Articles

A Study on the Structure and Thermal Property of Cu^{2+} and NH_4^+ Ion-Exchanged Zeolite A

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The frameworks of $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$-A·$zH_2O$ which were prepared by the ion-exchange of zeolite A with ammoniac cupric nitrate solution are more stable than those of Cu_xNa_{12-2x}-A obtained by the ion exchange with aqueous cupric nitrate solution are more stable than those of Cu_xNa_{12-2x}-A obtained by the ion exchange with aqueous cupric nitrate solution. An energetic calculation was made on the relatively stable $(CuOH^+)_2(NH_4^+)_{10-}$A·$2H_2O$ prepared by the partial evacuation of $(Cu(NH_3)_3OH^+)_2(NH_4^+)_{10}$-A·$zH_2O$. The mean stabilization energies of water, OH-, and NH_4^+ ions are -30.23 kcal/mol, -60.24 kcal/mol, and -16.65 kcal/mol, respectively. The results of calculation were discussed in terms of framework stability. The $(Cu(NH_3)_3OH^+)_2(NH_3^+)_{10}$-A·$zH_2O$ zeolite shows two step deammoniation reactions. The first deammoniation around 210℃ (third DSC peak) was attributed to the decomposition of $[Cu(NH_3)_3OH)]^+$ ion and the second one around 380℃ (fourth DSC peak) was ascribed to the decomposition of NH_4^+ ion. The activation energies of the first and second deammoniation reactions were 99.75 kJ/mol and 176.57 kJ/mol, respectively.

Introduction

Zeolites are a class of aluminosilicates with relatively rigid anionic frameworks which have the well-defined channels and cavities,[1] and they contain exchangeable cations and removable guest molecules inside their framework.

They are used widely as catalysts, ion exchangers, and selective sorbing agents[2] due to their structural characteristics and unusual physicochemical properties.

The framework of zeolite A can be considered as a rigid polydentate ligand within which the exchangeable 12 Na^+ ions are located at suitable sites inside the framework. The structure of Zeolite A can be described in terms of a simple cubic arrangement of the sodalite unit (β-cage) enclosing a cavity with a free diameter of 6.6 Å. The cubic D4R units ($Al_4Si_4O_{16}$) are placed in the centers of edges of the cube (12.3 Å) and are bridged with sodalite units. A large cavity (α-cage) with a free diameter of 11.4 Å is formed in the center of unit cell.

The most definite structural informations on the zeolites are obtained from single crystal X-ray diffraction and neutron diffraction. Infrared,[3] Raman,[4] EPR,[5] and solid NMR[6] spectroscopy are also useful means to study the zeolite structure.

Recently, many theoretical studies have been made to obtain the structural and energetic informations on the zeolite framework using some potential functions.[7-9] and molecular orbital method.[10-12]

It is generally believed that the nature of cations, such as their locations, coordination environments, and oxidation state are responsible for the profound effects on the physicochemical properties of zeolites.[13] Sometimes, the ion-exchange of zeolite is accompanied by dramatic alterations of stability, adsorption behavior, catalytic activity, and other physicochemical properties.

It has been reported that the structures of some cation-exchanged zeolites are lost when they are evacuated at higher temperature due to their instability of their framework.[14,15]

In this work, the framework stability and deammoniation reaction of hydroxotriammineCu(II)- and NH_4^+-exchanged zeolite A, $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$-A·$zH_2O$, will be examined by means of powder X-ray diffraction, FT-IR, and thermal analysis. At the same time, an energetic calculation will be made on the relatively stable $(CuOH^+)_2(NH_4^+)_{10}$-A·$2H_2O$ prepared by the partial evacuation of $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$-A·$zH_2O$ (where $x=2.0$), and the calculated structure and stabilization energies will be discussed in terms of the framework stability.

Experimental

Since the extensive ion exchange of Cu^{2+} ion into zeolite A with aqueous cupric nitrate solution damage the zeolite structure, ammoniac cupric nitrate solution was used for ion exchange in this work.

