

## A study of the luminescence mechanism of Ag-type Zeolite-A

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### 1 Introduction

Zeolites are crystalline aluminosilicates showing unique properties due to the presence of cavities and cages in the structure. Some cations are easily exchange to  $\text{Na}^+$  ions in the original Na-type zeolites and they show various physical and chemical properties [1]. The Ag-type zeolite-A cooled to room temperature after heated at 500 C for 24 hours under vacuum or in the atmosphere shows a strong PL band around 2.1eV [2]. It was known that the intensity of PL band was influenced by conditions of the heating steps and the kinds of atmospheric gases introduced after cooling. However, the detail mechanism of PL still has not been clear. On the other hand, when the Ag-type zeolite is heated, the lattice water molecules are removed and then the  $\text{Ag}^+$  ion is reduced to  $\text{Ag}^0$  forming Ag clusters. At the previous study, it was predicted that the Ag clusters are key species of the PL [2]. So we had carried out Ag-K-edge XAFS measurement to examine the relation of Ag cluster and intensity of PL band. From the result of Ag K-edge XAFS analysis, it was confirmed that Ag clusters were generated by heating process but the Ag clusters were broken down after the process of cooling and exposing to air. Strong intensity of PL band is observed under air condition after heating and cooling treatment. That is, Ag clusters do not exist even if the strong PL band appears [3]. It was suggested that the decomposition of Ag clusters plays an important role of generation of PL bands and the framework change by formation and decomposition of Ag clusters operates the PL peaks. Our previous study [3] strongly suggested that the change of frameworks structure of zeolite affected the mechanism of the PL. In this report we discussed the results of IR absorption spectra and XAFS measurement of Al K-edge for Ag-type zeolite-A to reveal the properties of frameworks of zeolite.

### 2 Experimental

#### 2.1. Sample preparations

The fully  $\text{Ag}^+$ -exchanged zeolite A (hydrated 12Ag-A) powder samples were prepared by immersing the hydrated 12Na-A in 0.1 M  $\text{AgNO}_3$  solution for 24 h at 25 C. The solution was stirred every an hour. After careful filtration the 12Ag-A powder was dried under air at RT in the darkroom [2].

#### 2.2 XAFS measurements

X-ray absorption spectra of Al K-edge (1559.6 eV) were measured at BL-11A at Photon Factory in KEK with fluorescence mode using SDD. The EXAFS oscillation function was extracted from the X-ray absorption spectra and Fourier transformed by XANADU code [4]

We carried out XAFS measurement about Al K-edge only vacuum condition because K-edge energy of Al (1559.6eV) is so low that X-ray is absorbed by atmospheric gasses. We show the outline of experiments in Fig.1.

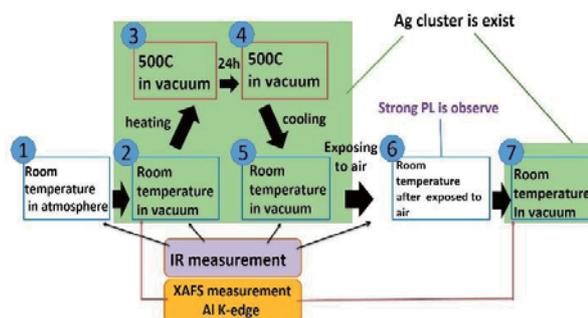


Fig.1 Schematic outline of experiments.

Ag-type zeolite is heated at 500 C in vacuum for 24hours and cooled to room temperature. The Ag clusters are generated by these heating and cooling process [3]. And then, air is introduced. Ag cluster is broken down by expose to air and strong PL is appear [3]. Next, sample is returned to vacuum condition to measure XAFS spectrum of Al K-edge. In Fig.1, each step of zeolite samples are numbered from ① to ⑦. In this report we use these numbers to indicate the state of sample.

#### 2.3 Infrared measurement

The IR absorption spectra were obtained at normal incidence of radiation. Measurements were conducted using a spectrometer (MB-100; ABB Bomem) equipped with a DTGS detector at  $4 \text{ cm}^{-1}$  resolution with 128 interferometric scans. A high-purity Si single crystal wafer was used as substrate for the infrared measurements. Zeolite powder sample was deposited on the wafer. Temperatures were controlled within  $\pm 1 \text{ }^\circ\text{C}$ . Details of IR measurements are described elsewhere [5].

