Preparation of Transparent TS-1 Zeolite Film by Using Nanosized TS-1 Particles

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Zeolites are crystalline oxides that have high surface-to-volume ratios, which are able to recognize, discriminate, and organize molecules with differences of <1 Å.[1] These are widely used in many chemical and physical processes such as catalysis reaction, ion exchange, separation, and chemical sensing technology.[2−4] Recently, much research has been focused on the synthesis of zeolite membranes because of their uniform pore size in molecular level and resistance to high temperature.[5−7] Zeolite membranes have been made by in situ crystallization of zeolite on ceramic, metal, metal oxide, Teflon, or glass substrate.[8] As an alternative method, the zeolite crystals were incorporated into the polymeric matrix such as silicone rubber[9] or a glassy silica matrix.[10,11] In the former case using in situ crystallization, zeolite particles were mainly crystallized on the substrate surface due to the local supersaturation caused by evaporation of water. In the incorporation method, zeolite particles were thoroughly mixed with polymer precursors and casted to make a composite membrane containing zeolite. In this case, the zeolite could not be fully utilized because most of the zeolite surface was embedded inside of polymer matrix. Therefore, a zeolite film made up of the crystals themselves may be more effective than the zeolite composite membrane.

Nanosized crystallites of various materials have received a great deal of attention.[12−17] Several researchers have studied the application of nanocrystallites to semiconductors. Among them, nanosized semiconductors incorporated into zeolite host are also known to have quantum size effects (QSE).[18] Srdanove et al. suggested that nanosized semiconductor particles became transparent to light because photons with lower energy transmitted the particles.[19] In optics, Engel et al. synthesized zeolite which was almost completely transparent down to 200 nm.[20] The nanosized crystallites would be very attractive for applications such as advanced optical materials. In their applications for zeolites, several researchers have synthesized nanosized zeolites.[21] Though nanosized zeolites were synthesized, synthesis and new applications of nanosized zeolites are not well studied because rapid crystallization occurs at high temperatures (>100 °C) under autogenous pressures in a hydrothermal autoclave reactor system.[22] Therefore, the size control of zeolite particles would be an important factor in the study of nanozeolites. In our previous work, we synthesized nanosized TS-1 zeolite particles having monosized distribution of crystallites at atmospheric pressure and 80 °C.[23] As a new application of nanosized TS-1 zeolite, we have tried to make the zeolite film from the nanosized TS-1 zeolite obtained in our laboratory. Recently, Tsapasis et al. synthesized zeolite L and formed transparent zeolite L film on a petri dish from the colloidal suspension.[21] However, there is currently no report on the preparation of optically transparent TS-1 zeolite film in visible range from crystallized zeolite particles.

In this paper, we report the first success in the preparation of transparent TS-1 zeolite film on micro slide glass using nanosized TS-1 zeolite crystals. The nanosized TS-1 zeolite was crystallized at 80 °C and 1 atm, as in our previous report.[23] Tetraethyl orthosilicate (TEOS, Aldrich), titanium butoxide (Aldrich), and 20% aqueous tetrapropylammonium hydroxide (TPAOH, Aldrich) solution were used for Si and Ti precursors and template, respectively. TEOS and TPAOH solution were mixed homogeneously with agitation. In a separate vessel, titanium butoxide solution diluted with isopropyl alcohol (Yakuri) was slowly dropped into the mixture of TEOS and TPAOH with vigorous stirring. After the removal of alcohol from the mixture, deionized water was added to the reaction mixture. The composition of initial reaction mixture in terms of molar ratios is as follows:

$$\text{Ti:Si:H}_2\text{O:TPAOH: 2-propanol} = 0.03\sim0.05\text{:1:25:0.32:0.77}$$

Before crystallization, a clear solution was obtained, and it was heated in polypropylene bottle submerged in a silicone oil bath preheated at 80 °C with stirring under reflux conditions.

