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Ionothermal synthesis of LTA-type aluminophosphate molecular sieve membranes with gas separation performance

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ABSTRACT

LTA-type aluminophosphate molecular sieve membranes with gas separation performance were ionothermally synthesized by using δ-alumina substrates as both the supports and the aluminum sources. The effects of the synthesis parameters, such as the concentrations of H_3PO_4, TAMOH, and HF, and the detailed formation process of the membrane were thoroughly investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). Furthermore, the subsequent membrane syntheses by using recycled mother liquids were also studied. The results demonstrated that continuous and compact LTA molecular sieve membranes can be prepared over a relatively wide range of the synthesis composition. The membranes prepared with fresh and recycled mother liquids exhibit the same crystallinity, morphology and the gas separation performance. Typically, for single-component gases at 293 K, the ideal separation factors of H_2/CO_2, H_2/O_2, H_2/N_2, and H_2/CH_4, are 10.9, 8.1, 6.8, and 4.8, respectively, which suggests the good gas separation performance of the membranes.

1. Introduction

Molecular sieve membranes are highly attractive for applications in the separation of gases and liquids due to their unique properties such as uniform micropores, superior hydrothermal and chemical stabilities [1,2]. Generally, there are two major approaches to fabricate molecular sieve membranes: an in situ method and a secondary (seeded) growth method [2]. The in situ method is the most widely used, in which the membrane is prepared by the direct crystallization of molecular sieves on a support. As for the in situ method, the membrane quality depends largely on the physicochemical properties of the support surface [3,4], as well as the synthetic procedures and conditions [5,6]. The secondary growth method, which involves coating seeds on the substrate followed by secondary growth, is more practical in preparing a high quality membrane [7,8]. However, the seeding step complicates the synthesis process, especially on a tubular support. Both of these methods are typically performed under hydrothermal conditions at high autogenous pressure, which introduces safety concerns and hinders scale-up preparation [9–11]. Further, the utilization ratio of reactant materials is relative low since the crystallization takes place mainly in the solution phase, and only a fraction of nutrients are consumed for the growth of the membrane, which increases the synthesis cost. In addition, the waste mother liquids containing toxic organic amines also bring environmental pollution.

To date, much attention is paid to aluminosilicate-based molecular sieve membranes [12–14], whereas investigations toward the synthesis and characterization of aluminophosphate-based membranes are somewhat limited [15–19]. Ionothermal synthesis has been proved to be an effective approach to synthesize microporous aluminphosphate molecular sieves [20–27]. Compared with traditional hydrothermal and solvothermal syntheses, ionothermal synthesis can be performed at ambient pressure due to the negligible vapor pressure of ionic liquids. Moreover, ionothermal synthesis provides an alternative method to fabricate aluminophosphate molecular sieve membranes. For instance, $AlPO_4$-11 and SAPO-11 films with anti-corrosion

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performance have been fabricated by in situ and electrochemical ionothermal synthesis, respectively [28,29]. Recently, we have developed a substrate surface conversion method to ionothermally prepare aluminophosphate molecular sieve membranes [30,31]. In the synthesis, a moderately active δ-alumina (a metastable phase between γ and α-alumina) substrate acts as both the support and the sole aluminum source. The detailed formation mechanism of a CHA-type membrane shows that the crystallization takes place merely on the surface of the substrate via a solid-state transformation mechanism [32]. Due to the excellent thermal stability of ionic liquids, we expect that the mother liquids could be reused, which will reduce the synthesis cost and environmental pollution.

The LTA-type aluminophosphate molecular sieve ($AlPO_4$-42) is a representative member of the $AlPO_4$-n family, which consists of three-dimensional 8-ring channels with a pore diameter of 0.4 nm [33]. The small pore size, together with its neutral framework, makes the aluminophosphate LTA membrane a promising material for the separation of light gases by the molecular sieving effect. Huang et al. reported the hydrothermal preparation of an $AlPO_4$-LTA membrane with high hydrogen selectivity by the secondary seeded method, in which the expensive crown ether compound Kryptofix 222 was used as the structure-directing agent [18,34].

In the present work, we report a facile and green ionothermal route for the synthesis of LTA-type $AlPO_4$ membranes with gas separation performance. The effects of the synthesis parameters and the formation process of the membrane were investigated in detail using XRD, SEM, and EDX techniques. The subsequent membrane syntheses by using recycled mother liquids were also investigated. The gas permeation properties of the membranes prepared with freshly made and recycled mother liquids were determined using the Wicke–Kallenbach technique.

