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In-situ XAFS Study of Ag Clusters in Ag-type Zeolite-A

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1 Introduction

We studied structural changes of Ag-type zeolite-A in which the mole ratio of Si and Al is 1. The Ag-type zeolite-A cooled to room temperature after heated at 500 C for 24 hours under vacuum or air shows the strong PL (photo luminescence) peaks around 2.1eV. It is reported that the intensity of PL peak is influenced by conditions of the heating step and the kind of atmospheric gas introduced after cooling. As the example the PL curves for various introducing gases are shown in Fig. 1. However, the detail mechanism of PL has not been clear. On the other hand, when the Ag-type zeolite is heated the lattice water molecules are removed, and then the Ag^+ ion is reduced to Ag^0. It is known that the Ag^0 species forms Ag clusters so it was predicted that the existence of Ag cluster plays an important role on PL mechanism.[1, 2]

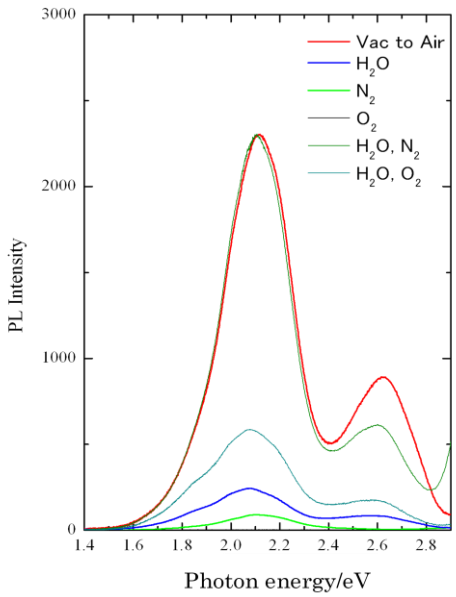

Fig.1: Intensity of PL for various introductory gases.

We have carried out XAFS analysis to study the structure of Ag-zeolite and the role of Ag clusters under various conditions. We investigated the relation between the Ag clusters and the intensity of PL peaks. At the result of previous study, it was concluded that the PL of the Ag-type Zeolite-A is attributed to the Ag clusters [1]. However the conclusion may be somewhat skeptical because the measurement condition of PL and the measurement condition of XAFS analysis are not completely the same. PL intensity measured at 24 hour passed after air is introduced after cooling. On the other hand, XAFS measurement carried out at almost 1 hour passed after air is introduced because we assumed that the structure of Ag-type zeolite should not change any more than 1 hour. In order to obtain a further exact result, we carried out XAFS measurement at the same condition of PL measurement. And we tried the introduction to other gasses; oxygen, nitrogen, water vapor, and their mixtures to study the origin of the deformation of the Ag clusters.

2 Experiment

We carried out XAFS analysis to study the structure of Ag-zeolite and the role of Ag clusters under various conditions. X-ray absorption spectra of K-edge of Ag were measured at NW-10A with transmission mode. A Si(311) monochrometer was used. The EXAFS oscillation function extracted from the X-ray absorption spectra was Fourier transformed by XANADU code [3]. In order to obtain the structural parameters, the EXAFS function was fitted by a non-linear least-squares method using the theoretical parameters calculated by FEFF 8.10 [4].

Figure 2 shows the Ag K-edge Fourier transform spectrum for Ag zeolite-4A at room temperature. measured in atmosphere. The peak around 1.7 Å corresponds to the first neighbor atom of O, the second peak around 2.7 Å corresponds to the second neighbor atom of O and Ag. We carried out 3 shell fitting (1st neighbor atom of O1 and 2nd neighbor atom of O2 and Ag) and investigate the coordination number *N* and atomic distance ***r*** each other**.** We discuss the existence of Ag clusters by the result of curve fitting.

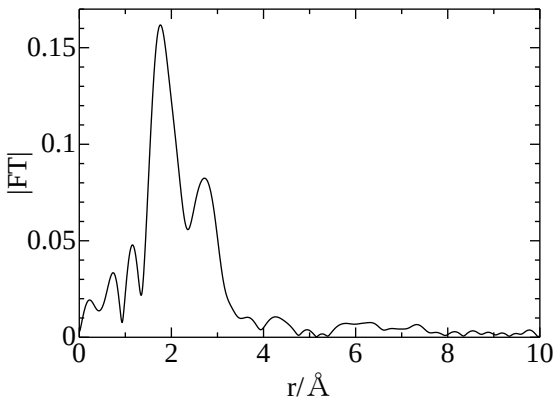

Fig.2: The Ag K-edge Fourier transform spectrum for Ag zeolite-4A measured in atmosphere

Ag type zeolite was heated at 500 C in vacuum. It is reported that Ag clusters were generated by the heating

from the our previous study. After keeping 500 C for 24 hours, they were cooled to room temperature and then various gases are introduced.