The ion-exchange of zeolite A with ammoniac cupric nitrate solution which was prepared by adding 5 m*l* of 16 M NH_4OH to 95 m*l* of 0.1 M $Cu(NO_3)_2$ solution yielded hydroxotriammineCu(II)- and NH_4^+- exchanged zeolite A, $(Cu(NH_3)_3OH^-)_x(NH_4^+)_{12-x}$-A·$zH_2O$ ($x=0.85$, 1.24, and 2.00). Further ion-exchange above $x=2.0$ was not achieved with this ion-exchanging solution at room temperature.

Powder X-ray diffractograms within $2°<2θ<50°$ were recorded on the Rigagu Geigerflex D/Max diffractometer with Ni-filtered CuKα radiation. All samples were scanned at the rate of 2° (2θ) per minute under the condition of time constant=1, CPS/FS: 2000, the power: 40 kV and 30 mA.

The IR spectra in the region of 400-2000 cm^{-1} were obtained using Mattson-Polaris TM spectrometer.

The thermograms of differential scanning calorimeter

(DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTA) were recorded on a Rigagu Thermal Analyzer TAS 100 system at ambient.

Calculation

Model Compound

The geometry of partially dehydrated $(CuOH^+)_{2.0}(NH_4^+)_{10.0}$-A·$2H_2O$ was taken from X-ray crystallographic study.[3]

Optimization

The positions and stabilization energies of NH_4^+, OH^-, and water molecules inside partially dehydrated $(CuOH^+)_{2.0}$ $(NH_4^+)_{10.0}$-A·$2H_2O$ were determined using some potential functions and optimization program.[16]

The total stabilization energy (V_{tot}) is expressed as a sum of electrostatic energy (V_{el}), polarization energy (V_{pol}), dispersion energy (V_{disp}), and repulsion energy (V_{rep}).

$$V_{tot} = V_{el} + V_{pol} + V_{disp} + V_{rep}$$

Electrostatic energy(V_{el}). The net charges of the atoms are considered as point charge. Electrostatic energy is given as

$$V_{el} = \sum_i^{(1)} \sum_j^{(2)} (\delta_i \delta_j)/DR_{ij}$$

where δ_i and δ_j are the charges of the ith and jth atoms, respectively and R_{ij} is their interatomic distance. The dielectric constant D was determined by comparing the calculated average binding energy of water molecules with the dehydration enthalpy measured by DSC. The optimum value of dielectric constant in this work was 2.9. i and j represent framework atoms.

The net atomic charges are calculated using Hueey's electronegativity set and Sanderson's electronegativity equalization method. The calculated net atomic charges are: δ_{T1} = 0.5861, δ_{T2} = 0.5861, δ_{Na} = 0.625, $\delta_{O(1)}$ = -0.4509, $\delta_{O(2)}$ = -0.4548, $\delta_{O(3)}$ = -0.4458, δ_{Cu} = 1.250.

Polarization energy(V_{pol}). Polarization energy is given as follows:

$$V_{pol} = -1/2 \sum_i^{N^-} \bar{a}_i \left[\left(\sum_{j \neq i} \bar{\epsilon}_{ij}^{\rightarrow x} \right)^2 + \left(\sum_{j \neq i} \bar{\epsilon}_{ij}^{\rightarrow y} \right)^2 + \left(\sum_{j \neq i} \bar{\epsilon}_{ij}^{\rightarrow z} \right)^2 \right]$$

Table 1. The Coordinates of Framework Atoms and Cu^{2+} Ions in $(Cu(OH)^+)_2(NH_4^+)_{10}$-A·$2H_2O$[3]

