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Mn^{2+}-치환 제올라이트 A의 수화 및 탈수 구조에 관한 연구

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A Study on the Hydrated and Dehydrated Mn^{2+}-Exchanged Zeolite A

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요 약. Mn^{2+}-치환 제올라이트 A는 가열 탈수되어도 그 구조가 열적으로 안정하였다. $Mn_{4.5}Na_3$-A의 수화상태 및 탈수상태에 있어서의 골조원자, 이온 및 물분자들의 위치와 결합에너지를 몇가지 퍼텐셜 함수들을 써서 계산하여 구하였다. 탈수상태의 $Mn_{4.5}Na_3$-A에 있어서 골조원자들의 결합에너지는 열적으로 안정한 것으로 알려져 있는 탈수상태의 Ca^{2+}-치환 제올라이트 A(Ca_6-A) 및 Co^{2+}-치환제올라이트 A(Co_4Na_4-A)의 그것과 비슷하였다. Mn^{2+}-치환 제올라이트 A 골조 내에는 결합에너지와 결합형식이 서로 다른 세 가지 그룹의 물분자들 즉 인접 물분자 또는 골조 산소원자와 수소결합을 하고 있는 물 ; W(I), Na^+이온에 배위되면서 인접 물 분자와 수소결합을 하는 물 ; W(II) 및 Mn^{2+}에 배위면서 수소결합을 하는 W(III)그룹의 물분자들이 존재하였으며 그들의 결합에너지 및 탈수반응의 활성화에너지의 크기 순서는 W(III) > W(II) > W(I)이었다.

ABSTRACT. The positions and interaction energies of framework atoms and water molecules of Mn^{2+}- exchanged zeolite A were calculated using some potential energy functions and an optimization program. The sum of interaction energies of framework atoms in dehydrated $Mn_{4.5}Na_3$-A was approximately the same as those of thermally stable Ca^{2+}- or Mg^{2+}-exchanged zeolite A. Since Mn^{2+} ions can form good coordination bonds with framework oxygens even in dehydrated state, Mn^{2+}- exchanged zeolite A is considered to be thermally stable. The optimized positions of framework atoms and ions in this work are agreed well with the crystallographic data[1]. Three groups of water molecules are found in hydrated Mn^{2+}-exchanged zeolite A; W(I) group of water molecules having only hydrogen bonds, W(II) group coordinated to Na^+ ion, and W(III) group coordinated to Mn^{2+} ion. The average binding energy of each group of water molecules decrease in the order of W(III) > W(II) > W(I). The activation energies in the dehydration reaction of each group of water molecules increased in accordance with their binding energy.

INTRODUCTION

Zeolites are a class of aluminosilicates with relatively rigid anionic frameworks, and crystallographically well-defined channels and cavities. These contain exchangeable cations and removable guest molecules such as water.

Since zeolites have been widely used as molecular sieves, catalysts, adsorbents, and ion exchangers, many researches on the physicochemical properties of zeolite have been made.

Zeolite A exchanged with Ca^{2+}, Zn^{2+}, Sr^{2+} or

Co^{2+} ion are stable on dehydration upon heating or under vacuum, while some divalent cations exchanged zeolite A with such as Ba^{2+}, Cr^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}, or Hg^{2+} are thermally unstable on dehydration.[2-5]

In recent years, many theoretical studies on the structure and stability of zeolite framework by the calculation of interaction energy have been reported.[6-12]

In this work, three kinds of Mn^{2+}-exchanged zeolite A having different compositions ($Mn_x Na_{12-2x}$-A; $x=1$, 2, and 4.5) were prepared by static ion exchange method.

Thermal stability of Mn^{2+}-exchanged zeolite A was investigated by means of powder x-ray diffraction, infrared spectroscopy, and thermal analysis (TG, DSC). The interaction energies were calculated using some potential energy functions and an optimization program VA10A.[13]

An explanation on the thermal stability of Mn^{2+}-exchanged zeolite A could be made by the analysis of the theoretical and experimental results.

EXPERIMENTAL

Zeolite A was purchased from Toyo Soda Ind. Co. and ion exchange were carried out with 0.1 *M* solution of $Mn(ClO_4)_2\ 6H_2O$ by static ion exchange method, and three compositions of Mn^{2+}-exchanged zeolite A; $Mn_xNa_{12-2x}Si_{12}Al_{12}O_{48}\ zH_2O$ ($x=1$, 2, and 4.5) were obtained.