3 Results and Discussion

First of all, we show the result of curve fitting before the gases are introduced in Fig.3.

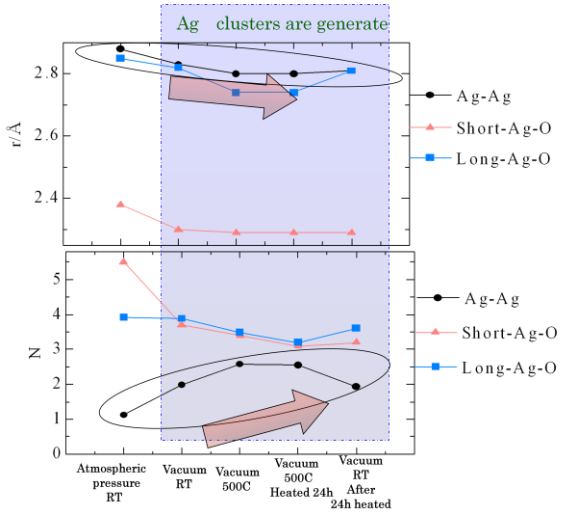

Fig. 3: The change of *r* and *N* before the gases were introduced.

It was observed that Ag clusters were generated by heating in vacuum, and the Ag clusters remains after cooling.

Next, we show the result of curve fitting after various gases were introduced. We introduced 4 gases; air, oxygen, water and oxygen, and water and nitrogen. Each curve fitting result is described below. The results are compared with two states; at room temperature in atmosphere and at room temperature in vacuum after heated 24hour.

(Ⅰ) Air

Figure 4 shows the curve fitting result for the species at 24 hours passed after air were introduced. Strong PL peak is observed when air is introduced. After introducing air, the states of Ag clusters were changed. The value of *N* and *r* is similar to the state of room temperature in atmospheric pressure. It indicates the breakdown of the Ag clusters. This result is different from the previous result. It indicated that air lead to break down of Ag clusters, but it needs long time enough to break down the Ag clusters and exists of Ag cluster is not necessary to appear the property of PL.

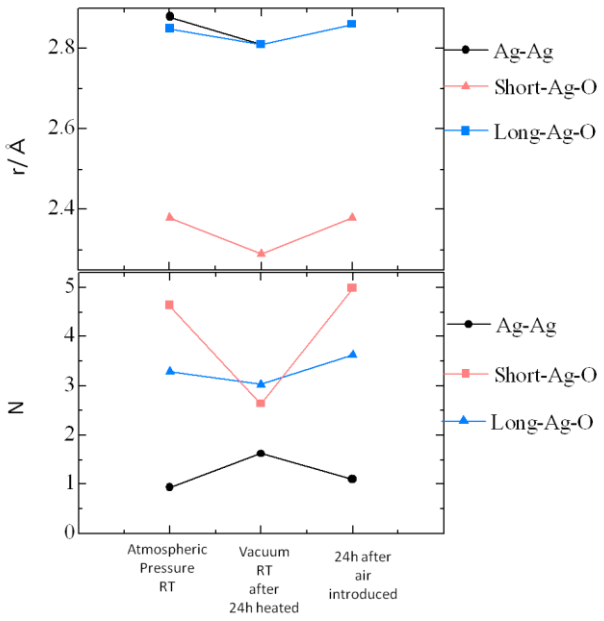

Fig. 4: The change of *r* and *N* after the air was introduced.

(Ⅱ) Oxygen gas

Figure 5 shows the result of curve fitting at 3 hours passed after oxygen introduced. PL peak is not observed when the oxygen is introduced. The values of *N* and *r* have not been changed as before the oxygen gas was introduced. It indicated that Ag clusters are exists.

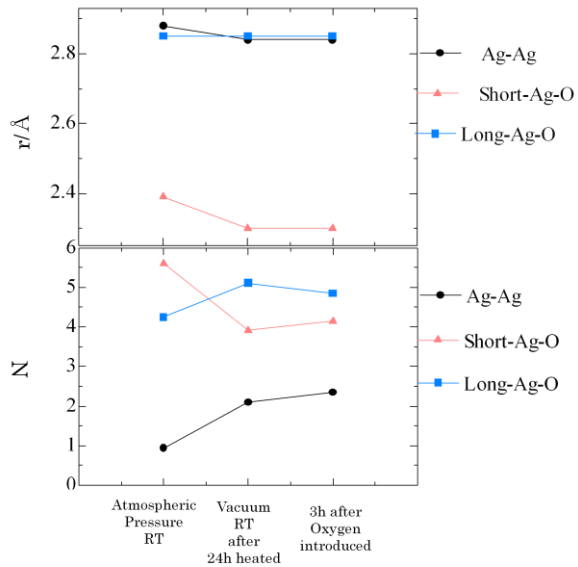

Fig. 5: The change of *r* and *N* after oxygen gas was introduced.

