

Thermogravimetric Studies of Hydrated Zeolite Type A: Effect of Transition Metal Ion Exchange on Zeolitic Water

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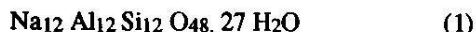
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Summary: The crystal structure of fully hydrated synthetic zeolite type A has been described. Co^{2+} , Ni^{2+} , Cu^{2+} and Mn^{2+} ions have been exchanged to different extents (from 16.6% up to 81.6%) into zeolite A and their zeolitic water contents have been measured thermogravimetrically. The gravimetric studies showed complete loss of water molecules in dynamic vacuum (10^{-6} torr) at 623 K. Turnover numbers for H_2O increase smoothly with increasing transition metal divalent ions in the zeolite framework. The water content is closely related to the nature and number of the cations incorporated into the zeolite lattice. The sequence of the number of water molecules per unit cell was $\text{Ni A} > \text{Co A} > \text{Cu A} > \text{Mn A} > \text{Na A}$. Thus the water content increases with decreasing ionic radius of the cation, from 27 for Na^+ ($r = 0.98 \text{ \AA}$) to 47.8 for Ni^{2+} ($r = 0.69 \text{ \AA}$)

Introduction

Thirty five years ago the synthesis and properties of industrially important zeolite type A having no natural counterpart was first described [1]. Type A zeolite, which ever since its discovery, has been the subject of numerous studies and discussion [2]. Its structure is thought to be the most reliable established of all the synthetic zeolites characterized to date. The formula per unit cell is,



in the form in which zeolite A is synthesized, and should be considered as follows:

the 12 Na^+ ions are ion-exchangeable; $\text{Al}_{12} \text{Si}_{12} \text{O}_{48}^{12-}$ comprises a relatively rigid anionic framework in the zeolite A arrangement, and the 27 H_2O molecules can be baked out to leave intracrystalline volume into which other guest molecules can be sorbed. The aluminosilicate framework is composed of AlO_4 and SiO_4 tetrahedra bonded together to form truncated octahedral with eight hexagonal faces and six square faces. These truncated cubo octahedra are called sodalite or β -cages

and are in turn bonded together by cubes on their square faces to form a large cavity or α -cage. Each unit cell has one large cavity and one sodalite cavity; each cavity is approximately spherical with mean free diameters when empty of 11.4 and 6.6 \AA and the void volumes are 775 \AA^3 and 151 \AA^3 respectively. Therefore, total void volume per unit cell is 926 \AA^3 .

The zeolitic water exists in both α - and β -cavities [3]. Each sodalite cavity contains four water molecules in a distorted tetrahedron with four edges of 2.2 \AA and the remaining two of 3.3 \AA with bonding to O(3) at 2.8 \AA and Na (1) at 2.9 \AA . Each large cage contains two sets of water molecules which could correspond to 20 H_2O molecules, which are lying at the corners of cubically distorted pentagonal-dodecahedron. Distances indicated bonding of H_2O to Na (1) and O(3). [Note :- O(3) and Na(1), the bracketed numbers mentioned above is an arbitrary number to distinguish crystallographically distinct portions]. Such an arrangement of water molecules is well known in clathrate hydrates. The configuration of the clus-

ter of water molecules within the α -cavity of hydrated Na A is shown in figure 1. The radius of this cluster is about 3.85 \AA . Three water molecules per unit cell may be located in the 8-rings. Of the water molecules in the cluster those in 8-rings form part of the Na^+ ion coordination. The water molecules forming this cluster are thus all linked to a sodium or oxygen atom of the framework. The pentagonal dodecahedron contributes to the stability of the hydrate type A zeolite and allows the relatively open aluminosilicate framework to form. Yanagida and Seff [4] reported that when NH_3 is sorbed into anhydrous NaA zeolite, a similar pentagonal dodecahedron of 20 NH_3 molecules is formed in the α -cavity. Breck [2] suggested that in general, in small zeolite cavities like the β -cavity, the cations are in contact with few water molecules. As the cavity increase in size, the cations may be surrounded by water molecules, and in large cavities water may behave as an isolated liquid phase.

This paper is intended to review that framework structure of the fully hydrated synthetic Na A-zeolite and to investigate systematically the effect on the zeolitic water after exchanging Na^+ ions by Co^{2+} , Ni^{2+} , Cu^{2+} and Mn^{2+} ions to different degrees.