Thermograms of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were recorded on a Rigaku Thermal Analyzer TAS100 system. Diffractograms within $5° < 2\theta < 40°$ were obtained by using Rigaku Geigerflec D/Max. IIIA differactometer. Infrared spectra of Mn_xNa_{12-2x}-A zeolites were recorded on a Matterson-Polaris TM spectrometer.

METHODS OF CALCULATION

(a) Model compound; In this study, the geometry of Mn^{2+}-exchanged zeolite A were taken from x-ray crystallographic study.[1]

(b) Refinement of potential energy function; The parameters of potential energy functions were refined by constraint method.

The potential parameters were obtained by the minimization of the following function.

$$\sum_{i=1}^{k}\sum_{l=1}^{N}\sum_{j=1}^{3}\partial/\partial\alpha_i[\partial V^o/\partial q_l^{o1}]=f,\ j=1,2,3 \quad (1)$$

where

$$V=V[\alpha_1, \alpha_2, \cdots \alpha_n, q_1^1, q_2^1, \cdots, q_3^N] \quad (2)$$

$$V^o=V[\alpha_1, \alpha_2, \cdots, \alpha_n, q_1^{o1}, q_2^{o1}, \cdots q_3^{oN}] \quad (3)$$

where α_i is ith potential parameters, q_j^l and q_j^{ol} represent the jth coordinate of the lth atom and that in an equilibrium structure, respectively.

The stabilization energy (V) of the model is expressed as a sum of several energy terms.

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

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

$$\vec{F}_i^n=-(\partial V/\partial\vec{q}_i^n)\,q_1^1 q_2^1\cdots q_3^N \quad (5)$$
$$n=1,2,3,\cdots, N$$
$$i=1,2,3\ [\text{or } x, y, z]$$

and the force constant is expressed as follows;

$$K_{i,j}^{m,n}=[\partial^2 V/\partial q_i^m\,\partial q_j^n]\,q_1^1, q_2^1, \cdots, q_3^N \quad (6)$$

(1) Electrostatic energy (V_{el})

The net charges of the atoms are considered as point charges and electrostatic energy is given as

$$V_{el}=\sum\sum_{m>n}\delta_m\delta_n/r_{mn} \quad (7)$$

where δ_m and δ_n are the net atomic charges of the mth and nth atoms, respectively, and r_{mn} is

their interatomic distance. The net atomic charges are calculated using Hueey's electronegativity set[14] and Sanderson's electronegativity equalization method.[15]

$$\sum_{i \neq Na} \delta_i = -\delta_{Na} \tag{8}$$

$$a_i + b_i\delta_i = a_i + b_j\delta_j, \quad i, j \neq Na \tag{9}$$

where i *and* j represent T_1, T_2, $O_{(1)}$, $O_{(2)}$, and $O_{(3)}$ $O'_{(3)}$, and T_1 and T_2 are Si or Al atom.

The calculated net atomic charges are as follows;

$$\delta_{Na}=0.625, \quad \delta_{Mg}=1.250, \quad \delta_{O(1)}=-0.4509, \quad \delta_{O(2)}=-0.4548$$
$$\delta_{O(3)}=-0.4458, \quad \delta_{O(3)}=-0.4458, \quad \delta_{T_1}=0.5861, \quad \delta_{T_2}=0.5861$$

(2) Polarization energy (V_{pol})

$$V_{pol}=-1/2\sum_{i}^{N}\bar{\alpha}_i\left[\left(\sum_{j\neq i}\vec{\varepsilon}_{ij}^{x}\right)^2+\left(\sum_{j\neq i}\vec{\varepsilon}_{ij}^{y}\right)^2+\left(\sum_{j\neq i}\vec{\varepsilon}_{ij}^{z}\right)^2\right] \tag{10}$$

where α_i is the atomic polarizability of the ith atom and $\vec{\varepsilon}_{ij}^{x}$ is the electric field in the x- direction at the ith atomic position created by jth atom.

(3) Harmonic potenntial energy ($V_{T\text{-}O}$)

For T-O bonds, the harmonic function is as follows,

$$V_{T-O}=1/2\sum_{i}\sum_{j>i}k_{ij}\left[r_{ij}-r^{o}_{ij}\right]^2 \tag{11}$$

where k_{ij} and r^{o}_{ij} are harmonic potential parameters and r_{ij} is an interatomic distance.