Particle size and crystallinity of TS-1 zeolite were measured by using dynamic light scattering (DLS) and

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Table 1. Effect of TS-1 Solid Contents and Crystal Size on the Formation of TS-1 Zeolite Film

sample	TS-1 solid content[a] (wt %)	particle size	formation of TS-1 zeolite film[b]
1	0.2	80 nm	good
2	1.0	80 nm	no good
3	10.0	80 nm	no good
4[c]	0.2	1−2 μm	no good

[a] TS-1 particle (g)/H_2O (g) × 100. [b] Zeolite film was formed on the micro slide glass (25 mm × 75 mm). Micro slide glass was cleaned by heating at 70 °C for 1 h in acid solution (a mixture 5:5 (v/v) of 98% HCl and deionized water) followed by washing with acetone and ethanol solution. Finally, micro slide glass was cleaned and air-dried. [c] TS-1 particles with the size of 1−2 μm was synthesized by using hydrothermal synthesis at 150 °C for 4 days in Teflon-lined stainless steel autoclave reactor.

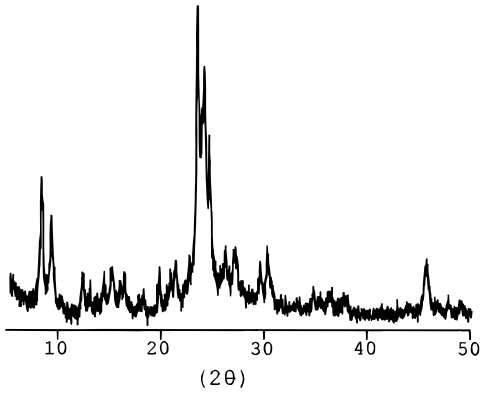

Figure 1. X-ray diffraction (XRD) pattern of TS-1 zeolite film as-prepared.

X-ray diffraction (XRD). After crystallization at 80 °C, nanosized TS-1 zeolite (80−90 nm) was obtained, and the crystallinity of TS-1 zeolite was more than 95%. After separating the TS-1 crystals from the mother liquid by centrifugation, TS-1 crystals were redispersed in deionized water. When TS-1 zeolite particles were dispersed in deionized water, there was no precipitation due to the Brownian motions of nanosized TS-1 particles.[24] TS-1 zeolite film was formed on the surface of micro slide glass by dipping the micro slide glass into the dispersed TS-1 solution and drying the solution at 100 °C when the TS-1 solid content is below 0.2 wt % (Table 1). However, the transparency of zeolite film decreased with the increase of TS-1 solid content. When we tried to make the TS-1 zeolite film with the TS-1 particles larger than 1 μm, film was not formed on the micro slide glass. The TS-1 particles were aggregated on the surface of slide glass.

This result implies the importance of nano size of TS-1 particles for the formation of TS-1 zeolite film. After preparing the TS-1 zeolite film, they were calcined in stagnant air at 550 °C for 2 h to remove the trapped organic molecule, TPAOH. To identify the crystal structure and the crystallinity of TS-1 zeolite film, XRD was measured. Figure 1 shows the XRD pattern of the TS-1 zeolite film obtained. It shows that TS-1 zeolite film has the MFI-type structure with an orthorhombic symmetry, which is the same result reported by other researchers.[22] After calcining up to 550 °C, apparently there was no crack on the surface of TS-1 zeolite film, and the zeolite film showed optical transparency (Figure 2a). To investigate the surface morphology of zeolite film, atomic force microscopy (AFM) was used. Figure 2b clearly shows that TS-1 particles (80 nm) were well packed on the surface of micro slide glass. Sano et al. have suggested that opaque zeolite film could be made with zeolite particles 3−5 μm in diameter by intergrowth among the zeolite primary particles under hydrothermal synthesis conditions.[8] This opaque film may stem from the particle size of zeolite with 3−5 μm in diameter. From the nanorange ceramic particles, Daganis suggested that a fairly transparent ceramic