Results and Discussion

The composition of unit cell of Na A is given in the formula (eq 1) and the zeolite samples prepared by ion exchange and their water contents obtained by thermogravimetric method using Mc Bain spring balance are given in Table 1. The table also shows the colours of the fully hydrated and dehydrated samples. X-ray powder diffraction of the transition metal exchanged zeolites showed no evidence of structural breakdown. The low temperature (77K) adsorption of krypton confirmed the stability of the structures of the dehydrated zeolite samples with the exception of highly exchanged zeolites such as $\text{Co}_{4.9}\text{A}$, $\text{Ni}_{4.6}\text{A}$ and $\text{Cu}_{4.9}\text{A}$ where at high-temperature partial lattice instability occurred [5-6]. The gravimetric studies showed complete loss of water molecules at 723 K in dynamic vacuum (10^{-6} torr).

The lattice constant of the unit cell of Na A zeolite is 12.3 \AA [2]. When Na A is dehydrated the unit cell constant decreased by only about 0.02 \AA .

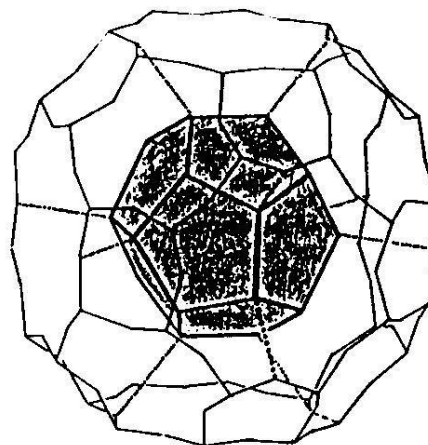


Fig. 1: Cluster of water molecules in hydrated synthetic NaA-zeolite. The water molecules lie at the corners of the pentagonal dodecahedron, and the framework T and O atoms of the α -cavity lie at the intersections of the thin lines. Dotted lines show shortest $\text{H}_2\text{O} - \text{O}$ distances [3].

Table 1: Physical characteristics of Co^{2+} , Ni^{2+} , Cu^{2+} and Mn^{2+} exchange A-zeolites.

Zeolite sample	unit cell composition	colour on exchange	H_2O molecular per unit cell	colour after dehydration
$\text{Co}_{1\text{A}}$	$\text{Co}_1\text{Na}_{10}\text{A}$	very light pink	30.5	pale blue
$\text{Co}_{1.7\text{A}}$	$\text{Co}_{1.7}\text{Na}_{8.6}\text{A}$	light pink	31.0	pale blue
$\text{Co}_{2.8\text{A}}$	$\text{Co}_{2.8}\text{Na}_{6.4}\text{A}$	pink	33.5	pale blue
$\text{Co}_{3.4\text{A}}$	$\text{Co}_{3.4}\text{Na}_{5.2}\text{A}$	bright pink	35.8	pale blue
$\text{Co}_{4.9\text{A}}$	$\text{Co}_{4.9}\text{Na}_{2.2}\text{A}$	bright pink	38.8	pale blue
$\text{Ni}_{1\text{A}}$	$\text{Ni}_1\text{Na}_{10}\text{A}$	very light green	32	yellow
$\text{Ni}_{2.4\text{A}}$	$\text{Ni}_{2.4}\text{Na}_{6.2}\text{A}$	light green	34	dirty yellow
$\text{Ni}_{3.15\text{A}}$	$\text{Ni}_{3.15}\text{Na}_{5.7}\text{A}$	green	39.34	dark yellow
$\text{Ni}_{3.9\text{A}}$	$\text{Ni}_{3.9}\text{Na}_{4.2}\text{A}$	bright green	45.3	brown
$\text{Ni}_{4.6\text{A}}$	$\text{Ni}_{4.6}\text{Na}_{2.8}\text{A}$	bright green	47.8	black metallic
$\text{Cu}_{1\text{A}}$	$\text{Cu}_1\text{Na}_{10}\text{A}$	light turquoise blue	30.32	pale blue
$\text{Cu}_{3\text{A}}$	$\text{Cu}_3\text{Na}_6\text{A}$	Turquoise blue	31.52	pale blue
$\text{Cu}_{3.5\text{A}}$	$\text{Cu}_{3.5}\text{Na}_5\text{A}$	Turquoise blue	32.72	pale blue
$\text{Cu}_{4\text{A}}$	$\text{Cu}_4\text{Na}_4\text{A}$	Turquoise blue	33.22	pale blue
$\text{Cu}_{4.9\text{A}}$	$\text{Cu}_{4.9}\text{Na}_{2.2}\text{A}$	Turquoise blue	34.73	pale blue
$\text{Mn}_{3.5\text{A}}$	$\text{Mn}_{3.5}\text{Na}_5\text{A}$	very pale	29.4	white

