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Preparation and characterization of A-type zeolite/SiO₂ molecular sieving membranes^①

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Abstract: To deal with the brittleness and crystal grain interfacial defects of zeolite membranes, and to confine the pore size distribution of inorganic membranes in a limited range, a process method for composite membranes of A-type zeolite/SiO₂ was described. A silica sol was mixed with nanocrystals of zeolite 4A in a suitable proportion, then the supported membranes was prepared by dip coating method. The composite membranes prepared in first step was treated hydrothermally again, so nanocrystal zeolite 4A formed and located in the mesopores of the membranes, and the microstructure and pore size distribution of the membrane were modified greatly. The thermal stability, mineral phase, microstructure, and pore size distribution were examined via DTA-TG, X-ray diffractometer, scanning electron microscope (SEM), and BET equipment. The structure of the composite membranes remains high stability below 800 °C. Its average pore size in a very limited range is smaller than that in the untreated membranes in hydrothermal condition, and the peak bands of the membrane pores are 4×10^{-10} m, 1.8×10^{-9} m, respectively.

Key words: composite membrane; zeolite 4A; SiO₂; sol-gel; molecular sieving

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1 INTRODUCTION

Inorganic membrane for gas separation, liquid permeation is one of the advanced technologies, which would be most possible to be used in the industries of chemical engineering, electron, spinning, metallurgy, petroleum, and medicine etc. Ceramic membranes with an average pore size of 3–5 nm^[1] are commercially available, however, such membranes are not suitable for high temperature gas separations or membrane reactor applications because of their modest selectivity determined by the Knudsen separation factor. So far series of research have been reported that microporous membranes possessing micropore sizes (5×10^{-10} – 8×10^{-10} m) could be prepared successfully by the sol-gel method^[2–4], but the uncertainty in engineering defect-free supported membranes is still a major problem^[5]. Defects can be formed during dipping and drying or subsequent sintering stages.

The A-type zeolite membranes was one of developed molecular sieving membranes, whose pore size is 0.3–0.5 nm. Sürer et al^[6] prepared zeolite-filled polymer membrane mixed using polyethersulfone and zeolite 4A. Yamazaki et al^[7] and Masuda et al^[8] prepared A-type zeolite membranes on the outer surface of an alumina filter by hydrothermal synthesis, but no separation properties were

reported. Okamoto and his coworkers^[9–10] synthesized A-type zeolite membranes on a seeded porous alumina support. These membranes were highly permselective to water with respect to organic solvents dissolved in water because of the hydrophilicity of the membranes. However, gas permeation tests revealed that gases permeate through the membranes by Knudsen diffusion mechanism. It indicated that gaseous molecular passes through the grain boundaries, and not through the lattice pores. Wang et al^[11] also conducted gas permeation tests using an A-type zeolite membrane which was deposited on a porous substrate by a hydrothermal process. It showed that permeation rates are dominated by surface diffusion through grain boundaries, and not by molecular sieving diffusion through zeolite crystals. Silicalite and ZSM-5 membranes have been prepared with good selectivities for gas separations. Several of these membranes revealed n-butane: isobutane selectivities as high as 90 at room temperature and about 10 at around 200 °C^[12]. Other membranes showed the opposite temperature dependence, e. g., n-butane: isobutane selectivity of 18 at room temperature and 31 at 185 °C^[13]. The variation of selectivity among membranes obtained by different preparation protocols is most likely due to differences in the number size of defects present in these membranes. In this paper, a partic-

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ular process of composite membranes was presented throughout combining the synthesis of A-type zeolite hydrothermally and dipping method by using silica-sol.

