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快 报

清液体系中高性能 T 型沸石分子筛膜的合成

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摘 要：由摩尔组成为 $SiO_2:Al_2O_3:Na_2O:K_2O:H_2O$=1:0.015:0.25:0.08:25 的澄清溶液，在预涂晶种的管状莫来石支撑体上水热合成 T 型沸石分子筛膜。在高于 100 ℃清液体系中合成出了高性能 T 型沸石分子筛膜。用 X 射线衍射(X-ray diffraction, XRD)仪和扫描电子显微镜(scanning electron microscope, SEM)对 150 ℃下合成 35 h 的分子筛膜进行了表征。XRD 谱表明：T 型沸石分子筛成功地生长在预涂晶种的支撑体上。支撑体的外表面覆盖着 20 μm 厚有取向的晶体层。从 SEM 照片判断，起到分离作用的是生长致密的中间层，而不是表层。在 150 ℃下制备的膜，对水/乙醇、水/异丙醇混合物具有高渗透汽化分离性能。优异的渗透汽化性能归因于在涂有晶种的多孔支撑体上生长了一层高结晶度且缺陷较少的 T 型沸石分子筛晶体层。

关键词：T 型分子筛；分子筛膜；晶体生长；渗透汽化
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SYNTHESIS OF ZEOLITE T MEMBRANES WITH HIGH PERFORMANCE FROM CLEAR SOLUTIONS

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Abstract: Zeolite T membranes were prepared on pre-seeded mullite tubes by hydrothermal synthesis from clear solutions with a molar composition of $SiO_2:Al_2O_3:Na_2O:K_2O:H_2O$=1:0.015:0.25:0.08:25. The synthesis of high performance zeolite T membrane above 100 ℃ from clear solutions was reported. The membrane synthesized at 150 ℃ for 35 h was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD pattern indicated that the zeolite T crystals were successfully grown onto the pre-seeded mullite tube support. The outer surface of the porous support was covered with oriented zeolite T crystals of about 20 μm in thickness. The intermediate layer packed densely with zeolite T crystals would act as an active layer for separation rather than the top layer, judged from SEM observation. The membrane prepared at 150 ℃ showed high pervaporation properties for water/ethanol and water/isopropanol liquid mixtures. The good pervaporation performance would be attributed to the high crystallinity and the few defects contained in the zeolite T crystal layer grown on the seeded porous tube.

Key words: zeolite T; zeolite membrane; crystal growth; pervaporation

Zeolite membranes have attracted intensive interest because of their promising applications for pervaporation, gas separation and membrane reactors. Zeolite T with a Si/Al molar ratio of 3:4 is an intergrowth-type zeolite of erionite and offretite. Due to its effective pore size (0.36 nm×0.51 nm) and hydrophilicity, zeolite T membranes have great potential applications in pervaporation and gas separation. Although some studies have reported the synthesis of zeolite T membranes from a milk-like aluminosilicate gel or a clear solution,[1–4] the synthesis temperatures are around 100 ℃. To our knowledge, no reports deal with the preparation of zeolite T membranes at the synthesis temperature above 100 ℃, which is a favorable condition for crystal growth of zeolite T.[5–9] In this work, the synthesis of zeolite T membranes from clear solutions was carried out at the temperature above 100 ℃, and the pervaporation performance of the membrane was improved significantly.

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1 Experiment

1.1 Membrane preparation

The clear solution for the synthesis of zeolite T membrane was prepared by mixing colloidal silica (Aldrich, Ludox TM–40), aluminum hydroxide (Wako Pure Chemical), sodium hydroxide (Shanghai Chemical Reagent Research Institute, reagent grade) potassium hydroxide (Shanghai Lingfeng Chemical Reagent Co., Ltd., reagent grade) and distilled water. The mixture was then stirred vigorously for 1 h at room temperature. The molar composition of the solution was $1SiO_2:0.015Al_2O_3:0.25Na_2O:0.08K_2O:25H_2O$. The tubular mullite support, which was 12 mm in outer diameter, 2 mm in thickness and 1 μm in average pore size, was prepared by our Membrane Science & Technology Research Center. It was polished with SiC paper (#800), and then rubbed with water slurry of zeolite T particles. The seeded tube (10 cm in length) was vertically placed in a stainless steel autoclave filled with synthesis solution. After crystallization at a given temperature for 35 h, a membrane was obtained. Then the membrane was washed thoroughly with deionized water, and dried at 100 ℃.