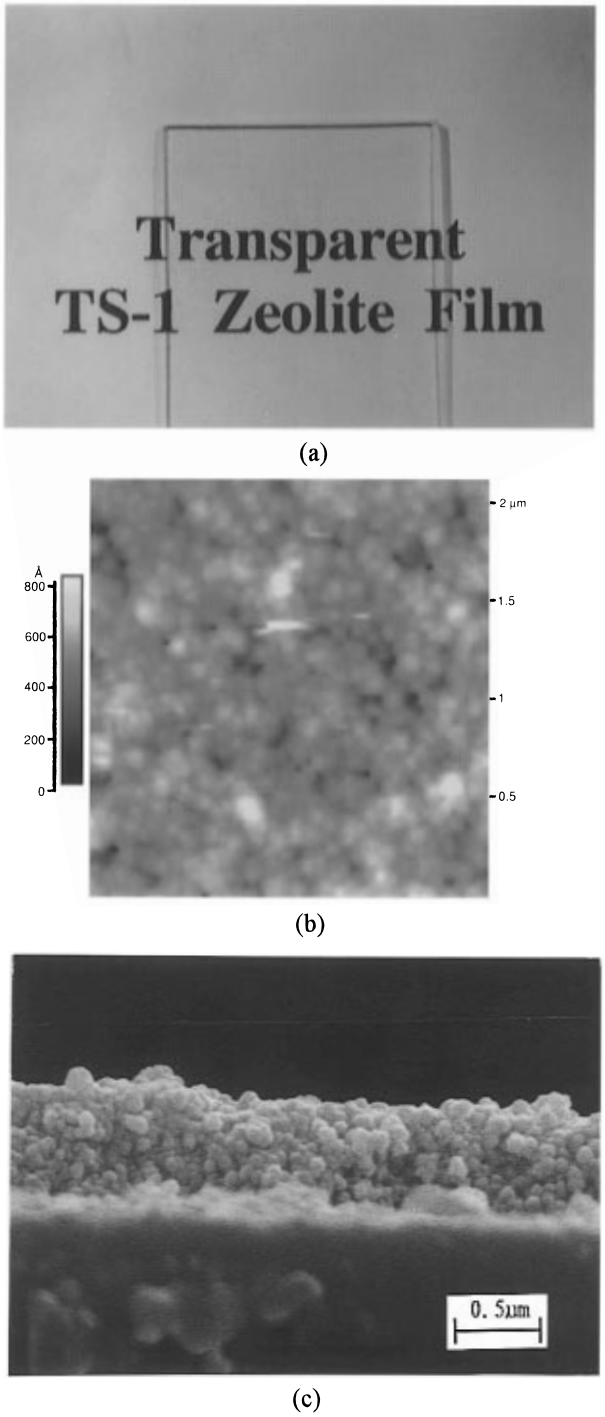

Figure 2. TS-1 zeolite film prepared by nanosized TS-1 particles (<100 nm): (a) optical microphotograph of zeolite film, (b) 2 × 2 μm AFM scan of the surface of zeolite film, and (c) scanning electron micrograph of the fracture of zeolite film.

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disk could be obtained because these samples do not scatter much light due to the size.[25] In inorganic−organic composite system, Schmidt also suggested that a high transparent property could be obtained by using nanoscaled metals or ceramics as inorganic materials.[26] In our case, transparent property of zeolite film result from the use of nanosized TS-1 zeolite. The size of TS-1 particles (80 nm) are below the wavelength of visible light (400−700 nm) and there are no secondary larger pores, which make zeolite film opaque, due to the dense packing of particles (Figure 2a,b). Therefore, the zeolite film does not scatter much light and shows transparency. This transparent property of zeolite could be applicable to the advanced optical materials such as photocatalysis, optical switching, hole burning, and laser focusing.[27] Figure 2c shows SEM image of the fracture of zeolite film coated on the micro slide glass after calcining at 550 °C. As shown in the SEM image, the thickness of the zeolite film was about 0.7 μm and TS-1 zeolite particles with about 80 nm were densely packed on the surface of micro slide glass to form film.

Nanosized zeolite is indispensable for making film and minimizing the force of gravitation acting on the TS-1 particle. In dipping process of the micro slide glass to the dispersed TS-1 solution, an intensive water flux carries the suspended TS-1 particles toward the surface of the micro slide glass. When the top of the particles protrudes from the aqueous solution due to the moving downward of the solid−liquid boundary, ordered state of TS-1 aggregates appear from disordered states which forms nucleus for multilayer stacking of TS-1 particles on the micro slide glass. A successive multilayer stacking of TS-1 particles could occur by water flux caused by the further evaporation of water. At this moment, we could find highly densified particles on the glass wall surface as a film. These densified particles resulted from the capillary force were appeared in colloidal systems such as latex and gold particle during the drying of the droplet of colloid solution in a horizontal system.[28]

In conclusion, the formation of a TS-1 zeolite film was mainly affected by the particle size and the solid content of TS-1. The nanosized TS-1 zeolite may provide a new method for preparing the optically transparent film. It could open new applications of optozeolite in advanced functional materials.

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