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Performance of Ceramic Composite Membrane for the Separation of VOCs

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Abstract−Zeolite composite membranes were prepared for the separation of VOCs by the pressurized coating method. On the top of the composite membrane, TiO_2, polyimide or polyethersulfone were coated by the same technique. 100 nm-sized ZSM-5 coated membranes show higher selectivity for n-hexane in n-hexane/benzene mixture than 500 nm sized ZSM-5 coated membrane. Composite membrane coated with 100 nm zeolite and polymer showed the highest selectivity (44) for n-hexane/benzene.

Key words: Zeolite, VOC, Membrane

INTRODUCTION

Many chemical industrial processes such as surface coating, petroleum refining, or paint baking produce waste air stream containing low concentrations of volatile organic compounds (VOCs), such as benzene, toluene, xylene. VOCs are directly hazardous to human health and can damage plants and building material. In past years several procedures for dealing with VOCs, such as carbon adsorption, incineration, etc., were introduced in the industry [Huang et al., 1997]. The membrane process has recently emerged as an attractive alternative to the conventional methods. Polymeric materials are typically employed in membrane separation processes. However, these materials suffer from some limitations including thermal and chemical stability. In this sense, a polymer-based system mostly has been used below 100 °C, needing a precooling system before the membrane in the process operating at high temperature [Kim et al., 2001].

Ceramic membranes have many properties, which makes them especially appealing for use in gas phase separations [So et al., 1999]. Of particular interest is their stability under a wide range of conditions, e.g., exposure to high and extremely low temperatures and contact with organic solvents. Their stability makes these membranes appropriate for VOCs emission control systems at high temperature. Zeolite, which has an inorganic crystalline structure with pores of the same size as small molecules, can be used at high temperatures and is resistant to chemical degradation. When zeolite is prepared as continuous membrane films, they provide an opportunity to greatly expand the use of membrane technology. Several recent publications report the high separation performances of cyclic, branched, and linear hydrocarbon mixtures through zeolite membranes [Funke et al., 1997; Coronas et al., 1998]. Because of their separation properties, zeolite membranes have received much attention for gas separation in the petrochemical industry. For industrial applications, zeolite membrane must possess good selectivity and high permeability. Although very good separation factors have been obtained in the past, it has proved difficult to achieve a high permeance due to the thick zeolite layers [Xu et al., 2000].

Zeolite membranes are commonly prepared by liquid-phase hydrothermal synthesis, in which the porous support is immersed into the zeolite precursor gel. According to Graff et al., the synthesis procedure of zeolite film is difficult to control. About 80% of all attempts to synthesize a membrane fail. This lack of reproducibility is a general problem [Graaf et al., 1998].

As a new process, the pressurized coating method [Hyun et al., 1993] was introduced to form the separation layer into the support. By this process, inorganic particles and organic materials could be packed into the pore of support. It also gives crack-free and reproducible nanocomposite membranes. Because of these advantages, the pressurized coating method could be useful for the fabrication of the zeolite membrane.

In this study, nano zeolite particles with different sizes were prepared for the preparation of zeolite composite membranes [Jung et al., 1997]. These nano zeolite particles were packed into the support by using the pressurized coating method [Kim et al., 1998]. And then, polyimide, polyethersulfone, and TiO_2 were coated on the top layer of this composite membrane to fill the intraparticle gap among zeolite particles. N-hexane/Benzene permeation test was carried out to characterize the performance of the zeolite composite membranes.

