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Ionothermal Synthesis

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Ionothermal Synthesis of Aluminophosphate Molecular Sieve Membranes through Substrate Surface Conversion**

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Applications of zeolite membranes in separation, chemical sensors, and catalytic membrane reactors have led to extensive studies on their fabrication.[1,2] To date, mainly silicate-based zeolite membranes of the structure types MFI,[3] DDR,[4] LTA,[5] and FAU[6] have been synthesized on different substrates and evaluated for single- or multiple-gas permeation. Routes for the synthesis of zeolite membranes can be broadly classified into two categories:[7] in situ and secondary growth synthesis, both of which are derived from the strategy of hydrothermal zeolite synthesis. However, the high autogenous pressure[8] associated with hydrothermal procedures is inconvenient for preparation of zeolite membranes, especially for large-scale production, due to safety concerns and the risk of molecular sieve collapse. On the other hand, although aluminophosphate[9,10] and silicoaluminophosphate[11,12] membranes for gas separation have been prepared, there are few reports on the preparation of aluminophosphate molecular sieve membranes,[9–12] which suggests that hydrothermal preparation of such membranes may be difficult.

Ionothermal synthesis,[13] which uses ionic liquids as reaction media instead of water or organic solvents, allowed highly efficient preparation of aluminophosphate molecular sieves under ambient pressure.[13–15] Ionic liquids (ILs) are commonly defined as salts that consist of organic cations and inorganic anions with melting temperatures below 100 °C.[16] ILs are well known as environmentally benign and designable solvents,[17] which endow ionothermal synthesis with interesting features and many potential advantages over the hydrothermal method. As a result of the negligible vapor pressure of ILs, ionothermal synthesis can take place at ambient pressure, which eliminates safety concerns. The organic cation of the IL can act as a structure-directing agent (SDA),[13c] or play a cooperative structure-directing role together with introduced amines and quaternary ammonium compounds.[18–20] AEL, AFI, CHA, LTA, and −CLO types of aluminophosphate molecular sieves have been successfully synthesized by ionothermal methods.

Ionothermal synthesis is a promising method for the preparation of aluminophosphate molecular sieve membranes under ambient pressure. Yan and co-workers prepared AlPO-11 and SAPO-11 films on aluminum alloys as anti-corrosion coatings by in situ ionothermal synthesis.[21] To the best of our knowledge, no permeable membrane has been previously prepared on a porous substrate by the ionothermal method. Here we report an ionothermal method for the synthesis of permeable aluminophosphate molecular sieve membranes on porous alumina disks by substrate-surface conversion.

Molecular sieve membranes of types AEL, AFI, CHA, and LTA were prepared by placing homemade δ-alumina substrates (2.0 mm thickness, 20 mm diameter, and 10 nm average pore size; see Supporting Information for details) in a solution of IL, phosphoric acid, hydrofluoric acid, and, if required, organic amines with no additional source of Al. Table 1 lists the initial solution composition, crystallization conditions, and framework types of the products, while the detailed synthesis procedure is described in the Experimental Section. Although the synthesis is carried out in sealed vessels to prevent the evaporation of SDAs and HF, no autogenous pressure is produced under our experimental conditions.[22] The presence and identity of the membranes were confirmed by XRD patterns (Figure 1). No byproducts were found. SEM images (Figure 2) show that all of the synthesized membranes are dense and continuous. No cracks, pinholes, or other defects were observed.

Table 1: Details of initial solution and crystallization conditions for the preparation of molecular sieve membranes on δ-alumina substrates.

