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Hollow silicalite-1 sphere-polymer mixed matrix membranes for gas separation

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ABSTRACT

Mixed matrix membranes (MMMs) were prepared combining two different polymers (polysulfone Udel® and polyimide Matrimid®) and hollow silicalite-1 spheres (HZSs) with about 4 μm in diameter. These HZSs were obtained by hydrothermal synthesis from solid mesoporous silica spheres (seeded with silicalite-1 nanocrystals). With filler loadings varying between 0 and 16 wt.%, the MMMs were applied to the separation of H_2/CH_4, CO_2/N_2, and O_2/N_2 mixtures. For all the gas pairs tested, it was found that with a loading of 8 wt.% the MMMs performed better than those prepared with pure polymer, other different loadings and conventional silicalite-1 crystals of similar size to that of the HZS diameter. The highest selectivities obtained here for H_2/CH_4, CO_2/N_2, and O_2/N_2 mixtures were 180 (H_2 permeability = 38.4 Barrer), 41.7 (CO_2 permeability = 7.2 Barrer), and 8.5 (O_2 permeability = 2.8 Barrer), respectively.

1. Introduction

Over the last decade, to establish a membrane with higher gas separation performance relative to the pure polymeric membrane material, various polymers have been changed to produce mixed matrix membranes (MMMs) [1,2] with the incorporation of inorganic fillers, such as zeolites, ordered mesoporous silica, non-porous silica, carbon molecular sieves, and carbon nanotubes. When using nanoporous materials, MMMs have the advantage of combining the benefits of both phases: the superior gas transport properties and thermal resistance of molecular sieves with the desirable mechanical properties, low price and good processability of polymers.

Of the mentioned nanoporous fillers, zeolites are one of the most versatile from the point of view of chemical composition, particle size, shape, and possibility of chemical adaptation for improving interaction with polymer material. A recent zeolitic development includes the layer-by-layer (LbL) procedure used for engineering particle surfaces and fabricating hollow zeolite spheres (HZSs) [3], a new kind of self-bonded molecular sieve structure that have been found application as guest encapsulates [4], controlling release systems [5], and adsorbent materials [6].

Lately, it has been shown that spherical particles of ordered mesoporous silica MCM-41 with narrow particle size distribution (in the 2–4 μm diameter range) would facilitate the preparation of highly homogeneous MMMs [7]. This spherical filler would minimize agglomeration and hence improve dispersability and interaction with the polymer for two reasons: (i) the spherical shape limits the contact between silica particles, and (ii) the micrometer size spherical particles provide a lower external surface area to volume ratio than that used in other reports (for instance, with approximately 80 nm MCM-41 particles [8]). Alternative approach to obtain MMMs would consist in the use of HZS particles. The obtained HZS-MMMs would benefit from the advantages of zeolites, as microporous and crystalline molecular sieves, and those of the spherical particles above mentioned. To date, a recent communication has addressed the preparation of HZS-PDMS MMMs [9] and also a few publications use hollow silica spheres for the same purpose of obtaining composite membranes [10,11]. However, there is no detailed report describing the preparation and gas phase application of MMMs using HZSs as filler. Therefore, the aim of this study is the preparation and characterization of HZS-MMMs able to produce an enhancement in terms of selective gas transport. Even though a considerable research effort has been done on the use of nanoporous materials in polysulfone (PSF)- and polyimide (PI)-based MMMs, a challenge remains when the improvement of permeability–selectivity binomial is taken in consideration for gas mixtures such us H_2/CH_4, CO_2/N_2, and O_2/N_2. Finally, it must be pointed out that HZSs give rise to a new kind of MMM with potential applications no yet studied. As hollow particles they could incorporate a third encapsulated component to the polymer film different from the polymer and the zeolite itself. Then, the membrane could be applied as a drug delivery system, sensor material or active package.