EXPERIMENTAL

1. Materials

The zeolites used in this work were ZSM-5, nano TS-1, and nano ZSM-5. The synthesis mixture of TS-1 was composed of tetraethylorthosilicate (TEOS, Aldrich Co.), titanium butoxide, tetrapropyl ammonium hydroxide (TPAOH, Aldrich Co.), isopropyl alcohol (IPA, Hyman Co.) and hydrogen chloride(HCl, Yakuri Co.). The molar ratio of these components was Ti : Si : H_2O : TPAOH : IPA= 0.03 : 1 : 25 : 0.32 : 0.77. The mixture solution was crystallized at 80 °C and atmospheric pressure for 100 hrs and then it was centrifuged at 15,000 rpm to obtain TS-1 solids [Jung and Shul, 1998]. In the case of nano ZSM-5, aluminum sec-butoxide was used as

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aluminum precursor instead of titanium butoxide. NaOH was added to the mixed solution with de-ionized water. The other method is the same with the synthesis of TS-1 zeolite [Jung et al., 1997]. Conventional ZSM-5 was synthesized under autogenous pressure. As sources of silica, aluminum and alkali, sodium silicate, sodium aluminum sulfate solution and sodium chloride were used, respectively. Tetrapropyl ammonium bromide was selected as a templating agent. The crystallization took place at 175 °C. After the crystallization, the layer was rinsed with water and dried in air.

The polyimide was synthesized by the polycondensation of polyamic acid. 4,4'-hexafluoroisopropylidene diphtalic anhydride (6FDA, Aldrich Co.) and 4,4'-oxydianiline (4,4'ODA, Aldrich Co.) The monomers were purified by vacuum sublimation before preparing polyamic acid used in this study. N,N'-dimethylactamide (DMAc, Aldrich) was used for solvent without further purification. The polyamic acid solution was prepared with 15% solid contents of solution in nitrogen environment [Chun et al., 1999]. The polyethersulfone was the commercial polyethersulfone of Dupont and the solvent was Dimethylformamide (Duksan, DMF). TiO_2 sol was prepared by the conventional sol-gel technique. Titanium tert-isopropoxide (TTIP, Fluka) and 2,4-pentandion (acetylacetone, Aldrich) were added to isopropyl alcohol (IPA, Hyman Co.).

2. Pressurized Coating

[Hyun et al., 1992]. Tubular support used in this work was 0.95 mm-thick α-Al_2O_3 membrane with 1 μm pore size and porosity 0.3. All membrane was prepared by repeating the pressurized coating on the α-Al_2O_3 support in order to obtain the top layer without pinholes or defects. The coating solutions were 0.05% zeolite suspension in DI water, 1% polyamic acid in DMAc, 1% polyethersolfone in DMF and TiO_2 sol. Pressurizing gas was N_2 and the pressure was about 50 psi to coat the α-Al_2O_3 membrane. The zeolite particles were first coated on the pore (1 μm) of α-Al_2O_3 substrate. And then, thin composite membrane was dried at 100 °C. TiO_2 sol or polyimide was coated on this composite membrane by pressurized coating method to fill the intraparticle gaps between zeolite particles. TiO_2 sol-coated membrane was dried at room temperature and calcined at 450 °C. Polyimide-coated membrane was dried in vacuum oven at 80 °C and imidized at 350 °C.

3. Characterization of Membranes

Membranes were observed with a scanning electron microscope (SEM, JEOL). The crystal structures of ZSM-5, nano TS-1, nano ZSM-5 and TiO_2 were determined by using x-ray diffraction (XRD, Rikaku). Infrared spectra (Genesis FT-IR spectrophotometer) of the polyamic acid and polyimide were taken to confirm the degree of imidization. Particle size and distribution of ZSM-5, nano ZSM-5, nano TS-1, and TiO_2 sol were measured by using dynamic light scattering (DLS, Brookhaven Particle Sizer, Zetaplus). BET (Fison sorptomatic 1900) was used for the pore size distribution of membrane.

4. Separation Measurement

Fig. 1 shows the separation and permeance measurement apparatus. The separation experiments were performed in a continuous flow system with N_2 carrier gas. Hexane and benzene mixture was fed with saturator as liquids, and then N_2 was fed to saturator to supply the vapor of n-hexane and benzene mixture to the separation module. The stream was analyzed with a GC equipped with FID (Simadzu 8A). The total organic feed concentration was maintained between 20 and 30 mol% for the pure and mixed feed studies.

