



# Characterization of thermally treated $\text{Co}^{2+}$ -exchanged zeolite X

Hoon Young Jeong<sup>a</sup>, Dong-Chan Koh<sup>b</sup>, Kwang-Sik Lee<sup>c,\*</sup>, Hyun Hwi Lee<sup>d,\*\*</sup>

<sup>a</sup> Department of Geological Sciences, Pusan National University, Busan 609-735, South Korea

<sup>b</sup> Geologic Environment Division, Korea Institute of Geoscience & Mineral Resources, Daejeon 305-350, South Korea

<sup>c</sup> Division of Earth and Environmental Science, Korea Basic Science Institute, Ochang, Chungbuk 363-883, South Korea

<sup>d</sup> Pohang Accelerator Laboratory, Pohang University of Science and Technology (POSTECH), Pohang 790784, South Korea

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## ABSTRACT

This study investigated thermal stabilization of  $\text{Co}^{2+}$ -exchanged zeolite X (Co–X) using scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD), X-ray absorption spectroscopy (XAS), and leaching tests. From SEM-EDX analysis, cobalt was dispersed randomly at  $\leq 600^\circ\text{C}$ , suggesting its presence as an extraframework cation in exchange sites. At  $\geq 800^\circ\text{C}$ , cobalt was locally concentrated with Al on the vitreous surface. Consistent with such observations, XRD data indicated that Co–X maintained the zeolite framework at  $\leq 600^\circ\text{C}$ , and that it became vitrified and transformed to nepheline ( $\text{NaAlSiO}_4(\text{s})$ ) and cobalt aluminate ( $\text{CoAl}_2\text{O}_4(\text{s})$ ) at  $\geq 800^\circ\text{C}$ . Cobalt-K edge XAS was subjected to both X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) analyses. In XANES spectra, the pre-edge peaks and edge-shoulders, characteristic of 4-fold coordinated cobalt (e.g.,  $\text{CoAl}_2\text{O}_4(\text{s})$ ), were not evident at  $\leq 600^\circ\text{C}$ , but such features were strong at  $\geq 800^\circ\text{C}$ . The EXAFS spectra of Co–X at  $\leq 600^\circ\text{C}$  lacked in the coordination shells beyond the first Co–O shell. In contrast, Co–X at  $\geq 800^\circ\text{C}$  showed the EXAFS spectra similar to  $\text{CoAl}_2\text{O}_4(\text{s})$ . Taken together, cobalt was likely present as 6-fold coordinated  $\text{Co}^{2+}$  in exchange sites at  $\leq 600^\circ\text{C}$  and mainly incorporated into a non-exchangeable  $\text{CoAl}_2\text{O}_4$ -like phase in both vitreous and crystalline forms at  $\geq 800^\circ\text{C}$ . In agreement with this proposition, leaching tests with concentrated  $\text{CaCl}_2$  solutions supported the greater stability of cobalt at  $\geq 800^\circ\text{C}$ .

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## 1. Introduction

Nuclear fuel reprocessing and nuclear energy generation produce large amounts of radioactive liquid wastes [1]. Such liquid wastes may contain the radioactive isotope  $^{60}\text{Co}$ , one of the most hazardous pollutants present in low-to-intermediate level liquid radioactive wastes [2]. Before disposal, the radioactive cobalt is treated with ion exchangers such as organic resins, clay minerals, and zeolites to prevent it from being introduced into environments [3]. Among them, zeolites are most commonly employed to remove radioactive cations from nuclear wastewaters due to the higher selectivity and capacity for radioactive cations [4] and the greater radiational and thermal stability [5]. Through cation exchange, zeolites sorb radionuclides including  $^{60}\text{Co}^{2+}$  from nuclear wastewaters [2]. However, the reversible nature of ion exchange makes the once-sorbed nuclides re-exchanged by other cations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc.) in groundwaters [5]. Thus,  $\text{Co}^{2+}$ -exchanged zeolites are often

thermally treated (calcinated) to have radioactive cations in vitreous lattices or non-exchangeable crystalline phases [1,3].

