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Direct observation and structural characterization of natural and metal ion-exchanged HEU-type zeolites

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ABSTRACT

The atomic structure of natural HEU-type zeolite and two ion-exchanged variants of the zeolite, Ag^+ (Ag-HEU) and Zn^{2+} (Zn-HEU) ion exchanged HEU-type zeolites, are investigated using advanced transmission electron microscopy techniques in combination with X-ray powder diffraction and X-ray absorption fine structure measurements. In both ion-exchanged materials, loading of the natural HEU zeolite is confirmed.

Using low-voltage, aberration-corrected transmission electron microscopy at low-dose conditions, the local crystal structure of natural HEU-type zeolite is determined and the interaction of the ion-exchanged natural zeolites with the Ag^+ and Zn^{2+} ions is studied. In the case of Ag-HEU, the presence of Ag^+ ions and clusters at extra-framework sites as well as Ag nanoparticles has been confirmed. The Ag nanoparticles are preferentially positioned at the zeolite surface. For Zn-HEU, no large Zn(O) nanoparticles are present, instead, the HEU channels are evidenced to be decorated by small Zn(O) clusters.

1. Introduction

HEU-like zeolites are three-dimensional framework structures consisting of $(Si,Al)O_4$ tetrahedra, in which each oxygen is shared between two neighboring tetrahedra. Substitution of Si^{4+} by Al^{3+} results in a deficiency of positive charge in the zeolite framework. The net negative charge produced is usually balanced by cations, mainly Na^+, K^+, and Ca^{2+} for natural zeolites, which are situated in the cavities within the structure [1–3]. These extra-framework cations are mobile and can therefore be exchanged by other metal ions. Zeolites are known to have high cation exchange and adsorption capacities; generally, zeolite cation exchange capacities (CEC) are a factor of two to three higher than those of most smectites and vermiculites [4]. Furthermore, as zeolite pores are a natural consequence of the zeolite crystal structure, they possess a constant geometry. This constant geometry combined with their high specific surface area is of interest for applications such as catalysis and molecular sieving (straight and branched hydrocarbons). The cavities and channels in zeolites can also serve as hosts for e.g. metals or metal-oxide clusters or nanoparticles, forming novel composite materials [5]. The wider the zeolite channels, the larger the clusters that can be introduced into the structure.

Natural zeolites have attracted worldwide interest for use in a broad range of applications, even though they may contain more impurities as compared to their synthetic counterparts. Many of these applications are in medicine, as natural zeolites are generally cheaper and less toxic than their synthetic counterparts. Since natural zeolites are abundant in nature, they are easily available and environmental friendly [6–9]. HEU-type zeolites (clinoptilolite and heulandite; monoclinic crystal structure, space group C2/m, cell parameters $a \approx 17.7$, $b \approx 17.9$ and $c \approx 7.4$ Å [10]) are the most abundant minerals on earth exhibiting a zeolite structure, making them low-cost industrial minerals with several commercial applications [1,11]. According to the Zeolite Subcommittee of the Commission on New Minerals and Mineral Names of the International Mineralogical Association, heulandite is defined as the zeolite mineral which has the framework topology of heulandite and a ratio $Si/Al < 4$, while clinoptilolite is defined as the series with the same framework topology but with $Si/Al > 4$ [1]. For clarity, in this

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manuscript our natural zeolite will be referred to as HEU-type zeolite, even though the Si/Al ratio in our samples is always in correspondence with heulandite. (See supplementary information).

Transmission electron microscopy (TEM) is a valuable technique for the characterization of zeolites [12], as important information such as crystal/defect structure [13,14] and identification of loaded materials like metal or metal-oxide nanoparticles inside the matrix [15,16], can be derived from TEM data. The problem with TEM characterization of natural zeolites is that they generally contain a large amount of water. Degradation of the zeolite structure under electron beam irradiation, caused mainly by radiolysis, occurs very fast and makes it extremely difficult to acquire HRTEM images and consequently perform a full structural characterization based upon these data. Being able to perform stable TEM measurements would be of especially great value in the characterization of modified HEU-type zeolites, ion-exchanged with extra-framework guests like metallic cations or clusters through the use of e.g. ion exchange. In this type of loaded zeolite materials, knowledge on the size, shape and distribution of the constituting ions/clusters/nanoparticles would then be directly accessible by TEM.

In this work, we report the first characterization of the atomic structure of a HEU-type zeolite through use of low voltage aberration corrected transmission electron microscopy under low dose conditions [17,18]. The sensitivity of this type of zeolite to the electron beam is in the typical range for natural zeolites and therefore the described measuring procedures for TEM imaging of intact HEU-type zeolites are applicable to many other sensitive, natural zeolites. This will provide a deeper understanding of the structure of the zeolite and the interaction of exchanged ions or clusters with the framework pores. As Diaz &Mayoral [20] reported, there are only few studies which have focused on the observation of guest materials within a zeolite structure through use of low electron dose conditions and short exposure times [19,20]. We will also provide more information on the morphological and structural properties of the HEU-type zeolite after ion exchange with Ag^+ and Zn^{2+} ions by combining the TEM data with X-ray powder diffraction (XRPD) and X-ray absorption fine structure (XAFS) spectroscopy. The element selective character of the latter allows the determination of the bonding environment of the exchanged ions (in this case for Zn^{2+}), irrespective of the crystalline or amorphous character of the host lattice, and has previously already been used for the study of Zn-exchanged zeolites [21,22].