### 3 Results and discussion

First, we discuss about results of Al K-edge XAFS analysis. Figures 2 and 3 show EXAFS  $\chi(k)$  spectrum for sample ② and ⑦ about Ag-type zeolite-A and Na-type zeolite-A, respectively. It can be seen the change of  $\chi(k)$  spectrum after  $4.5 \text{ \AA}^{-1}$  in Ag-type zeolite-A. In contrast, difference of  $\chi(k)$  spektrum of sample ② and ⑦ of Na-type zeolite-A is almost not obserbed. It indicates that the framework of Na-type zeolite-A is not influenced, but Ag-type zeolite-A is influenced by heating and cooling treatment.

Figures 4 and 5 show the Al *K*-edge EXAFS Fourier transform spectra for sample ② and ⑦ about Ag-type zeolite-A and Na-type zeolite-A, respectively. The peak around 1~1.5 Å corresponds to the first neighbor atom of O, the second peak around 2.5~2.8 Å corresponds to the second neighbor atom of cations, Ag or Na. To pay attention to the first peak of Ag-type zeolite-A, the peak position moved to shorter and the intensity of the peak decreased by heating and cooling treatment. This change of the peak position indicated that bond distance of Al-O becomes shorter, and that of peak intensity indicated increase of Debye Waller factor or loss of Oxygen atom at framework. It is noted that the spectra for the Na-type zeolite-A do not change after heat treatment.

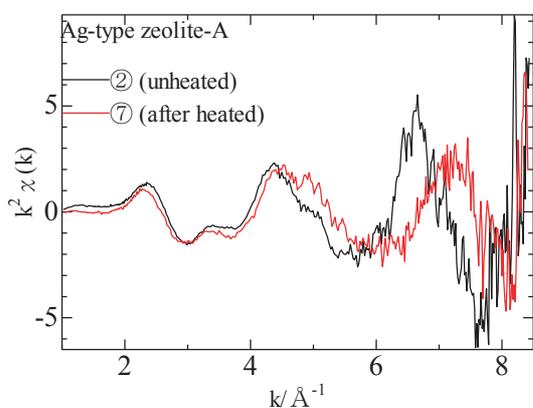


Fig.2 Al *K*-edge EXAFS  $k^2 \chi(k)$  spectrum of sample ② and ⑦ about Ag-type zeolite-A.

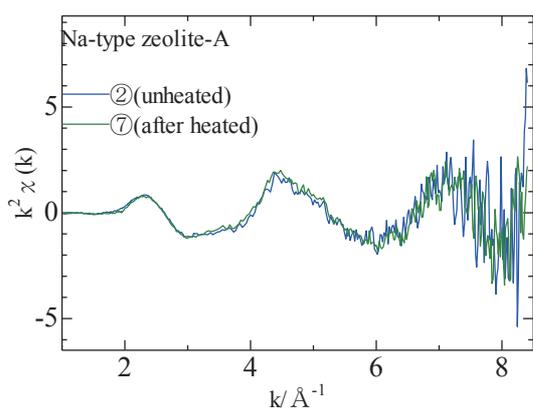


Fig.3 Al *K*-edge EXAFS  $k^2 \chi(k)$  spectrum of sample ② and ⑦ about Ag-type zeolite-A.

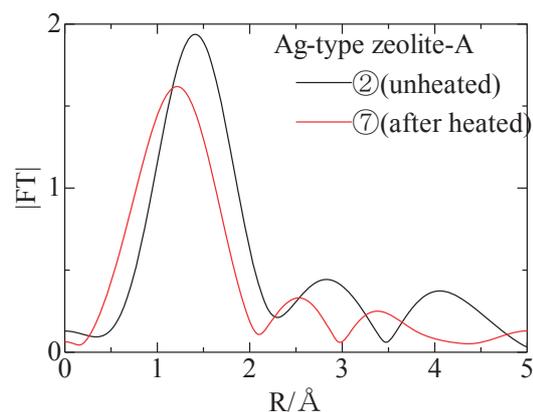


Fig.4 Al *K*-edge EXAFS Fourier transform spectrum for state ② and ⑦ about Ag-type zeolite-A.

