Amorphous materials prepared by heat treatment at low temperature for partially Ag-exchanged Na-P1 type zeolites and their photoluminescence properties

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Partially Ag-exchanged Na-P1 type zeolites were prepared using an Na-P1 type zeolite and a silver nitrate solution. Emission spectra of the samples prepared at various concentrations of the silver nitrate solution and at various subsequent heat-treatment temperatures were compared. The structure of the Na-P1 type zeolites was changed to an amorphous phase by the heat-treatment at 400°C or higher. When the amorphous materials were irradiated with 254 nm ultraviolet light, these samples showed a high intensity violet luminescence with an emission peak around 390 nm.

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1. Introduction

Zeolites are porous aluminosilicates and widely used in industry as ion-exchange materials for the purification of water and soil.¹⁾ One of the promising properties is the photoluminescence (PL) for partially Ag⁺ exchanged zeolites. Up to now, the A-,^{2)–4)} Y-,^{5),6)} X-types of zeolites have been studied as host materials.⁷⁾ The mechanism of the PL has been attributed to the formation of a silver cluster, which is formed by heat treatment in the range of 300–800°C. The zeolite frame was maintained and dehydrated to form the silver cluster by the heat treatment. The dehydrated zeolite hydrates again in ambient air at room temperature. The excitation wavelength was different for each Ag-zeolite. Although an Na-P1 type zeolite (Na₆Al₆Si₁₀O₃₂·12H₂O) having a high cation exchange capacity (CEC) is one of the host materials, the PL properties have not been reported for the Ag-containing Na-P1 type zeolite. In addition, the formation of a homogeneous amorphous phase is expected for the Ag⁺-substituted Na-P1 zeolite at a lower temperature, because the frame for the Na-P1 type zeolite is not stable even at 400–500°C. The heat-treatment of the Ag-containing Na-P1 type zeolite is a new preparation method at low temperature for the homogeneously Ag⁺-containing amorphous Ag₂O–Na₂O–Al₂O₃–SiO₂ system. We considered that the silver cluster also forms in the amorphous phase during the heat-treatment.

In this study, we synthesized partially Ag-exchanged Na-P1 type zeolites and the PL properties were obtained by the heat-treatment of the new Ag-containing amorphous materials.

2. Experimental

For the preparation of the Na-P1 type zeolite, a sodium silicate solution (14.47 g, JIS-K1408, No. 3, Daiso Company, Limited) and NaAlO₂ (3.00 g, Wako Chemical) were dissolved in a NaOH

solution (NaOH = 2.00 g and H₂O = 38.86 mL). The total elemental ratios for the starting materials were Na:Al:Si = 3.6:1.0:2.0. This mixed solution was heated at 120–190°C for 3 or 6 h in an autoclave. The powder was collected and washed several times by centrifugal separation, then dried at 80°C. The synthesized Na-P1 zeolite (1.0 g) was completely exchanged to Na⁺ in 24 h using a NaCl solution (0.1 mol/L, 20 mL) at room temperature. For the Ag⁺ partial substitution, a 0.05–0.75 mmol/100 mL Ag⁺ solution was prepared using AgNO₃ in deionized water. A 100 mL Ag⁺ solution was added to 1.0 g of the Na-P1 zeolite powder, then the mixture was slowly shaken (1 Hz) for 24 h using a shaking machine at room temperature. The mixture was filtered and washed with deionized water. After the powder was dried at 50°C, it was then heated at various temperatures in the range of 100 to 900°C for 2 h in ambient air. The X-ray diffraction (XRD) patterns of the heated powders were recorded using a Rigaku Rint 2000 diffractometer with Cu-K-alpha radiation (Scanning rate = 2°/min at 40 kV and 20 mA). The elemental ratio of Ag, Na, Al, and Si was analyzed by X-ray fluorescence (XRF, Model RIX2100, Rigaku Co.). The fluorescent signals were measured using a fluorescence spectrophotometer (Hitachi F-7000) at 254 nm UV.

