Effect of coexisting lithium content on fluorescent properties of silver ion-exchanged LTA zeolite

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The effect of the lithium ion coexistence on the fluorescent properties was studied for a partially Ag-exchanged LTA (A-type) zeolite. A series of Ag–Li-LTA zeolite samples was prepared by mixing the LTA zeolite powder (1.0 g) with aqueous solutions (100 mL) containing AgNO₃ (0.5 mmol) and various amounts of LiNO₃ (0–100 mmol). Although the fluorescence intensity was hardly observed in the unheated state for the Ag-LTA and the Ag–Li-LTA zeolites, the intensity was enhanced by the heat-treatment and showed the maximum value for the samples heated at 600 °C. A dramatic enhancement in the fluorescence intensity was observed by increasing the amount of the Li addition with a heat treatment at 600 °C. The highest fluorescence intensity was reached for the Ag(2.8 %)-Li(72.6 %)-LTA zeolite doped using the solution containing 0.5 mmol/g AgNO₃ and 100 mmol/g LiNO₃. Furthermore, the fluorescence shifted from a 605 nm (yellow) to the shorter wavelength of 505 nm (green) with the increasing Li amount. The fluorescent intensity due to the coexisting lithium ion for the Ag-exchanged LTA zeolite was significantly superior to those of the Ag–Li-FAU(X- and Y-types) zeolites.

Key-words : Fluorescence, Lithium, Silver, LTA zeolite

1. Introduction

A fluorescent is a substance that converts energy from the outside into light. It is used everywhere in our life as the lighting of fluorescent lights and LEDs, liquid crystals of smart phones and televisions, etc. In addition, the fluorescent is composed of a host material and a fluorescent center. The rare earth elements, such as Eu or Ce, are used for the fluorescent center. However, these rare earths are limited natural materials because of their cost and supply shortage. Therefore, studies of rare earth-free fluorescent materials are now being conducted.

In the rare earth-free silver ion-exchanged zeolite, Ag acts as a fluorescent center replacing the rare earth and the zeolite functions as the host material. The advantage of this material is that it is inexpensive and does not contain toxic elements. Zeolite is a general term for a crystalline porous aluminosilicate composed of SiO₄ and AlO₄ tetrahedrons bonded in a three-dimensional network. The AlO₄ tetrahedron has a negative charge, which is neutralized by a cation for charge compensation. Based on this structure, the zeolite has ion exchange characteristics, adsorption characteristics, molecular sieve properties, and catalytic properties. Among them, the silver exchanged zeolite fluorescent materials have been confirmed as various zeolite types, including the A type, X type, Y type, etc. Many studies have investigated the appearance of fluorescence on a Ag-exchanged zeolite after heating at 400 °C or higher temperature. The fluorescence was ascribed to the formation of Ag clusters in the zeolite cavities caused by reduction of Ag⁺ to Agₐ⁺. However, one of the problems is the low fluorescent intensity. Based on some previous studies, it is known that changes in the environment surrounding Ag are important for improving the fluorescent properties of the silver exchanged zeolite fluorescence. The affecting factors include (1) the structure of the zeolite as the host material, (2) the atmosphere during heat treatment and storage, (3) the presence or absence of crystal water, and (4) the presence of cations in the zeolite. Among these factors, “the presence of cations in the zeolite” was emphasized. E. Coutino-Gonzalez et al. reported the improvement of the fluorescence properties for the partial silver-ion exchanged type LTA (A-type) zeolite fully containing lithium. However, the effects of the changes in the lithium content on the fluorescent properties have not been reported for the hydrated LTA zeolite.

