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Separation of Dichlorinated Hydrocarbons by Pervaporation Using ZSM-5 Zeolite Membrane

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Abstract: Pervaporation with a membrane is one of the economic technologies for separation of liquid mixtures including organic/water mixtures. The ZSM-5 membrane was used for pervaporation of dichloromethane, 1,2-dichloroethane and trans-1,2-dichloroethylene from their aqueous solutions since its physical property shows very hydrophobic. ZSM-5 crystals were hydrothermally grown and deposited on the inside of a porous sintered stainless steel tube by the secondary growth method. Fluxes of dichlorinated organic compounds were observed to be 50~429 g/m^2/h while separation factors were 15~320 depending on a mole fraction of a dichlorinated organic compound in a feed solution ranged from 0.0001 to 0.001 mole fraction and the operation temperature between 25°C and 35°C.

Keywords: *organic/water separation, dichlorinated compounds, pervaporation, zsm-5, zeolite membrane*

1. Introduction

Because of their unique pore structure, mechanical, chemical and biological stabilities, zeolite membranes have been widely studied on various applications: gas permeation, vapor permeation, pervaporation, etc[1-3]. Pervaporation is not only an economic separation technology since it needs electric powers to maintain the permeate side in vacuum but also an environmentally clean technology in which potential pollution sources such as entrainers for azeotropic distillation are not needed[4,5]. A hydrophobic membrane could be used to separate organic compounds from their aqueous solution. Separation of organic compounds from aqueous solutions is very important in a point of view from either prevention of water pollution or recycle of valuable materials. Even if hydrophobic polymer membranes might show a high selectivity, their operation conditions such as a concentration and a temperature may limit their application. Also thermal, chemical and mechanical stabilities of polymer membrane are not good enough for a certain usage. On the other hand, a zeolite membrane might be used for organic separation with pervaporation technique since it shows not only molecular sieve effects but also good physicochemical stabilities[6].

Chlorinated organic compounds are useful materials which have been used for various application purposes such as solvents, coating agents, extractants, cleaning agents, dry cleaning and so on[7]. Chlorinated organic compounds are strongly regulated on discharges so that air and water pollutions could be prevented.

Organics might be separated economically from their aqueous solution by pervaporation using a ZSM-5 membrane. Li *et al.*[8] reported ZSM-5 seeds could grow under the identical secondary growth conditions, suggesting that the phase of the secondary grown zeolite membrane can be controlled by the seed. Preparation of crack-free ZSM-5 membranes has been achieved on the surface of an asymmetric α-Al_2O_3 support under the proper condition. The water content

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in the secondary growth mixture strongly influences the growth rate of zeolite crystals. ZSM-5 seeds grow at a slow rate in a concentrated mixture and the grown crystals with a shape of thin hexagonal plate are stacked on the support surface with a poor intergrowth, while ZSM-5 crystals via the secondary growth in a diluted mixture are a shape of rectangular parallelepiped and are in a highly intergrowth to a continuous zeolite layer on the support surface. In either case, the crystals in the secondary grown were observed to be in a random orientation.

Noack *et al.*[9] prepared a ZSM-5 membrane on the Al_2O_3 support in a wide range of Si/Al-ratio with or without template. The TPA template concentration in a synthesis gel strongly influences the Al content in the MFI-layer. While a low template concentration results in a high Al-content, but a high template concentration results in a low Al-content in the MFI- crystals. This observation seems to be important since in many cases only the Si/Al-ratio of the synthesis mixture is known. MFI-membranes with a high Al-content show a high permeance and a low selectivity due to the high degree of intercrystalline defect. For water/i-propanol mixtures, the maximum of the permselectivity was found at Si/Al = 119.

