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Hydrovapothermal conversion of tetraethoxysilane vapor to polycrystalline zeolite layer by *in situ* gelation†

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Zeolite membrane has been fabricated on porous alumina substrate in a single continuous process of gelation and subsequent crystallization while suppressing nucleation of zeolite powder in the bulk.

Fabrication of membrane is pivotal for zeolite-membrane-based technology and continues to draw considerable attention in research and development due to its indisputable control over the microstructure and sorption properties of the membrane.[1–12] The lack of simple, reproducible and economic method producing high performance membrane in large scale poses the hardest obstacle to the industrial realization of many desirable processes implementing a robust zeolite-membrane-based technology. Commercialization of zeolite membrane has been achieved only recently for the dehydration of alcohol.[11] From this perspective, we intend to explore a simple and scalable method to fabricate zeolite membrane on porous α-alumina tubular substrates (pore size 0.1–1.0 μm).

We anticipate that a zeolite membrane can be fabricated by confining a thin solution-envelope of structure-directing-agent(SDA)/aluminium/alkali-metal-ions in water, around the substrate surface, and carrying out the crystallization in presence of the substrate-solution assembly, and the vapor of tetraethoxysilane (TEOS). Using silica in the vapor phase, gelation and successive nucleation and growth can be tuned. Gelation can occur *in situ* by the hydrolysis of TEOS in the vapor–liquid interface, under heating. To explore such possibilities, we investigated a simple, economic and distinct method in which crystallization was carried out in a TEOS vapor environment on a substrate that is either dipped into or soaked with the aqueous alkaline solution of SDA or Al-source and alkali-metal-ions. Under such circumstances, consumption of silica by the alkaline solution would probably be controlled by the vapor-liquid equilibrium and hydrolysis of TEOS that is followed by the diffusion of hydrolyzed species from the surface to the bulk of the liquid. Successive process probably follows the hydrothermal crystallization. From this perspective, the present method is a hydrothermal process induced by vapor phase transport[13] of TEOS (or in short, a hydrovapothermal process). Additionally, use of TEOS in vapor phase would reduce side effects of any impurities from the silica source.

Here, we demonstrate fabrication of MFI membrane. Fig. 1a shows the schematic of the synthesis vessel. A cleaned α-alumina substrate (length 3 cm, i.d. 0.8 cm, o.d. 1 cm , pore size 1 μm) was fixed vertically in a 55 ml Teflon®cup (Cup A, i.d. 3.3 cm) while keeping it completely immersed in 24 g of 0.2 M TPAOH solution. The inner top level of cup A, was fixed with another smaller Teflon® cup, B (i.d. 2. 2 cm, o.d. 2.4 cm, height 2 cm), containing 2 g of TEOS. Teflon® cup A was then tightly capped and put in a stainless steel bomb. Crystallization was carried out at 170 °C for 96 h. XRD data (Fig. 2) and SEM (Fig. 3) image of the MFI layer, thus produced, confirms feasibility of the present method. A highly crystalline MFI layer with a uniform thickness of *ca.* 20 μm was obtained only on the outer surface of the substrate. Effect of spilling was always negligible. Homogeneous growth along the length of the substrate was evident from the textural homogeneity of the MFI layer that would be otherwise does the diffusion of silicate species from the surface to the bulk of the alkaline solution and the gravity develops a steep concentration gradient along the height of the liquid column during the course of the crystallization. Assuming a compact 20 μm as-synthesized silicalite layer with a density of 2.03 g cc^{-1} [calculated assuming negligible intercrystalline void space and framework density of $(17.97SiO_2 + 0.37TPA_2O)/1000$ Å^3][14,15] on a 3 cm long tubular substrate of 1 cm o.d., the total MFI loading in the membrane can be calculated as 0.038 g (while neglecting any contribution of MFI formed in the pores of the substrate). On the other hand, only 0.037 g of MFI powder was produced in the bulk of TPAOH solution in cup A. Thus, a relative amount of MFI formed per unit volume is considerably larger in the vicinity of the substrate as compared to that in the bulk of TPAOH solution indicating a substrate induced driving force for the growth of the MFI layer. Further, wastage due to powder formation in the bulk of the alkaline solution is considerably less.

