

Preparation of Zeolite T Membranes with Different Ratios of Water and SiO₂

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ABSTRACT

In the present work, effect of water content in the synthesis solution on the membrane performance and structure was studied. It was found that water content will affect the compactness and thickness of the functional layer. It also affected the crystal size and morphology. When the $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ was 20, the membrane showed rod zeolite T crystals. More water will cause thinner zeolite membrane and loose structure with some defects. When $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ reached 30, dense zeolite T membrane was formed with rod crystals. The obtained T-type zeolite membranes were used to separate isopropanol/water mixed solution containing 90 wt.% isopropanol at 348 K, the permeation flux was $3.34 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and the separation coefficient was 2536.

Keywords: Zeolite T membrane, pervaporation, isopropanol, dehydration

1.0 INTRODUCTION

Pervaporation (PV) including vapor permeation (VP) has attracted researchers' attention because of its energy saving and environmental friendliness for the separation of organic solvents, especially for azeotropes and close-boiling mixtures [1]. Due to the good chemical and thermal stability, uniform zeolite pores, adsorption and molecular sieving, zeolite and corresponding membranes showed efficient and selective separation performance [2, 3]. Zeolite A membranes with high hydrophilicity are good for alcohol dehydration and have been commercialized for the dehydration of solvents and biofuels in small- to medium-scale plants [4, 5]. However, zeolite A membranes [6] were unstable under acidic conditions

because Al content in the zeolite LTA framework will dissolve in an acidic media. T type zeolite membrane with relatively high hydrophilicity and good acid resistance [7, 8] was found to be potential candidate, which can be applied in pervaporation and vapor permeation dehydration organics especially in acid conditions.

There are many studies have been made to synthesize and utilize T-type zeolite membranes. Okamoto *et al.* [8] obtained zeolite T membrane, which showed stable results in 50 wt. % acetic acid/water solution at 348 K for 7 days, neither Si/Al ratio nor XRD pattern changed. Yang *et al.* [9] synthesized zeolite T membranes and studied their hydrothermal stability for in 20 wt. % ethanol/water mixtures and acid stability for the same solution after adding acetic acid to pH 3 at 338

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K for 164 h, indicating good hydrothermal and acid stability. Kita *et al.* [10] also applied zeolite T membrane for ethanol/water mixtures and ethanol/water/acetic acid mixtures, which displayed good stability. Gu *et al.* [11] developed zeolite T membrane on the hollow fibers supports, good acid stability were obtained by them. Wang *et al.* [12] utilized ultrasonic-assisted pretreatment prior to hydrothermal synthesis to prepare T-type zeolite membranes on Al₂O₃ hollow fibers. Zhou *et al.* [13] prepared zeolite T membranes on the α -Al₂O₃ tubes by microwave-assisted hydrothermal synthesis, which was the first time to change the way of heating on zeolite T membrane preparation. Zhou *et al.* [14] first reported the preparation of zeolite T membranes on mullite supports in a clear solution. In their work, the crystallization temperature of membranes was high to 423 K and the pervaporation flux of zeolite T membranes was improved significantly. Subsequently, they [15] added F⁻ into synthesis solutions and successfully obtained high flux zeolite T membranes in fluoride media.

Although there are a lot of work focused on the preparation of zeolite T membrane. The application of zeolite T membrane in dehydration of organic mixtures is still little. First of all, the preparation method of zeolite T membrane is often complicated which often needs long synthesis time and some toxic additives. Also, the cost of supporting membrane with precise pores is relatively high [16, 17]. In this work, zeolite T membranes with high performance was prepared with one step synthesis method in an organic template-free solution, which only require a short synthesis time and without additives. In order to decrease the cost of the zeolite T membrane, macroporous α -alumina tubes with average pore size of 2 μ m were

selected as the supporting membrane. The effect of water content on the growth and performance of the zeolite T membranes on macroporous Al₂O₃ tubes was investigated systematically to reveal the formation evolution process of the zeolite T membranes. Furthermore, the pervaporation performance for isopropanol/water mixtures was evaluated.

2.0 EXPERIMENTS

2.1 Materials

Tetramethylammonium hydroxide (TMAOH, 75 wt.%, Alladin, Shanghai, China) was used as template in the preparation of seeds. NaOH, KOH and NaAlO₂ (analytical grade, Sinopharm Chemical Reagent Co., Ltd, Shanghai, China) were used as alkali and Al source. Silica sol (40 wt. % in water, Aldrich) was used as silica source. Macroporous α -alumina tubes (porosity: 30%~40%; average pore size: 2 μ m; outer diameter: 13 mm; inner diameter: 9 mm; length: 5 cm, Foshan Ceramics Research Institute (FCRI), China) were served as supporting membranes.

