

## Support Information

# Synthesis of NaA zeolite membrane by maintaining pressure difference between the two sides of the support

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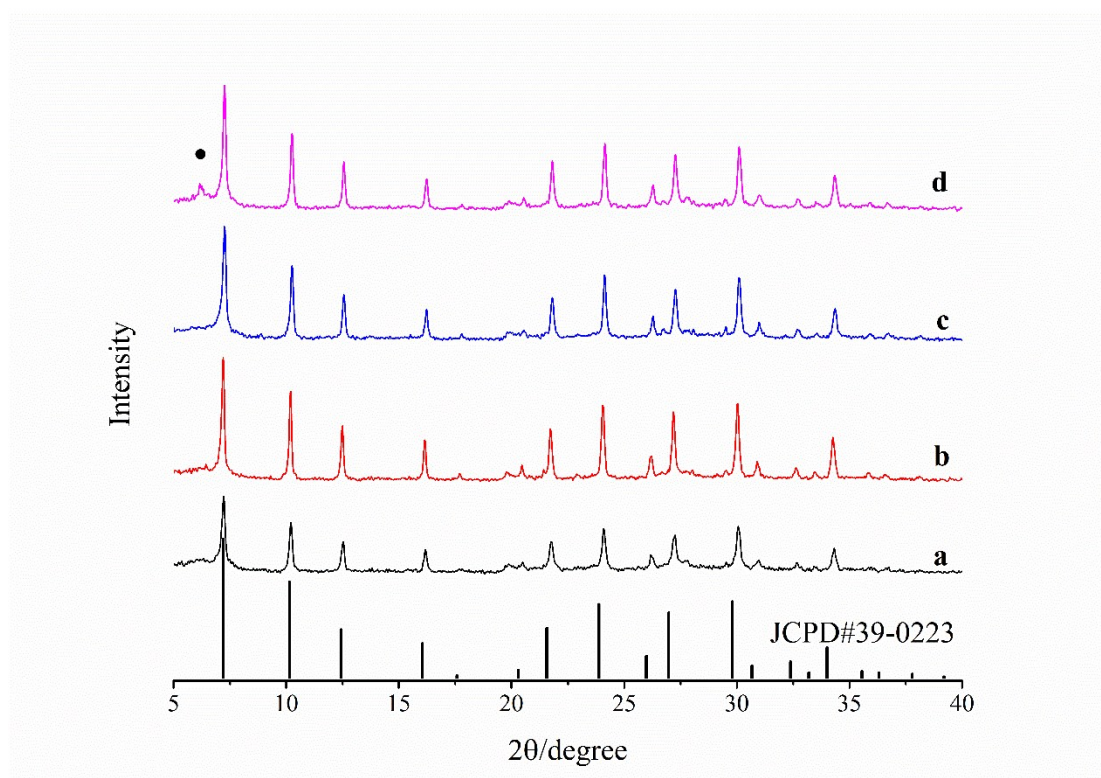
## **1. Synthesis of NaA zeolite seeds**

NaA zeolite seeds were synthesized with space confinement additive described by Wang *et al.*<sup>1</sup>, and employed microwave heating method. 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 Na<sub>2</sub>O: 2.7 SiO<sub>2</sub>: 1.00 Al<sub>2</sub>O<sub>3</sub>: 182 H<sub>2</sub>O. After aging for 12h at 298K, 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.

## **2. XRD patterns of the powders**

### **2.1 XRD patterns of the powders synthesized at different**

## temperatures

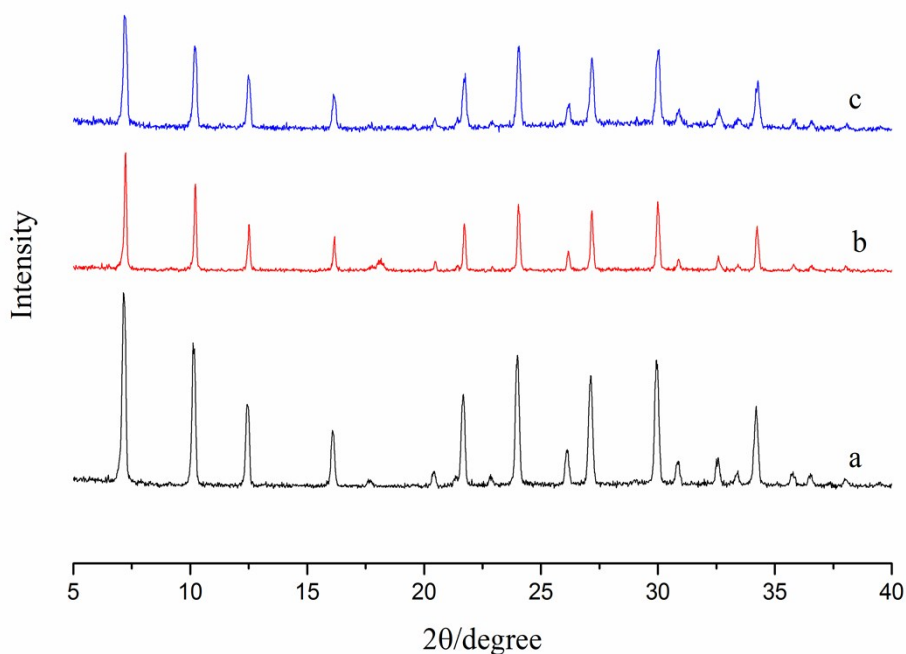


**Fig. S1** XRD patterns of powders generated accompanied by the zeolite membrane synthesis at different temperatures; (a) M2 membrane; (b) M3 membrane; (c) M5 membrane and (d) M6 membrane. (The peak marked by the symbol ● is NaX zeolite and the other peaks are NaA zeolite. The standard diffraction pattern for NaA zeolite (JCPDS#39-0223) is also shown by the vertical lines above x axis).

