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Microwave-Assisted Hydrothermal Synthesis of [Al(OH)(1,4-NDC)] Membranes with Superior Separation Performances

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Abstract: In this study, we report a facile ligand-assisted in situ hydrothermal approach for preparation of compact [Al(OH)(1,4-NDC)] (1,4-NDC = 1,4-naphthalenedicarboxylate) MOF membranes on porous γ-Al_2O_3 substrates, which also served as the Al^{3+} source of MOF membranes. Simultaneously, it was observed that the heating mode exerted significant influence on the final microstructure and separation performance of [Al(OH)(1,4-NDC)] membranes. Compared with the conventional hydrothermal method, the employment of microwave heating led to the formation of [Al(OH)(1,4-NDC)] membranes composed of closely packed nanorods with superior H_2/CH_4 selectivity.

Owing to their unprecedented pore architectures and adsorption functions, metal organic frameworks (MOFs) in form of membranes have shown great potential in gas separation such as H_2 purification,[1] CO_2 capture[2] and olefin/paraffin separation.[3] Apart from framework topology and elemental composition, the performance of MOF membranes was also significantly influenced by their microstructures. For instance, it has been demonstrated that ZIF-8 membranes prepared at room temperature generally showed much higher C_3H_6/C_3H_8 selectivity ($\approx$50) in comparison with those synthesized under solvothermal conditions due to reduced intercrystal defect densities.[4] At present, diverse methodologies and technologies (such as microwave-assisted heating,[1a,5] counter diffusion,[3d,6] chemical vapor deposition[7] and electrospray deposition[8]) had been employed to exert precise control over their microstructures. Among them, microwave-assisted heating is particularly noteworthy since not only the reaction time could be reduced significantly, but also their microstructures and separation performances may be tuned effectively.[1a,5] For instance, Caro first reported the synthesis of well-intergrown ZIF-8 membranes by relying on microwave heating. Compared with conventional solvothermal methods, not only the nucleation density on porous TiO_2 substrates was greatly enhanced, but also the synthesis time was significantly reduced.[1a] At present, microwave synthesis has been employed in the synthesis of a wide range of high performance MOF membranes (like ZIF-7,[5a] MOF-5,[5b] CAU-10-H[5c] and NH_2-MIL-125(Ti)[5d]). Very recently single-mode microwave heating was employed in the synthesis of highly *c*-oriented NH_2-MIL-125(Ti) membranes. Owing to the improved microwave field uniformity, enhanced nonthermal effects and higher absorption efficiency of single-mode microwave heating, the undesired twin growth was effectively suppressed.[5d] It was noted that although it has been proved that microwave-assisted heating could be employed to fabricate MOF membranes, a straightforward comparison of microstructures and separation performances of MOF membranes prepared by conventional and microwave methods under identical synthetic conditions was still rare. Moreover, the role of microwave irradiation played in MOF membrane synthesis still awaits further elucidation.

[Al(OH)(1,4-NDC)] is representative of MOF materials with two independent pore apertures of 7.4 Å × 7.4 Å and 3.0 Å × 3.0 Å, respectively (Figure 1).[9] Moreover, it further exhibits preferential adsorption behaviors and exceptional aqueous stability. All these properties made [Al(OH)(1,4-NDC)] membranes potentially attractive candidates for gas separation. Such stud-

