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

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Abstract. We studied the relation between structure of the Ag clusters produced in Ag-type zeolite-A and properties of photo luminescence (PL) by use of in-situ X-ray absorption fine structure (XAFS). Ag clusters are generated in the cavity of Ag-type zeolite-A which is cooled to room temperature after heated at 500°C for 24 hours under vacuum or atmosphere. We investigated the change of the Ag clusters in the zeolite cavity when various gases are introduced: oxygen, nitrogen, water vapor, and their mixture. The Ag clusters were breakdown when H$_2$O gas was introduced and the fact of the breakdown of the cluster is necessary for appearing the strong PL band. It was suggested that the structural change in the zeolite induced by the formation and breakdown of the Ag clusters is key point of the PL mechanism.

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 Na$^+$ ions in the original Na-type zeolites and they show various unique physical and chemical properties [1]. The Ag-type zeolite-A cooled to room temperature after heated at 500°C for 24 hours under the vacuum or in the atmosphere shows a strong PL band around 2.1 eV [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 Ag$^+$ ion is reduced to Ag$^0$, the “Ag clusters” are produced inside the cavity of zeolite [2]. In the cavity of the zeolite, a part of Ag ions are still connected to oxygen atoms at the zeolite lattice, but we call such “Ag aggregation” as “Ag cluster” according to our previous paper [2].

In this paper we investigated the relation between the existence of Ag clusters and the intensity of PL band to reveal the PL mechanisms using X-ray absorption fine structure (XAFS), which has advantages for the local structure analyses in the field of nano scaled sciences. In the result of previous study, it was concluded that the PL of the Ag-type zeolite-A is attributed to the Ag clusters [2]. However the conclusion may be somewhat skeptical because the measurement conditions of PL and XAFS are not completely the same. The strong PL band was appeared even at 24 hours passed after the air was introduced. In order to obtain a further exact result, we carried out in-situ XAFS measurement at the same condition of PL measurements. And further we tried to introduce various gases; oxygen, nitrogen, water vapor, and their mixtures into zeolite after heating to study the origin of the structural change of the Ag clusters.
2. Experimental

2.1. Sample preparations
The fully Ag⁺-exchanged zeolite A (hydrated 12Ag-A) powder samples were prepared by immersing the hydrated 12Na-A in 0.1 M AgNO₃ solution for 24 hours 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. Ag-type Zeolite-A was heated at 500°C in vacuum to produce the Ag clusters [2]. After keeping at 500°C for 24 hours, they were cooled to room temperature, and then, various gases: oxygen, nitrogen, water vapor, their mixtures and air are introduced. In-situ XAFS measurements were performed on each process.

2.2. PL measurements
The PL measurements were performed on a UV-VIS spectrometer (SPM-002; KLV) and a 405 nm violet laser (SU-61-405; audio-technica) light source was used. The chamber for high vacuum (RVX-3) was used in order to PL spectra measurement at various atmospheric conditions. PL measurements were performed 24 hours after the gases were introduced.

2.3. XAFS measurements
X-ray absorption spectra of K-edge of Ag (25.5 keV) were measured at NW10A at Photon Factory in KEK with transmission mode. A Si (311) monochrometer was used. The EXAFS oscillation function extracted from the X-ray absorption spectra and Fourier transformed by XANADU code [3]. In order to obtain the structural parameters, the EXAFS function was fitted in k-space by a non-linear least-squares method using the theoretical parameters calculated by FEFF 8.10 [4].

3. Results and discussion
First, we discuss the result of the PL measurements. Figure 1 shows the PL curves for various introduction gases. The strongest intensity of PL band around 2.1 eV was observed when the air or the mixture of the water vapor and nitrogen are introduced. It is suggested that the combination of the water vapor and the nitrogen is important for the strong PL band. On the other hand, PL is not observed when the oxygen was introduced. In the present stage the reasons of these phenomena are unclear.

Figure 2 shows the Ag-K EXAFS \( k^2 \chi(k) \) spectra for the Ag-type zeolite-A at room temperature in atmosphere (black solid line) and that at room temperature in vacuum after heated (red dashed line). It is found that the structure around 3.5 Å⁻¹ is especially changed after heating process, which is the characteristic feature by producing the Ag clusters [2]. Figure 3 shows the EXAFS \( k^2 \chi(k) \) spectra for Ag-type Zeolite-A after following gases were introduced; air (black solid line), H₂O (blue slid line) and O₂ (red dashed line). The structure around 3.5 Å⁻¹ is returned to initial state when air or H₂O+N₂.
were introduced. This reversible change in $k^2 \chi(k)$ spectra indicates the breakdown of the Ag clusters. On the other hand, the $k^2 \chi(k)$ spectra was not changed when O$_2$ gas was introduced.