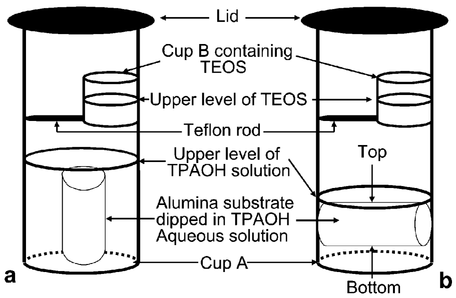

Fig. 1 Sketch of synthesis vessel with; a) vertical and b) horizontal placement of substrate.

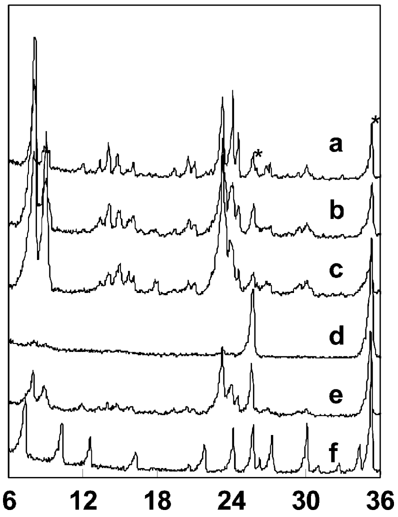

Fig. 2 X-Ray diffraction pattern of; MFI membrane obtained on a) vertically placed substrate, b) horizontally placed substrate (bottom side), c) horizontally placed substrate (top side), and d) silicalite seed coated substrate, e) MFI membrane obtained after secondary growth, and f) LTA coating obtained on vertically placed substrate (100 °C, 6 h crystallization). '*'indicates reflections from α-alumina tubes

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† Electronic supplementary information (ESI) available: SEM images and seeding method. See http://www.rsc.org/suppdata/cc/b4/b400207p/

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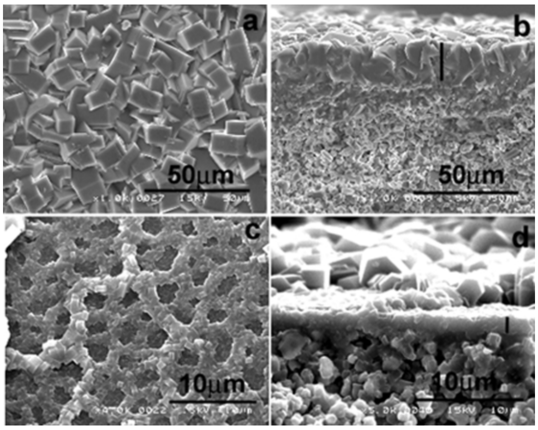

Fig. 3 SEM image of, (a) surface, b) cross section of thick MFI membrane and c) surface, d) cross section of thin MFI patterned coating obtained on vertically placed substrate. Vertical bars indicate cross section.

