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RESEARCH ARTICLE

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Preparation of mordenite composite membranes with seeding

Abstract Mordenite composite membranes were prepared by means of coating a porous α-alumina support with nanosized mordenite seeds followed by hydrothermal crystallization. A systematic investigation was performed on the influence of several factors such as ageing of the reaction mixture, alkalinity, salt addition and temperature on the formation of a mordenite membrane on the seeded support. The ageing of the reaction mixture reduces the growth rate of mordenite crystal along *a*-axis and *b*-axis but hardly influences the growth rate along *c*-axis. As a result, the boundaries between the surface crystals become a little larger with prolonging the period of ageing time. The growth rate of the mordenite crystal along individual axes increases first and then decreases with increasing concentration of sodium hydroxide. A higher alkalinity is unfavorable for the formation of a continuous mordenite membrane. The addition of salt in the reaction mixture has different effect on the growth rate of the mordenite crystal along each axis. With increasing the amount of salt, there was hardly influence on the growth rate along *c*-axis, whereas an obvious decline was observed in the growth rate along either *a*-axis or *b*-axis, which enlarges the boundaries between the surface crystals. The growth rate of the mordenite crystal increases more along *c*-axis than that along *a*-axis or *b*-axis with increasing temperature for hydrothermal crystallization. The use of a temperature as high as 473 K produces a membrane composed of bar-like crystals with larger boundaries.

Keywords mordenite membrane, seeding, zeolite membrane

1 Introduction

Zeolite membranes have potential applications in the membrane separation processes [1] and membrane reactors [2] due to their attractive features such as high thermal resistance, chemical inertness, mechanical strength as well as the unique pore structure of molecular dimension. In recent years, zeolite membranes, as an important research field of inorganic membranes, have been investigated extensively [3].

A zeolite membrane is generally prepared by forming a continuous zeolite layer on or in a porous support. The formation of a zeolite layer is a rather complex process, of which the mechanism is not yet very clear. Myatt et al. have proposed four possible processes for a zeolite membrane to grow on the surface of a support [4]: (i) nucleation and growth occurring in the bulk solution, followed by deposition on the support surface; (ii) nucleation occurring in the bulk solution followed by attachment and growth on the support surface; (iii) formation of a gel layer on the support surface, followed by nucleation and growth in the gel; (iv) direct nucleation on the support surface followed by growth.

So far several approaches or techniques have been proposed for the preparation of zeolite membranes. Among these, the secondary growth method, based on the idea of the growth process (iv), has been recognized as one of the most promising approaches [5]. In this approach, nanosized zeolite crystals as seeds are first coated on the surface of a porous support. These seeds are then grown into larger crystals under hydrothermal conditions to eliminate the voids between the seeds, leading to a continuous zeolite layer. There are already many reports on the preparation of zeolite membranes such as LTA [6–8], FAU [8, 9] and MFI types [10–12] by the secondary growth method, while few examples have been reported for other zeolite types.

Mordenite is a silica-rich zeolite. Owing to its controllable pore size by ion exchange, strong hydrophilicity, and high resistance to acid, mordenite has also been studied as an attractive membrane material. Mordenite membranes

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would find their uses for dehydration of organic acids and in membrane reactors such as esterification reactions. In previous studies [13, 14], we have proposed a simple method for preparing nanosized mordenite crystals from commercially available mordenite powder and have investigated the influence of silica source and water content on the growth of a mordenite membrane. In this study, the details are reported on the effect of other factors such as ageing of the reaction mixture, alkalinity, salt addition and crystallization temperature on the formation of a mordenite membrane on the seeded porous support.

2 Experimental

2.1 Reagents and materials

Reagents used in this study include silica sol (30～31 wt.% SiO_2, Nissan Chemical Industries Ltd., Japan), sodium aluminate (34.0～39.0 wt.% Al_2O_3, Kanto Chemical Co., Inc., Japan), sodium hydroxide (97.0 wt.%, Kanto Chemical Co., Inc., Japan), and deionized water. Asymmetric porous α-alumina plates (2 cm×2 cm, NGK Insulators Co., Japan) with the average pore size of ca. 100 nm in the top layer were used as supports for membrane preparation. These supports were successively cleaned in acetone and water in an ultrasonic bath for 20 min each and dried at 393 K before use.

2.2 Membrane preparation

A colloidal mordenite crystal suspension (the solid content=ca. 3 g/l and pH=6.0), which was prepared from commercially available mordenite powder following our previous protocol [13], was used for seeding as follows. The cleaned α-alumina support was dipped in the colloidal suspension for 2 min, withdrawn vertically at a slow rate, and then dried for 30 min at 293 K and subsequently for 30 min at 373 K. This seeding process was run twice.