Mabande *et al.*[10] studied the growth of Al-ZSM-5 and silicalite-1 membranes on a relatively rough porous stainless steel support (d_p~270 nm). Much higher H_2/SF_6 ideal permselectivities were achieved for Al-ZSM-5 membranes compared to silicalite-1 membranes synthesized under a similar condition. A high H_2/SF_6 ideal permselectivity of 356 was achieved for a 10 μm thick Al-ZSM-5 membrane which was crystallized for 48 h at 458 K.

Tuan *et al.*[11] separated organics from water by pervaporation with isomorphously-substituted MFI zeolite membranes. Substituted ZSM-5 membranes showed a higher methanol/water separation factor than silicalite-1. The B-ZSM-5 membrane had a methanol/water separation factor of 101. The separation factors and fluxes in prevaporation through substituted ZSM-5 membranes (except Ge-ZSM-5) were in the order: methanol 〉 ethanol 〉 1-proranol 〉 2-propanol. A B-ZSM-5membrane was selective for separation of acetone and MEK from water. Separation factors at 333 K for 5% feeds were ranged from 380 to 440.

2. Experimental

2.1. Preparation and Analysis of Membrane

ZSM-5 zeolite membranes were synthesized from liquid mixtures in which the chemical compositions were 1 TPABr : 50 SiO_2 : 3 NaOH : 987 H_2O. Ludox As 40 (Dupont, U.S.A.) was used as a source material for Si; sodium hydroxide (Daejung, Korea) was used as a source chemical for Na; tetrapropylammonium bromide (Aldrich, U.S.A.) was used as a template. After preparing a Si solution and a template solution, the template solution was added to the Si solution. The synthesized ZSM-5 zeolite powder was used as a seed crystal; they were rubbed on the inside surface of a support tube (sintered stainless steel tube, Mott. Co., O.D. 9.5 mm, I.D. 6.4 mm, mean pore size 0.5 μm) using a sponge brush. ZSM-5 zeolite membranes were synthesized under the reaction temperature of 150~180°C and the reaction time of 8~16 hours. After 2~3 times of synthesis, washing and drying, ZSM-5 membranes were calcined at upto 480°C.

The crystal structure of the zeolite membrane was confirmed with a XRD (D/Max-2200 Ultima/PC, Rigaku Co., Japan, 30 kV, 15 mA) and the morphology was analyzed with a SEM (JSM-6300, Jeol Ltd., Japan).

2.2. Pervaporation

The pervaporation experiments were carried out using a pervaporation apparatus designed and set up as schematically shown in Figure 1. The membrane was installed in a membrane test cell. The aqueous feed solutions were fed and circulated with a diaphragm pump (DMA-05, Daekyung, Korea). The feed concentration was regulated upto the solubility of dichlorinated organic compounds in water. The permeate was

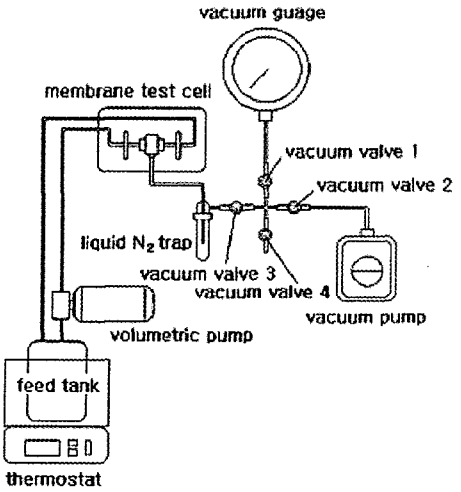


Fig. 1. A schematic diagram of pervaporation apparatus.

