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Characterization of the formation of NaA zeolite membrane under microwave radiation

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Zeolite membranes have gained much attention in recent years, due to their potential application in various fields such as catalysis, gas separation, pervaporation, etc. [1–4]. There are many reports on the synthesis, characterization and applications of zeolite membranes [1–4], but literatures about the formation mechanism of zeolite membrane are fewer [5–7]. To prepare zeolite membranes, many methods have been developed, including hydrothermal crystallization [8], vapor phase synthesis [9], and microwave heating [10, 11]. It was reported that microwave heating and crystal seeding could help the formation and improve the performance of zeolite membranes [10]. It was proposed that the formation of zeolite membranes included the following three stages: sol or gel adhesion on the substrate to form the gel layer, the nucleation and crystallization stage, and the dissolving stage [10, 12, 13]. However, there are few reports on the direct observation of these stages, especially under microwave radiation. In this report, by using scanning electron microscopy (SEM), the formation stages of zeolite NaA membrane in microwave radiation environment were observed and confirmed with the results from X-ray diffraction (XRD) and gas permeation measurements.

The disk shaped substrates (30 mm in diameter, 3 mm in thickness) used were porous α-Al_2O_3 made by casting, with pore radius of 0.3–0.5 μm and ca. 50% porosity. The precursor of the gel was prepared by mixing sodium hydroxide, sodium aluminate, water glass and water, and aging for 24 h with vigorous stirring. The final molar composition of the gel was $3Na_2O$: Al_2O_3: $2SiO_2$: $200H_2O$. After one face of the substrates was rubbed with zeolite NaA crystals as seeds, the substrates were put vertically in Teflon vessels containing 120 ml gel. Then the vessels were transferred into a microwave oven, heated up to 90 °C within 1 min, and reacted for a range of specified times. After the reaction, the membranes were vigorously ultrasonically vibrated in water for 10 min to remove the species physically absorbed on the substrates, washed by de-ionized water to pH = 7.0 and dried at 150 °C for 3 h. The membranes were characterized by scanning electron microscopy (SEM) on a JEM-1200E scanning electron microscope and X-ray diffraction (XRD) using Cu K_α ($\lambda = 0.154$ nm) radiation operating at 40 kV and 100 mA on a Rigaku D max /b powder diffractometer. The integrity of the membrane was evaluated with gas permeation tests. The membrane was sealed in a permeation module with the zeolite membrane on the high-pressure side. The gas permeances of the membrane were measured by a soap-film flowmeter under a pressure difference of 0.10 MPa at 25 °C. The permselectivity of A/B, $\alpha_{A/B}$, is defined as the permeance ratio of gas A to gas B.

The SEM images (Fig. 1) demonstrate the growth process of the zeolite membranes. After 5 min reaction, the substrate was covered with a very thin layer of gel $\approx$ 1 μm, and almost no well-grown crystals were seen (Fig. 1(1a), (1b)). After 15 min, the thickness of the adsorbed gel layer increased to 4 μm, and the gel layer was slightly crystallized (Fig. 1(2a), (2b)). After 25 min, the thickness remained almost the same, but the crystals were well developed with regular cubic shape and were highly intergrown, forming a continuous zeolite layer (Fig. 1(3a), (3b)). As the reaction time was extended to 40 min, some holes and indentations appeared in the NaA zeolite crystals, and the thickness was slightly decreased, which meant that dissolution had begun (Fig. 1(4a), (4b)). The SEM results displayed the formation process of the zeolite membrane: adsorbing (0–15 min), crystallizing (15–25 min) and dissolving (>25 min). During the first stage, the reaction mixture was continuously adsorbed and piled up onto the surface of the substrate to form a gel layer until equilibrium between the adsorption and desorption was established. Many nuclei were developed in the gel layer around the active sites and the seeds on the surface of the substrate. As the reaction continued, the gel layer gradually and simultaneously crystallized into cubic NaA crystals. When the reaction was extended to long times, the formed crystals gradually dissolved and could further transform to other type of zeolite crystals [10, 12–14].

The SEM observation results were confirmed by the XRD patterns in Fig. 2. The peaks from the synthesized membranes consist of those of the NaA crystals and of the α-Al_2O_3 substrate, which confirmed that the membranes formed were typically NaA zeolite membranes. After 5 min microwave radiation, the diffraction peaks of NaA were very weak, their intensities increased as the reaction was extended to 25 min, and then slightly decreased after 40 min reaction, which suggested that the main growth and crystallization process occurred in 5–25 min.