(4) Dispersion and Repulsion energy ($V_{d\text{-}r}$)

(a) Lennard-Jones (6-12) type potential function was used for describing non-bonding interactions of the O-O, O-Na, and O-Mn atomic pairs in dehydrated Mn^{2+}-exchanged zeolite A.

$$V_{d-r(L-J)}=4\sum_{i}\sum_{j>i}\varepsilon_{ij}\left[(\sigma_{ij}/r_{ij})^{12}-(\sigma_{ij}/r_{ij})^{6}\right] \tag{12}$$

where ε_{ij} and σ_{ij} are L-J parameters and r_{ij} is an interatomic distance.

(b) A modified Kitaigorodskii potential function[16]:

Table 1. The refined potential parameters of dehydrated $Mn_{4.5}Na_9$-A

	Parameter		Parameter
$r^{o}_{T\text{-}O(1)}$	1.8611	$\varepsilon_{O\text{-}O}$	0.4481
$r^{o}_{T\text{-}O(2)}$	1.6778	$\varepsilon_{O\text{-}Na}$	0.1980
$r^{o}_{T\text{-}O(3)}$	2.2122	$\varepsilon_{O\text{-}Mn}$	0.2182
$\sigma_{O\text{-}O}$	2.776	$k_{T\text{-}O(1)}$	0.4464
$\sigma_{O\text{-}Na}$	1.1335	$k_{T\text{-}O(2)}$	0.5508
$\sigma_{O\text{-}Mn}$	2.5930	$k_{T\text{-}O(3)}$	0.1818

Table 2. The optimized positions and energies of framework atoms and ions in dehydrated and hydrated $M_{n4.5}Na_9$-A (in parenthesis; the energy calculated at crystallographic position[1])

atom	dehydrated state			(energy)	hydrated state			(energy)
	x(Å)	y(Å)	z(Å)	(kcal/mol)	x(Å)	y(Å)	z(Å)	(kcal/mol)
T_1	1.6071	6.0875	3.8595	-197.95				
	(1.6071	6.0875	3.8595	-197.75)	(1.5826	6.1340	3.8890	-236.40)
O_3	2.2086	7.4724	4.6502	1.94				
	(2.1306	7.4633	4.7117	2.90)	(1.9751	7.5203	4.7477	-26.10)
O_2	2.5164	6.0273	2.5067	3.68				
	(2.4837	6.0875	2.4837	3.89)	(2.5395	6.1340	2.5395	-55.21)
T_2	3.8586	6.0891	1.6072	-186.21				
	(3.8595	6.0875	1.6071	-186.20)	(3.8890	6.1340	1.5826	-234.18)
O_3	4.7127	4.7127	2.1287	-8.07				
	(4.7117	4.7117	2.1306	-8.02)	(4.7477	4.7477	1.9751	-65.58)
O_1	3.6721	6.0501	-0.0232	8.57				
	(3.6769	6.0875	0.0000	8.65)	(3.4288	6.1340	0.0000	-102.84)
E_{tot}				-378.04				(-720.31)
				(-376.73)				

Table 3. The optimized positions and interaction energies of water molecules in hydrated $Mn_{4.5}Na_3$-A