Several mechanisms have been proposed for thermal stabilization of radioactive cations in zeolites. Thermal treatment of zeolites causes dehydration, which in turn results in the redistribution of extraframework cations among different types of exchange sites [6]. The dehydration of zeolite X was found to cause  $\text{Co}^{2+}$  in site I' to migrate into site I, the more restricted and less exchangeable site [7]. Thermal treatment also led to the closure of open channels, making sorbed cations no longer available for ion exchange [8]. For example, the melting of the zeolite surface may develop vitreous coating on the surface [3]. These processes account for the increased stability of radionuclides before the whole framework of zeolites breaks down. Upon the collapse of the zeolite framework at higher calcination temperatures, sorbed radionuclides become entrapped within the glassy material or non-exchangeable crystalline phases [1,3]. By thermal treatment,  $\text{Co}^{2+}$ -exchanged zeolite X was found to transform into cobalt aluminate ( $\text{CoAl}_2\text{O}_4$ ) along with amorphous phase(s) [1].

Despite the aforementioned stabilization mechanisms, the exact chemical nature of cobalt in thermally treated zeolites has not been fully understood. To date, the structure of  $\text{Co}^{2+}$ -exchanged zeolites during thermal treatment has been investigated largely based on

\* Corresponding author. Tel.: +82 43 240 5337; fax: +82 43 240 5319.

\*\* Corresponding author. Tel.: +82 54 279 1551; fax: +82 54 279 1599.

E-mail addresses: [hjeong@pusan.ac.kr](mailto:hjeong@pusan.ac.kr) (H.Y. Jeong), [chankoh@kigam.re.kr](mailto:chankoh@kigam.re.kr) (D.-C. Koh), [kslee@kbsi.re.kr](mailto:kslee@kbsi.re.kr) (K.-S. Lee), [hleec@postech.ac.kr](mailto:hhleec@postech.ac.kr) (H.H. Lee).

**Table 1**  
Physicochemical properties of zeolite X.<sup>a</sup>

Chemical formula	Particle size	Pore size	Bulk density
Na <sub>86</sub> Al <sub>86</sub> Si <sub>106</sub> O <sub>384</sub> ·xH <sub>2</sub> O	125–150 μm	~13 Å	~0.65 g/mL

<sup>a</sup> The data are obtained from the supplier.

XRD method [1,3]. Since XRD is sensitive to the long-range ordering, the information attained by this technique is mostly restricted to the identity of crystalline phases, leading to the incomplete understanding of thermal stabilization mechanisms. Few exceptions have resulted from the structural refinement analysis of XRD data [7,9], by which the local coordination of Co in zeolites can be fully resolved. Yet, most previous studies utilizing such a laborious refinement analysis were not originally intended for thermal treatment of Co<sup>2+</sup>-exchanged zeolites. Consequently, the calcination temperatures used in those studies were limited, and the experimental conditions were often irrelevant for the purpose of thermal treatment (e.g., heating under vacuum). Furthermore, when the sorbed phase becomes associated with or incorporated into amorphous phases during thermal treatment of zeolites, the information on the coordination structure of cobalt cannot be obtained by XRD. The coordination information is necessary given that the stability of sorbed cobalt is determined by the strength of its bonds to the bulk phase(s). In this study, thus, the local coordination structure of cobalt was examined using XAS. Since the XAS signals originate dominantly from a few coordination shells of atoms close to the absorbing atom, it can serve as an effective local structure probe [10]. Besides, SEM and XRD were employed to have the bulk-phase structural information. Leaching tests were also performed to supplement the results from SEM, XRD, and XAS analyses. With these methods, we aimed to investigate the structural changes of Co<sup>2+</sup>-exchanged zeolites as a function of thermal treatment temperature and time for a better understanding of thermal stabilization mechanisms for cobalt.

Besides the use for the safe disposal of nuclear wastes, zeolites can be effective decontaminants in treating radionuclide-contaminated sites [11,12] or back-fill materials in nuclear waste repositories [13]. In such applications, zeolites tend to receive great amounts of heat and radiation dose, both of which gradually amorphorize zeolites over time [8]. Even before the complete amorphorization of zeolites, sorbed radionuclides were found to be more stabilized [14]. Nonetheless, most previous researches have been mainly focused on the thermal stabilization of sorbed radionuclides in zeolites at temperatures at which amorphorization occurs. Thus, it was also our goal to examine the structure of thermally exposed, yet crystalline zeolites for the prediction of the stability change of cobalt over a wide range of temperatures.

