

## Diffuse Reflectance Spectroscopic Investigation of Partially and Fully Rehydrated Cobalt (II) Exchanged A-Zeolites

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**Summary:** The formation of complexes of  $\text{Co}^{2+}$  ion with  $\text{H}_2\text{O}$  molecules in the framework of synthetic molecular sieve A, at different stages of rehydration have been investigated by diffuse reflectance spectroscopy. The results showed that  $\text{Co}_{1\text{A}}$ ,  $\text{Co}_{1.7\text{A}}$ ,  $\text{Co}_{2.8\text{A}}$  and  $\text{Co}_{3.4\text{A}}$  regained their initial structures after complete rehydration. The spectrum of fully rehydrated  $\text{Co}_{4.9\text{A}}$  was nearly similar as of its fully hydrated sample [1], except a weak band at  $17300\text{ cm}^{-1}$  instead of weakly emerged shoulder. The rate of rehydration was observed to decrease on increasing the  $\text{Co}^{2+}$  ion loadings in the zeolite.

### Introduction

By using combined results of gravimetric and optical spectroscopic techniques, the structures of five samples of hydrated, partially and fully dehydrated Co Na A-zeolites have been described previously [2]. As far as the authors are aware no systematic study by using reflectance spectroscopy of a series of varying concentration of partially and fully rehydrated cobalt (II) A-zeolites has been reported yet. The present paper illustrates the measurement of the diffuse reflectance spectra of five samples of synthetic Na A-zeolites in which the charge balancing sodium ions have been replaced by 1, 1.7, 2.8, 3.4, and 4.9  $\text{Co}^{2+}$  ions per unit cell. The aim of this work was to investigate the formation of the complexes of  $\text{Co}^{2+}$  ion in the framework of A-type zeolite during its different degrees of rehydration and finally to examine whether

Co A-zeolites regain their initial structures after complete rehydration.

### Experimental

The parent zeolite was Na A (lot no 4941040757) kindly supplied by the Union Carbide Co. (United States). The preparation of Co Na A samples and their chemical analysis carried out as previously described [3]. X-ray diffraction and low temperature adsorption of krypton indicated the stability of crystalline aluminosilicate framework of all samples except  $\text{Co}_{4.9\text{A}}$  which showed partial collapse of structure during dehydration in vacuo.

The diffuse reflectance spectroscopy was carried out at room temperature (298K) on a Pye Unicam SP-800 spectrophotometer using a SP-890 diffuse reflectance accessory. The spectra were recorded in the visible UV range

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(11,500 to 32,500  $\text{cm}^{-1}$ ). For taking reflectance spectra of the samples after different degree of rehydration at room temperature first a vacuum upto  $10^{-6}$

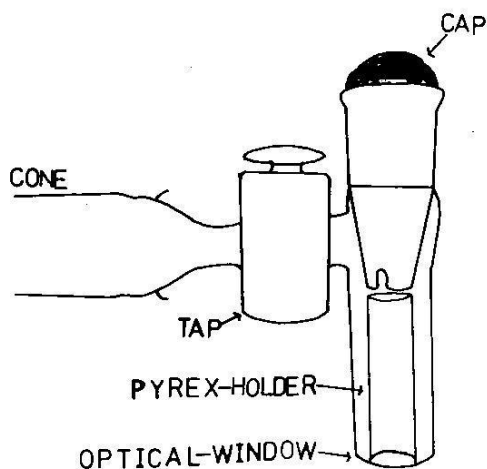


Fig.1: Vacuum cell for reflectance spectrum measurement.

torr was produced in the Pyrex glass standard high vacuum system by using both the rotary oil pump and mercury diffusion pump. The vacuum cell (Fig. 1) containing a fully hydrated disc of sample was connected to the main vacuum apparatus. The sample was outgassed at 620K for several hours till complete dehydration occurred [4]. The cell was disconnected from the vacuum apparatus. After taking the spectra of partially rehydrated samples, at different degree of rehydration, finally they were kept in a desiccator over saturated calcium nitrate solution for complete rehydration. In case of  $\text{Co}_{4.9}\text{A}$  (82% exchanged), the partially rehydrated samples was ground and mixed with deionized water and left in the water for different periods. It was filtered and dried at room temperature for recording the spectrum.

