In-situ XAFS study of Ag clusters in zeolite 4A

Takafumi MIYANAGA1*, Yushi SUZUKI1, Hideoki HOSHINO2, Naoyuki MATSUMOTO1, Takeshi AINAI2

1 Faculty of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561, Japan
2 Faculty of Education, Hirosaki University, Hirosaki, Aomori 036-8560, Japan

Introduction

In the fully Ag+-exchanged zeolite 4A (Ag-4A) the 12 Ag+ ions are present inside of the zeolite cages, as needed to balance the anionic charge of the zeolite framework. The white color of the hydrated Ag-4A changes through yellow to brown by heating under vacuum. These changes in color are related to the formation of silver clusters by dehydration [1]. In this report, we study the structural change of Ag-4A by in-situ XAFS measurements.

Experimental

Ag-4A powder samples were prepared by immersing Na-4A (Na12[(AlO2)12(SiO2)12]27.5H2O) zeolite in an aqueous AgNO3 solution at 25°C[2,3]. The air-dried Ag-4A was set into the in-situ XAFS measurement cell in which the sample can be heated under vacuum. Ag K-edge EXAFS spectra were measured at BL-10B. A Si(311) channel-cut monochrometer was used, and energy and current of the storage ring were 3.0 GeV and 250~300 mA, respectively. The analyses were performed by XANADU code [4] and FEFF6 code [5].

Results and Discussion

Figure 1 shows the change of $k\chi(k)$ EXAFS spectra measured for 2 minutes (2 minutes scan EXAFS) for Ag-4A by keeping the evacuation of the sample at room temperature. After 12 minutes evacuation, any more changes cannot be observed in the spectra.

The corresponding change of Fourier transforms is shown in Fig. 2. First peak is assigned to short Ag-O distance and second peak to long Ag-O and Ag-Ag [3]. It is observed that the intensity of the second peak increases continuously during the evacuation.

![Fig. 1](image1)

![Fig. 2](image2)

Table 1 Structural parameters obtained from 20 minutes scan EXAFS.

<table>
<thead>
<tr>
<th></th>
<th>short Ag-O</th>
<th>long Ag-O</th>
<th>Ag-Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r$ (Å)</td>
<td>$N$</td>
<td>$r$ (Å)</td>
</tr>
<tr>
<td>1 atm</td>
<td>2.38</td>
<td>5.7</td>
<td>2.87</td>
</tr>
<tr>
<td>Vac.</td>
<td>2.28</td>
<td>3.3</td>
<td>2.86</td>
</tr>
</tbody>
</table>

References


*takaf@cc.hirosaki-u.ac.jp*