(A = $\text{Al}_{12}\text{Si}_{12}\text{O}_{48}^{12-}$)

This confirms the very rigid nature of the aluminosilicate framework. Since the total void space must remain constant within the rigid zeolite crystal, the volume occupied by various cations will effect the number of water molecules that can subsequently be added. Barrer and Meier [7] investigated the structural and ion sieve properties of synthetic Na A zeolite. The zeolite exhibits ion sieving properties just as it possesses molecule

sieving characteristics. They found that the crystal exhibits an ion sieve effect which depends on the size of the exchanging ion.

The presence of cations in the zeolitic voids may affect the pore volume. It was reported [2] that in zeolite A exchange of Na^+ by Tl^+ reduces the pore volume per unit cell approximately 30%. From the crystal structure analysis of Tl A [8] the cations are located well into the main α -cage on the three-fold axis, and therefore should interfere with the water adsorption. The exchange of Na^+ by Ca^{2+} increases the pore volume since the total cation density is reduced by 50%. The zeolitic water falls with increasing ionic radius of monovalent cations and is higher in the form containing bivalent cations. The water content increases with decreasing the ionic radius of the monovalent cation in zeolite A in the following sequence [2].

Tl A = 22.6 H_2O , KA = 25.2 H_2O , Na A = 27 H_2O

Ion ic radii $\text{Tl}^+ = 1.49 \text{ \AA}$, $\text{K}^+ = 1.33 \text{ \AA}$, $\text{Na}^+ = 0.98 \text{ \AA}$

For bivalent cation: Ca A = 30.4 H_2O , $\text{Ca}^{2+} = 1.06 \text{ \AA}$.

The zeolitic water fills the cavities and are localized near the cations. It has been indicated that at room temperature the water molecules are highly mobile.

Considering the above mentioned scientific information, the results of each transition metal exchanged A-zeolite of the table will be discussed individually as below.

Cobalt A zeolites

The formula (eq 1) shows that the number of water molecules per unit cell of hydrated Na A zeolite is 27. The table 1 indicates that the number of water molecules per unit cell of hydrated Co(II) A zeolites increases with increasing the number of Co^{2+} ions per unit cell in the zeolite. It has already been mentioned above that the presence of different cations in the zeolite A voids affects the pore volume. A small divalent cation increasing the space unoccupied. According to the valence rule 2Na^+ ions are exchanged by 1 Co^{2+} ion,

moreover, the Pauling's ionic radii for Co^{2+} and Na^{1+} are 0.74 and 0.95 \AA respectively [9], therefore, the empty space in the cavities increases by exchanging Na^+ ions by Co^{2+} ions. In addition to this, Co^{2+} ions have the capability of forming complexes with water molecules, in which the water molecules are strongly co-ordinated with Co^{2+} ions and they are therefore tightly packed. The number of water molecules of fully hydrated Co A zeolites shown in the table are in good agreement with those obtained by Riley and Seff [10], Gal *et al.* [11] and Coughlan and Shaw [12] for Co₄A, Co_{5.4}A and Co_{5.62}A respectively by X-ray diffraction data, weight loss at 873K and thermogravimetric analysis by heating at 973K. They reported 35, 39 and 42.90 water molecules per unit cell respectively for Co₄A, Co_{5.2}A and Co_{5.52}A-zeolites. According to Riley and Seff [10], the 4 Co^{2+} ions in hydrated Co₄A are located at two distinct crystallographic sites. The first Co^{2+} ion which enters in zeolite A by ion exchange resides in the β -cavity where it is coordinated by regular octahedron of water molecules. The other 3 Co^{2+} ions which enter by ion exchange are distributed about equivalent sites on unit cell three fold axes. It has been suggested that each Co^{2+} ion entering into the structure of zeolite A after the first Co^{2+} ion is responsible for the addition of three water molecules to the zeolite framework. The results of the table are also supported by their suggestion.