water group	water molecule	atom	coordinate (Å) X	Y	Z	energy (kcal/mol)
		H	2.0991	2.1160	1.7013	
W(I)	w1	O	2.4904	2.4904	2.4904	-6.97
		H	3.1535	1.8556	2.7557	
		H	1.8036	-2.0272	-2.0101	
	w2	O	2.4904	-2.4904	-2.4904	-6.16
		H	3.1095	-1.8102	-2.7442	
	w3	H	8.0360	-2.0272	-2.0102	
		O	-2.4904	2.4904	-2.4904	-4.22
		H	3.1095	-1.0102	-2.7442	
		H	-2.7853	-1.7081	2.9601	
	w4	O	-2.4904	-2.4904	-2.4904	-3.11
		H	-1.7579	-2.1851	1.9561	
		H	-1.8114	-2.9361	-2.9953	
	w5	O	-2.4904	-2.4904	-2.4904	-2.31
		H	-3.3003	-2.9462	-2.7226	
		H	-3.2812	2.8468	2.8958	
	w6	O	-2.4904	2.4904	2.4904	-5.81
		H	-1.7833	2.7380	3.0847	
		H	-0.6856	-2.5032	-4.0528	
	w7	O	0.0100	-2.2450	-3.4473	-6.23
		H	-0.4229	-1.6680	-2.8180	
		H	-3.0566	-3.9554	0.0151	
	w8	O	-2.2450	-3.4473	0.0100	-7.15
		H	-2.2165	-3.0475	-0.8574	
		H	0.0309	2.8658	4.1757	
	w9	O	0.0100	2.2450	3.4473	-6.94
		H	-0.2438	1.4138	3.8476	
		H	0.3028	-1.8141	4.2515	
	w10	O	0.0100	-2.2450	3.4473	-8.78
		H	0.8122	-2.3993	2.9517	
		H	0.4724	6.2267	-0.7666	
W(II)	w11	O	0.0100	5.3979	-0.8710	-10.35
		H	0.9183	5.6348	-0.8482	
		H	-0.8144	-5.3572	0.3865	
	w12	O	0.0100	5.3979	0.8710	-11.80
		H	0.1194	-6.3254	1.0807	
		H	2.9709	3.9863	-0.3030	
	w13	O	2.2450	3.4473	0.0100	-9.40
		H	1.4600	3.9484	-0.2184	
		H	-4.3042	-4.3129	-4.2993	
	w14	O	-4.8581	-4.8581	-4.8581	-10.02
		H	-5.7492	-4.6908	-4.5451	
		H	-1.5366	4.0898	0.0041	

water group	water molecule	atom	coordinate (A) X	Y	Z	energy (kcal/mol)
	w15	O	-2.2450	3.4473	0.0100	-10.66
		H	-3.0039	3.9293	0.3395	
		H	2.0489	-4.3055	0.3905	
	w16	O	2.2450	-3.4473	0.0100	-10.17
		H	2.2155	-2.8452	0.7544	
		H	-2.6964	0.3921	1.7903	
	w17	O	-3.4473	0.0100	2.2450	-11.08
		H	-3.5909	0.5863	2.9958	
		H	-4.2567	-0.0543	-2.7523	
	w18	O	-3.4473	0.0100	-2.2450	-9.19
		H	-2.9592	-0.7826	-2.4740	
		H	3.8073	-0.2330	3.0990	
	w19	O	3.4473	0.0100	2.2450	-9.96
		H	4.2048	0.0360	1.6634	
		H	3.9072	0.3738	-3.0016	
	20	O	3.4473	0.0100	-2.2450	-11.83
		H	4.0258	0.1813	-1.5049	
		H	0.6254	2.9578	-3.6012	
	w21	O	0.0100	2.2450	-3.4473	-10.83
		H	0.1239	1.6627	-4.2031	
		H	4.6262	4.3352	5.6256	
W(III)	w22	O	4.8581	4.8581	4.8581	-20.43
		H	5.6382	4.4384	4.0548	
		H	4.3960	-5.6337	-4.5219	
	w23	O	4.8581	-4.8581	-4.8581	-20.76
		H	4.2759	-4.5135	-5.5329	
		H	-4.5806	4.1901	-5.4948	
	w24	O	-4.8581	4.8581	-4.8581	-16.22
		H	-5.6481	4.4856	-4.4631	
		H	-4.6240	-4.3323	5.6260	
	w25	O	-4.8581	-4.8581	4.8581	-14.89
		H	-5.6281	-4.4157	4.4963	
		H	-5.3298	0.3788	0.8282	
	w26	O	-5.3979	0.8710	0.0100	-16.66
		H	-6.2737	0.6685	-0.3192	

($V_{d-r(kil)}$) was used for the description of dispersion and repulsion between water molecules and framework atoms or ions in hydrated structure.

$$V_{d-nkl0}=\sum_{i}\sum_{j>i} k_i k_j [-A/Z^4+(1-\delta_i/N_i^{val})(1-\delta_j/N_j^{val})\,C\exp(-\alpha Z)] \quad (13)$$

where $Z=R_{ij}/R^{O'}$ and $R^{O'}{}_{ij}=[(2R_i^w)(2R_j^w)]^{1/2}$ where R_i^w and R_j^w are the van der Walls radii of atom i and j. The parameter A, C, and α are 0.214 kcal/mol, 47000 kcal/mol, and 12.35, respectively. The multiplication factor k_i, and k_j represents the nature of the interacting atom i *and*

j. The values used in this work are $K_H=1.00$, $K_O=1.36$[17], $K_T=2.10$, $K_{Na}=2.86$[17], δ_i is the net charge of atom i, and Ni^{val} is the number of valence electrons of neutral atom i. This modification scheme is also applied to the case of hydrogen bond.