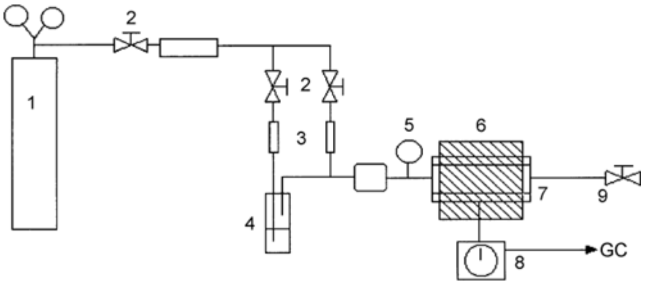

Fig. 1. Apparatus for n-hexane/benzene permeation test.

1. N_2 cylinder
2. Needle valve
3. Rotameter
4. Bubbler
5. Pressure guage
6. Heater
7. Membrane module
8. Gas flowmeter
9. Vent line

The selectivity of the membrane toward the i component in a mixture containing i and j components is determined from the retentate and permeate compositions as follows:

$$\alpha_{ij} = \frac{X_{i,p}/X_{j,p}}{X_{i,r}/X_{j,r}} \tag{1}$$

where $X_{i,p}$ and $X_{j,p}$ refer to the mole fractions of the components in the permeate and $X_{i,r}$ and $X_{j,r}$ refer to the mole fractions in the retentate.

RESULTS AND DISCUSSION

Fig. 2 illustrates the XRD patterns of ZSM-5, nano TS-1, and nano ZSM-5 particles. The XRD patterns of zeolite were compared

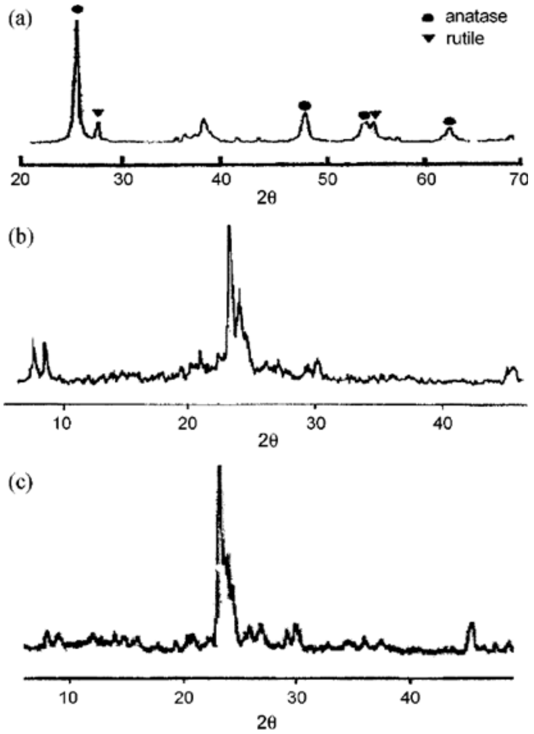

Fig. 2. XRD patterns of TiO_2, nano TS-1, nano ZSM-5.

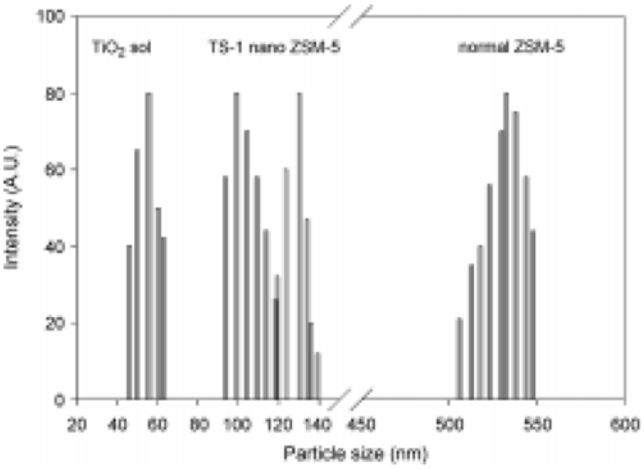

Fig. 3. Particle size distributions of TiO$_2$ sol, nano TS-1, nano ZSM-5 and ZSM-5.