Table-1: Composition per unit cell of dehydrated Co A-zolites.

Zeolites	Exchange (%)	$\text{Co}^{2+}$	$\text{Na}^+$
$\text{Co}_1\text{A}$	16.6	1	10
$\text{Co}_{1.7}\text{A}$	28.3	1.7	8.6
$\text{Co}_{2.8}\text{A}$	46.6	2.8	6.4
$\text{Co}_{3.4}\text{A}$	56.6	3.4	5.2
$\text{Co}_{4.9}\text{A}$	81.6	4.9	2.2

where A is abbreviation for configuration  $[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}]^{-12}$

## Results

The results of the chemical analyses of all samples are given in Table 1. The spectra recorded after different degrees of rehydration were similar for all samples except that of  $\text{Co}_{4.9}\text{A}$ .

All dehydrated discs of the samples changed their colours from pale blue to bright blue immediately on exposure to atmospheric water vapours. The reflectance spectra of  $\text{Co}_{2.8}\text{A}$ , after exposing the dehydrated disc to air for 4 (5 or 7), 36,60 mins and 10 weeks are shown in Fig. 2 by curves 1,2,3 and 4 respectively. Curves 1,2,3 and 4 of Fig. 2, show band maxima at 17200, 17300, 17300 and 19800  $\text{cm}^{-1}$  respectively. The spectra of  $\text{Co}_{4.9}\text{A}$  after exposing the dehydrated disc of the sample to air for 5, 30 (or 60) mins are shown in Fig. 3, by curves 1 and 2 respectively.

The diffuse reflectance spectra of fully rehydrated samples (Pink in colour) of  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$ ,  $\text{Co}_{2.8}\text{A}$ , and

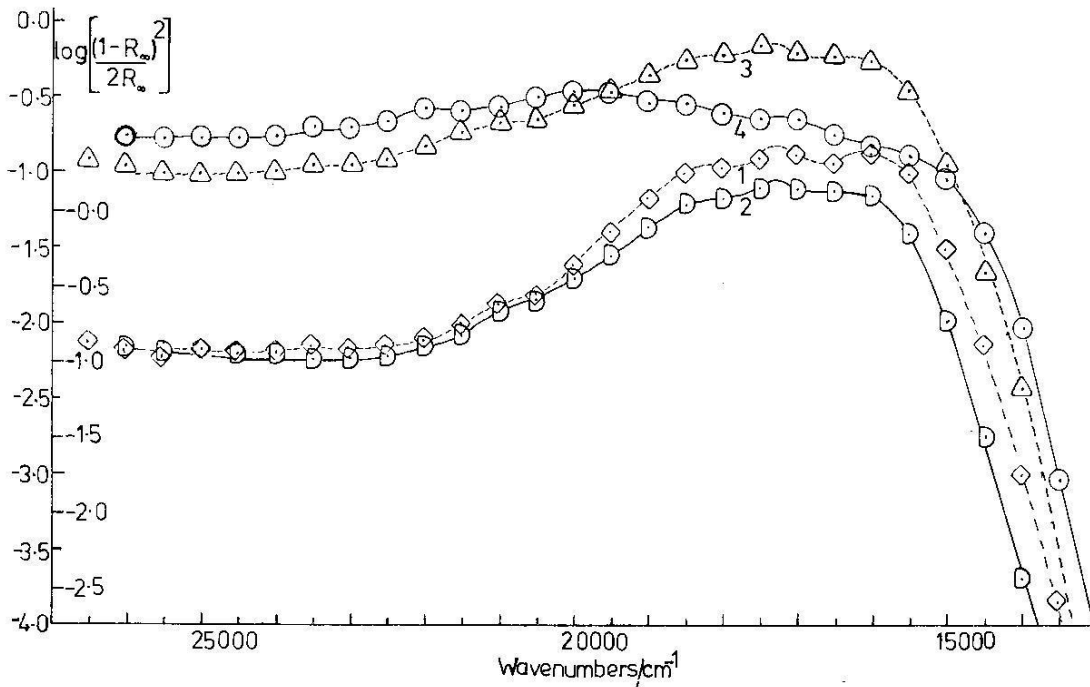


Fig.2:

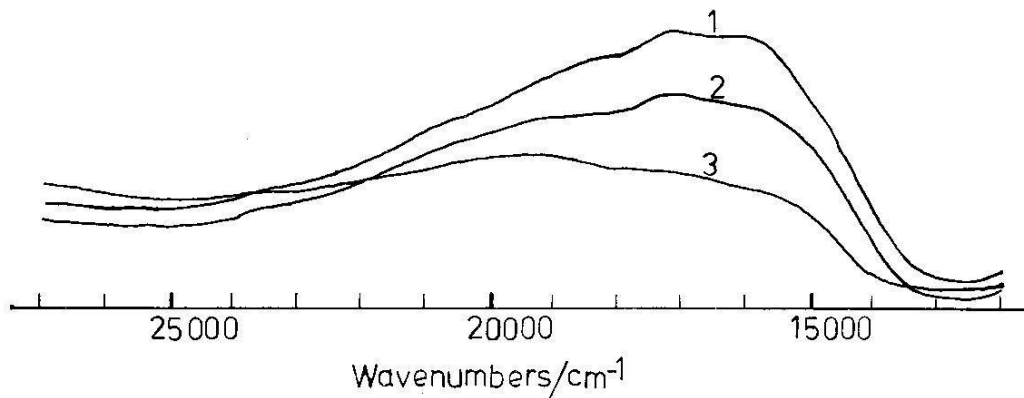


Fig. 3: Reflectance spectra of the rehydrated  $\text{Co}_{4.9}\text{A}$ : (1) the dehydrated sample was exposed to water vapours for 5 mins; (2) for 30 mins; (3) for 3 months.

$\text{Co}_{3.4}\text{A}$  except  $\text{Co}_{4.9}\text{A}$  were the same as their hydrated spectra [1]. Curve 4 (Fig.2) shows the spectrum of fully rehydrated  $\text{Co}_{2.8}\text{A}$  sample. The partially rehydrated disc of  $\text{Co}_{4.9}\text{A}$  was stored over saturated calcium nitrate solution in a desiccator for 8 weeks and its reflectance spectrum was

recorded as shown by curve 3 in Fig. 3. The band maxima of curves 1, 2 and 3 of Fig.3 are lying at 17150, 17150 and  $19300\text{ cm}^{-1}$  respectively. Then the partially rehydrated disc of  $\text{Co}_{4.9}\text{A}$  was ground and mixed with deionized water and left in the water for 24 hours. It was filtered and dried

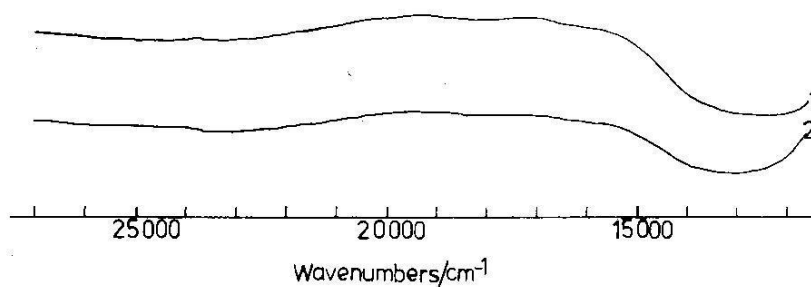


Fig.4: The rehydrated spectra of  $\text{Co}_{4.9}\text{A}$ : (1) the partially rehydrated sample was mixed with deionised water, filtered and after drying at room temperature, recorded the spectrum; (2) the above sample was kept in water for four weeks, then filtered after drying at room temperature, recorded the spectrum.

at room temperature, the spectrum was taken and is shown in Fig. 4 by curve 1. The above sample of  $\text{Co}_{4.9}\text{A}$  was then kept in water for an additional 4 weeks and its reflectance spectrum was measured, which is shown by curve 2 in Fig.4. The band maximum of curve 2 of Fig. 4 is at  $19500\text{ cm}^{-1}$  whereas its hydrated spectrum shows at  $19300\text{ cm}^{-1}$  [1]. The other differences lie in that the hydrated spectrum shows the weakly emerged shoulders at ca.  $15700$ ,  $17300$  and  $21700\text{ cm}^{-1}$ , whereas the spectrum 2 of Fig. 4 shows weakly emerged shoulders at ca.  $15500\text{ cm}^{-1}$ ,  $21500\text{ cm}^{-1}$  and also a weakly emerged band at  $17400\text{ cm}^{-1}$ .