The location of each ion and water molecule has been optimized by minimizing the interaction ennergy using the optimization program VA10A developed by Fletcher.[13]

The refined potential parameters of dehydrated $Mn_{4.5}Na_3$-A are listed in *Table* 1 and the optimized positions and interaction energies of framework atoms in dehydrated and hydrated $Mn_{4.5}$ Na_3-A are listed in *Table* 2. The binding energies of water molecules in hydrated $Mn_{4.5}Na_3$- A at their optimized positions are shown at *Table* 3.

RESULTS AND DISCUSSION

Typical results of powder x-ray diffraction and infrared spectroscopy experiments on Mn^{2+}- exchanged zeolite A are shown in *Fig.* 1 and 2.

It was reported that when the thermally unstable Ba^{2+}-exchanged zeolite A are heated at 300°C, all x-ray diffraction peaks disappear because of the collapse of zeolite framework.[4, 5] Ni^{2+}-exchanged zeolite A in our work were also thermally unstable. When Ni_5Na_2-A zeolite is heated at 300°C, no x-ray diffraction peaks are observed. But Mn^{2+}-exchanged zeolite A (Mn_x Na_{12-2x}-A; $x=1$, 2, and 4.5) heated at 300°C for 5 hours shows almost the same strong peak intensities and patterns of x-ray diffraction regardless of the contents of Mn^{2+} ion (see *Fig.* 1). This means that the framework of Mn^{2+}-exchanged zeolite A is stable even after heating and dehydration.

In recent years, many systematic investigations on the framework structures of various synthetic zeolites have been carried out by infrared spectroscopic methods.[18, 19]. The interpretations of these

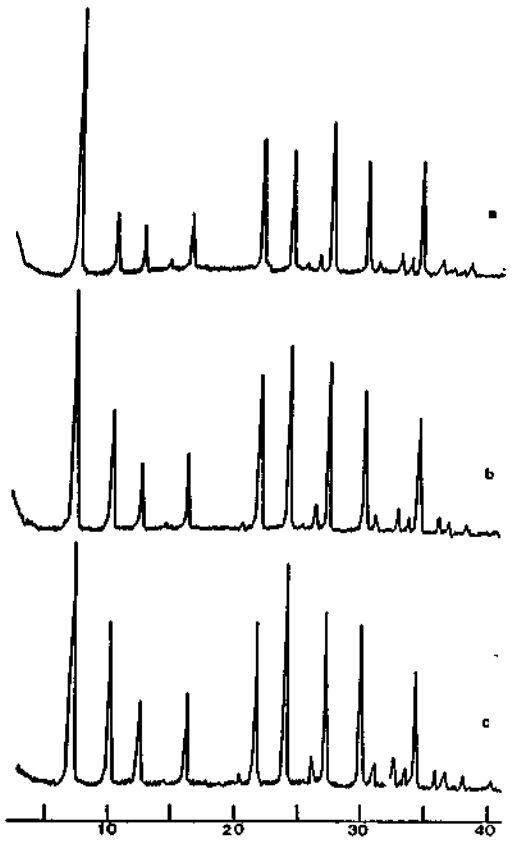

Fig. 1. The x-ray diffraction patterns of Mn^{2+}-exchanged zeolite A heated at 300°C. ; $Mn_{4.5}Na_3$ A, b; Mn_2Na_8 A, c; Mn_1Na_{10} A.

spectra are based on assignment of infrared bands to certain structural groups in various zeolite frameworks.