Nickel A zeolites

The table shows the gradual increase of water contents per unit cell of hydrated Ni A-zeolites with increasing the Ni^{2+} ions per unit cell. The same reasons are suggested for increased water content of Ni A zeolites as have been given for Co A zeolites. The table indicates that, in general, the number of water molecules per unit cell of Ni A zeolites is higher than Co A zeolites. The reasons are suggested below.

The size of Ni^{2+} ion is smaller than Co^{2+} ion [9]. This shows a high degree of ordering of water molecules around Ni^{2+} ion and hence greater hydration ability of Ni^{2+} than Co^{2+} in hydrated A-zeolite.

In general, the values of water molecules per unit cell of the table agree reasonably well with the literature values. Gal *et al.* [11] reported 44.7 H_2O

molecules per unit cell for Ni_{4.9}A-zeolite. Dyer and Wilson [13] and Coughlan *et al.* [14] showed the increase of water contents per unit cell of a number of Ni A zeolites with increasing degrees of exchange.

The table shows that the colours of dehydrated Ni_{3.9}A and Ni_{4.6}A became brown and black metallic respectively. Amaro *et al.* [15] also reported that the colour of dehydrated Ni_{2.5}A became black and had a metallic lustre. They investigated dehydrated Ni_{2.5}A by X-ray diffraction technique and suggested that Ni²⁺ had disproportionated to some degree to give Ni⁰ and Ni³⁺ or Ni⁴⁺. The formation of the same species is expected here for the metallic-black dehydrated Ni_{4.6}A zeolite. Lattice instability of Ni_{4.6}A is suggested on outgassing in vacuum above room temperature [5].

Copper and manganese A zeolites

The table shows that the number of water molecules per unit cell of Cu A zeolites increases with increasing the Cu²⁺ content in the zeolite A. The same reasons can be given for the increase in the water content of Cu A zeolites as suggested for Co A zeolites. The number of water molecules per unit cell for Cu_{1.8}A zeolite reported by Coughlan and Carrol [16] are 29.7. Thus the values of the table and reported in the literature indicate that the increase in the number of water molecules per unit cell of Cu A zeolites is less than cobalt and nickel A zeolites. This might be in addition to greater ion radius of Cu²⁺ ion, due to less ordering H₂O molecules around Cu²⁺ as compared to Co²⁺ and Ni²⁺ ions. The table shows that the number of water molecules per unit cell of Mn_{3.5}A is 29.4. Yanagida *et al.* [7] reported 29.5 water molecules per unit cell of hydrated Mn_{3.5}A zeolite by X-ray diffraction techniques. Their result supports the water content reported here for Mn_{3.5}A zeolite.

Experimental

Synthetic Na A zeolite (Lot No. 494104075) binderless powder form, white in colour, provided by Union Carbide Corporation, Linde Division, with unit cell composition given in the formula (eq. 1). The exchange of Na A zeolite was carried out to various degrees with Co²⁺, Ni²⁺ and Cu²⁺ cations, only one sample of Mn²⁺ exchange A zeolite

was prepared. Exchanging solutions were made from CoCl₂.6H₂O, NiCl₂.6H₂O, Cu(NO₃)₂.3H₂O and MnCl₂.4H₂O of B.D.H. Chemicals Ltd. The extent of ion exchange was governed by the concentration of the appropriate transition metal ion solution, contact time and solution temperature. The following procedure, to prepare Cu₅A is typical of the exchange methods used. The Na A zeolite (5g) was slurried in 75 cm³ deionized water. The pH of the slurry was recorded by an E.I.L. direct reading pH meter. The pH of slurry was initially about 11.2. The pH was then reduced to 7.0 with constant stirring by adding dropwise very dilute (0.01 mol dm⁻³) hydrochloric acid. A solution of Cu(NO₃)₂.3H₂O (200 cm³, 0.057 mol dm⁻³) was added slowly stirring and the mixture stirred for 50 hours at 343 K. The pH after completing stirring was 5.1. The slurry was filtered and the exchanged sample washed several times with hot, deionized water. The wet sample was dried in an oven overnight at 343 K and then stored over saturated calcium nitrate solution in a desiccator at room temperature for at least 24 hours for complete hydration. The copper content of the solution was analysed before and after exchange, by titration against 0.01 mol dm⁻³ EDTA, with murexide as indicator. The structural integrity of the zeolite samples prepared were checked by X-ray diffraction and physical adsorption. In all sixteen samples of transition metal ions exchanged A-zeolites were prepared (Table 1).