2.2 Preparation of Zeolite T Membranes

The traditional hydrothermal method was used to prepare zeolite T seed crystals with TMAOH used as template. The molar composition of the synthesis solution was 20 SiO₂:1 Al₂O₃:5.2 Na₂O:1.8 K₂O:600 H₂O:1.8 TMAOH. The alkali source and template TMAOH were dissolved in deionized water in a beaker. Then add silica sol to the liquid drop by drop, continue to stir (aging) at room temperature for a certain time. After 72 h crystallization, the precursor solution is poured into the autoclave which is

sealed and placed in the oven at 100°C for hydrothermal crystallization. The product was washed with deionized water to neutral, and dried at 80 °C. At last the product was placed in muffle furnace at 550 °C for calcination.

Zeolite T membranes were hydrothermally synthesized on macroporous α -alumina tubes. The surfaces of the tubes were polished with 800 and 1500 grit-sand paper and cleaned with deionized water before utilization. 3.0 wt.% seeds suspension was prepared with the assistance of ultrasonic for 30 min to avoid the formation of aggregates. The outer surface of support was immersed into the 3.0 wt.% seeds suspension by vacuum seeding method for 30 s contact time. Then the support was dried at 483 K for 3 h. After cooling down, the outer surface of the support was rubbed carefully to remove the exterior large seeds until there were no obvious seeds on the surface. At last, the dried seeded support was calcined at 453 K for 3 h to consolidate the seed

layer and remove the template in the crystals.

The seeded support tube was sealed with Teflon caps at both ends and placed vertically in a Teflon autoclave filled with an organic template-free synthesis solution. The synthesis solution was obtained by mixing aluminate solution with silica sol. The aluminate solution was prepared by dissolving KOH and NaOH in deionized water, then adding NaAlO₂ into the solution until the solution became clear. Subsequently, the silica solution was added dropwisely. The synthesis solution was aged in water bath and vigorously stirred for 24 h at 298 K. The resulted autoclave containing the seeded support and synthesis solution was moved to a 423 K preheated oven for 4 h crystallization reaction. The resultant membrane was thoroughly washed with water and dried at 373 K for several hours. The synthesis conditions of the membranes are listed in Table 1.

Table 1 The Synthesis Conditions for the Membranes

Samples	Solution composition	Synthesis time	Synthesis temperature
M1	20 SiO ₂ :1 Al ₂ O ₃ :5.2 Na ₂ O:1.8 K ₂ O:400 H ₂ O	4 h	423 K
M2	20 SiO ₂ :1 Al ₂ O ₃ :5.2 Na ₂ O:1.8 K ₂ O:500H ₂ O	4 h	423 K
M3	20 SiO ₂ :1 Al ₂ O ₃ :5.2 Na ₂ O:1.8 K ₂ O:600 H ₂ O	4 h	423 K
M4	20 SiO ₂ :1 Al ₂ O ₃ :5.2 Na ₂ O:1.8 K ₂ O:700 H ₂ O	4 h	423 K
M5	20 SiO ₂ :1 Al ₂ O ₃ :5.2 Na ₂ O:1.8 K ₂ O:800 H ₂ O	4 h	423 K

2.3 Characterization of Zeolite T Membranes

The morphologies of zeolite T seeds and as-synthesized membranes were characterized by X-ray diffraction (XRD) with a Philips Analytical X-ray

diffractometer using Cu K α radiation (30 mA and 40 kV) and scanning electron microscopy (SEM) using a NOVA NANO SEM 450 (FEI Company) at an acceleration voltage of 20 kV. Before scanning, the membranes are coated with gold. The

composition of the membrane was characterized with X-ray photoelectron spectroscopy (XPS USA Thermo Fisher ESCALAB 250 X).

2.4 Pervaporation Measurements

The properties of zeolite T membranes were evaluated by pervaporation separation of 90 wt.% isopropanol/water mixtures by using a laboratory-scale batch PV experimental apparatus. The feed solution was continuously pumped into the module. The pervaporation tests were controlled by thermocouple at 348 K. The inside of the membranes was connected by a vacuum pump and the permeate was collected by a cold trap cooled by liquid nitrogen with a pressure of 200 Pa. The concentrations of the feed and permeate solution were characterized with a gas chromatograph (GC7890T, Techcomp, Shanghai, China). The separation performance of membranes was evaluated by the permeation flux (Q , $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and the separation factor (S.F., α). The permeation flux was calculated by the mass of the permeate in a given time interval. The membrane

S.F. was defined as:

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

where X_A and X_B denote the mass fraction of components A and B respectively in the feed side, respectively; Y_A and Y_B the mass fractions of components A and B in the permeate that is collected by a cold trap cooled by liquid N_2 , respectively; A and B represent for water and isopropanol component, respectively.