(Ⅲ) Water vapor and Oxygen gas

Figure 6 shows the curve fitting results at 3 hours passed after water and oxygen were introduced. Feeble PL is observed when the water and oxygen were introduced. The result of curve fitting indicated breakdown of the Ag

clusters similar to the case of atmospheric gas is introduced.

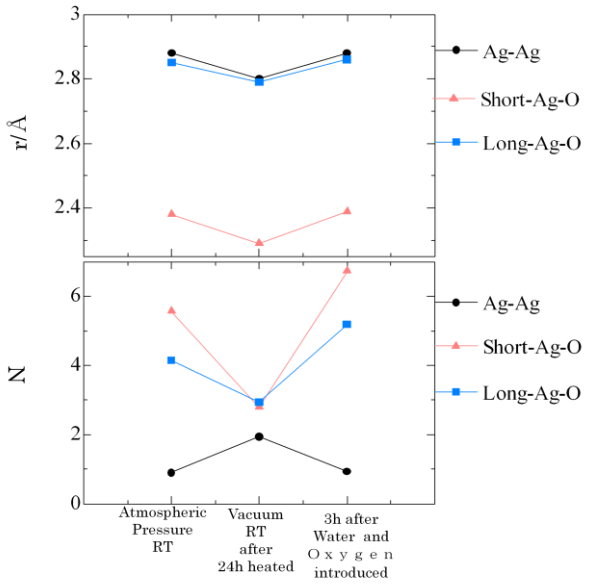

Fig. 6: The change of *r* and *N* after water vapor and oxygen gas was introduced.

(IV)Water vapor and nitrogen gas

Figure 7 shows the result of curve fitting at 18 hours passed after the water and nitrogen introduced. Strong PL is observed when water and nitrogen are introduced. The result of curve fitting indicated the breakdown of Ag clusters.

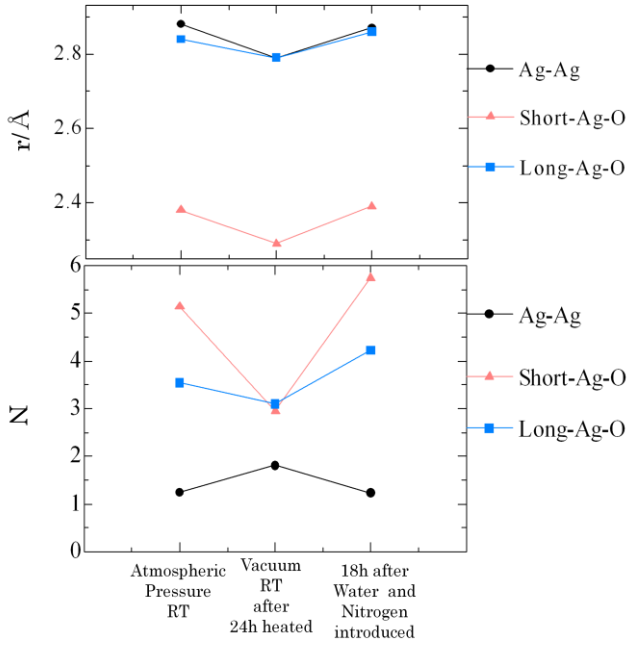

Fig. 7: The change of *r* and *N* after water vapor and nitrogen gas were introduced.

These results are summarized in Table 1. The results of the process for the nitrogen gas and for the water vapor are additionally presented. From the present results, it was found that the Ag clusters breakdown when the water vapor is introduced. We consider that the deformation of Ag clusters plays an important role of generation of PL peals and the framework change by formation and deformation of Ag clusters operates the PL peaks.

Table 1. The relation between the intensity of PL peaks and the existence of Ag cluster for various introductory gases.

	Air	Oxygen	Water	Nitrogen	Water and Nitrogen	Water and Oxygen
Intensity of PL	Strong	Not observed	Weak	Weak	Strong	Weak
Existence of Ag cluster	Not exist	Exist	Not exist	Exist	Not exist	Not exist

References

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