

Thermal Studies of NaX Zeolite with Different Degrees of Cadmium Exchange

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Summary: Type X-zeolite in which 14.6, 31.00, 42.40, 57.80 and 59.00 Na⁺ ions have been exchanged with Cd²⁺ ions at 60 °C. The decrease in % Cd²⁺ ion exchange with increase in concentration of cadmium chloride solution is attributed to 'salt imbibent' and 'concentration valency effect'. Thermogravimetric analysis (TGA) has been used to ascertain the zeolitic water content of all samples investigated. The thermal stability of NaX and CdX-zeolite samples were studied by using differential thermal analysis (DTA) curves as a function of calcination temperature up to 1000 °C and degree of Cd²⁺ exchange in type X-zeolite. The number of water molecules increases with increasing the Cd²⁺ ions per unit cell (p.u.c) in the zeolite. The DTA curves indicated that dehydrated NaX retained its crystal stability from 400 °C to 560 °C and then re-crystallized to another form from 580 to 840 °C, while CdX-zeolite samples from 400 °C to 840 °C and then re-crystallized from 860 to 900 °C. The structures of NaX at above 880 °C and of CdX at above 960 °C collapse to an amorphous residue.

Introduction

A zeolite is crystalline aluminosilicate with a 4-connected tetrahedral framework structure enclosing cavities occupied by cations and water molecules both of which have considerable freedom of movement, permitting ions exchange and reversible rehydration [1,2]. More than 60 natural zeolites [3] and more than 200 synthetic zeolites are known [4] and many of these zeolites display Si / Al ratios continuously varying in quite extended ranges with Si / Al = 1 to ∞ [5,6]. As the Si / Al ratio of the framework increases, the hydrothermal stability as well as the hydrophobicity increases. The fact that zeolites retain structural integrity upon loss of water makes them different from other porous hydrates such as CaSO₄.

Variations in structure, cation sites, cation population and distribution lead to considerable variations in the ion exchange behavior. Zeolite type X in its sodium bearing form is called NaX is an ideal material for studying cation exchange phenomena in zeolites. The NaX-zeolite has a general unit cell formula, Na₈₆. [(AlO₂)₈₆ (SiO₂)₁₀₆]. m H₂O where m is the number of water molecules. The silica and alumina tetrahedra are coupled to form a truncated

octahedron known as the sodalite unit. The sodalite units have square faces and hexagonal faces. When the sodalite units are interconnected by hexagonal prisms on their hexagonal faces we have the X-zeolite structure, which is shown in Fig. 1 [7,8]. 86 Na⁺ ions may occupy up to five different sites in the hydrated X-zeolite as shown in Table-1. In type X-zeolite the easily accessible cations are located at sites II and II' of the remaining Na⁺ ions could not be located by X-ray diffraction and were believed to be mobile, hydrated cations in the supercages. In zeolite X entrances to the sodalite cages are small rings of six tetrahedra (6-rings) with a free diameter 2.5 Å. The entrances to the supercages are large rings of 12 tetrahedra (12-rings) with a free diameter 8-9 Å [9, 10].

The aim of this work was to introduce Cd²⁺ ions to different degrees into zeolite X by conventional ion-exchange techniques and then thermal analysis measure the (TGA and DTA) to get information about the zeolitic water and on the cadmium ions load to the zeolite and on the crystal-line phase transformations as well. The TG curves provided the % loss in weight up to 1000 °C from which number

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Table-1: Distribution of Na⁺ ions at different sites in zeolite X structure.

Position	Site	No. of sites p.u.c. [†]	Na ⁺
Center of hexagonal prism	I	16	4
In sodalite cage, adjacent to hexagonal prism	I'	32	32
In supercage, adjacent to the six ring outside of sodalite cage	II	32	32
In sodalite cage, adjacent to the single six ring.	II'	32	-
In supercage, neighborhood of the four ring	II''	48	4