3. Results and discussion

For the zeolite preparation, the single phase Na-P1 type zeolite was obtained after heating at 150 and 160°C for 3 h in an autoclave. The crystalline phase was not obtained at a lower temperature than 150°C. The intensity of the XRD peaks for the Na-P1 type zeolite was higher for the sample heated at 160°C. An analcime (Na₁₆Al₁₆Si₃₂O₉₆·16H₂O) phase as the second phase formed during the heat treatment at a higher temperature than 160°C. The formation of the analcime was also observed when the sample was heated for longer than 6 h at 160°C. Based on these results, we adopted the heating at 160°C for 3 h as the synthesis conditions of the Na-P1 type zeolite.

Figure 1 shows the relationship between the concentration of the Ag⁺ solution and the elemental Ag/(Ag+Na) ratio of the

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Fig. 1. Relationship between the amount (mmol/100 mL) of silver nitrate solution and Ag^+ exchange rate (mol %).

Fig. 2. XRD results of Ag^+ exchange Na-P1 type zeolites heat-treated at 100–900°C.

Ag^+ exchanged Na-P1 zeolite. The Ag exchange rate increased with the increase in the Ag^+ concentration, and it agreed with the theoretical ratio when the Ag^+ was completely exchanged with the Na^+ ion in the zeolite. **Figure 2** shows the XRD peaks for the heat-treated Ag^+ exchanged Na-P1 zeolite using the 0.125 mmol/100 mL solution. In this material, the Ag^+ exchange rate to the Na^+ site was 1.4%. The XRD pattern of the heat-treated sample at 100°C showed the single phase of the Na-P1 type zeolite. The peak intensity decreased with an increase in the heat-treatment temperature. The Na-P1 phase disappeared and small peaks of the $\text{Na}_{6.4}\text{Al}_{6.4}\text{Si}_{9.6}\text{O}_{32} \cdot 4.2\text{H}_2\text{O}$ phase (Powder Diffraction Datafile 00-024-1046) were detected for the samples heated at 400–600°C. The amorphous material was obtained for the samples heated at 700–800°C. A nepheline (NaAlSiO_4) phase was formed at 900°C.

Figure 3 shows the emission spectra of the heat-treated Ag^+ -exchanged Na-P1 zeolite using the 0.125 mmol/100 mL solution. The weak emission peak around 400 nm was observed for the crystalline materials of the Ag^+ -substituted Na-P1 zeolite for the samples heated at 100–200°C. The wavelength of the emission peak is very low compared to 500–560 nm for the A-, Y-, and X-

Fig. 3. Emission spectra of Ag^+ exchanged Na-P1 type zeolite heat-treated at 100–900°C excited by 254 nm.

Fig. 4. Emission spectra for the heat-treated (800°C for 2 h) amorphous materials of the Ag^+ zeolites using various Ag^+ solutions (0.05–0.75 mmol/100 mL) excited by 254 nm.

type zeolites.⁷⁾ The intensity of the emission strongly increased with the increasing heat-treatment temperature. The maximum intensity was obtained for the amorphous sample heated at 800°C. Two emission peaks at around 330 and 390 nm were observed for the nepheline-containing sample heated at 900°C, but the emission intensity was much lower than that of the amorphous sample heated at 800°C. **Figure 4** shows the emission spectra for the heat-treated materials at 800°C of the Ag^+ zeolites using the various Ag^+ solutions. The XRD results indicated that these were amorphous materials. The emission peak of the Ag^+ zeolite shifted to a higher wavelength from 360 to 390 nm with an increase in the Ag^+ content of the zeolite. The maximum intensity was obtained for the Ag^+ -substituted sample using a 0.25 mmol/100 mL solution. The depression of the intensity for the high Ag^+ -substituted sample would be due to concentration quenching.

Figure 5 shows photos of the UV (254 nm) irradiated powder materials. Bright violet emissions were observed from these amorphous powder materials.

Fig. 5. Photos of UV (254 nm) irradiated powder materials. The samples were prepared by the heat-treatment (800°C for 2 h) of the Ag^+ zeolites using various Ag^+ solutions (0.05–0.75 mmol/100 mL).

Based on these results, the amorphous samples prepared by the heat treatment of the partially Ag^+ -substituted Na-P1 type zeolite showed a high intensity violet luminescence with an emission peak around 390 nm. In other words, this luminescence is derived from the amorphous Ag_2O – Na_2O – Al_2O_3 – SiO_2 system. The preparation method using the homogeneous Ag^+ substitution in the Na-P1 zeolite would be the most important parameter to produce this new amorphous luminescent material.

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