Framework atom	Coordinate		
	x (Å)	*y* (Å)	*z* (Å)
T₁	1.5694	6.1400	3.8805
O(3)	1.9230	7.5178	4.7622
O(2)	2.5395	6.1400	0.0000
T₂	3.8805	6.1400	1.5694
O(3)'	4.7622	4.7622	1.9230
O(1)	3.3795	6.1400	0.0000
Cu(1)	3.8498	3.8498	-3.8498
Cu(2)	-3.8498	-3.8498	3.8498

$$V_{pol(i,j)} = V_{pol(i \rightarrow j)} + V_{pol(j \rightarrow i)}$$

where $\bar{a}_i$ is the atomic polarizability of the ith atom and $\bar{\epsilon}_{ij}$ is the electric field created by jth atom at the position of ith atom in the x-direction

Dispersion and repulsion energy $(V_{d \cdot r})$. A modified Kitaigorodskii potential function[17] was used for the description of dispersion and repulsion between all i and j atom.

$$V_{d \cdot r} = V_{dis} + V_{rep}$$

$$V_{d \cdot r} = \sum_i \sum_{j > i} k_i k_j \left[-A/Z^6 + (1 - \delta_i/N_i^{val}) \right.$$
$$\left. (1 - \delta_j/N_j^{val})C \exp(-\alpha R_{ij}/R_{ij}^{o'}) \right]$$

where R_{ij} is an inter atomic distance, $Z = R_{ij}/R_{ij}^{o'}$ and $R_{ij}^{o'} = [(2R_i^o)(2R_j^o)]^{1/2}$ and R_i^w, R_j^w are the van der Waals radii of atom i and j. The parameter A, C, and α are 0.214 kcal/mol, 47,000 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, k_T = 2.10, k_{Na} = 2.86, $k_{Cu(II)}$ = 3.00. δ_i is the net charge of atom i, and N_i^{val} is the number of valence electrons of neutral atom i. This modified function was also applied to the case of hydrogen bond.

Table 1 shows the coordinates of framework atoms and Cu^{2+} ions in partially dehydrated $(Cu(OH)^+)_2(NH_4^+)_{10}$-A·$2H_2O$. The optimized positions and stabilization energies of water

Table 2. The Opitimized Positions and Stabilization Energies of OH^- Ions and Water Molecules in $(CuOH^+)_2(NH_4^+)_{10}$-A·$2H_2O$ in parenthesis; crystallographic data[3]

Group	Atom	Coordinate			Stabilization
		x (Å)	*y* (Å)	*z* (Å)	energy (kacl/mol)
w(1)	H	2.6628	2.8481	-1.7454	
	O	2.6828(2.6844)	2.6824(2.6844)	-2.6880(-2.6844)	-29.716
	H	1.7849	2.4317	-2.9056	
w(2)	H	-2.6997	-2.5383	1.7391	
	O	-2.6851(-2.6844)	-2.6829(-2.6844)	2.6853(2.6844)	-30.747
	H	-1.8376	-3.0960	2.8517	
OH(1)	O	5.0907(5.0937)	5.0899(5.0937)	-5.1005(-5.0937)	-63.857
	H	5.4187	5.8345	-5.6047	
OH(2)	O	-5.0950(-5.0950)	-5.0908(-5.0950)	5.0953(5.0950)	-58.626
	H	-5.5955	-5.0908	5.7906	

Table 3. The Optimized Positions and Stabilization Energies of NH_4^+ Ions in $(CuOH^+)_2(NH_4^+)_{10}$-A·$2H_2O$. in Parenthesis; Crystallographic Data[3]

