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Incorporating one-dimensional aminated titania nanotubes into sulfonated poly(ether ether ketone) membrane to construct CO_2-facilitated transport pathways for enhanced CO_2 separation

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ABSTRACT

One-dimensional aminated titania nanotubes were prepared by a facile distillation-precipitation polymerization method and were incorporated into sulfonated poly(ether ether ketone) (SPEEK) to fabricate mixed matrix membranes (MMMs). The aminated titania nanotubes (TNT-IM) with abundant amine groups increased the CO_2-facilitated transport sites in MMMs. Moreover, the CO_2-facilitated transport pathways (CO_2-FTP) were constructed from aminated titania nanotubes in polymer matrix, and acted as the fast CO_2 transport channels to transfer CO_2 molecules continuously and smoothly. Water uptake and water state in MMMs also played an important role in the gas separation performance. The relationship between the water content and CO_2 separation performance was investigated. Nanotubes as fillers showed water retention properties during water evaporation from the MMMs at low humidity. The highest ideal selectivities of the SPEEK/TNT-IM MMMs for CO_2/CH_4 and CO_2/N_2 were 56.8 and 62.0, respectively, with a CO_2 permeability of 2090 Barrer.

1. Introduction

Membrane gas separation technology continues to grow in importance due to its advantages over the traditional absorption and cryogenic distillation processes in terms of low capital and operating cost, low energy requirements, ease of operation and environmental friendliness [1]. The mixed matrix membrane (MMM) comprising a polymer bulk phase and a filler phase has attracted considerable attention for CO_2 separation since it provides an effective strategy to overcome the Robeson's upper-bound tradeoff line [2–7]. A well-designed MMM combines the benefits of both phases leading to enhanced gas transport property, thermal resistance and mechanical property. According to their dimensions, the fillers commonly used in MMMs include zero dimensional (0D) oxide materials (e.g., SiO_2, Ag_2O and MgO) [8,9], one dimensional (1D) materials (e.g., nanotubes) [10], two dimensional (2D) materials (e.g., flake graphite, layered titanosilicate) [8,11] and three dimensional (3D) materials (e.g., zeolite, MOFs) [12,13]. Nanotubes as one-dimensional materials used for fabricating MMMs have received significant attention on account of their inherent smooth surface and high modulus, strength, aspect ratio, *etc* [14–18].

One-dimensional tubular nanostructure was investigated for efficient gas transport and separation [19–23]. Holt et al. [18] investigated gas flow through carbon nanotube-based membrane with carbon nanotube diameters less than two nanometers, and the gas permeability of the carbon nanotube-based membranes was several orders of magnitude higher than that of commercial polycarbonate membranes. Skoulidas et al. [19] theoretically investigated the diffusivities of H_2 and CH_4 in carbon nanotubes, and came to the conclusion that transport rates of H_2 and CH_4 in nanotubes were orders of magnitude faster than in other two kinds of siliceous zeolites (silicalite and ZSM-12) with comparable pore sizes. Sholl et al. [20] reported that gas diffusion through single-walled carbon nanotube (SWCNT) membranes was much higher than other known nanoporous materials such as zeolites. They also predicted that SWCNT membranes showed high selectivity for CH_4 over H_2, which was mainly attributed to the adsorption selectivity of SWCNTs for CH_4 over H_2. Kim et al. [21] incorporated SWCNTs into a polyimide siloxane matrix to fabricate MMMs and found that the permeability of O_2, N_2 and

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CH_4 increased as the content of SWCNTs increased in MMMs. Nair et al. [22] developed an analytical model to describe molecular transport in composite membranes with tubular fillers. They reported that for a membrane with randomly oriented fillers, a high aspect ratio was preferred since it provided a higher effective permeability. Consequently, tubular nanostructure materials with intrinsically excellent separation properties could be exploited as promising fillers to fabricate MMMs. However, despite the unique transport and separation property of nanotubes, the poor compatibility between polymer chain and nanotubes is still a challenge for MMMs [23].

A facile method of surface modification of nanotubes was used to avoid the formation of undesirable voids at the interface between the filler and polymer and thus enhancing gas separation performance. In the fabrication of nanotubes-based MMMs, the pretreatment and modification of nanotubes by physical or chemical methods has been widely studied to obtain homogenous dispersion in membrane matrix [24–26]. Ismail et al. [24] acquired an good dispersion of carbon nanotubes (MWCNTs) in polyethersulfone matrix by functioning multi-walled carbon nanotubes (MWCNTs) with 3-aminopropyltriethoxysilane. Aroon et al. [25] wrapped chitosan as a hydrophilic polymer onto MWCNT to achieve the improved dispersion of MWCNT in polyimide matrix. Wang et al. [26] pre-dispersed MWCNTs in PEG solutions and transferred the whole suspension into Pebax®1657 solutions to fabricate the MMMs. The PEGs could endow hydrophilic modification to MWCNTs and improved their dispersion. To obtain a good dispersion in solutions, CNTs were sonicated with ultrasound in a PVAm solution, and then the CNTs dispersed PVAm solution was blended with PVA solution. A carbon nanotube (CNT) reinforced polyvinylamine/polyvinyl alcohol (PVAm/PVA) blend membrane was developed by Hägg et al. [27] and showed promising gas separation performance. Moreover, the presence of CO_2-facilitated transport sites in membrane has been effective to enhance gas separation performance due to the reversible reaction between CO_2 and facilitated transport groups [28–39]. Incorporation of fillers functionalized with CO_2-facilitated transport sites into polymeric membranes has been explored recently. Ismail et al. [38] investigated the facilitated transport effect of Ag^+ ion by incorporating Ag^+ exchanged halloysite nanotubes (HNTs) into membranes on the CO_2/CH_4 gas separation performance. Wang et al. [39] explored high performance MMMs by incorporating polyaniline nanoparticles into polyvinylamine matrix for CO_2/N_2 separation.

