O 2\textit{p} partial density of states in Sn β-zeolite by soft x-ray emission spectroscopy

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1 Introduction

Zeolites are functional materials that are mostly composed of aluminosilicate networks with a considerable number of pores with nanometer size. Zeolites possess a surface area (up to 600 m\textsuperscript{2}/g) in the structure. In addition to traditional applications of molecular sieves and adsorbents, radioactive Cs ions etc, new applications have recently been developed, such as high durable exhaust gas purification devices, petro-chemical catalysts, antibacterial agents, and so on. Therefore, more than two million tons of zeolites per year are produced all over the world, and nowadays, human lives cannot work without zeolites.

Increasing attention is being paid to technologies for the heterogeneous catalysts with isolated metal centers which exhibit unique catalytic activities. Since the first report of Sn containing zeolites inside the framework structure, Sn β-zeolites \cite{1}, they have gained much attention due to their Lewis acidic features, with which these zeolites exhibited high performance in some isomerization reactions.

Wakihara and coworkers recently succeeded in manufacturing Sn β-zeolites with 1% of Sn/(Sn+Si) contents in 4 days (Fig. 1(a)) or 2% in 8 days (Fig. 1(b)) by using a mechanochemical treatment of mixed oxide composites \cite{2}. This is much faster than the conventional method (usually takes longer than one month) to introduce Sn atoms in the framework structure \cite{3}. Since the fraction of Sn directly reflects the performance in the isomerization reactions, it is important how to increase the substitution amount and to control the crystallographic site.

2 Experiment

The powder sample of Sn β-zeolites with a Sn content of 2% was manufactured at the University of Tokyo by the mechanochemical method together with the reference pure silicate zeolite.

SXES experiments were carried out at BL13A of the PF-KEK. Figure 2 shows a schematic view of the SXES apparatus installed at BL13A of the PF-KEK. Synchrotron radiation from an undulator insertion device was monochromatized by using a varied-line-spacing plane grating. SEXS spectra were measured by using a Rowland-type monochromator with a spherical grating with a radius of 5 m and a line density of 1,200 line/mm and a photon detector with a CsI-coated multichannel plate. The total energy resolution of SXES was ~0.5 eV. Details of the experimental setups are given elsewhere \cite{4,5}.

![Fig. 1: SEM images of Sn β-zeolites with (A) 1% in 4 days or (B) 2% in 8 days.](image)

![Fig. 2: Schematic view of SXES apparatus.](image)
were carried out at room temperature under an ultrahigh vacuum condition of less than $10^{-7}$ Pa.

3 Results and Discussion

Top panel of Fig. 3 shows O 1s-2p SXES spectra on β-zeolites with 2% and without Sn elements. The spectra have main peaks composed of the lone-pair band and some structures corresponding bonding states of O atoms with Si/Sn ones. Both the spectra are very similar to each other. It should be noted that the spectra also resemble well those of SiO$_2$ crystal and glass [6], indicating that Si(Sn)O$_4$ tetrahedral configurations are the constituent blocking units of these zeolites.

To clarify the effect of Sn additives in detail, the Sn contribution is estimated by carefully obtaining the difference between these SXES spectra, which is displayed in the bottom panel of Fig. 3 indicated by the red curve. In comparison, the SXES spectrum was measured on the reference SnO$_2$ crystal, where sixfold Sn and threefold O are linked to each other different from those of SiO$_2$ (fourfold Si and twofold O). The contrast by Sn impurities in the β-zeolite is very similar to that of the host β-zeolite, indicating that Sn may form a fourfold SnO$_4$ atomic arrangement similar to the SiO$_4$ tetrahedral one. On the other hand, SnO$_2$ with the different atomic arrangement shows different SXES spectral features, such as the energy shifts and magnitude changes in the peaks of lone pair and bonding states.

4 Summary

O 1s-2p resonant SEXS spectra were measured on β-zeolites with 2% and without Sn impurities to obtain O 2p partial DOSs, in which the Sn additives are very effective for the CO$_2$ adsorbent property. These spectra as well as a small contrast by the Sn impurities are similar to one another. On the other hand, SXES spectrum of SnO$_2$ reference crystal with sixfold Sn and threefold O configurations has a different spectral feature, and thus, Sn atoms in β-zeolite may form SnO$_4$ atomic arrangements similar to SiO$_4$ tetrahedral units in β-zeolite.

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References


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