In this study, we described a dramatic increase in the fluorescent intensity of the Ag partially exchanged LTA zeolite by changing the Li ion amount, and decided the suitable Ag and Li contents in the zeolite and its calcination temperature for the formation of the Agₐ⁺ clusters.
2. Experimental

2.1 Sample preparation of the Ag-exchanged LTA zeolite

For the preparation of the Ag-exchange LTA (A-type, Na\textsubscript{12}Al\textsubscript{12}Si\textsubscript{12}O\textsubscript{48}·27H\textsubscript{2}O) zeolite, 100-mL solutions containing various amounts of AgNO\textsubscript{3} (0.0–1.0 mmol) were prepared. Each solution and 1.0 g of the commercial Na-form of the LTA zeolite powder (Wako Pure Chemical Industries, Ltd.) were placed in an Erlenmeyer flask and shaken for 24 h in a shaker at room temperature. The flasks were covered with aluminum foil during the shaking to prevent light exposure. Finally, the zeolite samples were filtered with suction and dried at 50 °C.

After drying, the samples were placed in an alumina crucible and subjected to heat treatment in a muffle furnace. The temperature was first raised to 50 °C and held for 1 h, then increased to the desired temperatures at the rate of 100 °C/h. The heat treatments were carried out at 300 to 800 °C for 2 h in the ambient air, then cooled in the same atmosphere.

2.2 Sample preparation of the Ag-exchanged LTA zeolite containing coexisting cation

To study the effect of coexisting cation species, 100-mL solutions containing 0.5 mmol AgNO\textsubscript{3} and various cations of MNO\textsubscript{3} (M = Li, K, Cs, 5.0 mmol) or M(NO\textsubscript{3})\textsubscript{2} (M = Mg, Ca, Sr, Ba, 2.5 mmol) were prepared. To determine the effect of the coexisting Li\textsuperscript{+} content, 100-mL solutions containing 0.5 mmol AgNO\textsubscript{3} and various amounts of LiNO\textsubscript{3} (0.0–100 mmol) were prepared. Each solution and 1.0 g of the commercial Na-form of the LTA zeolite powder were placed in an Erlenmeyer flask and shaken for 24 h in a shaker at room temperature. The flasks were covered with aluminum foil during the shaking. Finally, the zeolite samples were filtered with suction and dried at 50 °C. For further change in the Li exchange rate, the dried Ag–Li-LTA zeolite samples using the 0.5 mmol AgNO\textsubscript{3} and the maximum amount (100 mmol) of the Li solution were additionally treated using a pure 100-mL LiNO\textsubscript{3} solution (10, 50, and 100 mmol).

After drying, the samples were placed in an alumina crucible and subjected to heat treatment in a muffle furnace. The temperature was first raised to 50 °C and held for 1 h, then increased to the desired temperatures at the rate of 100 °C/h. The heat treatments were carried out at 600 °C for 2 h in the ambient air.

For simplicity, the obtained Ag and Li exchanged zeolite samples were abbreviated Ag-LTA and Ag–Li-LTA for the LTA zeolite treated only with the AgNO\textsubscript{3} (0.5 mmol) solution (LiNO\textsubscript{3} = 0 mmol) and for the LTA zeolite treated with the AgNO\textsubscript{3} (0.5 mmol) and LiNO\textsubscript{3} solutions, respectively. The original LTA zeolite was labelled Na-LTA.

2.3 Measurements

The elemental ratio was analyzed by X-ray fluorescence (XRF, Model RIX2100, Rigaku Co.). The ion exchange ratio of Ag was obtained from Eq. (1). Since Li could not be measured by XRF, it was calculated from the decrease in the amount of Na using Eq. (2).

$$\text{Ag ion exchange rate (\%)} = \frac{\text{Ag amount of Ag-LTA or Ag–Li-LTA}}{\text{Na amount of Na-LTA}} \times 100$$ \hspace{1cm} (1)

$$\text{Li ion exchange rate (\%)} = \frac{(\text{Na amount of Na-LTA}) - [(\text{Ag} + \text{Na}) \text{ amount of Ag–Li-LTA}]}{\text{Na amount of Na-LTA}} \times 100$$ \hspace{1cm} (2)

The X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku Rint 2000 X-ray diffractometer with Cu-K alpha radiation (Scanning rate = 2°/min at 40 kV and 20 mA). The fluorescence spectra were measured using a fluorescence spectrophotometer (Hitachi F-7000) with excitation at 275 nm. The thermal dehydrate process of the zeolite was studied (heating rate 100 °C/h) by a thermogravimetric analysis (TGA) along with a differential thermal analysis (Seiko Instrument TG/DTA 6200) in the ambient air.

