

## Thermal Analysis of Hydrated Cobalt (II) Exchanged X-type Zeolites

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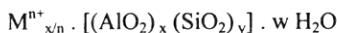
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**Summary:** A series of five samples (6.80, 15.80, 20.10, 21.45, 22.00 Co<sup>2+</sup> ions per unit cell) of Co<sup>2+</sup> exchanged X - zeolites were prepared by cation exchange method. The decrease in percentage exchange with increase in Co<sup>2+</sup> ions in exchange solution suggests replacement of NaX ions from the supercages and also "volume effect". The zeolitic water contents and thermal stability of hydrated zeolite samples both unexchanged and exchanged were investigated by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) techniques, under a constant flow of nitrogen as a purge gas. The TGA study indicated total weight loss percentage of the zeolite samples from 18.87 to 26.70. The zeolitic water contents and thermal stability increased with increase Co<sup>2+</sup> ions in the zeolite X. Two exothermic DTA curves at 585 °C and 887 °C for NaX and one up to about 830 °C were recorded for Co X-zeolite samples, which indicated the collapse of crystalline aluminosilicate framework.

### Introduction

Zeolites and more generally, molecular sieves are micro porous crystalline aluminosilicates composed of TO<sub>4</sub> tetrahedra (T = Si, Al) with O atoms connecting neighboring tetrahedra. Each Al<sup>3+</sup> ion in the framework requires a compensating cationic charge to ensure neutrality. The compensating charges usually originate from extra-framework cations (inorganic and organic cations can satisfy this requirement) within the structure to keep the overall framework neutral. The framework consists of cages and channels of different sizes, accessible for various guest molecules. The zeolite composition can be best described as having three components.



extra framework cations framework sorbed phase

The extra framework cations are ion exchangeable and give rise to the rich ion exchange chemistry of these materials. The novelty of zeolites stems from their micro porosity and is a result of the topology of the framework [1-3].

The zeolite type X was synthesized in 1959 by Milton at Union carbide corporation, U.S.A. This zeolite is called NaX as it is synthesized in the sodium bearing system and is also called 13X due to

presence of large supercage of diameter 13 Å with pore diameter of 7.4 Å in its frameworks structure [4-7]. There are also smaller cages of 6.6 Å in diameter (β-cages) joined by 6-rings of 2.2 Å in diameter. These small cavities are accessible only for a few water molecules. Zeolite X has at least five-cation sites. Sites I lie at the center of hexagonal prisms. Sites II lie on the 6-ring faces of the sodalite cages, on the supercage side. Sites I' and II' lie on the other side of the corresponding 6-rings of the sites I and II respectively, within the sodalite cage. Sites III are in the supercage and in the sodalite 4-ring. Cations located near the sites III are said to occupy the sites III' [8-10]. The water molecules are present in clusters, which seem to be joined into a continuous intracrystalline phase. The zeolite is referred to as a nonstoichiometric hydrate because the water is present as a guest molecule in the host structure [7]. Even though many new frameworks have been discovered since 1959, this zeolite still enjoys tremendous academic and commercial importance.

This paper intends to carry out the thermogravimetric study by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) techniques of NaX and after exchanged to different extents by Co<sup>2+</sup> ions. Thermal analysis gives zeolitic water contents and thermal stability of crystals. Prediction of thermal behavior of NaX and cobalt

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Table -1: Preparation and analysis of  $\text{Co}^{2+}$  exchanged X-zeolites

Sample No.	$\text{CoCl}_2$ Solution M $\times 10^2$	% Exchanged	No of $\text{Na}^+$ ions replaced per unit cell	Unit cell formula of CoX Zeolite*
1	0.94	98.94	13.6	$\text{Co}_{6.80}\text{X}$
2	2.26	96.02	31.6	$\text{Co}_{15.80}\text{X}$
3	3.16	87.34	40.2	$\text{Co}_{20.10}\text{X}$
4	3.68	82.31	42.2	$\text{Co}_{21.45}\text{X}$
5	4.92	5.96	42.9	$\text{Co}_{22.00}\text{X}$

exchanged X-zeolite can provide useful information for possible application to catalysis in the case of high thermal stability [11-12].

