The region of integration represented the figures ABCDEO (● is K^+(1) Ion of D site).

Potential Maps. The potential map of the adsorbate molecule was determined on basis of the calculated values of potential energy. At first, the potential energies for various orientations of molecule determined by Euler's angles θ, ϕ and Ψ were calculated at an arbitrary point of the plane BOF in *Fig.* 1a and were registered on a computer. Next, the potential minimum at the point corresponding to cylindrical coordinates ρ, θ' and z (the coordinate z is zero) was found in the registered potential energies, and the equipotential lines were estimated. Here the numbers of steps along the coordinates ρ, θ', θ, ϕ and Ψ were 20, 31, 3, 3 and 3, respectively.

RESULTS AND DISCUSSION

Potential maps for the adsorbate in a part of

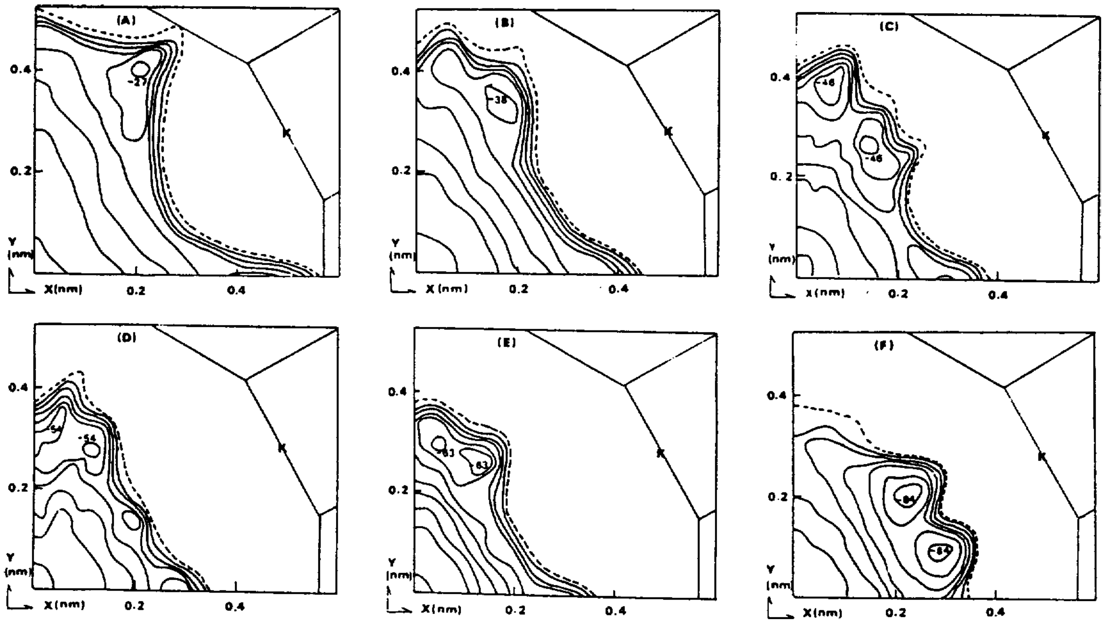

Fig. 2. Potential maps of molecules in the main channel of K–L; A: CH_4, B: C_2H_6, C: C_3H_8, D: n-C_4H_{10}, E: neo-C_5H_{12}, and F: C_6H_6 (The values on curves are represented as in kJ mol^{-1}; Contours start at the deepest equipotential lines and are at equal intervals 4.2 kJ mol^{-1} but 8.4 kJ mol^{-1} for benzene; K represents $K^+(1)$ ion of D site; The K^+ ion of A site toward +y axis is occupied; potential energies between molecules and zeolite lattice are positive above the dashed lines.)

the main channel are shown in *Fig.* 2. The potential energy is essentially dependent on the size and geometry of the adsorbate molecule. As can be seen in *Fig.* 2, the larger the size of the alkane molecule is, the larger the region of the negative potential is. For the relatively small molecules such as CH_4, C_2H_6 and C_3H_8 the deepest potential minima lie near to the wall of the main channel. However all the maps except that of ben K^+ zene show similar patterns.

In spite of the fact that benzene molecule is the relatively large molecule, the deepest potential minima lie nearer to K^+ ion of *D* site than those of *n*-C_4H_{10} and *neo*-C_5H_{12} are. This confirms that the contribution of ϕ_e arising from quadrupole moment of benzene is large as shown in *Table* 3.

The distance between K^+ ion and the deepest potential minimum of benzene is longer compared with the equilibrium distance of isolated K^+-C_6H_6 pair. This suggests a strong screening of the adsorbate molecule by the anionic oxygens of the framework. For this reason ϕ_e of benzene in zeolite is a little larger than that of isolated K^+-C_6H_6 pair. *Table* 3 also shows that a large difference between ϕ_p or ϕ_d of benzene in the main channel and that of isolated K^+-C_6H_6 interaction must come from the numerous and polarizable anionic oxygens, and that the contribution of ϕ_d to ϕ is large for alkanes in the main channel.

Table 3. The deepest potential minima (in kJ mol^{-1}) of adsorbate molecules in the main channel of K–L

Adsorbate	$-\phi_e$	$-\phi_p$	$-\phi_d$	ϕ_r	$-\phi$
CH_4		13.1	27.6	13.3	27.4
C_2H_6		21.1	34.8	17.7	38.2
C_3H_8		16.7	52.0	21.9	46.8
n-C_4H_{10}		23.9	46.8	15.9	54.8
neo-C_5H_{12}		30.1	66.2	33.5	62.8
C_6H_6	30.8	31.5	62.0	38.0	86.3

$\Delta\overline{U}_1$ and $q_{st,1}$ at zero coverage are summariz-

Table 4. Thermodynamic characteristics of the adsorption of adsorbate molecules in the main channel of K-L

Absorbate	T (K)	$-\Delta\bar{U}_1$(kJ mol^{-1})	$q_{st,1}$(kJ mol^{-1})	
		calc.	calc.	exp.
CH_4	90	25.1	25.8	20.1[a]
C_2H_6	188.5	32.8	34.3	29.3[a]
C_3H_8	269	42.4	44.6	38.5[a]
n-C_4H_{10}	273	50.0	52.3	47.7[a]
neo-C_5H_{12}	303	56.2	58.7	50.2[a]
C_6H_6	298	79.7	82.2	67.0[b]

[a] from ref. 22, [b] from ref. 23.

ed, together with the corresponding experimental data of $q_{st,1}$ in *Table* 4. The temperature considered for calculations were that of the experimental data. *Table* 4 shows the calculated values of $q_{st,1}$ agree faily well with experimental data for alkanes, whereas the calculated $q_{st,1}$ for benzene is greater by 15 kJ mol^{-1} than its experimental one.

The accuracy of the calculations of the potential energy is important in obtaining the correct values of thermodynamic characteristics. Particularly for the potential energy calculations of molecules with electric moments with zeolite lattice, a careful selection of the values of ρ_i is necessary. The quantum chemical study of Beran[24] revealed that the charge on the exchangeable cations in zeolites decreases in the order K>Na>Li. Other authors[1,4,18,25] achieved a good agreement between the calculated and the experimental $q_{st,1}$ or Herny constant for several molecules in zeolites when the charge of zeolitic cation was rather underestimated. Therefore, to calculate the correct values of thermodynamic characteristics the parameter ρ_i of all the type zeolites must be improved in future.

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