2.4 Sample preparation of other Ag and Ag–Li zeolites for comparison

For comparison, the Ag-FAU and Ag–Li-FAU zeolites were also synthesized using the Na-form of FAU (X- and Y-types) zeolites (Wako Pure Chemical Industries, Ltd.). For the Ag-FAU zeolites, the preparation method and wavelength for the excitation were the same with samples having the maximum intensity.\textsuperscript{12,13} For the Ag–Li-FAU zeolites, they were prepared using 1.0 g of the FAU zeolite powder and the 100 mL solutions containing AgNO\textsubscript{3} (X-type 1.0 mmol, Y-type 0.5 mmol) and LiNO\textsubscript{3} (100 mmol).

3. Results and discussion

3.1 Effect of Ag-exchange ratio and heating temperature

The Ag\textsuperscript{+} ion in the AgNO\textsubscript{3} (0.0–1.0 mmol) solution was partially exchanged to one gram of the LTA zeolite and heated for 2 h in the ambient air. The XRD patterns did not change up to the heating temperature at 800 °C for all the Ag-LTA zeolites, indicating that the zeolite structure was maintained. However, the XRD peaks disappeared at 900 °C as the structure of the zeolite was destroyed and became amorphous. Figure 1 shows the fluorescent spectra for the typical Ag-exchanged LTA zeolite (Ag-LTA) samples (Ag = 0.5 mmol) heated at 300 to 800 °C in the ambient air by excitation at a 275 nm wavelength. For the non calcined sample, the fluorescent spectra were hardly observed for the LTA sample. All the samples exhibited a broad fluorescent in the visible light range from 520 to 750 nm with a maximum band at around 605 nm. The
maximum intensity of all the examined Ag-LTA zeolites was obtained for the sample heated at 600 °C. The intensity was reduced by the higher calcination temperature. The heat-treatment at 600 °C was suitable to obtain the high intensity for the Ag-LTA zeolites. The change in the weight with the heat process was confirmed by TGA analysis in the ambient air. The Ag-LTA zeolite was dehydrated during the heating at 600 °C to 78.0 %, which agreed with the theoretical 78.1 % assuming the formation of the dehydrated Ag-LTA zeolite. After the heat treatment, the weight of the zeolite completely returned to the initial hydrated value during the cooling process in the ambient air. Therefore, the zeolites obtained by the heat treatment in this study are hydrates. This improvement in the intensity of the fluorescent spectra is due to the formation of Ag clusters \([\text{Ag}_4(\text{H}_2\text{O})_4]^2+\) as luminescent centers in the sodalite cage of the LTA zeolite by heat treatment and rehydration.18)

Figure 2 shows the Ag ion exchange ratio and the maximum peak intensity of the fluorescent spectra versus the amount of Ag in the solution for the Ag-LTA calcined at 600 °C. The Ag content in the zeolite depended on the concentration of the \(\text{Ag}^+\) ion. The maximum intensity of the fluorescent spectra was obtained for the samples around 0.3–0.5 mmol/g whose Ag exchange ratio was around 1.5–3.0% in the zeolite. The intensity gradually decreased with the increasing amount of \(\text{Ag}^+\) due to the concentration quenching. Based on these experiments, the Ag content was fixed at 0.5 mmol/g for the study of the cation coexisting LTA zeolites. However, the fluorescence spectra were quite poor even for the heated Ag-LTA zeolite samples.