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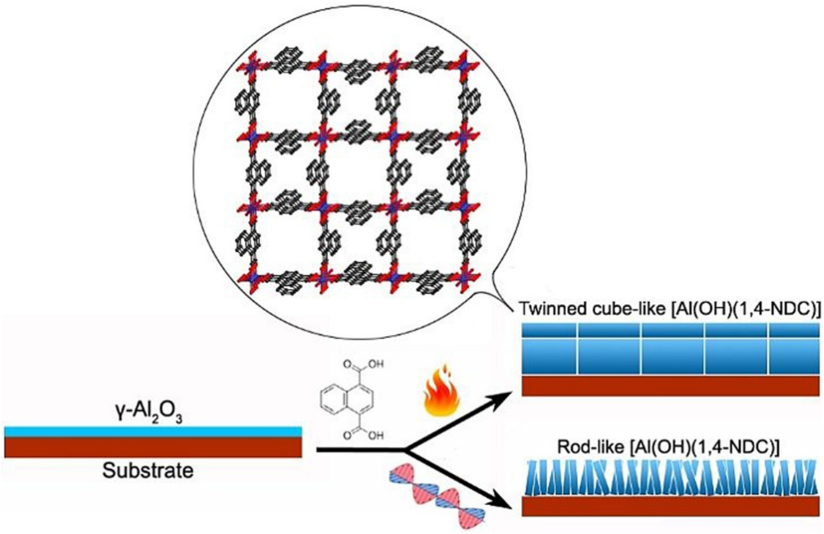

Figure 1. Schematic illustration of the concept of microwave-assisted hydrothermal synthesis of [Al(OH)(1,4-NDC)] membranes. γ-Al_2O_3 plates were served as the substrate as well as Al^{3+} source.

ies, however, have not been carried out except a tentative synthesis on dense Si wafers.[10]

In this study, both conventional and microwave-assisted heating were employed for in situ fabrication of [Al(OH)(1,4-NDC)] membranes. Commercially available porous γ-Al_2O_3 substrates, which served as the sole Al^{3+} source of [Al(OH)(1,4-NDC)], were used. The precursor solution was prepared by mixing the ligand 1,4-NDC in distilled and de-ionized (DDI) H_2O under vigorous stirring. In the next step, in situ hydrothermal growth was carried out under both conventional and microwave conditions (details were shown in experimental section). Our results indicated that microwave irradiation exerted significant influence on both microstructures (evolving from twinned cube-like to rod-like shape) and separation performances (4.2- and 1.6-fold increases in H_2 permeance and mixed H_2/CH_4 selectivity, respectively) of [Al(OH)(1,4-NDC)] membranes. To the best of our knowledge, such huge discrepancies in microstructures and separation performances of MOF membranes caused by microwave-assisted heating have been rarely observed before.

Initially conventional hydrothermal growth was employed for in situ fabrication of [Al(OH)(1,4-NDC)] membranes. After the synthesis a well-intergrown [Al(OH)(1,4-NDC)] membrane with a thickness of 2 μm was formed on the substrate (shown in Figure 2 a,b,c). Moreover, it was observed that the membrane surface had been fully covered with 1 μm-sized, twinned cube-like crystallites. XRD pattern further confirmed that the formed layer indeed belonged to [Al(OH)(1,4-NDC)] phase (Figure 3 a,b).

In contrast, microwave-assisted heating not only led to a significant reduction in reaction time, but also gave rise to a significant microstructural change. As shown in the Figure (Figure 2 d,e), after the synthesis rod-like [Al(OH)(1,4-NDC)] crystallites with an average diameter of 200 nm and length of 2 μm were readily formed and in situ attached to the substrate (Figure 2 e). Moreover, most crystallites should be vertically aligned on the substrate as confirmed by the cross-sectional image (Figure 2 f). In contrast, the use of conventional heating under the same reaction condition only led to sparse distribution of [Al(OH)(1,4-NDC)] particles on the substrate surface, although in some areas [Al(OH)(1,4-NDC)] particles were relatively densely packed (SI-1).