2 EXPERIMENTAL

2.1 Materials

The raw materials were tetraethylorthosilicate (TEOS, $\text{SiO}_2 > 18\%$), hydrochloric acid (AR, $\text{HCl} > 36\%$), Sodium hydroxide (NaOH) (AR), aluminum hydroxide ($\text{Al}(\text{OH})_3$) (AR) and sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$). All reactants above were obtained from Jinshan corporation, Shanghai. Sodium dodecylbenzenesulfonate (SDF) and NaCl were used to adjust the crystallization process of hydrothermal system, which were from Hong Xing corporation, Shanghai.

2.2 Characterization

The mineral phases and crystallinity of the membranes were examined by XRD (Siemens D5000-2CU: Cu, 40 kV-mA). Thermal stability of the membranes was tested by differential thermal analysis (DTA) and thermogravimetry (TG). The microstructure of the membranes was observed by scanning electron microscope (SEM, in Changsha Institute of Mining and Metallurgy, China). The pore sizes distribution was examined by American AP-2400 BET equipment.

The $\alpha\text{-Al}_2\text{O}_3$ support was bought from Zibo Ceramic Institute, Shangdong, China. The pore size of the support was $1 \sim 2 \mu\text{m}$, with porosity of 0.5, gauge of $10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$.

2.3 Samples preparation

The molecular sieving membranes was prepared by sol-gel method and hydrothermal synthesis in situ. The steps were as follows.

The first step was to prepare the composite sol of silica/A-type zeolite (diameter $< 100 \text{ nm}$). The silica-sol was prepared via hydrolysis of TEOS precursors under acid-catalyzed condition. A mixture of TEOS, distilled water, and hydrochloric acid (HCl) in a proportion of $\varphi(\text{HCl}) : \varphi(\text{H}_2\text{O}) : \varphi(\text{TEOS}) = 0.1 : 5.8 : 1$, was stirred vigorously at room temperature until the mixture temperature did not rise after about 30min. Then distilled water was added into the mixture to adjust the composition as $\varphi(\text{HCl}) : \varphi(\text{H}_2\text{O}) : \varphi(\text{TEOS}) = 0.1 : 100 : 1$, followed by 2 h refluxing at 60°C under stirring. So the silica-sol was obtained.

Secondly the nano-crystals of A-type zeolite was prepared under hydrothermal condition. The composition of reaction system was $\varphi(\text{Na}_2\text{O}) : \varphi(\text{Al}_2\text{O}_3) : \varphi(\text{SiO}_2) : \varphi$

$(\text{H}_2\text{O}) = 3 : 1 : 2 : 180$. A small amount of SDF (sodium dodecylbenzenesulfonate) and sodium chloride (NaCl) were added to the system, in general, $w(\text{NaCl})/w(\text{SiO}_2) = 1\%$, $w(\text{SDF})/w(\text{SiO}_2) = 0.01\%$. Before crystallization, $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was dissolved in distilled water in a glass flask, then the solution A was obtained. $\text{Al}(\text{OH})_3$ and NaOH were prepared and added into the solution of sodium metalluminate in another flask, which was solution B. Then the solution A was stirred vigorously meanwhile the solution B was dropped slowly into solution A. In the process the milk white gel was formed. The gel was crystallized at 80°C for 2 h. And the products was washed and filtered until $\text{pH} = 8$. At the last time, it was washed with alcohol, then dried at 110°C .

Thirdly a desired volume of nano-crystals of A-type zeolite was added into silica-sol under vigorous stirring, then a composite gel of A-type zeolite/silica was obtained.

The forth, one face of the support disk was polished with 600 grit sand-paper, then the disk was washed with water and dipped flatly into the composite gel with the fresh face for 10 s, subsequently dried naturally at room temperature. The process was repeated twice. The dried sample was placed into a furnace and sintered according to the sintering routine (Fig. 1). The sample CM was obtained.