Group	Atom	Coordinate			Stabilization energy (kacl/mol)
		x (Å)	y (Å)	z (Å)	
NH_4(I)	N	3.0842(3.0860)	3.0874(3.0864)	3.0864(3.0860)	
	H	2.9878	4.0063	2.6787	
	H	2.3813	2.9599	3.8004	−16.378
	H	4.0021	2.9965	3.4980	
	H	2.9656	2.3867	2.3687	
//	N	−3.0863(−3.0868)	−3.0879(−3.0860)	−3.0833(−3.0860)	
	H	−3.1840	−2.1673	−3.4873	
	H	−3.2063	−3.7863	−3.8031	−16.485
	H	−3.7888	−3.2176	−2.3688	
	H	−2.1681	−3.1804	−2.6740	
//	N	−3.0868(−3.0860)	3.0855(3.0860)	3.0851(3.0860)	
	H	−3.1814	4.0062	2.6796	
	H	−3.7904	2.9579	3.7982	−16.801
	H	−2.1694	2.9927	3.4971	
	H	−3.2059	2.3874	2.3656	
//	N	3.0842(3.0866)	−3.0855(−3.0860)	3.0883(3.0860)	
	H	3.0687	−2.9528	2.0871	
	H	2.1391	−3.0754	3.4444	−16.209
	H	3.6137	−2.3406	3.5182	
	H	3.5153⁻	−3.9732	3.3033	
//	N	3.0842(3.0860	−3.0892(−3.0860)	−3.0846(−3.0860)	
	H	2.9853	−2.1694	−3.4901	
	H	2.9653	−3.7890	−3.8032	−18.247
	H	2.3829	−3.2188	−2.3694	
	H	4.0033	−3.1796	−2.6758	
//	N	−3.0868(−3.0868)	3.0824(3.0860)	−3.0888(−3.0860)	
	H	−3.1025	3.0824	−2.0901	
	H	−4.0138	3.8378	−3.4077	−16.984
	H	−2.4470	2.3318	−3.3065	
	H	−2.7842	3.9280	−3.5509	
NH_4(II)	N	5.7504(5.7507)	0.4170(0.4175)	−0.4180(−0.4175)	
	H	5.7506	−0.5867	−0.4178	
	H	6.9378	0.8016	−0.1901	−16.361
	H	5.7112	0.6450	0.5653	
	H	4.9460	0.8082	−0.8870	
//	N	−0.4095(−0.4175)	5.6506(5.7507)	−0.4145(−0.4175)	
	H	−0.4398	5.9903	0.5361	
	H	−0.7001	4.6838	−0.4365	−15.223
	H	0.5333	5.3726	−0.7689	
	H	−1.0306	6.2024	−0.9889	
//	N	−0.4167(−0.4175)	0.4167(0.4175)	5.7505(5.7507)	
	H	−0.4669	−0.0815	6.6276	
	H	0.5341	0.4049	5.4100	−16.548
	H	−0.7126	1.3724	5.8890	
	H	−1.0214	−0.0290	5.0753	
NH_4(III)	N	−4.7597(−4.7585)	4.7530(4.7530)	−4.7628(−4.7628)	
	H	−4.7697	4.8481	−3.7574	
	H	−5.6970	4.5741	−0.0938	−17.228
	H	−4.1589	3.9836	−5.0220	
	H	−4.4133	5.6060	−5.1781	

(a)

(b)
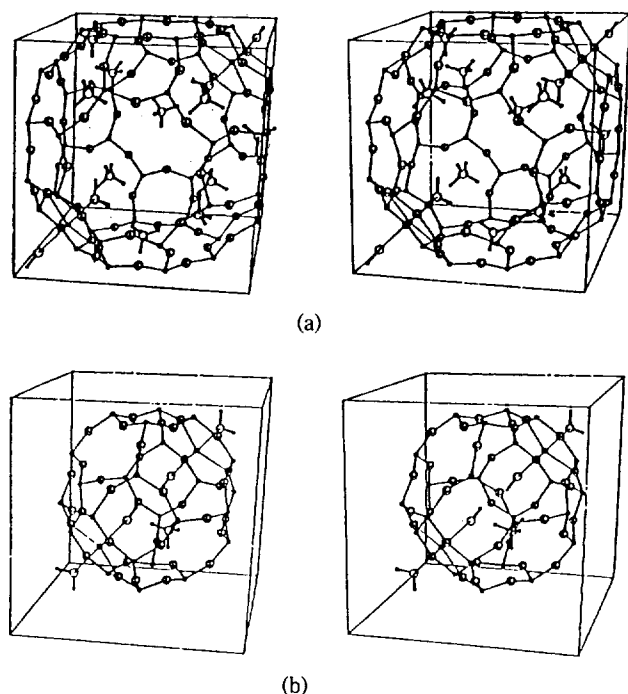
Figure 1. The stereoview of the large cavity (a) and sodalite cage (b) of partially dehydrated $(CuOH^+)_{2.0}(NH_4^+)_{10.0}$-A·$2H_2O$.