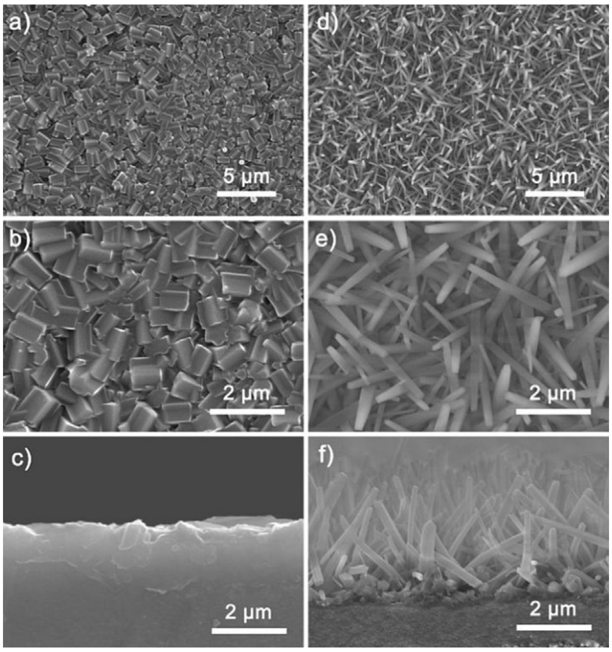

Figure 2. SEM images of [Al(OH)(1,4-NDC)] membranes prepared by (a, b, c) conventional hydrothermal growth at 180 °C for 24 h, and (d, e, f) microwave-assisted hydrothermal growth at 160 °C for 2 h.

The distinct discrepancies in membrane microstructures could be reasonably attributed to the uniform and high nucleation rate of [Al(OH)(1,4-NDC)] grains on the substrate in a supersaturated precursor solution under microwave irradiation.[11] It should be noted that such a morphological discrepancy was

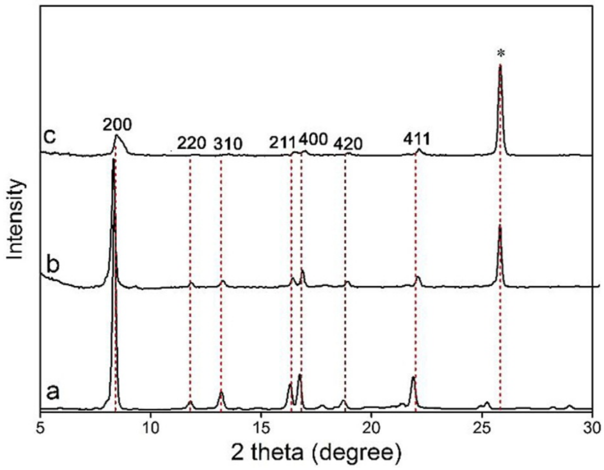

Figure 3. XRD patterns of (a) [Al(OH)(1,4-NDC)] powders and related membranes prepared by (b) conventional hydrothermal growth and (c) microwave-assisted hydrothermal growth. Diffraction peaks derived from porous γ-Al_2O_3 substrates were indicated by asterisk.

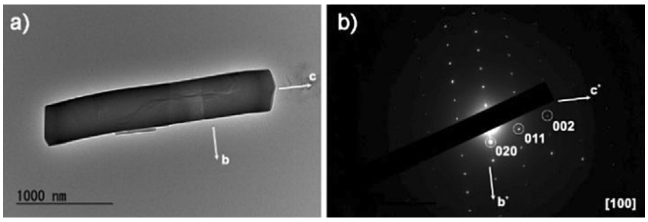

Figure 4. a) The TEM image of rod-shaped [Al(OH)(1,4-NDC)] powders prepared by microwave-assisted hydrothermal growth at 160 °C for 2 h and b) the corresponding SAED pattern.