2. Experimental

Pure faintly-white natural HEU-type zeolite crystals and crystals ion-exchanged with Ag^+ and Zn^{2+} were used in this work. The Zn- and Ag-exchanged forms of the HEU-type zeolite crystals (indicated/denoted as Zn-HEU and Ag-HEU respectively) were prepared in two steps; (1) the preparation of a Na homoionic form of the zeolite and (2) Na-exchange with Zn- and Ag-ions.

In order to prepare the Na homoionic form used as precursor for Zn-HEU, 1 g of the pulverized raw materials was treated for 24 h with 50 mL of a 2 M NaCl solution under refluxing. For the Na homoionic form used as precursor for Ag-HEU, only 0.65 g of pulverized raw material was treated with the same procedure.

The Na homoionic forms of the zeolite were separated by centrifugation, washed with double distilled water until they become Cl^- free and finally dried at 70 °C. A quantity of about 0.50 g of the prepared Na homoionic forms of the HEU-type zeolite crystals was treated under refluxing for 24 h with 50 mL of a 0.5 M $Zn(NO_3)_2$*$4H_2O$ and for 24 h with 50 mL of a 0.3 M $AgNO_3$ solution for the preparation of its Zn-HEU and Ag-HEU forms respectively. After separation of the solid from the liquid phase by centrifugation, the Zn-HEU and Ag-HEU were washed with double distilled water and dried at 80 °C. The reagents used for the preparation of the Na-form of the HEU-type zeolite, Zn-HEU and Ag-HEU forms (NaCl, $Zn(NO_3)_2$*$4H_2O$ and $AgNO_3$) were of analytical grade and used without further purification.

Samples suitable for TEM and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were prepared by mechanical grinding and polishing the HEU-type zeolite crystals followed by ion milling in a Balzers Ar^+ ion mill. High resolution TEM (HRTEM) and HAADF-STEM images were acquired on an aberration-corrected FEI Titan 'Cubed' microscope operated at 80 kV. In order to minimize beam damage to the sample, all images were acquired using a low electron dose in the range of 50–150 e/$Å^2$ s. The exposure time in TEM was limited to 0.1 s, and a beam blanking system was used in between acquisitions to minimize exposure of the sample to the electron beam. Image simulations were performed using the JEMS software package. Fourier filtering in Fig. 4 was performed using the Digital Micrograph software suite. Tomography series were acquired on a FEI Tecnai G2 microscope, operated at 200 kV acceleration voltage in STEM mode with an angular range from −70° to +65° for Zn-HEU and −70° to +70° for the Ag-HEU with a tilt increment of 5°, in order to minimize beam damage. A Fischione tomography holder (model 2020) was used and the series were acquired automatically using the Xplore3D software. The alignment of the series was performed with the Inspect 3D software. 3D reconstruction was performed using the Simultaneous Iterative Reconstruction Technique (SIRT) as implemented in the Inspect 3D software package (FEI Company).

XRPD analysis of the materials was performed using a Philips PW1710 diffractometer with Ni-filtered Cu-Ka radiation operating at 40 kV and 30 mA. The unit cell parameters of the HEU-type zeolite were refined by the Le Bail fitting of the XRPD data using the JANA2006 software [23].

The X-ray Absorption Fine Structure (XAFS) spectra were recorded at the Zn–K-edge at the KMC-II beamline of the BESSY-II storage ring of the Helmholtz Zentrum Berlin. The beamline is equipped with a double SiGe (111) graded-crystal monochromator and a Röntec XFlash fluorescence detector that was used in order to electronically discriminate the Zn K_α photons. The detector was positioned in the horizontal plane at right angle to the incident beam. The angle of incidence was 80° to the sample surface. A ZnO powder sample was used as reference material after proper corrections for self-absorption. The spectra were normalized with the signal of an ionization chamber positioned in front of the sample. A Zn thin foil measured in the transmission mode was used for the correction of the energy shifts induced by the monochromator and as a reference material.

3. Results and discussion

3.1. Structural characterization of the pure HEU-type zeolite

To date, the main technique to study the structure of natural HEU-type zeolites has been single crystal X-ray diffraction [1]. However, XRPD collects structural information from a large area to reveal an average structure, and therefore does not provide local information. In order to gain more information on the pure HEU-type zeolite at a local level, low voltage aberration corrected TEM was used in this study. To keep the HEU framework from collapsing under the electron beam illumination, high resolution images were acquired from different crystal projections, while keeping the electron dose as low as possible through use of a low intensity beam and the lowest possible magnification. A beam blanking system was also used in between acquisitions to minimize exposure of the sample to the electron beam.

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