

# Separative capability of $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified by ZIF-8

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**Abstract**—Several precursors such as zinc nitrite, zinc chloride, zinc acetate and zinc sulfate were used to synthesize ZIF-8. These zeolitic imidazolate frameworks synthesized from different zinc precursors under different reaction conditions were characterized by XRD, SEM and FTIR. The synthesis of ZIF-8 was not sensitive to zinc precursor and reaction parameter. Subsequently, we used ZIF-8 to modify the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane, expecting improvement of separation performance in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane. The experimental results indicated that the permselectivity of hydrogen/nitrogen was enhanced in the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8, although the gas permeance through the modified membrane slightly decreased. In addition, the modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane was used to separate the binary systems containing ethanol-water and acrylic acid-water. The separation factor of ethanol to water is 3.1, while it is 2.6 as for acrylic acid-water. Furthermore, the permeance in the former is about five times than that of the latter.

**Key words:** Zeolitic Imidazolate Frameworks,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Porous Inorganic Membrane, Modification, Separation Efficiency

## INTRODUCTION

Porous ceramic membrane has some unique advantages, such as technical resistance, chemical inactivity, non-swelling, thermal stability, and easy cleaning [1-3]. Compared with dense membrane, porous ceramic membrane has also a high permeance. Thus, ceramic membrane is widely used in the separation process and as membrane reactor at high temperature. However, unmodified membrane has a low separation factor, and this has limited its application in some areas. To enhance the separation efficiency, work on modifying porous ceramic membrane should be developed.

Zeolitic imidazolate frameworks, a subfamily of metal-organic frameworks, have received much attention because of their exceptional thermal and chemical stability [4-16]. As one of the most important members in this family, ZIF-8 (with the formula zinc(2-methylimidazolate)<sub>2</sub>) represents an appropriate model system and has found wide applications [17,18], such as selective adsorption, separation hybrid membrane and catalysis.

Separation for alcohol/water is viewed as one of the most important in the biochemical process. For example, ethanol is produced by fermentation of amyllum using enzyme in aqueous solution. Using an economical separation, a large amount of water is separated from the reaction system, which has been increasingly focused on by many researchers in recent years. Acrylic acid and its esters have found a wide application; its production methods include the oxidation of propylene, hydrocarboxylation of acetylene, dehydration of lactic acid, etc. [19-28]. As for a renewable method, dehydration of lactic acid has a potential application in an era facing a shortage of petroleum. To obtain high concentration of acrylic acid, a large quantity of water has to be separated from the reaction system. Although polymeric membrane has displayed an excellent separa-

tion performance for liquid mixture at relative low temperature, the permeance is lower and its separation efficiency decreases with increase of time at relatively high temperature. Thus, it is very important for us to find an efficient way with a low cost for separation of water.

The aim of this work is to use ZIF-8 to modify the surface of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane with a high permeance and enhance the separation efficiency. Ethanol-water and acrylic acid-water were chosen as separation systems because their separation consumes a large amount of energy using traditional separation of distillation. In this work, we reported that the modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane was used to separate ethanol, acrylic acid from water system using pervaporation separation.

## EXPERIMENTAL

### 1. Materials

Zinc nitrate, zinc chloride, zinc acetate, zinc sulfate and 2-methyl imidazole were purchased from Aldrich and were used without further purification. Sodium formate, methanol were supplied by Chengdu Kelong Chemical Reagent Co., China.

### 2. Synthesis of ZIF-8 and Characterization

The method for synthesis of ZIF-8 was similar to that described previously [11,15,29]. In a typical synthesis, a solid mixture of 0.002 mol zinc chloride, 0.003 mol 2-methyl imidazole and 0.001 mol sodium formate was dissolved in 25 ml methanol by ultra sonic treatment. Subsequently, at room temperature (25 °C), the above reaction mixture continued to react for 3 hours under a stirring state. Or by a solvothermal mode at 150 °C, the above reaction mixture was transferred to a 100 ml autoclave made of stainless steel (316L) and continued to react for 3 hours under continuous stirring. ZIF-8 was characterized by XRD, SEM and FTIR, respectively. Powder X-ray diffraction measurement was conducted on a Dmax/Ultima IV diffractometer operated at 40 kV and 20 mA with Cu-K $\alpha$  radiation.

