

Support Information

Methylcellulose-assisted synthesis of compact and thin NaA zeolite membrane

Xue-Ling Wei^a, Shuai Liang^a, Yao-Yi Xu^a, Ya-Li Sun^a,
Jun-Fang An^a, Zi-Sheng Chao^{a, b, *}

^a *College of Chemistry and Chemical Engineering, State Key Laboratory of Chemo/Biosensing and Chemometrics, Hunan University, Changsha, Hunan 410082, China*

^b *College of Materials Science and Engineering, Changsha University of Science & Technology, Changsha, Hunan 410114, China*

**Corresponding authors: Prof. Zi-Sheng Chao;*

Tel & Fax: +86-731-88713257;

E-mail: zschao@yahoo.com; chao_zs@aliyun.com

1. Experimental

1.1 Materials

All the chemicals, sodium aluminate (Chemical Pure), colloidal silica solution (30 wt%), sodium hydroxide (Analytical Reagent), methylcellulose (average viscosity 20/mPa·s for a solution of 20 g/L at 20 °C) and ethanol (Analytical Reagent), were purchased from commercial companies, and they were used as purchased without further purification.

1.2 Synthesis of NaA zeolite seeds

A sodium silicate solution was first prepared by dissolving sodium hydroxide into colloidal silica solution under heating and stirring, and then, it was cooled to room temperature and mixed with sodium aluminate aqueous solution under agitation. This resulted in a synthesis gel with molar composition 5.85 Na₂O: 2.7 SiO₂: 1.00 Al₂O₃: 182 H₂O. After that, MC powders were dispersed into the above synthesis gel according to a weight ratio solid/ liquid = 1/ 11, at room temperature and under vigorous stirring. The resultant mixture was charged into a Teflon container and heated for 15 minutes in a household microwave oven (Panasonic NN-K5541JF) under ambient pressure and refluxing condition, using a microwave power of *ca.* 150 W. Finally, solid was recovered by centrifugation, washing with deionized water repeatedly, and then, dried at 383 K. The above-obtained solid was identified by XRD to be pure NaA zeolite and by SEM to possess an average crystal size of *ca.* 100 nm,

and it was employed to provide NaA zeolite seeds in the subsequent synthesis of NaA zeolite membrane.

1.3 Introduction of NaA zeolite seeds to α -Al₂O₃ support disc

Home-made porous α -Al₂O₃ discs (22 mm × 1.5 mm) with porosity of 68 %, and average pore size of 100–300 nm were employed as supports for the preparation of NaA zeolite membranes. The support discs were first polished by 1000 grit-sand paper, followed by pretreating in a 12 mol/L sodium hydroxide solution for 12 h, and then, ultrasonically cleaned with deionized water until pH = 7. After that, the support discs were dried at 383 K for 12 h, and they were directly subjected to the loading of NaA zeolite seeds, without cooling.

The NaA zeolite seeds were dispersed into ethanol, according to a ratio solid / liquid = 5 g / 1000 mL, and ultrasonically treated for 1 h. The resultant suspension was employed to load NaA zeolite seeds on the surface of support disc, using a hot dip-coating method ¹ described as follows: One side of a hot support disc (383 K) was kept in contact with the surface of NaA zeolite seeds suspension for 10 seconds, allowing an enough adsorption of NaA zeolite seeds onto the support disc. After that, the support disc was gently slid and pulled up from the surface of NaA zeolite seeds suspension, and then, it was dried at 383 K for 1 h. This hot dip-coating procedure was repeated for three times to enable a uniform distribution of NaA zeolite seeds on the surface of support disc. The

thus-obtained seeded support disc was employed in the subsequent synthesis of NaA zeolite membrane.

1.4 Preparation of NaA zeolite membrane without the addition of MC

A synthesis gel with molar composition 3 Na₂O: 2 SiO₂: 1 Al₂O₃: 200 H₂O was first prepared via the similar procedure as that for the synthesis gel in the preparation of NaA zeolite seeds. Then, a 30 mL of the above synthesis gel was carefully poured into a 50 mL Teflon reactor, in which the seeded support disc had been vertically mounted. After that, the reactor was transferred into a microwave oven (Panasonic NN-K5541JF) and heated for 15 min under ambient pressure and refluxing condition, using a microwave power of *ca.* 150 W. Finally, the support disc was washed with deionized water several times until pH = 7, followed by drying at 308 K in air for 3 h and at 323 K in vacuum overnight. The thus-obtained NaA zeolite membrane was named as M1. Basing on the M1 membrane as support, another membrane, namely M2, was also prepared by the same procedure as above for the M1 membrane.

1.5 Preparation of NaA zeolite membrane with the addition of MC

MC powder was first dissolved into the synthesis gel involved in section 1.4 at room temperature and under vigorously stirring, according to a weight ratio solid / liquid = 3.13 / 100. The obtained mixture was continuously stirred for 3 h, generating a MC-containing gel.

