



Title	Preparation of hydrophilic silicalite-1 nanocrystal-layered membranes and their application to separating water from water–acetone solution
Author(s)	Tago, Teruoki; Nakasaka, Yuta; Kayoda, Ayaka; Masuda, Takao
Citation	Microporous and Mesoporous Materials, 115(1-2), 176-183 <a href="https://doi.org/10.1016/j.micromeso.2007.12.035">https://doi.org/10.1016/j.micromeso.2007.12.035</a>
Issue Date	2008-10-01
Doc URL	<a href="http://hdl.handle.net/2115/34883">http://hdl.handle.net/2115/34883</a>
Type	article (author version)
File Information	Revised_MICMAC-IZMM4-20_TAGO.pdf



[Instructions for use](#)

**Preparation of hydrophilic silicalite-1 nanocrystal-layered membranes and their application to separating water from water-acetone solution**

**Teruoki Tago\*, Yuta Nakasaka, Ayaka Kayoda, and Takao Masuda**

5 Group of Chemical Engineering, Division of Chemical Process Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido 060-8628, JAPAN

Email address; [tago@eng.hokudai.ac.jp](mailto:tago@eng.hokudai.ac.jp)

## Abstract

Separation of water from a water–acetone solution was carried out by a pervaporation method using a hydrophilic silicalite-1 membrane. Silicalite-1 nanocrystals were piled up on the outer surface of cylindrical alumina ceramic filters, followed by a hydrothermal synthesis to form a silicalite-1 protection layer on the nanocrystal layer. In other words, the membrane consisted of a silicalite-1 nanocrystal layer and a silicalite-1 protection layer (the nanocrystal–layered membrane). In order to achieve high hydrophilic properties of the membrane with the remaining silanol group, the liquid–phase oxidation technique was applied to remove the template. From the SEM observation, the nanocrystal layer and the protection layer were clearly observed, and the silicalite-1 protection layer was uniformly formed on the nanocrystal-layer. Pervaporation experiments to separate water from the water-acetone solution were conducted using the nanocrystal-layered membrane. It was considered that the secondary growth of the nanocrystals around the interface between the nanocrystal and protection layers affected the separation properties. The effects of the nanocrystal size on the separation properties were examined. The membrane exhibited selective permeation as well as a high flux of water, and these properties were improved with a decrease in the size of the nanocrystals. Moreover, the layered membrane exhibited high hydrophilic properties regardless of the acetone concentrations.

Keywords: Pervaporation, Hydrophilic zeolite membrane, Silicalite-1, Silicalite-1 nanocrystal, Water-acetone solution

## 1. Introduction

Separation and purification processes for liquid-mixtures are one of the most important unit-operations in petrochemical industries, and are primarily carried out by distillation columns. Moreover, recently, the efficient utilization of biomass to produce energy and base chemicals has become an important function that will contribute to environmental protection by decreasing CO<sub>2</sub> emissions. The biomass-derived chemicals, such as ethanol, acetic acid, and acetone are usually obtained as water-mixture solutions, so that effective separation methods for water from the solutions are required.

In carrying out high-purity separations by distillation, a huge amount of energy is consumed due to the large number of plates in the distillation columns and a high reflux ratio above 20. Accordingly, in order to decrease the large energy consumption for separation, methods for high-purity separation have been desired, and a pervaporation technique could be a promising solution.

In the pervaporation method, feed liquid mixtures are in contact with one side of the membrane (feed side), and the target components in the mixture permeating through the membrane are removed as a vapor from the other side of the membrane (permeate side). Since an affinity (*e.g.* hydrophilic or hydrophobic interaction) between the membrane and the component in liquid solution causes selective permeation, the pervaporation membranes are more selective than distillation [1], which relies on vapor-liquid equilibrium to achieve separation.

Zeolite membranes [2,3] have been prepared and studied as potential pervaporation membranes [4–11] due to their high stability at high temperature and their strong resistance to organic solvents. For

dehydration of organic solvents such as ethanol, iso-propanol, and acetone, several types of zeolite membranes are applied. The selective dehydration by pervaporation using zeolite membranes is due to their hydrophilic properties, which depend on the composition of elements composing the frameworks, *e.g.* the Si/Al ratio. In the case of zeolites containing Al<sub>2</sub>O<sub>3</sub>, the dealumination, however, proceeds in acid solutions, resulting in a decrease in the separation factor due to the generation of defects after long-term use. Therefore, Al<sub>2</sub>O<sub>3</sub>-free zeolite membranes with hydrophilic properties are desired.

Silicalite-1 with MFI structure is one of Al<sub>2</sub>O<sub>3</sub>-free zeolites, which avoid dealumination. Since the silicalite-1 exhibits hydrophobic property, there are few reports concerning a preparation of hydrophilic silicalite-1 membranes. We have successfully prepared hydrophilic and Al<sub>2</sub>O<sub>3</sub>-free silicalite-1 membrane by hydrothermal synthesis of a silicalite-1 zeolite layer on an alumina ceramic filter [12, 13]. These silicalite-1 membranes have a marked amount of hydrophilic silanol groups, on which water molecules are selectively adsorbed. Moreover, it was revealed that the water-silanol networks formed on the non-zeolitic pores among the silicalite-1 crystals are the dominant channels for permeation of water molecules, which allows only water molecules to diffuse through the network, resulting in a high separation factor [12].