The reaction mixture was prepared by mixing silica sol, sodium aluminate, sodium hydroxide and deionized water. The mixture was stirred at 323 K for 4 h before being transformed into a 40 ml Teflon-lined autoclave, in which the seeded support was vertically mounted in a Teflon holder. The autoclave was then put in a preheated oven for hydrothermal crystallization. After 14 h at a specified temperature, the autoclave was taken out and water-quenched to room temperature. As-synthesized samples were thoroughly washed with deionized water and dried at 393 K prior to characterization.

2.3 Characterization

The phase of the zeolite layer formed on the support surface was determined by X-ray diffraction (XRD, Rigaku RINT 2100) using Cu K_α radiation at 40 kV and 20 mA with a scanning speed of 2° (2θ) /min. The results confirmed that the crystals grown on the seeded support surface under all conditions employed here had a MOR-type structure. The nanosized particles in the colloidal suspension and the seeded support were characterized by field emission scanning electron microscope (FE-SEM, Hitachi S4500S) operated at 15 keV. The morphology of the zeolite layer was observed by scanning electron microscope (SEM, Hitachi S-2150) operated at 15 keV.

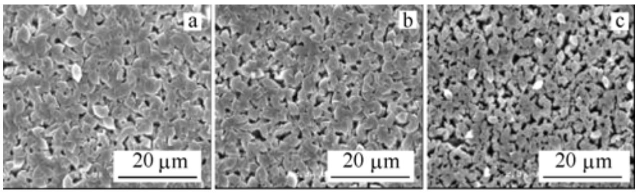

Fig. 1 SEM images for mordenite composite membranes prepared at 453 K in the aged reaction mixtures for different periods with the molar composition of $10Na_2O:36SiO_2: 0.15Al_2O_3:440H_2O$. (**a**) 1d; (**b**) 9d; (**c**) 24d

3 Results and discussion

3.1 Effect of ageing of the reaction mixture

Ageing of the reaction mixture is a common technique in the synthesis of zeolite powder. Ageing often results in an increase in the number of nuclei and accelerates the crystallization process. Figure 1 shows the SEM images of mordenite membranes prepared at 453 K using the reaction mixtures aged for different periods of time. It can be seen that the boundaries between the surface crystals become larger slightly with prolonging the ageing time. It suggests that the growth rate along the *a*-axis and *b*-axis of mordenite crystal becomes a little smaller with the ageing time. On the other hand, the cross-section images (not shown) show that the thickness of the zeolite layer hardly changes with the ageing time, indicating that ageing of the reaction mixture has less effect on the growth rate along *c*-direction. These results might be explained as follows. As stated above, ageing of the reaction mixture normally increases the number of nuclei in the bulk solution. The growth of the crystals in the solution competes with the growth of the crystals on the support surface in consuming structural units present in the solution. The excess of nuclei in the solution reduces the growth of the crystals on the support surface. Zhang et al. [15] have studied the effect of ageing on the growth of mordenite crystals on the unseeded α-alumina support. They also observed that the crystal size appeared to be smaller when an aged reaction mixture was used, which is in agreement with our results. Furthermore, the comparison of our results with theirs also shows that the effect of ageing becomes less important when the support surface was coated with seeds.

3.2 Effect of alkalinity

Alkalinity of the reaction mixture is another important factor influencing the crystallization process of zeolite. In this study, the alkalinity was adjusted by changing the amount of sodium hydroxide. Thus, the effect of alkalinity on the formation of a mordenite membrane can be considered as a combined result of sodium and hydroxide ions.

Hydroxide is an excellent mineralizer and will help in the uptake of material from the solid phase into solution. The increase in the hydroxide content of the system facilitates the dissolution of the gel and therefore increases the degree of saturation and promotes nucleation and crystal growth. On the other hand, the excess of hydroxide ions will also accelerate the dissolution of the formed crystals. As a consequence, there must be an optimum for the hydroxide ion concentration. This agrees with the tendency as shown in Fig. 2.

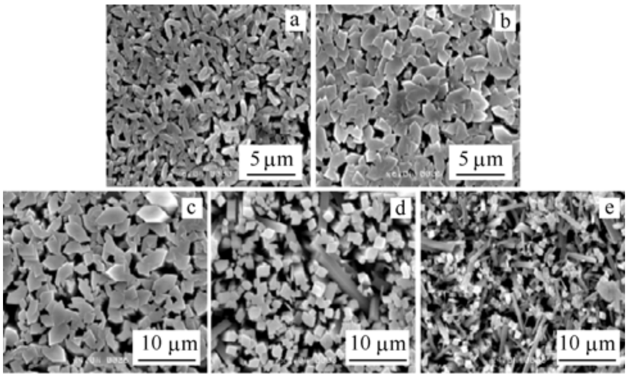

Fig. 2 SEM images for mordenite composite membranes prepared at 453 K in the reaction mixture with the molar composition of $nNa_2O:36SiO_2:0.15Al_2O_3:440H_2O$ with different alkalinity. (**a**) n=8; (**b**) n=9; (**c**) n=10; (**d**) n=11; (e) n=12

Besides acting as counterions to balance the zeolite framework charge, sodium cations present in the reaction mixture often appear as the dominant factor for structure direction.It seems that an increase in the concentration of sodium cations would accelerate nucleation and growth rate and larger crystals would thus be produced. As shown in Fig. 2, however, the variation of the crystal size is not monotonous. With an increase in the concentration of sodium hydroxide, an initial rise in crystallite size is observed, followed by a decline in size.