## 2. Experimental

### 2.1. Sample preparation

Zeolite X, a synthetic Al-rich zeolite with the faujasite framework [15], was purchased from Sigma–Aldrich (see Table 1 for its physicochemical properties and Fig. A.1 in Supplementary Material for the structure). The zeolite powder was pretreated as follows: 100 g of the powder was equilibrated with 1000 mL of 5 M NaCl solution for 7 days, after which it was washed out with deionized water several times to remove the residual NaCl and oven-dried at 60 °C. To prepare Co<sup>2+</sup>-exchanged form (Co–X), the pretreated sample (80 g) was reacted at pH ~ 6.3 with 1000 mL of 0.32 M CoCl<sub>2</sub> solution for 48 h on a magnetic stirrer. The slightly acidic condition in preparing Co–X was chosen to prevent the precipitation of Co(OH)<sub>2</sub>(s) and minimize the exchange of proton for Na<sup>+</sup> in zeolite

[7]. Following the exchange of Co<sup>2+</sup> for Na<sup>+</sup>, the resultant sample was thoroughly rinsed with deionized water to remove the residual CoCl<sub>2</sub> and then oven-dried at 60 °C. A portion of Co–X samples was digested with a mixture of nitric, hydrofluoric, and perchloric acids at 200 °C for overnight, and then was analyzed for the composition of Na, Co, and Al using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Approximately 58% of the total exchange sites in Co–X were found to be occupied by Co<sup>2+</sup>, with the resultant unit formula of Na<sub>36</sub>Co<sub>25</sub>Al<sub>86</sub>Si<sub>106</sub>O<sub>384</sub>. Such incomplete Co<sup>2+</sup> occupancy has been previously observed for zeolite X [7].

Co–X samples were thermally treated using a chamber furnace with a SiC rod (Nabertherm, Inc.) under the atmosphere. The furnace temperature was ramped at a rate of 20 °C/min and kept isothermal at the target treatment temperatures (400, 600, 800, 1000, and 1200 °C) for 2–24 h. Such treatment conditions covered where the zeolite structure was retained and collapsed. The similar temperatures were previously employed in thermal treatment of Co<sup>2+</sup>-exchanged zeolite X [1]. After thermal treatment, the samples were quickly removed from the furnace and allowed to quench at room temperature. Prior to use, thermally treated samples were stored inside air-tight serum vials to prevent the absorption of moisture from the atmosphere. As described in the following sections, the samples were subjected to leaching tests as well as solid-phase characterization using SEM, XRD, and XAS techniques.

### 2.2. SEM and XRD

The effect of thermal treatment on the size and morphology of particles and the distribution of elements was examined using a scanning electron microscope (HITACHI 6853-H) equipped with an energy dispersive X-ray spectroscope at voltages of 5–15 kV. Sample powders were applied on a conductive carbon tape and then coated with a Pt film. Image processing and analysis were performed using ImageJ 1.42 (National Institutes of Health, USA).

XRD provides information on changes of the crystallinity and mineralogical composition of Co–X by thermal treatment. Each powder sample was loaded into a quartz capillary. X-ray diffraction measurements were performed with an 18 keV X-ray beam at beamline 5A at Pohang Accelerator Laboratory (PAL). Diffraction patterns were recorded on a MAR345 image plate, and the data were then processed using the Fit2d suite [16]. For the samples maintaining the zeolite framework, the unit cell parameter was extracted from the reflection peak positions.

### 2.3. XAS

Cobalt-K edge XAS spectra were collected at ambient temperature at beamline 10B (2.5 GeV, ~150 mA) at PAL using an unfocused beam with a Si(1 1 1) double-crystal monochromator. Transmission and fluorescence signals were simultaneously measured using high precision ionization chambers (IC-SPEC) and a bent crystal Laue analyzer, respectively. The monochromator was detuned at minimum 50% at the highest energy of the scan to reject the contribution from high-order harmonics. The beam energy was calibrated for each scan using a Co foil at Co-K edge (7709 eV). XAS spectra were obtained for both thermally treated samples and reference compounds including aqueous Co<sup>2+</sup>(aq), Co(OH)<sub>2</sub>(s), and Co<sub>3</sub>O<sub>4</sub>(s). The aqueous Co<sup>2+</sup> was prepared by dissolving Co(NO<sub>3</sub>)<sub>2</sub> salt in water to have the resultant Co concentration of 0.1 M. Four to nine scans were collected to enhance the signal-to-noise ratios. The XAS spectrum of cobalt aluminate (CoAl<sub>2</sub>O<sub>4</sub>(s)) was provided by Maurizio et al. [17].

XAS analysis was performed using SixPACK [18]. Individual scans were averaged, and the background absorbance was removed by a linear fit through the pre-edge region. X-ray absorption

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