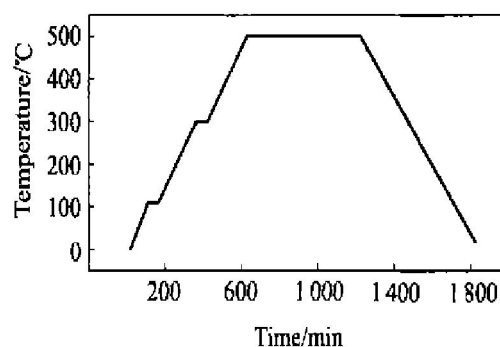


Fig. 1 Sintering routine of composite membranes

The fifth, the sample CM was dipped into solution A and solution B in sequence, and solutions A and B were absorbed into pores of the composite membranes. Meanwhile the gel particles for A-type zeolite were formed in the pores. This procedure was repeated twice. After each time, the membranes were dried at low temperature. Then the membranes was placed into hydrothermal mixture for synthesis of A-type zeolite, and the composition of the system was same as that mentioned in the second step above. The system was kept at 100°C for $1 \sim 3 \text{ h}$. So the molecular sieving membranes was obtained at last.

3 RESULTS AND DISCUSSION

3.1 Thermal stability

Fig. 2 shows the TGA/DTA curves of the composite gel membranes of A-type zeolite/SiO₂ before it was sintered. It shows that the endothermic peak appears at 85–250 °C. The mass loss was about 10% before 250 °C. Solvent was vaporized at 80–100 °C, and the organic agents remaining in the gel were oxidized above 221.9 °C. Above 350 °C, there is no evidence of mass loss, endothermic and exothermic changes. It was proposed that, water, organic agents and other solvent could be eliminated above 400 °C, which was the temperature designed for sintering of the molecular sieve membranes. Fig. 3 shows the DTA analysis curve of the last sample of the molecular sieving membranes sintered (forth step) and treated under hydrothermal condition for zeolite 4A (fifth step). It is showed that a wide lower endothermic peak appears before 221.9 °C, which presents the vaporization of water. No change was observed at 221.9–800 °C, which shows the thermal stability of the molecular sieve membranes is excellent. A gently exothermic peak appears above 800 °C, which was caused by microstructure collapse of A-type zeolite.

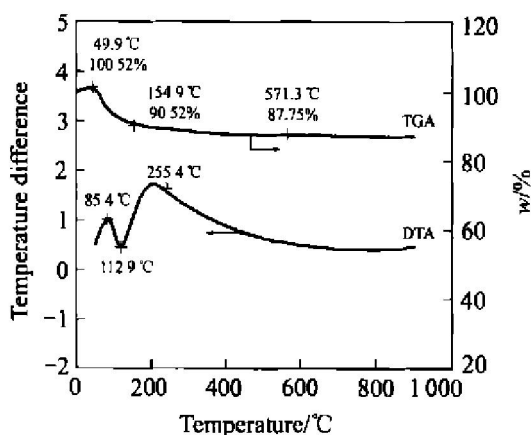


Fig. 2 TGA-DTA curves of composite gel membranes

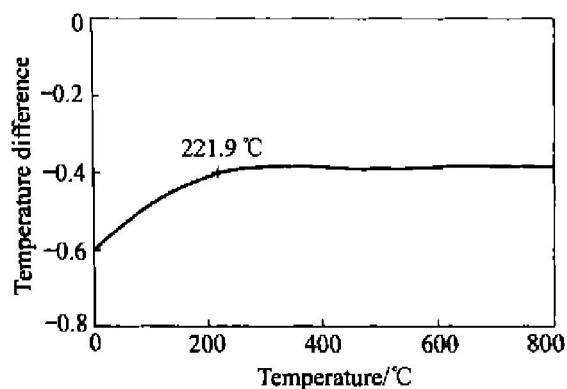


Fig. 3 DTA curve of molecular sieving membranes sintered

3.2 X-ray diffraction analysis

X-ray powder diffraction analyses of the samples of the molecular sieving membranes are showed in Fig. 4. All samples were the last ones prepared according to steps above, and their crystallization (or hydrothermal treatment) time were 0, 1.5, 2 h respectively under 100 °C in static system. The diffraction peak of A-type zeolite couldn't be observed with sample (a). Just a wide excursive peak of silica appeared. The obvious diffraction peaks of A-type zeolite appeared in sample (b). Its crystallinity was respectively high, and the all unique peaks of A-type zeolite could be observed clearly. The peaks were respectively higher in sample (c) than those in sample (b). So the crystallinity and the value of A-type zeolite in the membranes increased with crystallization time. This results was identical with SEM observation.

