

Diffuse Reflectance Spectroscopy of Dehydrated Cobalt-Exchanged Faujasite-Type Zeolites: A New Method for Co²⁺ Siting

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The diffuse reflectance spectra of cobalt in X- and Y-type zeolites with varying Co²⁺ contents have been investigated after dehydration at 400 and 500 °C. A novel method for the determination and characterization of Co sites in dehydrated zeolites is developed. The spectra were resolved with a decomposition program in five or six Gaussian bands in the visible region (12 500–22 500 cm⁻¹) and three Gaussian bands and two Lorentz bands in the near infrared region (4000–10 000 cm⁻¹). Interactive self-modeling analysis showed the presence of three independent Co species, called pure components. In the visible region component A appeared at 20 000–17 800 cm⁻¹, component B appeared in the 18 800–15 300 cm⁻¹ region with three band maxima, and component C appeared with main purity at 13 700–14 900 cm⁻¹. In the near infrared region component B appeared as a triplet in the 4600–7000 cm⁻¹ region together with two components of framework hydroxyls at 4500 and 7600 cm⁻¹. With the aid of additional experiments on dehydrated lanthanum-, cesium-, and ammonium-exchanged Co zeolites, the three cobalt-related components (A, B, and C) were assigned as follows: A, (pseudo)octahedral cobalt in the hexagonal prisms (I); B, (pseudo)tetrahedral cobalt at I' (II',II); and C, trigonally coordinated cobalt at the same sites. These findings are discussed in relation with XRD results of Co siting.

Introduction

For all applications of transition metal ion (TMI) exchanged zeolites there is a great interest in locating and characterizing the preferred positions of the TMI in order to understand complexation and catalytic properties. The coordination sites can be obtained with X-ray diffraction (XRD), however, such studies are only possible for high TMI loadings. For a study of the coordination at lower loadings a spectroscopic approach, such as diffuse reflectance spectroscopy (DRS), is recommended.

Klier was the first to develop a ligand field model to explain the d-d transitions of the 3d TMI, coordinated to six-rings of oxygens in zeolite A.^{1,2} Similar six-rings occur in zeolites X and Y, together with other coordination sites, all of which can be occupied simultaneously. In this paper we have chosen cobalt as a probe for studying the cation siting in X- and Y-type zeolites. The most important cation sites are indicated with Roman numbers in Figure 1. It has been established that during dehydration the hexaquo complex Co(H₂O)₆²⁺ (O_h symmetry) in the supercage loses water and migrates toward the sodalite cages where it is coordinatively bound to three oxygen ions of the structure and one extra-lattice OH⁻ or O²⁻ group at sites I' and II'.^{3–8} The electronic spectrum becomes that of a tetrahedral Co²⁺ species with two ranges of absorption:⁹ the visible (VIS), 20 000–15 400 cm⁻¹, and the near infrared (NIR), 8300–5900 cm⁻¹. In each range, a 3-fold band splitting is often observed. Above 250 °C, a large part of the tetrahedral species migrates in the hexagonal prisms (octahedral site I), but yet a part stays tetrahedrally coordinated at II' or I' as evidenced by XRD.¹⁰ As a consequence, the DRS spectra of Co²⁺ in X and Y are a superposition of spectra, due to Co²⁺ on different sites. Up to now, no method has been developed to decompose these spectra into their individual components.

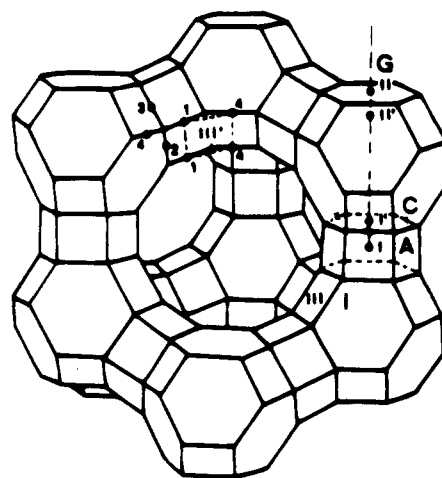


Figure 1. Faujasite structure with indication of cation sites. Numbers refer to the four crystallographically different oxygens.

We propose a new approach for the spectroscopic speciation of Co²⁺ on different sites in dehydrated zeolites X and Y. The method is based on (1) decomposition of spectra of homogeneous series of dehydrated Co zeolites into Gaussian and/or Lorentz bands and (2) an interactive self-modeling analysis of these series of spectra.^{11–15}

Experimental Section

1. Sample Preparation and Characterization. *1.1. CoNaX–CoNaY.* Commercial X- and Y-type zeolites from Ventron were stirred in 0.01 M NaCl, washed Cl⁻ free, air-dried, and stored over a saturated NH₄Cl solution prior to use. Cobalt zeolites with variable cobalt content were prepared by ion exchange of the so-obtained NaX or NaY in solution (1 g/L) with the amount of CoCl₂·6H₂O necessary to obtain the desired exchange level at room temperature. The exchange time was 24 h.

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