molecules and OH^- ions are listed in Table 2, and those of NH_4^+ ions are shown in Table 3, respectively.

Figure 1 shows the stereoview of the α-cage and sodalite unit of partially dehydrated $Cu(OH^+)_{2.0}(NH_4^-)_{10.0}$-A·$2H_2O$ plotted using ORTEP program.[18]

Results and Discussion

Calculation. The optimized positions and stabilization energies of NH_4^+, OH^-, and water molecules inside the partially dehydrated $(CuOH^+)_2(NH_4^+)_{10}$-A·$2H_2O$ were obtained using above potential energy functions and optimization program. The calculated positions of nitrogen atoms in NH_4^+ and those of oxygen atoms in both OH- and water molecules are agreed well with crystallographic data[3] (in parenthesis of Table 2 and 3).

This calculation show that Cu^{2+} ion lies on a three-fold axis, nearly in the O(3) plane of a 6-ring and this is coordinated equatorially with three O(3) framework oxygens and also axially with one H_2O and one OH^- ion in nearly trigonal bipyramidal manner. This agresse well with Herman's report.[19]

He observed that Cu^{2+} ions are coordinated octahedrally with framework oxygens and water molecules in hydrated state but upon evacuation, their coordinations are changed in trigonal bypyramidal manner having three coordinations with 6-ring oxygens and two coordinated water molecules axially.

The calculated bond angles of O(3)-Cu-O(4) and O(3)-Cu-O(5) are 91° and 88.5°, respectively. The distance between Cu^{2+} ion and oxygen atom O(5) of water molecule was 2.155 Å. The distance is good agreement with the single crystal X-ray diffraction data 2.150 Å.

The stabilization energies of w(1) and w(2) water molecules which are located in α-cage near 6-ring along c_3-axis are

−29.716 kcal/mol and −30.747 kcal/mol, respectively.

The OH^- ions lie in the sodalite unit along c_3-axis and they are coordinated axially with Cu^{2+} ion more strongly than H_2O. The mean stabilization energy of OH^- ion is −61.242 kcal/mol. This large stabilization energy of OH^- ion will contribute to stabilize the framework of partially dehydrated $(CuOH^+)_2(NH_4^+)_{10}$-A·$2H_2O$.

The distance between Cu^{2+} and oxygen (O(4)) of OH^- is 2.019 Å and can be compared with crystallographic data (2.020 Å).

The nitrogen atoms of $NH_4(I)$ group locating in large cavity are 2.64 Å apart from three O(3) framework oxygen atoms, and three hydrogen atoms of ammonium ion of this group are directed toward O(3) framework oxygen atoms to make hydrogen bonds. Three NH_4^+ ions of $NH_4(II)$ group lies at a site near the plane of 8-ring. The nitrogen atoms of this group are 3.02 Å apart from two O(1) and 3.03 Å apart from one O(2), respectively.

The similar locations of NH_4^+ ions in partially dehydrated $(CuOH^+)_2$ $(NH_4^+)_{10}$-A·$2H_2O$ had been found in dehydrated $(NH_4)_{12}$-A zeolite.[20] The remaining one NH_4^- ion of $NH_4(III)$ group is located in the sodalite unit opposite a 6-ring which was already associated with one NH_4^+ ion of $NH_4(II)$ group. The nitrogen atom of $NH_4(III)$ group is 2.84 Å apart from three O(3) framework oxygen.