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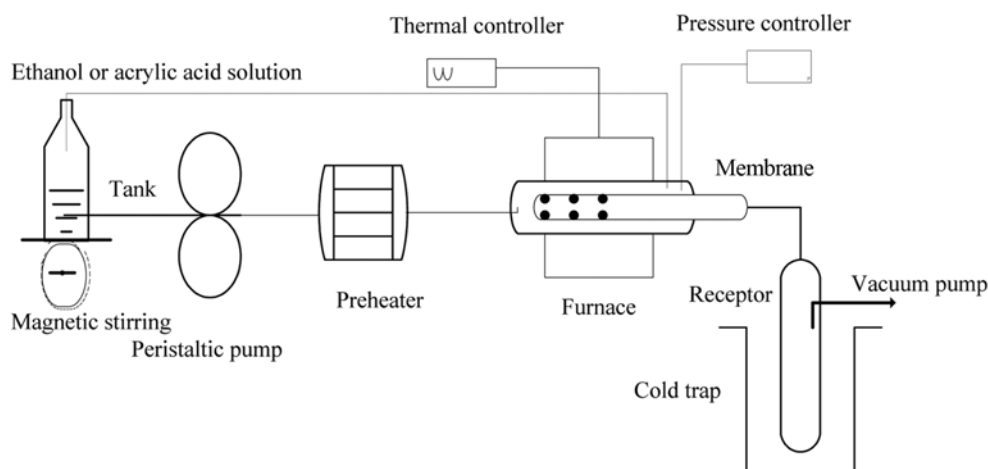


Fig. 1. Experimental setup.

The FTIR spectra were recorded in the range of 500–4,000  $\text{cm}^{-1}$  on a Nicolet 6700 spectrometer. The morphology was examined by using a scanning electron microscope (SEM, JSM-6510).

### 3. $\gamma\text{-Al}_2\text{O}_3$ Porous Ceramic Membrane and Modification

The asymmetric alumina membrane consists of a support and a skin layer. Porous  $\gamma\text{-Al}_2\text{O}_3$  tube (avg. pore size=0.1  $\mu\text{m}$ , i.d.=9 mm, o.d.=13.5 mm, Fusan Institute of Ceramics) used as the support was cleaned successively in anhydrous ethanol, and distilled water each for 20 min at least five times, and dried at 120  $^\circ\text{C}$  overnight. The top layer  $\gamma\text{-Al}_2\text{O}_3$  with pore diameter of about 4 nm was prepared on the outer surface of the support by a sol-gel technique [30,31]. The length of  $\gamma\text{-Al}_2\text{O}_3$  porous section is 30 mm and the total length of tube is 400 mm. The other part of the membrane except for  $\gamma\text{-Al}_2\text{O}_3$  porous section was sealed using superior glaze under the calcination for 20 min at 950  $^\circ\text{C}$ .

$\gamma\text{-Al}_2\text{O}_3$  porous ceramic membrane was modified by impregnation method. A clean and dried  $\gamma\text{-Al}_2\text{O}_3$  porous ceramic membrane was immersed into reaction mixture solution during the synthesis of ZIF-8 and left standing for 30 min. Subsequently,  $\gamma\text{-Al}_2\text{O}_3$  porous ceramic membrane was taken out and washed at least three times with methanol and dried at room temperature and further dried at 120  $^\circ\text{C}$  for 3 hours in a drying oven.

### 4. Gas Permeance Test

The gas permeance through the porous membrane with or without modification was measured in a dead-end permeate unit. Nitrogen or hydrogen gas from a gas cylinder by reducing pressure was directly fed into the membrane module. The module consisted of a stainless-steel casing (i.d.=21 mm and o.d.=27 mm), inside which the ceramic tube was placed and sealed to the stainless-steel casing using Swagelok fittings and Teflon tape wrapped around the membrane. Tightness at the joint between the fitting and the membrane was very important to make a good seal. The membrane module was placed in an oven, so that the system was operated under isothermal conditions. The temperature in the membrane module was measured by a type-K thermocouple, and the pressure of the shell side was measured by precision instrument for testing pressure. The output of permeate stream was measured by soap bubble meter.