3.0 RESULTS AND DISCUSSION

3.1 Preparation of Zeolite T Membrane

The seeds used in this work were characterized with SEM and XRD as shown in Figure 1. Figure 1a was the SEM of the seeds, which showed about 2~3 μm in size. Figure 1b showed the XRD patterns of the zeolite T seed. The characteristic peaks of zeolite T ($2\theta=7.7^\circ$, 13.3° , 20.5° , 23.7° , 31.4°) demonstrates the successful preparation of zeolite T seeds.

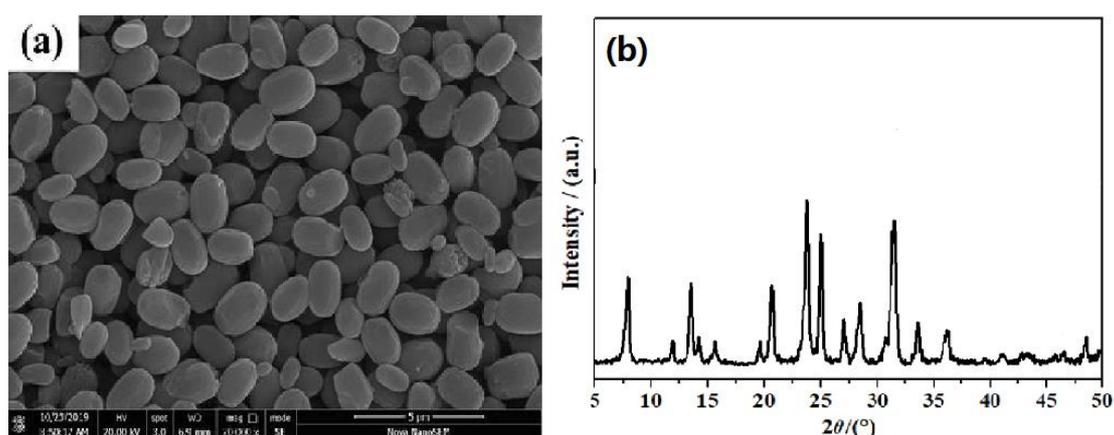


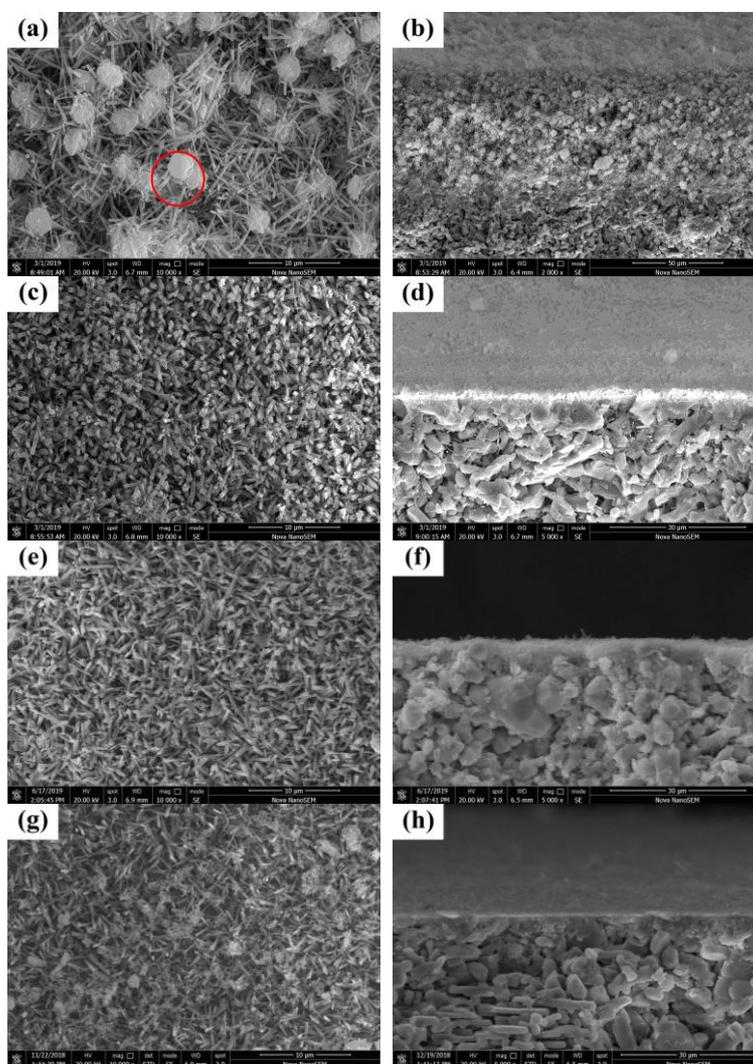
Figure 1 SEM and XRD patterns of large T zeolite seeds