The order of mean stabilization energy of ammonium ions in each group is $NH_4(III)$: −17.228 kcal/mol > $NH_4(I)$: −16.851 kcal/mol > $NH_4(II)$: −16.004 kcal/mol.

Framework Stability. Some of the cation-exchanged zeolite A, such as K^+, Mg^{2+}, Ca^{2+}, and Sr^{2+}-exchanged zeolite A are stable upon dehydration at higher temperature, but some others, such as Ba^{2+}, Fe^{2+}, and Ni^{2+} ion-exchanged zeolite A are thermally unstable and their framework are almost collapsed by dehydration around 200℃.[21]

In this work, the X-ray diffraction and FT IR experiment show that the hydroxotriammineCu(II)- and NH_4^+-exchanged zeolite-A, $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$-A·$zH_2O$, which were prepared by the ion exchange of zeolite A with ammoniac cupric nitrate solution are more stable than Cu_xNa_{12-2x}-A zeolites obtained by the ion-exchange with aqueous cupric nitrate solution.

All the samples of Cu^{2+} and NH_4^+ ion-exchanged zeolite A show the similar X-ray diffraction patterns and intensities as those of thermally stable zeolite A $(Na_{12}$-A) even after evacuation at 300℃ for 5 hours (Figure 2). In spite of the same contents of Cu^{2+} ion, $(CuOH^+)_2(NH_4^+)_{10}$-A shows stronger XRD intensities than that of $Cu_{2.0}Na_8$-A prepared by the ion-exchange with aqueous cupric nitrate solution (Figure 2).

The IR spectroscopy also shows that the framework of $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$-A·$zH_2O$ are relatively stable (Figure 3). It is well known that the IR band at 550 cm^{-1} due to external linkages, D4R, is sensitive to the zeolite structure.

The decrease in intensity and the broadening of this band indicates the disruption and decomposition of zeolite framework.

Figure 3 clearly shows that $(CuOH^+)_x(NH_4^+)_{12-x}$-A zeolites show the same IR absorption bands and intensities at 1000 cm^{-1} (asymmetric stretching band of TO_4), 550 cm^{-1} (vibration of double 4-ring), and 670 cm^{-1} (symmetric stretching vibration of TO_4) as those in zeolite A after evacuation at
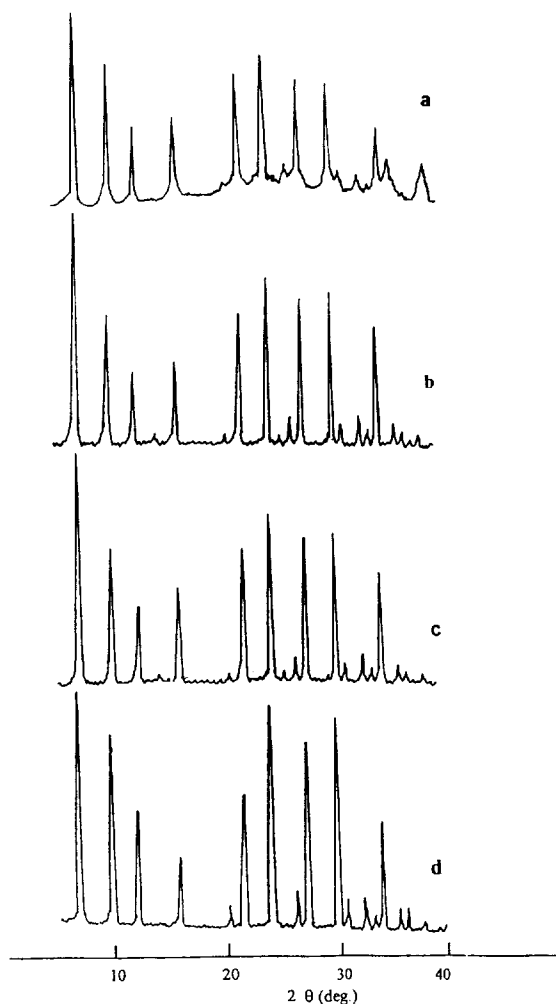
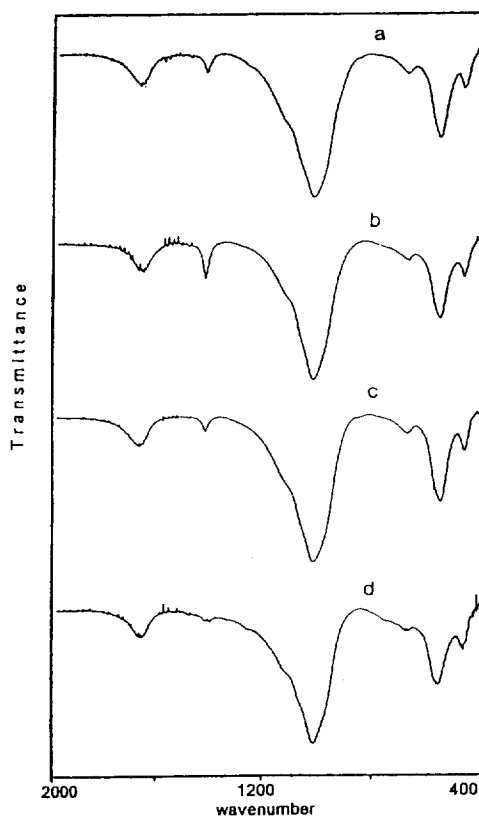**Figure 2.** The X-ray diffractograms of Cu^{2+} and NH_4^+ ion-exchanged zeolite A heated at 300℃. a: $Cu_{2.0}Na_{8.0}$-A, b: $(CuOH^+)_{2.0}$ $(NH_4^+)_{10.0}$-A, c: $(CuOH)_{1.24}(NH_4^+))_{10.76}$-A, d: zeolite A $(Na_{12}$-A).

