

## Gravimetric and Optical Spectroscopic Studies of Fully Hydrated Cobalt (II) Exchanged A-Zeolites

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**Summary:** This paper reports the water content per unit cell and diffuse reflectance spectra of five samples of fully hydrated Co(II) A-zeolites with different Co<sup>2+</sup> ion loadings. It is suggested that each of the hydrated Co A-zeolite investigated contains per unit cell one Co (H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> complex in the centre of beta cavity (or sodalite unit) [1] and the other Co<sup>2+</sup> ions reside as hexa-aquo complexes in the alpha cavity of the zeolite framework. Small shift of band maxima towards higher frequency for samples with lower Co<sup>2+</sup> ion loadings was measured and interpreted.

### Introduction

Since the synthesis of Na A-zeolite by Breck et.al. [2], its structure has been thoroughly investigated and now the crystalline aluminosilicate framework of type A-zeolite is well understood [3,4]. The thermally stable and polar environments of the structure of crystalline aluminosilicate network of synthetic zeolites lends them to catalytic applications [5]. The incorporation of transition metal ions in the crystal lattice of synthetic zeolite, to promote catalytic activity has been investigated by using a myriad of techniques.

Optical spectroscopy is a useful technique for locating the sites of catalytically important transition metal ions in zeolite framework. The structures of hydrated, partially dehydrated and dehydrated Co A-zeolites using reflectance spectroscopy

have been reported by Klier [6] and Akbar et.al. [7]. This paper illustrates the effect on the position of band maxima with change in the concentration of Co<sup>2+</sup> ions in the framework of hydrated type A-zeolite. The ion-exchanged samples are designated according to the number of Co<sup>2+</sup> ions incorporated per unit cell of the zeolite matrix. Thus, for example Co<sub>2.8</sub> A indicates the sample in which 5.6 Na ions in Na A have been replaced by 2.8 Co<sup>2+</sup> ions.

### Experimental

The starting zeolite material was a synthetic Na A-zeolite in powder form (Lot. No. 4941040757) with unit cell formula Na<sub>12</sub>[(AlO<sub>2</sub>)<sub>12</sub>(SiO<sub>2</sub>)<sub>12</sub>]

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$x\text{H}_2\text{O}$ , without binder-clay, kindly supplied by the Union Carbide (United States). Five samples of the cobalt (II) exchanged zeolites were prepared by ion exchange of the parent material with cobalt (II) chloride (of B.D.H. Chemicals Ltd.) solutions. The extent of ion exchange was governed by the concentration of the  $\text{Co}^{2+}$  ion in cobalt (II) chloride solution, contact time and solution temperature. For preparation of each sample of cobalt (II) A-zeolite, a slurry of 5 gram of fully hydrated Na A zeolite was made with  $75\text{ cm}^3$  of deionized water. The pH of the slurry was initially about 11.2. The pH was reduced to 7 with constant stirring by adding very slowly very dilute (0.01 M) hydrochloric acid. A quantity of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  calculated to give the desired number of  $\text{Co}^{2+}$  ions per unit cell of the zeolite was dissolved in  $200\text{ cm}^3$  of deionised water. The  $200\text{ cm}^3$  solution of cobalt (II) salt was added slowly in small quantities to the slurry. The solution was stirred at temperature  $\sim 353\text{ K}$  with a magnetic stirrer, until it was believed that maximum exchange had occurred. After stopping the ion exchange process, the pH of the solution was measured at room temperature. The solution was filtered and exchanged sample was thoroughly washed several times with deionised hot water. The filtrate and washing were retained for determination of the amount of unexchanged  $\text{Co}^{2+}$  ions. Each wet Co A sample prepared was dried in an oven at  $343\text{ K}$  for overnight. The dried sample (partially dehydrated) was transferred to a desiccator and stored in a constant humidity chamber over saturated calcium nitrate solution at  $298^\circ\text{K}$  for at least 24 hours for complete rehydration. The exact number

of  $\text{Co}^{2+}$  ions per unit cell in the exchanged sample was found by carrying out volumetric analysis.

The amount of  $\text{Co}^{2+}$  ions in the original salt solution and the filtrate was determined. The difference indicated the number of  $\text{Co}^{2+}$  ions introduced in to the zeolite. The cobalt (II) exchanged zeolites have the following composition per unit cell:  

$$\text{Co}_x\text{Na}_{(12-2x)}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]$$

$$\text{WH}_2\text{O}$$

where  $x=1, 1.7, 2.8, 3.4, \text{ or } 4.9$   
 $\text{Co}^{2+}$  and W is the number of water molecules. In this work the above formula is written in the abbreviated form as  $\text{Co}_x\text{A}$ .

