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Synthesis and characterization of high performance NaA zeolite-polyimide composite membranes on a ceramic hollow fiber by dip-coating deposition

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ABSTRACT

NaA zeolite membranes were synthesized on a porous seeded α-Al_2O_3 ceramic hollow fiber substrate via microwave heating method. Dense intergrown NaA zeolite-polyimide (PI) composite membranes were prepared by dip-coating with polyamic acid solution and imidization process on the NaA zeolite membranes. The composite membranes were characterized by XRD, FT-IR, SEM, gas permeation and pervaporation tests. The differences in morphology, structure and gas permeability between NaA zeolite and NaA zeolite-PI composite membranes were explored. XRD results show that only NaA zeolite emerges on the support, and FT-IR results show that PI has been successfully synthesized on NaA zeolite membranes surface. The SEM images show that the particles are twinborn by well intergrowth on the composite membrane surface. Gas permeation tests on H_2, O_2, N_2 and C_3H_8 under different temperatures display that the permeance of H_2 on the NaA zeolite-PI composite membranes is lower than that of NaA zeolite membranes, and the permselectivity of H_2/C_3H_8 on the former membranes is higher than that of the latter. Pervaporation experiments of the as-synthesized membranes on various alcohol mixtures indicate that the maximum selectivity of NaA zeolite-PI composite membranes on EtOH/H_2O solution with the water content of 10 wt.% was much higher.

1. Introduction

In the past decades, zeolite supported membranes have been extensively developed in view of their potential applications in modern industrial fields as energy issues become increasingly important [1,2]. Their intrinsic properties on preferential adsorption, differences in diffusion rates and molecular sieving effects make them broadly applicable in petrochemical processes [3], fine chemical and pharmaceutical production [4,5], contamination abatement [6–8], membrane reactor[9–11] and sensors [12–14].

So far, high performance zeolite membranes of all sorts (LTA, MFI, FAU, DDR, SAPO-34, CHA, et al.) have been successfully prepared by different preparation methods, such as in-situ hydrothermal synthesis [15–17], secondary growth method [18,19], vapor phase transport [20,21] and microwave heating method [22,23].

NaA zeolite, a crystalline aluminosilicate with uniform micrometer-sized pores, has a unit cell formula of $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ with crystalline hydrated 18~22%, containing cages with orthogonal 3-D oriented apertures of approximately 4.1 Å[24]. As a result, the hydrophilic NaA zeolite membrane was widely used for removal of water from organic solutions by PV or VP and extremely selective for small molecules as well, such as hydrogen. Mitsui Engineering and Shipbuilding Co. Ltd. in Japan made the first large scale PV plant in 1998 using tubular NaA zeolite membranes for dehydration of organic solvents by employing Kita group's technology and then brought it to the market as the first semi-technical zeolite membrane, which was a milestone in the commercialization and industrialization of zeolite membranes [25,26]. However, the space yield of PV on this plant turned out to be not very efficient compared to the polymeric membrane because of its low packing density. Then, ceramic hollow fiber membranes with a relatively high packing density are becoming more and more attractive to researchers. X. C. Xu et al. synthesized a relatively high quality NaA zeolite membrane of about 5 μm on a ceramic hollow fiber support with an outer diameter of 400 μm, a thickness of 100 μm and an average pore radius of 0.1 μm [27]. A zeolite LTA membrane with a high flux of 9.0 kg/m^2 h and high water/ethanol separation factor of 10,000 was prepared by Z. B. Wang et al. on a ceramic hollow fiber by a novel seeded method—dipcoating-wiping [28].

In order to obtain an ideal selectivity when applied in separation processes, the zeolite membrane must be dense and defect free. Nevertheless, as to NaA zeolite membrane, the synthesis of defect-free membrane is still challenging although various approaches have been developed to improve the quality of the membrane, just like addition of intermediate silane layer to increase the adhesion between gel layers and supporting substrate [29]. In addition, looking into the fields of organic membranes, polyimide (PI) membranes have come into

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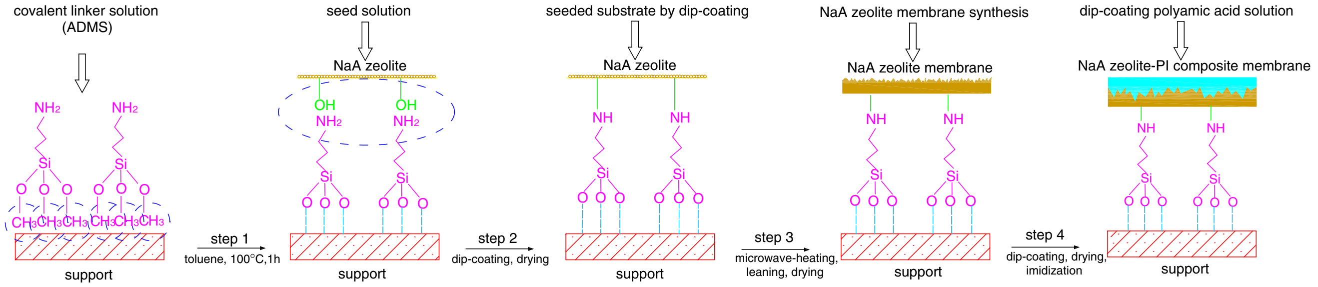

Fig. 1. Schematic diagram for preparation of NaA zeolite-PI composite membranes by using APTES as a covalent linker between the NaA zeolite membranes and the α-Al_2O_3 substrate.