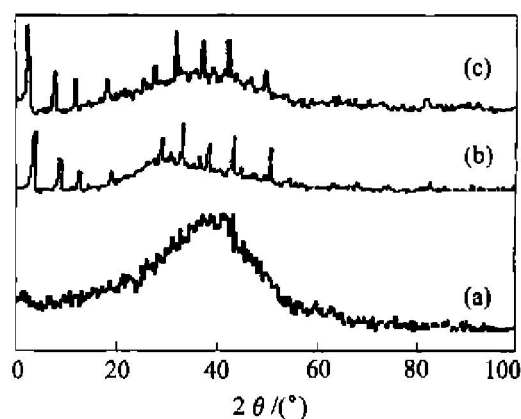


Fig. 4 XRD analysis of samples

3.3 Microstructure

The SEM micrographs of the samples are shown in Fig. 5. Sample (a) had not been treated in hydrothermal system for zeolite 4A. Its microstructure was constructed mainly by silica particles, which were gray. A few scattering of nano-crystals of zeolite 4A which was white piece in Fig. 5(a) existed between silica particles. The both particles size were about 50nm. The interface, interspace and pinhole could be observed clearly. Meanwhile some conglomeration of zeolite 4A existed in it. A large number of A-type zeolite crystal appeared in Fig. 5(b) and Fig. 5(c). According to XRD analyses and SEM observation, the content of A-type zeolite in membranes samples were about 5%, 30% and 35% respectively. The content of zeolite 4A in Fig. 5(c) was more than that in Fig. 5(b), and the microstructure observed in Fig. 5(c) was more tight or better. The larger crystals were in consequence of recrystallization of nano-crystals mixed into the composite sol before, and the crystal size was about 100 nm. The smaller crystals (nanometer) were formed in the process

of hydrothermal treatment, and the size was about 50 nm. In Fig. 5(b) and Fig. 5(c), silica particles and the crystals of A-type zeolite were joined together tightly, the interspace between the both was in tendency of disappearance. And some interface or interspace disappeared, which was just a transition layer connected with crystal of zeolite 4A and silica particle. The color of the transition layer was from gray to white in direction from silica to zeolite. As desired, nano-crystals were located in the pores and interspace of the composite membranes, namely the mesopores and defects were minimized by hydrothermal synthesis of A-type zeolite in the pores in situ. With nano-crystals formed in mesopores, the mesopores were modified into micropores for gas separation.