### 5. Pervaporation Permeance Test

Similarly, a dead-end permeate unit was adopted for testing per-

vaporation permeance; the experimental setup is shown in Fig. 1. Before each pervaporation permeance experiment, nitrogen and hydrogen gas permeance was performed to check the integrity of the membrane. If a defect of the membrane occurs, the gas permeance will change greatly. A peristaltic pump was used to transport solution from its tank to the system. The flow rate of feed was controlled by tuning the rotating rate. The system was allowed to reach steady state at 90  $^\circ\text{C}$ , which took around 60 min, and then the pressures both in the shell side and inside of ceramic tube were recorded. The experiment was repeated at different feed flow rates. The retention side pressure is above 0.02 MPa at which no vapor is formed for ethanol-water or acrylic acid-water with low concentration in shell side. The permeate side pressure was less than an atmospheric pressure in all cases. Permeate vapor was first cooled to liquid by cold salt water, and the liquid sample was collected to be analyzed by a gas chromatograph. In the process for testing permeance, in order to reduce the volatilization of sample, the liquid sample was further cooled using cold trap with the liquid nitrogen, received using a test tube with cap. The mass was measured by analytical balance.

### 6. Gas Permeance and Permselectivity

Permeance and permselectivity are respectively defined as follows:

$$J_{\text{gas}}/\text{mol}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa}) = \frac{V}{S \cdot p \cdot t}, \quad \alpha_{A/B} = \frac{J_A}{J_B}$$

where,  $J_{\text{gas}}$  represents gas permeance ( $\text{mol}/(\text{m}^2\text{sPa})$ ),  $V$  is permeate gas volume (L) in permeate side at standard conditions,  $S$  is porous membrane area ( $\text{m}^2$ ),  $p$  is average across membrane pressure difference (Pa),  $t$  is permeate time (s), and  $\alpha_{A/B}$  is permselectivity for single component A to single component B at the same temperature and pressure.

### 7. Pervaporation Permeance and Separation Factor

Similarly, pervaporation permeance and separation factor are respectively defined as follows:

$$J_p/\text{g}/(\text{m}^2 \cdot \text{s} \cdot \text{Pa}) = \frac{m}{S \cdot p \cdot t}, \quad \alpha_{\text{inside/outside}} = \frac{C_{\text{inside}}}{C_{\text{outside}}}$$

where,  $J_p$  represents pervaporation permeance ( $\text{g}/(\text{m}^2\text{sPa})$ ),  $m$  is pervaporation permeate weight (g),  $S$  is porous membrane area ( $\text{m}^2$ ),

$p$  is average across membrane pressure difference (Pa),  $t$  is permeate time (s), and  $\alpha_{\text{inside/outside}}$  is separation factor for the ratio of concentration of ethanol or acrylic acid inside the modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic tube to concentration of ethanol or acrylic acid outside the modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic tube.

## RESULTS AND DISCUSSION

### 1. Synthesis of Zeolitic Imidazolate Framework and Characterization

To expand substrates and search for the optimal synthetic conditions in synthesis of zeolitic imidazolate framework, several precur-

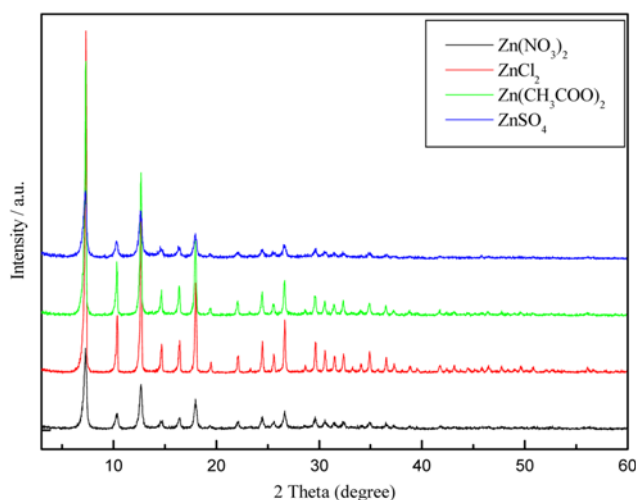


Fig. 2. XRD of ZIF-8 synthesized from different zinc precursors.