with the literature [Jung et al., 1997, 1998; Treacy et al., 1996]. It shows that crystallization was successfully completed. Nano TS-1 particles were separated in 100 hours and nano ZSM-5 were in 554 hours. After separating the zeolite particles from the mother liquid, TS-1 and ZSM-5 were redispersed in de-ionized water to make zeolite sol. When particles were dispersed in the water, there was no precipitation and the sol behaved like a colloidal suspension. Fig. 3 shows the nano TS-1, nano ZSM-5, ZSM-5 and TiO$_2$ sol particle size distribution. It was found that the monodisperse distributions of particles were obtained from the reaction mixtures. The size of nano TS-1 is about 100 nm, that of nano ZSM-5 is 130 nm, that of ZSM-5 is about 500 nm, and the TiO$_2$ sol size is about 50 nm. We can expect that all inorganic particles could be packed into the 1 mm pore of Al$_2$O$_3$ support.

1. Zeolite Particle Size Effect

Fig. 4 shows N$_2$ permeances of membranes coated with 500 nm and 100 nm ZSM-5 particles. Increasing the number of the zeolite coatings resulted in a reduction in N$_2$ permeances. Zeolite particles might block the pore of alpha alumina support. The decrease of permeances indicates that the pressurized coating of zeolite particles could control the pore size of the alumina membrane. ZSM-5 coated composite membrane with 100 nm particles showed much lower permeance. The smaller particle size may be effective to reduce the pore size of support.

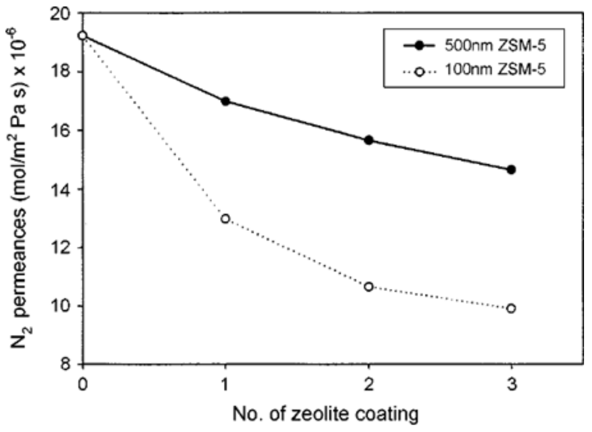

Fig. 4. N$_2$ permeances of 500 nm and 100 nm size ZSM-5 coated membrane.

The SEM images of α-Al$_2$O$_3$ and ZSM-5 coated membrane are shown in Fig. 5. Zeolite particles were coated on the surface and inside of the support. 500 nm-sized ZSM-5 coated membrane represented the sparse surface. Zeolite layer was found near the surface of Al$_2$O$_3$ substrate. Most of the particles did not penetrate into the deep pore and made the ununiform layers as shown in Fig. 5(b). On the other hand, the membrane coated with 100 nm particles showed fine surface. Nano-sized ZSM-5 particles infiltrated into the pore of support membrane. The penetration depth of nano particle was less than 5 μm.

Fig. 6 shows the results of the benzene permeances for the composite membranes coated with the 500 nm and 100 nm ZSM-5 particles. The permeance of 100 nm ZSM-5 coated membrane is lower than 500 nm ZSM-5 coated membrane. This result suggests that 100 nm particles homogeneously fill the pore of support membrane and make a denser layer than large particle as shown in SEM images.

N-hexane selectivity of ZSM-5 coated membrane for the n-hexane/benzene mixture is shown in Fig. 7. Higher selectivity for n-hexane (44-33) was obtained for composite membrane. Differences in permeance and selectivity for n-hexane depending on the size of ZSM-5 particle were obvious. 500 nm ZSM-5 might not penetrate into the support and make more nonzeolitic pores than 100 nm ZSM-5. This nonzeolitic large pore may make a significant contribution to reduce the selectivity of n-hexane.