In our previous paper [13], the membrane was prepared using silicalite-1 nanocrystals, which were successfully prepared via hydrothermal synthesis utilizing a water/surfactant/oil solution [14,15]. In order to keep silanol groups in the membrane, asprepared membrane was treated by a liquid phase oxidation technique with H<sub>2</sub>O<sub>2</sub> to remove template molecules. In the membrane, the water-silanol networks were formed on the non-zeolitic pores surface among the nanocrystals, which were the main channels for water

permeation. The main objective of this paper is to develop a silicalite-1 nanocrystal-layered membrane with hydrophilic properties. First, the membranes were prepared using the silicalite-1 nanocrystals with different crystal sizes, and the effects of the amount of nanocrystals loaded on alumina filters and crystal sizes of nanocrystals on the separation properties of water from water–acetone solution through the layered-membrane were examined. Usually zeolite membranes formed on alumina filter are confronted with the serious problem of the mismatch regarding the expansion coefficients of the zeolite layer and alumina filter. However, in the nanocrystal-layered membrane, the thick nanocrystal layer can compensate the mismatch because the separation region was formed around the interface between nanocrystal and protection layers. Second, the effects of acetone concentrations in feed solution on the separation properties were examined to evaluate the hydrophilic properties of the membrane.

## **2. Experimental**

### *2.1 Preparation of silicalite-1 nanocrystal-layered membrane*

Mono-dispersed Silicalite-1 nanocrystal with different crystal sizes of approximately 60 nm, 100 nm, and 150 nm was prepared via hydrothermal synthesis in water/surfactant/oil solution. A water solution containing Si sources was prepared by hydrolyzing a metal alkoxide (tetraethylorthosilicate, Wako Chemicals) with a dilute tetra-n-propyl ammonium hydroxide/water solution (Wako Chemicals). The concentrations of TEOS and the molar ratio of TEOS to template were 1.6 mol/l and 3.0, respectively.

Polyoxyethylene-(15)-oleylether (Nikko Chemicals) and cyclohexane were employed as a surfactant and organic solvent, respectively. The water solution was added to surfactant/organic solvent solution at 50°C, and the mixture was magnetically stirred for 1 h. The mixture was then placed in a Teflon-sealed stainless bottle, heated to 120 degrees C, and held at the desired temperature for 50 h with stirring to produce silicalite nanocrystals. The preparation procedure was described in detail in our previous paper [14,15].

The silicalite-1 nanocrystals thus obtained were ultrasonically dispersed in alkaline water solution at a pH of approximately 10. The concentration of nanocrystals in the alkaline water was in the range of 0.0025–0.01 g/L. The dispersed nanocrystals were layered on the outer surface of cylindrical alumina ceramic filters (NGK insulators) by a filtration method with evacuation on the permeate side. The inner and outer diameters, and the length of the filter were 6 mm, 11 mm, and 50 mm, respectively. The thickness of the silicalite-1 nanocrystal layer piled up on the ceramic filter can be controlled by changing the concentration of the silicalite-1 nanocrystal in the water solution. Finally, to protect the nanocrystal layer against mechanical shock, a silicalite-1 layer (protection layer) was hydrothermally formed on the nanocrystal layer. A sodium silicate solution (Na<sub>2</sub>SiO<sub>3</sub>: 5.38 g; NaOH: 0.28 g; H<sub>2</sub>O: 58.5 g) and a template solution (tetra-n-propyl ammonium bromide (TPABr): 1.18 g; H<sub>2</sub>O: 86.0 g) were used as precursor solutions to form the protection layer. The alumina filter with a silicalite-1 nanocrystal layer was immersed in the precursor solution, and the silicalite-1 layer was formed hydrothermally for 24 h. The preparation procedure for the silicalite-1 protection layer has been described previously [13].

Prepared MFI type zeolites are usually calcined in air stream at 803 K, to burn off organic templates within the zeolite. During this procedure, silanol groups undergo the dehydration, yielding siloxane bonds. Silicalite-1 thus obtained has low hydrophilic properties. Moreover, it was revealed that the dehydration of silanol groups occurs at the calcination temperature above 670 K, leaving siloxane bonds [12]. Hence, in order to achieve high hydrophilic properties of silicalite-1 by remaining silanol groups, low temperature oxidation technique was required. The ozonation method at low temperature of 473 K reported by Heng et al. [16] is an effective method to remove the template without dehydration between silanol groups. In this study, in order to achieve high hydrophilic properties of the membrane with the remaining silanol group, the liquid-phase oxidation technique using hydrogen-peroxide solution at the reflux condition was applied [12] to remove the template. Firstly, 800 g of 1 N nitric solution and three prepared silicalite-1 membranes were put in a separable flask, and heated up to 373 K by stirring the solution. Then, 80 g of 30 wt.% H<sub>2</sub>O<sub>2</sub> solution was fed at the feed rate of 0.16 kg h<sup>-1</sup>, and held for 24 h. This sequence was repeated at three times. The treated membrane was washed by distilled water, dried in air stream, and then used in the further experiments.

15

## *2.2 Pervaporation experiments using the nanocrystal-layered membrane*

Pervaporation experiments were carried out by a conventional method at temperatures ranging from 30 to 110 degrees C using the stainless-steel autoclave vessel shown in Fig. 1. An acetone-water mixture (150 ml, acetone; 90 wt%) was used as the feed solution of the pervaporation. A new acetone-water

20



solution was used at each pervaporation temperature. Prior to the pervaporation experiment, nitrogen gas was fed into the gas phase of the vessel (upper side) at room temperature for 5 minutes to exchange air for nitrogen. Thereafter, the inlet and outlet valves on the top of the vessel were closed, and the vessel was heated to pervaporation temperatures. One end of the layered membrane was sealed, and nitrogen was fed to the sealed end of the membrane from a pipe inserted through the inside (permeate side) of the membrane. Nitrogen flowed backward to sweep out molecules permeating from the feed side to the permeate side of the membrane. The composition of the exit gas obtained from the permeate side of the membrane was measured by on-line gas chromatography (Shimadzu, GC-8A) with a TCD and FID detectors and a porapak-Q column. The water and acetone fluxes reached constant values after approximately 2 hours, with these values being used as the experimental data in this study.