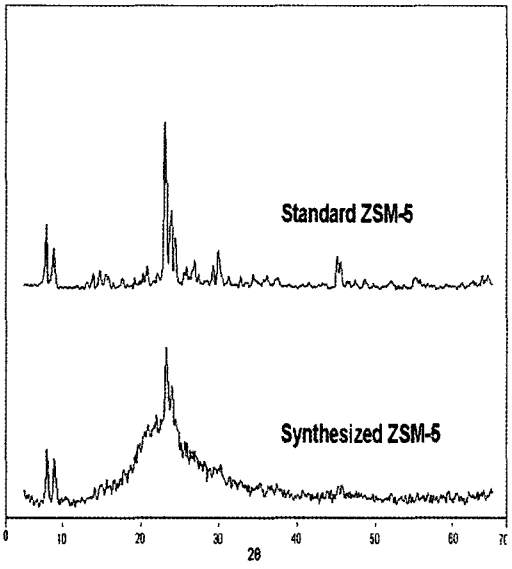
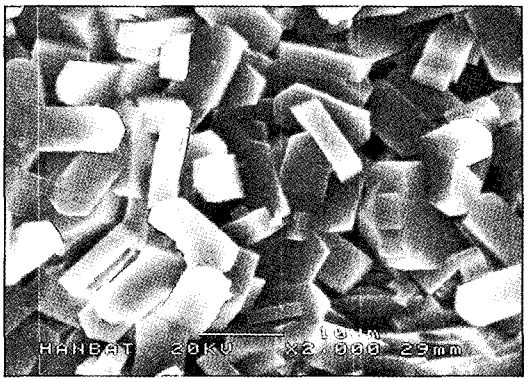
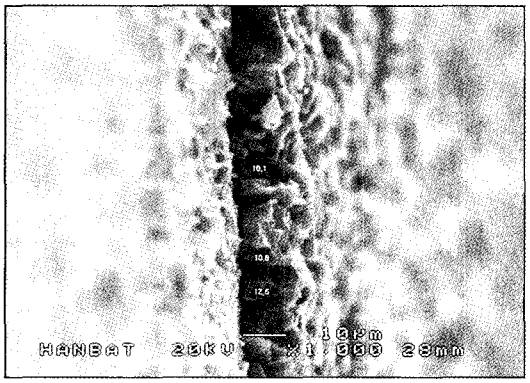


Fig. 2. XRD pattern of ZSM-5 zeolite membrane.

collected in a liquid N_2 trap in which the pressure was controlled to be about 5 mmHg. The experiment was performed at the temperature ranged from 25°C to the boiling point of a dichlorinated organic compound. Both the feed and the permeate concentrations were analyzed with a gas chromatograph (M600D, Younglin Co., Korea) where Porapak Q (Supelco, U.S.A.) column was equipped. A FID (flame ionization detector) was used to determine the concentration of organic compounds.



(a) a top view



(b) a cross-sectional view

Fig. 3. SEM images of the ZSM-5 membrane.

3. Results and Discussion

3.1. Membrane Characterization

Figure 2 shows XRD patterns of the synthesized ZSM-5 and the standard ZSM-5 which was confirmed by the reference[12].

The synthesized ZSM-5 was confirmed as a MFI structure since the XRD pattern was the same as that of the standard ZSM-5 zeolite.

SEM images of the synthesized ZSM-5 membrane were shown in Figure 3. As shown in Figure 3, the synthesized ZSM-5 zeolite crystals were randomly grown to the size of about 10 μm and the thickness of the zeolite layer was found to be about 10 μm.

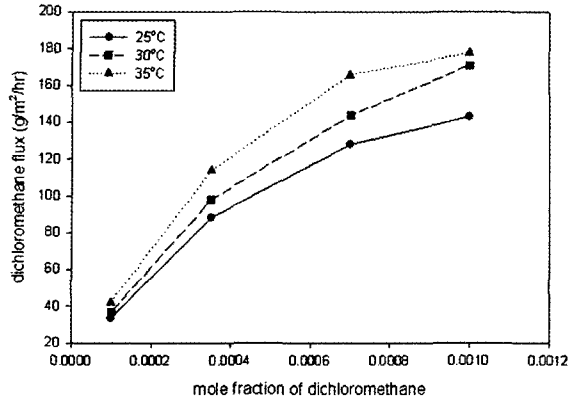


Fig. 4. Dichloromethane fluxes through ZSM-5 membranes.