2. Experimental

2.1. Materials

Phosphoric acid (H_3PO_4, 85 wt% in water, AR), hydrofluoric acid (HF, 40 wt% in water, AR) and tetramethylammonium hydroxide (TMAOH, 25 wt% in water, AR) were purchased from Tianjin Kermel Chemical Reagent Co. and used as received without further purification. 1-butyl-3-methylimidazolium bromide ([BMIm]Br), was prepared by neutralization of redistilled N-methylimidazole (Kaile Chemical Factory, Zhejiang, China, 99.9%) and 1-bromobutane (Sinopharm Chemical Reagent Co., Ltd.) according to the procedure reported elsewhere [21]. δ-alumina disks with 2.0 mm thickness and 20 mm diameter were prepared according to the method reported elsewhere [30].

2.2. Molecular sieve membrane syntheses using fresh mother liquid

Table 1 summarizes the detailed synthesis conditions and product structures. The typical synthesis procedure can be described as follows: the synthesis solution was prepared by mixing 21.9 g (0.1 mol) of [BMIm]Br and the required quantities of H_3PO_4, TMAOH and HF with vigorous stirring. Notably, no additional aluminum source was added into the synthesis solution. Afterward, the solution was transferred into a Teflon-lined autoclave in which a δ-alumina substrate prepared in-house was placed vertically with a Teflon holder. The crystallization was performed in an air oven at 180 °C for 0.5–24 h. The as-synthesized samples was washed with distilled water by ultrasonication and dried overnight at 110 °C. To remove the template, the samples were calcined at 500 °C for 8 h with heating and cooling rates of 0.2 °C/min.

Table 1
Details of initial solution compositions, crystallization conditions and product structures.

Sample	H_3PO_4:TMAOH:HF:ILs (molar ratio)	T (°C)	t (h)	Product
1	1.0:1.0:0.7:100	180	24	LTA
2	2.0:1.0:0.7:100	180	24	LTA
3	4.0:1.0:0.7:100	180	24	LTA
4	6.0:1.0:0.7:100	180	24	LTA
5	8.0:1.0:0.7:100	180	24	LTA+AEL
6	4.0:0:0.7:100	180	24	AEL
7	4.0:0.5:0.7:100	180	24	LTA+AEL
8	4.0:0.7:0.7:100	180	24	LTA
9	4.0:2.0:0.7:100	180	24	LTA
10	4.0:4.0:0.7:100	180	24	LTA
11	4.0:1.0:0:100	180	24	Amorphous
12	4.0:1.0:0.2:100	180	24	LTA
13	4.0:1.0:1.0:100	180	24	LTA
14	4.0:1.0:0.7:100	180	2	LTA
15	4.0:1.0:0.7:100	180	6	LTA
16	4.0:1.0:0.7:100	180	12	LTA

2.3. Molecular sieve membrane syntheses using recycled mother liquids

In the recyclable syntheses, about 21 g of mother liquids were collected by simply removing the membrane. Prior to the second and third syntheses cycles, the chemical composition of the mother liquids was adjusted by adding proper amount of H_3PO_4, HF and TMAOH. The added amount of H_3PO_4 was determined by ICP-OES to keep the H_3PO_4/[Bmim]Br ratio constant. The added amount of TMAOH and HF was half of the initial amount. The detailed synthesis information is presented in Table 2. The other procedure was identical to that prepared with fresh reactants. The amount of the unreacted H_3PO_4 and compensated reagents is listed in Table 2. The other synthetic procedures are identical to that prepared using fresh reactant materials.

2.4. Characterization of the membranes

XRD analysis was carried out on a PANalytical X'Pert PRO diffractometer fitted with a CuKα radiation source (λ = 1.5418 Å) operating at 40 mA and 40 kV. The relative crystallinity was calculated based on the ratio of the intensities of the Bragg reflection (200) for LTA for each sample compared to sample 3. SEM was performed on a Phenom scanning electron microscope (FEI Electron Optics). EDX was carried out on a Hitachi S4800 field emission scanning electron microscope. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis was carried out on a Perkin–Elmer Optima 7300 DV spectrometer.

Single and mixture gas permeation tests were performed according to procedure outlined in reference [35] at 293 K followed by a modified Wicke–Kallenbach technique. The permeate side was swept with N_2 (except for the N_2 permeation measurement where CH_4 was employed as the sweep gas). The fluxes of the feed and

Table 2
The amounts of unreacted H_3PO_4 and added reagents.

Membranes	Unreacted H_3PO_4 (g)[a]	Added reagents		
		H_3PO_4 (g)	TMAOH (g)	HF (g)
M1	0	0.39	0.091	0.014
M2	0.253	0.14	0.046	0.007
M3	0.298	0.10	0.046	0.007

[a] Measured by ICP-OES. M1, M2 and M3 represent the membranes prepared from the first, second and third syntheses cycles, respectively.