	Solution composition[a]	*t* [d]	*T* [°C]	Product
a	$1.0\,H_3PO_4:2.0\,HF:40.0\,[EMIm]Br$	3	170	HO[b] AEL
b	$1.0\,H_3PO_4:0.2\,HF:40.0\,[EMIm]Br$	3	170	AEL
c	$1.0\,H_3PO_4:0.2\,HF:0.1\,TEAC:60.0\,[BMIm]Br$	1.5	150	AFI
d	$1.0\,H_3PO_4:1.0\,HF:1.0\,N\text{-}MIm:40.0\,[EMIm]Br$	3	170	CHA
e	$1.0\,H_3PO_4:0.2\,HF:0.2\,TMAH:30.0\,[BMIm]Br$	4	160	LTA

[a] [EMIm]Br: 1-ethyl-3-methylimidazolate bromide; [BMIm]Br: 1-ethyl-3-butylimidazolate bromide; *N*-MIm: *N*-methylimidazole; TEAC: tetraethylammonium chloride; TMAH: tetramethylammonium hydroxide.
[b] HO: highly oriented.

The most significant feature of this novel method is that the porous alumina substrate acts as both support and Al

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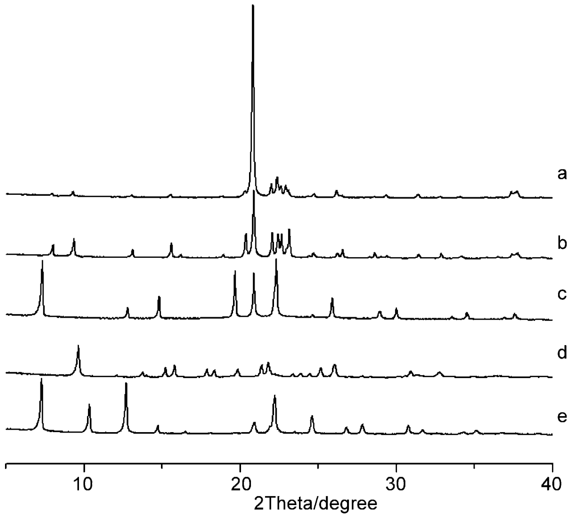

Figure 1. XRD patterns of membranes. a) *c*-Oriented AEL, b) AEL, c) AFI, d) CHA, and e) LTA.

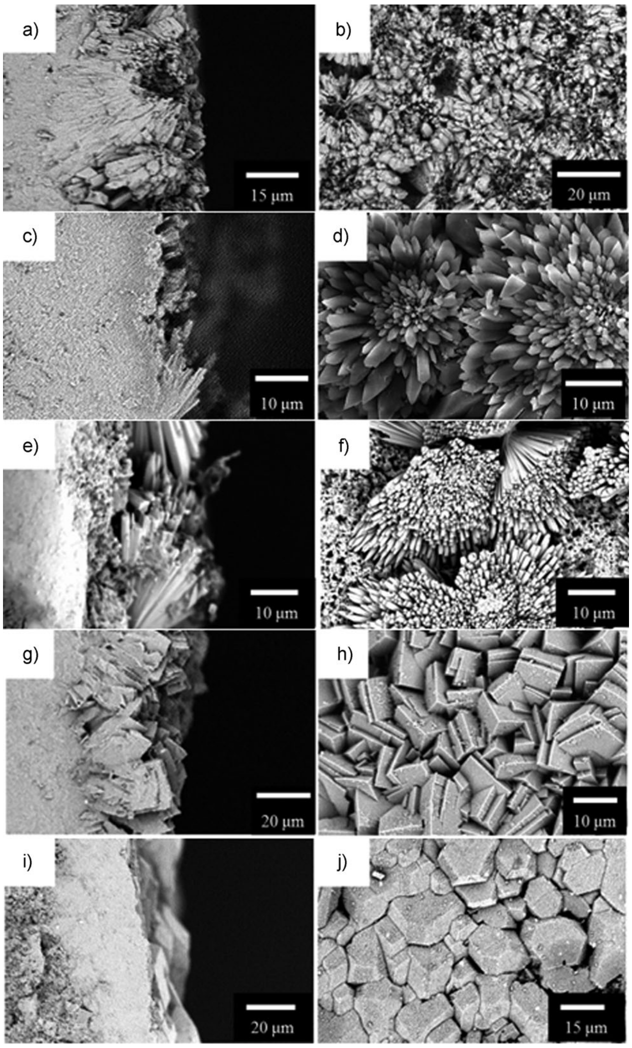

Figure 2. SEM images of as-synthesized membranes. a) *c*-Oriented AEL (cross section), b) *c*-oriented AEL (surface), c) AEL (cross section), d) AEL (surface), e) AFI (cross section), f) AFI (surface), g) CHA (cross section), h) CHA (surface), i) LTA (cross section), and j) LTA (surface).