The technique for determining the water contents of the samples was the same as reported previously (7). Diffuse reflectance spectra of the fully hydrated Co A-zeolites in the powder form were recorded at room temperature ( $298\text{K}$ ) on a Pye Unicam SP 800 spectrophotometer using a SP 890 diffuse reflectance accessory. X-ray diffraction and low temperature adsorption of research grade krypton studies showed that no structure breakdown resulted from the exchange process.

## Results

A summary of results of preparation and thermogravimetric data of cobalt (II) exchanged A-zeolites are given in tables 1 & 2 respectively. The table 2 shows that water content per unit cell of hydrated Co A-zeolites increases with increasing the number of  $\text{Co}^{2+}$  ions per unit cell of the zeolite. The diffuse reflectance spectra of hydrated  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$ ,  $\text{Co}_{2.8}\text{A}$ ,  $\text{Co}_{3.4}\text{A}$ , and  $\text{Co}_{4.9}\text{A}$  are shown in the figure, by curves 1,2,3,4, and 5 respec-

Table-1: Summary of preparation and analysis of Cobalt (II) exchanged A-zeolites

Sample attempted to prepare	Molarity cobalt (II) chloride salt solu. (M cm <sup>-3</sup> )	Period for cation-exchange (hours)	pH after cation exchange	% of cation exchange sample	Composition of exchange sample	Colour of hydrated sample
Co <sub>1</sub> A	1.15 × 10 <sup>-2</sup>	6	6.5	100	Co <sub>1</sub> A	Very light pink
Co <sub>1.7</sub> A	1.95 × 10 <sup>-2</sup>	17	6.5	99	Co <sub>1.7</sub> A	light pink.
Co <sub>3</sub> A	3.45 × 10 <sup>-2</sup>	10	6.8	94.5	Co <sub>2.8</sub> A	Pink
Co <sub>4</sub> A	4.64 × 10 <sup>-2</sup>	6	5.5	84.8	Co <sub>3.4</sub> A	Bright Pink
Co <sub>6</sub> A	6.9 × 10 <sup>-2</sup>	60	6.4	81	Co <sub>4.9</sub> A	Bright pink

\*200 cm<sup>3</sup> × M of Cobalt (II) chloride solution was used for preparation of every cobalt (II) A-zeolite.

