Chinese Chemical Letters Vol. 14, No. 8, pp 874 – 877, 2003
http://www.imm.ac.cn/journal/ccl.html

Synthesis of Compact NaA Zeolite Membrane by Microwave Heating Method

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Abstract: A continuous and dense NaA zeolite membrane was synthesized by microwave heating method while employing a multi-step seeding LTA zeolite with the average size of 120 nm. The gas H_2/N_2 mixture separating results indicated that the mixture selectivity increased with increasing of synthesis times. In addition, selectivity of the three-step synthesis was higher than the value(3.74) expected from Kundsen diffusion.

Keywords: Microwave heating, NaA zeolite membrane, gas separation.

Another candidate for use as membrane for gas separation is the zeolite A membrane, the pore size of which is 0.3~0.5 nm. Because of the small pore size, the zeolite A membrane may be selective for small molecules[1,2,3,4,5]. There are reports about synthesis of zeolite A membrane by microwave heating[4,6,7], whereas the gas separation only depended on single gas permeance and less studied about separation of the mixture components on them. This paper reports novel synthesis of continuous and dense NaA zeolite membrane by microwave heating using a method of the multi-step seeding LTA zeolite with the average size of 120 nm .

Experimental

One side of polished and pretreated ã-alumina substrates (24 mm in diameter, 1.5 mm in thickness, 100 nm~300 nm in pore radius, by homemade) were coated LTA zeolite with the average size of 120 nm as have prepared in the literature[8]. The seeded substrates which were calcined at 550 °C for 3 h to remove template were vertically placed into a Teflon vessel loading a gel solution with a composition of $3Na_2O:2SiO_2:1Al_2O_3:150H_2O$. The reactant mixture was prepared by dissolving $Al(OH)_3$ in NaOH solution, and then adding to SiO_2 sol (25 mass% in water) by stirring at room temperature. The reactant mixture formed above was transferred into teflon vessel and then heated repeatedly for 20 min in household microwave oven at atmosphere pressure and under reflux. The as-synthesized membranes were washed several times by deionized water until the pH value of the washings was neutral, and then dried at 393 K.

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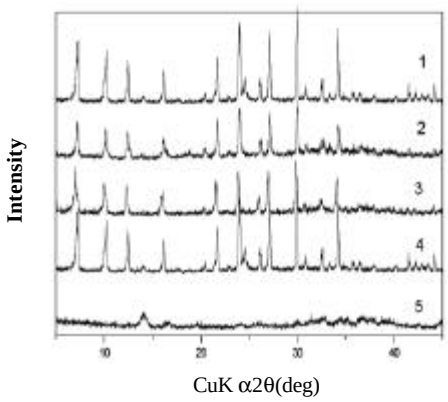
The mixture gas (H_2/N_2, 50: 50 v/v) testing was performed with similar Wicke-Kallenbach method at room temperature. Both sides of membrane maintained at pressure difference of 0.10 MPa using helium as sweep gas at a flow rate of 30 mL/min in permeating side. The permeating side was maintained at atmosphere pressure with on-line analysis of GC.

Finally, the formation of the zeolite membrane was confirmed by X-ray diffraction(XRD) using a Rigaku Rotaflex D/MAX-C powder diffractometer with Cu K_α (λ=0.154 nm) radiation, with operation condition at 40 kV and 30 mA. Electron micrographs were recorded with Hitachi S-520 scanning electron microscope.

Results and Discussion

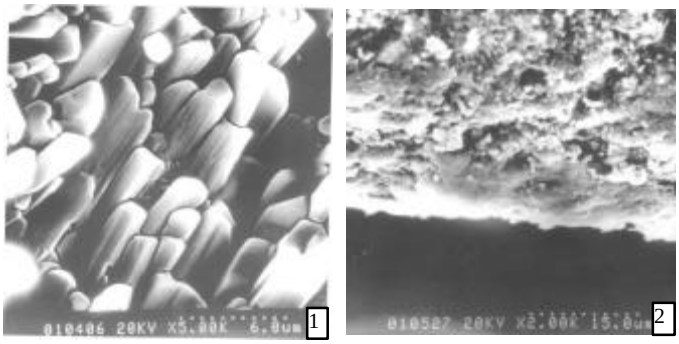
As shown in **Figure1**, besides the combining peaks of NaA zeolite and γ-alumina after one, two and three-step synthesis, there aren't the peaks of other crystal, indicating that the pure NaA zeolite membrane grew on ã-alumina substrate. From SEM images shown in **Figure2**, it can be seen that the substrate is completely covered the NaA zeolite crystal, with highly intergrown and randomly oriented morphology. In addition, the membrane consists of the larger rectangle crystals and the thickness of the membrane is about 7 μm. As the results of permeating testing show in **Table 1**, the selectivity indicate that the defect of NaA membrane decreases with increasing of synthesis times. After three-step synthesis, the selectivity is higher than the value (3.74) expected from Knudsen diffusion, confirming the membrane is highly compact.

Figure 1 XRD patterns of the as-synthesized membranes



1:First time；2: Second time；3:Three time；4: NaA zeolite; 5: ã-alumina substrate

Figure 2 SEM images of the as-synthesized membranes after three-step synthesis



1: Top view, 2: Cross-section view

Table 1 Effects of synthesis times on permeance and selectivity

Synthesis times	Permeance ($\times 10^{-8}$ mol/Pa·m^2·s)		H_2/N_2 Selectivity
	H_2	N_2	
First time	120.7	41.7	2.88
Second time	75.0	22.0	3.40
Third time	51.5	12.9	3.97

Acknowledgment

We are grateful to the Ministry of Science and Technology of China for the Financial support (Grant No. G1999022408)

References

1. Y. H. Ma, Y. J. Zhou, R. Poladi, E Engwall, *Sep. Purif. Technol.*, **2001**, *2*, 235.
2. K. Aoki, K. Kusakabe, S. Morooka, *J. Membr. Sci.*, **1998**,*141*, 197.
3. X. C. Xu, W. S. Wang, J. Liu, *et al.*, *Chem.Commun.*, **2000,** *7*, 603.
4. X. C. Xu, W. S. Yang, J. Liu, L.W. Lin, *Adv. Mater.*, **2000**, *12*, 195.
5. X. C. Xu, W. S. Yang, J. Liu, L. W. Lin, *Sep. Purif. Techno*l., **2001**, *25*, 475.
6. Y. Han, H. Ma, S. L. Qiu, F. S. Xiao, *Micropor. Mesopor. Mat.*, **1999**, *30*, 321.
7. X. C. Xu, W. S. Yang, J. Liu, L. W. Lin, *Sep. Purif. Technol.*, **2001**, *25*, 241.
8. J. Hedlund, B. Schoeman, J. Sterte, *Chem.Commun*.,**1997,** 1193.

Received 5 September, 2002