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Gas permeation characteristics of heterogeneous ODPA–BIS P polyimide membranes at different temperatures

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Abstract

Heterogeneous carbon molecular sieves and hypercrosslinked polystyrene microparticles adsorbent-based membranes with a (ODPA–BIS P) polyimide binder were prepared. The effect of adsorbent particles on the gas transport properties of heterogeneous membranes was studied. Permeability, diffusion and solubility coefficients of He, CO_2, O_2 and N_2 were estimated for homogeneous and heterogeneous membranes at a feed pressure of 1 atm for different temperatures between 25 and 60 °C. It was observed that adsorbent-filled (ODPA–BIS P) polyimide membranes exhibit higher gas permeability in comparison with adsorbent-free membrane, while permselectivity is maintained. The results also showed that the adsorbents enhance significantly gas diffusivity in (ODPA–BIS P) polyimide membrane, whereas the gas solubility is clearly reduced. In both type of heterogeneous membranes, gas permeation and diffusion are thermal activated processes described by the Arrhenius equation, whereas the sorption process is exothermic. The addition of both type of adsorbents to the (ODPA–BIS P) polyimide membrane increases the activation energy of permeability, this is mainly due to a significant increase of the heat of sorption, because the activation energy for diffusion is slightly decreased.

Keywords: Heterogeneous membrane; Carbon molecular sieve; Polymer adsorbent; Gas permeation; Polyimide

1. Introduction

The polyimides exhibited very good thermostability; therefore it is interesting to look at the separation properties of such membranes at enhanced temperature. The polyimide (PI) membranes have a good separation properties, but outstanding in permeabilities. A promising route to improve the gas permeability of polyimides consists in the incorporation of microporous materials into polymer matrix, such as carbonaceous materials, silica and polymer adsorbents, among others. Koros and coworkers used mixed matrix membrane films based on carbon molecular sieves (CMSs), which have been incorporated into polyimide matrices, for separation of gas mixtures [1]. It was shown that the CMS particles produced a mixed matrix or heterogeneous membrane having significantly enhanced effective permselectivities (CO_2/CH_4 and O_2/N_2) and fast-gas permeabilities (CO_2 and O_2) over the intrinsic properties of the pure polymer matrix phase alone [2,3]. Kim et al. [4] prepared CMS membranes using aromatic polyimide (PI) and polyvinylpyrrolidone (PVP) polymer blends. Gas permeability of pure gases He, H_2, CO_2, O_2 and N_2 was measured at 1 atm and 25 °C. It was found that the permeability decreases with increasing gas kinetic diameter, with the exception of H_2. It was reported that the membranes exhibit better permselectivity (H_2/N_2, He/N_2, CO_2/N_2 and O_2/N_2) in comparison with polymeric PI membranes. The gas permeation behavior of the CMS membranes was explained in terms of two transport mechanisms, that is, a molecular sieving mechanism (dependent on the kinetic diameter of the gas molecules) and a surface diffusion mechanism (dependent on the solubility of the gas molecules). Xu et al. [5] prepared nanocomposite membranes of polystyrene (PS) and poly(styrene-co-vinylpyridine) (PSVP) nanoparticles with polyimide precursor. Permeability and diffusion coefficients of CO_2, O_2, N_2 and CH_4 in the membranes were determined at 1 and 10 atm for different temperatures between 30 and 75 °C. The gas permeability coefficients and selectivity values

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for PI/PS-nanoparticle composite membranes decrease with the increase of PS-nanoparticles in the membranes. These are due to the increase in gas diffusion coefficients and the decrease in diffusion selectivities. For PI/PSVP-nanoparticle composite membranes, both increases in gas permeabilities and selectivities were observed when the PSVP-nanoparticles increase from 10 to 20 wt.% in the membranes, while the diffusion coefficients and diffusion selectivities show both decrease.

The three-dimensional networks, in which linear polymer chains are interconnected by a separate chemical reaction following the polymerization, are called hypercrosslinked, macronetwork polymers, or simply macronets. Hypercrosslinked polymers are usually produced in the presence of a solvent in such a way that the resulting material has a relatively 'floppy' structure and is capable of reabsorbing large quantities of solvents. The hypercrosslinked polymeric beads open new possibilities because they absorb large amounts of various organic vapors from air, as well as organic compounds from their aqueous solutions. The sorption capacity proved to be always higher than that of common polymeric, inorganic, and even carbonaceous sorbents. Recently, hypercrosslinked polymer beads were prepared [6–8] by post-crosslinking of polystyrene. The post-crosslinked polymers showed high surface areas (1000 m^2/g), a narrow distribution of small pores, and good mechanical stability and thermal resistance (till 400 °C). The sorption capacity of hypercrosslinked copolymers is up to three times higher than that of macroporous samples. The hypercrosslinked polymeric adsorbents are able to trap repeatedly large quantities of adsorbates.

