Preparation of hydrophilic silicalite-1 nanocrystal-layered membrane and its application to selective removal of water from raw acetone by pervaporation

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We have successfully prepared hydrophilic silicalite-1 nanocrystal-layered membrane. Mono-dispersed Silicalite-1 nanocrystals with different crystal sizes of 60 nm, 100 nm and 150 nm were used. The nanocrystals could be uniformly piled up on the alumina ceramic filter, followed by hydrothermal formation of silicalite-1 layer as protective coat. Mixture of acetone-water (raw acetone, acetone: 90 wt%, water: 10 wt%) was used as the solution in the feed side of the pervaporation. These membranes permitted only water permeation and the flux of water increased with decreasing the size of the silicalite-1 nanocrystals.

Introduction

In chemical industry, separation and purification processes for liquid-mixtures are the important unit-operations, which are mainly operated by distillation towers. In high purity separation by distillation, a large amount of energy is consumed due to a number of plates in the towers and reflux ratio of above 20. A pervaporation technique using zeolite membranes [1-4] is one of promising methods for high purity separation due to their high stability at high temperatures and strong resistance to organic solvent. We have successfully prepared hydrophilic silicalite-1 dense membrane by hydrothermal synthesis of silicalite-1 zeolite layer on an alumina ceramic filter [4]. This silicalite-1 membrane has large amount of hydrophilic silanol group, on which networks of water molecules were formed via hydrogen bonds. The networks allow only for water molecules to diffuse through the network, resulting in high separation factor. Moreover, it was revealed that the water-silanol networks formed on the non-zeolitic pores among the silicalite-1 crystals which were the dominant channels for permeation of water molecules.

In this study, to obtain the high flux of water by pervaporation, the increase in the amount of channels for water permeation was investigated. For this purpose, the membrane was made of the silicalite-1 nanocrystals, which was successfully prepared via hydrothermal synthesis using water/surfactant/oil solution [4]. The number of pores among the silicalite-1 crystals increases, which leads to the high flux of water through the membrane. The main objectives of this study are to prepare the silicalite-1 nanocrystal-layered membrane and to apply it to perm-selective membrane in raw acetone.

Experimental

Mono-dispersed Silicalite-1 nanocrystals with different crystal seizes of 60 nm, 100 nm and 150 nm were prepared via hydrothermal synthesis in water-surfactant-oil solution, which was described in detail in our previous paper [5,6]. The silicalite-1 nanocrystals were ultrasonically dispersed in alkaline water solution at pH of 10, and layered on the outer surface of cylindrical alumina ceramic filters (NGK Insulator, Co. Ltd.) by a filtration method with low-pressure vacuum in the permeate side. Finally, to protect the nanocrystal layer against mechanical shock, silicalite-1 layer as protective coat was hydrothermally formed on the nanocrystal layer. In order to achieve high hydrophilic properties of the membrane by remaining silanol group, the liquid phase oxidation technique was applied [4] to remove template molecules in silicalite-1.

The pervaporation experiments were carried out by a conventional method in temperature ranging from 30 to 110 degree C. Raw acetone (acetone: 90 wt%, water: 10 wt%) was used as the solution in the feed side of the pervaporation. The composition of the exit gas obtained from the permeate side of the membrane was measured by an on-line gas chromatography (Shimadzu, GC-8A) with a TCD detector and a porapak–Q column.

Results and Discussion

Figs. 1(a) and 1(b) shows SEM photographs of the silicalite-1 nanocrystal used in this study.

