Effect of mesoporous silica modification on the structure of hybrid carbon membrane for hydrogen separation

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ABSTRACT

An SBA-15/carbon molecular sieve (CMS) composite membrane, using polyetherimide as a precursor and mesoporous silica as filler, was fabricated for hydrogen separation. The effect of mesoporous SBA-15 on the gas transport properties of the composite membrane was evaluated. The permeability and selectivity coefficients of H_2, CO_2, O_2, N_2, and CH_4 were estimated for the pure CMS and SBA-15/CMS composite membranes at a feed pressure of 2–7 atm for 30 °C. The SBA-15/CMS composite membrane had a gas permeability higher than that of the pure CMS membrane, whereas its selectivity was the same. The permeability was found to be independent of pressure; this indicates that the gases are transported through the membrane by a molecular sieve mechanism. The membranes appeared to have a more microporous structure when the mesoporous silica SBA-15 was incorporated. These results concur with the hypothesis that SBA-15 improves gas diffusivity by increasing pore volume.

1. Introduction

Membrane separation processes have become one of the emerging technologies undergoing rapid growth during the last few decades [1–3]. Recently, inorganic membranes, such as micro and mesoporous silica [4], zeolite [5], and carbon molecular sieve (CMS) membranes [6], have been developed. These offer outstanding potential, including greater mechanical strength, chemical inertness, high temperature stability and time-independent performance for gas separation applications such as hydrogen production from ethanol steam reforming [7,8]. Among these inorganic membranes, the CMS membrane has been recognized as an attractive gas separation material because its pores approach the molecular diameters of small gases (<6 Å), and the main mechanism of separation in the CMS membrane is molecular sieving [9–12].

The separation takes place based on size exclusion and is therefore independent of pore wall-gas molecule interactions or feed pressure [9].

CMS membranes are usually fabricated by the carbonization of suitable polymeric precursors, such as polyimide [13–16], polyacrylonitrile [17], phenolic resin [3,18] polyfurfuryl alcohol [19–21], polyetherimide (PEI) [22], and poly(vinylidene chloride-co-vinyl chloride) [23]. In general, polymeric membrane preparation conditions, pre-treatment of the precursor, pyrolysis conditions, and post-treatment of pyrolyzed membranes all play important roles in the CMS membrane pore structure and result in different gas transport properties.

Though great progress has been made in the field of CMS membranes, permeation flux through CMS membranes is considerably reduced as gas selectivity increases because of

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the disordered pore structure and diffusion resistance of the membranes. To address this issue, almost all efforts for CMS membranes have been directed toward the production of microporous molecular sieving carbon (MSC), or the incorporation of nano-scaled materials, such as Ag-nanocluster [9], palladium nano-particles [24], zeolite [25–27], metal oxides [28], carbon nanotubes [29,30] and silica [10,31,32], during synthesis. In spite of these developments, the fabrication of the composite carbon membrane must be simplified, and its reproducibility must be improved.

In this paper a simple strategy to incorporate mesoporous silica, SBA-15, into carbon membranes is proposed, which could significantly improve gas flux without losing selectivity. As ordered mesoporous silica, SBA-15 has many unique characteristics, such as a large surface area, narrow pore distribution, long pore diameter, large pore volume, and high mechanical strength sustained by a thick wall [33,34]; thus, it is suitable as a filler for pore structure modification. The present work examined the effect of SBA-15 filler on the gas permeation properties of CMS composite membranes derived from the PEI precursor. The variation of the filling weight of SBA-15 was studied, and single gas permeation experiments with H_2, CO_2, O_2, N_2, and CH_4 were performed for pure, PEI-derived CMS and composite SBA-15/CMS membranes at different feed pressures between 2 and 7 atm at 30 °C. These membranes were analyzed by X-ray diffraction (XRD), field emission-scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) to evaluate the surface morphology and thermal stability of the composite CMS membranes.

2. Experimental methods

2.1. Materials

For the synthesis of SBA-15 mesoporous materials, TEOS (tetraethyl orthosilicate, 98%, Aldrich) and Pluronic P123 (an amphiphilic triblock copolymer containing ethylene oxide (EO) and propylene oxide (PO) in the empirical ratio of $EO_{20}PO_{70}EO_{20}$, Aldrich) were used as a Si source and template (structure-directing agent), respectively. An aqueous solution of HCl (37%, Sigma–Aldrich) was also used to control the pH of the reaction system.