## Results and Discussion

The results of exchange experiments are reported in Table-1. All samples of CoX-zeolites

\*Where 'X' is abbreviation for configuration  $[(\text{AlO}_2)_8(\text{SiO}_2)_{106}]^{86-}$

were of pink colors characteristic of hexa-aqua  $\text{Co}^{2+}$  complexes [13-15] because  $\text{Co}^{2+}$  ions exist as fully hydrated octahedrally coordinated species in zeolite X [16-17] as also in zeolite A [18]. The table indicates that percent exchange of  $\text{Co}^{2+}$  ions in zeolite X decreases with increasing the concentration of the  $\text{CoCl}_2$  solution. As mentioned earlier X-zeolite has at least five cation sites [19-20] the molecules larger than water can access only the large supercages and cannot pass into the empty space inside sodalite cages and hexagonal prisms (network of small cages). Thus the possible reason for the decrease in the percentage exchange with increasing the concentration of  $\text{CoCl}_2$  solution is the inaccessibility of certain ion exchange sites (like sodalite and hexagonal prism cages) at temperature of exchange by hydrated cobalt complexes [13-15]. As in NaX, 82% of  $\text{Na}^+$  ions are located in the super cages [21] therefore, most likely when too many of large complex cations such as  $\text{Co}^{2+}(\text{H}_2\text{O})_6$  move into the super cages they crowd out some of the  $\text{Na}^+$  ions into the sodalite cages. One could look at this as a "volume effect" [22]. Thus, it is the size of the hydrated cobalt ion that inhibits movement into the small cages. It has also been suggested that when the ingoing ion is more highly charged than the outgoing ion, the preference for the ingoing ion decreases with increasing solution concentration [23]. Therefore the  $\text{Co}^{2+}$  ions have displaced  $\text{Na}^+$  ions only from the supercages.

Representative example of TGA and DTA curves of  $\text{Co}_{22}\text{X}$ -zeolite are shown in figures 1 and 2 respectively. The DTA curve of NaX-zeolite for

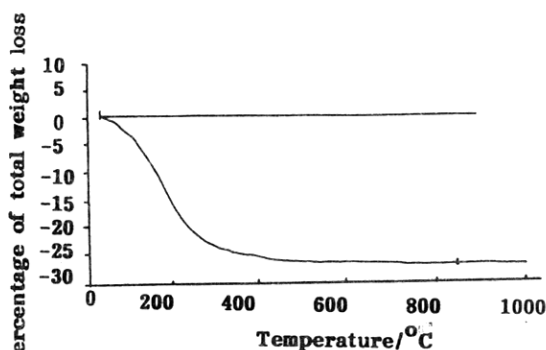


Fig. 1: Thermogravimetric curve of  $\text{Co}_{6.80}$  X-Zeolite.

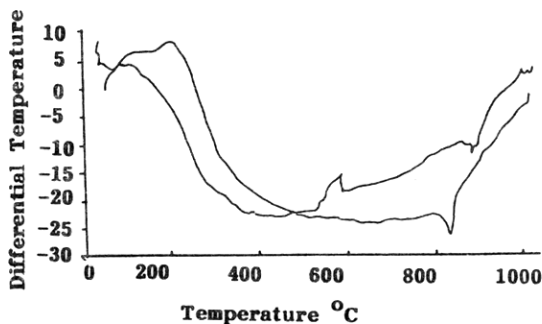


Fig. 2: Differential thermal analysis (DTA) curves for (a), NaX and (b)  $\text{Co}_{6.80}$  X-Zeolite.

comparison with  $\text{Co}_{22}\text{X}$  is also shown in Fig. 2. The thermogravimetric analysis (TGA) curves for all zeolite samples investigated were continuous and smooth and showed that most water is lost by 400 °C and dehydration completed at different temperatures depending on the loading of  $\text{Co}^{2+}$  ions in zeolites X (Table-2). The Total water losses observed and zeolite samples dehydration behavior are summarized in Table-2. The Table shows that the maximum weight loss for NaX is at 260 °C and for  $\text{Co}^{2+}$  zeolite is at about 280 °C. It has been reported by Breck and Flanigen [24] that DTA curve of NaX zeolite indicated the loss of water started above room temperature to about 350 °C with maximum at about 250 °C. This water is assumed to be sorbed and free

Table-2: Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) Of  $\text{Co}^{2+}$  exchanged X-Zeolites

Zeolite	Dehydration Starts at $^{\circ}\text{C}$	Dehydration completed at $^{\circ}\text{C}$	Exothermic Peak at $^{\circ}\text{C}$	Total weight loss%	Number of $\text{H}_2\text{O}$ molecule per unit cell of zeolites
NaX	40	840	580, 850	23.78	232
$\text{Co}_{0.80}\text{X}$	50	840	900	25.42	259.22
$\text{Co}_{15.80}\text{X}$	60	900	880	25.68	261.40
$\text{Co}_{20.10}\text{X}$	60	950	865	26.63	272.20
$\text{Co}_{21.45}\text{X}$	60	950	860	26.65	275.96
$\text{Co}_{22.00}\text{X}$	60	950	880	26.70	277.17

mobile water inside the supercages and the water lost above  $260^{\circ}\text{C}$  was that forming hydration complexes with the cations 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  $\text{CoX}$  samples at about  $975^{\circ}\text{C}$  may be due to dehydroxylation [25-27].