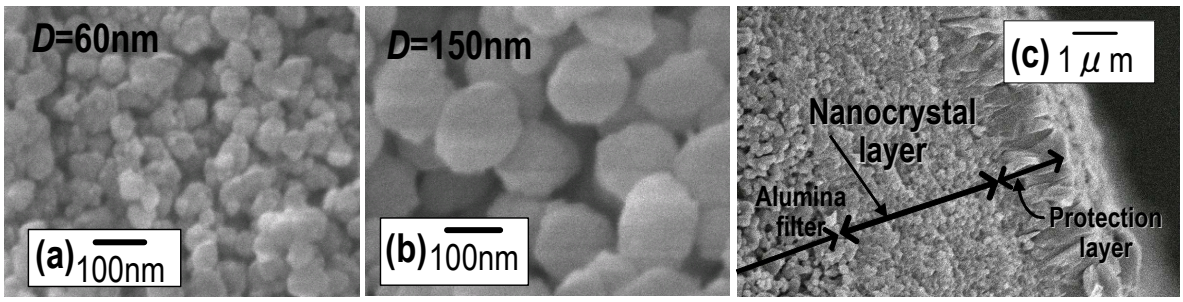

Figure 1: SEM photographs of (a) silicalite-1 nanocrystal and (b) cross section of nanocrystal-layered membrane.

Mono-dispersed silicalite-1 nanocrystals with a crystal size of approximately 60 nm could be observed. The X-ray diffraction patterns of the samples showed peaks corresponding to MFI type zeolite. Fig. 1(c) shows the SEM photographs of the cross sectional area of the silicalite-1 nanocrystal-layered membrane after formation of the silicalite-1 protective coat. The silicalite-1 protective coat was hydrothermally synthesized on the nanocrystals layer at 140 degree C for 24 h. As shown in the figure, the nanocrystals were uniformly piled up on the alumina ceramic filter, on which the silicalite-1 protective coat was synthesized. The thicknesses of the nanocrystal layer and the protection layer were approximately 3.5 μm and 1.5 μm, respectively. Moreover, as can be seen from Fig. 1(c), the nanocrystals around the interface between two layers grown during the formation of the protective coat via hydrothermal synthesis. It is considered that the pores among the silicalite-1 nanocrystals around the interface are dominant channels for permeation of water molecules where the water networks are effectively formed via hydrogen bond [4].

While the water as well as acetone permeated through these membranes at the initial stage of the experiments, the acetone flux decreased with time and was reached to zero after approximately 8 hours. The decrease in the flux was ascribed to the formation of the water-silanol networks via hydrogen bonds on the outer surface of the silicalite-1 nanocrystals, and the flux of water was higher than that of acetone at the steady state. Accordingly, the fluxes after reaching the constant values were used as the fluxes.

Figure 2 shows the effect of the permeation temperatures on the fluxes of water through the layered membranes. The water flux through the dense silicalite-1 membrane prepared by a previous method [4] was also shown in this figure for comparison. The fluxes of water through the layered membranes increased with increasing the permeation temperatures. Moreover, as the sizes of silicalite-1 nanocrystals decreased, it was found that the water fluxes extremely increased even though the acetone permeation could not be observed. As the crystal size decreased, the number of channels for the water permeation increased, which led to the increase in the water flux. The water flux of the layered membrane prepared using the silicalite-1 nancrystals with a diameter of 60 nm is approximately 100 times higher than the values of the dense membrane.

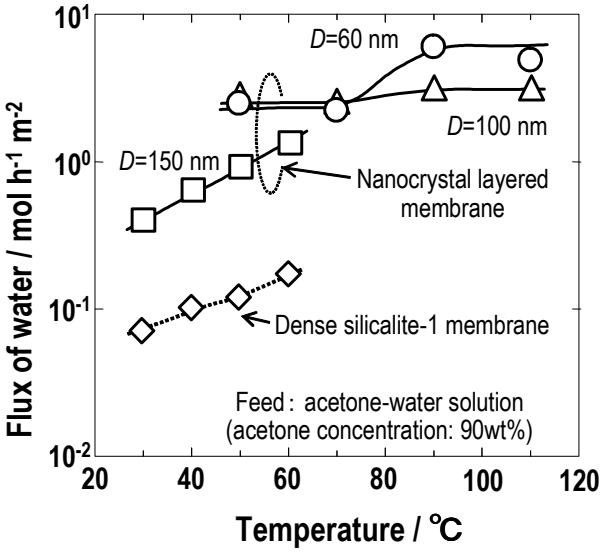

Figure 2: Effect of the permeation temperature on the flux of water.

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