The polymeric precursor used in this research to prepare carbon membranes was commercial PEI (Mw of repeated unit = 592 g/mol, Aldrich). The N-methyl-2-pyrolidone (NMP) supplied from Mallinckrodt Chemicals Co., USA was used as a solvent. A porous α-alumina support disk with an average pore size of 0.14 μm, diameter of 1.6 cm and porosity of 40–48% was purchased from Ganya Fine Ceramics Co., LTD (Taiwan). Gases for permeation tests were supplied from Toyo Gas, Taiwan, with purity higher than 99.99%. All materials were used as received.

2.2. Preparation of the CMS composite membranes

The preparation of the SBA-15-filled CMS composite membrane involved three steps. The first step was to prepare the mesoporous silica SBA-15, which has been described in detail elsewhere [35]. Five grams of Pluronic P123 were dissolved in 2 M, 156 ml HCl. TEOS (11.5 ml) was added in drops to the acidic solution of P123 with vigorous stirring at 40 °C. After 3 h, a gel was formed and then continuously stirred and aged at 90 °C for 24 h. After cooling down to room temperature, the resulting precipitation was filtered and washed with deionized water and acetone to facilitate the template extraction. It was dried at 90 °C overnight, and calcined in air at 500 °C for 6 h, with a slope heating rate of 1.5 °C/min.

The second step was to prepare the SBA-15-filled PEI coating suspension. The composition of the coating suspension is listed in Table 1. The desired loading weight of SBA-15 with a media particle size of 1–2 μm was dispersed into the NMP solution of PEI. To disperse the SBA-15 homogeneously in the solution, a high-intensity ultrasonic processor was used to sonicate the coating suspension for about 30 min. This sonication step provided powerful shearing of the SBA-15 particles, breaking up aggregates of particles and enhancing homogeneity during the intense agitation.

The third step was to prepare the SBA-15/CMS composite membrane by slide casting, curing and carbonization. The curing and carbonization trajectory used here followed the TGA results (see next paragraph). In these processes, the SBA-15-mixed PEI coating suspension was spread on the porous α-alumina support disk by a slight casting technique, resulting in a thin film of the polymer on the support. After casting, the membranes were dried overnight. The polymeric membrane was cured in a tubular furnace under an air gas stream from room temperature up to 240 °C, with a heating rate of 1.0 °C/min, and held at this temperature for 12 h. After curing, the membrane was carbonized under vacuum from 240 °C to 600 °C, with a heating rate of 1 °C/min, and kept at this temperature for 2 h. The membranes were then carefully taken from the quartz tube in the furnace and eventually stored in a desiccator containing silica gel. In this study, the membranes were denoted as SPEI-x composite membrane, where x means the SBA-15 loading weight.

2.3. Characteristics of SBA-15

The structure regularity of the SBA-15 was determined by small-angel powder XRD (D/max-2400, Rigaku, Japan) from $0.4°–5°$ using Cu Kα radiation. The Fourier transform infrared (FTIR) spectroscopy of SBA-15 was recorded on JASCO 5300 FTIR (Nicolet, USA). The size and shape images of SBA-15 were recorded by FE-SEM analysis using a JEOL JSM-6700F, OXFORD INCA ENERGY 400. Transition electron microscopy (TEM) measurements were made with a JEOL JSF-2000FX TEM (JEOL, Inc., Kyoto, Japan) operating at an excitation voltage of 120 kV. Before analysis, the samples were prepared by dispersing the powders in water-free ethanol. The samples were then deposited on a copper grid covered with a holey carbon thin film. The N_2 sorption isotherms were measured with an ASAP 2010 apparatus (Micromeritics, Norcross, GA). The Brunauer–Emmett–Teller (BET) surface area, S_{BET}, was calculated from the linearity of the BET equation. The surface area, volume and pore diameter of the BJH were obtained from the pore size distribution curves using the Barrett–Joyner–Halenda (BJH) formula.