source. Our previous attempts to prepare molecular sieve membranes by in situ ionothermal synthesis[21] with Al[OCH-$(CH_3)_2]_3$ as added Al source were not successful (Supporting Information, Table S1). Crystallization occurred only in the solution phase, and a continuous membrane could not be formed on porous substrates. In the in situ process, the crystal nuclei, which are formed in bulk solution, are attached to the substrate surface as a result of favorable electrostatic and van der Waals interaction,[23] and then develop into a continuous molecular sieve layer. However, the attachment between the crystal nuclei and the substrate surface could be interrupted by the ionic environment of the solvent under ionothermal conditions.[16] To increase the probability of nucleation on the substrates, we eliminated the Al source ($Al[OCH(CH_3)_2]_3$) from the solution with the expectation that the alumina substrates would react with the P source and SDA in the solution and form nuclei on the substrates. Substrates made of different aluminas were tried out in our experiments (Supporting Information, Table S1). The pseudoboehmite substrate was completely dissolved during the reaction, while no crystals were formed with α-alumina substrate due to its low reactivity. Continuous membranes can only be obtained on the surface of δ-alumina substrates. This suggests that appropriate reactivity of the substrate is the key factor in the synthetic procedure.

Figure 3 shows a cross-sectional SEM image of a CHA membrane. Energy-dispersive X-ray spectroscopy (EDX) was scanned from the boundary of the membrane into the depth of the substrate (along the arrow in Figure 3a). The thickness of the molecular sieve layer is about 100 µm, and the P/Al ratio is almost unity, which is in accordance with the stoichiometry of aluminophosphate molecular sieves. On passing through an intermediate layer of about 20 µm thickness, the P/Al ratio drops to zero when the alumina substrate is reached. On the basis of these results, we propose a mechanism for substrate-surface conversion. At the beginning of the process, the δ-alumina substrate reacts with H_3PO_4 in solution and forms an aluminophosphate precursor layer on its surface. Nucleation of the molecular sieve occurs at the layer/solution interface, where both the SDAs and P source are present in abundance.[24] Subsequently, the nuclei grow to larger crystals and form a continuous membrane. Formation of the aluminophosphate precursor layer and crystallization are continuous processes until the interaction between the substrate and the H_3PO_4 is obstructed by formation of a continuous membrane. Crystallization occurs only on the surface area, and the substrates keep their original shape and strength during synthesis.

Different types of membranes can be synthesized by adjusting the kind of IL and organic amines in the initial solution. AEL membranes are synthesized in EMImBr solution without organic amine (Table 1, Figure 1). A CHA membrane is obtained by the addition of *N*-MIm to the EMImBr solution. AFI and LTA membranes are prepared in BMImBr solution by addition of TEAC and TMAH, respectively. Synthesis of molecular sieves usually involves addition

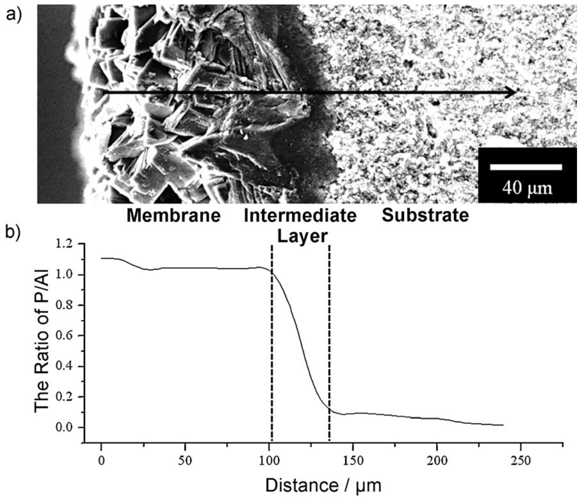

Figure 3. a) Cross-section SEM image of CHA membrane. The arrow represents the path of the EDX line scan. b) P/Al ratio along the path of the EDX line scan.