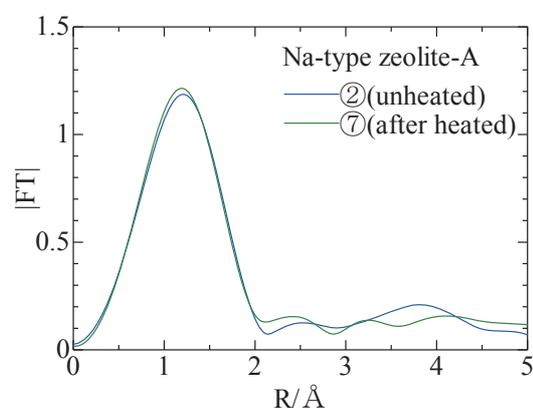


Fig.5 Al *K*-edge EXAFS Fourier transform spectrum for state ② and ⑦ about Na-type zeolite-A.

Next, we discuss about results of IR measurement. Figure 6 shows the change of IR spectrum about Ag-type zeolite-A. The IR spectra show large changes by heating and cooling in vacuum. We estimate this change of spectra appears due to the existence of Ag-clusters in zeolite cavity. Since Ag clusters existing in the cavity are broken down by exposing to air, the spectrum of IR changed nearly to the sample ① by exposed to air. From the result of XAFS measurement of Ag *K*-edge of previous study [3], the EXAFS  $\chi(k)$  spectra of the sample ① and ⑥ were completely same. But the IR spectra of ① and ⑥ were different. So, this change of IR spectrum ① to ⑥ is not due to change of the local structure around Ag atoms. From the result of Al *K*-edge XAFS analysis, described above, zeolite frameworks is changed by heating treatment. Furthermore, it is predicted that site of Ag ions in the zeolite cavity is changed by the formation and decomposition of Ag clusters. We predict this difference of IR spectrum of ① and ⑥ is due to change of zeolite frameworks and site of Ag ions.

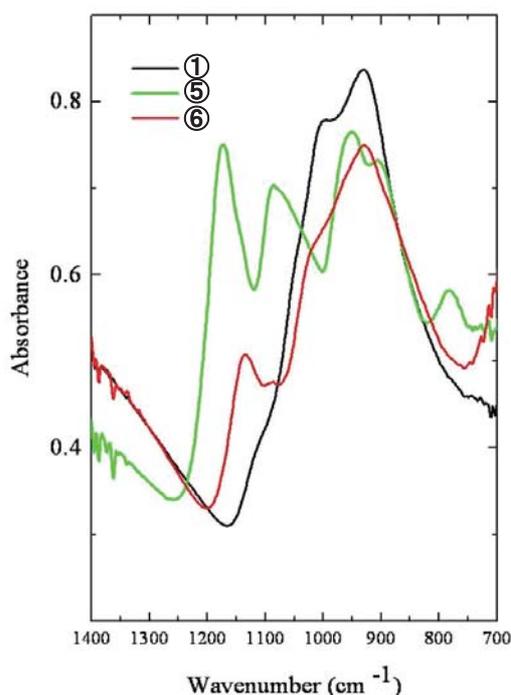


Fig.6 IR absorption spectrum for sample ①, ⑤ and ⑥ about Ag-type zeolite-A.

#### 4 Conclusion

We studied the structural change of zeolite framework by Al K-edge XAFS measurement and IR light absorption measurement to elucidate the luminescence mechanism of Ag-type Zeolite-A. From the result of experiments, we found that the state of framework of Ag-type zeolite-A is changed by heating and cooling treatment, and this change is not appear at Na-type zeolite-A. We conclude the framework of Ag-type zeolite-A is influenced by generation and breakdown of Ag-cluster. This change of framework affected by Ag atoms is key point to elucidate of PL mechanism.

#### References

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