3.4 Pore size distribution

The pore size, pore volume and pore size distribution

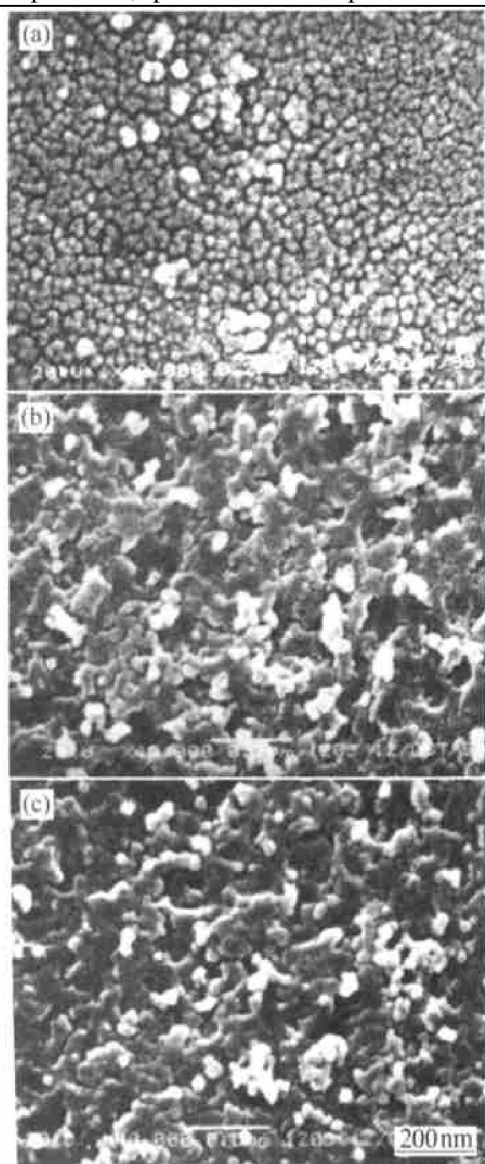


Fig. 5 Micrographs of membrane samples
(a) —Composite membranes untreated in hydrothermal condition;
(b) —Treated for 2 h;
(c) —Treated for 3 h. (White were crystals of zeolite 4A; gray were particles of silica)

of the membranes were examined by nitrogen adsorption isotherms measured and using an adsorption porosimeter (micrometrics, ASAP2400). Fig. 6 shows the curves of pore size distribution of the membranes. Curve 2 was the membrane untreated in hydrothermal system for zeolite 4A, and curve 1 was that treated for 2 h. From curve 2, there was only one wide rambling peak in range of 10^{-1} – 80 nm. This was related to pores between silica particles. But three new peaks appeared in curve 1 of the pore size distribution of treated membranes in hydrothermal condition, which were 3×10^{-10} – 5×10^{-10} m (first band), 10×10^{-10} – 20×10^{-10} m (second band), $> 20 \times 10^{-10}$ m (third band). The first, and the second bands were related to A-type zeolite, interspace between crystals of zeolite 4A and silica particles or pores of silica particles. So it could be learned that the pores of composite silica membranes could be modified efficiently by crystals of zeolite 4A during hydrothermal treatment. The existence of the second pore size peaks was due to imperfect modification (or assembling) by crystals of zeolite 4A in the pores of silica particles.

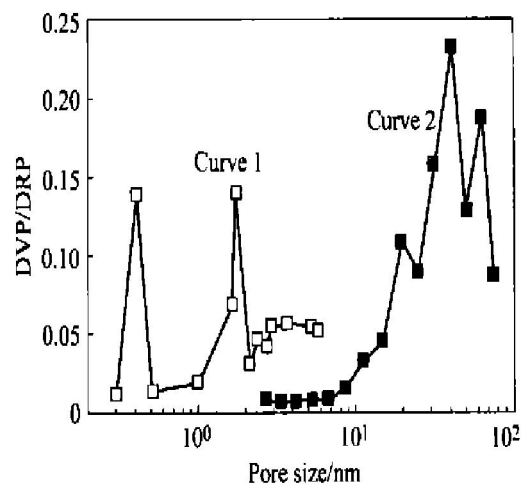


Fig. 6 Pore size distribution of samples

1 —Treated sample in hydrothermal condition;
2 —Untreated sample in hydrothermal condition

4 CONCLUSIONS

The resulted microporous (or molecular sieving) membranes can be prepared from silica-sol containing zeolite A by sol method and hydrothermal synthesis method very well. The pore size distribution of composite membranes is modified efficiently by crystals of zeolite 4A during hydrothermal treatment. The main phases of this composite membrane were zeolite A and amorphous silica. The size of A-type zeolite crystals examined by TEM in the membrane is about 50 nm and the pore size of the membranes is in two bands, 4×10^{-10} m and 18×10^{-10}

m. The microstructure frame of the membranes is kept very well below 800 °C.

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