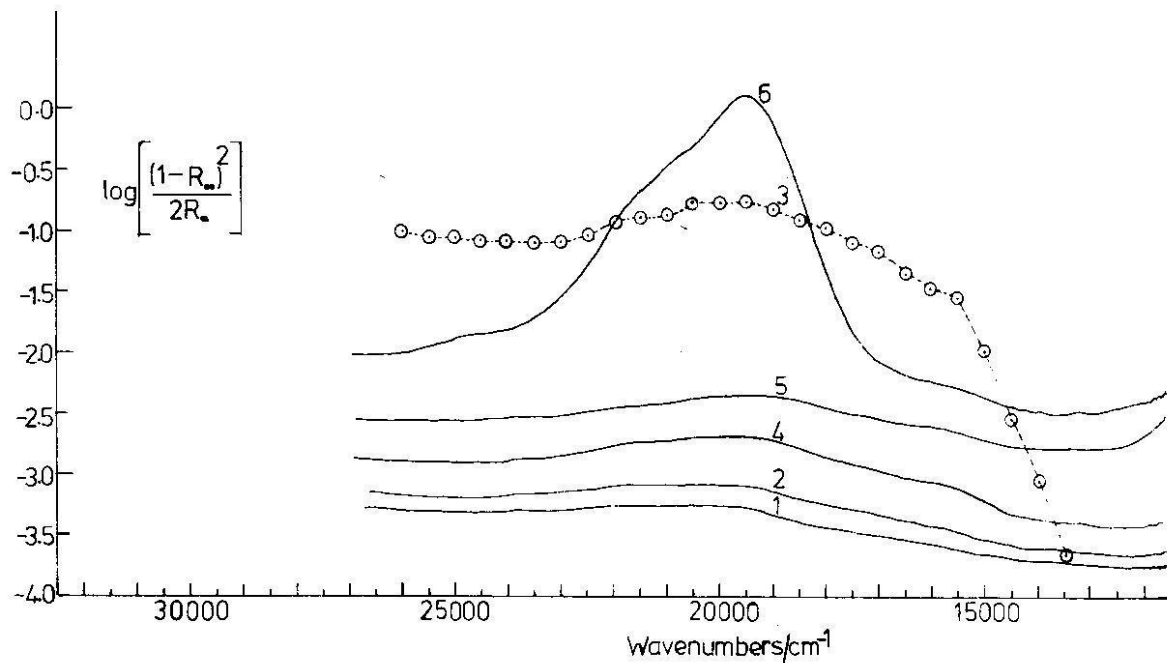


Fig.1: Comparison of the reflectance spectra of hydrated Co<sup>2+</sup> A-zeolites with transmittance spectrum of CoCl<sub>2</sub> solution; (1) Co<sub>1</sub>A; (2) Co<sub>1.7</sub>A; (3) Co<sub>2.8</sub>A; (4) Co<sub>3.4</sub>A; (5) Co<sub>4.9</sub>A; (6) CoCl<sub>2</sub> solution. [Scale of  $\log \left[ \frac{(1-R_\infty)^2}{2R_\infty} \right]$  is only for curve 3]

Table-2 Zeolitic water molecules per unit cell

Na A	30.0
Co <sub>1.0</sub> A	30.5
Co <sub>1.7</sub> A	31.0
Co <sub>2.8</sub> A	33.5
Co <sub>3.4</sub> A	35.8
Co <sub>4.9</sub> A	38.8

tively. Only curve 3 of the figure is plotted as the  $\log_{10}$  of the Schuster Kubelka-munk function versus wave numbers [8], the other curves are in the same forms as they were recorded. Curve 6 of the figure shows the transmittance spectrum of cobalt (II) chloride solution. The fig.1 shows the band maxima of curve 6 at  $19300 \text{ cm}^{-1}$  and also weakly emerged shoulders at ca. 15500, ca.20800 and ca. 21500  $\text{cm}^{-1}$ . The figure indicates the spectra of hydrated Co A-zeolites are similar to the spectrum of  $\text{CoCl}_2$  solution with small shifts of band maxima towards higher frequency with decreasing the cobalt (II) ion concentration in the zeolite.

### Discussion

The results of table 2 indicate that the number of water molecules of Co A-zeolites increases with raising the number of  $\text{Co}^{2+}$  ions in the zeolite frameworks. It was shown by Breck (3) that the presence of different cations in the voids of the type A-zeolite affects the pore volume. A small divalent cation

increases the empty space in the framework for filling with water molecules. As  $2\text{Na}^+$  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  $\text{Å}$  (9) respectively, the total empty space in the cavities increases by exchanging  $\text{Na}^+$  ions by  $\text{Co}^{2+}$  ions. It was indicated by Breck (3) that both  $\alpha$  and  $\beta$ -cavities are easily accessible to water molecules. In addition, it is well known that 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. Thus the above mentioned facts support the results of the table 2. Moreover, the number of water molecules of hydrated Co A-zeolites of the table are in good agreement with those previously reported [1, 10,11] by using different techniques for  $\text{Co}_{5.4}\text{A}$ ,  $\text{Co}_4\text{A}$  and  $\text{Co}_{5.62}\text{A}$ . Gravimetric results are also close to the suggestion (1) that after the first  $\text{Co}^{2+}$  ion, each  $\text{Co}^{2+}$  ion entering in to the structure of zeolite A, adds about  $3\text{H}_2\text{O}$  molecules.

The curve 6 of the figure shows that the absorption spectrum of  $\text{CoCl}_2$  solution resembles the diffuse reflectance spectra (curves 1,2,3,4 and 5) of hydrated Co- A-zeolites, but for a hypsochromic shift of ca. 1000, ca.900, ca.700, ca.500 and ca.200  $\text{cm}^{-1}$  respectively for  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$ ,  $\text{Co}_{2.8}\text{A}$ ,  $\text{Co}_{3.4}\text{A}$ , and  $\text{Co}_{4.9}\text{A}$ . Hydrated  $\text{Co}_{4.9}\text{A}$  (curve 5) shows the band maximum at ca. 19500  $\text{cm}^{-1}$  where about the band maximum of cobalt (II) chloride solution lies. It is well known that hydrated

cobaltous salts contain  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  (9) and that the reflectance spectra of hydrated  $\text{Co}^{2+}$  A-zeolites can be interpreted as due to  $\text{Co}^{2+}$  ion in an octahedral field of water molecules and forming hexa-aquo complex. In addition, the following reasons are suggested for the formation of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  complexes in the framework of hydrated Co A-zeolites.