[†]p.u.c (per unit cell) for convenience

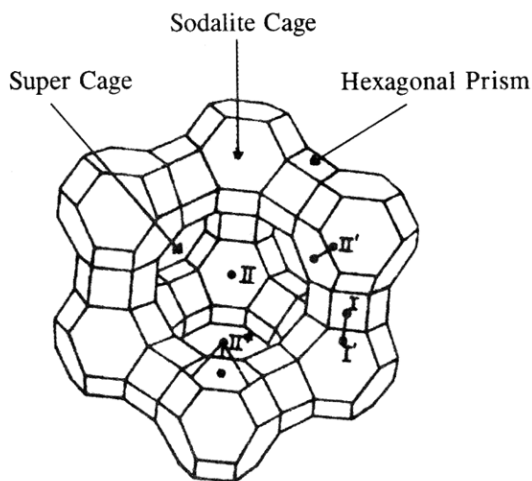
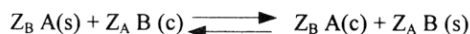


Fig. 1: A structure model of type X-zeolite composed of sodalite units connected by hexagonal prisms, cation site locations are designate by I, I', II, II' and II''.

of water molecules per unit cell formula of Cd²⁺ exchanged X-zeolite samples were calculated. The DTA curves from room temperature to 1000 °C provided the information about the changes in the crystalline aluminosilicate framework.

Results and Discussion

The cadmium exchanged X-zeolite samples were prepared from synthetic NaX-zeolite which has anhydrous unit cell formula, Na₈₆ [(AlO₂)₈₆ (SiO₂)₁₀₆], their degrees of exchange are given in Table-2. The Cd exchanged X-zeolite samples prepared by cation exchange manner. Any binary ion-exchange reaction in a zeolite may be written [11] as,



Where Z_A and Z_B refer to the valences of the ions A^{Z_A} and B^{Z_B} respectively, and (c) and (s) refer to

crystal and solution phases. Thus, for cadmium exchange into X type-zeolite, A^{Z_A} is Cd²⁺ and B^{Z_B} is Na⁺ ions and (c) is the crystal lattice of zeolite X. considering the locations of Na⁺ ions in NaX (Fig. 1) exchange takes place in two steps, a fast initial step followed by an over-lapping slow step. The cation exchange in NaX involves Na⁺ ions located in the supercages that diffuse rapidly through the main channels, and sodium ions in the β-cage that exchange, in a slow step, with mobile ions in the supercage

The Table-2 indicates that as the concentration of CdCl₂ solution increases the percentage ion exchange decreases at 60 °C for a particular fixed time. The following reasons are suggested for decrease of % exchange.

1. As in NaX-zeolite, 82 % of Na⁺ ions are located in the supercages [10] therefore, most likely when too many of Cd²⁺ ions move into the supercages they crowd out some of the Na⁺ ions in to the sodalite cages. One could look at this as a 'volume effect'. Thus, it is the size of hydrated Cd²⁺ ions that inhibits movement into the small cages, therefore, Na⁺ ions replacement seem impossible.

2. If the salt concentration is very high, anions can diffuse into the zeolite and carry along cations to preserve neutrality in both phases. Thus, at high CdCl₂ concentration in the solution the concentration gradient overwhelms the Donnan potential and salt imbibent may take place [12]. It increases with increasing salt concentration [13].

3. The third reason is the 'concentration valency effect' [14-15]. According to which when the exchange ions have different valences (e.g. Na⁺ and Cd²⁺) the ion exchange behavior of the system depends strongly on the total concentration of the aqueous solution, and the selectivity of the zeolite for the ion of higher valence becomes progressively greater with increasing dilution.

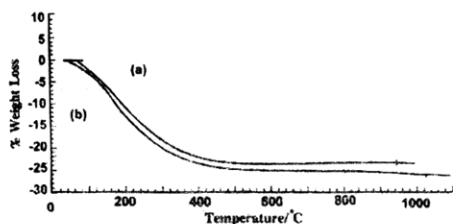
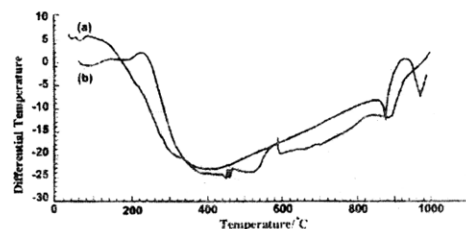
Table-2: Preparation and analysis of Cd²⁺ exchanged X-zeolites.