The separation factor,  $\alpha$ , was defined as

$$\alpha = \frac{F_W / F_A}{C_W / C_A} \quad (1)$$

where  $F_W/F_A$  is the molar flux ratio of water to acetone on the permeate side of the membrane, and  $C_W/C_A$  is the molar concentration ratio on the feed side. The total amount of water and acetone permeating through the membrane during each experiment was less than approximately 3 percent of the initial amount of acetone–water solution. Accordingly, the initial concentrations of  $C_W$  and  $C_A$  were used.

### 3. Results and Discussion

#### 3.1 Preparation for Silicalite-1 nanocrystal-layered membrane

Figures 2(a)–2(c) show SEM photographs of the silicalite-1 nanocrystals used in this study. Mono-dispersed silicalite-1 nanocrystals with different crystal sizes of approximately 60 nm, 100 nm, and 150 nm were observed. From X-ray diffraction analysis, the nanocrystals showed peaks corresponding to MFI-type zeolite [14]. Figures 3(a) and 3(b) show SEM photographs of the cross-sectional area of the silicalite-1 nanocrystal-layered membranes. The size of the nanocrystal was 60 nm, and the hydrothermal temperatures to form a silicalite-1 protection layer were (a) 100 degrees C and (b) 140 degrees C. As can be seen from these figures, a nanocrystal layer with a thickness of approximately 4.0  $\mu\text{m}$  could be clearly observed on the alumina filter, and the columnar crystal orientation of the silicalite-1 protection layer with a thickness of approximately 1.2  $\mu\text{m}$  was observed on the nanocrystal-layer. Figure 3(c) shows SEM photograph of the top views of the membrane prepared at the hydrothermal temperature of 140 degrees C. The crystal size of the protection layer was approximately 500–1000 nm, and was much bigger than that of the nanocrystal. Though there was no crack at the top surface of the membrane, lots of pores among the silicalite-1 crystals of the protection layer can be observed.

The effects of the hydrothermal temperatures on the formation of the silicalite-1 protection layer and the separation properties were examined in order to determine the appropriate hydrothermal temperature. The pervaporation temperature and acetone concentration were 90 degrees C and 90 wt%, respectively. The experimental results are listed in Table 1. Though the morphology of the membrane and the thickness of the protection layer were almost identical, as shown in Fig. 3, the separation properties depended on the hydrothermal temperature. Judging from the crystal size and thickness of the protection layer shown

in Figs. 3, it was considered that there was almost no separation ability in the protection layer. However, since the nanocrystal-layered membrane exhibited the separation ability, the separation region was considered to be the interface between the nanocrystal and protection layers. We have previously revealed [13] that the growth of nanocrystals occurs during the formation of the protection silicalite-1 layer, and that the secondary growth of the nanocrystals around the interface between these layers affects the separation properties. Accordingly, the dependency of the separation properties on the hydrothermal temperature was ascribed to the difference in the secondary growth of silicalite-1 around the interface, which was discussed below in detail. Moreover, it was considered that at the low hydrothermal temperature below 120 degrees C, the amorphous and/or poor crystallinity phase is formed on the surface of the silicalite-1 crystal, which caused a decrease in the separation factor. From this perspective, the hydrothermal temperature in the formation of the protection layer was determined to be 140 degrees C.

### *3.2. Effect of the thickness of nanocrystal layer on permeation properties*

The effect of the thickness of the nanocrystal layer on the separation properties was investigated. The thickness can be easily controlled by changing the concentrations of nanocrystals in the water solution when piling up the nanocrystals on the alumina filter. The thickness of the nanocrystal layer was a monolayer, 1.3  $\mu\text{m}$ , and 4.0  $\mu\text{m}$ , and after piling up the nanocrystals, the silicalite-1 protection layer was formed at a hydrothermal temperature of 140 degrees C. Figure 4 shows the effects of the thickness of the nanocrystal layer on the separation properties of water through the layered membrane.  $\alpha$  in Fig. 4

represents the separation factor. In the membrane prepared without nanocrystal, the silicalite-1 layer was directly formed on the alumina filter by hydrothermal synthesis.

The membrane without nanocrystal showed no separation ability, indicating that the silicalite-1 nanocrystals layer played an important role in the separation property. In contrast, in the nanocrystal-layered membrane, the separation properties were extremely improved. Though the layered-membrane with the nanocrystal monolayer showed no flux of water, the membrane with the nanocrystal layer of 1.3  $\mu\text{m}$  and 4.0  $\mu\text{m}$  thickness exhibited high water fluxes and high separation factors. This result indicated that the separation properties of the membrane depended on the amount of nanocrystals loaded on the alumina filter. Pera-Titus et al. [17] and Hasegawa et al. [18] have reported that the amount of the seed crystals on a support affected the membrane performances for pervaporation and gas-separation, which was in agreement with our result.

Yokoi et al. [19] have reported that the pore size among silica nanospheres with periodic arrangement was approximately 3.2 nm. Accordingly, it was considered that pore sizes among the nanocrystals prior to hydrothermal synthesis to form the protection layer were bigger than 3.2 nm, which had no selective permeation ability. The dependency of the membrane performance on the amount of silicalite-1 nanocrystals was ascribed to the difference in the secondary growth during hydrothermal synthesis. In the membrane with a nanocrystal monolayer, it was considered that a dense silicalite-1 layer was formed, so that the water as well as acetone molecules could not permeate the membrane. In the membrane with a nanocrystal layer of 1.3  $\mu\text{m}$  and 4.0  $\mu\text{m}$  thickness, it was considered that the appropriate pores for selective permeation of water were formed by the secondary growth. After the liquid-phase oxidation

using H<sub>2</sub>O<sub>2</sub>, the silanol groups remained, where water-silanol networks formed, especially on the non-zeolitic pores surface among the nanocrystals.