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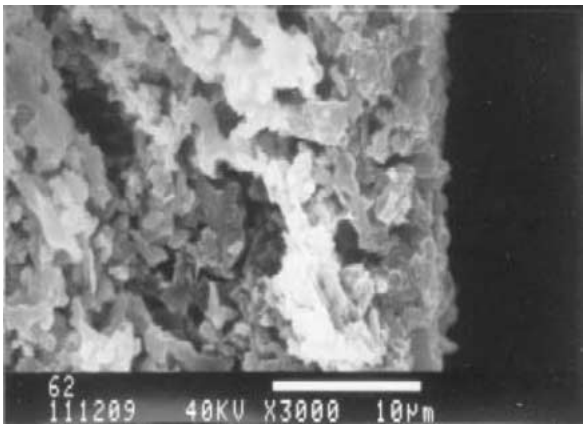
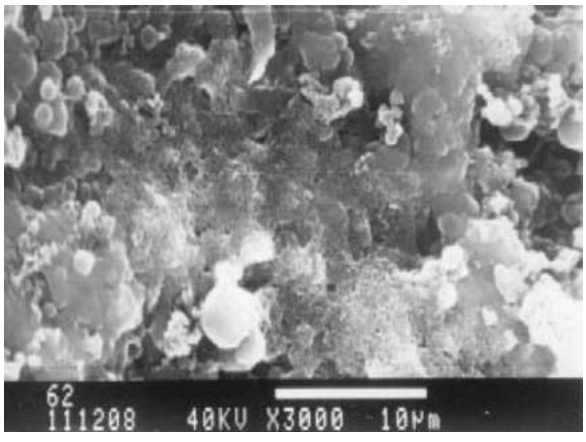
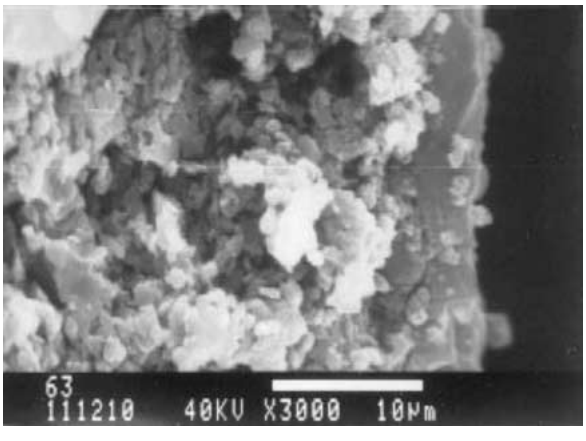


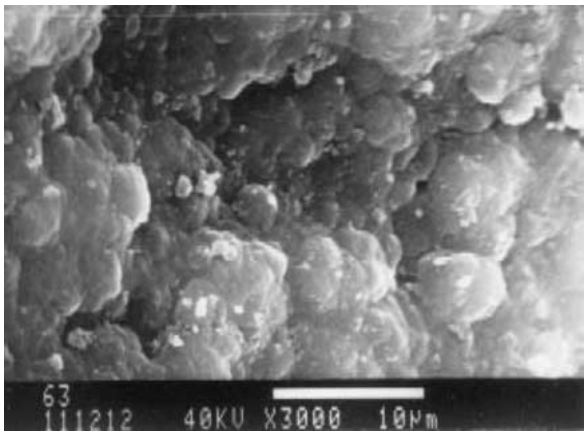
(1a)



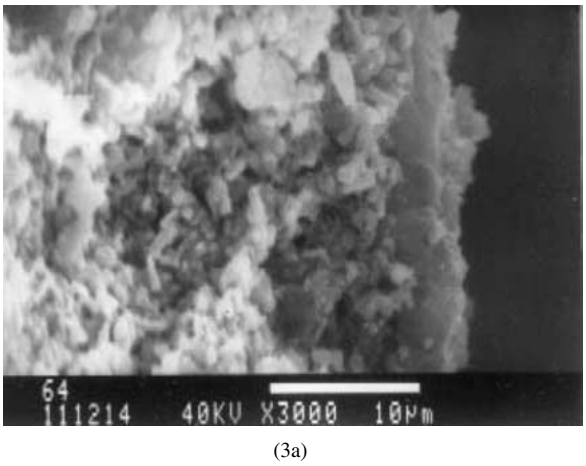
(1b)



