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Silver-exchanged zeolite LTA molecular sieving membranes with enhanced hydrogen selectivity

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ABSTRACT

In the present work, we report a new road to enhance the gas separation performances of the zeolite Na-LTA membrane by tuning the pore size of zeolite LTA through silver cation exchange. Through the functionalization of the alumina support by using 3-aminopropyltriethoxysilane (APTES), a thin, phase-pure and well intergrown zeolite Na-LTA membrane with a thickness of about 5.0 μm can be facilely prepared on the APTES-modified macroporous α-Al_2O_3 tube. After a following silver exchange treatment of the as-synthesized zeolite Na-LTA membranes, the sodium ions in zeolite Na-LTA framework are replaced by silver ions, thus forming zeolite Ag-LTA membranes with a narrower pore diameter. The zeolite Ag-LTA membranes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). It is found that both the morphology and structure of the zeolite Na-LTA membrane keep unchanged after silver-exchange, and no cracks, pinholes or other defects are observed in the membrane layer. The zeolite Ag-LTA membrane shows high hydrogen selectivity due to the reduction of pore size of the zeolite Ag-LTA. For the separation of the binary mixture at 50 °C and 2.0 bar, the separation factor of H_2/C_3H_8 is $\alpha \approx 120.8$, which by far exceeds $\alpha \approx 19.4$ of the starting Na-LTA membrane, and are also much higher than the separation factors previously reported for the H_2/C_3H_8 mixture on zeolite membranes.

1. Introduction

During the past a few decades, owing to the uniform pore structure and high thermal and chemical stability, zeolite membranes have been extensively investigated as separators, reactors, sensors [1–8]. Various types of zeolite membranes (LTA [9–20], MFI [21,22], FAU [23–26], T-type [27,28], DDR [29,30], MOR [31], AEI [32,33], SAPO-34 [34,35]) have been successfully prepared on different supports. Among these membranes, zeolite LTA membranes have attracted intensive interest for its potential application on gas or liquid separation. On one hand, the Na-zeolite LTA membrane with Si/Al ratio of 1 shows a strong hydrophilicity, and thus have displayed excellent performances in hydrophilic separation, especially in the separation of water/organic mixtures by pervaporation and steam permeation [14–20]. Indeed, the zeolite Na-LTA membranes have been used for the first time at an industrial scale for the de-watering of bio-ethanol by Mitsui Engineering and Shipping Co. Ltd. [36]. Recently, more and more plants equipped with zeolite Na-LTA membrane tubes have been set up for the ethanol dewatering. On the other hand, the pore size of zeolite Na-LTA membrane is about 0.4 nm, which is usually smaller than the kinetic diameter of the short-chain alkanes (> 0.43 nm), thus Na-LTA membranes are promising for the separation of small molecules such as hydrogen by molecular sieving [9–13]. However, there are only a few reports on successful shape-selective separations of gas mixtures on zeolite Na-LTA membranes [10–13]. Due to the strong negative surface charge (zeta potential) of zeolite LTA building blocks, inter-crystalline defects can form easily during the growth of zeolite LTA membrane [37]. Therefore, it is still a challenge to prepare zeolite LTA membranes with molecular sieving properties.

Recently, we have developed a seeding-free synthesis strategy for the preparation of supported zeolite LTA molecular sieve membranes by using APTES [38–40], 1,4-diisocyanate (DIC-4) [41], 3-chloropropyltrimethoxysilane (CPTMS) [42], and polydopamine (PDA) [43] as covalent linkers between the zeolite layer and the porous α-Al_2O_3 support. By covalent bonds, the zeolite precursors are effectively attached and anchored onto the support surface to promote the nucleation and growth of a continuous zeolite LTA membrane layer, thus improving the gas separation performances of zeolite LTA membranes. Despite this progress, we have to admit that the gas separation performance of the zeolite Na-LTA

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membranes is still far from our expectation.

It is well known that the pore size of the zeolite Na-LTA can be tuned by cation exchange: about 0.3 nm for K-LTA (3 A) and about 0.5 nm for Ca-LTA (5 A) [44,45]. Therefore, it can be expected to improve tune the gas separation performances of the zeolite Na-LTA membranes by tuning the pore size of the zeolite Na-LTA through cation exchange [46–49]. So far, there are only a few reports on ion-exchanged zeolite Na-LTA membranes. Guan et al. reported the preparation and gas permeation properties of the ion-changed LTA zeolite membranes [46]. It is found that the K-exchanged zeolite LTA membranes showed a higher H_2/N_2 selectivity due to the decrease of the pore size, while the Ca-exchanged zeolite LTA membranes showed a higher gas permeance than the zeolite Na-LTA membranes due to the increase of the pore size. Varela-Gandía et al. reported the preparation of ion-exchanged zeolite LTA membranes on the macroporous discs through secondary growth method for the separation of H_2/CO [47]. It is reported that the ion-exchanged LTA membranes showed better performances for the purification of H_2. Shirazian et al. reported the synthesis of K-exchanged zeolite LTA membranes for the dehydration of natural gas via secondary growth method [48]. However, the separation factors of the ion-exchanged zeolite LTA membranes are still close to the coefficients of Knudsen diffusion.

