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Location of extra-framework Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} cations in natural and dealuminated clinoptilolite

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ABSTRACT

In the present work a combination of chemically constrained Rietveld refinement and computer simulation is used for the determination of the positions of the extra-framework cations Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} in the channels of clinoptilolite. The analysis of the metal rich clinoptilolites with two different Si/Al ratio (4.7 and 7.8) demonstrates that most of the cations are located in two extra-framework sites, the first one in the center of channel **A** and the second one in the center of channel **B**. In the case of the Cu^{2+} exchanged zeolite with high Si/Al ratio (4.7), a third site is found. This site is located at 1.65 Å of the center of the **A** channel and can be considered as a highly disordered first site. All the metal ions are coordinated to water molecules with no coordination to the zeolite framework. The presence of hydronium cations controls the relative occupancy of the transition metals in the observed sites.

1. Introduction

Clinoptilolite is the most abundant natural zeolite, exhibiting the same framework topology of heulandite with a higher Si/Al ratio (for clinoptilolites Si/Al > 4, while for heulandites Si/Al < 4) [1]. The abundance, low extraction cost and high chemical stability of clinoptilolite account for massive applications in agriculture and wastewater treatments [2–4]. Comparatively, catalytic and adsorption applications have been much less exploited [5–8], which is due to the fact that this zeolite usually appears in relatively inhomogeneous tuffs accompanied by other phases like volcanic glass, quartz, clays, feldspars and metal oxides and hydroxides. However, in certain cases deposits contain high clinoptilolite content or simple mineral enrichment procedures can be applied to obtain samples with higher than 90% zeolite concentration [9,10]. Therefore, it is a valuable strategy to focus our attention on the study of possible new catalytic and sorption properties of clinoptilolite. In this context, it is worth noting that, for these applications, transition metal exchanged synthetic zeolites have shown great performance [11–14].

The effectiveness of zeolites in catalytic and sorption applications can be maximized on the basis of the detailed knowledge of the structural features associated to the extra-framework cations (EFC). However, this is usually a difficult task in the case of clinoptilolite, because single crystals are very scarce and the powder diffraction patterns feature strong peak overlap. A computational assisted structural approach is, then, required in order to overcome such experimental limitation, as have been applied in other zeolites [15–22]. As a typical illustration, combining high-resolution X-ray powder diffraction, with XPS and molecular modeling allowed Milanesio and co-workers to explore the Cu location in over-exchanged Cu-MCM22 zeolite [18]. More recently, some of us introduced an approach for locating the extra-framework cations in low-silica zeolites that is based on *in-house* powder diffraction measurements, combined with inverse and real space analysis methods, further assisted by computational modeling [9]. The best solutions are subject to full Rietveld refinement. The quality of the results is also improved when the zeolite framework is subject to lattice energy minimization using the experimental cell parameters. The methodology was successfully applied to two samples of those typically used in wastewater environmental applications, *i.e.* Ni and Co rich clinoptilolite containing also a considerable amount of the native cations [9].

The framework of clinoptilolite (IZA code HEU) is built up by 4-4-1 secondary building units, and consists of three channels

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connected in two dimensions: two of them formed by 8-membered rings and the third one by 10-membered rings. The 10-membered channel (**A**) and one of the 8-membered channels (**B**) run parallel to the crystallographic axis **c**, with the second 8-membered (**C**) parallel to the **a** axis (Fig. E.S.I.1 in Electronic Supporting information). A very common assumption is that only four EFC sites exist in HEU-type zeolites (clinoptilolite and heulandite) following Koyama and Takeuchi early work [23]. However, in a previous paper, we identified 18 different EFC sites separated by, at least, 1 Å, reported in the literature [9].

Studies of cation location in clinoptilolite exchanged with the four metals treated in this paper are scarce and ambiguous. Godelitsas and co-workers suggested that Ni^{2+} and Co^{2+} are likely to be fully coordinated with water molecules with no coordination to the framework [24–26]. de las Pozas et al. concluded, based on of the analysis of the cation exchange of Ni^{2+} on Na^{1+}, K^{1+}, Ca^{2+}, and Mg^{2+} enriched clinoptilolite, complemented with NH_3 adsorption and Ni reducibility, that Ni atoms seem to be located at sites M1 and M2 (M*i*, *i* = 1, 2, 3 and 4 are the Koyama and Takeuchi sites [23]) when the ion exchange is with Na and K rich samples, and M3 when starting from Ca and Mg enriched clinoptilolite [27]. For the case of Cu^{2+} exchanged clinoptilolite Armbruster et al. [28] reported two crystallographic sites, one located in the center of the **A** channel forming a disordered $(Cu(H_2O)_6)^{2+}$ complex, occupied by 45% of the total amount of Cu^{2+}. The second preferential site is present in the **B** channel with 43% of total Cu^{2+}, forming an approximately square planar H_2O complex. Cerjan Stefanovic et al. studied Zn^{2+} exchanged clinoptilolites using EXAFS. While they were not able to provide a definitive location of the Zn atoms in the zeolite, they suggested that tetrahedrally coordinated Zn in the exchanged natural sample and the octahedral Zn in the sodium pretreated sample are coordinated to both, framework oxygen and water molecules, while the octahedral Zn in the calcium pretreated sample is in the center of the channel, not coordinated to the framework [29].

