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Simultaneous Time-Resolved Photoluminescence and X-Ray Absorption Fine Structure Operando Measurement during Ag Cluster Formation in Ag Zeolite X

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Abstract

We use operando X-ray absorption fine structure (XAFS) to analyze the relation between the properties of photoluminescence (PL) and the structures of Ag clusters and Ag ions. The Ag clusters are generated by evacuation in the cavity of Ag-type zeolite-X. The Ag clusters in the zeolite cavity collapse when exposed to the atmosphere. The results reported herein indicate that the collapsing Ag cluster plays an important role in generating strong PL bands and that Ag clusters might not be a direct species of PL. Results of XAFS analysis show that the Ag cluster formed in the zeolite cavity by evacuation can be tetrahedral with four atoms. By evacuation, 9 or 10 Ag tetrahedral are formed, two of which are expected to be responsible for strong PL. This result suggests that the Ag ion position after cluster collapse plays an important role in PL band generation and that Ag clusters are not direct luminescent species of PL.

Keywords: zeolite, Ag cluster, photoluminescence, XAFS, operando measurement

1. Introduction

Zeolites are crystalline aluminosilicates with large ordered cavities (cages) that exhibit unique properties because of their cages [1–4]. They are used widely in applications such as catalysis, ion exchange, and separation [5–9].

The fact that Ag-exchanged zeolites exhibit luminous properties despite containing no rare earth metal component indicates zeolite as a promising luminescent material for future use. In recent years, many researchers have investigated the luminescence behavior of silver-exchanged zeolites [10–18]. Many reports have described that Ag clusters formed with a zeolite framework are luminescent species. In studies using inorganic material matrices such as silica, light emission from silver clusters formed in the matrix has been confirmed [19, 20]. However, the existence

of Ag clusters in PL studies of zeolites has been confirmed only indirectly. In earlier studies, PL and XAFS measurements of zeolites were taken to confirm the relation between PL bands and the local structure of Ag clusters [21, 22]. Results confirmed that Ag clusters were formed during heat treatment processing, however, the Ag cluster decomposed when cooled to room temperature (RT). The XAFS spectra of the unheated sample and the sample cooled after heating were very similar. The Ag clusters formed during heating but collapsed after cooling.

To elucidate the PL mechanism of Ag zeolite, it is fundamentally important to elucidate the relation between the formation and collapse processes of Ag clusters and PL. Accurate PL cannot be observed by thermal excitation. Therefore, it is impossible to observe this process by heat treatment. Ag clusters can be formed not only by heat treatment but also by evacuation. In the case of evacuation, clusters can form at RT. Therefore, as described herein, Ag clusters are formed by evacuation; then the clusters are destroyed by introducing air. In these processes, the relation between cluster formation/collapse and PL is elucidated by the time-resolved operando measurement of PL and XAFS.

For these purposes, we developed an in-situ/operand measurement cell, which can be possible to measure XAFS and PL simultaneously. In this chapter, we discuss the result for time-resolved operando measurement of PL and structure change measured by Quick measurement mode-XAFS.

2. Experimental

2.1 Sample preparation

Fully Ag⁺-exchanged zeolite X (hydrated 86Ag-X) powder samples were prepared by immersing the hydrated 86Na-X (Na₈₆[(AlO₂)₈₆(SiO₂)₁₀₆], purchased from Tosoh Corp.) in 0.1 M AgNO₃ solution for 24 h at 25°C. The solution was stirred continuously with a magnetic stirrer during ion exchange. After careful filtration, the 86Ag-X powder was dried under air at RT in the darkroom.

2.2 PL measurements

The PL measurements were taken using a UV-VIS spectrometer (flame; Ocean Insight) and a 313 nm UV light source (UVF-203S; San-Ei Electric) with a bandpass filter (313 nm, Edmund Optics Inc.).