In general, infrared spectra of zeolites consist of strongest asymmetric streching vibration of internal tetrahedron (Al, Si)O_4 found at 950-1250 cm^{-1}, next strong T-O bending mode and symmetric streching vibration modes of internal tetrahedron (TO_4) at 420-500 cm^{-1} and 650- 820 cm^{-1}, respectively, and the vibration mode due to double ring of external linkage in the region of 500-650 cm^{-1}, etc.[20]

The hydrated Mn_1Na_{10}-A and partially dehydrated Mn_xNa_{12-2x}-A ($x=1$, 2, and 4.5) showed strong absorption bands at 675 cm^{-1} (T-O bending), 550 cm^{-1} (vibration of D4R), 675 cm^{-1}

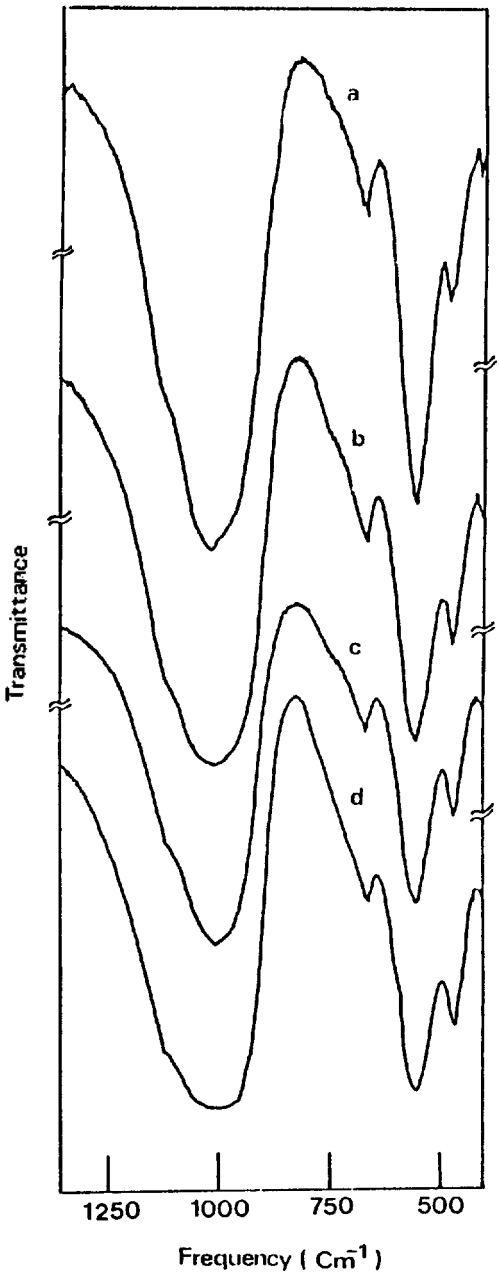

Fig. 2. Infrared spectra of Mn^{2+}-exchanged zeolite A, a,b,c; heated at 300°C, a; $Mn_{4.5}Na_3$ A, b; Mn_2Na_8 A, c; Mn_1Na_{10} A, d; $Mn_1Na_1Na_{10}$ A (unheated).

(symmetric streching of internal tetrahedron, (Al, Si)O_4, and 1020 cm^{-1} (asymmetric streching of internal tetrahedron) in *Fig.* 2.

In our earlier study[5], when Ba_6-A is heated above 200°C, the bands found in the above regions almost disappeared. This might be closely related to the collapse of zeolite frameworks upon dehydration. The fact that infrared spectra related to the framework of Mn^{2+}-exchanged zeolite A heated at 300°C remains with strong intensities without any great changes discloses that Mn^{2+}-exchanged zeolite A is thermally stable.

Using the refined potential parameters and potential energy functions, the coordinates and binding energies of the framework atoms of dehydrated and hydrated $Mn_{4.5}Na_3$-A were calculated and then compared with crystallographic data. The optimized coordinates are agreed well with the x-ray crystallographic results.[1]

The sum of the binding energies of framework atoms in the reduced system[21] (AlO_2SiO_2) of the hydrated $Mn_{4.5}Na_3$-A was -720.31 kcal/mol and that of the dehydrated $Mn_{4.5}Na_3$-A was -378.04 kcal/mol. This indicates that the hydrated structure is more stable by 342.27 kcal/mol.

The sum of the binding energies of the framework atoms of dehydrated $Mn_{4.5}Na_3$-A is almost the same as those of dehydrated Ca_6-A (-373.02 kcal/mol) and Co_4Na_4-A (-365.39 kcal/mol)[22] which are known to be stable in their dehydrated state. Therfore, it may be concluded that Mn^{2+}-exchanged zeolite A is thermally more stable than others due to the greater binding energy of its framework even in dehydrated state.