Tables-2 shows that NaX-zeolite contains 232 water molecules per unit cell after dehydration at  $840^{\circ}\text{C}$  and other authors have reported 243.6 [28] by the weight loss at  $800^{\circ}\text{C}$  and 264  $\text{H}_2\text{O}$  molecules per unit cell of NaX-zeolite [19, 29]. The number of  $\text{H}_2\text{O}$  molecules in zeolite depends on the number of Al ions in the structure of zeolite [30]. The number of Al per unit cell of NaX varies from 96 to about 77 [30]. As the ratio Si/Al increases, the lattice constant of the zeolite decreases in accordance with the variations in Al-O, and Si-O distance and the hydrothermal stability as well as the hydrophobicity increases [19, 31].

The Table-2 indicates that zeolitic water of  $\text{CoX}$  zeolite increases with increasing  $\text{Co}^{2+}$  ions per unit cell. This is probably due to hydration capacity for the  $\text{Co}^{2+}$  ions. Similar result has been observed by Bhomrah and Kulkarni [32]. Most of the water is in the supercages together with cations [33]. The zeolitic water content depends on the nature and size of the mobile cations [19]. As according to valance rule 2  $\text{Na}^+$  ions were exchanged by 1  $\text{Co}^{2+}$  ion, moreover since the pauling's ionic radii for  $\text{Co}^{2+}$  and  $\text{Na}^+$  ions are 0.74 and 0.95 Å [34] respectively, therefore, the total empty space of the zeolitic cavities increased in the  $\text{CoX}$ -zeolite samples. Thus, the increased space in  $\text{CoX}$  zeolites has been occupied by water molecules. In addition, the  $\text{Co}^{2+}$  ions have the capability of forming complexes with water molecules, in which the water molecules are strongly coordinated with  $\text{Co}^{2+}$  ions and are tightly packed. Hercigonja *et al.*, [28] also reported that in cobalt exchanged samples the water content per u.c was found to be larger than NaX zeolite. They food

by thermogravimetric technique 311.3  $\text{H}_2\text{O}$  molecules for  $\text{Co}_{32}$  X- zeolite. The increase in zeolitic water 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  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  complexes. Water molecules interact with cations present in the zeolite and form hydrogen bonds with negatively charged oxygen ions associated with the zeolite lattice.

Differential thermal analysis (DTA) curves are useful in characterizing zeolites. The endothermic curves of the DTA shown in Fig. 2 indicate a continues loss of water over a broad range commencing from slightly above room temperature to about  $350^{\circ}\text{C}$  for NaX and  $380^{\circ}\text{C}$  for  $\text{CoX}$ -zeolite. The DTA exothermic temperatures in Fig. 2 are for peaks corresponding to the collapse of the crystalline structure. The two exothermic peaks for NaX at  $580$  and  $850^{\circ}\text{C}$  indicate decomposition of the lattice followed by recrystallization at  $585$  and at  $865^{\circ}\text{C}$  and at above  $900^{\circ}\text{C}$  the zeolite becomes amorphous. Breck and Flanigen reported [24] that DTA exothermic peaks at  $772$  and  $933^{\circ}\text{C}$  indicated decomposition followed by recrystallization at  $800$  and  $1000^{\circ}\text{C}$ . The different Si / Al ratios of the zeolites were found to be responsible for their different thermal behavior [30-31]. The Table-2 indicates the exothermic peaks for  $\text{Co}^{2+}$  exchanged X-zeolites are higher (up to  $900^{\circ}\text{C}$ ) than NaX-zeolite. The reasons for exothermic curves and more thermal stability of  $\text{CoX}$ - zeolite samples are given below. The thermal collapse of a crystalline zeolite structure does not represent a true melting point, but rather a gradual degradation that is dependent only on temperature but also on time, the presence of water vapour, 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 [30]. The results of thermal analysis shown in Table-2 are in agreement qualitatively with those reported by other authors [31]. However, quantitative agreement among authors is poor. Many factors influence the temperature at which the exotherm is 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. As in Table 2 the temperatures of exothermic peaks associated with crystal collapse are higher than NaX, so the thermal stability of CoX- zeolites are more than NaX - zeolite. Some general behavior of increasing thermal stability with cations size has been observed for other zeolites including type A [30]. It has been attributed the relation to the relative stability of the various cations to fill the voids in the crystal after dehydration [30].  $\text{Co}^{2+}$  cations augment the stability of type X - zeolite probably because of formation of a complex inside the sodalite cage with framework oxygens during dehydration process as in type A zeolite [35-37].