The membrane with a thin nanocrystal layer of 1.3 μm exhibited lower water flux than that in the membrane with a nanocrystal layer of 4.0 μm. In the layered membrane with a thin nanocrystal layer of 5 1.3 μm, it was considered that the excessive secondary growth of the nanocrystals occurred to decrease the pore sizes for the water permeation, as compared to the membrane with a nanocrystal layer of 4.0 μm. Accordingly, the thickness of the nanocrystal layer was determined to be 4.0 μm.

Moreover, as shown in Fig. 4, the membranes with a nanocrystal layer of 1.3 μm and 4.0 μm showed almost the same water fluxes as the membranes without nanocrystals at a pervaporation temperature of 50 10 degrees C, even though the separation factors were differed. This result was ascribed to the rate-limiting step for water permeation through the membrane. In the nanocrystal-layered membrane, the selective channels for water permeation were formed among the crystals by the silanol–water networks due to its hydrophilic properties. In contrast, because there was no selective channels for water permeation within the membrane without nanocrystals, the separation factor of the membrane was low. However, at a low 15 pervaporation temperature of 50 degrees C, since the rate-limiting step for water permeation through the membrane was considered to be the heat transfer required for the heat of water evaporation, these membranes showed almost the same water fluxes.

### *3.3. Effect of the size of nanocrystal on the permeation properties*

Figure 5 shows the effects of the sizes of silicalite-1 nanocrystals on the separation properties of the water from water–acetone solution through the layered membranes. The hydrothermal temperature to form the protection layer and the thickness of the nanocrystal layer were 140 degrees C and 4.0  $\mu\text{m}$ , respectively.  $D$  and  $\alpha$  in Fig. 5 represent the size of the nanocrystal and the separation factor, respectively.

5 The water fluxes through the dense silicalite-1 membrane prepared by the previous method are also shown in this figure for comparison.

The fluxes of water through the layered membranes increased with increases in the permeation temperatures, and the water flux of the layered membrane prepared using the silicalite-1 nanocrystals with a diameter of 60 nm was approximately 100 times higher than the values of the dense membrane. As the  
10 sizes of the silicalite-1 nanocrystals decreased, it was found that the water fluxes as well as the separation factors increased dramatically. Hasegawa et al. [18] have examined the preparation of MFI-type zeolite membrane by secondary growth of seeds with different particle sizes. They reported that the amount and size of the seed crystals influenced on the separation performance. The experimental results shown in Fig.5 were in agreement with Hasegawa's report. Moreover, they have also revealed that the permeation  
15 behavior was mainly affected by pores spaces having diameters of approximately 1 nm in gas separation [20]. Though their research is in gas separation using MFI-type zeolite membrane, their results indicated that the pore spaces among crystals formed during the secondary growth is important for separation membranes. As shown in Fig. 3(c), the silicalite-1 protection layer has almost no separation properties because of many pore observed on the top surface of the membrane. Accordingly, it is considered that the

pore spaces formed by the secondary growth of the nanocrystals around the interface between the nanocrystal and protection layers are important for water separation.

As shown in Fig.5, the water flux as well as the separation factor affected the sizes of nanocrystal. As the size of nanocrystal decreased, the pore sizes among the crystal prior to the formation of protection layer decreased, which led to the decrease in the sizes of pore spaces formed by the secondary growth. Accordingly, the separation factor increased with the decrease in sizes of nanocrystal. Moreover, the decrease in the size of nanocrystal led to an increase in the number of hydrophilic channels among the crystals, where the water–silanol network was formed for the selective permeation of water molecules. Accordingly, the decrease in the crystal sizes led to an increase in the water flux.

10

#### *3.4. Effect of acetone concentrations in the feed solution on permeance*

In the above discussion, the acetone concentrations in the feed solution were fixed to be 90 wt% (0.74 mol%) to determine the appropriate preparation conditions for the silicalite-1 nanocrystal layered membranes. In order to evaluate the hydrophilic properties of the layered membrane, the effects of acetone concentrations on the separation properties were investigated. The concentrations of acetone were changed in the range from 10 wt % to 97 wt%, which corresponded to the range of an acetone molar ratio from 0.03 to 0.91. Figure 6 shows the permeance of water and the molar ratio of acetone in the vapour phase (permeate side) as a function of the molar ratio of acetone in the feed solution. The vapour–liquid

equilibrium line of acetone–water solution is also shown in this figure. The pervaporation temperatures were 50, 70, and 90 degrees C.

In the equilibrium line, the vapour component is primarily acetone in the low acetone concentration region, and in the high acetone concentration region, the molar ratios of acetone in the vapour and liquid phases exhibit almost the same values. The reverse triangles in the figure represent the molar ratio of acetone on the permeate side at a pervaporation temperature of 50 degrees C. Almost no acetone permeation was observed in the layered membrane (separation factors above 900). As mentioned above, the hydrophilic properties of the membrane resulted from the silanol groups formed on the non-zeolitic pore surface, where water molecules were preferentially sorbed to form water-silanol networks for the water permeation. Accordingly, silanol–water networks exhibiting the hydrophilic properties of the membrane can be formed in all acetone concentration regions, leading to excellent separation properties.

The permeance of the membrane apparently depended on the acetone concentrations in the feed solution. Since the adsorption and vaporization of water molecules within the membrane occurred during water permeation, the dependency of the permeance on the acetone concentration was ascribed to the difference in the number of vaporizing water within the membrane. In the low acetone concentration region (high water concentration), the rate of heat transfer was not enough to vaporize water because the water flux was high due to the high water concentrations. As the acetone concentrations increased, the flux of water through the membrane decreased because of the decrease in water concentrations, indicating that the number of water molecules vaporized decreased. Accordingly, the permeance of water through



the membrane apparently increased with increase in the acetone concentrations (decreasing the water concentrations).