The sum of binding energies of framework atoms in dehydrated Ni_3 Na_6-A is -257.17 kcal/mol which is smaller than that of Mn^{2+}-exchanged zeolite A. The lower binding energy of Ni^{2+}-exchanged zeolite A is responsible for the accumulation of protons produced by hydrolysis of Ni $(H_2O)_n^{2+}$. It is proposed that the attack of protons to framework oxygen atoms makes the framework of zeolite unstable.

In general, the cations in the zeolite structures move toward the framework oxygen atoms upon dehydration.[4, 5]

Table 4. The number and average binding energies of three different groups of water molecules in hydrated $Mn_{4.5}Na_3$-A

group	Tm of DSC (°C)	Number of water molecules by TG	by calculation	Average binding energy by calculation (kcal/mol)
W(I)	87.0	9.86	10	-5.77
W(II)	147.8	10.94	11	-10.48
W(III)	217.0	5.20	5	-17.79
Total binding energy of 26 H_2O by calculation;				-261.193
Dehydration energy per unit cell by DSC;				253.76

It is known that when Mn^{2+}-exchanged zeolite A is dehydrated, Mn^{2+} ions move from the deep position in -cage to near the center of 6-ring plane. The ionic radius of Ba^{2+} ion is 1.34 Å. Since the large Ba^{2+} ions can not move into the vicinity of the 6-ring plane, Ba^{2+} ions can not form good coordination bonds with the framework oxygens. Therefore, the hydrated Ba^{2+}- exchanged zeolite A is unstable upon dehydration. However, the relatively small Mn^{2+} ions (ionic radius of Mn^{2+} = 0.81 Å) can easily approach and make stable bonds with framework oxygens, O(3)'s. Therefore, the Mn^{2+}-exchanged zeolite A is stable even after heating and dehydration.

The position and binding energy of twenty six water molecules are calculated and are shown in *Table* 3. Water molecules can be easily classified into three major catergories by the type of bonds and binding energies. That is, W(I) group where water molecules are hydrogen bonded with other water molecules or framework oxygens, W (II) group where water molecules are coordinated to Na^+ ions and also hydrogen bonded with either adjacent water molecules or framework oxygens, and W(III) group where water molecules are coordinated to Mn^{2+} ions and hydrogen bonded.

Mn^{2+} ions in the hydrated $Mn_{4.5}Na_3$-A form a trigonal bipyramidal structure with three framework oxygen, O(3)'s and two water

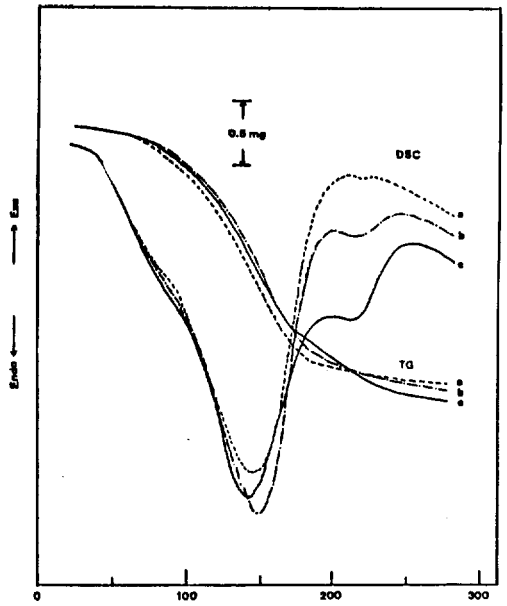

Fig. 3. The TG and DSC thermograms of hydrated Mn^{2+}-exchanged zeolite, A, a; Mn_1Na_{10} A, b; Mn_2Na_8 A, c; $Mn_{4.5}Na_3$ A, heating rate; 10 °C/min.

molecules. Water molecules in the α-cage form a distorted dodecahedron. *Table* 4 shows that there are ten water molecules in W(I) group, eleven water molecules in W(II) group, and five water moleucles in W(III) group. The average binding energies are -5.77 kcal/mol, -10.48 kcal/mol, and -17.79 kcal/mol for W(I), W(II), and W(III) groups, respectively. As expected, the W(III) group of water molecules has strong bonds, while the W(I) group has weak bonds.

The sum of dehydration energies of twenty six water molecules per unit cell is approximately 253.76 kcal. This energy amount is almost the same as the absolute value of the calculated total binding energies of twenty six water molecules (-261.93 kcal).

There appeared three endothermic peaks in the DSC thermograms of Mn^{2+}-exchanged zeolite A.