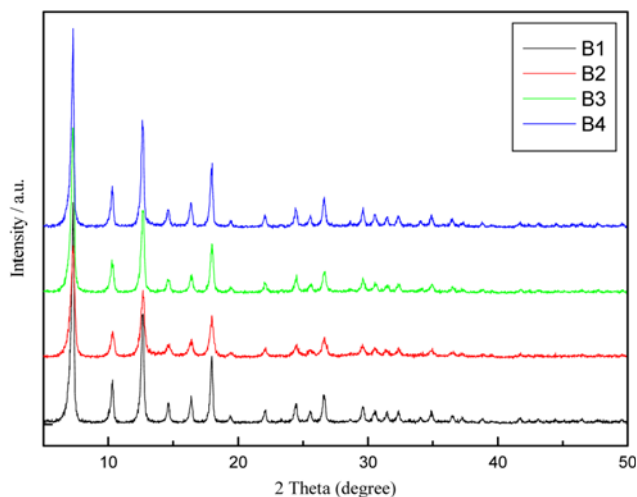


Fig. 3. XRD of ZIF-8 synthesized from reaction of zinc nitrate with 2-methyl imidazole under different conditions. Conditions: B1: ZIF-8 synthesized through solvothermal mode at 150 °C in autoclave lined inside using polytetrafluoroethylene with a continuous stirring for 5 hours; B2: ZIF-8 synthesized through solvothermal mode at 150 °C in autoclave lined inside using glass with a continuous stirring for 5 hours; B3: ZIF-8 synthesized at 25 °C in glass tube with a continuous stirring for 5 hours; B4: ZIF-8 synthesized at 25 °C in glass tube without stirring for 5 hours.

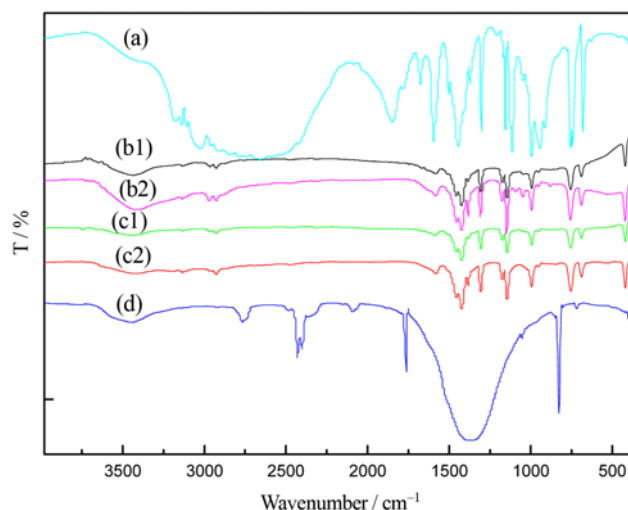


Fig. 4. FTIR spectra of ZIF-8 together with 2-methyl imidazole and zinc nitrate. (a) 2-Methyl imidazole; (b1) ZIF-8 synthesized through solvothermal mode at 150 °C in autoclave lined inside using polytetrafluoroethylene with a continuous stirring for 5 hours; (b2) ZIF-8 synthesized through solvothermal mode at 150 °C in autoclave lined inside using polytetrafluoroethylene without stirring for 5 hours; (c1) ZIF-8 synthesized at 25 °C in glass tube with a continuous stirring for 5 hours; (c2) ZIF-8 synthesized at 25 °C in glass tube without stirring for 5 hours; (d) zinc nitrate.