A recent work by Rodriguez-Iznaga and co-workers have shown that, when forming binary metallic systems in clinoptilolite, the properties of the prepared materials dependent on which metal was first incorporated in the zeolite. They suggested that the observed behaviors are likely to be due to differences in metal location that seems to be a function of the order of metal incorporation [30–32].

In a previous work we studied the Co and Ni positions in natural clinoptilolite containing a significant presence of the native cations. In this work we determine the positions of Co, Ni, Cu and Zn in clinoptilolite with potential application in catalysis and gas adsorption. The samples were obtained from the purified natural zeolites by a chemical treatment that eliminates the native cations. The samples were also partially dealuminated in order to study the effect of the varying Si/Al ratio on the cation positions and, possibly, on the zeolite properties. It is interesting to note that while the location of EFC in high silica zeolites is directed by the position of the Al atoms, as has been detected by spectroscopic methods [33], in low silica zeolites cation–cation repulsion rules out such relationship as have been suggested by computer modeling studies [34]. It is therefore interesting to see whether differences appear or not in the location of the metals at the two Si/Al ratios analyzed in this work.

2. Experimental

2.1. Sample preparation

The clinoptilolite used in this work is the main phase present in the zeolitic rock (the raw mineral) from the Caimanes deposit, Moa (Cuba). In addition, Mordenite, Quartz, Feldspar and Montmorillonite are present, as was revealed in a mineralogical investigation using a variety of techniques, including X-ray diffraction and scanning electron microscopy [35]. The raw mineral was ground and sieved to 32–90 μm grains and then purified by washing with distilled water in a constant-flux fluidized bed process to remove the non-zeolitic mineral phases. In addition, the denser and lighter fractions were discarded, since they often contain feldspar and clays, to obtain a material more rich in clinoptilolite phase. After vacuum filtration and drying, this procedure resulted in a mixture of about 87% clinoptilolite, 8.5% quartz and 4.5% Mordenite [9]. Herein this sample is referred to as purified clinoptilolite or natural zeolite (NZ).

Since starting from metal-rich HEU type zeolites might lead to cation-exchanged materials with high content of native cations [9,36], here we apply a decationization treatment to the samples before the transition metal cation exchange. We converted NZ to its acid form, through ammonium exchange and calcination, as described in details elsewhere [37]. Considering that in partially dealuminated zeolites synergic effects might improve the catalytic and adsorption properties, we also prepared dealuminated samples exchanged with transition metals. For this dealumination, consisting in extracting two Al atoms per unit cell without altering the framework, we applied the recently developed stepwise procedure [37]. Since we have zeolites with two different Si/Al ratios, hereafter we refer to them as Si/Al-1 and Si/Al-2 for the natural (Si/Al = 4.7) and the dealuminated (Si/Al = 7.8) samples, respectively.

The metal exchanged forms were obtained by ion exchange at 100 °C in reflux and agitation with 0.2 mol/L aqueous chloride solutions of Co, Ni, and Zn and 0.2 mol/L aqueous nitrate solution of Cu. The initial pH of the solutions was slightly acid, around 6. The solutions were changed nine times every 8 h. The solid/liquid ratio was 1 g of solid/10 ml of solution. The solids were washed with distilled water until no salt anions (chloride or nitrate) were detected in the washed water, then dried at 60 °C overnight. The samples were labeled as Me-Si/Al-*x*, where Me represents the metal (Co, Ni, Cu or Zn), and *x* (1 or 2) stands for the Si/Al ratio, as defined above.

2.2. X-ray diffraction and general characterization

Powder X-ray diffraction patterns (XRD) were collected in Bragg–Brentano geometry at room temperature on a STOE goniometer using the Cu Kα radiation ($\lambda = 1.5406$ Å) produced by an ENRAF–NONIUS FR571 rotating anode generator. A Moxtek 2500 Silicon drift energy sensitive detector was used in order to minimize the background level. The patterns were measured in the 2θ interval from 5° to 70°, with a step size of 0.02° and 24 s counting time per step. Other details of crystallographic data and Rietveld refinement are summarized in Tables 1a and b.

No violation of the $C2/m$ space group symmetry was observed and then it was used in the structural refinement of all samples. Corrections due to the anomalous dispersions were done for the zeolites containing Co, Ni and Cu metals. The framework (Si and O) model for Rietveld refinement was taken from Koyama and Takeuchi data [23], but for each case the coordinates were again optimized by computer modeling fixing the lattice parameters at the experimental values. For this purpose we use the code Gulp [38,39], with widely used interatomic potentials [40].

The Fourier density map is calculated and analyzed following a procedure described elsewhere [9]. Peaks found in the electron density maps can be attributed to metal, water oxygen or hydronium oxygen atoms; hence, a detailed combinatorial analysis is required for their identification. Compared to our previous work on Ni and Co enriched clinoptilolite obtained directly from a natural clinoptilolite, here we do not have the presence of Na^{+}, Ca^{2+}, and Mg^{2+}, as will be shown below; however, we detect the presence of H_3O^{+} cations. In the procedure for finding the EFC location, these