**Figure 2.** The EXAFS $k^2 \chi(k)$ spectra for Ag type Zeolite-A at room temperature in atmosphere and that at room temperature in vacuum after heated. **Figure 3.** The EXAFS $k^2 \chi(k)$ spectra for Ag type Zeolite-A after following gases were introduced; Air, H$_2$O+N$_2$, O$_2$.

Figure 4 shows the Ag K-edge Fourier transform spectrum for Ag zeolite-4A measured at room temperature in atmosphere and that after following gases were introduced: Air, O$_2$, H$_2$O, N$_2$, and H$_2$O+O$_2$. The peak around 1.7 Å corresponds to the first nearest neighbor O1 atom, the second peak around 2.7 Å corresponds to the second nearest neighbor O2 and Ag atom. We carried out the 3-shell fitting and obtained the structural parameters; the atomic distance $r$ and the coordination number $N$ for each shell.

**Figure 4.** Fourier transform spectrum of Ag K-edge; unheated in atmosphere, introduction Air, O$_2$, H$_2$O+O$_2$, H$_2$O+N$_2$.

|                  | $r_{O1}$ (Å) | $N_{O1}$ | $r_{O2}$ (Å) | $N_{O2}$ | $r_{Ag}$ (Å) | $N_{Ag}$ |
|------------------|--------------|----------|--------------|----------|--------------|----------|
| Atmospheric pressure at RT | 2.38         | 5.51     | 2.85         | 3.92     | 2.88         | 1.12     |
| Vacuum at RT     | 2.30         | 3.70     | 2.82         | 3.89     | 2.83         | 1.98     |
| Vacuum at 500°C  | 2.29         | 3.40     | 2.74         | 3.49     | 2.80         | 2.58     |
| Vacuum at 500°C after 24h heated | 2.29       | 3.10     | 2.74         | 3.20     | 2.80         | 2.55     |
| Vacuum at RT after 24h heated | 2.29     | 3.14     | 2.81         | 3.61     | 2.81         | 1.93     |
In Table 1, the results of the curve fittings at the processes before introducing the gases are summarized. When the sample was evacuated, $N_{Ag}$ increases from 1.12 to 1.98, which indicates producing Ag clusters. Then it was observed that the Ag clusters were grown by heating in vacuum ($N_{Ag} \sim 2.58$), and they remain after cooling to room temperature ($N_{Ag} \sim 1.93$).

Now we discuss the structure of the Ag clusters after the various gases are introduced. The structural parameters after the gases are introduced are summarized in Table 2. As shown in Fig. 1, the strong PL band is observed when the air is introduced. After introducing the air, the Ag clusters were disappeared. The values of $r_{Ag}$ and $N_{Ag}$ are nearly same as those at the room temperature in atmospheric pressure. The air leads to breakdown of the Ag clusters, but it takes long time enough.

Judging from the results of the PL and the XAFS, the existence of the Ag clusters is not necessary to make the strong PL band. The PL band is not observed when the oxygen is introduced. The $r_{O1}$ and $r_{Ag}$ have not been changed after the oxygen gas is introduced, and the $N_{Ag}$ is still large ($N_{Ag} \sim 2.35$). This indicates that the Ag clusters exist after oxygen gas is introduced. Finally we discuss the results after the mixed gases of (1) water and oxygen, and (2) water and nitrogen were introduced. Feeble PL was observed when two gases of (1) were introduced. On the other hand, strong PL band was observed when two gases of (2) were introduced. The results of curve fitting indicate the breakdown of the Ag clusters as same as the case of the introduction of the air for both cases (1) and (2).

| Table 2. The structural parameters; $r$ and $N$ for the process after the various gases are introduced. |
|-----------------------------------------------|
| $r_{O1}$(Å) | $N_{O1}$ | $r_{O2}$(Å) | $N_{O2}$ | $r_{Ag}$(Å) | $N_{Ag}$ |
|----------------|---------|----------------|---------|-------------|---------|
| Air             | 2.38    | 4.57            | 2.86    | 2.96        | 2.86    | 1.40    |
| Oxygen          | 2.30    | 4.14            | 2.85    | 4.85        | 2.84    | 2.35    |
| $H_2O+O_2$      | 2.39    | 6.73            | 2.86    | 5.19        | 2.88    | 0.94    |
| $H_2O+N_2$      | 2.39    | 5.75            | 2.86    | 4.23        | 2.87    | 1.23    |

4. Conclusion

We studied the in-situ XAFS for the structural changes of Ag cluster after introduction of various gases. It was found that the Ag clusters were broken when the water vapor is introduced. It is suggested that the deformation of the Ag clusters after the introduction of the water vapor as primary and the nitrogen gas as secondary plays an important role of generation of the strong PL band. Ag clusters might be not direct species for the PL. We predict as one possibility that the structural change in the zeolite cavity induced by the formation and breakdown of Ag clusters is key point of the PL mechanism.

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