3.2 Effect of coexisting cation species

The Ag–M-LTA zeolites \((M = \text{Li, K, Cs, Mg, Ca, Sr, Ba})\) were prepared to study the effect of the coexisting cation species. Figure 3 shows the fluorescent spectra for the Ag–M-LTA zeolite \((\text{Ag} = 0.5 \text{ mmol}, M = \text{Li, K, Cs} = 5.0 \text{ mmol}, M = \text{Mg, Ca, Sr, Ba} = 2.5 \text{ mmol})\) heated at 600 °C. The fluorescent spectra for the Ag–M-LTA zeolites were strongly reduced for these coexisting sample except for the Li. For the Li coexisting sample \((\text{Ag} = 0.5 \text{ mmol}, \text{Li} = 5.0 \text{ mmol})\), the intensity of the fluorescent spectra was increased ca. 6 times compared to that of the Ag-LTA zeolite. Among these coexisting cations, Li possessed particular characteristics in the LTA zeolites. The small ionic radius and high affinity to the coordinated oxygen would be of particular interest for the stabilization of metal guests within the LTA zeolites.15) It suggested that the Li cations facilitated the stabilization of the Ag clusters within the zeolite cavities without any strong and direct involvement in the chemical reactions with the metal guest.
3.3 Ag–Li-LTA zeolites

Figure 4 shows the Ag and Li ion exchange rates for the Ag–Li-LTA samples versus the amount of Li in the solution. The data were calculated based on the XRF analysis results using Eqs. (1) and (2). Based on this result, it was confirmed that the amount of Ag was nearly constant irrespective of the amount of added Li. For the highest amount of Li, the amount of the added Li was about 200 times more than the added Ag (Li\(^+\) added = 100 mmol/g; Ag\(^+\) added = 0.5 mmol/g), but the Ag exchange rate was constant (2–3%), indicating that Ag has a high selectivity compared to the Li ion for the LTA zeolite. It was confirmed that the ion exchange rate of Li increased as the amount of added Li increased. For the samples with the higher (100 mmol) amounts of added Li, the exchange rate was approaching saturation at 72.6%. This saturation would occur due to competition with the Na ions eluted by the Li ion exchange. To increase the Li exchange rate, the saturated Ag–Li-LTA zeolite (Li = 100 mmol) powder (1.0 g) was treated again using a pure LiNO\(_3\) solution (10, 50, and 100-mmol) in 100 mL solutions. Table 1 shows the Ag and Li ion exchange rates for the retreated Ag–Li-LTA samples. The Li ion exchange rate for these samples of 10, 50, and 100 mmol was increased without a decrease in the Ag content to 76.5, 84.2, and 89.7%, respectively. The XRD patterns were not influenced by Ag\(^+\) and Li\(^+\) substitution for all the examined samples.

These Ag–Li LTA zeolites were heated for 2 h to confirm the effect of the Li coexistence. Although the XRD patterns did not change up to the heating temperature of 600 °C for the typical Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 100.0 mmol), the peaks disappeared at 700 °C as the structure of the zeolite was destroyed and became amorphous. Figure 5 shows the fluorescence spectra at EX = 275 nm of the typical Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 100.0 mmol) heated at various temperatures and the unheated sample. The spectra of the Ag-LTA sample heated at 600 °C are also shown in the figure.

### Table 1. Ag and Li ion exchange rates of the retreated samples using LiNO\(_3\) solution (10, 50, and 100 mmol) for the saturated Ag–Li-LTA zeolite (Ag = 0.5 mmol, Li = 100 mmol)

| Added Li (mmol) | Ag exchange rate (%) | Li exchange rate (%) |
|----------------|----------------------|---------------------|
| 10 mmol        | 2.7                  | 76.5                |
| 50 mmol        | 3.1                  | 84.2                |
| 100 mmol       | 2.5                  | 89.7                |

Fig. 4. Ag and Li ion exchange rates for Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 0–100.0 mmol) with various amounts of added Li.