In the high acetone concentration region, since the permeance of water was higher than that in the low acetone concentration region, the separation of water from the solution by pervaporation is suitable as compared with distillation. In contrast, in the low acetone concentration region, the permeance of water was found to be low. Moreover, in the vapour-liquid equilibrium line shown in Fig. 6, the acetone concentrations in the vapour phase are much higher than those in the liquid phase, so that the distillation is adequate in the low acetone concentration region. Therefore, from this perspective, we have proposed a new separation process consisting of distillation and pervaporation; the separation of acetone by distillation in the low acetone concentration region and the separation of water by pervaporation in the high acetone concentration region results in high-purity acetone from the acetone-water solution. The combination process is expected to decrease the scale of the distillation column and the reflux ratio, leading to the decrease in the cost imposed on the separation process.

Mordenite membranes also possess a resistance to strong acid and alkali environment, and are applied for water separation from acid solution [21,22]. Compared to the hydrophilic silicalite, the hydrophilic property of mordenite is strong because the mordenite have ion exchange sites in its framework, which lead to high flux of water. Though the water flux is not sufficient in the hydrophilic silicalite-1 nanocrystal-layered membrane, this membrane has two advantages as follows; one is the absence of Al in the zeolite structure, leading to the strong resistance to acid solution, and the other is the inhibition of the

mismatch regarding the expansion coefficients of the zeolite layer and alumina filter because of the thick nanocrystal layer. These advantages are expected to improve life time of the membrane.

#### 4. Conclusions

5

Hydrophilic silicalite-1 nanocrystal-layered membrane was successfully prepared. Mono-dispersed silicalite-1 nanocrystal with different crystal sizes of 60 nm, 100 nm, and 150 nm was used to prepare the layered membrane. From the SEM observation, the nanocrystal and protection layers were clearly observed, and the silicalite protection layer was uniformly formed on the nanocrystal-layer. To remove the template, a liquid-phase oxidation was carried out using hydrogen peroxide at reflux conditions. Silanol groups existed on the zeolite surface, and the water-silanol networks were formed on the non-zeolitic pores surface among the nanocrystals, which were the main channels for water permeation. As the size of the nanocrystals decreased, the water flux as well as the separation factor improved. The increase in the flux of the layered membrane was ascribed to the increase in the number of channels for water permeation through the membrane. Moreover, no acetone permeation was observed in the acetone concentration range from 10 wt% to 97 wt%. From the dependency of the permeance of water through the membrane, a new separation process consisting of distillation and pervaporation was suitable to obtain high-purity of acetone from acetone-water solution.

20

## References

- [1] R. W. Baker, Membrane Technology and Applications, Chapter 9 Pervaporation, McGraw-Hill.
- [2] F. Mizukami, Study in Surface Science and Catalysis 125 (1999) 1.
- [3] T. Sano, Y. Kiyozumi, M. Kawamura, F. Mizukami, H. Takaya, T. Mouri, W. Inaoka, Y. Toida, M.  
5 Watanebe, K. Toyoda, Zeolites 11 (1991) 842.
- [4] T. Sano, S. Ejiri, K. Yamada, Y. Kawakami, H. Yanagishita, Journal of Membrane Science 123  
(1997) 225.
- [5] T. C. Bowen, R. D. Noble, J. L. Falconer, Journal of Membrane Science 245 (2004) 1.
- [6] T. Masusda, H. Hara, M. Kouno, H. Kinoshita, K. Hashimoto, Microporous Materials 3 (1995) 565.
- 10 [7] H. Kita, K. Horii, Y. Ohtoshi, K. Tanaka, K. Okamoto, Journal of Materials Science Letters 14 (1995)  
206.
- [8] M. Kondo, M. Komori, H. Kita, K. Okamoto, Journal of Membrane Science 133 (1997) 133.
- [9] M. Noack, P. Kolsch, J. Caro, M. Schneider, P. Toussaint, I. Sieber, Microporous Materials 35 (2000)  
253.
- 15 [10] X. Lin, E. Kikuchi, M Matsukata, Chemical Communication 11 (2000) 957.
- [11] Y. Hasegawa, K. Watanabe, K. Kusakabe, S. Morooka, Journal of Membrane Science 208 (2002)  
415.
- [12] T. Masuda, S. Otani, T. Tsuji, M. Kitamura, S. R. Mukai, Separation and Purification Technology 32  
(2003) 181.
- 20 [13] T. Tago Y. Nakasaka, A. Kayoda, T. Masuda, Separation and Purificatio Technology, in press

- [14] T. Tago, M. Nishi, Y. Kouno, T. Masuda, *Chemistry Letters* 33 (2004) 1040.
- [15] T. Tago, K. Iwakai, M. Nishi, T. Masuda, *Studies in Surface Science and Catalysis* 159 (2006) 185.
- [16] S. Heng, P. P. S. Lau, K. L. Yeung, M. Djafer, J. C. Schrotter, *Journal of Membrane Science* 243 (2004) 69.
- 5 [17] M. Pera-Titus, J. Llorens, F. Gunill, R. Mallada, J. Santamaria, *Catalysis Today* 104 (2005) 281.
- [18] Y. Hasegawa, T. Ikeda, T. Nagase, Y. Kiyozumi, T. Hanaoka, F. Mizukami, *Journal of Membrane Science*, 280 (2006) 397.
- [19] T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo, T. Tatsumi, *Journal of the American Chemical Society*, 128 (2006) 13664.
- 10 [20] Y. Hasegawa, T. Nagase, Y. Kiyozumi, F. Mizukami, *Journal of membrane Science*, 294 (2007) 186.
- [21] G. Li, E. Kikuchi, M. Matsukata, *Separation and Purification Technology*, 32 (2003) 199.
- [22] L. Casado, R. Mallada, C. Tellez, J. Cornas, M. Menendez, J. Santamaria, *Journal of Membrane Science*, 216 (2003) 135.

Figure 1. Schematic of the stainless-steel autoclave vessel used for pervaporation experiments.

Figure 2. SEM photographs of silicalite-1 nanocrystals with different crystal size.