also observed in conventional and microwave-assisted synthesis of [Fe(OH)(1,4-NDC)] powders (an isostructural compound of [Al(OH)(1,4-NDC)]),[12] and some unique phenomenon like enhanced heating rate, superheating, hot pots and enhanced dissolution of precursors induced by microwave-assisted heating may account for their morphological discrepancies.[13] On the other hand, their discrepancy in crystallographic preferred orientation could be interpreted by considering the tendency of [Al(OH)(1,4-NDC)] crystals to be attached to porous γ-Al_2O_3 substrates through their largest facets. In effect, this principle has proven to be universal and has been widely reported in the literature.[14,15] For instance, a previous study on self-assembly of zeolite microcrystals with different morphologies on 3-chloropropyl-coated glass (CP-g) plates indicated that in case cylindrical-shaped zeolite microcrystals were attached onto CP-g plates, zeolite crystals self-assembled very tightly and vertically. In contrast, hexagonal columnar zeolite microcrystals self-assembled horizontally.[15] Such a difference in orientation was attributed by the tendency of zeolite microcrystals to be attached onto substrates through their largest facets. By analogy, herein it was reasonable to assume that twinned cuboid-shaped [Al(OH)(1,4-NDC)] microcrystals prepared under conventional hydrothermal conditions tended to attach to the substrate along the *ab*-axis direction whereas cylinder-shaped [Al(OH)(1,4-NDC)] crystals synthesized by microwave heating were inclined to adhere to the substrate along the *c*-axis direction. It should be emphasized that the selected area electron diffraction (SAED) pattern of [Al(OH)(1,4-NDC)] powders prepared by additional hydrothermal growth clearly demonstrated that the nanorod shown in the TEM bright-field image (Figure 4a) was oriented almost along the [110] zone axis so that the longitudinal axis of the nanorod was indeed along the *c*-axis (Figure 4b).

In the next step, gas permeation tests were carried out. Initially, [Al(OH)(1,4-NDC)] membranes prepared under both conventional and microwave conditions were impermeable to any gas molecules since their micropores were still fully occupied with solvent molecules. To open micropores, an on-stream thermal activation was carried out by using a Wicke-Kallenbach permeation cell by gradual increasing the operating temperature to 120 °C (ramping speed was 0.3 °C min^{-1}) with H_2-CH_4 mixture as the feed gas and He as the sweep gas ($P_{H2}=P_{CH4}=P_{He}=50\ mL\,min^{-1}$). Under this condition, the permeance and selectivity of H_2/CH_4 gas mixtures through [Al(OH)(1,4-NDC)] membranes were further measured at 120 °C and 1 bar (more details are shown in SI-2). It was found that the [Al(OH)(1,4-NDC)] membrane prepared under conventional conditions showed a H_2/CH_4 selectivity as high as 8.6, which had by far exceeded the Knudsen value (2.8) and thus was a clear indication of the domination of molecular sieving mechanism (Figure 5). In contrast, the membrane prepared under microwave conditions showed a H_2/CH_4 selectivity of 13.3. Simultaneously, there was a 4.2-fold increase in H_2 permeance demonstrating convincingly that microwave-assisted heating was indeed more effective for preparing high performance [Al(OH)(1,4-NDC)] membranes.

Lower H_2 permeance of the conventionally synthesized [Al(OH)(1,4-NDC)] membrane could be partially ascribed to the twinned microstructure (Figure 2a). As was demonstrated in previous studies, the generation of twins in molecular sieve membranes would remarkably increase their mass transfer bar-

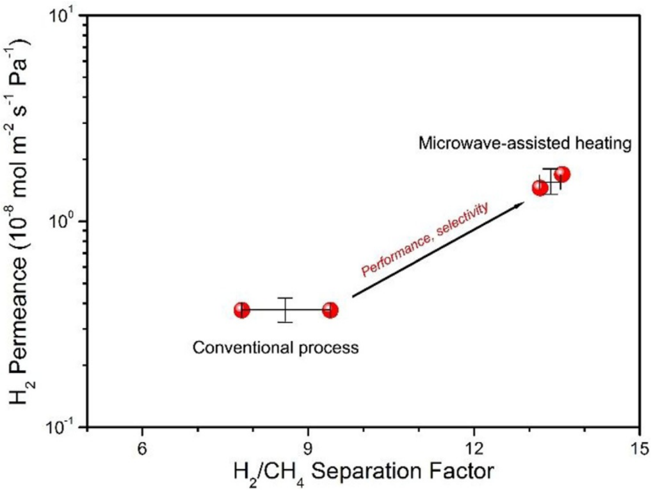

Figure 5. Mixed H_2/CH_4 selectivity and H_2 permeance of [Al(OH)(1,4-NDC)] membranes prepared by conventional hydrothermal growth and microwave-assisted hydrothermal growth, respectively.