Figure 3. The infrared spectra of $(CuOH^+)_x(NH_4^+)_{12-x}$-A zeolite heated at 300℃. a: $(CuOH^+)_{2.0}(NH_4^+)_{10.0}$-A, b: $(CuOH^+)_{1.24}(NH_4^+)_{10.76}$ -A, c: $(CuOH^+)_{0.85}(NH_4^+)_{11.15}$-A, and d: zeolite A $(Na_{12}$-A).

Figure 4. The DSC and TG thermograms of solvated $(CuOH^+)_2$ $(NH_4^+)_{10}$-A zeolite.

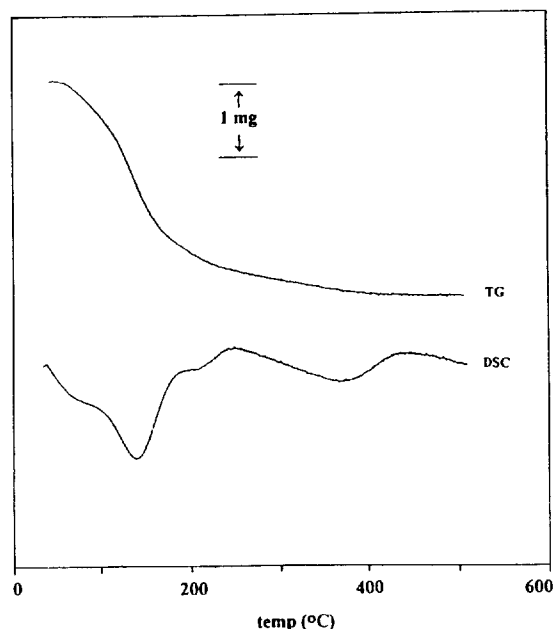300℃. This indicates that the framework of $(Cu(NH_3)_3OH^+)_x$ $(NH_4^+)_{12-x}$-A·zH_2O are relatively stable.