5 Figure 3. Cross-sectional SEM images (3(a) and 3(b)) and top view (3(c)) of the nanocrystal layered membrane. Hydrothermal temperatures to form the silicalite-1 protection layer were (a) 100 degrees C and (b and c) 140 degrees C.

Figure 4. Effects of the thickness of the nanocrystal layer on the water flux through the layered membrane.

10 The size of the nanocrystal, the hydrothermal temperature, and the acetone concentration were 60 nm, 140 degrees C, and 90 wt%, respectively.

Figure 5. Effect of the nanocrystal size on the water flux through the layered membrane. *D* represents the sizes of the nanocrystals used for preparation of the membrane.

15

Figure 6. Effect of the acetone concentration in the feed solution on the permeance and acetone concentrations on the permeate side.

Table 1 Effect of the hydrothermal temperatures on the formation of the silicalite-1 protection layer and

20 the separation properties.

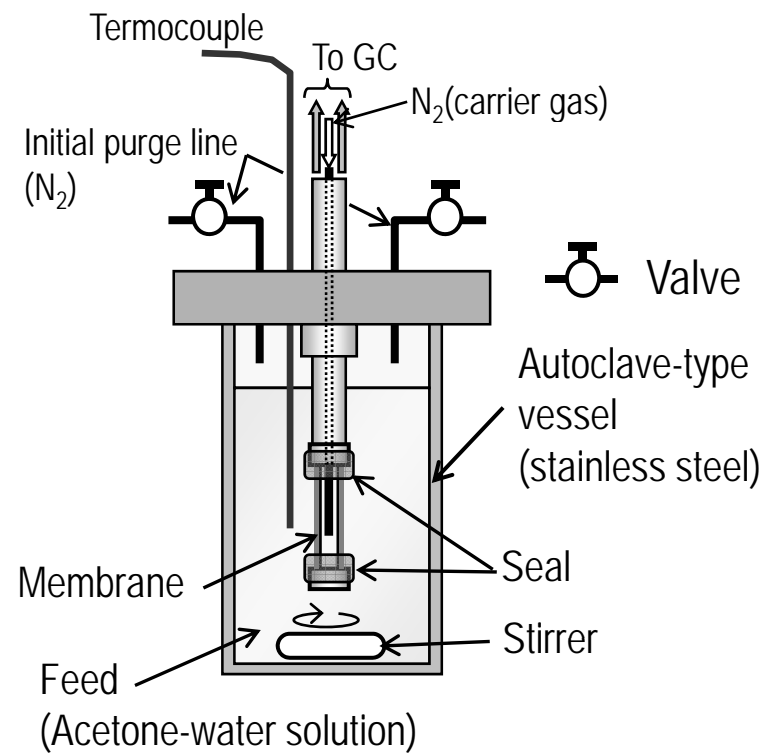


Fig. 1

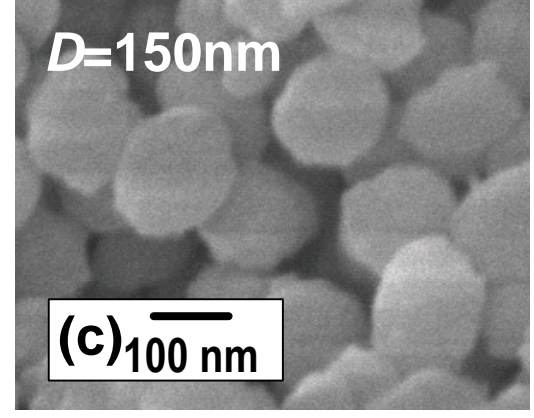
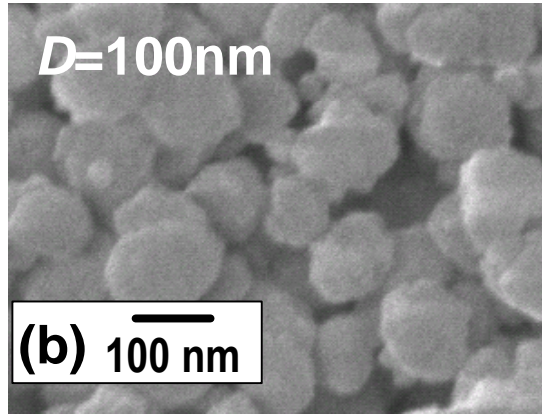
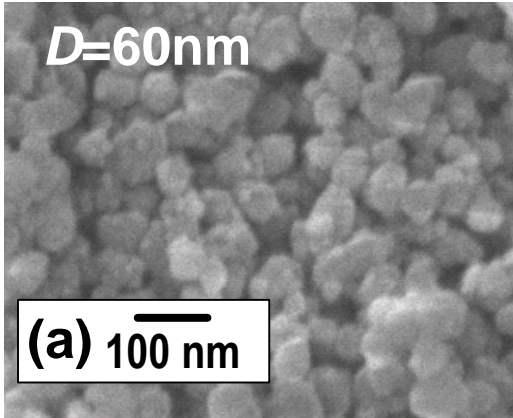