During zeolite T membrane preparation, synthesis solution parameters especially the water content

affect the membrane compactness and PV performance obviously because water content will directly affect the

dispersion of the solute in the synthetic gel and overall uniformity of the synthetic solution. So the water content in the synthesis solution will determine the amount of nutrients, and then affect the crystalline form, morphology and PV properties of the synthesis membrane. In this work, different water/SiO₂ ratios 20, 25, 30, 35 and 40 were investigated to prepare zeolite T membrane with high performance. As shown in Figure 2, the membrane M1 showed loose structure in the surface. Also, the membrane layer showed relatively high thickness but large

pores which is negative to the PV performance. When the water content was increased, the crystals in the membrane surface are all zeolite T. When the ratio of n(H₂O):n(SiO₂) was 30, the prepared membrane M3 is very dense without defects in the surface. The membrane thickness was about 5 μm. However, when the water content was increased further, the crystals in the membrane surface became thin. Maybe the dilute synthesis solution causes less crystals and loose structure. So membrane M3 was studied in detail.



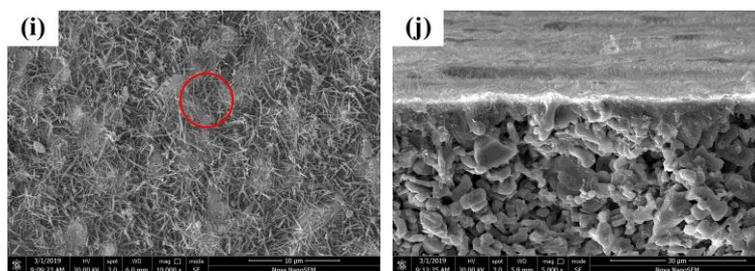


Figure 2 Surface and cross section SEM images of T-type zeolite membranes synthesized with different $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ ratios ((a, b)-M1; (c, d)-M2; (e, f)-M3; (g, h)-M4; (i, j)-M5)

The membranes are characterized with EDS and the results are shown in Figure 3. It was found that the Al content was increased with the water content and Si content was decreased gradually in contrast. The ratios of $n(\text{Si})/n(\text{Al})$ were 4.2, 2.3, 1.7, 1.1 and

0.8, respectively which caused by the decreased concentration of synthesis solution. All the membranes showed high peaks of Al because the EDS characterization penetrated the thin layer and detected the Al_2O_3 membrane.