Sample No.	CdCl ₂ solution Mx10 ⁻²	Cd ²⁺ ions % exchanged p.u.c	No. of Na ⁺ ions released p.u.c	Unit cell formula of anhydrous CdX-zeolite*
1	1.02	98.53	14.60	Cd _{7.30} Na _{71.40} X
2	2.15	99.07	31.00	Cd _{15.50} Na ₅₅ X
3	3.02	96.69	42.40	Cd _{21.20} Na _{43.60} X
4	4.60	86.30	47.80	Cd _{28.90} Na _{28.20} X
5	5.02	80.88	59.00	Cd _{29.30} Na ₂₇ X

*X = [(AlO₂)₃₆(SiO₂)₁₀₆]⁸⁶⁻

Table-3: Thermal analysis (TGA, DTA) data of NaX and CdX-zeolites.

Zeolites	% loss in wt.	Dehydration Started	Min. of endothermic peaks	Completed dehydration	Max. of exothermic peaks	No. of H ₂ O molecules p.u.c
NaX	23.78	40	585, 880	840	580, 850	232
Cd _{7.30} X	24.00	40	872, 980	900	840, 940	257.63
Cd _{15.50} X	24.19	40	840, —	900	820, 920	261.03
Cd _{21.20} X	25.02	50	830, 988	910	830, 930	263.57
Cd _{28.90} X	25.71	50	865, 962	930	840, 920	277.64
Cd _{29.30} X	26.07	50	850, 955	930	835, 930	280.26

Fig. 2: Thermograms of (a) NaX and (b) Cd_{28.90} X-zeolites.Fig. 3: DTA profiles for (a) NaX and (b) Cd_{28.90} X-zeolites.

The typical thermograms of TGA curves of NaX and Cd_{28.9}X are shown in figure 2 and differential thermal analysis (DTA) curves of NaX and Cd_{28.90}X - zeolites are shown in figure 3, by curve (a) and (b) respectively. The thermograms of all zeolite samples investigated were continuous and smooth and showed that the dehydration starts between 38 and 50 °C and maximum weight losses

(23.78 to 26.07 %) occurred at about 400-450 °C and dehydration completed at about 840 to 930 °C depending on the nature and number of Na⁺ and Cd²⁺ ions in the zeolite samples (Table-3). There are at least two types of water, mobile and immobile ones, in the narrow phase zeolite, while there is only mobile water in the wide pore zeolite [16]. The thermograms showed that the maximum weight losses occurred at 280 °C for NaX and for CdX-zeolite samples at 280 °C-310 °C depending on the number of Cd²⁺ ions in the zeolite type X. This water is assumed to be sorbed and free mobile water inside the supercages and the water lost above 280 °C was that forming hydration complexes with the cations. The Cd²⁺ ions are octahedrally coordinated to three framework oxygens and three water oxygens such as Cd (H₂O)₃ (Ox)₃ (where Ox denotes an oxygen in the zeolite lattice) [17] and near the periphery of supercage tightly bonded to framework oxygens and in the small cages and pores of the zeolite samples. A slight weight loss in NaX at 840 °C and in CdX-zeolites at 888 to 930 °C may be due to dehydroxylation [18-19]. For strongly polarizing cations, a water molecule yields a hydroxyl bonded to the cation plus a proton, which attaches itself to frame-work oxygen. Ultimately as the temperature rises, the hydroxyls are destroyed with expulsion of water.

The Table-3 indicates that NaX-zeolite contains 232 H₂O molecules p.u.c and other authors have reported 243.6 [20] by the weight loss at 800 °C and 254.9 [8] and 251.7 [11]. The zeolitic water content

depends on the number of Al ions in the structure of zeolite [21]. The number of Al per unit cell of NaX varies from 96 to about 77. As the ratio Si / Al increases, the lattice constant of the zeolite decreases in accordance with the variation in Al—O (1.728Å) and Si—O (1.608Å) distance and the hydrothermal stability as well as the hydrophobicity increases [6, 22].

The Table-3 shows that the zeolitic water contents increase with increasing the degrees of Cd exchange p.u.c of the zeolite X. This result is in consistent with values of water molecules for CdX – zeolite reported in the literature [11, 23]. Gal and Radovano reported 281, Fletcher and Townsend reported 264.9 H₂O for Cd_{42.2} X and Cd_{43.4} X respectively. The zeolitic water content depends mainly on the nature and size of the mobile cations. The following reasons are described for more water molecules per p.u.c of CdX-zeolites than NaX-zeolite.