As discussed above, the effect of sodium hydroxide is a collective result of sodium and hydroxide ions. It is difficult to discuss the effect of individual ions. To solve this problem, the effect of addition of sodium salt in the reaction mixture was investigated.

3.3 Effect of salt addition

Figures 3 and 4 show the SEM images of mordenite membranes prepared after the addition of sodium chloride and sodium bromide in the reaction mixture, respectively. On comparing these two figures, it can be seen that the effect of addition of sodium chloride is similar to that of sodium bromide on the formation of mordenite membrane. This suggests that the nature of halogen anions has almost no effect on the membrane growth. The effect of sodium halogen salt can thus be approximately considered as the effect of sodium cations. Figures 3 and 4 show that the habit of mordenite crystal changes from prism to needle-like shape, indicating that the growth rate of the crystal along the *c*-direction is hardly influenced while that along the *a*-direction or *b*-direction reduces with increasing salt concentration. This might be due to an increase of the viscosity of the reaction mixture upon the addition of salt, which influences unfavorably the transport of structural units to the growing site on the crystal surface.

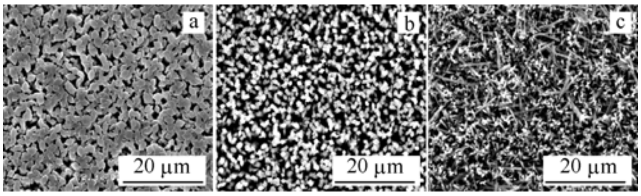

Fig. 3 SEM images for mordenite composite membranes prepared at 453 K in the reaction mixture with the molar composition of $10Na_2O:36SiO_2:0.15Al_2O_3:440H_2O$: *n*NaCl. (a) *n*=0.5; (b) *n*=1.0; (c) n=2.0

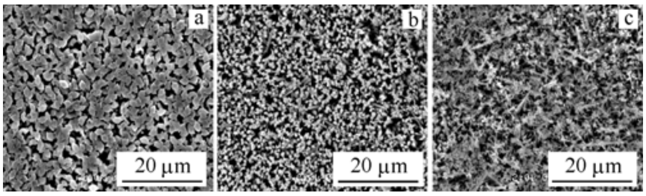

Fig. 4 SEM images for mordenite composite membranes prepared at 453 K in the reaction mixture with the molar composition of $10Na_2O:36SiO_2:0.15Al_2O_3:440H_2O$: nNaBr. (a) *n*=0.5; (b) *n*=1.0; (c) *n*=2.0

3.4 Effect of crystallization temperature

Temperature is an important factor strongly influencing the rate of crystallization and the zeolite phases obtained. Since the crystallization of a zeolite phase is an activated process, zeolite crystals grow faster at high temperatures. It seems that a higher temperature would be favorable for the formation of a continuous zeolite layer. The fact, however, is not so simple. As shown in Fig. 5, the voids between the surface crystals become larger with an increase in temperature. This might be due to the reason that the temperature dependence of the growth rate is different along individual directions for the mordenite crystal. The growth rate along the *c*-axis increases much faster than that along either *a*-axis or *b*-axis, which results in the formation of bar-like crystals and the greater voids between the surface crystals. The facilitated dissolution of seeds at a higher temperature may also be responsible for the formation of larger voids.

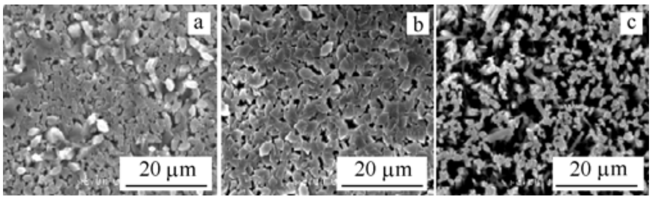

Fig. 5 SEM images for mordenite composite membranes prepared in the reaction mixture with the molar composition of $10Na_2O:36SiO_2:0.15\ Al_2O_3:440H_2O$ at different crystallization temperatures. (**a**) 438 K; (**b**) 453 K; (**c**) 473 K

4 Conclusions

It has been demonstrated that the factors such as ageing of the reaction mixture, alkalinity, salt addition and temperature impose effects to some extent on the formation of a mordenite membrane on the seeded support. SEM characterization results show that ageing of the reaction mixture reduces the growth rate along the *a*-axis or *b*-axis while hardly influencing the growth rate along the *c*-axis. As a result, the voids between the crystals appear to be larger slightly with ageing time. In addition, it is unfavorable for the formation of a continuous mordenite membrane with higher alkalinities, or with higher concentrations of sodium ions, or at temperatures higher than 453 K.

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