The secondary coating materials, that is, TiO$_2$, polyimide, polyethersulfone, reduced the gas permeance further as shown in Figs. 6 and 8. Figs. 7 and 9 show that the n-hexane selectivity in composite membranes coated with ZSM-5 (130 nm) or TS-1 (100 nm) is over 35. However, the selectivity of n-hexane for the TiO$_2$ coated membrane is about 30. It means that polyimide and polyethersulfone were more effective to make a dense film by filling the nonzeolitic pores than TiO$_2$. As the size of TiO$_2$ sol is 55 nm shown in Fig. 3, it would be hard to fill the nonzeolitic pores like polymer.

In Figs. 6 and 8, increasing the membrane temperature, the permeance of benzene was also increased. It is due to an increase in the benzene permeance as reported by Funke et al.

2. Pore Size Distribution

The permeance was decreased with increasing the number of zeolite coatings in Fig. 4. It suggests the reduction of pore by pressurized coating of zeolite. Fig. 10 shows the pore size distribution of the zeolite composite membranes. The narrow pore size distributions below 2 nm in diameter were obtained after the coating of polymer and TiO$_2$. Polymer and TiO$_2$ sol might fill the pores which were formed among the zeolite particles (non zeolitic pore). The main peak appears at 1 nm. However ZSM-5/TiO$_2$ composite membrane has 1.5 nm pores in diameter. The polymer seems to be more effective to fill up the gap in zeolite particles than TiO$_2$. It suggests that the pore size of zeolite composite membrane can be controlled by repeating the pressurized coating with proper materials such as polyimide and polyethersulfone.

3. Discussion

Composite membrane coated with 100 nm ZSM-5 showed a selectivity of 40 and permeance of 1×10^{-6} mol/m^2 Pa s in n-hexane/benzene mixture. For the hydrothermally prepared zeolite membrane, Funke et al. reported that the selectivity was 200 and the per-