sors such as zinc nitrite, zinc chloride, zinc acetate and zinc sulfate were used to synthesize ZIF-8. Subsequently, we examined the synthetic conditions for production of ZIF-8. Fig. 2 shows the wide-angle X-ray diffraction (XRD) patterns of ZIF-8 synthesized from different zinc precursors. According to the wide-angle XRD, all kinds of Zn precursors may be used to synthesize ZIF-8. But, zinc chloride as precursor, ZIF-8 displayed the strongest intensity peak, indicating that it has a high crystallinity. Furthermore, with zinc nitrite as precursor, we changed reaction conditions to synthesize ZIF-8 characterized by XRD and FTIR, respectively, as given in Fig. 3 and Fig. 4. From Fig. 3, it is clear that synthetic conditions have an influence on the crystal structures of ZIF-8 and stronger intensive peaks at 7.2°, 10.2°, 12.5°, 17.9°; in conditions B1 (solvothermal synthesis in polytetrafluoroethylene reactor with continuous stirring) and B4 (synthesis at 25 °C in glass reactor without stirring) are observed, suggesting that ZIF-8 from synthetic conditions B1 and B4 has a higher crystallinity. Thus conditions of B1 and B4 are better for synthesis of ZIF-8. In Fig. 4, peak positions of ZIF-8 characterized by FTIR are well in agreement with previous reports [11,32]. Wavenumbers 750 cm<sup>-1</sup>, 690 cm<sup>-1</sup>, are ascribed to bending vibration of imidazole ring, and 422 cm<sup>-1</sup> is ascribed to stretching vibration of V<sub>ZnN</sub>. Whether it was continuous stirring or no stirring in the process of synthesis, ZIF-8 displays a spherical shape.

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane was modified by ZIF-8 synthesized from reaction of zinc nitrate with 2-methyl imidazole at 150 °C in polytetrafluoroethylene reactor. Fig. 5(a) shows the top-view of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8, while Fig. 5(b) gives the EDX analysis of the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous membrane modified with ZIF-8. Fig. 6 shows the SEM image of the cross section of a simply broken porous alumina membrane

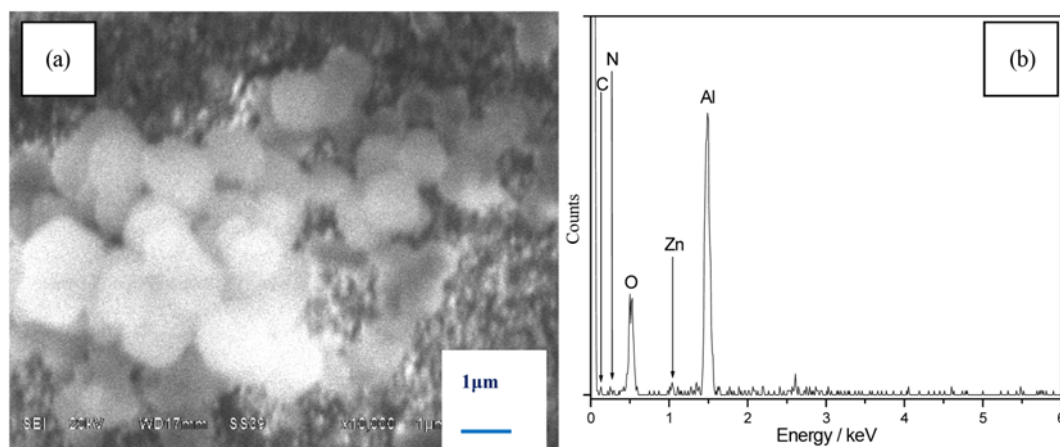


Fig. 5. (a) Top-view of  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane modified with ZIF-8; (b) EDX analysis of the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$  porous membrane modified with ZIF-8.

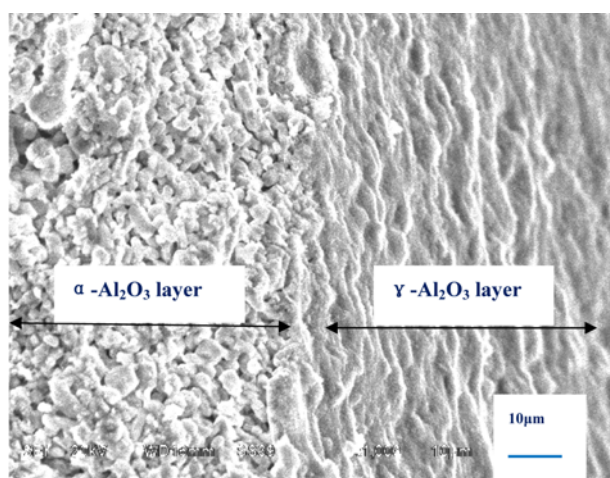


Fig. 6. SEM image of the cross section of a simply broken porous alumina membrane modified with ZIF-8.

modified with ZIF-8. From Fig. 5 and Fig. 6, ZIF-8 was really supported the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$  porous membrane. Thus, the property of the surface of  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane was modified and this may have improved the separation of  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane, although ZIF-8 had not formed a dense membrane.