1.2 Characterization and pervaporation test

The as-synthesized membrane was characterized by X-ray diffraction (XRD, BRUKER, D8 ADVANCE). The morphologies of seed crystals and zeolite T membranes were observed by scanning electron microscope (SEM, FEI, QUANTA 200).

The pervaporation (PV) tests for water/ethanol (10%/90%, in mass, the same below) and water/isopropanol (10%/90%) mixtures were carried out at 75 ℃. The membrane used for the PV test had an effective area of about 19 cm^2, and the inside of the membrane tube was evacuated through a vacuum line. The membrane separation performance was evaluated by the permeation flux [$Q/(kg\cdot m^{-2}\cdot h^{-1})$] and the separation factor (α). The permeation flux was calculated by the mass of the permeate, which was collected by a liquid-nitrogen trap. The separation factor was determined as

$$\alpha_{A/B}=(Y_A/Y_B)/(X_A/X_B) \quad (1)$$

where X_A, X_B, Y_A, and Y_B denote the mass fractions of components A and B in the feed and permeate sides, respectively.

2 Results and discussion

Figure 1 shows the XRD patterns of the as-synthesized membrane, zeolite T powders and porous mullite tube. The XRD patterns from the as-synthesized membrane showed the presence of zeolite T and the mullite that came from the support. As a result, the zeolite T crystals were successfully grown on the seeded support.

Figure 2 shows the SEM images of the seed crystals and the seeded tube. It was clear that the rod-like zeolite

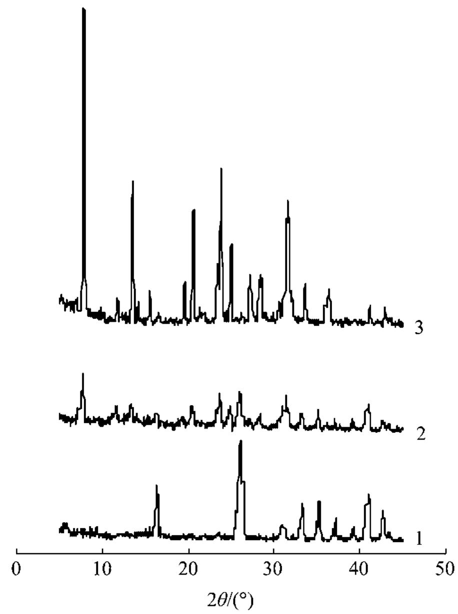
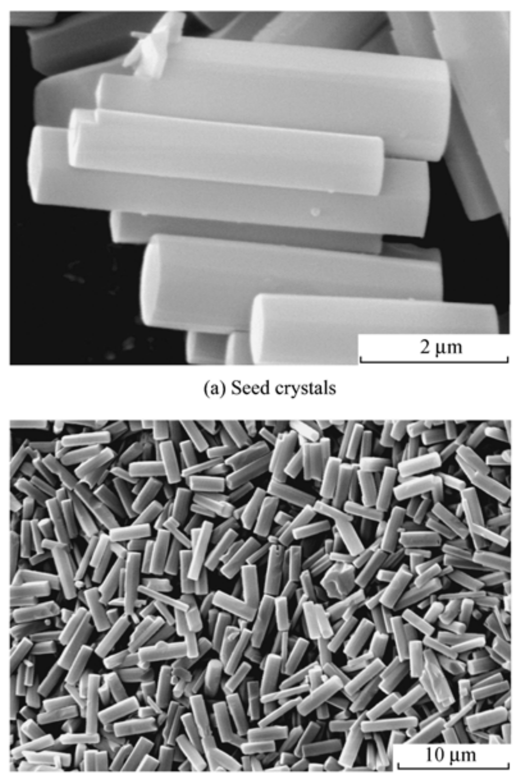


