Electronic structures of an Ag-containing 4A zeolite

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Valence- and Conduction-band O $2p$ partial density of states (DOS) on an Ag-containing (about 10 at.%) 4A-type (Ag4A) zeolite being utilized for antibacterial materials together with the reference Na4A zeolite were measures by soft x-ray emission and absorption spectroscopies (SXES and SXAS) using O $1s$-$2p$ resonant technique, respectively. A density functional theory (DFT) was applied to obtain the electronic DOS on the Ag and Na4A zeolite to clarify the origin of antibacterial function of Ag4A zeolite by comparing with the reference Na4A zeolite.

1 Introduction

Natural zeolite minerals are created under high temperature and high pressure in the earth, and have been utilized as several kinds of functional materials. They are composed of aluminosilicate networks with a considerable number of pores with a nanometer size [1]. Zeolites have many applications, such as classical molecular sieves, and adsorbents for moistures, radioactive Cs ions, and so on. Recently, synthetic zeolites doped with a small amount of heavier elements are used for catalysts. For example, P, Fe, or Cu-including zeolites can work as high durable purification devices for exhaust gas, and Sn containing zeolites are promising for a CO_2 adsorber with a Lewis acidic feature [2]. Ag-containing zeolites, handled in this paper, have antibacterial functions, which can drastically improve health conditions in developing countries inexpensively, and are already commercialized.

To investigate properties of such useful functions of zeolites, three hierarchical parts of zeolites should be carefully considered, i.e., 1) aluminosilicate framework made of mainly Si, Al, and O atoms, 2) cations located at pore surfaces like Na+ compensating fourfold Al ions, and 3) molecules or nanosized atomic group adsorbing into pores. Although applications of zeolites are widely available in human lives, basic knowledges on zeolite materials are not rich, and thus, higher functional improvements were not made on the basis of fundamental properties of zeolites. This was because most of active sites in three hierarchical structures have no long-range periodicity, which makes very difficult to exactly determine atomic positions by usual diffraction methods. Concerning electronic structures, it is difficult to measure photoelectron spectroscopy since zeolites are highly insulating.

To measure electronic density of states (DOS) for insulating materials, soft x-ray emission and absorption spectroscopies (SXES and SXAS) are available, both of which have element and orbital angular momentum number-selective [3]. By using these methods, we previously measured O $2p$ partial DOS of typical highly insulating materials of SiO_2 [4] and B_2O_3 [5] glasses. In this article, we report results of SXES, and SXAS spectra on a Ag-containing (about 10 at.%) 4A zeolite (($Ag_{0.1}Na_{0.9}$)$_2$O·Al_2O_3·$2SiO_2$, Ag4A) for investigating why this zeolite has an antibacterial function by comparing with those of the original 4A zeolite (Na_2O·Al_2O_3·$2SiO_2$). The Ag composition was obtained by an inductively coupled plasma mass spectrometry (ICP-MS). Moreover, theoretical calculations were performed by a density functional theory (DFT) for the comparison with the experimental data, as performed in our recent paper on a Mordenite zeolite [6].

2 Experiment

Synthetic 4A zeolite, Na_2O·Al_2O_3·$2SiO_2$ (Na4A), with pores of about 4 nm in an inner diameter and a crystal size of about 1 μm was purchased from Tosoh Corp. The zeolite powder was washed by distilled water, and a part of the sample was ion-exchanged with Ag+ by infiltrating in an $AgNO_4$ aqueous solution, which is named as Ag4A zeolite. The powder sample was pressed to make a pellet with a diameter of 10 mm and a thickness of about 1 mm.

SXES and SXAS experiments were performed at the beamline BL13A of the Photon Factory located in the High-Energy Accelerator Organization (PF-KEK) in Tsukuba, Japan. There, synchrotron radiation from a linear undulator device was monochromatized by using a variable-included-angle Monk-Gilliesen-type monochromator with a varied-line-spacing grating with a line density of 1000 lines/mm [7]. The energy resolution of the incident soft x-rays was higher than 0.1 eV FWHM. Emitting photons of SXES were measured by using a Rowland-type monochromator with a spherical grating of 5 m in a radius and a line density of 1200 lines/mm, and a photon detector with a CsI-coated multichannel plate. The energy resolution of SXES was about 0.3 eV. The details of the experimental setups are given elsewhere [8].

The sample for these measurements was dehydrated by

heating at about 150°C under a vacuum condition in the sample introduction device of the spectrometer. SXES spectra of O 2p valence-band partial DOS were obtained with incident photon energies of 535-554.7 eV, beyond the O K absorption edge. SXAS spectra of O 2p conduction-band DOS were measured around the O K absorption edge in total electron yield mode. All the SXES and SXAS experiments were performed at room temperature under ultrahigh vacuum condition of 10^{-9} Torr level.