2.3 XAFS measurements

The X-ray absorption spectra of *K*-edge of Ag (25.5 keV) were measured at NW10A of the Photon Factory at KEK using transmission mode. A time-resolved operando measurement of Quick-XAFS was performed during the evacuation process and the air introduction process. In addition, step scan XAFS measurements with high spectral quality were taken in the atmosphere before evacuation, in a vacuum, and after introduction into the atmosphere. The EXAFS oscillation function was extracted from the X-ray absorption spectra and Fourier transformed by XANADU code [23]. To obtain the structural parameters, the EXAFS function was fitted in *k*-space using the nonlinear least-squares method with theoretical parameters calculated using FEFF 8.10 [24]. Experimental details are presented in reports of several earlier studies [25, 26].

Figure 1.
Schematic drawing of zeolite sample holder for simultaneous time-resolved PL and XAFS operando measurements.

2.4 Simultaneous time-resolved operando measurement of PL and quick-XAFS

The transmission method must be adopted to ensure the spectrum quality by Quick-XAFS. Performing the transmission method with PF-AR NW10A requires the setting of the sample vertically because of the beam-line structure. A cover must have necessary powdery zeolite material installed vertically. Earlier studies have used microscope coverslips [26]. However, the inflow and outflow of air from the front are interrupted in the case of glass. The inflow and outflow of air only from the side face take a long time, especially in the process of introducing air. To date, long-term evacuation and atmospheric exposure have been used to avoid this shortcoming. However, time-resolved measurement has no such time margin. Therefore, a PTFE membrane filter (0.5 μm , T050A025A; Advantec) was used for the cover. With a membrane filter, air can enter and exit from the sample surface at a sufficiently high speed. For the sample, a prepared glass plate with a hole was used as a spacer for filling. The simultaneous time-resolved operando measurement of PL and Quick-XAFS has been realized. **Figure 1** portrays a schematic diagram. The time resolution of PL measurements and Quick-XAFS measurements was set to 1 min.

3. Results of PL and XAFS spectra

First, we discuss the PL measurement results. **Figure 2** shows a time-resolved operando measured PL curve of Ag-zeolite in the evacuation process (a) and the air introduction process (b). In both cases, a PL band having a peak near 556 nm is observed. When the evacuation was started, the PL band intensity decreased sharply and then decreased gradually. Similarly, during the air introduction process, the PL band intensity recovered rapidly in the early stage. Subsequently, it increased gradually.

Figure 3 shows the normalized operando time-resolved Quick-XAFS measurement spectra obtained for the Ag-X zeolite sample with step scan XAFS spectra in

Figure 2.
Evolution of the photoluminescence spectra of 86Ag-X: (a) evacuation process and (b) air introduction process.

Figure 3.
Evolution of the X-ray absorbance spectra of 86Ag-X: (a) evacuation process and (b) air introduction process.

Figure 4.
(a) The $k^2\chi(k)$ spectra and (b) their Fourier transforms of 86Ag-X.

the evacuation process (a) and the air introduction process (b). In both the evacuation process and the atmosphere introduction process, the XAFS spectrum changes continuously from the initial state to the final state. It is exciting that well-defined isosbestic points (e.g., marked by circles in **Figure 3(B)**) exist, which indicates that no clear intermediate state exists. The transient spectrum is a mixed spectrum of the initial sample and the final sample [27].

Figure 4 shows (a) the $k^2\chi(k)$ spectra and (b) their Fourier transforms for before and after evacuation and air introduction. To elucidate the structural parameters around Ag atom, we applied least-squares fitting (curve-fitting) to XAFS data. These results are discussed later.

4. Discussion

To reproduce XAFS spectrum of the intermediate state, a linear combination of the step scan spectra under atmospheric and vacuum conditions was made. The XAFS spectra simulated from the linear combination of them is shown in **Figure 5**.

Least-squares method was then used to ascertain which intermediate state spectra could be approximated by which linear combined spectra. Based on the results, we were able to plot the proportion of the XAFS spectrum in the atmosphere as a function of the evacuation time as shown in **Figure 6** (as open circle). In this figure, the integrated intensity of the PL band measured simultaneously is also shown (closed circles). Similarly, the results obtained during the process of introducing air are depicted in **Figure 7**.