Carbonaceous adsorbent materials have suitable sorption properties. Many polymers and copolymers have been described as starting materials for carbonization, e.g. polyacrylonitrile, polyethylene, polypropylene, polystyrene, among others. Among different methods, carbon molecular sieves can be prepared by microwave treatment of strong acid ion exchangers based on styrene–divinylbenzene matrix [9]. Microwave irradiation is preferred to conventional heating in preparation of CMSs due to the short reaction time and easy process control. In addition, the prepared CMSs had high specific surface areas, rather low pore volumes and, therefore, very low pore diameters.

This paper examines heterogeneous CMSs and hypercrosslinked polystyrene adsorbent-based membranes with a polyimide binder. In particular, the present study deals with the effect of temperature on gas permeation, diffusion and sorption properties of heterogeneous membranes based on (ODPA–BIS P) polyimide. With this aim, single gas permeation experiments with He, CO_2, O_2 and N_2 were performed for homogeneous and heterogeneous (ODPA–BIS P) polyimide membranes at a feed pressure of 1 atm for different temperatures between 25 and 60 °C.

2. Experimental part

2.1. Materials

4,4′-Oxybis(phthalic anhydride) (ODPA) (Chriskev, USA) was heated to 180 °C overnight in vacuum before use. 4,4′-[(1,4-Phenylene)dipropane-2,2-diyl]dianiline (BIS P) (Aldrich, Czech Republic) was used as received. *N*-methylpyrrolidone (NMP) (Merck, Czech Republic) was distilled in vacuum over phosphorus pentoxide. Ostion LG KS 0803, strong acid ion exchangers based on styrene-divinylbenzene matrix (Spolchemie a.s. Ústí n. Labem, Czech Republic, particle size 16 μm, 4.2% SO_3^{2-} groups) was used for carbonization.

2.2. Procedures

2.2.1. Synthesis of hypercrosslinked microparticles

Hypercrosslinked polystyrene microparticles were prepared by Friedel–Crafts reaction of polystyrene with chloromethyl methyl ether (CMME) in 1,2-dichlorethane solution using $SnCl_4$ catalysis. The polystyrene (PSt) was dissolved in 1,2-dichloroethane and cooled to −15 °C. Then, CMME was added to the solution, and the reaction was started by addition of $SnCl_4$ under intensive stirring. The mixture was heated for 12 h at 80 °C. The product was filtered and washed three times with 1,2-dichloroethane, then three times with acetone and finally, dried under vacuum pump. Prepared particles were first washed with 1,2-dichloroethane, then with methanol and water, and finally were dried.

2.2.2. Synthesis of carbonized particles

Strong acid ion exchangers based on styrene–divinylbenzene matrix (Ostion LG KS 0803, Spolchemie a.s. Ústí n. Labem, Czech Republic, particle size 16 μm, 4.2% SO_4^{2-} groups) (100 g) was immersed into a solution of 7 wt.% of NH_4Cl, 13% $FeCl_3$ and 7% $ZnCl_2$ in 100 cm^3 of water for 1 h. It was then dried in a rotation drier under air. Carbonization of polymer was occurred by heating in a microwave oven (Sharp R-7E45(B)/(W), Japan) with energy intensity 500 W for 8 min in air atmosphere. After heating, the sample was washed with 1 M HCl, water and ethanol, and finally was dried.

2.2.3. Membrane preparation

In the case of homogeneous membrane, the precursor polyamic acid (PAA) was synthesized by the reaction of equimolar amounts of 4,4′-oxybis(phthalic anhydride) (ODPA) and 4,4′-oxydianiline (ODA) or 4,4′-[(1,4-phenylene)dipropane-2,2-diyl]dianiline (BIS P) in *N*-methylpyrrolidone (solid content 10 wt.%) at room temperature for 24 h. A PAA solution in *N*-methylpyrrolidone with the adsorbent was spread onto a glass substrate and kept at 60 °C/12 h, 100 °C/2 h, 150 °C/2 h, 200 °C/2 h, and finally at 240 °C/2 h. The structure of the prepared membranes was confirmed by attenuated total reflectance (ATR) spectra (zinc selenide crystal, incidence angle 45°) [9]. The chemical structure of polyimide binder was shown in Fig. 1.

Heterogeneous membranes were prepared by dispersion of the filler (carbonized ion exchanger or hypercrosslinked microparticles) in NMP solution of PAA by stirring for 5 h. Then, the mixture was poured on a glass substrate and heated similarly as it was described in the homogeneous membranes preparation. The content of fillers in the films was 10 wt.%, such amount was considered optimal based on previous studies [9,10]. The adsorbent-filled polyimide membranes prepared