DFT calculations were performed with a generalized gradient approximation [9] for exchange-correlation energy by using the CP2K program package [10]. Goedecker-Teter-Hutter pseudopotentials [11] were employed for the electron-ion interaction with the valence electron configurations of $4d^{10}5s^{1}5p^{0}$, $3s^{2}3p^{1}3d^{0}$, $3s^{2}3p^{2}3d^{0}$, and $2s^{2}2p^{4}$ for Ag, Al, Si, and O elements, respectively. The electronic electron density was expanded by using plain wave basis sets with cutoff energies of 400 Ryd. We used totally 168 atoms (2Ag, 22Na, 24Al, 24Si, and 96O) under a periodic boundary condition. Calculations were carried out with a constant-temperature constant-volume canonical ensemble using a generalized Langevin equation thermostatat at 300 K [12,13] for 5000 steps in time steps of 1.0 fs with two of a supercell size of 1.22775 nm cubic. Physical quantities of our interest were obtained by averaging over 1 ps after equilibration of 4 ps. The initial atomic positions were set by an XRD result of Na4A [14].

3 Results and Discussion

Figure 1 shows the SXAS spectra of Ag4A (red) and Na4A (blue) zeolites near the O K absorption edge, corresponding to the O 2p conduction-band partial DOS. At a glance, no clear differences are observed by exchanging Na^{+} with Ag^{+} ions, i.e., they show relatively distinct primary peaks at about 540 eV with some small structures below and beyond the peaks, which are indicated by arrows. Compared with SXAS spectra of Mordenite being a SiO$_2$-rich zeolite (Na$_2$O·Al$_2$O$_3$·20SiO$_2$) [6] or SiO$_2$ crystal (quartz) [4], the primary peak is much prominent, suggesting that the primary peak in 4A zeolites is dominated by O-Si covalent bonding. The energies marked by the arrows were chosen as incident photon energies, E_0, for SXES measurements.
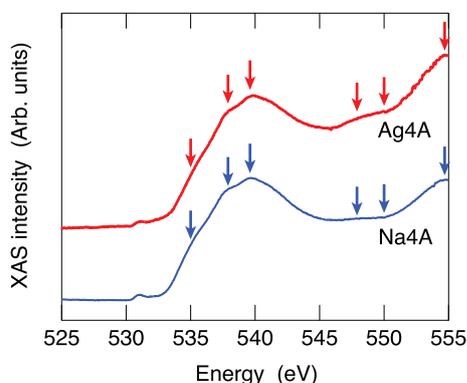
Fig. 1: SXAS spectra of Ag4A (red) and Na4A (blue) zeolites near the O K absorption edge

Figure 2 shows SEXS spectra of (a) Ag4A and (b) Na4A zeolites, corresponding to the O 2p valence-band partial DOS, at several E_0 values from 535.0 to 554.7 eV. The SXES spectra exhibit mainly four characteristic structures of a primary peak at 525.3 eV, a shoulder at 524.5 eV, a small peak at 522.0 eV, and a small shoulder at about 519.5 eV. By exchanging Na with Ag, it appears no spectral changes. Note that these spectral features are almost the same as those on Mordenite [6] or even SiO$_2$ crystal [4]. In case of SiO$_2$ or highly hydrophobic Mardenite, the prominent peak is made of O lone-pair (LP) electrons and three structures at the lower energies correspond to the O-Si bonding (σ) states. Therefore, the O 2p partial DOS in Ag4A zeolite is dominated by the O-Si covalent bonding.
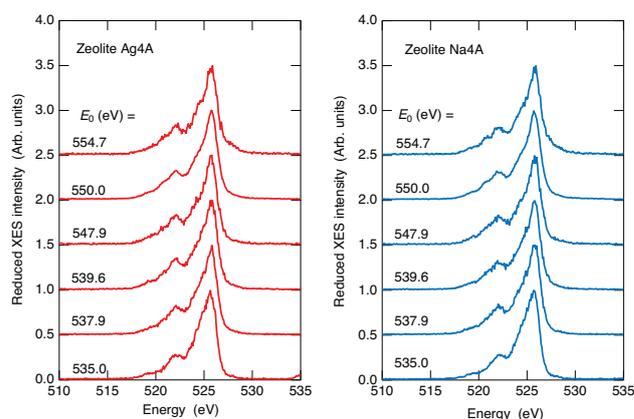
Fig. 2: SXES spectra of Ag4A (red) and Na4A (blue) zeolites near the O K absorption edge

Figure 3 shows atomic configurations obtained from the DFT calculation of (a) the initial positions (the XRD result for Na4A [14]), relaxed atomic configurations for (b) Na4A and (c) Ag4A. Yellow, purple, and red balls indicate Si, Al, and O atoms in the frame, respectively. Light and dark blue represent Na and Ag atoms, respectively. The Ag atoms in (c) are given by dashed circles for clarity. The positions of two atoms at the pore center in the initial state (a) slightly shift from the center, and the remaining one moves near the surface of the pore in (b) and (c). Interestingly, the Ag atoms selectively travel to the surface. On the other hand, the frames seem not to move by the DFT calculation.