The same procedure as mentioned in section 1.4 for the preparation of M1 membrane was conducted, except that the M1 membrane was used as support (substrate membrane) and the above MC-containing gel as synthesis gel. The thus-obtained NaA zeolite membrane was named as M3 membrane.

1.6 Characterization of NaA zeolite membrane

X-ray diffraction (XRD) spectroscopy was conducted over a Bruker D8 Advance X-ray diffraction equipment, under the following conditions: Cu target $K\alpha$ ray ($\lambda = 1.54187 \text{ \AA}$); scanning voltage 40 KV; scanning current 40 mA; scanning speed 0.5 s; scanning step 0.02° .

Scanning electron microscopy (SEM) was carried out over a FEI Quanta-200 scanning electron microscope, operated at an accelerating voltage of 20 kV. The crystal size of NaA zeolite was measured by Nano Measurer software based on SEM photograph.

Fourier transform infrared spectroscopy (FT-IR) was performed with a Varian 3100 instrument, under the following conditions: wavelength 400 to 4000 cm^{-1} ; scanning number 32; resolution 2 cm^{-1} .

1.7 Evaluation of gas permeation

The evaluation of permeation performance of NaA zeolite membrane was carried out over a self-designed equipment, which was

similar as reported in the literature². The dried disc-shaped zeolite membrane, M1 or M3, was sealed in the permeation cell with the zeolite layer on the high-pressure side. The effective membrane area was ca. 2.01 cm². The pressure value of high-pressure side was determined by pressure gauge.

In the measurement of the permeation of single gas, the flow rate of permeated gas was determined by a soap-film flow meter. The permeances J (mol·m⁻²·s⁻¹·Pa⁻¹) and ideal permselectivity α were respectively calculated according to Eqns. (1) and (2):

$$J (\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}) = \frac{n}{St\Delta p} \quad (1)$$

$$\alpha_{A/B} = \frac{J_A}{J_B} \quad (2)$$

where n represented the moles of permeated gas and Δp the pressure difference between the two sides of zeolite membrane, respectively; S referred to the permeating area of zeolite membrane and t to the permeating time, respectively; A and B was the determined gases, respectively.

The permeation of binary mixture consisting of H₂ and another gas (CO, CO₂, N₂, CH₄ and C₃H₈) was measured using the Wicke-Kallenbach technique. The sweep gas was fed on the permeate side to take away as quickly as possible the permeated gas from the permeation cell. CH₄ was employed as sweep gas for the determination of H₂/N₂ and N₂ for that of

H₂/other gas, respectively. Both the fluxes of feed and sweep gases were regulated by mass flow controllers, and the composition of mixed gas was determined by a SP-6890 gas chromatograph. The real permselectivity for gas A over gas B in the mixed gas is calculated according to Eqn. (3):

$$\alpha_{A,B}^* = \frac{y_A/y_B}{x_A/x_B} \quad (3)$$

where y_A and y_B were the mole fractions of gas A and B in the permeate gas and x_A and x_B the corresponding mole fractions in the feed gas, respectively.

2. Results and discussion

2.1 XRD characterization

Fig. S1 shows the full width at half maximum (FWHM) of XRD peak at $2\theta = 7.26^\circ$ ((200) diffraction) for various membranes. The FWHM can be employed to evaluate the size of particles of crystals, according to Scherrer equation (eqn (4)):

$$D = K\lambda/\beta\cos\theta \quad (4)$$

where D is the average size of the ordered (crystalline) domains, which may be smaller or equal to the grain size; K is a dimensionless shape factor, usually with a value of ca. 0.9; θ is the Bragg angle; β is the line broadening, obtained via subtracting the instrumental line broadening

from FWHM. One can see that the FWHM for the membranes has an order $M3 > M2 > M1$. The calculation based on Fig. S1 shows that the average sizes of NaA crystals are 312.4, 59.4 and 49.0 nm for M1, M2 and M3 membrane, respectively, which are smaller than those obtained from SEM micrographs (see Fig. 3). It is indicated that the crystals as observed from SEM micrographs are in fact the aggregations of smaller crystals of NaA zeolite. One may have noted that the average size of NaA crystals