In **Figure 6**, whereas the XAFS spectrum changes almost linearly from the initial state to the final state, the PL intensity decreases immediately after the start of evacuation. At 8 min after the start of evacuation, the change in XAFS is about one-fifth from the initial state, whereas the PL intensity has decreased to 1/12.5. In other words, the PL spectrum intensity change speed preceded the local structure change speed. No simple correlation was found between the speeds of both changes. This finding suggests that the PL almost disappears when about 20% of the Ag in the Ag-X zeolite changes from the initial state. However, in the process of introducing the atmosphere

Figure 5.
Linear combination of step scan XAFS spectra under atmospheric and vacuum conditions.

Figure 6.
Evolution of the PL intensity (solid circle) and the proportion of the XAFS spectrum (open circle) in the evacuation process as a function of the evacuation time.

(**Figure 7**), the XAFS changes almost linearly, whereas the change in PL intensity is somewhat complicated. The PL increases rapidly for about the first 10 min after the introduction of the atmosphere. Thereafter, the PL intensity increases slightly until about 35 min. Subsequently, the PL intensity again shows a gradual decrease. The change in the XAFS spectrum ends approximately 40 min after introduction into the atmosphere. Even in the process of introducing the atmosphere, the change in PL intensity and the change in the XAFS spectrum do not match. The XAFS spectrum

Figure 7. Evolution of the PL intensity (solid circle) and the proportion of the XAFS spectrum (open circle) in air introduction processes as a function of the introduction time.

shows a 20% change after about 7 min, at which time the PL intensity had reached about 60% of the maximum intensity.

The **Table 1** presents the structural parameters obtained from the curve-fitting to Ag *K*-edge XAFS. Especially, we specifically examine the coordination number ($N_{\text{Ag-Ag}}$) to Ag-Ag atom in the zeolite.

The values of $N_{\text{Ag-Ag}}$ of Ag-X zeolite in air and vacuum are, respectively, 1.55 and 2.07. The Ag species which might be present in Ag-X include the following: isolated Ag ($N_{\text{Ag-Ag}} = 0$), pairs ($N_{\text{Ag-Ag}} = 1$), linear (or bent) triples ($N_{\text{Ag-Ag}} = 1.33$), triangles ($N_{\text{Ag-Ag}} = 2$), tetrahedrons ($N_{\text{Ag-Ag}} = 3$), and octahedrons ($N_{\text{Ag-Ag}} = 4$).

Now we consider the models of Ag clusters produced in the zeolite cavity in air and vacuum deduced from EXAFS results. Several possible combinations can satisfy both the coordination number of Ag-X in the atmosphere ($N_{\text{Ag-Ag}} = 1.55$) and the coordination number in vacuum ($N_{\text{Ag-Ag}} = 2.07$), such as “pair and triangle”, “pair and tetrahedron”, and “triple and triangle”. Among them, it is considered that the change from the triple ($N_{\text{Ag-Ag}} = 1.33$) to the triangle ($N_{\text{Ag-Ag}} = 2$) can simply represent the change from 1.55 to 2.07. However, no direct conversion occurs from triple to triangle. For example, if one atom of a triple forms a triangle with another triple, a pair is also formed simultaneously, which is inconsistent with the existence of an isosbestic point. Based on the findings presented above, the simple combination most likely to satisfy the coordination number of Ag-X zeolite is considered as the combination of a pair and tetrahedron. When two pairs are twisted and the distance among the four atoms is coordinated, a tetrahedron is formed. A schematic drawing is presented in **Figure 8**.

Unheated sample	$r_{\text{O1}}(\text{\AA})$	N_{O1}	$\sigma_{\text{O1}}(\text{\AA})$	$r_{\text{O2}}(\text{\AA})$	N_{O2}	$\sigma_{\text{O2}}(\text{\AA})$	$r_{\text{Ag}}(\text{\AA})$	N_{Ag}	$\sigma_{\text{Ag}}(\text{\AA})$
in atmosphere	2.37	3.6	0.14	3.05	0.5	0.08	2.97	1.55	0.15
in vacuum	2.29	3.4	0.14	2.94	0.4	0.1	2.84	2.07	0.15

Table 1. Structural parameters r , N and σ for $\text{Ag}_{86}\text{-X}$ for unheated samples in atmosphere and vacuum.

Figure 8.
Schematic drawing of mutual conversion model between pairs and tetrahedron.