rier[16–18] possibly due to the narrowed cross-section of micropores[19] or higher framework density at grain boundary regions.[20] These effects might become more obvious with further reduction of the grain size of [Al(OH)(1,4-NDC)] crystallites due to a higher grain boundary density. On the other hand, the vertical alignment of microwave-synthesized [Al(OH)(1,4-NDC)] crystallites may also contribute to the increased H_2 permeance due to an equivalent reduction in membrane thickness. It should be emphasized that although there existed open space between neighboring [Al(OH)(1,4-NDC)] grains, the bottom section of the [Al(OH)(1,4-NDC)] membrane remained defect-free and well-intergrown (shown in SI-3) thus maintaining a high H_2/CH_4 selectivity.

To summarize, in this study [Al(OH)(1,4-NDC)] membranes were in situ fabricated under both conventional and microwave conditions. Porous γ-Al_2O_3 disks, which also served as Al^{3+} sources of MOF membranes, were utilized as substrates. It was demonstrated that microwave irradiation not only remarkably reduced the reaction time from 24 h to 2 h, but also exerted significant influence on both microstructures and separation performances of [Al(OH)(1,4-NDC)] membranes. In particular, [Al(OH)(1,4-NDC)] membranes prepared by microwave-assisted heating showed dual enhancement of both H_2 permeance and H_2/CH_4 selectivity. We firmly believe that microwave-assisted heating will further contribute to the performance enhancement of other MOF membranes.

Experimental Section

Chemicals, substrates and apparatus: 1,4-Naphthalenedicarboxylic acid (1,4-NDC, 95.0 wt.%) was bought from Wako Co. Ltd. without further purification. Porous γ-Al_2O_3 asymmetric porous substrates were supplied by Fraunhofer IKTS. Diameter and thickness of the substrate were 18 mm and 1 mm, respectively. The mean pore diameter was 5 nm. Alternatively, Porous γ-Al_2O_3 substrates could also be easily prepared by first dip-coating thin layer of γ-AlOOH[21] on one side of porous α-Al_2O_3 substrates followed by calcination at 500 °C. The microwave reaction was conducted on "flexiWAVE"-type microwave synthesis system of Milestone Company.

Preparation of the precursor solution: The precursor solution was prepared by adding 0.324 g 1,4-NDC in 60 mL of DDI H_2O. Afterwards the solution was vigorously stirred for 30 min before use.

In situ hydrothermal growth of [Al(OH)(1,4-NDC)] membrane: A porous γ-Al_2O_3 asymmetric porous substrate was vertically placed into a 50 mL Teflon-lined stainless vessel, and 30 mL precursor solution was poured into the vessel. The vessel was sealed and put into a convective oven with the temperature pre-heated to 180 °C. After an elapsed time of 24 h, the vessel was taken out and naturally cooled to room temperature in air. Finally, the film was taken out, washed with copious amount of water and dried in a convective oven at 60 °C overnight.

Microwave-assisted synthesis of [Al(OH)(1,4-NDC)] membrane: A porous γ-Al_2O_3 asymmetric porous substrate was vertically placed into a 200 mL Teflon-lined plastic vessel, and 60 mL precursor solution was poured into the vessel. The vessel was sealed and put into the microwave-heating apparatus with the Max. Power of 400 W. The reaction temperature was heated to 160 °C in 10 min and maintained at this temperature for 2 h. Consequently, the vessel was taken out and naturally cooled to room temperature. Finally, the film was taken out, washed with copious amount of water and dried in a convective oven at 60 °C overnight.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: gas separation · hydrothermal growth · membrane · metal-organic frameworks · microwave heating

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