#Sulfonated poly(ether ether ketone) (SPEEK) as a glassy polyelectrolyte has recently been used as a potential gas separation membrane materials [40,41]. In this study, one-dimensional aminated titania nanotubes with abundant amine groups were prepared by a facile distillation–precipitation polymerization method, and the one-dimensional aminated titania nanotubes were filled into SPEEK matrix to fabricate MMMs for CO_2/CH_4 and CO_2/N_2 separation. CO_2-facilitated transport pathways (CO_2-FTP) were expected to construct within SPEEK membrane by incorporating aminated titania nanotubes. The effects of the titania nanotubes content, operating pressure and temperature on gas separation performance were investigated.

2. Experimental

2.1. Chemicals and materials

Poly(ether ether ketone) (PEEK) was acquired from Victrex High-performance Materials (Shanghai, China) Co., 3-(methacryloxy) propyltrimethoxysilane (MPS, Fig. 1(a)), 2-azodiisobutyronitrile (AIBN) and ethyleneglycol dimethacrylate (EGDMA, Fig. 1(b)) were obtained from Aldrich. Rutile-type titanium dioxide powders and 1-vinylimidazole (IM, Fig. 1(c)) were purchased from Aladdin reagent (Shanghai, China). N, N-dimethylformamide (DMF, 99.8%) was purchased from Tianjin Guangfu Fine Chemistry Institute (Tianjin, China). Acetonitrile (> 99.5%) and anhydrous ethanol (> 99.5%) were purchased from Tianjin Jiangtian Chemicals Ltd (Tianjin, China).

SPEEK was prepared *via* post sulfonation method [42]. The fully dried PEEK (28.0 g) was gradually added into sulfuric acid solution (98 wt%, 200 mL) and then stirred vigorously for 3.5 h at 25 °C to dissolve PEEK. The reaction mixture was continued to stir vigorously for 10 h at 50 °C, and was added to excess water under mechanical agitation. The precipitated SPEEK was washed with water until neutral pH was reached. The as-prepared SPEEK was dried at room temperature for one week, and then was placed in a vacuum oven at 60 °C for 24 h. The degree of sulfonation of SPEEK was 69% determinated through titration method.

2.2. Preparation of aminated titania nanotubes and membranes

The pure titania nanotubes (TNT) were prepared by a hydrothermal reaction as reported in the literature [43]. In a typical procedure, 2 g of rutile TiO_2 powders were dispersed in 85 ml of an aqueous solution of NaOH (10 M), and then heated at 150 °C for 72 h in a hydrothermal reactor. After cooling to 30 °C, the titania nanotubes were separated by centrifugation, and washed with water. Subsequently, the titania nanotubes were immersed in hydrochloric acid (0.1 M) for 2 h, followed by washing with water to neutral pH. The as-prepared pure titania nanotubes were obtained and dried at 80 °C in a vacuum oven. For aminated titania nanotubes, MPS and IM were applied for modification reagents in succession (Fig. 2). Firstly, the as-synthesized titania nanotubes were reacted with MPS to introduce carbon-carbon double bonds, which was used as grafting sites for the following 1-vinylimidazole polymerization. Briefly, 0.5 g titania nanotubes were dispersed in 50 ml of ethanol under sonication for 30 min, and then 1.0 ml of MPS was added into the above solution under stirring at 50 °C for 24 h. The polymerization of 1-vinylimidazole on the MPS-modified nanotubes was prepared by distillation-precipitation polymerization [44]. Secondly, the MPS-modified nanotubes (0.05 g) were dispersed in acetonitrile under sonication for 60 min, and the monomer IM (0.6 ml), crosslinker EGDMA (0.4 ml) and initiator AIBN (0.02 g) were then added into the above solution. The mixture was heated from ambient temperature till boiling state at about 80 °C and then the solvent was distilled off from the reaction vessel. After 90 min, the reaction was terminated and the aminated titania nanotubes were purified with water and anhydrous ethanol, respectively. The obtained MPS-modified titania nanotubes and the further aminated titania nanotubes were designated as TNT-MPS and TNT-IM, respectively.

#Before membranes fabrication, both the SPEEK and fillers were placed in a vacuum oven at 110 °C for 48 h to remove the adsorbed water. A certain amount of the TNT and TNT-IM were dispersed into DMF (10.0 g) under ultrasonic treatment for 12 h to obtain a suspension, and SPEEK (0.6 g) was added into the suspension under stirring vigorously at room temperature for 24 h. The resultant solution was then cast onto a glass plate and heated at 60 °C for 12 h and at 80 °C for another 12 h in succession, followed by annealing at 110 °C for 48 h. The as-prepared MMMs were designated as SPEEK/TNT-X or SPEEK/TNT-IM-X, where X (=1, 2, 5 or 8) was the weight percentage of the nanotubes to SPEEK. The average thickness of the membrane was in the range of 60–80 μm.