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Significantly enhanced CO_2 capture properties by synergy of zinc ion and sulfonate in Pebax-pitch hybrid membranes

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ABSTRACT

For high-performance hybrid membranes, it is crucial to design multi-functional filler to rationally manipulate the structure-property relationship. In this study, a novel kind of hybrid membrane was fabricated by incorporating zinc ion loaded sulfonated pitch (SP-Zn^{2+}) nanofillers into poly (ether-block-amide) (Pebax) matrix for CO_2/CH_4 separation. Sulfonated pitch (SP) with high sulfonate content was functionalized by zinc ion (Zn^{2+}) via complexation reaction to synthesize SP-Zn^{2+} nanofillers with high Zn^{2+} loading. Mixed gas separation performances of membranes with different SP-Zn^{2+} loading were conducted. Meanwhile, the effect of operating pressure on separation performance and long-term operation stability were investigated. The hybrid membranes displayed significantly enhanced permeability and CO_2/CH_4 selectivity. First, the hydrophilic sulfonate group in SP had good compatibility with Pebax matrix and effectively suppressed interfacial defects. Second, zinc ions and sulfonate group could form zinc-sulfonate complex network. The sulfonated moiety afforded strong affinity toward CO_2 due to multiple interactions whereas the Zn^{2+} moiety afforded a transport highway for CO_2. Third, the incorporation of SP-Zn^{2+} nanofillers could disturb the Pebax chain packing and optimize the free volume characteristics. Particularly, Pebax/SP-Zn^{2+}(2) membrane exhibited an increment of 104% and 70.2% in CO_2 permeability and CO_2/CH_4 selectivity respectively, much higher than that of Pebax membrane.

1. Introduction

Energy-efficient carbon capture from flue gas and other sources has been considered as a feasible way for greenhouse gas emission control and reutilization of CO_2 [1]. Among various separation technologies, membrane-based gas separation technology has unique advantages such as energy efficient and environmentally benign [2,3]. Currently, polymers with excellent processability constitute the most promising candidates for large-scale applications [4]. However, conventional polymeric materials often suffer from high chain flexibility and low physicochemical stability [5]. Hybrid membranes inheriting the merits of both polymer bulk phase and filler phase have aroused widespread interests due to the multiple interactions, multiscale structures and multiple functionalities [6,7].

For gas separation applications, hybrid membranes have another unique superiority. For example, different separation mechanisms can be integrated within hybrid membrane through the incorporation of multi-functional fillers [8,9]. In most cases, gases like CO_2 permeate through membranes following a well-known solution-diffusion mechanism [10,11], which encompasses the solution mechanism and the diffusion mechanism. The solution of CO_2 refers to the adsorption and dissolution of CO_2 in the membrane, principally depending on the affinity between CO_2 and polymer membranes. The solution mechanism can be intensified by introducing oxygen-containing hydrophilic groups like ethylene oxide [12,13] or sulfonate group (RSO_3^-) [14,15]. The diffusion mechanism refers to separation of gases with different diffusion rates, which primarily depends on free volume characteristics of membranes [16]. The diffusion mechanism can be intensified by interfering with polymer chain packing and increasing the free volume fraction [17–19]. Besides the solution-diffusion mechanism, membranes with facilitated transport mechanism have become broadly concerned [20–22], in which CO_2 can react reversibly with the carriers such as metal ions. In recent years, majority researches focus on the synergistic optimization of two transport mechanisms, particularly solution-diffusion mechanisms [23–25], while much less researches focus on simultaneous intensification of all the three transport mechanisms

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[26]. As mentioned above, it is crucial to design multi-functional fillers to integrate multi-selective mechanisms for high-performance membrane.

Sulfonated pitch (SP) is a kind of hydrophilic polymer materials with high content of sulfonate groups (> 10 wt%) [27–30], which confers strong molecular interactions with CO_2 and favorable affinity toward CO_2 [31–33], rendering sulfonation a promising strategy for the modification of diverse kinds of materials to intensify the CO_2 solution mechanism in CO_2/N_2 and CO_2/CH_4 separations. Maletzko et al. [34] found that blending of a polymer of intrinsic microporosity and partially sulfonated polyphenylenesulfone (sPPSU) could remarkably improve the gas separation performance of the hybrid membranes. The higher degree of sulfonation in sPPSU resulted in higher gas separation performance because the sulfonate groups of sPPSU could form hydrogen bonding and have strong molecular interactions with CO_2. Oliver et al. [35] synthesized a sort of organosulfonate-based metal-organic framework (MOF) which exhibited prominent enhanced CO_2 capture capabilities outperforming conventional carboxylate-based MOF. The high polarity of sulfonate groups could promote the CO_2-sulfonate interaction, rendering favorable CO_2 affinity of sulfonate-functional MOFs. Meanwhile, sulfonated pitch has good compatibility with polymeric matrix owing to their similar chemical properties. Good compatibility can mitigate interface defects and further regulate effective fractional free volume for enhanced CO_2 diffusion [36]. Subsequently, the facilitated transport mechanism of CO_2 to the permeate side of membranes can be optimized by introducing zinc ions because CO_2 with the double bond can react reversibly with zinc ions to form a π-bonded complex [37,38]. In addition, zinc ions and sulfonate group can form zinc-sulfonate complex ligand network [39], which has hydrogen bonding and electrostatic interactions with CO_2.

