SHORT NOTE

Preparation of Analcime Film from Hydrogels

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Inorganic membranes such as zeolite films have become of interest in connection with application to separation technology(1)(2). Zeolite membranes have been usually obtained by embedding high-silica zeolite crystals in polymer or ceramic matrices(3). Lately, polycrystalline analcime film with a low Si/Al ratio of 2.0 has been prepared onto the alumina support by the hydrothermal treatment of hydrogels containing colloidal silica, NaOH and powdered natural zeolites(4). The analcime film was found to have a strong ion-sieve ability to Cs+ and was proved to be effective for the mutual separation of Cs and Rb(4). The separation of these elements is important for the partitioning of high-level liquid wastes. The present study deals with the preparation of analcime film from hydrogels with different chemical compositions under hydrothermal conditions.

1. Experimental

(1) Starting Materials

Hydrogels were prepared by adding colloidal silica (abbreviated as CS) with a particle size of 10–20 μm (Cataloid S-20L, Catalysts & Chemical Ind. Co. LTD.) to NaOH solution containing powdered natural zeolites. Two kinds of natural zeolites, clinoptilolite (below 200 mesh (<0.074 mm), Itaya, Yamagata Pref., CP) and mordenite (below 200 mesh, Itaoroshi, Miyagi Pref., NM) were used as the sources of the components, Si, Al and Na. The compositions of these zeolites were determined by electron probe micro analysis (EPMA, Hitachi X-650S) to be 68.0 wt% SiO₂, 10.1 wt% Al₂O₃, 0.85 wt% Na₂O for CP and 69.6 wt% SiO₂, 11.4 wt% Al₂O₃, 3.0 wt% Na₂O for NM, respectively.

(2) Preparation and Surface Analyses

The basic composition of hydrogel was (Na₂O)₆₇.₅ (Al₂O₃)₁₀ (SiO₂)₆₇.₅ (H₂O)₃₃₆₀, which was used for the formation of analcime film in a previous paper(4). The amount of each component and molar ratio in the hydrogel were varied as follows:

CS: 0 ~ 8.3 wt% (SiO₂/Al₂O₃=11.4 ~ 84.2, Na₂O/Al₂O₃ = 67.5),
NaOH: 0 ~ 2.67 M (=mol/dm³)
(SiO₂/Al₂O₃=0.14 ~ 67.5),
CP or NM: 5.0 x 10⁻³ ~ 0.3 g
(SiO₂/Al₂O₃=67.5 ~ 3.37 x 10³, Na₂O/Al₂O₃=67.5 ~ 4.04 x 10³),

where the weight of CP and NM corresponds to the amounts added to 15 cm³ of hydrogel.

Preparation of analcime film from hydrogels was performed in a similar manner described in a previous paper(4); the hydrogel and a porous alumina support (corundum type, 5 x 5 x 2 mm; 76.0 wt% Al₂O₃, 23.0 wt% SiO₂) were treated under hydrothermal conditions in an autoclave: 180°C for 1 d. The sample treated was washed with deionized water and then dried at 80°C for 1 d. The identification of the films obtained was achieved by X-ray diffractometry (XRD, Rigaku RAD-B). The surface and the cross section of the films were characterized by scanning electron microscope (SEM) and electron probe microanalyzer (EPMA, Hitachi X-650S).

2. Results and Discussion

(1) Effect of Concentration of Colloidal Silica

Photographs 1(a)~(c) show the surface morphology of the samples treated with different concentrations of CS. At lower concentration of CS below 1.8 wt%, the surface was covered with amorphous needle-like deposits which contained Na, Al, Si and Fe (Photo. 1(a)). The element of Fe probably came from CP which contained Fe₂O₃ as an impurity. A large number of spherical analcime (NaAlSi₂O₆,H₂O) particles of about 40 μm in diameter accumulated on the surface of the support contacted with 3.3 wt% CS, however, the crystallinity of these particles were rather low (Photo. 1(b)). The crystallinity of analcime particles was enhanced at higher concentration of CS; above 4.6 wt% CS, the film consisted of well-crystallized analcime of 30-hedron was formed on the surface of the support, and the particles are seen to have a uniform size of about 30 μm in diameter (Photo. 1(c))(4).

In-depth profile near the surface was further examined to estimate the film thickness and the alteration of the support. Photograph 2 shows the SEM image of the cross section of the sample treated with 4.6 wt% CS. The surface are seen to be covered with analcime film of about 200 μm in thickness; the film thickness was estimated by line analysis of Si-Kα. The analcime crystals are found to accumulate on the altered part of the
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Figure 1 shows the effect of CS concentration on the estimated thickness of analcime film. No films were formed on the surface at lower concentration below 1.8 wt% (SiO₂/Al₂O₃ ≤ 22.6), beyond which the film thickness markedly increased with CS concentration, and a relatively thick film of about 200 μm in diameter accumulated on the surface above 4.6 wt% (SiO₂/Al₂O₃ ≥ 45.1).

(2) Effect of Concentration of NaOH

The concentration of alkali component such as NaOH is a dominant factor for the formation of zeolite crystals. Figure 2 shows the effect of NaOH concentration on the thickness of analcime film. No analcime particles were formed on the surface at lower concentration of NaOH below 0.73 M. The formation of spherical analcime particles of about 40 μm in thickness was observed in the presence of 1.3 M NaOH, however, the surface was partially covered with the particles. At higher concentrations above 1.8 M, polycrystalline analcime film accumulated on the surface. Its particle size increased with increasing NaOH concentration and the crystallinity were also enhanced. The analcime film of about 200 μm in thickness was obtained at higher con-
centration of NaOH above 2.3 M (Na₂O/Al₂O₃ ≥ 54.0).

(3) Effect of Amount of Natural Zeolites

Photographs 3(a) and (b) show the surface morphology of the samples treated with either 15 cm³ of hydrogel free from CP or 15 cm³ of hydrogel containing 0.1 g of CP. Even in the absence of CP, the surface was covered with well-crystallized analcime forming twins (Photo. 3(a)). In this case, the analcime crystals were probably formed through hydrothermal alteration of the alumina support incorporating Na⁺ and CS⁴⁺; the surface of the support consisted of the mixtures of both phases of analcime and alumina. On the other hand, a large number of analcime crystals with a uniform size of about 30 μm in diameter were formed by the treatment of the hydrogel containing 0.1 g of CP (Photo. 3(b)). The film thickness markedly increased with the amounts of CP added (Fig. 3). The size of analcime crystal also increased with the amounts of CP added and the crystallinity was enhanced. The well crystallized film of above 100 μm in thickness was obtained above 0.1 g of CP added (SiO₂/Al₂O₃ ≤ 1.8 × 10², Na₂O/Al₂O₃ ≤ 2.0 × 10⁸). In the case of natural mordenite, similar results were obtained for the formation of analcime film.

3. Conclusions

The effects of composition of hydrogels on the formation of analcime film were examined under hydrothermal conditions. The polycrystalline analcime film of about 200 μm in thickness was formed by the hydrothermal treatment of hydrogels containing colloidal silica (CS) above 4.6 wt% (SiO₂/Al₂O₃ ≥ 45.1) and NaOH above 2.3 M (Na₂O/Al₂O₃ ≥ 54.0). The crystallinity and film thickness proportionally increased with concentration of CS and NaOH. The well crystallised analcime film of above 100 μm in thickness was also obtained above 0.1 g of CP added (SiO₂/Al₂O₃ ≤ 1.8 × 10², Na₂O/Al₂O₃ ≤ 2.0 × 10⁸).

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