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Partial density of states in functional zeolite by soft x-ray emission spectroscopy

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1 Introduction

Zeolites are functional materials that the nature is manufactured by self-organization. They are mostly composed of aliminosilicate networks with a considerable number of holes with a nanometer size [1], and one gram of zeolite possesses a surface of holes with an area wider than a tennis court. Zeolites have many applications, such as classical ones of molecular sieves and adsorbents for moistures, radioactive Cs ions etc., or recently high durable exhaust gas purification devices by P-including ones, petrochemical catalysts by hydrophobic ones, antibacterial agents by Ag in their holes, and so on. More than two million tons per year are manufactured all over the world, and thus, human lives do not work without zeolites.

To consider the functions of zeolites, three parts should be carefully discussed, i.e., 1) frameworks made of mainly Si, Al, and O atoms, 2) Cations located at the hole surface like Na^+ compensating the fourfold Al^- ions, and 3) molecules or nano-scaled atomic groups adsorbing into the holes. Although the applications of zeolites are widely spread in the human lives, basic knowledges on these materials are not so rich, and thus, higher advancements are not improved on the basis of the fundamental understandings of basic scientific properties. This was because in addition to complex structures of zeolites, most of active sites for the functions, such as Al^- ions in the frameworks, cations at the hole surfaces, and adsorbed atomic groups, have no long-range periodicity, which makes difficult to determine atomic positions by usual diffraction methods. As regards the electronic structures, it is difficult to measure photoemission spectroscopy since they are insulators.

To investigate electronic density of states (DOS) for insulating materials, soft x-ray emission spectroscopy (SXES) and soft x-ray absorption spectroscopy (SXAS) are available with element- and angular momentum quantum number-selective [2]. By using these methods, we previously measured O 2*p* DOS of SiO_2 [3] and B_2O_3 [4] glasses. In this article, we report results of SXES and SXAS spectra on one of the typical zeolites, mordenite ($Na_2O\cdot Al_2O_3\cdot 20SiO_2$), and discuss the O 2*p* DOS.

2 Experiment

Synthetic mordenite powder with an one-dimensional holes of about 0.66 nm and a sample size of about 1 μm was supplied by Toyo Soda Manufacturing Co., Ltd. (No. TSZ 640NAA). The mordenite powder was washed by distilled water. The powder sample was pressed to make a pellet with a diameter of 10 mm and a thickness of about 1 mm. It was dehydrated by heating it at 150°C under vacuum in the sample introduction device.

SXES and SXAS measurements were carried out at BL13A of the PF-KEK. The SXES spectra were measured by using a Rowland-type monochromator with a spherical grating with a radius of 5 m and a line density of 1200 line/mm and a photon detector with a CsI-coated multichannel plate. The energy resolution of SXES is about 0.3 eV. Details of the experimental setups are given elsewhere [5].

The SXES spectra of O 2*p* valence-band partial DOS were obtained with incident photon energies of 535-550 eV, beyond the corresponding 1*s* absorption edge. The SXAS spectra of O 2*p* conduction-band partial DOS were measured around the O 1*s* absorption edge in total electron yield mode. The energy resolution of SXAS was higher than 0.1 eV. All the SXES and SXAS experiments were carried out at room temperature under ultrahigh vacuum condition of less than 10^{-7} Pa.

3 Results and Discussion

Figure 1 shows the SXAS spectra of mordenite near the O *K* absorption edge, corresponding to the O 2*p* conduction-band partial DOS. At a glance, the spectral features are very similar to those of crystalline and glassy SiO_2 [3]. However, the pre-shoulder structures are very prominent at 533-535 eV, which may be related to the covalent-ionic bonding to the Al^+ ions. Besides, there are several characteristic structures as indicated by arrows,

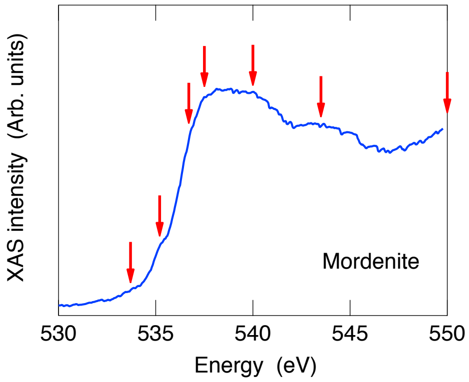

Fig. 1: The SXAS spectra of mordenite near the O *K* absorption edge.

which were used for the incident photon energies, E_0, for the subsequent SXES measurement.

Figure 2 shows the SXES spectra of mordenite, corresponding to the O 2*p* valence-band partial DOS, at several E_0 values from 533.7 to 550 eV. The SXES spectra exhibit four characteristic peaks and shoulders as indicated by dashed lines. Most of the structures do not change with varying E_0.

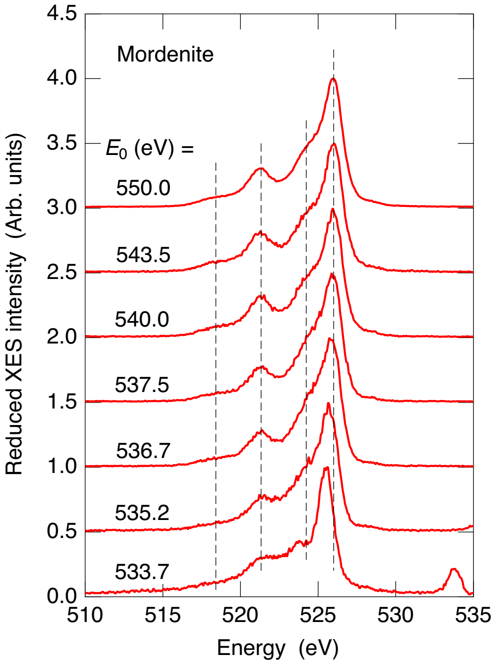

Fig. 2: SXES spectra of mordenite at several E_0 values.

At the lower E_0 values of 533.7 and 535.2 eV, however, the prominent peak at about 526 eV shifts towards the lower energies, and the shoulder at about 524 eV changes the spectral shapes. These anomalies would be related to the origin of the pre-shoulder in Fig. 1, or in other words, the dispersion relations of O 2*p* electronic bands near the band gap, reflecting the bond natures of O atoms with Al and Si atoms.

An *ab initio* molecular dynamics simulation is now in progress for calculating the electronic DOS and for clarifying the role of Al$^-$ ions for the electronic properties of mordenite. The most serious problem for simulating it in a first principle sense is a large size of unit cell containing one hundred atoms, which will be sophisticatedly solved very soon.

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