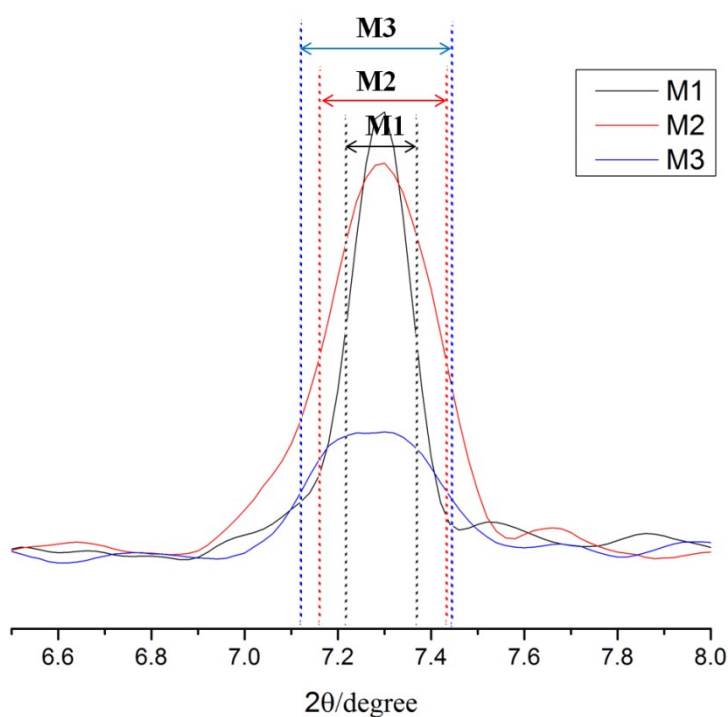


Fig. S1 XRD spectra at $2\theta = 7.26^\circ$ for various membranes. The double-headed arrow illustrates the full width at half maximum (FWHM) of the XRD peak.

from XRD determination is larger for the M1 membrane than for the M2 membrane; however, the order of the average size of NaA crystals from SEM identification for the two membranes is reversed. This may be most probably due to the Ostwald ripening effect, i.e., during the formation of the M2 membrane, with the M1 membrane as support, a proportion of NaA zeolite crystals, particularly those with smaller size, may become smaller due to their partial dissolution by the caustic synthesis solution, while another proportion of NaA zeolite crystals become larger due to their continuous growth in the synthesis solution. The presence of smaller crystals of NaA zeolite contributes to the broadening of the XRD peak for the M2 membrane than for the M1 membrane. This result also hints that the crystal size distribution of NaA zeolite for the M2 membrane should be wider than for the M1 membrane, and also, the crystal size distribution curve for the M2 membrane can be expected to possess dual peaks. In fact, the above deductions have been evidenced by the determination of crystal size distribution, as shown in Fig. S3. Nevertheless, the result derived from Fig. S1 indicates that the NaA zeolite crystals for the M3 membrane are smaller than for the M1 and M2, being consistent with that derived from Fig. 3 (SEM characterization).

2.2 FT-IR characterization

Fig. S1 shows the FT-IR spectra for NaA zeolite powders synthesized with the addition of MC, before and after the removal of MC by washing

repeatedly with deionized water. As a comparison, the FT-IR spectrum of pure MC is also included in Fig. S1. The characteristic peaks of pure MC employed in this work (Fig. S1 a) are well consistent with those reported in the literatures³. The band at 2924 cm^{-1} is attributed to the C-H asymmetric stretching vibration and that at 1056 cm^{-1} to the C-O-C stretching mode, the band at 941 cm^{-1} is related to OCH_3 group, while the bands 1377 cm^{-1} and 1466 cm^{-1} are assigned to the C-OH vibration and CH_2 scissoring vibration, respectively. These bands are present over the NaA zeolite before the removal of MC (Fig. S1 b) but absent after the removal of MC (Fig. S1 c), indicating clearly that MC has been removed completely after washing repeatedly with deionized water. In addition, the characteristic peaks of NaA zeolite synthesized in this work are same with those reported in the literature⁴. The bands at 1008 and 672 cm^{-1} are respectively attributed to the T-O-T (T = Al or Si) asymmetric and symmetric stretching vibrations and that at 467 cm^{-1} to the T-O bending mode. The band at 560 cm^{-1} is related to the presence of double 4 ring dominating secondary building unit in the LTA zeolite structure, which demonstrates that considerable amount of amorphous precursor gel have been transferred into crystalline NaA zeolite⁵.

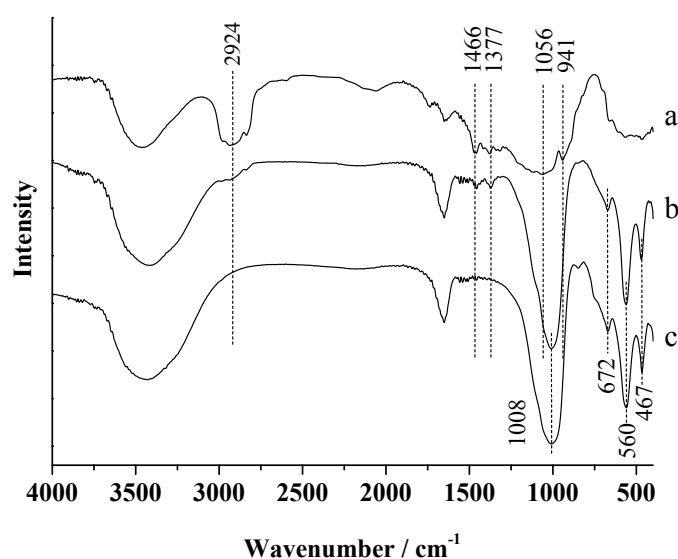


Fig. S2 FT-IR spectra of (a) commercial pure MC; (b) synthesized NaA zeolite without removing MC and (c) synthesized NaA zeolite with removing MC repeatedly with deionized water.