In this study, multi-functional SP-Zn^{2+} nanofillers were fabricated by complexing sulfonated pitch with zinc ions. The resultant SP-Zn^{2+} nanofillers were incorporated into Pebax to prepare Pebax/SP-Zn^{2+} hybrid membranes for CO_2/CH_4 separation. The morphology, structure and thermal stability of prepared nanofillers were characterized by transmission electron microscope (TEM), Fourier transform infrared spectrometer (FT-IR), X-ray photoelectron spectroscopy (XPS), Raman spectrometer and thermal gravimetrical analysis (TGA). Furthermore, the cross-sectional morphology, chemical structure, polymer chain mobility, crystalline property, free volume characteristic and mechanical stability of hybrid membranes were evaluated. Finally, the gas separation performance of mixed CO_2/CH_4 system was analyzed.

2. Experimental

2.1. Materials

Pebax® MH 1657 composing of 60 wt% of polyethylene oxide (PEO) and 40 wt% polyamide 6 (PA6) was purchased from Qingdao Tianhe Graphite Co., Ltd. (China). Sulfonated pitch (SP) containing sodium sulfonate (> 10 wt%) was obtained from Yanggu Shandong Jiangbei Chemical Co., Ltd. (China). Zinc chloride ($ZnCl_2$) and anhydrous ethanol (C_2H_5OH) were produced from Aladdin (China). Concentrated hydrochloric acid (HCl) was received from Tianjin Jiangtian Chemical Technology Co., Ltd. (China). All chemicals were of analytical grade or purer without further purification. Deionized water purchased from the Millipore system (Milli-Q) was used throughout the study.

2.2. Preparation of SP-Zn^{2+} nanofillers

A specified amount of SP was first dispersed in water at room temperature with ultrasonic to get an aqueous solution. The solution was further under centrifugal treatment at the speed of 3000 r/min to remove large impurities. The resultant suspension was concentrated by evaporation in an oven at 60 °C for 24 h followed with lyophilization to obtain the high purity SP powder.

A certain amount of $ZnCl_2$ powder was added into 40 mL of deionized water. The solution was treated by magnetic stirring for 30 min followed with addition of small amount of dilute hydrochloric acid to obtain transparent $ZnCl_2$ solution. The SP powder (0.1 g) was added to 20 mL of deionized water with ultrasonic for 40 min to acquire homogeneous SP solution. The SP solution was dissolved in $ZnCl_2$ solution with magnetic stirring for 24 h and the solid precipitation was collected by centrifugation (10,000 r/min). After washed completely with water for 3 times to remove unreacted Zn^{2+} and Cl^-, the SP-Zn^{2+} powder was obtained through lyophilization treatment.

2.3. Preparation of hybrid membranes

First, 5 g Pebax was dissolved in the mixture of 70 g ethanol and 30 g water at temperature of 80 °C for 2 h to get a 5 wt% homogeneous Pebax solution. Certain amount of SP and SP-Zn^{2+} were treated in water under ultrasonic dispersion. Then they were added respectively in Pebax solution and dispersed by stirring for 2 h to obtain casting solution. After removing bubbles, the final solutions were cast on Teflon molds and dried under ambient conditions for 24 h. Then the membranes were further dried in a vacuum oven at 45 °C for 24 h to remove the residual solvent. For comparison, the pristine Pebax membrane was prepared by the same method following with the same drying process as mentioned above. The resultant membranes with 70 ± 5 μm thickness were named as Pebax/SP(x) or Pebax/SP-Zn^{2+}(x) respectively, where x (= 1, 2, 5, 10) referred to the content (wt%) of the nanofillers in the Pebax matrix.

2.4. Characterization

The morphology and size of SP or SP-Zn^{2+} nanofillers were obtained by transmission electron microscope (TEM, PHILIPS TECNAI G2 F20). The FT-IR spectra for SP, SP-Zn^{2+} nanofillers and corresponding membranes were determined to measure chemical structures by using a BRUKER Vertex 70 Fourier transform infrared spectrometer (FT-IR) with a scanning range of 4000–400 cm^{-1} and a resolution of 1.93 cm^{-1}. The formation of SP-Zn^{2+} complex reflecting the chemical structure was conducted by DXR Smart Raman Spectrometer with a scanning range of 3500–100 cm^{-1} and a resolution of 1 cm^{-1}. The surface elemental composition (especially sulfur and zinc) and the energy level of SP and SP-Zn^{2+} nanofillers were obtained by an X-ray photoelectron spectrometer (XPS, PHI-1600, Perkin-Elmer Co., USA). The thermal gravimetrical analysis (TGA, Perkin-Elmer) was performed in order to analyze the thermal stability of SP and SP-Zn^{2+} nanofillers. The dispersion of SP (or SP-Zn^{2+}) nanofillers and cross section morphology in membranes were tested with a field emission scanning electron microscope (SEM, Nanosem 430, operated at 10 kV). Crystallization condition of Pebax hybrid membranes was examined by the X-ray diffractometer (XRD, Rigaku D/max 2500 v/pc) with a range of 5–65° and a scan rate of 3°min^{-1}. The glass transition temperatures (T_g) and the polymer chain mobility of Pebax hybrid membranes were examined by the differential scanning calorimetry (DSC, Netzsch 200F3). The fractional free volume of Pebax hybrid membranes was measured by the positron annihilation lifetime spectroscopy (PALS, EG & GORTEC, 22Na, 195 ps). The mechanical property of resultant hybrid membranes was analyzed by using an instron mechanical tester (Yangzhou WDW-02).

2.5. Gas permeation experiments

The gas separation performances of the prepared membranes were estimated with the fixed pressure/variable volume method by a self-built permeation measurement equipment, which was described previously [40]. Mixed gas system (CO_2/CH_4 30/70 vol%) was applied as testing gas. Pebax/SP or Pebax/SP-Zn^{2+} membranes with different nanofiller loading were measured under 30 °C. Pure N_2 was applied as