Fig. 5. The fluorescence spectra (EX = 275 nm) of the typical Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 100.0 mmol) heated at various temperatures and the unheated sample. The spectra of the Ag-LTA sample heated at 600 °C are also shown in the figure.
amounts of Li from 0.0 to 100.0 mmol at the heat treatment temperature of 600 °C. Based on this result, it was confirmed that the fluorescent intensity dramatically increased along with the increasing amount of added Li. The highest fluorescent intensity was reached when the zeolite was treated with 0.5 mmol of Ag and 100.0 mmol of Li. The fluorescent intensity of this sample was about 15 times higher than that of the zeolite treated with only Ag. Along with this, a blue shift, which is a peak shift from 605 nm (yellow) to 505 nm (green) of the shorter wavelength side, was also confirmed. These phenomena may occur because the Ag cluster tended to be stabilized by the presence of Li.

**Figure 6.** The excitation-emission profile for the Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 100.0 mmol) heated at 600 °C.

**Figure 7.** Changes in the fluorescent spectra (EX = 275 nm) for the Ag–Li-LTA samples with the change in the amount of the added Li.

**Figure 8.** The fluorescent spectra for the additional Li treated samples using Li solution (10, 50, and 100 mmol) for the saturated Ag–Li-LTA (Ag = 0.5 mmol, Li = 100 mL).

**Figure 9.** Relationship between the Li ion exchange rate and the maximum intensity of the fluorescence spectra (EX = 275 nm) for the Ag–Li-LTA zeolites.

A quantum efficiency of some selected samples was measured and presented in **Table 2**. For the Li free Ag-
Table 3. The sample preparation conditions for the amount of AgNO₃ and LiNO₃ and calcination temperature (CT) and wavelength for the excitation (EX)

| Sample                  | Ag (mmol) | Li (mmol) | CT (°C) | EX (nm) |
|-------------------------|-----------|-----------|---------|---------|
| Ag-LTA                  | 0.5       | 0         | 600     | 275     |
| Ag-Li-LTA              | 0.5       | 100       | 600     | 275     |
| Ag-FAU (X-type)        | 1.0       | 0         | —       | 311     |
| Ag-Li-FAU (X-type)     | 1.0       | 100       | —       | 308     |
| Ag-FAU (Y-type)        | 0.5       | 0         | 500     | 302     |
| Ag-Li-FAU (Y-type)     | 0.5       | 100       | 500     | 305     |

Fig. 10. The fluorescence spectra for Ag-LTA and Ag–Li-LTA and FAU (X- and Y-type) zeolites.

LTA sample (Ag = 0.5 mmol, heated at 600 °C), the internal quantum yield was 24.2%. This value was enhanced to 47.2% for the Li co-exchanged Ag–Li-LTA samples (Ag = 0.5 mmol, Li = 100.0 mmol, heated at 600 °C). The absorbance of UV light (275 nm) and the external quantum yield of the material were also higher for the Ag–Li-LTA zeolite.

3.4 Comparison with other Ag and Ag-Li zeolites

In our previous papers, the silver exchanged zeolites were reported for the FAU (X- and Y-type) zeolites. The same materials having the highest fluorescent intensity in these studies were prepared for comparison. In addition, the Ag–Li zeolites were also prepared by the Li co-substitution using 100.0 mmol/g Li. Table 3 shows the conditions of the sample preparation. Figure 10 shows the fluorescent spectra for the Ag and Ag–Li zeolites. For the FAU (X and Y type) zeolite, the intensity was not strongly changed by the Li co-substitution. Although the fluorescent intensity for the Ag-LTA zeolite was low among the three Li free Ag-zeolites, the highest value was obtained for the Ag–Li-LTA zeolite.

4. Conclusion

The Ag–Li-LTA zeolite showed the highest intensity of the fluorescent spectra among the typical examined zeolites. The suitable preparation methods, such as the cation (Ag and Li) contents and the heat temperature were studied for the superior Ag–Li-LTA zeolite. The highest fluorescent intensity having the green color around 500 nm was obtained by the calcination at 600 °C for the Ag(1.5–3.0%)–Li(ca. 75%)-LTA zeolite. This study is considered to provide a guideline for improving the fluorescent characteristics of a rare earth-free silver ion exchanged zeolite.

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