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2. Experimental

2.1. Materials

The chemicals used for the synthesis of mesoporous silica spheres and hollow silicalite-1 spheres were as follows: sodium metasilicate, Na_2SiO_3 (Sigma–Aldrich), cetyltrimethylammonium bromide, CTABr, $C_{19}H_{42}NBr$ (Sigma–Aldrich), ethylacetate, $CH_3COOC_2H_5$ (Sigma–Aldrich), TPAOH, tetra-propyl ammonium hydroxide, 1 M solution (Sigma–Aldrich), and the silica and ethanol source here was TEOS, tetra-ethyl ortho silicate (98%, Sigma–Aldrich). Polysulfone (PSF) Udel® P-3500 and polyimide (PI) Matrimid® 5218 were kindly supplied by Solvay Advanced Polymers and by Huntsman Advanced Materials, respectively.

2.2. Synthesis of hollow zeolite spheres (HZSs)

Mesoporous silica spheres (MSSs) were synthesized following the experimental procedure given by Schulz-Ekloff et al. [12], but including slight variations in the molar composition of the synthesis sol [6]. To prepare the MSSs used in this work sodium metasilicate, CTABr, and ethylacetate as an initiator for the particles formation were used. The chemicals were mixed in order to obtain a synthesis gel with the following molar composition: $1.5Na_2SiO_3$:1CTABr:$361H_2O$:$7.4CH_3COOC_2H_5$. Once mixed, the resulting sol was kept in a closed polypropylene flask at room temperature. Whitish color dispersion was achieved 5 h later indicating the silica condensation. Subsequently, the synthesis proceeded at 90 °C for 50 h in the same open flask, without stirring. The final product was washed several times in distilled water and ethanol, and then filtered. To remove the structural agent from the pores and activate the mesoporous structure MSSs were calcined at 600 °C for 8 h with heating and cooling rates of 0.5 °C/min and maintained at 600 °C.

Silicalite-1 seeds (labeled S1S), approximately 100 nm in size, were prepared using a sol with the molar composition of 9TPAOH:$25SiO_2$:$408H_2O$:100EtOH [13] which was autoclaved for 20 h at 100 °C. To improve the electrostatic interaction between the spheres and the seeds, 2 mL of an aqueous 0.5 M NaCl solution containing 2 mg PDDA (poly(diallyl di-methyl ammonium chloride)) were added to 0.2 g of MSSs dispersed in 2 mL distilled water. Then, to remove the excess of polyelectrolyte, the dispersion obtained was washed with distilled water and centrifuged at 9500 rpm for 20 min four times. The resulting suspension was evaporated at 100 °C, leaving 2 mL of PDDA-MSS suspension. The PDDA-MSS suspension was placed in contact with 16 mL of diluted NH_4OH (pH 9.5), and 0.25 wt.% silicalite-1 seeds. The excess of silicalite-1 seeds was removed by washing four times with distilled water and centrifugation at 9500 rpm for 20 min. This layer-by-layer seeding procedure was performed only once, producing, in principle, silicalite-1 monolayer coated MSSs. Finally, silicalite-1 seeded MSSs were subjected to hydrothermal synthesis at 175 °C for 12 h (the heating time, approximately 0.5 h, is not included) with the following molar composition: KOH:TPABr:$8SiO_2$:$2130H_2O$ [6]. TPABr (tetra-propyl ammonium bromide, 98%) was purchased from Sigma–Aldrich and KOH (in pellets, 85%) from Merck. During this synthesis procedure, silica was converted to zeolite giving rise to hollow zeolite (silicalite-1) spheres (HZSs).

To compare, silicalite-1 crystals (labeled S1C) with dimensions of around $0.3\,\mu m \times 1\,\mu m \times 2.0\,\mu m$ were also prepared according to a previous work [14]. These crystals were synthesized by hydrothermal growth at 150 °C for 20 h in a mixture with a molar composition of $5SiO_2$:1TPAOH:$500H_2O$:20EtOH. Subsequently, the mixture was washed by repeating 4 centrifugation steps. All the zeolitic materials (including HZSs) were calcined at 480 °C for 8 h with heating and cooling rates of 0.5 °C/min.