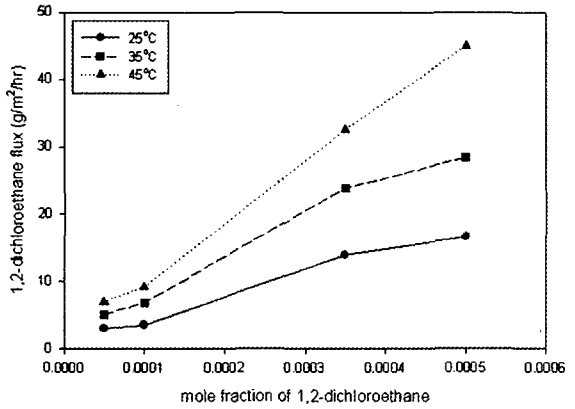


Fig. 5. 1,2-dichloroethane fluxes through ZSM-5 membranes.

3.2. Pervaporation Characteristics

Pervaporation characteristics might be presented in terms of a flux and a separation factor defined as follows:

$$Flux = \frac{P}{A \cdot t}, \quad Separtionfactor = \frac{y_{DCOr} / y_{H_2O}}{x_{DCOr} / x_{H_2O}}$$

where P represents a weight of permeate (g), A denotes a membrane area (m^2) and t is a permeation time (hr). y_{DCOr} and y_{H_2O} refer to mole fractions of dichlorinated organic compounds and water at the permeate side, respectively. x_{DCOr} and x_{H_2O} represent mole fractions of water and ethanol at the feed side, respectively.

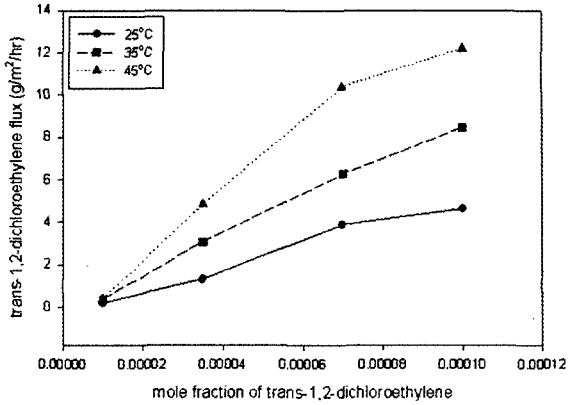


Fig. 6. Trans-1,2-dichloroethylene fluxes through ZSM-5 membranes.

3.2.1. Organic Flux

Fluxes of dichlorinated organic compounds through the ZSM-5 membrane are shown in Figure 4~6. The flux of a dichlorinated organic compound increases as either their mole fraction increases or the temperature increases. This may be due to the increment of the partial vapor pressure of dichlorinated organic compounds, which is the driving force of pervaporation. The increment of either the concentration or the temperature results in the increment of a partial vapor pressure since the partial vapor pressure is a function of the concentration and the temperature. In Figure 4, the dichloromethane flux increased from 32 to 180 g/m^2/h with the feed concentration of 10^{-4}~10^{-3} mole fraction of dichloromethane and the temperature of 25~35°C. In Figure 5, the 1,2-dichloroethane flux increased from 3 to 46 g/m^2/h for the feed concentration of 5×10^{-5} ~5×10^{-4} mole fraction of 1,2-dichloroethane and the temperature of 25~45°C. In Figure 6, the trans-1,2-dichloroethylene fluxes increased from 0.2 to 13 g/m^2/h with a operating condition of the feed concentration of 10^{-5}~10^{-4} mole fraction of trans-1,2-dichloroethylene and the temperature of 25~45°C.

3.2.2. Separation Factor

In Figure 7~9, the separation factors of dichlorinated organic compounds were plotted as a function of the feed mole fraction of dichlorinated organic compounds.