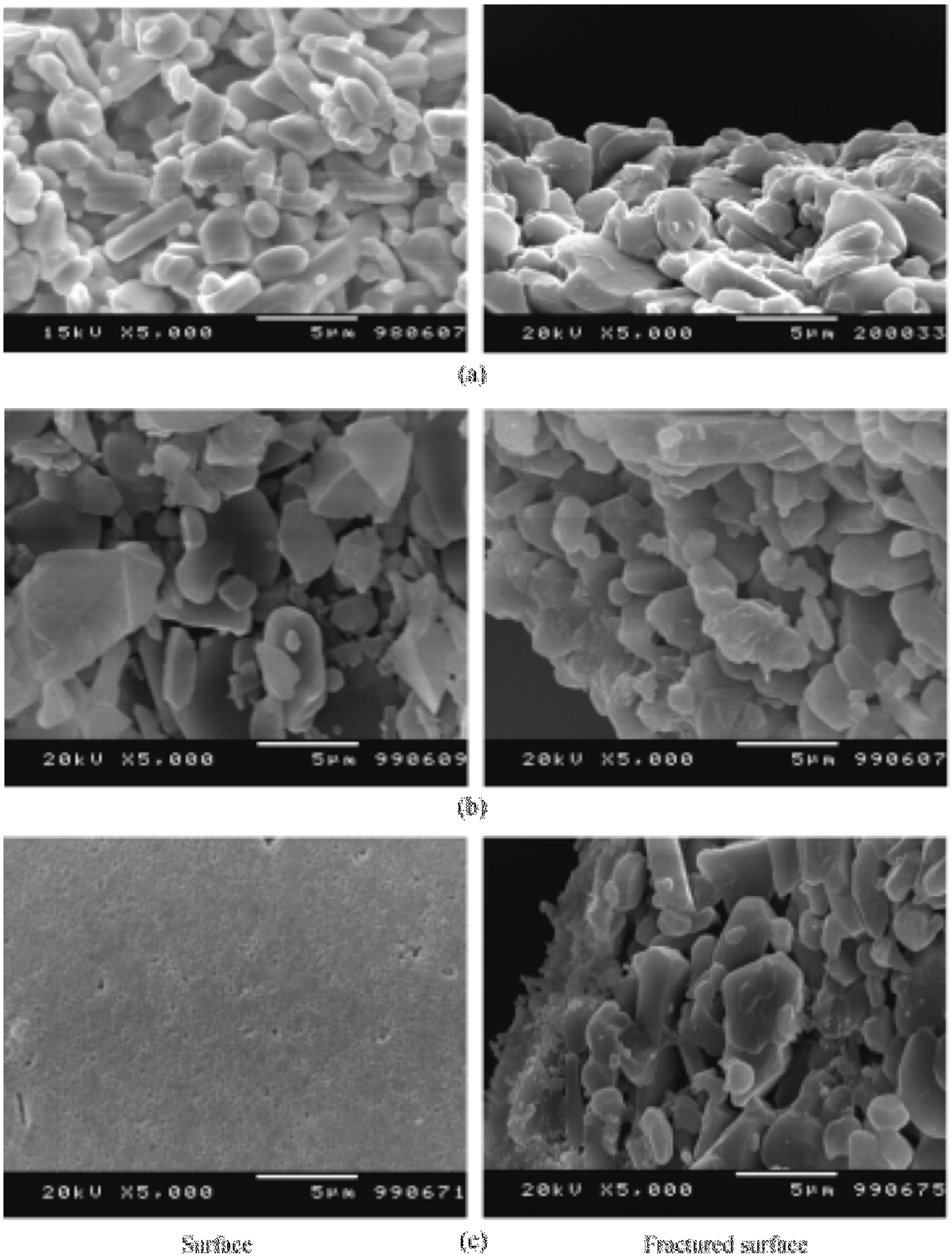

Fig. 5. Surface and fractured surface of Al_2O_3 support (a), 500 nm sized ZSM-5 coated membrane (b) and 100 nm sized ZSM-5 coated membrane (c).

meability was 1×10^{-8} mol/m^2 Pa s using the silicalite membrane [Funke et al., 1997]. Kita et al. reported that the selectivity was 29 and the flux was 0.05 kg/m^2 h using the NaY type composite membrane [Coronas et al., 1999]. The membrane prepared in this study shows higher selectivity than Kitas membrane and higher permeance than Funkes membrane.

Selectivity is generally inverse to the permeance; the composite membrane coated with zeolite particle in this study shows fairly high permeability with relatively high selectivity for n-hexane compared with the ideal selectivity, which was just below 2. This high permeance might be due to the membrane pore structure. The zeolite particles were infiltrated into the pore of support by pressurized coating method. And then, the polymer and inorganic fine particles filled up the gap between particles and non-zeolitic pores. This structure leads to both high permeability and selectivity in benzene/n-hexane separation.

CONCLUSION

TiO_2, polyimide, and polyethersulfone were used for the modification of zeolite-coated membrane. Zeolite composite membrane was successfully prepared by the pressurized coating method. The ceramic composite membrane prepared by the 100 nm size zeolite particle showed higher selectivity of n-hexane in n-hexane/benzene mixture than that by 500 nm size zeolite particle. In particular, polyimide or polyethersulfone composite membrane showed higher