2.3. Mixed matrix membrane (MMM) fabrication

Plain PSF and PI membranes were prepared to evaluate their gas separation performance with those of films containing increased amounts of HZSs (loadings of 4, 8 and 16 wt.%) as dispersed phase. Before the preparation of the MMMs, the polymers were dried overnight under vacuum (10 mbar) at 100 °C (for PSF membranes) and 150 °C (for PI membranes) to remove adsorbed water. To prepare the pure polymer membranes, polymer was dissolved (in a percentage of 10 wt.% polymer) in chloroform, allowing good viscosity of the casting solution. This percentage was kept constant for the hybrid membranes. To fabricate MMMs, the synthesized zeolitic materials were dispersed in chloroform (around 90 wt.% of solvent-10 wt.% combined inorganic filler plus polymer mixture) in an ultrasonic bath for 15 min. The polymer (PSF or PI) was then added and the resulted dispersion was magnetically stirred at room temperature for 24 h. Before the membrane casting three intervals of sonication of 15 min were carried out to guarantee a well-dispersed solution. Subsequently, the homogeneous solution was poured on a plain glass surface and left overnight partially covered at room temperature for natural evaporation. The last step was the vacuum treatment under 10 mbar of pressure to remove the solvent remaining within the membrane. The treatment took place in a vacuum oven at 100 °C for PSF and at 150 °C for PI, respectively. Membrane thicknesses were measured by a Digimatic Micrometer 0–30 mm (accuracy $\pm 1\,\mu m$). For permeation testing membrane circular areas of about $15.2\,cm^2$ were cut from the films.

2.4. Characterization

MSSs and HZSs were observed by a scanning electron microscope (SEM, JEOL JSM 6400, Jeol Corp. Ltd., Tokyo, Japan, operating at 20 kV) and by transmission electron microscopy (TEM, JEOL-2000 FXII, Jeol Corp. Ltd., Tokyo, Japan, operating at 200 kV). The materials were characterized by X-ray diffraction using a D-Max Rigaku diffractometer with a copper anode and a graphite monochromator to select Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5418$ Å). Low angle X-ray diffraction (LA-XRD) spectra of calcined MSSs were recorded on a Philips X'Pert diffractometer (PANalytical B.V., The Netherlands) with Bragg–Brentano geometry and CuKα radiation.

N_2 adsorption–desorption isotherms of both MSSs and HZSs were measured at −196 °C using a porosity analyzer (TriStar 3000, Micromeritics Instrument Corp.). The samples were outgassed at 350 °C for 8 h. BET specific surface areas were measured from the adsorption branches in the relative pressure range of 0.05–0.25 and the pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model form the adsorption branches. The sorption properties of the main material examined in this study were tested at 35 °C for CO_2, N_2, O_2 and CH_4 using a system described elsewhere [15]. Samples (around 30 mg) were pretreated under vacuum overnight at 180 °C.

Membrane SEM images were obtained by previous freeze-fracturing after immersion in liquid N_2, while collecting TEM micrographs needed to embed a portion of the membrane in an Epofix™ cold-setting embedding resin (Electron Microscopy Sciences, Hatfield, PA). For this purpose, 15 parts of embedding resin and 2 parts of hardener (in volume) were mixed and cured during 8 h at room temperature, so that the cross-section pieces could be sliced into the desired sections thin enough to be transparent for the electron beam. The slices were cut at 30–60 nm thickness using a RMC MT-XL ultramicrotome (RMC Products, Tucson, AZ) with a Standard Ultraknife 45°, 3 mm diamond blade (Drukker Ultramicrotome knife, Elementsix™, Cuijk, The Netherlands). The sliced sections were stained in aqueous solution and placed on carbon copper grids for TEM observation.