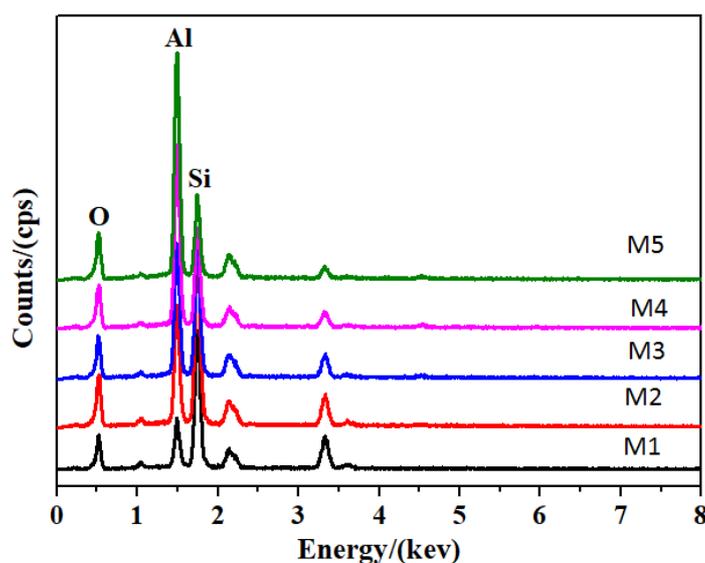


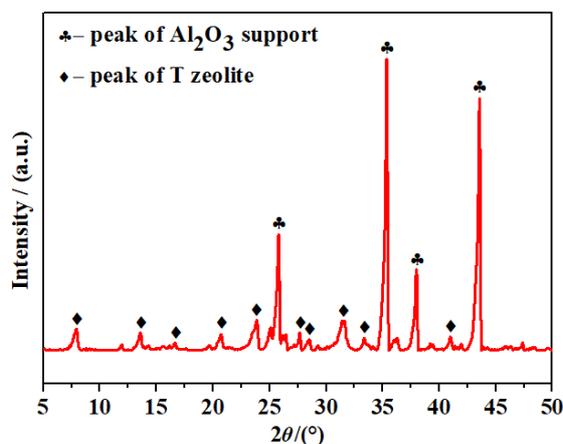
Figure 3 EDS images of T-type zeolite membranes synthesized with different $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ ratios

The membrane M3 with $30n(\text{H}_2\text{O}):n(\text{SiO}_2)$ was characterized with XPS and XRD. As shown in Table 2, the corresponding Atom content of Al2p and Si2p was 22.1% and 77.9%, respectively. The silica-alumina ratio is 3.5 which is in accordance with the T zeolite. As shown in Figure 4, except

the peaks of supporting layer, they are all of the characteristic peaks of T (zeolite $2\theta=7.7^\circ, 13.3^\circ, 20.5^\circ, 23.7^\circ, 31.4^\circ$) which further demonstrates the successful preparation of zeolite T membrane.

Table 2 XPS data of membrane M3

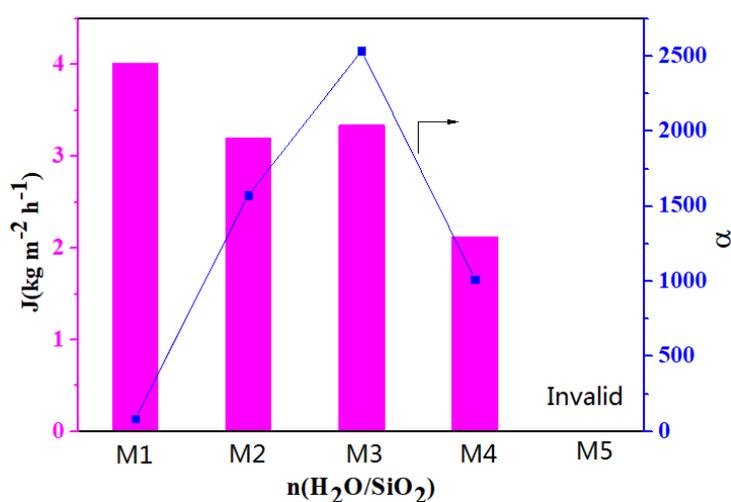
Name	Height CPS	FWHM (eV)	Area (P) CPS.(eV)	Area (N) TPP-2M	Atomic (%)
Al2p	1058.43	1.39	1726.72	0.07	22.1
Si2p	5409.56	1.66	9734.27	0.24	77.9

**Figure 4** XRD patterns of membrane M3

3.2 PV of IPA/Water Mixture

Zeolite T membranes prepared with different water/SiO₂ ratios are carried PV test at 348 K for 90 wt. % isopropanol/water separation. As shown in Figure 5, the membrane M5 was invalid because of many defects in the functional layer. Membrane M1

showed high flux but low separation factor. For the membrane M3, it showed high permeation flux and separation factor because of dense and thin functional zeolite membrane layer. During the separation of isopropanol/water mixed solution, the permeation flux reached 3.34 kg·m⁻²·h⁻¹ with a high separation factor of 2536.

**Figure 5** Pervaporation performance of membranes M1~M5 synthesized with different $n(\text{H}_2\text{O}) / n(\text{SiO}_2)$ ratios

4.0 CONCLUSION

In the present work, dense zeolite T membrane was synthesized in clear liquid in 5 h. They are characterized by XRD, SEM, EDS, XPS and PV test. When 2 μm seed was used, the prepared membrane showed smooth and flat surface which can effectively coat the porous Al_2O_3 supporting layer. Effect of water content in the synthesis solution on the membrane performance and structure was studied in detail. When $n(\text{H}_2\text{O})/n(\text{SiO}_2)$ reached 30, dense zeolite T membrane was formed with rod crystals. When it was used to separate isopropanol/water mixed solution containing 90 wt.% isopropanol at 348 K, the permeation flux was $3.34 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ and the separation coefficient was 2536.

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