**Fig. S1** shows the XRD patterns of powders generated accompanied by the zeolite membrane synthesized at different temperatures. It is found that the XRD peak intensity for NaA zeolite is particularly weak and a broad peak from  $20^\circ$  to  $30^\circ$  is appeared at M2 membrane, indicating that the crystallinity of the NaA zeolite crystal is not high and some amorphous materials are still present after synthesizing at  $60^\circ\text{C}$  for 12 h. The peak intensity of NaA zeolite gradually increases with the synthesis

temperature, indicating a higher degree of crystallinity at higher temperature. However, besides NaA zeolite crystals, the diffraction peak of NaX zeolite appears when the synthesis temperature up to 90 °C, meaning that the type of zeolite crystal transforms from NaA zeolite to NaX zeolite at high temperature. This occurrence can be attributed to the fact that the higher of the synthesized temperature, the more favorable for the crystal growth until the temperature is so high that the type of crystal exchanges, which is agreed with the references <sup>2 3</sup>.

## 2.2 XRD patterns of the powders synthesized at different pressure difference produced by vacuuming



**Fig. S2** XRD patterns of powders generated accompanied by the zeolite membrane synthesis at different pressure difference produced by vacuuming: (a) M7 membrane; (b) M8 membrane and (c) M9 membrane.

The powders deposited in the reactor during the synthesis process are also collected and characterized by XRD. However, no powders are collected during the M10 membrane synthesis process due to the pressure difference between the two sides of the support is so great that all of the synthesis solution flows out from the inside of the support. Fig. S2 shows the XRD patterns of powders generated accompanied by the zeolite membrane synthesis at different pressure difference produced by vacuuming. It is found that the XRD patterns of the all the powders are consistent well with the standard peaks of NaA zeolite (JCPDS file #39-0223), indicating that a pure-phase NaA zeolite is obtained after synthesis at 60 °C for 24h. It also turns out that a NaA zeolite layer has been formed on the surface of all the supports. Meanwhile, one can see that the peak intensity for NaA zeolite gradually decreases with the pressure difference. This occurrence can be attributed to the fact that the greater of the pressure difference between the two sides of the support, the more water in the synthesis solution flows out from the inside of the support, making the increase of the alkalinity. The high alkalinity is not only unfavorable to the conversion of the Si/Al active ingredients into zeolite crystals, but also will dissolve and destroy the original zeolite crystals. Accordingly, the peak intensity for NaA zeolite gradually decreases with the pressure difference.

### **3. Reproducibility of M8 membrane**

Table S1 The repeat results of M8 membrane

number	1	2	3	4	5	6	7	8	9	10
H <sub>2</sub> (mol/m <sup>2</sup> s <sup>-1</sup> Pa <sup>-1</sup> )	3.67 E-05	1.88 E-05	1.45 E-05	8.90 E-06	8.22 E-06	4.33 E-06	3.99 E-06	3.01 E-06	2.73 E-06	1.11 E-06
N <sub>2</sub> (mol/m <sup>2</sup> s <sup>-1</sup> Pa <sup>-1</sup> )	1.04 E-05	4.87 E-06	3.72E -06	2.15 E-06	1.90 E-06	8.64 E-07	7.64 E-07	5.63 E-07	4.93 E-07	1.95 E-07
$\alpha(\text{H}_2/\text{N}_2)$	3.54	3.86	3.90	4.13	4.33	5.01	5.22	5.35	5.54	5.70

In order to determine the reproducibility of M8 membrane, the repeat experiment is carried out with ten ceramic tubes and the detailed results are list on Table S1. From the table, one can see that, five samples show both the permeances and the permselectivities of H<sub>2</sub> over N<sub>2</sub> are closed to the results of M8 membrane (Selectivity ranged from 5.00 to 5.70), meaning that the reproducibility of M8 membrane reaches to 50%. According to the statistical of the permselectivity, it is found that the average permselectivity is 5.34 and the standard deviation is 0.25. However, the selectivities of the remaining ceramic tubes are closed to Knudsen diffusion coefficient and the permeances are significantly higher than that of other tubes, meaning that defects exist in the zeolite membranes. The porous supports used for the grown of zeolite membrane may cause seeds infiltrate into the pores, resulting in reduced the density of the seed layer and the compactness of the zeolite membrane<sup>4</sup>. In any case, to a certain extent, the repeat experiment illustrates the feasibility of this strategy.

## References

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