## 2. Performance of Separation in Alcohol-water, Acrylic Acid-water

### 2-1. Gas Permeance of Hydrogen and Nitrogen

Hydrogen, nitrogen permeance tests were performed prior to permeance test of the binary systems containing alcohol-water, acrylic acid-water, and the results are shown in Fig. 7. From Fig. 7(a), gas permeance in the unmodified  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane is about  $10^{-6}$  mol/(m<sup>2</sup>sPa) at 25 °C, as for hydrogen  $7.5\text{--}9.5 \times 10^{-6}$  mol/(m<sup>2</sup>sPa), nitrogen,  $2.5\text{--}3.0 \times 10^{-6}$  mol/(m<sup>2</sup>sPa), while the permselectivity value for hydrogen/nitrogen is about 2.9–3.4, lower than that for Knudsen diffusion of hydrogen/nitrogen (3.74) [33]. Compared with that in the unmodified membrane, the  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane modified using Zn based zeolitic imidazolate framework (ZIF-8) has lower permeance for hydrogen and nitrogen, and the permselectivity value for hydrogen/nitrogen is higher, 3.1–3.7 in Fig. 7(b). In terms of permeance for hydrogen and nitrogen, the  $\gamma$ -

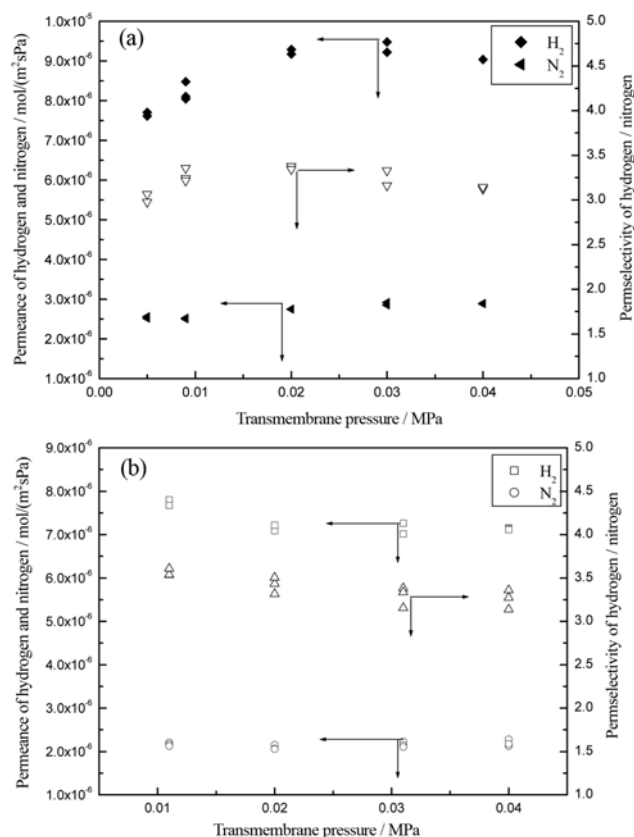


Fig. 7. Nitrogen, hydrogen permeance and permselectivity of hydrogen/nitrogen in  $\gamma$ - $\text{Al}_2\text{O}_3$  porous ceramic membrane at 25 °C. (a) Unmodified with Zn based zeolitic imidazolate framework; (b) modified with Zn based zeolitic imidazolate framework.