Gonzales et al. assigned the double positively charged $\text{Ag}_4(\text{H}_2\text{O})_4$ and $\text{Ag}_4(\text{H}_2\text{O})_2$ clusters to the PL emission species by XEOL measurement [28]. However, the light observed by XEOL is an emission band excited by an energy of about 25.5 keV. No evidence exists that it is the same species as PL species excited by UV-Vis light. We measured PL and XAFS simultaneously and clarified that the formed cluster was not a PL luminescent species.

Assuming that the ratio of the number of pairs to tetrahedra is 31:6, then the average coordination number is 1.558, which is approximately equal to the coordination number in the atmosphere of 1.55. However, if the ratio of the number of pairs to tetrahedrons is 21:11, then the average coordination number is 2.023, which is close to 2.07 in a vacuum. From these results, a model is conceivable by which evacuation increases the tetrahedral clusters from 6 to 11. The pairs decrease from 31 to 21: about 10 pairs (20 Ag ions) of Ag change into tetrahedrons when Ag clusters are formed. Results presented in **Figures 5 and 6** show that only 2 Ag pairs (4 Ag ions) form clusters, causing a rapid decrease in PL. In addition, during the collapse process, only one tetrahedron becomes two pairs. The PL increases rapidly. This model, which can clearly represent the change between the two states of Ag cluster formation and collapse, is called the “pair and tetrahedron model” (PTM).

Importantly, PL is lost when clusters are formed by evacuation (**Figure 6**). This result indicates that the cluster formed by the evacuation is not a PL luminescent species. In Ag-A, when Ag clusters are formed by heat treatment and are then collapsed, the PL intensity is increased considerably, but no change in local structure is observed by XAFS [21, 22]. These facts suggest that a “metastable site contributing to light emission” exists very close to the “stable site”. Unlike Ag-X, Ag-A and Ag-Y show almost no PL when not heated [29]. This phenomenon is explainable by considering that Ag-X has 86 Ag per unit cell, which is higher than other types (Ag-A = 12, Ag-Y = 51.2), and that Ag is located not only at stable sites but also at metastable sites. Then, in the cluster formation process, Ag that is coordinated to an unstable metastable site is consumed preferentially for cluster formation. Consequently, PL is lost. However, in the cluster collapse process, PL recovers rapidly because the cluster preferentially coordinates to metastable sites as the cluster collapses (**Figure 7**, 10 min). It is conceivable that the two pairs coordinated to the metastable site move to the more “stable site” over time. Subsequently, the collapsed Ag coordinates to this vacant metastable site. The Ag exchange is considered to occur at the metastable site. In other words, the increase in Ag at the metastable site becomes slower by the amount of Ag moving to the stable site. Accordingly, the PL intensity increases gradually (**Figure 7**, 10–35 min). The change in XAFS has stopped in 40 min. The

collapse of the Ag cluster is completed in 40 min. The decrease in PL intensity after 40 min is explainable by considering that Ag is moving gradually from the metastable site to the stable site. Considering the existence of metastable sites contributing to PL, one can explain the phenomenon by which PL disappears because of the formation of a small amount of Ag cluster. The PL intensity increases considerably because of the slight collapse.

5. Conclusion

This study was conducted to elucidate the PL mechanism of Ag-type zeolite by the construction of a model that can explain the PL expression mechanism. For that purpose, XAFS measurements that can analyze local structure are combined with PL measurements. Simultaneous operando time-resolved measurements of PL and transmission Quick-XAFS during evacuation and introduction to the atmosphere were taken to elucidate the formation and collapse processes of Ag clusters. Based on those findings, we attempted to ascertain the PL mechanism. From results of this experiment, the formation and collapse processes of Ag clusters in Ag-X zeolite are explainable by Ag species of two types: a pair and a tetrahedron. Then we confirm that the Ag cluster is not related directly to light emission. We predict the existence of metastable sites in zeolite as PL emission species. Furthermore, we propose a PTM that can explain only two pairs of Ag (4 Ag) that contribute to PL.

Acknowledgements

Synchrotron radiation experiments were conducted at the Photon Factory at KEK under Proposals 2016G056, 2018G070, and 2020G070. This work was supported by JSPS KAKENHI Grant Number JP17K05026, JP21K04858 and JP20K05295.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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