According to valence principle 2 Na⁺ ions are replaced by one Cd²⁺ ion therefore the space left vacant in cages of the zeolite framework is filled by water molecules.

The pauling radius of Cd²⁺ is 0.97Å and that of Na⁺ is 0.95 Å, Cd²⁺ ion binds water molecules more strongly and form complexes [17] as described above. Further, in a structure as rigid as X-zeolite, the increase of zeolitic water occurs by a closer packing of water molecules around the ions [23], and that is exactly what the change of water concentration shows.

The increased in zeolitic water of CdX-zeolites can also be attributed to the high negative charge density of the framework of the zeolite X which makes possible a more dense packing of both water molecules and cadmium complexes. The water molecules interact with cations present in the zeolite structure and form hydrogen bonds with negatively charged oxygen ions associated with the zeolite lattice.

Differential thermal analyses (DTA) provided data to the thermal stability of the NaX and Cd exchanged forms of X-zeolite. The endothermic curves of the DTA shown in Fig. 3 indicate a continuous loss of water over a broad range commencing from slightly above room temperature to about 350 °C for NaX and 380 to 400 °C for CdX-

zeolites depending on number of Cd²⁺ ions per p.u.c. The increase in peak temperature of the DTA endotherm for CdX-zeolites suggests that water molecules are more strongly bonded to Cd²⁺ cations than Na⁺ cations. The exothermic temperatures of DTA are for peaks corresponding to the collapse of the crystalline structure. The two maxima of exothermic peaks of NaX at 580 and 850 °C indicate decomposition of the lattice followed by two minima of endothermic peaks of recrystallization in an other form at 585 and at 880 °C and at above 910 °C the zeolite becomes amorphous. Breck and Flanigen reported [24] that DTA exothermic peaks at 772 and 933 °C indicated decomposition of the lattice followed by recrystallization to a new phase at 800 and 1000 °C. It has been reported [6] that for NaX-zeolite most water is lost by about 400 °C, but strongly polarizations held the last water tenaciously and thermal breakdown of NaX is near 760 °C. Gal and Radovanov reported [23] breakdown of the zeolite framework by an exothermic peak for NaX at about 800 °C and for CdX at above 900 °C. The different Si / Al ratios of the zeolite were found to be responsible for their different thermal behavior [22,25,26]. In general, greater stability accompanies increase of the Si / Al ratio. The Fig. 3 shows that two maxima of exothermic peaks for Cd_{28.90} X at 835 and 930 °C indicate decomposition of the lattice followed by two minima of endothermic peaks of recrystallization at 850 and 930 °C and at above 1000°C the zeolite becomes amorphous. The Table-3 indicates that maxima of exothermic peaks of CdX-zeolites are higher than NaX-zeolite. The reasons for appearance of exothermic curves and more thermal stability of CdX-zeolites are suggested below.

The thermal breakdown of a crystalline structure of a zeolite represents a gradual degradation that is dependent only on temperature but also on time, the presence of water vapors, and probably on other factors. The exothermic nature of the crystal collapse has been attributed to the large amount of surface energy associated with the zeolite. At the temperature of framework collapse, the surface area decreases and the energy associated with the host surface appears in the form of liberated heat [25]. The data of thermal analysis reported in Table-3 agree qualitatively with those reported by other authors [26]. However, quantitative agreement among authors is poor. Many factors influence the temperatures at which the exothermic peaks are observed e.g. heating rate, the particular temperature used, atmosphere, sample size.

The nature and number of metal cations that are present contribute significantly to the stability exhibited by a particular zeolite structure [27]. The results of more thermal stability of CdX-zeolites than NaX-zeolite are in consistent with the results reported in literature [17, 23]. Some general behavior of thermal stability with cation size and nature has been observed for other zeolites including type A [25]. It has been attributed the relation to the relative stability of the various cations to fill the voids in the crystal after dehydration [28, 29]. It has been confirmed [17, 28] that in the case of dehydrated zeolites the Cd^{2+} ions are distributed preferentially in the sites, situated in the hexagonal prisms and sodalite and forming $\text{Cd}(\text{Ox})_3$ complexes. Thus in the dehydrated CdX-zeolite samples the Cd^{2+} ions are closer and more strongly associated with the framework than in the hydrated state and in this way the thermal stability of CdX-zeolite is augmented.