$\text{Al}_2\text{O}_3$  porous ceramic membrane with or without modification in this work is like that used in other literatures [1,33–36]. This indicates that hydrogen and nitrogen do not permeate the membrane through the pores of ZIF-8, but through  $\gamma$ - $\text{Al}_2\text{O}_3$  pores. If the gas permeated through the pores of ZIF-8, its permeance, ordinarily in  $10^{-8}\text{--}10^{-7}$  mol/(m<sup>2</sup>sPa), is far more lower than that tested at present [11,16,32,37]. Evidently, ZIF-8 should not form a dense layer of

**Table 1. Permeation performance of ZIF-8 modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ceramic membrane**

Separation system	EtOH-water	AA-water
EtOH or AA concentration in remaining side /mol/L	0.86	0.15
EtOH or AA concentration in permeate side /mol/L	2.67	0.39
Separation factor	3.1	2.6
Permeance of solution/g/(m <sup>2</sup> ·s·Pa)	6.23 × 10 <sup>-4</sup>	1.21 × 10 <sup>-4</sup>

Conditions: permeation temperature 90 °C, EtOH: Ethanol, AA: Acrylic acid, ZIF-8: was synthesized from reaction of zinc nitrate with 2-methyl imidazole

membrane on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane, but to an extent, the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane was modified by ZIF-8. This may favor an increase for permselectivity of hydrogen/nitrogen. The possible reason is that Zn atom of ZIF-8 has a weak coordination effect with N<sub>2</sub>, resulting in adsorption of N<sub>2</sub>, while a similar effect does not exist for H<sub>2</sub>. Thus, H<sub>2</sub>/N<sub>2</sub> permselectivity slightly increased for the modified porous ceramic membrane using ZIF-8.

#### 2-2. Permeability of Alcohol-water, Acrylic Acid-water

Here, we used the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified by ZIF-8 to separate water from binary systems including ethanol-water, acrylic acid-water (see Table 1). The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8 displays more efficient separation for ethanol-water than that of acrylic acid-water. As for the former, the separation factor for ethanol/water is 3.1, while as for the latter the separation factor for acrylic acid is 2.6. Concerning the permeability, permeance of the former is almost five-times higher than that of the latter. The obtained results may be ascribed to the polarity of the permeate and its molecular kinetic diameter. In the direction of polarity, the ethanol has less polarity than that of acrylic acid. In a recent report [11], the separation factor gradually increased in the order of ethanol-water, n-propanol-water and n-butanol-water, according with the decreased order of their polarity (Table 2). In addition, the permeance also increased from ethanol to n-butanol in their investigation [11]. To search for a further reason concerning separation for a binary system, we tested the surface property using water droplets (Table 3). For unmodified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane, water droplets quickly disappeared on the surface of mem-

**Table 2. Polarity of some materials**

	Ethanol	n-Propanol	n-Butanol	Acrylic acid
Polarity index	4.3	4.0	3.7	-

**Table 3. Water droplet disappeared time on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ceramic membrane modified by ZIF-8**

$\gamma$ -Al <sub>2</sub> O <sub>3</sub> ceramic membranes	No. 1	No. 2	No. 3
Water droplet disappeared time/s	5	65	420

No. 1,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ceramic membranes unmodified with ZIF-8;  
No. 2,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ceramic membranes modified a time with ZIF-8;  
No. 3,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ceramic membranes modified twice with ZIF-8

brane, indicating water permeated rapidly through the membrane. However, as for the modified membrane using ZIF-8, water droplets disappeared after long time. This showed that the hydrophobicity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane increased after it was modified with ZIF-8. The hydrophobicity of the membrane is a primary cause for improvement of the separation factor. Similar results were observed by Sekulic [38]. Thus, due to the hydrophobicity of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8, the membrane displayed an excellent separation performance, and more efficient separation for ethanol-water with a relatively less polarity than that of acrylic acid.

## CONCLUSIONS

$\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8 had a higher permselectivity for hydrogen/nitrogen than that of unmodified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane, although its permeance was slightly lower than that of unmodified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane. In separation of the binary systems, including ethanol-water and acrylic acid-water, the modified membrane displayed an efficient separation. Compared with that of acrylic acid-water,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8 has a higher separation factor for ethanol-water. The permeance of ethanol-water through the modified membrane is almost five-times than that of acrylic acid-water. This separation effect of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> porous ceramic membrane modified with ZIF-8 may be ascribed to its hydrophobicity. Hydrophobicity favored separation of binary systems, especially for a system with less polarity.

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