of SDAs, which can provide the initial building block for further crystallization of a particular structure type.[25] In ionothermal synthesis, the structure-directing role of ionic liquids and additional amines has already proved to be effective.[13a,18] By this method, the type of membrane can be efficiently controlled by choosing the SDA contained in the initial solution, and molecular sieve membranes with different structures are obtained.

Oriented molecular sieve membranes can be explored for many applications, such as size-selective chemical sensors, separation membranes, optical systems, and corrosion-resistant coatings.[26] The orientation of AEL molecular sieve membranes could be modified by adjusting the addition of HF. AEL consists of ten-membered-ring channels parallel to the *c* axis of the crystal, which is the fastest growing axis during the ionothermal procedure. During our synthesis, the XRD pattern of the membrane suggests a random orientation when the HF/IL ratio is 1/200 (Table 1, Figure 1 c and d). When the HF/IL ratio rises to 1/20, an AEL membrane with the preferred orientation is obtained. The strong (002) reflection peak in the XRD pattern indicates that the *c* axis of AEL crystals is perpendicular to the substrate surface (Table 1, Figure 1 a and b). In ionothermal synthesis, the dual action of fluoride ions as SDA and mineralizer increases the efficiency of crystallization.[13a] According to the two-stage model of Yan et al. for the ionothermal synthesis of oriented SAPO-11 film,[21] the space between growth centers may be limited by the abundant seeds formed in the first stage, which suppress in-plane growth of the crystal in the second stage. In our case, increasing addition of HF promotes nucleation of molecular sieve crystals at the interface. The abundant formation of nuclei suppresses in-plane growth of the crystals. Thus, the fastest, out-of-plane, *c*-oriented growth dominated the membrane crystallization process. A highly *c*-oriented AEL membrane is thereby formed.

The CHA membrane was taken as an example to investigate the permeability of molecular sieve membranes synthesized by this ionothermal method. The CHA-type molecular sieves, which have eight-membered rings with a small pore size of 0.38 nm, could provide a suitable membrane for separation of H_2 from gases with larger kinetic diameters, such as CO_2, N_2, O_2, C_3H_8.[27] Figure 4 shows the permeances of single gases through the CHA membrane as a function of the kinetic diameter of the permeating gas molecules. The permeance of H_2 is higher than those of the other gases (Figure 4), and the ideal separation factors for H_2 from CO_2, N_2, O_2, and C_3H_8, determined as the ratio of the single-component permeances, are 4.8, 4.1, 5.0, and 21 respectively, which are all higher than the corresponding Knudsen value, and suggest that the CHA membrane is gas-permeable. Compared with silicoaluminophosphate membranes with the same topology,[11,12] which always show high CO_2 permeance due to strong CO_2 adsorption affinity owing to their polar structure, the present CHA membrane shows no CO_2 affinity because of the neutral framework of the aluminophosphate structure. This result is in accordance with previous reports on aluminophosphate membranes.[9,10]

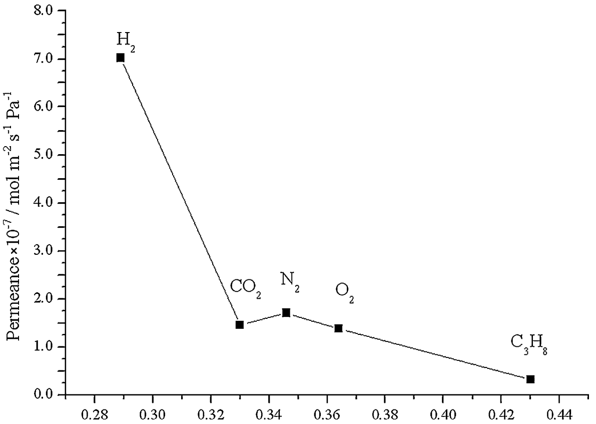

Figure 4. Single-gas permeances of different gases through the CHA-type membrane at 293 K as a functional of kinetic diameter.