Fig. 2

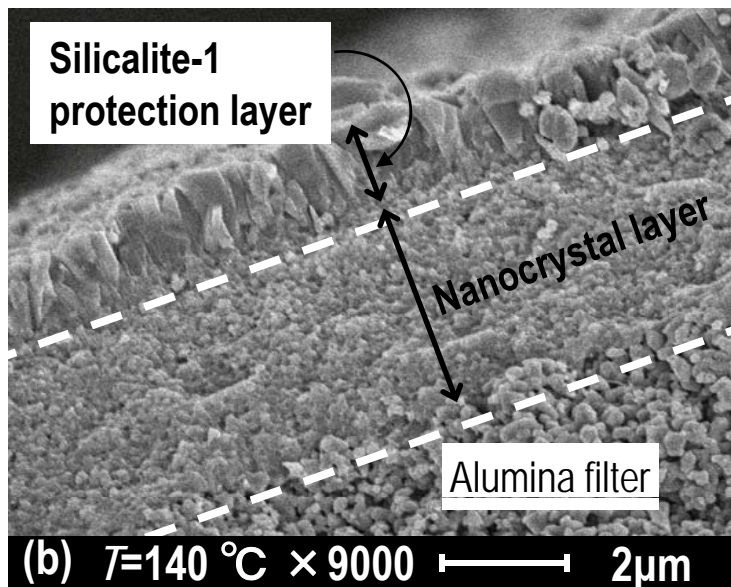
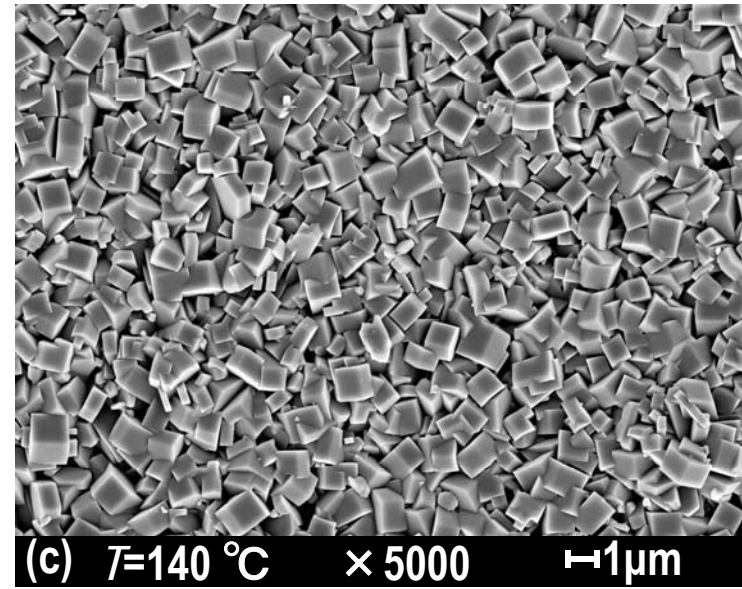
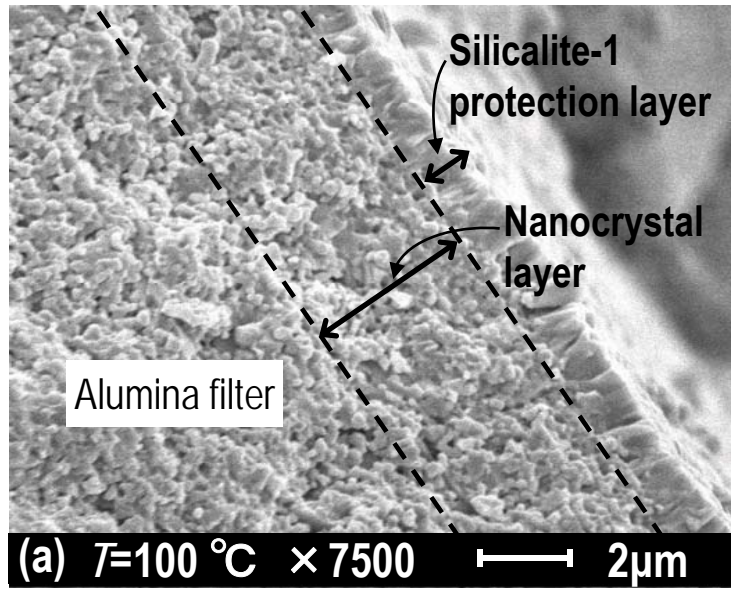