The composition of unit cells of all presented in Table-3 are related to the hydrated forms of investigated zeolites in which the sodium ions from the hexagonal prisms were obviously not exchanged.

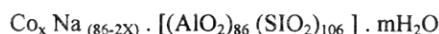
Table-3: Composition of  $\text{Co}^{2+}$  exchanged X-zeolites

Zeolite	Zeolite unit cell composition
NaX	$\text{Na}_{86} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 232\text{H}_2\text{O}$
$\text{Co}_{6.80}\text{X}$	$\text{Co}_{6.80}\text{Na}_{72.40} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 259.22\text{H}_2\text{O}$
$\text{Co}_{15.80}\text{X}$	$\text{Co}_{15.80}\text{Na}_{55.40} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 261.40\text{H}_2\text{O}$
$\text{Co}_{20.10}\text{X}$	$\text{Co}_{20.10}\text{Na}_{46.80} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 272.20\text{H}_2\text{O}$
$\text{Co}_{21.45}\text{X}$	$\text{Co}_{21.10}\text{Na}_{44.80} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 275.96\text{H}_2\text{O}$
$\text{Co}_{22.00}\text{X}$	$\text{Co}_{22.00}\text{Na}_{42.00} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 277.17\text{H}_2\text{O}$

## Experimental

The NaX (lot no. 96F0251) was purchased from Sigma used in powder form. The general formula of the Na X is:  $\text{Na}_{86} \cdot [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot m\text{H}_2\text{O}$ , where m is the number of water molecules (4). First the zeolite was kept in a desiccator over saturated  $\text{Ca}(\text{NO}_3)_2$  solution for several days to ensure its complete hydration. The exchange of NaX ions was carried out to various degrees with  $\text{Co}^{2+}$  ions. Cobalt chloride used for exchange solution was of analar grade and was used as such,  $\text{Co Cl}_2 \cdot 6\text{H}_2\text{O}$  (lot no 5233375) from E. Merck. The extent of ion exchange was governed by the concentration of the cobalt chloride solution, contact time and solution temperature. A slurry of 5g of fully hydrated NaX

zeolite was made with 75  $\text{cm}^3$  deionized water. 200cc of the transition metal solution was added slowly in small quantity to the slurry. The solution was stirred for a particular time at 60  $^\circ\text{C}$  controlling pH at 7. The solution was filtered and the  $\text{Co}^{2+}$  -exchanged form were dried in an oven at 100  $^\circ\text{C}$  for over night. The dried samples (partially dehydrated) were stored over  $(\text{CaNO}_3)_2$  solution in a desiccator for 24 hours for complete rehydration. The filtrate was used for determination of unexchange  $\text{Co}^{2+}$  ions by titration with EDTA using murexide as an indicator. Volumetric analysis confirmed that each  $\text{Co}^{2+}$  ions displaced two  $\text{Na}^+$  ions. The five samples of Co NaX - zeolites prepared with the general unit cell formula.



where x = 6.80, 15.80, 20.10, 21.45 and 22.00.

The zeolitic water and other information of the hydrated Co X-zeolite were obtained by thermogravimetric (TGA) and differential thermal analysis (DTA). Simultaneous thermal analysis STA -40, NETZSCH (Germany) was used for thermogravimetric studies of Co X-zeolites. 10-20mg of each sample was taken and temperature was raised from room temperature to 1000  $^\circ\text{C}$ . The heating rate employed was 10  $^\circ\text{C}$  per minute at chart speed of 2.5 mm/min. All experiments were performed with samples under a flow of pure nitrogen at the rate of 200cc per/min. The zeolitic water of all samples of zeolite was determined after complete weight loss at about 800  $^\circ\text{C}$  for NaX and from 840 to 950  $^\circ\text{C}$  for  $\text{Co}^{2+}$  exchanged zeolites. The thermal stability was found from exothermic curves of DTA profiles.

## Conclusions

The chemical analysis of Cobalt (II) exchanged X-zeolites indicated that  $2\text{Na}^+$  ions were exchanged by one  $\text{Co}^{2+}$  ion. The TGA results confirmed that zeolitic water increased by increasing the degree of exchange of  $\text{Co}^{2+}$  ions. The lumpy nature of TG curves proved the stability of zeolite structures and water loss occurred in stages in a wide temperature range. The DTA curves showed that substitution of  $\text{Na}^+$  ions in X-zeolite enhanced its thermal stability.

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