Thermogravimetric studies

The water contents per unit cell of fully hydrated zeolites after outgassing in vacuum at 623 K was determined gravimetrically on a Mc Bain spring balance. This was attached to a standard high vacuum system of Pyrex glass (Fig. 2). The high vacuum system consisted of rotary oil and mercury diffusion pumps, which could be evacuated to 10⁻⁶ torr. The vacuum of system could be checked by McLeod gauge. The mercury diffusion pump was connected by tap 3 to the rotary pump. C₁ was the cold trap for mercury diffusion pump. M₁ was the McLeod gauge. M_m was a mercury manometer, which was isolated from the vacuum system during the experiments by keeping the taps 5 and 7 closed. The reaction vessel was beyond the tap 9. The reaction vessel contained a calibrated quartz spiral which was suspended in a Pyrex glass case. The glass case consisted of two parts. The upper

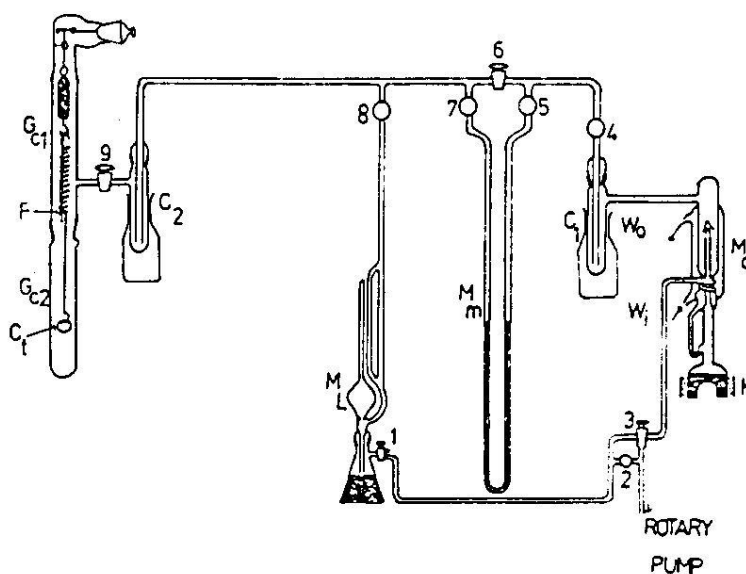
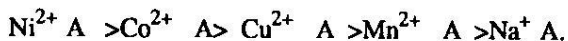


Fig. 2: High vacuum McBain spring balance (See text).

part of the (G_{c1}) was fixed and the lower part (G_{c2}) was mountable. To the lower end of the spiral was attached a small silica bucket for the sample. The fully hydrated samples were compacted without binder using a pressure of 2285 Kg cm^{-2} in a 13 mm diameter metallurgical dye. The specimens of the zeolites used here were in the form of small pieces (0.200 g) obtained by crushing the discs. A suitable point 'F' was chosen on the spiral as a reference point for measuring the extension using a cathetometer.

Conclusion

In general, the zeolitic water obtained per unit cell for Na^+ , Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} A zeolites was in the following sequence:



This order seems quite sensible, because the ionic radii [18] lie in the following order:-

Ni^{2+} ($r=0.69 \text{ \AA}$) < Co^{2+} ($r=0.72 \text{ \AA}$) = Cu^{2+} ($r=0.72 \text{ \AA}$) < Mn^{2+} ($r=0.80 \text{ \AA}$) < Na^+ ($r=0.98 \text{ \AA}$). Furthermore, in the framework of the hydrated zeolite type A, the transition metal ions form hexaquo complexes [19], therefore, due to lower coordinating abilities of Cu^{2+} and Mn^{2+} ions as compared to Ni^{2+} and Co^{2+} ions the Cu A and Mn A zeolites hold less number of water

molecules. An other reason for the least number of water molecules of $\text{Mn}_{3.5}\text{A}$ is its zero crystal field stabilization energy for octahedral complexes.

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