Fig. 3



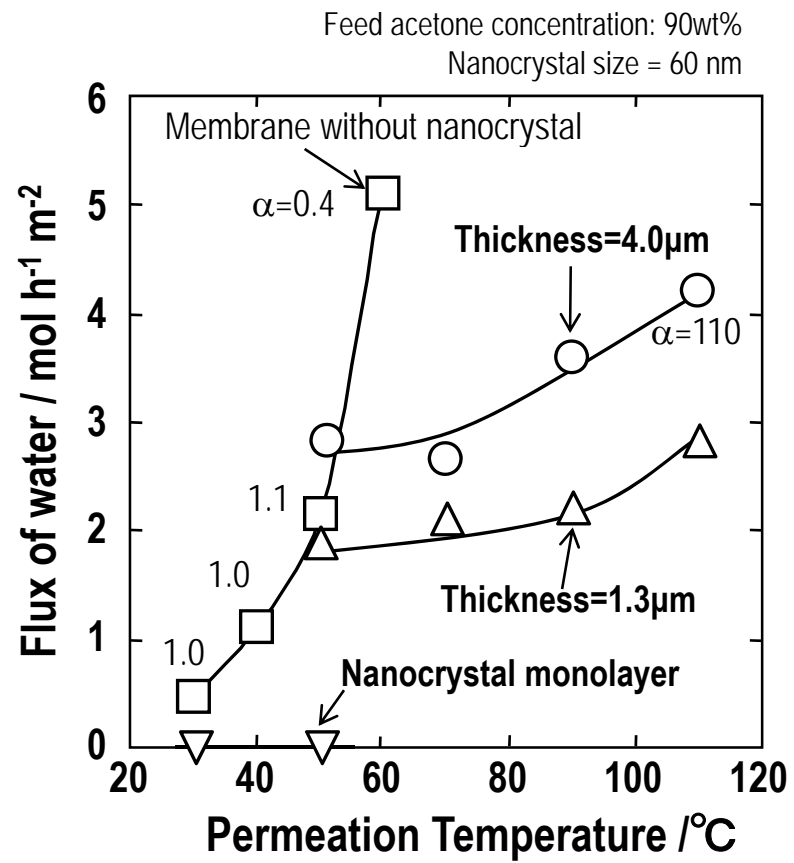


Fig. 4

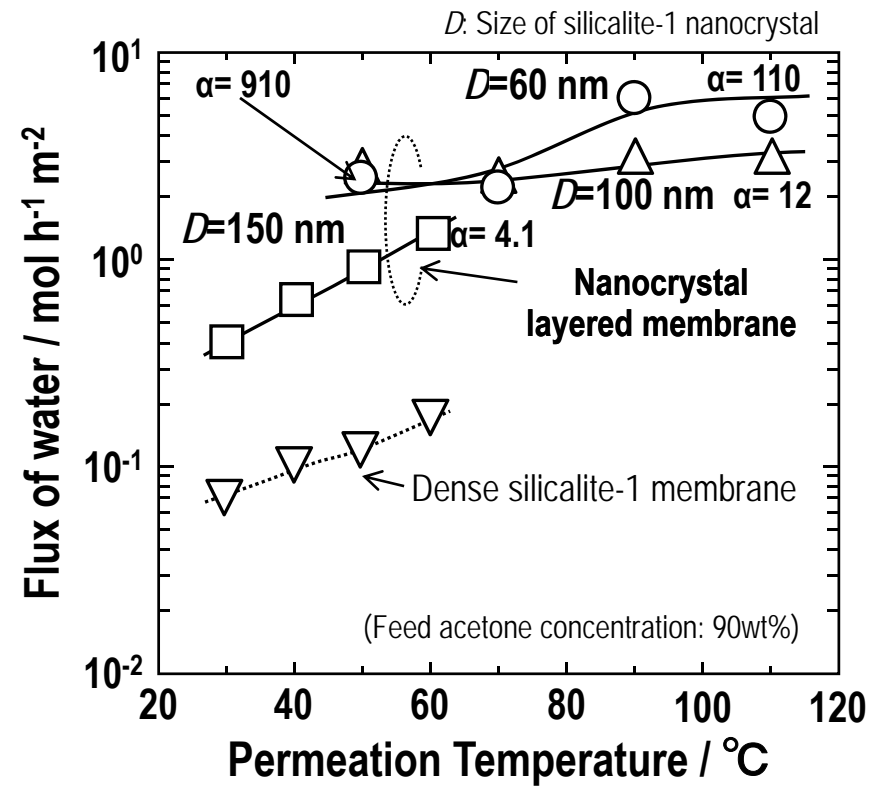


Fig. 5

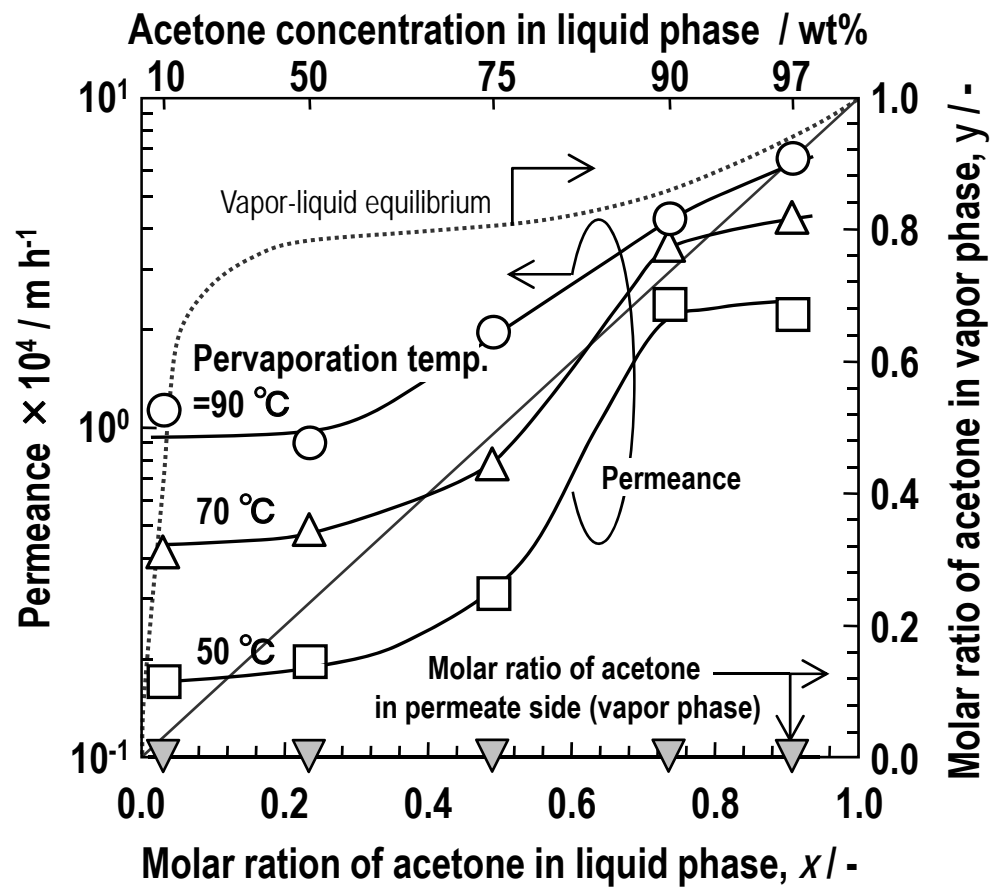


Fig. 6

Table 1

Hydrothermal temp. / degrees C	Thickness of silicalite-1 protection layer / $\mu\text{m}$	Flux of water / $\text{mol h}^{-1} \text{m}^{-2}$	Separation factor / -
<b>100</b>	<b>1.2</b>	<b>1.8</b>	<b>6.5</b>
<b>120</b>	<b>1.2</b>	<b>4.1</b>	<b>4.2</b>
<b>140</b>	<b>1.4</b>	<b>6.0</b>	<b>110</b>

Nanocrystal size :60 nm, Feed acetone concentration: 90 wt%, Pervaporation temp.:90 degrees C