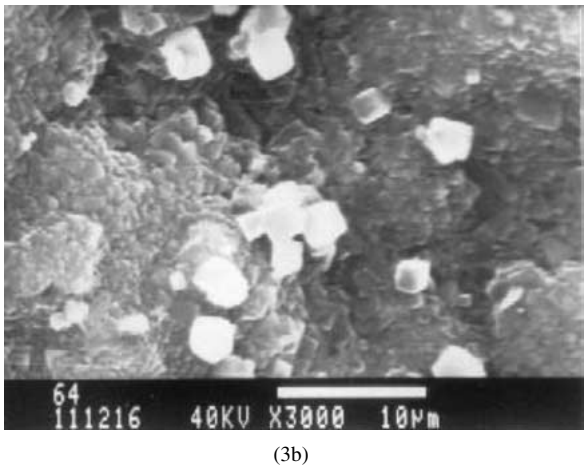
(2a)



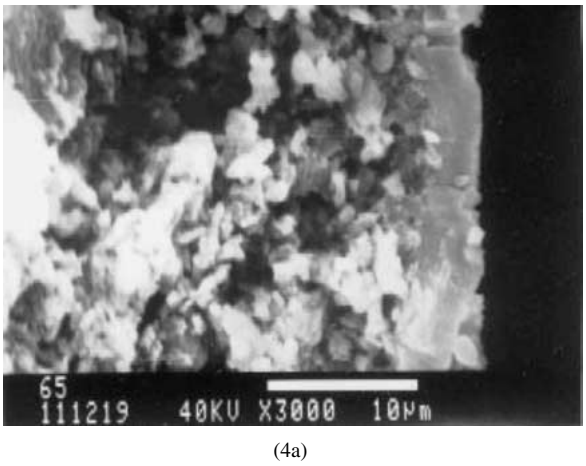
(2b)



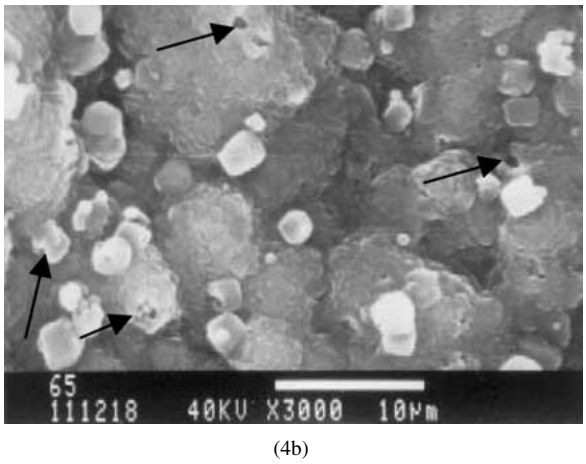
(3a)



(3b)



(4a)



(4b)

Figure 1 SEM images of zeolite membranes of different reaction time: (1) 5 min, (2) 15 min, (3) 25 min, (4) 40 min; (a) cross-section view and (b) top view.