Fig.1 XRD patterns for (1) mullite tube, (2) zeolite T membrane synthesized at 150 ℃ for 35 h, and (3) zeolite T powders



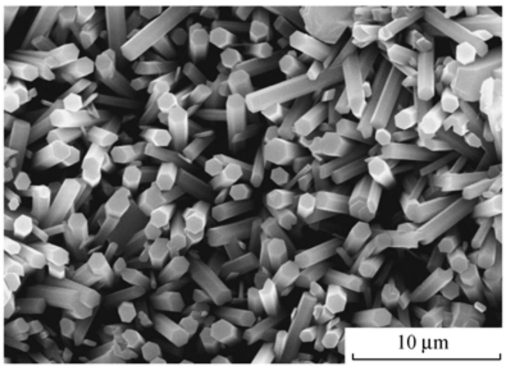
(a) Seed crystals

(b) Seeded tube

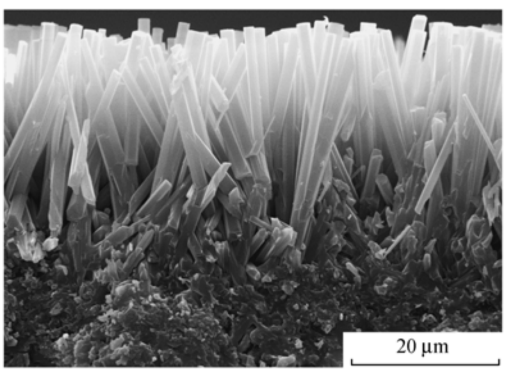
Fig.2 SEM photographs for (a) the seed crystals and (b) the seeded tube

T crystals deposited on the tube were rather continuous and uniform, and their average size was about 3 μm.

Figures 3a and 3b show the SEM photographs of surface and cross section of the as-synthesized membrane, respectively. From Fig.3a, it could be seen that the surface of the mullite support was covered with well oriented rod-like zeolite T crystals with loose packing. From Fig.3b, it was found that the thickness of the top crystal layer was approximately 20 μm. In addition, there was a continuous intermediate layer with about 20 μm in thickness between the top crystal layer and the support.



(a) Surface



(b) Cross section

Fig.3 SEM photographs for the zeolite T membrane synthesized at 150 ℃ for 35 h

Table 1 shows the pervaporation performance of the zeolite T membranes synthesized at different temperatures for water/ethanol and water/isopropanol liqiud mixtures. The membrane prepared at 100 ℃ showed no separation property. It was found that the PV performance of the membranes was improved with the increase of synthesis temperature. Especially, for the membrane prepared at 150 ℃, its separation factor was high, up to 2 800 for water/ethanol separation. Both the flux and separation factor were also improved significantly for water/isopropanol separation compared with the zeolite T membranes reported in the literature. It is also important to note that the intermediate layer packed densely with zeolite T crystals as shown in Fig.3 would act as an active layer for separation.

Table 1 Pervaportion performance of zeolite T membranes synthesized at different temperatures for water/ethanol and water/isopropanol liqiud mixtures

Synthesis Temperature /℃	Water/ethanol (10% water in mass)		Water/isopropanol (10% water in mass)		Reference
	Q/(kg·m^{-2}·h^{-1})	α	Q/(kg·m^{-2}·h^{-1})	α	
100	—	—			This work
125	0.92	2 300			This work
150	1.16	2 800	2.52	>10 000	This work
100	1.25	2 200	1.77	10 000	2
100	1.10	900	2.20	8 900	3

3 Conclusion

Zeolite T membranes were prepared on seeded porous tubes from clear solutions at temperature range from 100 ℃ to 150 ℃. The best pervaporation separation properties were obtained through the membrane synthesized at 150 ℃, and this resulted from the high crystallinity and the few defects contained in the zeolite T crystal layer grown on the seeded porous tube.

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