The high temperature exotherm is attributed to a structure collapse or phase transformation and it is taken as a measure of the thermal stability [28] of the zeolite. Thus, NaX is stable up to 910 °C and CdX-zeolites up to 1000 °C. The composition of unit cells of NaX and CdX-zeolites exchanged to different degrees are presented in Table-4.

Table 4:- Composition of NaX and Cd exchanged X-zeolites.

Zeolite	Unit Cell Composition
NaX	$\text{Na}_{86} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 232 \text{ H}_2\text{O}$
$\text{Cd}_{7,30}\text{X}$	$\text{Cd}_{7,30} \text{Na}_{71,40} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 257.63 \text{ H}_2\text{O}$
$\text{Cd}_{15,50}\text{X}$	$\text{Cd}_{15,50} \text{Na}_{55} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 261.03 \text{ H}_2\text{O}$
$\text{Cd}_{21,20}\text{X}$	$\text{Cd}_{21,20} \text{Na}_{43,60} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 263.57 \text{ H}_2\text{O}$
$\text{Cd}_{28,90}\text{X}$	$\text{Cd}_{28,90} \text{Na}_{28,20} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 277.64 \text{ H}_2\text{O}$
$\text{Cd}_{29,50}\text{X}$	$\text{Cd}_{29,50} \text{Na}_{26,90} \cdot [(\text{AlO}_2)_{86} (\text{SiO}_2)_{106}] \cdot 280.26 \text{ H}_2\text{O}$

Experimental

The exchanger studied was the zeolite designated NaX purchased from the Sigma Aldrich (USA). It was binderless crystalline white powder had a lot No. 96 Fo251. Before introducing cadmium ions into the framework of the zeolite it was equilibrated with the water vapours over a saturated solution of calcium nitrate in a sealed desiccator for several days to ensure a constant content of zeolitic water. Chemicals used for both analysis and exchange purposes were of analytical grade. All glass wares were of pyrex and water was distilled/ deionized.

A slurry of 5 g of fully hydrated NaX zeolite was made with 75cm³ deionized water. 200cm³ of the

CdCl_2 (E. Merck, Lot No. 366554) solution was added to the slurry of which PH was controlled at 7. The extent of ion exchange was governed by the concentration of the CdCl_2 solution, contact time and solution temperature. The solution was stirred with a magnetic stirrer hot plate at 60 °C for about 2 hours. The Cd exchanged sample was thoroughly washed several times with deionized hot water. Each wet Cd exchanged zeolite was dried in an oven at 110 °C for over night, then the dried sample was transferred to a desiccator and stored over saturated calcium nitrate solution for 24 hours for complete rehydration.

The exact number of Cd^{2+} ions per unit cell introduced into the zeolite X was found by carrying out chemical analysis of original CdCl_2 solution and the filtrate by EDTA as titrant and erichrome black – T as an indicator. The unit cell composition of various CdX-zeolite samples prepared are given in Table-2.

Thermal analyses were carried out using a Simultaneous thermal analyzer STA-40 NETZSCH (Germany) 10-15 mg of each sample was taken using high purity nitrogen as purge gas at the rate of 200 cm³ per minute, heating rates of 10 °C / min and chart speed of 2.5 mm/min. The zeolitic water was found by the % weight loss up to 1000 °C and thermal stability of the crystals was investigated by observing crystallinity changes in zeolite samples heated in the temperature range from room temperature up to 1000 °C.

Conclusions

The analysis of TGA/DTA curves, provided a useful tool to estimate changes in the thermal properties and modifications in the zeolitic framework as a consequence of cation exchange. The TGA results showed the increase of the zeolitic water with increasing the degrees of cadmium exchange. The order of introduction of the Cd^{2+} also affects the thermal stability of the zeolitic lattice. The DTA curves indicated that the calcined Na^+ retained its framework crystallinity from 350 °C to 900 °C and CdX from about 350 °C to 1000 °C.

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