### Discussion

The curve 1 of Fig. 2 matches the spectrum of partially dehydrated  $\text{Co}_{2.8}\text{A}$  at  $298\text{K}$  in vacuo [2]. The colour of the sample was bright blue. Thus for spectrum 1 (Fig. 2), tetrahedral  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  complex is suggested. The curves 2 and 3 of Fig. 2 probably show the formation of mixed complexes like  $[\text{Co}(\text{H}_2\text{O})_5]^{2+}$  and  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . The number of hexa-aquo complexes of  $\text{Co}^{2+}$  ions

increases with increasing the time of exposure of partially rehydrated samples to air. Curve 4 is similar in features like the spectrum of fully hydrated  $\text{Co}_{2.8}\text{A}$  [1]. The rehydrated sample of  $\text{Co}_{2.8}\text{A}$  was pink. Similarly the spectra of fully rehydrated  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$ , and  $\text{Co}_{3.4}\text{A}$  resembled the spectra of their hydrated samples [1]. The fully rehydrated samples of  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$  and  $\text{Co}_{3.4}\text{A}$  were pink colours like their fully hydrated samples. Therefore the above evidences suggest the  $\text{Co}_1\text{A}$ ,  $\text{Co}_{1.7}\text{A}$ ,  $\text{Co}_{2.8}\text{A}$  and  $\text{Co}_{3.4}\text{A}$ , zeolites regained their initial structures and reformed the hexaquo complexes upon complete rehydration.

The curves of Fig. 3 show that the process of rehydration was very slow. The spectra of Fig. 4 show that the process of rehydration can be made fast by mixing the partially rehydrated sample of  $\text{Co}_{4.9}\text{A}$  (Bluish pink) with deionised water. Spectrum 2 (Fig. 4) indicates that the dehydrated  $\text{Co}_{4.9}\text{A}$ -zeolite could not be fully rehydrated as it did not resemble the spectrum of fully hydrated  $\text{Co}_{4.9}\text{A}$  [1]. The colour of the fully rehydrated sample was pinkish. It seems likely that some

of the tetrahedrally coordinated  $\text{Co}^{2+}$  ion i.e.,  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  entered the sodalite cages during rehydration. Due to the small size ( $6.6 \text{ \AA}$  in diameter) of the sodalite cage (beta-cavity), it may not accommodate more than one  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex, which was indicated by Amaro et al [5] and Riley and Seff [6] by X-ray diffraction techniques. Moreover, Dyakonov et al [7] indicated that  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  has a diameter of  $4.78 \text{ \AA}$  obviously excludes the penetration of hexa-aquo complex through the 6-rings ( $2.8 \text{ \AA}$  diameter) of the sodalite unit to beta-cavity. Moreover, the surface area measurement of  $\text{Co}_{4.9}\text{A}$  indicated [3] the partial collapse of the structure after outgassing in vacuo. Therefore, it is suggested that all  $\text{Co}^{2+}$  ions of dehydrated  $\text{Co}_{4.9}\text{A}$  could not regain their initial hex-aquo complexes. As the extinction coefficient of tetrahedral cobalt (II) complex is 50 times greater than octahedral (II) complex [8], therefore the features of the spectrum 2 of Fig.4 indicate the presence of 98%  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  and 2%  $[\text{Co}(\text{H}_2\text{O})_4]^{2+}$  complexes. In general, the colours change of the rehydrated samples from pale blue to pink and their diffuse reflectance spectra showed that the speed of rehydration of  $\text{Co}^{2+}$  A-zeolites was in the following order:

$$\text{Co}_1\text{A} > \text{Co}_{1.7}\text{A} > \text{Co}_{2.8}\text{A} > \text{Co}_{3.4}\text{A} > \text{Co}_{4.9}\text{A}.$$

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