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# Enlarged Area A-type Zeolite Membranes Prepared by Vacuum Seeding Method

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**Abstract:** High quality A-type zeolite membranes, with enlarged area over 70 $cm^2$, were successfully synthesized on a tubular $\alpha$-$Al_2O_3$ support by applying the vacuum seeding method.

**Keywords:** A-type zeolite membrane, vacuum seeding, secondary growth.

Coating the zeolite seeds onto the support surface before hydrothermal treatment, which is also named secondary growth method, is an effective approach to synthesize high quality zeolite membrane. Compared to the *in situ* hydrothermal synthesis method, the secondary growth method exhibits many advantages such as better control over membrane microstructure (thickness, orientation), higher reproducibility, and so on. Up to now, many methods have been explored to coat support surface, including dip-coating[1], rub-coating[2], spin-coating[3] and pulsed laser deposition[4]. All these seeding methods were proved to be benefit to improve membrane synthesis. However, the area of the membranes prepared by the seeding methods mentioned above was usually small, which restrict the implement of zeolite membrane at large-scale. In addition, the reproducibility of the high quality membrane preparation was unsatisfactory. In the present work, a simple and effective seeding method, which is named vacuum seeding method, is developed to prepare high quality and enlarged area A-type zeolite membranes on the tubular $\alpha$-$Al_2O_3$ supports.

Porous $\alpha$-$Al_2O_3$ tubes (home-made: 11 mm in OD., 7 mm in ID, 270 mm in length, 0.5~1.0 μm pore radious, about 40% porosity) were used as supports. The seeding layer was coated onto the outer surface of the supports. The procedure for the vacuum seeding is described in **Figure 1**. As shown in **Figure 1**, the bottom end of the support was sealed and the upper end was linked to a water pump. The support was fixed vertically and immerged in a glass tube containing colloidal suspensions of the A-type zeolite seeds. When the valve to vacuum was open, pressure difference was created between the two sides of the support wall. Consequently, the A-type zeolite seed particles were transported and coated onto the support surface by vacuum force.

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**Figure 1** Apparatus for coating A-type zeolite seeds by vacuum seeding method

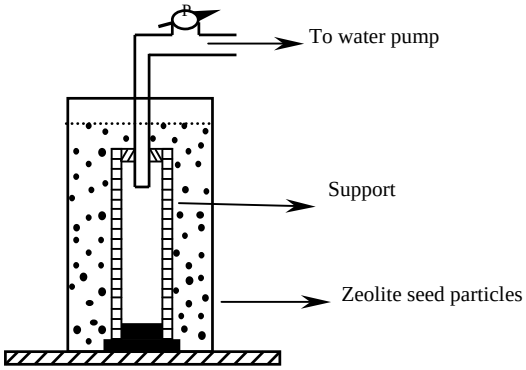
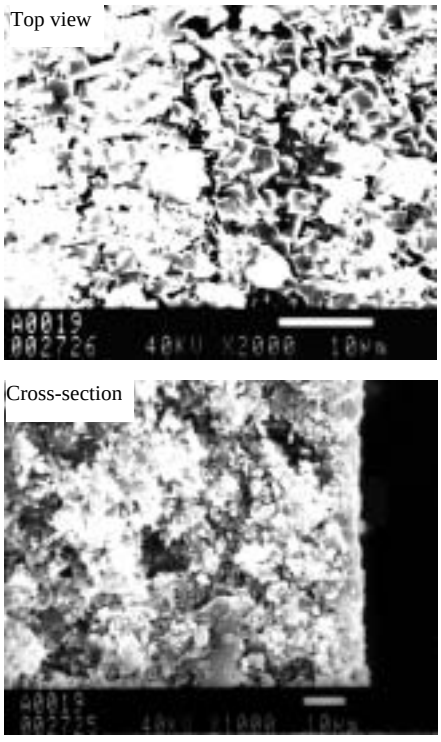



**Figure 2** SEM images of the as-synthesized A-type zeolite membrane prepared by vacuum seeding method




The solution for synthesizing A-type zeolite membrane was prepared according to the procedure reported previously[5]. The molar ratio of the synthesis solution was $50Na_2O$: $Al_2O_3$: $5SiO_2$: $1000H_2O$. The seeded support was placed vertically with a teflon holder in stainless steel autoclave. Synthesis solution was poured into the autoclave and then the autoclave was sealed. After crystallizing 24 h at 333 K, the membrane was washed with

deionized water, and then dried. The as-synthesized membrane was examined by SEM. The quality of the membranes was also evaluated by the pervaporation dehydration of isopropanol/water mixture.

**Figure 2** shows the SEM images of the as-synthesized A-type zeolite membrane. It can be seen that, the support surface is completely covered with A-type zeolite crystals with size of 2~4 μm, and the membrane thickness is about 5 μm judging from the cross-section view. More experiments indicate high quality A-type zeolite membranes can be easily prepared by vacuum seeding method under the optimized conditions: seed particle sizes of 500~1200 nm, suspension concentrations of 4~8 g/L, coating pressure difference of 0.0100~0.0150 MPa and coating time of 45~180 seconds. At 343 K, the separation factor ($H_2O$/isopropanol) is 5000~10000 at 95wt% feed isopropanol concentrations, and the flux is 1.02~1.78 Kg/m$^2$h, respectively. The reproducibility of the membrane preparation is satisfactory. **Table 1** gives some experiment results..

**Table 1** Membrane properties under optimized coating conditions

| Sample number | Seed size (nm) | C (seed) (g/L) | Vacuum (MPa) | Properties of the membranes | |
|---|---|---|---|---|---|
| | | | | Flux($H_2$0) (Kg/m$^2$h) | α ($H_2O$/IPA) |
| 1 | ~500 | 7 | 0.0150 | 1.24 | > 10000 |
| 2 | ~1200 | **7** | 0.0150 | 1.67 | > 10000 |
| 3 | ~1200 | 5 | 0.0150 | 1.47 | 7200 |
| 4 | ~1200 | 7 | 0.0100 | 1.78 | 6800 |

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## References

1. R. Lai, G. R. Gavalas, *Ind. Eng. Chem. Res.*, **1998**, *37*, 4275.
2. K. Kusakabe, T. Kuroda, A. Murata, S. Morooka, *Ind. Eng. Chem. Res.*, **1997**, *36*, 649.
3. S. Mintova, T. Bein, *Adv. Mater*., **2001**, *13*（24）, 1880.
4. T. Munoz Jr., K.J. Balkus Jr., *J. Am. Chem. Soc*., **1999**, *121*, 139.
5. X. C. Xu, W. S. Yang, J. Liu, L. W. Lin, *Microporous Mesoporous Mater*., **2000**, *43*, 299.

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