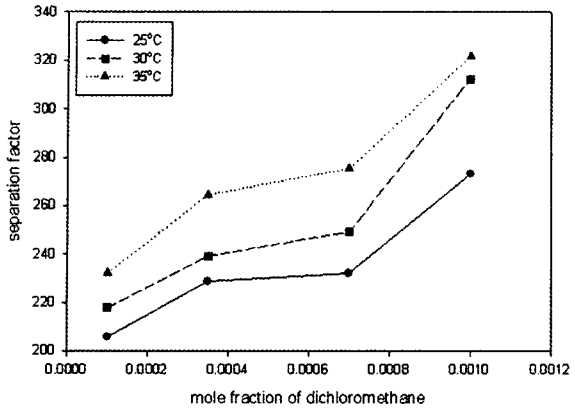


Fig. 7. Separation factor of dichloromethane through ZSM-5 membranes.

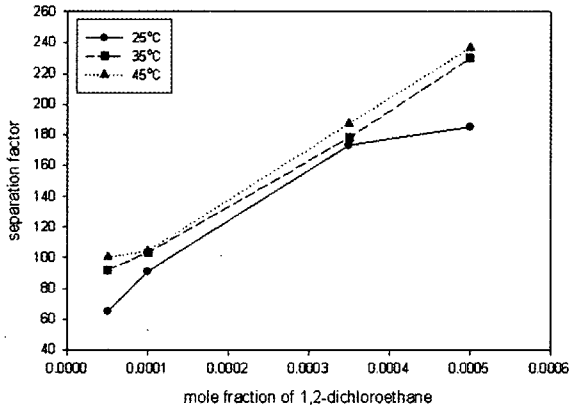


Fig. 8. Separation factor of 1,2-dichloroethane through ZSM-5 membranes.

The separation factor for the ZSM-5 membrane with respect to dichlorinated organic compounds increased as both a mole fraction of dichlorinated organic compounds and a temperature increased. As seen in the definition of the separation factor, while the numerator increased according to the increment of dichlorinated organic compounds fluxes as shown in Figure 4~6, the denominator decreased as the increment of the feed mole fraction, resulting in an increase of the separation factor. The separation factor of dichloromethane increased from 205 to 320 with the feed concentration of 10^{-4}~10^{-3} mole fraction of dichloromethane and the temperature of 25~35°C. Separation factor of 1,2-dichloroethane increased from 64 to 236 for the feed concentration of 5×10^{-5}~5×10^{-4} mole fraction

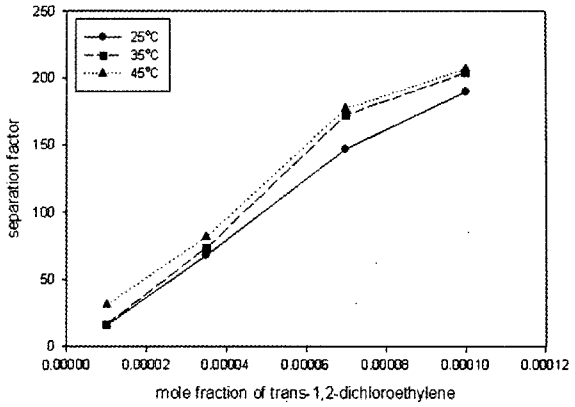


Fig. 9. Separation factor of trans-1,2-dichloroethylene through ZSM-5 membranes.

of 1,2-dichloroethane and the temperature of 25~45°C. The separation factor of trans-1,2-dichloroethylene increased from 15 to 206 with the feed concentration of 10^{-5}~10^{-4} mole fraction of trans-1,2-dichloroethylene and the temperature of 25~45°C.