When heated at the rate of 10°C/min, first endo peak appeared at approximately 82°C as a shoulder, second endo peak at 147.8°C, and third endo peak at 217°C (see *Table* 5 and *Fig.* 3)

Table 5. The activation energy in the dehydration reaction of hydrated Mn^{2+}-exchanged zeolite A by Ozawa method

	Heating rate (°C/min)	1st endo peak Tm (°C)	1st endo peak Ea (kcal/mol)	2nd endo peak Tm (°C)	2nd endo peak Ea (kcal/mol)	3rd endo peak Tm (°C)	3rd endo peak Ea (kcal/mol)
	6	68.0		136.4			
Mn_1Na_{10}-A	10	79.0	5.17	147.0	8.26		
	14	87.5		155.1			
	18	93.0		157.7			
	6	73.0		140.1		207.0	
Mn_2Na_8-A	10	85.5	5.26	150.1	9.08	216.0	14.30
	14	93.5		154.8		220.5	
	18	98.0		161.2		224.5	
	6	73.0		134.3		206.0	
$Mn_{4.5}Na_3$-A	10	82.0	7.02	141.9	9.86	210.8	15.72
	14	87.0		147.8		217.0	
	18	92.0		152.7		221.0	

As the content of Mn^{2+} ions per unit cell increased, the area of third endo peak at 217°C increased while that of second endo peak at 147°C decreased. These phenomena suggest that the first endo peak at 82°C is due to the dehydration of W(I) group, the second endo peak at 147°C due to the dehydration of W(II) group, and the third endo peak at 217°C due to the dehydrationn of W(III) group coordinated strongly to Mn^{2+} ions.

Ozawa[23] proposed that the activation energies may be estimated from the shifting of maximum deflection temperature (T_m) of DSC peaks as the heating rate (ϕ) is changed. We can evaluate the activation energy using the following Ozawa's equation.

$$\log \phi + 0.4567\, E_a/RT_m = \text{constant}$$

Plotting $\log \phi$ versus $1/T_m$ gives a straight line with a slope of $0.4567\, E_a/R$, and the activation energy (E_a) can be calculated from the slope. The activation energy in the dehydration of hydrated Mn^{2+}-exchanged zeolite A was obtained by Ozawa's method

Fig. 4 shows good linear relationships for all endothermic peaks in the dehydration reaction of $Mn_{4.5}Na_3$-A.

Table 5 shows that the activation energies of dehydration is greater at the higher dehydration temperature. This indicates that the greater are the binding energies, the larger activation energies are required for the dehydration of these water molecules.

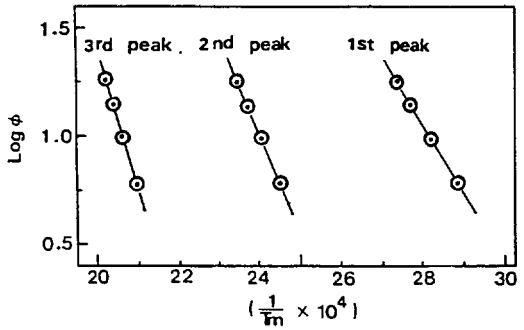

Fig. 4. Ozawa's plot of $\log \phi$ *vs.* $1/T_m$ for the hydrated $Mn_{4.5}Na_3$ A.

To summarize the present works, Mn^{2+}- exchanged zeolite A is stable even after heating and dehydration. The binding energies for the framework atoms of Mn^{2+}-exchanged zeolite A are almost the same as thermally stable Ca^{2+}- or Co^{2+}-exchanged zeolite A. The thermal stability of Mn^{2+}-exchanged zeolite A may be due to the fact that Mn^{2+} ion can have good coordination environments with the framework oxygen, O(3) after dehydration. The authors confirmed that Ni^{2+}-exchanged zeolite A is thermally very unstable. The instability of Ni^{2+}-exchanged zeolite A may due to the accumulation of H^+ ions

which are produced by the hydrolysis of $Ni(H_2O)_n^{2+}$ ion. The positions and binding energies of twenty six water molecules per unit cell were calculated and determined. These water molecules could be classified into three groups; W(I), W(II), and W(III) by the type of bonding and bond energies. The magnitude of their binding energies and the activation energies of dehydration decrease in the order of W(III) > W(II) > W(I).

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