To assess the compactness, gas permeation experiments were performed in a stainless steel module with a membrane fabricated at 170 °C (crystallization time – 96 h) on a 3 cm long horizontally placed substrate (pore size 0.1 μm) in presence of 13.2 g of 0.2 M TPAOH solution and 1.5 g TEOS. During synthesis, the substrate was fixed in a fashion so that a liquid layer of *ca.* 1–2 mm can be maintained on the top and bottom of the substrate (Fig. 1b). The deposition of zeolite from the bulk of the alkaline solution on to the top of the membrane is considerably less. No visible textural inhomogeneity was evident to the unassisted eye however, FE-SEM images indicate microstructural changes between the top and bottom surface of the as-synthesized membrane. Crystals at the bottom surface grown bigger as compared to that on the top. Unlike top surface, homogeneous growth causes unique particle size at the bottom. Thickness of the membrane was quite similar on both surfaces (*ca.* 20 μm). Preferential orientation was not observed on either surface (Fig. 2b and 2c). Membrane was calcined in air at 500 °C for 8 h. Result of single gas permeation (Table 1) is a clear indication of activated diffusion. At 107 °C, CO_2 was the fastest permeating gas with the CO_2/N_2 ideal selectivity of 2.3. Separation of 50/50 n-butane/iso-butane[16] mixture was carried out by Wicke–Kallenbach method. He-swept (40 ml min^{-1}) permeate was analyzed by gas chromatography. Under steady state condition at 150 °C, a separation selectivity of 10.9 was achieved with a n-butane permeance of 2.0×10^{-7} mol m^{-2} sec^{-1} Pa^{-1}. Selectivity increases with a corresponding decrease in permeance at lower temperature. Permeation results are indicative of a high performance MFI membrane.[5,12]

MFI membrane was also produced on a horizontally-placed silicalite-seeded[1,17] (see ESI†) substrate [seed loading = 0.0101 g/2.84 cm substrate (0.1 μm pores)] at 150 °C, using 13.24 g of 0.05 M TPAOH solution and 1.54 g TEOS. Pure MFI (Fig. 2e) layer was obtained within 12 h. FE-SEM image indicates formation of zeolite layer (< 5 μm) consists primarily of 4 μm crystals and is covered by loosely bound 500 nm crystals. At 120 °C, He permeance of the uncalcined seeded substrate was 1136×10^{-7} mol m^{-2} sec^{-1} Pa^{-1}, under 10 kPa pressure drop. Under similar conditions, He permeance for the as-synthesized uncalcined membrane falls below 0.01×10^{-7} mol m^{-2} sec^{-1} Pa^{-1} (Lower limit of the flow meter, Agilent ADM1000). The results confirm formation of defect-free as-synthesized membrane, in a short crystallization time.

Table 1 Single gas permeance measured on calcined MFI

T (°C)	Gas (k.d)	Pr/KPa	P × 10^7
360	He (0.26)	9.8	19.09
360	He	49.0	16.94
360	He	98.1	16.81
360	He	147.1	16.97
300	He	49	14.29
209	He	49	9.81
107	He	49	5.90
107	H_2 (0.289)	49	9.86
107	N_2 (0.364)	49	4.39
107	CO_2 (0.330)	49	10.08
31	He	98.1	3.97
31	SF_6 (0.550)	98.1	0.15

T = Temperature; k.d. = Kinetic diameter (nm); Pr = Pressure across the membrane; P = permeance (mol m^{-2} sec^{-1} Pa^{-1})

In another approach, the substrate was placed vertically in cup A after it soaked a 1 M TPAOH solution overnight. No additional solution except that trapped in the substrate, was used. A thin and net like patterned MFI layer was formed only on the lower few millimeters of the substrate (Fig. 3c & 3d). Pattern was formed over a thin (< 2 μm) and continuous primary MFI layer consisting of small crystals. The TPAOH solution trapped in the pores of the substrate possibly flowed down along the substrate due to the gravity on the onset of the crystallization. Continuous feeding of the TPAOH was maintained by the capillary effect up to few millimeters of height and a continuous zeolite layer could grow in this region only. An insufficient supply of TPAOH causes formation of thin amorphous silica layer[18] or scattered MFI crystals on the upper part of the substrate. The result apparently indicates possibilities of forming thin continuous MFI layer on horizontally placed porous flat substrates.

The present method is capable of producing LTA and FAU membrane as well. Preliminary trails produced pure LTA and LTA-FAU composite layer on α-alumina tubular substrate (Fig. 2 and ESI Fig. S1). A clear aqueous solution of NaOH and $NaAlO_2$ was used for the crystallization of LTA and FAU. Formation of large crystals is indicative of low nuclei density in the synthesis medium during crystallization by the present method that might have paramount importance in the fabrication of high performance zeolite membrane by secondary growth.[1,17]

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