Study on the Mechanism of Placed Ways of Seed Layer by Secondary Growth of MFI-type Zeolite Membranes Using Microwave

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Abstract. Effects of the placed ways of seed layer on secondary growth of MFI-type zeolite membranes using microwave was researched. The thickness of film was uneven and there were a large deposit on film surface while the seed layer upwards and vertical in synthetic reaction using microwave method, and MFI zeolite membrane surface was uneven with partial seeds falling off while the seed layer downwards.

Keywords: MFI-type Zeolite Membranes; Placed Ways of Seed Layer; Microwave.

1. Introduction

Zeolites are crystalline with well-defined pores of molecular dimensions as well as chemical and thermal stabilities [1-3]. Over the last decade increasing attention has been paid to the development of zeolite membranes, due to the successfully application of such membranes in a wide range of chemical industries including separation [4], catalytic reaction [5], chemical sensors, and microelectronic devices [6].

Significant progress has been achieved in the last years on microwave synthesis of zeolite membranes. NaA zeolite membranes were microwave synthesized on alumina support by Han et al. in 1999 [7]. Microwave heating greatly accelerated the crystalliza-tion rate and reduced the synthesis time to 10 min. In many cases, microwave synthesis has proven to remarkably reduce the synthesis time. Traditional MFI zeolite membrane hydrothermal synthesis needs more than ten hours [8-12], and synthesis time can be shortened by microwave hydrothermal synthesis [13-19].

A large number of publications reports on the synthesis of silicalite-1 membranes by a secondary growth method from seeded supports with microwave heating. Many synthesis parameters have been studied, such as the morphology, thickness, homogeneity, crystal preferential orientation and single gas permeation properties by Julbe et al [16, 17]. However, the placed ways of seed layer on substrates, which is an important factor in a secondary growth with microwave heating, is neglected in earlier researches.

The MFI-type zeolite membranes in this work were synthesized by a secondary growth on alumina substrates with microwave to reduce synthesis time. The placed ways of seed layer on substrates, as an important factor influencing the film-forming process, was detailed studied and discussed.

2. Experimental

2.1 Second Growth of MFI Zeolite Membrane Using Microwave Heating

MFI zeolite membranes were prepared on porous alumina substrates by using a secondary growth of seed layers. The supports used for zeolite membrane preparation were home-made α-Al2O3 disks, 2 mm thick and 20 mm in diameter. The treated a-Al2O3 substrate was seeded with silicalite-1 crystals by using a spin coater (TC108, sile corporation). Only one side was coated with seeds. The

MFI (silicalite-1) seeds (130 nm diameter) was prepared as previously reported [20]. In the process of spin-coating, the substrate was vacuum-locked, and dripped with 0.3 ml of colloidal silicalite-1 suspension (20g/L) using a injector. A uniform seed layer was prepared at a spinning rate of 4000 rpm for 40 s, which was accelerated at 2000 rpm/s. After being dried, the substrate was held by a Teflon holder with the seed layer upwards, vertical and downwards in the synthetic solution. The molar composition of the synthetic solution was 1TEOS: 0.2TPAOH: 200H2O.

A Berghof microwave MWS-2 was used for synthesizing the MFI zeolite mem-branes. About 30 ml precursor solution was used which filled about 2/3 of the vessels total capacity. In all synthesis experiments, a full MW power of 400W was used for the temperature ramping period. The synthesis duration was varied at 90min and temperature 448 K.

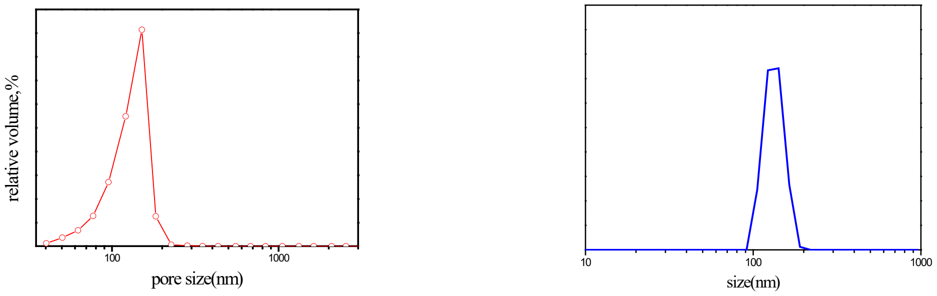
2.2 Characterization

The pore distribution of the home-made α-Al_2O_3 disks was characterized by Auto Pore IV 9500 (Micrometrics Instrument Corporation). The size distribution of the silicalite-1 seeds was investigated by Nano ZS90 (Malvern Corporation). The morphology of silicalite-1 films was investigated by scanning electron microscope (SEM, Philips XL30ESEM) operated at 20 kV.

3. Organization of the Text

3.1 Pore Size Distribution of Matrix and Particle Size Distribution of MFI Zeolite

Figure 1 presents that average pore diameter of α-Al_2O_3 substrates is 145 nm and mean size of silicalite-1 seeds is 130 nm. The mean size of silicalite-1 seeds is consistent with the literature [20], closing to the pore size of α-Al_2O_3 matrix.



(**a**) (**b**)

Figure 1. (**a**) pore distribution of α-Al_2O_3 disks, (**b**) size distribution of the silicalite-1 seeds.

3.2 Influence Mechanism of the Placed Ways of Seed Layer on Substrates to Forming MFI Zeolite Membrane

The surface morphology and cross-section of silicalite-1 membranes prepared with seeds layer upwards is shown in Figure 2. The thickness of film was uneven as seen in figure 2(b), and figure 2(a) indicated there was a large deposit on film surface.