prominence in recent years and have been applied in many fields, such as gas separation [30] and ultrafiltration with organic solvent [31] due to its good mechanic performance, high free volume, and high thermal and solvent resistance [32]. Subconsciously, many research efforts intended on preparing some organic–inorganic hybrid membranes so as to improve the quality of the membranes. Z. Huang et al. investigated the pervaporation dehydration of water–ethanol mixtures using MM membranes from crosslinked PVA incorporated with zeolite 4A, and the results showed that the total permeation and the water separation factor were improved upon adding zeolite 4A[33]. The void-free PI/zeolite 4A hybrid membrane synthesized by H. H. Yong et al. showed the lower permeability but higher permselectivity for He, N_2, O_2, CO_2, and CH_4[34]. However, there is no report about adding organics onto a ceramic hollow fiber supported NaA zeolite membrane surface.

In this study, NaA zeolite membranes were synthesized on a porous seeded α-Al_2O_3 ceramic hollow fiber substrate via microwave heating method firstly, and then we have attempted to coat PI film on the synthesized NaA zeolite membranes by dip-coating with polyamic acid DMF solution and imidization process to obtain NaA zeolite-PI composite membranes using 3-aminopropyl (diethoxy) methylsilane as covalent linker which enables the PI to connect with NaA zeolite tightly. The fabrication, characterization and separation performance of the NaA zeolite-PI composite membranes are detailed in this paper while the quality of the as-synthesized NaA zeolite-PI composite membranes was evaluated by gas permeation and alcohol/water pervaporation and our results show that the separating properties of NaA zeolite-PI composite membranes were very encouraging.

2. Experimental

2.1. Preparation of NaA zeolite seed suspension

NaA zeolite seed crystals A (SCA) were prepared starting from a clear solution with a molar ratio of $0.4Na_2O:Al_2O_3:3.5SiO_2:4.5(TMA)_2O:250H_2O$ (Sodium aluminum oxide, Alfa Aesar; NaOH pellets, AR, >96%, Aldrich; Sodium silicate, $Na_2SiO_3 \cdot 9H_2O$, Tianjin Kermel Chemical Reagents Ltd. Co.; Tetramethyl ammonium hydroxide 25%, Alfa Aesar; Colloidal silica suspension, 30% SiO_2 in water, Aldrich). The solution was heated at 90 °C for 6 h and the formed particles were removed by centrifugation, then the supernatant was placed in oven for an additional 15 h at 90 °C. Seed crystals B (SCB) were prepared using the same solution as in seed crystal A preparation, but were heated by a modified domestic microwave oven operating at 2450 MHz for 60 min at 90 °C. The particles finally formed were collected by centrifugation and washed to a pH of 8 and suspended in deionized water with ultrasonic treatment adding a small amount of PVA to stabilize the suspension. The concentration of suspension was adjusted to about 10 g/L. The suspension can keep stable for several days.

2.2. Substrate preparation and seeded

A self-made porous ceramic α-Al_2O_3 hollow fiber (1.6 mm in outer diameter, 1.2 mm in inner diameter, 100 mm in length, 0.1~0.2 μm pore radius, ~40% porosity) was used as the substrate. The substrate was cleaned in a deionized water bath by ultrasonic cleaner several times to remove the loose particles, and then dried in an oven at 60 °C for 12 h. The surface of the substrate was modified by reacting with the covalent linker 3-aminopropyltriethoxysilane (APTES, 98%, TCI Japan). It was placed in a 5 vol.% solution of APTES in toluene for 12 h to form APTES monolayer on the α-Al_2O_3 substrate surface, then dried at 120 °C for 12 h to remove toluene as well (see Fig. 1 step 1). A continuous NaA zeolite seeded layer consisting of mesopores (intercrystalline pores) and micropores (intracrystalline zeolitic pores) was coated on the surface of the treated hollow fiber substrate by dip-coating with the NaA zeolite seed suspension mentioned above, the seeded substrate was dried in air at 100 °C for 3 h(see Fig. 1 step 2).

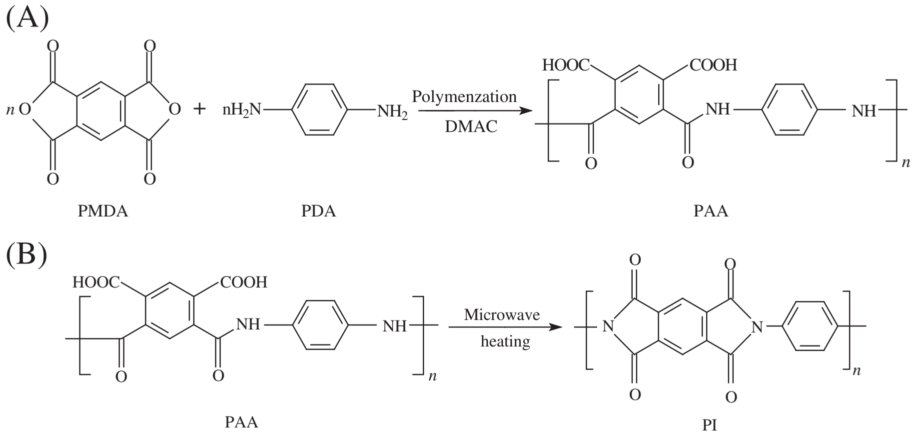

Fig. 2. Scheme of polymerization/dehydration reactions of polyimide.