Kim *et al.*[14] attributed the thermal instability of Ba^{2+} ion-exchanged zeolite A to the movement of large Ba^{2+} ion (1.34 Å) from the position of hydrated state toward the small 6-ring site where large Ba^{2+} ion can not be accommodated well enough upon dehydration. N. H. Heo and K. Seff[22] ascribed the thermal instability of Ni(II)-exchanged zeolite A to the attack of protons to the framework oxygen atoms while the protons are accumulated inside framework by the hydrolysis of Ni^{2+} ions.

Since the ionic radius of Cu^{2+} ion (r_+ = 0.71 Å) is quite smaller than Ba^{2+} ion (r_+ = 1.34 Å), the size effect of Cu^{2+} ion on the framework instability can not be expected. However, Cu^{2+} ion has the same charge and similar ionic size as Ni^{2+} and Fe^{2+} ion and it may cause the hydrated water molecules to be hydrolyzed likewise Fe^{2+} and Ni^{2+} ion. In fact, the hydrolysis constant of Cu(II) ion ($pK_{hCu(II)}$: ~10.36[23]) is comparable to those of Fe^{2+} and Ni^{2+} ($pK_{h(Ni(II))}$: ~9.86[22], $pK_{h(Fe(II))}$: ~9.50[23]).

It is well known that zeolite structure are damaged in acidic solution due to the attacking of proton to framework oxygen. In this work, the damage of zeolite framework could be reduced by making the exchanging solution high basic (pH = 12.3) by adding excess ammonia.

The relative high thermal stability of $(Cu(NH_3)_3OH^+)_x(NH_4^+)_{12-x}$

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-A·zH₂O ($x \leq 2.0$) zeolite also may be attributable to the formation of hydroxotriammineCu(II) complex ion which will reduce the ions hydrolyzing ability due to the reduced charge and decreased ionic potential ($\phi = z + /r_+$) by the coordination of OH⁻ ions and ammonia molecules.

Since the hydrated (Cu(NH₃)₃OH⁺)₂(NH₄⁺)₁₀-A·zH₂O showed a smooth and continuous weight loss due to the dehydration and deammoniation, a considerable overlaps between adjacent peaks are expected in thermogram.

The hydrated (Cu(NH₃)₃OH⁺)₂(NH₄⁺)₁₀-A·zH₂O showed four endothermic DSC peaks around 80℃ (shoulder), 140℃, 210℃, and 380℃, respectively. The first peak (80℃) may arise from the dehydration of waters bound weakly to the zeolite surface, and the second one (140℃) may be attributable to the dehydration of water molecules bound more strongly to the cations inside framework. As the temperature is raised above 190℃, the deep blue color of hydroxotriammine Cu(II) complex ion became gradually pale blue. The blue color was lost completely around 240℃ and changed to white indicating that hydroxotriammine Cu(II) complex ion have lost all of the coordinated ammonia. About six ammonia molecules (6.4 NH₃) were detected by the acid-base titration of evolved ammonia in the range of 190℃ to 240℃.

So the third DSC peak (T_m: 210℃) could be attributable to the deammoniation of the hydroxotriammine Cu(II) complex ion. At higher temperature ranging from 240℃ to 430℃, about ten ammonia molecules (9.3 NH₃) were evolved. It has been reported that NH₄⁻-exchanged zeolite X and Y show second endothermic DTA peak above 250℃ due to the deammoniation of ammonium ion and that the deammoniation are made more than 90% below 400℃ and almost completed at 500℃.[1b] Based on our experiments and previous reports,[1b] the fourth DSC peak (T_m: 380℃) ranging from 240℃ to 430℃ could be attributed to the deammoniation of ammonium ions.

The activation energies determined by Ozawa's[24] plot on the above thermal reactions are as follows; dehydration (second peak, around 140℃): 90.82 kJ/mol, deammoniation of hydroxytriammine Cu(II) ion (third peak around 210℃): 99. 97 kJ/mol, decomposition of ammonium ion (fourth peak around 380℃): 176.57 kJ/mol.

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