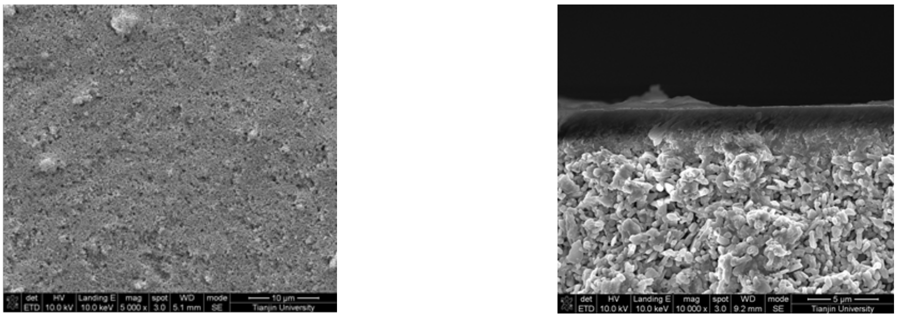
(**a**) (**b**)

Figure 2. SEM images of the membrane (**a**) top view and (**b**) cross section (seeds layer upwards)

A large number of crystal nucleus or crystal precursors with different size nucleate instantaneously with microwave. Useful components and useless components are produced on the surface of film respectively during hydrothermal synthetic process. Useful components referring to inter-grow to eliminate defects in zeolite membrane increase the active force between zeolite membrane and support. Useless components referring to hinder the efficient chemical crosslinking of useful components in forming continuous zeolite membrane lead to the generation of defects in zeolite membrane.

Figure 3. Sketch map of seeds layer upwards

The deposit to the membrane surface with the zeolite layer upwards for the second-time seeded growth under the condition of gravity, either in traditional hydrothermal way or microwave method, caused the membrane thicker and surface uneven, prone to defects, as shown in Figure 3.



(**a**) (**b**)

Figure 4. SEM images of the membrane (a) top view and (b) cross section(seeds layer vertical)

Figure 5 shows SEM top section and cross-section views of the film with the seeds layer vertical in growth. In the figure, there are still deposits on membrane surface. Generally speaking, membrane prepared with traditional hydrothermal method was good quality as tsapatsis reported[21] with seeds layer vertical in growth. Heating up and the nucleation rate are both slow in traditional progress, and then the accumulation rate is slow compared with the crosslinking rate, so the impact of useless component is small. However, deposition rate is greater than the speed of inter-growing for microwave method due to a large number of nucleation instantaneously and surface deposition occurred, causing the defects, which illustrates in Figure 5.

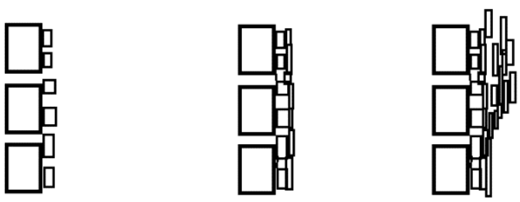


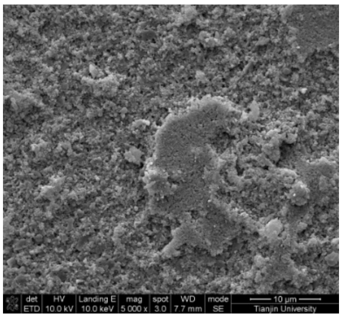
Figure 5. Sketch map of seeds layer vertical

And our experiments result in Figure 5 supports this hypothesis. So a thought comes out that the deposit impact of useless components maybe be eliminated by keeping the seeds layer downward in synthetic solution for the second growth like Figure 6a. Figure 7 shows the top section and cross-section of the film obtained by secondary growth with the seed layer downward at 448k when it grows.

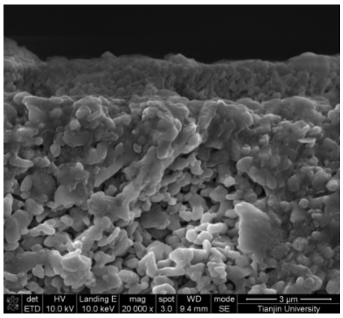
New problems occurred while the seed layer downward in microwave synthesis. MFI zeolite membrane surface was uneven with partial seeds falling off and continues film is not formed.

Figure 6. Sketch map of seeds layer downward (a) ideal situation (b) actual situation

There are two reasons for above phenomena. One, initial crosslinking did not produce due to the rapid nucleation without further intergrown of film. The other, the seeds fall off easily due to gravity with seeds layer downward. Therefore, repeatability of preparing film is low. Synthesis model illustrates in Figure 6b. The force between the substrate and the seed needs to be strengthened to prevent the crystal seeds in synthetic solution falling off due to gravity.



(a)



(b)

Figure 7. SEM images of the membrane (a) top view and (b) cross section(seeds layer downward)

4. Conclusion

It was found that the placed ways of seed layer in synthetic reaction showed great influences on MFI zeolite membrane formation in using microwave secondary growth method. The thickness of film was uneven and there was a large deposit on film surface while the seed layer upwards and vertical in synthetic reaction using microwave method, and MFI zeolite membrane surface was uneven with partial seeds falling off while the seed layer downwards. Therefore, these conventional placement methods need to be corrected in order to synthesize excellent molecular sieve membranes.

Acknowledgments

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