Figure 4 shows O 2p partial valence-band DOS obtained from the present DFT calculations for Ag4A (solid curve) and Na4A (dashed curve). As seen in the figure, the spectral shape for Ag4A is similar to that for Na4A, and only shifts to higher energy by about 1.5 eV. The DFT spectra for Na4A has features very similar to the experimental SXES data. On the other hand, the spectra do not coincide with the experiment in energy. One of the plausible reasons is that the Ag atoms are located well inside the surface of the zeolite sample as seen in Fig. 3(c) and the emitting photons from the O atoms surrounded by Ag cannot go outside of the zeolite sample. Thus, the

emissions are only from O atoms unrelated to the Ag atoms.
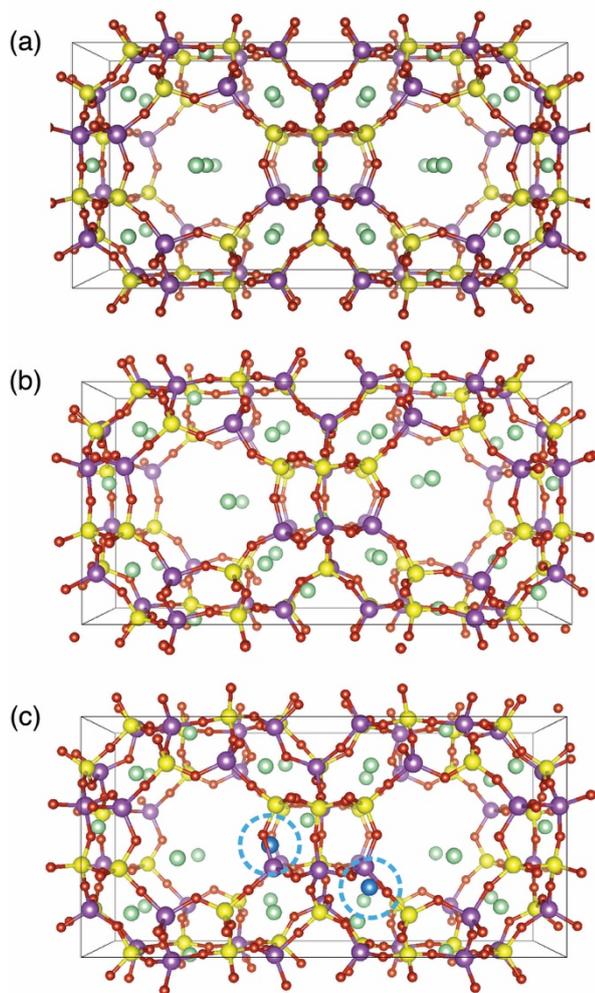
Fig. 3: Results of DFT calculation for atomic configurations. (a) the positions, relaxed atomic configurations for (b) Na4A and (c) Ag4A. The Ag positions in (c) are given by dashed circles.
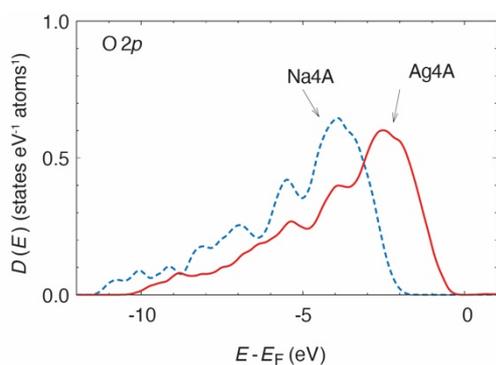
Fig. 4: O 2*p* partial valence-band DOS obtained from the present DFT calculations for Ag4A (solid curve) and Na4A (dashed curve).

Interestingly, the calculated spectrum for Ag4A shifts toward the Fermi edge energy, E_F, indicating a small charge transfer from O to probably Ag. This small charge transfer may cause the antibacterial functions in the Ag4A zeolite.

4 Summary

Electronic structures of an Ag containing 4A zeolite having an antibacterial function were investigated by SXES and SXAS at BL13A of the PF-KEK. The spectra were compared with the results of a DFT calculation. The reference Na4A data are well reproduced by the DFT results, while those of Ag4A are different in the spectral energies. The DFT calculation for the O 2*p* partial DOS reaches E_F, indicating the charge transfer between the O and Ag, which may be related to the antibacterial function in the Ag4A zeolite.

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