1. The table 2 shows that in each of the Co A-zeolite the ratio of number of water molecules at  $\text{Co}^{2+}$  ions per unit cell is greater than 6.
2. This result is in agreement with previous studies (6).
3. The colours of cobalt (II) chloride solution and hydrated samples of Co A-zeolites were pink (showing similar spectra).

Gal et.al. [10] reported that in hydrated  $\text{Co}_{5.4}\text{A}$ , on average,  $2\text{Na}^+$  and  $3\text{Co}^{2+}$  ions per unit cell are linked with the 6-oxygen rings of the framework, where each ion forming  $\text{Na}^+(\text{OX})_3(\text{H}_2\text{O})_3$  and  $\text{Co}(\text{OX})_3(\text{H}_2\text{O})_3$  complexes respectively, the remaining  $2\text{Co}^{2+}$  ions in the alpha cavity are fully aquated with octahedrally coordinated water molecules (OX refers to an oxygen atom of the zeolite 6-ring framework). The formation of  $\text{Na}^+(\text{OX})_3(\text{H}_2\text{O})_3$  complex is ruled out on the basis that  $\text{Na}^+$  ion has no ability of forming such type of complex. Moreover, in the presence of 'free' water molecules, whilst cations in hydrated type A zeolite are mobile (3), the formation of octahedral aquo-complexes  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  are more

likely than  $\text{Co}(\text{OX})_3(\text{H}_2\text{O})_3$  complexes. Furthermore Riley et.al. [1] reported through single crystal X-ray studies of hydrated  $\text{Co}_4$  A-zeolite that  $\text{Co}^{2+}$  ions are too far from the framework oxygen atoms to coordinate to them. In this work, we suggest that first exchanged  $\text{Co}^{2+}$  ion per unit cell in each hydrated Co A-zeolite investigated, most likely lies in the centre of  $\beta$ -cavity (or sodalite unit) in the form of octahedral aquo-complex  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  due to the following reasons:

1. Surface area measurement by krypton adsorption at 77K indicated (13) that the entry of first  $\text{Co}^{2+}$  ion in to zeolite framework occurred by the displacement of  $2\text{Na}^+$  ions from site I (6-ring), because the area of  $\text{Co}_1\text{A}$  was the same as that of unexchanged Na A. As  $4\text{H}_2\text{O}$  molecules occupy  $\beta$ -cavity in unexchanged hydrated Na A-zeolite (3), so that due to small size of  $\text{Co}^{2+}$  ion and its complex forming ability, it can easily be surrounded by  $6\text{H}_2\text{O}$  molecules.
2. The hydrated  $\text{Co}_1\text{A}$  (table 1) was of light pink colour, characteristic of hexaaquo Co (II) complex.
3. This suggestion, is also agreed with the result of Riley et.al. [1] who reported through single crystal X-ray diffraction techniques for hydrated  $\text{Co}_4\text{A}$ , the existence of one  $\text{Co}^{2+}$  ion forming  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  complex in the centre of the  $\beta$ -cavity.
4. The location of one  $\text{Co}^{2+}$  ion in the centre of  $\beta$ -cavity is possible, because in order to distribute the positive charge of the cations more uniformly, so as to minimize cation-

cation interaction as well as to neutralize negative charge of the framework. The remaining  $\text{Co}^{2+}$  ions of each hydrated Co A-zeolite are suggested to reside as fully aquated octahedrally coordinated species in the large  $\beta$ -cage of the zeolite framework.

The band maxima of hydrated  $\text{Co}_{4.2}$  A has been reported [12] to be at  $19500 \text{ cm}^{-1}$ , which is consistent with the result indicated here for  $\text{Co}_{4.9}$  A (curve 5). As far as small shifts of band maxima towards higher frequency for zeolites containing less than 4.9  $\text{Co}^{2+}$  ions per unit cell is concerned, similar results have been indicated previously (6,8).

In literature (6,8,12), different suggestions have been given for the shifts of the band maxima for hydrated Co A-zeolites. In this work, the following reasons are suggested for the bathochromic shifts of the band maxima with increasing  $\text{Co}^{2+}$  ions in type A-zeolite.

1. Increased structuring of the zeolitic water (3) which causes decrease in pressure on the complexes (14).

2. In agreement with Heilbron et al. [12] the increased interaction of the  $\text{Co}^{2+}$  ion electron could with framework oxygen ions, thus the  $\text{Co}^{2+}$  ion crystal field is influenced by the strong electric field of the zeolite framework.

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