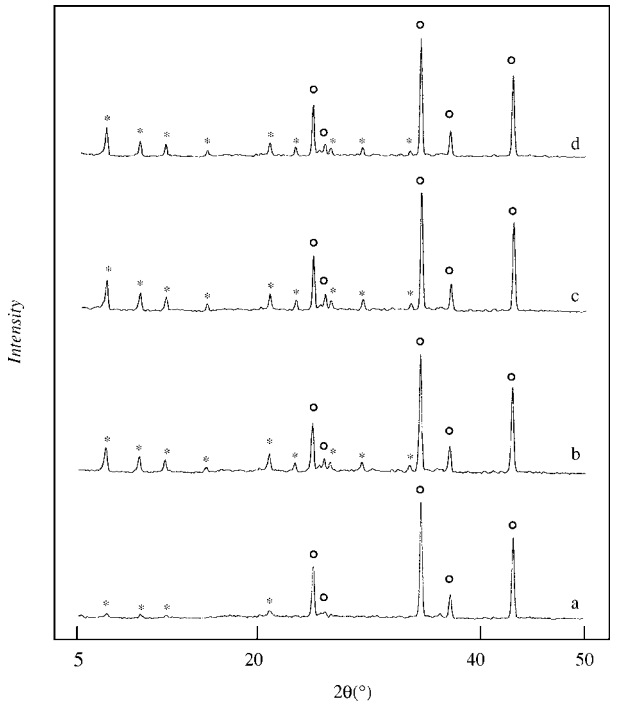


Figure 2 XRD profiles of the NaA zeolite membranes as reaction progressed: (a) 5 min, (b) 15 min, (c) 25 min, (d) 40 min NaA zeolite crystal (∗), the alumina substrate (○).

The SEM and XRD results were consistent with the results of gas permeation measurements. The H_2 and C_3H_8 permeances of the substrate were 1.79×10^{-5} and 1.47×10^{-5} $mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$. As the reaction progressed for 5, 15, 25 and 40 min, the permeance of H_2 changed to 9.37×10^{-6}, 2.93×10^{-6}, 1.79×10^{-5} and $5.81\ 1 \times 10^{-6}$ $mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$, while the permeance of C_3H_8 changed to 3.51×10^{-6}, 1.01×10^{-6}, 2.87×10^{-7} and 2.07×10^{-6} $mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$, respectively. Therefore, the corresponding H_2/C_3H_8 permselectivities were 2.67, 2.89, 6.23 and 2.81. Since the H_2/C_3H_8 permselectivity of the substrate and the Knudson diffusion are 1.15 and 4.69, the permeation result suggests that only the NaA membrane of 25 min microwave radiation had good quality of molecular sieving function, which is consistent with the high degree of crystallization from the SEM result. The amorphous profiles of NaA crystals of 15 min sample and the dissolution of NaA crystals found in 40 min sample are consistent with their poor gas selection performance controlled mainly by Knudson diffusion.

The SEM results in Fig. 1 also suggested that the thickness of the membrane was uneven from the first stage. Since the substrate was porous and had different sizes of pores, the strengths of capillary adsorption of the different sites of the surface were unequal and the surface activity of the substrate varied. This caused the uneven adsorbed gel layer and the later formed membrane. The strengths of the capillary adsorption and the viscosity of the reaction mixture controlled the equilibrium, and thus determined the thickness of the membrane formed [12, 13]. The thickness and the quality of continuum of the gel layer affected to a large extent the properties of the later formed membranes, such as their permeation and selectivity [10, 12, 13]. By adjusting the strengths of capillary adsorption of the different sites of the surface, it is possible to synthesize thin and even zeolite membranes with high integrity.

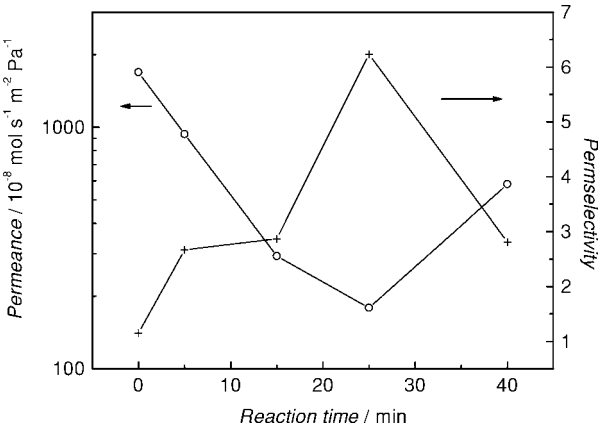


Figure 3 Evaluation of the NaA zeolite membranes by gas permeation. (○) H_2 permeance; (+) H_2/C_3H_8 permselectivity.

In conclusion, scanning electron microscope (SEM) identified similar formation stages of zeolite membrane under microwave radiation: namely the adsorbing stage, the nucleation and crystallizing stage and the dissolving stage, as found in traditional hydrothermal synthesis [5–7]. The results were consistent with the results of XRD and gas permeation measurements.

Acknowledgments

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14. The SEM image of the dissolvation and transformation of NaA crystals into other type of zeolite crystals such as hydroxy-sodalite zeolite was also clearly shown in the synthesis of NaA membrane on asymmetric alumina substrate in sol by microwave heating (Xiaobo Chen's MS thesis, unpublished results).

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