2.3 Determination on crystal size distribution

The crystal size distribution is measured by Nano Measurer software based on SEM photograph. From SEM micrograph, 100 points are randomly selected for the calculation of crystal size, resulting in the crystal size distribution curve, as shown in Fig. S3. One can see that the average crystal size for the M3 membrane is about 350 nm, being much smaller than those of M2 (*ca.* 1200 nm) and M1 (*ca.* 700 nm). In addition, the crystal size distribution of M3 is narrower (from 100 nm to 600 nm) than those for M1 and M2. It should be noted that the M2 membrane exhibits a bimodal distribution of crystal size, and this can be due to the Ostwald ripening effect as mentioned in the discussion on Fig. S1.

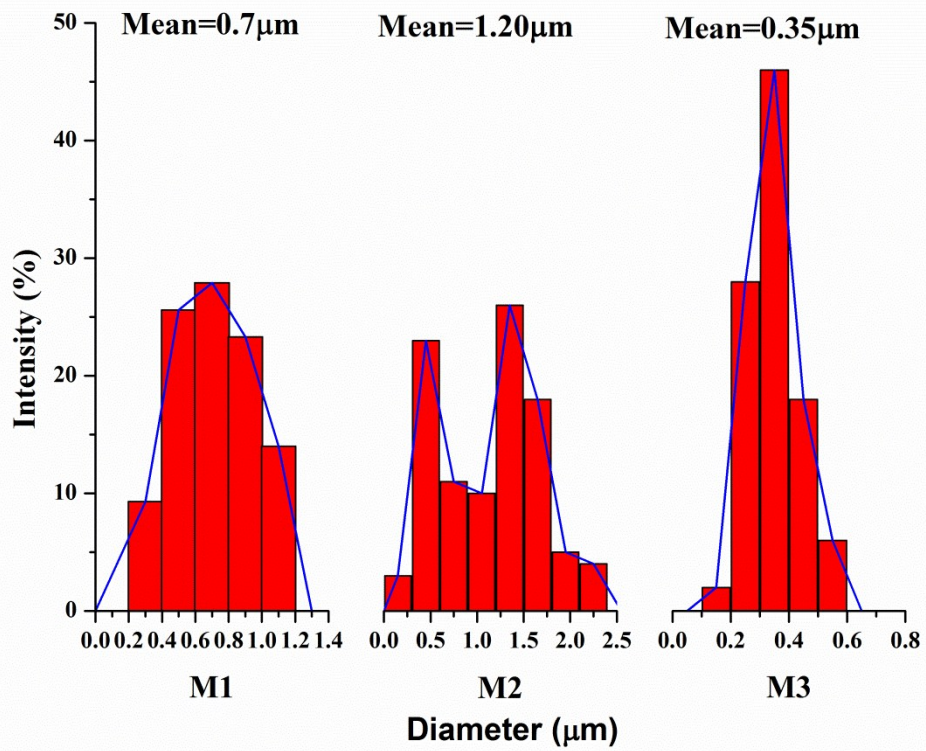


Fig. S3 Crystal size distributions of NaA zeolite for the M1, M2 and M3 membranes.

References

- 1 H. Li, J. Wang, J. Xu, X. Meng, B. Xu, J. Yang, S. Li, J. Lu, Y. Zhang and X. He, *J. Membr. Sci.*, 2013, **444**, 513.
- 2 A. Huang, F. Liang, F. Steinbach and J. Caro, *J. Membr. Sci.*, 2010, **350**, 5.
- 3(a) D. Maity, M. M. Mollick, D. Mondal, B. Bhowmick, M. K. Bain, K. Bankura, J. Sarkar, K. Acharya and D. Chattopadhyay, *Carbohydrate polymers*, 2012, **90**, 1818; (b) W. Siriprom, S. Kongsriprapan and K. Teanchai, *Advanced Materials Research*, 2014, **979**, 307.
- 4 P. Sharma, J.-g. Yeo, D. K. Kim and C. H. Cho, *J Mater Chem*, 2012, **22**, 2838.
- 5 L. Itani, Y. Liu, W. Zhang, K. N. Bozhilov, L. Delmotte and V. Valtchev, *Journal of the American Chemical Society*, 2009, **131**, 10127.