3.2.3. Comparison of Separation Behavior of Dichlorinated Organic Compounds

The organic flux at the same mole fraction of 10^{-4} in the feed solution are shown in Figure 10 to compare the pervaporation behavior among dichlorinated organic compounds as a function of the temperature. While dichloromethane showed the highest flux, 1,2-dichloroethane showed the lowest flux. This may be due to the partial vapor pressure difference of each compound due to the difference of their boiling points. Dichloromethane might be easily adsorbed and penetrated since not only it has the lowest boiling point of 39.8°C which results in relatively high partial vapor pressure among dichlorinated organic compounds but also its kinetic diameter of 4.898 Å[13] is small enough for its molecules to pass the pore of ZSM-5 zeolite which is known to be 5.1 Å~5.6 Å.

Even though trans-1,2-dichlorethylene and 1,2-dichloroethane might have a similar kinetic diameter, 1,2-dichlorothane flux is smaller than that of trans-1,2-dichlorothylene since its boiling point of 83.7°C is higher than that of trans-1,2-dichloroethylene (i.e. 48°C),

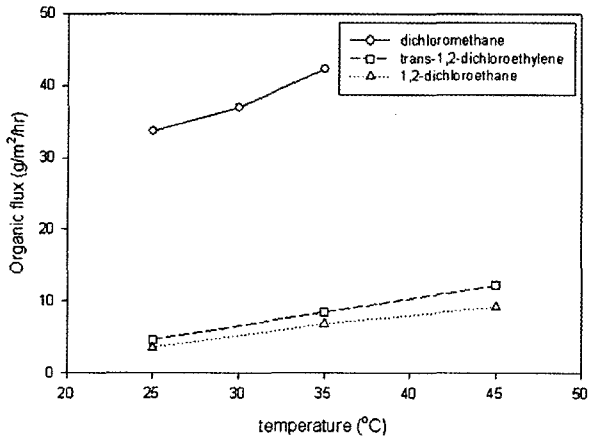


Fig. 10. Dichlorinated Organic compounds fluxes at a same feed mole fraction.

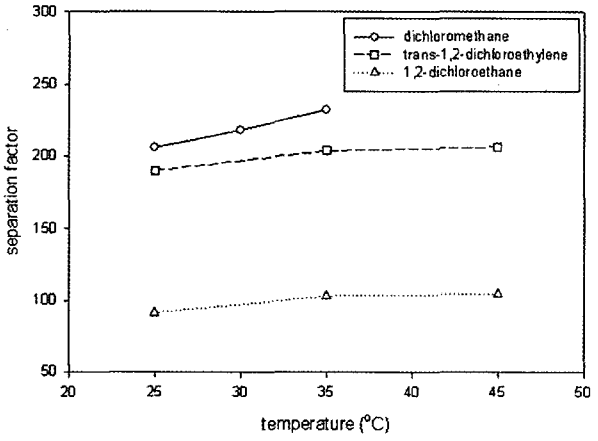


Fig. 11. Separation factor of dichlorinated Organic compounds at the same feed mole fraction.

resulting in a lower partial vapor pressure at the same temperature.

Separation factors of dichlorinated organic compounds at the same mole fraction in the feed of 10^{-4} are plotted in Figure 11. The separation factor of dichloromethane shows the highest and 1,2-dichloroethane shows the lowest. The separation factor difference among dichlorinated organic compounds might be explained by the difference of the permeation flux according to Figure 10. The separation factor increased as the temperature increased, which leads to the increment of the partial vapor pressure.

4. Conclusions

ZSM-5 membranes were successfully synthesized on the inside of a porous sintered stainless steel tube by the secondary growth method; they showed a high flux and a excellent separation factor for dichloromethane/water, 1,2-dichloroethane/water and trans-1,2-dichloroethylene/water mixtures. The flux and the separation factor through ZSM-5 zeolite membranes were strongly affected by both the feed concentration and the operating temperature. ZSM-5 membrane might be used as a pervaporation membrane to separate dichlorinated organic compounds from their aqueous solutions.

Acknowledgement

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