In conclusion, we have presented an ionothermal method for the synthesis of aluminophosphate molecular sieve membranes under ambient pressure by substrate-surface conversion. In the synthetic procedure, the alumina substrate acts as both support and source of Al. Different types of molecular sieve membranes were synthesized, including CHA, AEL, AFI, and LTA. The CHA membrane was shown to be gas-permeable. Aluminophosphate molecular sieves have been extensively studied owing to their complex structures and extensive applications since their discovery in 1982.[28] Ionothermal synthesis shows significant practical advantages over hydrothermal methods for the synthesis of molecular sieves owing to the unique properties of ionic liquids, including negligible volatility, excellent microwave absorption, designability, and so on. The presented synthesis of aluminophosphate molecular sieve membranes promises to be a safe, simple, and environmentally benign process suitable for large-scale production.

Experimental Section

Synthesis of membranes: A 100 mL beaker was charged with 0.1 mol of [BMIm]Br or [EMIm]Br, and the required quantities of phosphoric acid (85 wt% in water, AR) and hydrofluoric acid (40 wt% in water, AR) were added with vigorous stirring. Organic amines and Al[$OCH(CH_3)_2]_3$ (AR) were added if required. The solution was then poured into a Teflon-lined autoclave in which an alumina disk was previously placed vertically. The syntheses were performed at the required temperatures for certain times. After the synthesis, the coated sample was washed thoroughly with distilled water and acetone several times by ultrasonication and dried at 110 °C overnight. The synthesized membranes were gas-tight. To obtain a permeable membrane, the template was removed by calcination at 500 °C for 8 h with heating and cooling rates of 0.2 °C$\,$min^{-1}. One side of the disk was polished prior to calcination.

Substrate preparation: Different alumina disks with 2.0 mm thickness and 20 mm diameter were used as substrates. These substrates were made by uniaxial floating-die pressing of different alumina powders at 9000 kgf for 5 min into green disks. The δ-alumina and α-alumina powders were made from pseudoboehmite powder (purchased from Shandong Aluminium Industry Co.) by calcination at 850 and 1150 °C respectively. The green disks were then sintered at 150 °C for pseudoboehmite, 850 °C for δ-alumina, and 1150 °C for α-alumina for 20 h with heating and cooling rates of 100 °C$\,$h^{-1}. These disks were polished on both sides and subsequently cleaned several times by ultrasound.

Characterization of molecular sieve membranes: XRD analysis of the as-synthesized samples was performed on a PANalytical X'Pert PRO diffractometer fitted with a $Cu_{K\alpha}$ radiation source ($\lambda = 1.5418$ Å) operating at 40 mA and 40 kV. SEM was carried out on a Hitachi S4800 or Phenom scanning electron microscope (FEI Electron Optics). EDX was performed on a Hitachi S4800 field-emission scanning electron microscope.

Single-gas permeation experiments were conducted at room temperature in a self-made apparatus (Supporting Information, Figure S3). The feed gas was fed to the side of the membrane at a fixed pressure of $p = 0.1$ MPa while the permeation side was kept at atmospheric pressure. The gas flow rate $(V/t)_i$ through the membrane was measured with a soap-bubble flow meter. The data were taken on reaching the steady state. The permeance P_i for each gas was calculated as $P_i = [(V/t)_i/p]/S$, where S is the efficient permeation area of the membrane, which is about 7×10^{-4} m^2 in our case. The ideal separation factor $\alpha_{H_2/i}$ is equal to the ratio of P_{H_2} to P_i.

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