

Structural study of transition metal chalcogenide nanoclusters confined in the zeolite cages

Kenji MARUYAMA^{*1}, Makoto YAMAZAKI¹, Yuji KUROGOUCHI¹,
Hideoki HOSHINO², Takefumi MIYANAGA²
¹Niigata Univ., 8050 Igarashi-2, Niigata, 950-2181, Japan
²Hirosaki Univ., 1 Bunkyo-cho, Hirosaki, 036-8560, Japan

Introduction

Transition metal chalcogenides show the very interesting properties. In case of $\text{NiS}_{2-x}\text{Se}_x$, for example, its magnetism changes from Pauli para- to antiferromagnetic with increasing the value of x at low temperature. These features may be attributable to the interaction between 3d electrons of transition metal and lone pair electrons of chalcogen. So we expect that the nanocluster of these compounds show the new interesting properties by changing the interactions between adjacent clusters.

Recently we have succeeded to produce transition metal chalcogenide nanoclusters in the cage of zeolite LTA (11 Å diameter). In order to investigate the structures of these nanoclusters and its temperature dependence, we have performed EXAFS measurements for Ni-Se nanoclusters with various compositions.

Experimental

The Na^+ cations of zeolite LTA were exchanged with Ni^{2+} ions by using the aqueous $\text{Ni}(\text{NO}_3)_2$ solution. Zeolite powder was dehydrated at 400 °C under vacume of 10^{-6} Torr. Then it was heated with the weighed Se up to 450 °C in order to connect Se clusters in the cages. After that, it was heated in H_2 gas up to 350 °C for two hours. The obtained Ni-Se clusters were denoted as $\text{Se}_y\text{-A}(\text{Ni}_x)\text{red.}$, where x and y represent the number of Ni and Se atoms per cage, respectively, which were determined with ICP mass analysis.

EXAFS spectra around Ni and Se K edge were measured by using BL10B beam line. The samples were packed into a Teon cell in a glovebox to prevent containing water.

Results and discussion

EXAFS oscillation $\chi(k)$ of $\text{Se}_y\text{-A}(\text{Ni}_x)$ obtained around Ni K-edge at 20K were shown in Fig. 1. After the reduction, the profile of $\chi(k)$ changes very much. The $\chi(k)$ of $\text{Se}_{7.6}\text{-A}(\text{Ni}_{3.8})\text{red.}$ has larger amplitude in high k region ($k > 10 \text{ \AA}^{-1}$) than that of $\text{Se}_{3.8}\text{-A}(\text{Ni}_{3.8})\text{red.}$, which suggests the change of the coordination number of Se atoms around Ni atom.

Fig. 2 shows the $\chi(k)$ around Se K-edge for the same samples as Fig. 1. After the reduction, the amplitude of $\chi(k)$ in low k region becomes larger, which suggests the forming of Se-Ni bonds. With increasing the Se, the

amplitude of $\chi(k)$ around 5 \AA^{-1} becomes larger. This indicates that the structure of cluster was changed when the composition was changed.

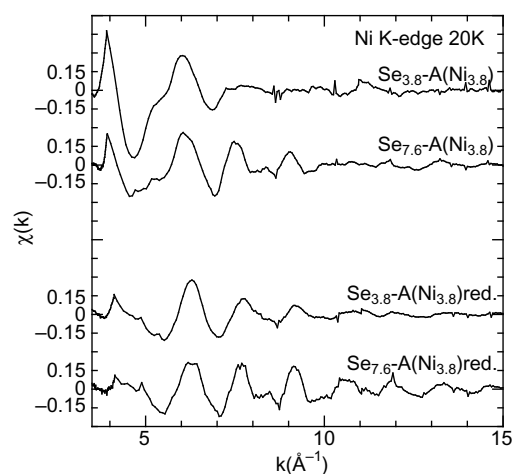


Fig. 1: The EXAFS oscillation $\chi(k)$ of Ni-Se clusters around Ni K-edge at 20K.

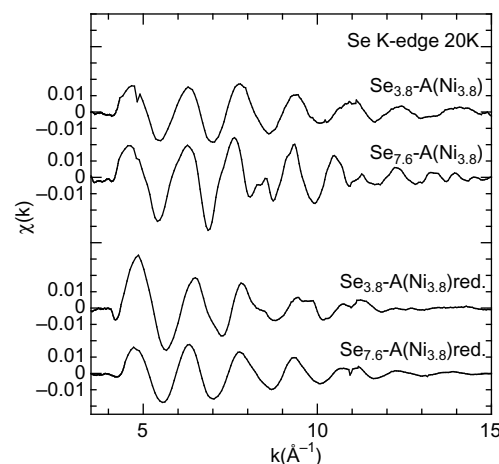


Fig. 2: The EXAFS oscillation $\chi(k)$ of Ni-Se clusters around Se K-edge at 20K.

*maruken@chem.sc.niigata-u.ac.jp