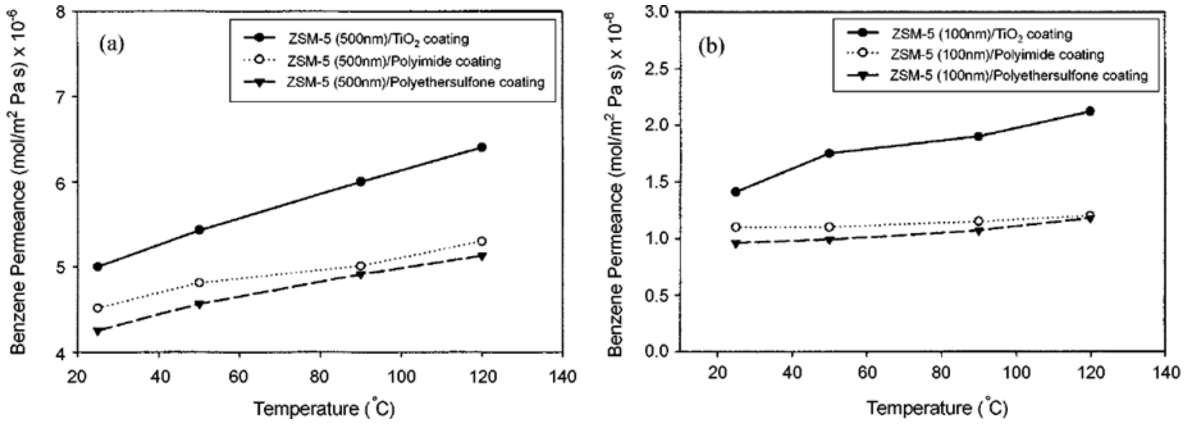

Fig. 6. Permeances of benzene for composite ceramic membrane coated with 500 nm sized ZSM-5 coated membrane (a) and 100 nm sized ZSM-5 coated membrane (b).

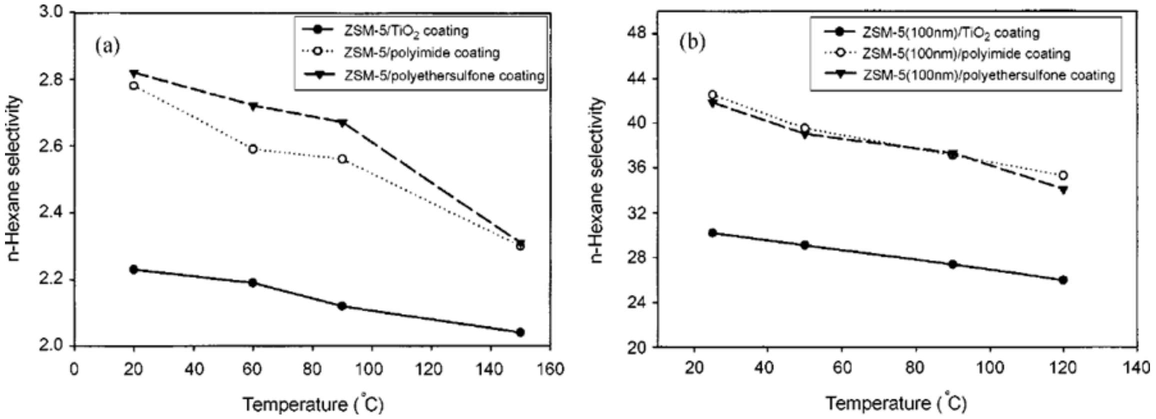

Fig. 7. n-Hexane selectivity of 500 nm sized ZSM-5 coated membrane (a) and 100 nm sized ZSM-5 coated membrane (b) in n-Hexane/ Benzene mixture.

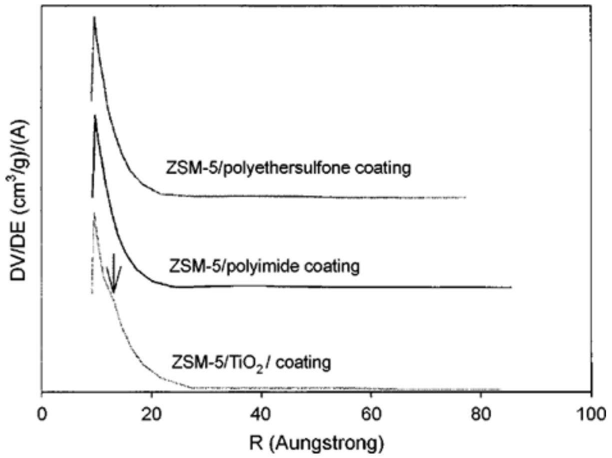

Fig. 8. Pore size distribution of ZSM-5 coated membranes.

selectivity than did TiO_2 coated membrane. The highest selectivity of n-hexane was 45 with 1×10^{-6} mol/m^2 Pa s permeance. This study showed the simple preparation procedures to make reliable ceramic composite membrane.

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