Since the ion size of silver ions (0.115 nm) is slight larger than that of sodium ions (0.102 nm) [50], the pore size of the silver-exchanged zeolite LTA (hereafter called zeolite Ag-LTA) membrane should be smaller than that of the starting zeolite Na-LTA membrane. Therefore, it can be expected that zeolite Ag-LTA membranes will display a higher gas separation performance in the separation of hydrogen (kinetic diameter 2.9 Å) than Na-LTA membranes. To the best of our knowledge, there is no study on the preparation of zeolite Ag-LTA membranes. In the present work, we reported the synthesis of phase-pure and well intergrown zeolite Ag-LTA membranes on the APTES-modified macroporous α-Al_2O_3 tubes, as shown in Fig. 1. Firstly, a thin, phase-pure and well intergrown zeolite LTA membrane layer is prepared on the APTES-modified α-Al_2O_3 tube. Second, zeolite Ag-LTA membrane is obtained through a following silver-exchange treatment of the as-synthesized zeolite Na-LTA membrane.

2. Experimental

2.1. Materials

Chemicals were used as received: LUDOX AS-40 colloidal silica (40% SiO_2 in water, Aldrich) as Si source; aluminum foil (Aladdin) as Al source; sodium hydroxide ($>$97%, Aladdin); 3-aminopropyltriethoxysilane (APTES, 99%, Aladdin); toluene (99%, Aladdin); silver nitrate (99.8%, Aladdin); ethanol (99.5%, Aladdin); doubly distilled water. Porous α-Al_2O_3 tubes (Jiexi Lishun Technology Co., Guangdong, China: 12 mm outside diameter, 9 mm inside diameter, 75 mm length, ca. 1.0 μm pore size, 30% porosity) were used as the supports.

2.2. Preparation of zeolite Ag-LTA particles

The molar ratio of the synthesis solution used for the hydrothermal synthesis of zeolite Na-LTA particles was 50 Na_2O:1 Al_2O_3:5 SiO_2:1000 H_2O. The aluminate solution was prepared by dissolving 22.22 g sodium hydroxide in 50 g deionized water, then adding 0.3 g aluminum foil to the solution at room temperature. The silicate solution was prepared by mixing 4.17 g LUDOX AS-40 colloidal silica and 47.5 g deionized water at 60 °C with vigorous stirring. And then, the prepared aluminum solution was added into the silicate solution and stirred overnight at room temperature to produce a clear, homogenous solution. After synthesis for 24 h at 60 °C, the resulting Na-LTA zeolite particles were centrifuged and washed with deionized water until the pH value of the wash liquor decreased to 7, and then the produced zeolite Na-LTA particles were dried in air at 110 °C over night for characterization and ion-exchange.

For silver ion-exchange, 1.5 g zeolite Na-LTA powder was added into 100 ml $AgNO_3$ ethanol solution (with $AgNO_3$ concentration of 0.05 mol/L), and then the mixture was stirred for 4 h at 50 °C in a temperature-controlled water bath. After ion-exchange, the zeolite Ag-LTA powder was filtered and washed with ethanol to remove all the unreacted cations, and then it was dried under nitrogen at 110 °C over night for characterization.

2.3. Preparation of zeolite Ag-LTA membranes

Before hydrothermal synthesis of the zeolite LTA membranes, the porous α-Al_2O_3 tubes were treated with 3-aminopropyltriethoxysilane (APTES, 0.45 mM in 10 mL toluene) at 110 °C for 1 h, leading to an APTES layer deposited on the support surface [38].

For the synthesis of zeolite Na-LTA membranes, a clear synthesis solution with the molar ratio of 50 Na_2O:1 Al_2O_3:5 SiO_2:1000 H_2O, was prepared according to the procedure reported elsewhere [38–42]. The APTES-modified α-Al_2O_3 tubes were vertically placed in a Teflon-lined stainless steel autoclave, and then the synthesis solution was poured into the autoclave. After in-situ growth for 24 h at 60 °C, the solution was decanted off and the zeolite Na-LTA membrane was washed with deionized water several times, and then dried in air at 110 °C over night for silver ion-exchange.

For preparation of zeolite Ag-LTA membranes, the as-synthesized zeolite Na-LTA membranes were placed in a Teflon-lined stainless steel autoclave, and then appropriate amount of 0.05 mol/L $AgNO_3$ ethanol solutions were poured into. After

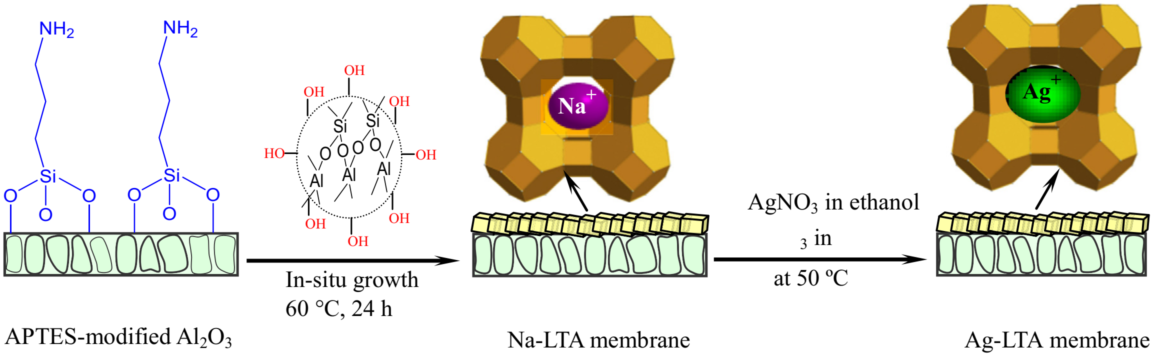

Fig. 1. Scheme of the synthesis of supported zeolite Ag-LTA membrane through silver ion exchange of zeolite Na-LTA membrane.