Chemical Engineering Science 66 (2011) 4221–4228

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Titanate nanotubes-embedded chitosan nanocomposite membranes with high isopropanol dehydration performance

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ARTICLE INFO

Article history:
Received 18 November 2010
Received in revised form
1 May 2011
Accepted 3 June 2011
Available online 13 June 2011

Keywords:
Membranes
Nanostructure
Diffusion
Dissolution
Separation
Titanate nanotube

ABSTRACT

Titanate nanotubes (TNTs) are prepared by a hydrothermal method, and then modified with poly(aspartic acid). Subsequently, they are incorporated into chitosan (CS) to fabricate the modified TNTs (MTNTs)-embedded chitosan hybrid membranes supported by the polyacrylonitrile (PAN) membrane (CS-MTNTs/PAN) and utilized for isopropanol dehydration. The physicochemical properties including physical morphology, chemical interaction, hydrophilicity, crystallinity, thermal stability and free-volume of CS-MTNTs hybrid separation layers are characterized by SEM, FTIR, water contact angle, XRD, TG and PALS analysis, respectively. It is found that the modification of poly(aspartic acid) can apparently improve the interfacial morphology and compatibility between TNTs and membrane matrix. Moreover, the superior isopropanol dehydration performance of CS-MTNTs/PAN composite membranes compared to pure CS membrane is verified via pervaporation experiments, which can be ascribed to the strong hydrophilicity and tubular structure of TNTs. For 90 wt% aqueous solution of isopropanol, the CS-MTNTs/PAN composite membrane containing 6 wt% MTNTs acquires the highest permeation flux and separation factor of 1498 g/m^2 h and 6237 at 80 °C, respectively. These results indicate the promising application potential of nanotube-filled membranes in the pervaporative dehydration of alcohols.

1. Introduction

Isopropanol (IPA) of high purity has great industrial demand since it is widely used as good solvent, cleaning agent, chemical intermediate for organic synthesis and particularly ethanol substitute. Accordingly, the IPA dehydration becomes an important industrial process. In recent years, much effort has been focused on the pervaporation (PV) dehydration technique because of its low energy consumption, high process efficiency and environmentally benign characteristics, compared to the traditional distillation technique (Bhat and Aminabhavi, 2007; Chapman et al., 2008). Among the IPA dehydration membranes, inorganic membranes usually have the best performance, i.e. high permeation flux and separation factor synchronously (Okamoto et al., 2001; Sommer and Melin, 2005; Verkerk et al., 2001; Van Veen et al., 2001); however, the expensive cost inhibits their extensive application. On the other hand, organic membranes have a much lower cost, but their permeation flux is often quite low (Chanachai et al., 2000; Dong et al., 2006; Kurkuri et al., 2002; Liu et al., 2007, 2008; Lee et al., 1999; Qiao et al., 2005; Rao et al., 2007; Svang-Ariyaskul et al., 2006; Zhang et al., 2007b; Zhao et al., 2009a).

Recently, organic–inorganic hybrid membranes have attracted tremendous interest due to the combination of the specific chemical reactivity and flexibility from polymer materials with good mechanical and thermal stability from inorganic materials. Till now, a number of inorganic particles, such as TiO_2 (Sairam et al., 2006), SiO_2 (Liu et al., 2005; Zhang et al., 2007a; Zhao et al., 2009b), zeolite (Kittur et al., 2005), phosphotungstic acid (Rachipudi et al., 2009), montmorillonite (Bhat and Aminabhavi, 2006; Choudhari and Karidurganavar, 2009), etc. have been incorporated into polymers to fabricate organic–inorganic hybrid membranes for IPA dehydration owing to their hydrophilicity or size-selective porous structure. However, majority of these inorganic particles are often of irregular granular shape, which is not in favor of mass transport within membranes. Recently, the polymer–carbon nanotubes hybrid membranes have been prepared and employed in direct methanol fuel cell (DMFC) (Chen et al., 2008; Joo et al., 2008; Thomassin et al., 2007) and pervaporation (Choi et al., 2009; Lu et al., 2007; Liu et al., 2009; Penkova et al., 2010). Because of large surface area, open end, tubular and layered-wall structure, carbon nanotubes can render desirable transport channels for water molecules, leading to the enhanced performance of the hybrid membranes (Ismail et al., 2009; Zheng et al., 2005). Nevertheless, the hydrophobicity of carbon nanotubes inhibits their application in alcohol dehydration. In comparison, incorporating titanate nanotubes (TNTs) with high

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doi:10.1016/j.ces.2011.06.005

hydrophilicity and tubular structure (Bavykin et al., 2006) into the polymers may endow the resultant hybrid membrane more favorable structural characteristics and separation performance. Although the TNTs-filled hybrid membranes have been already fabricated (Geng et al., 2010; Matos et al., 2007; Wang et al., 2010), their application in IPA/H_2O separation has not been reported as far as we know.

The aim of this work is to pursue high efficient dehydration of IPA using TNTs-embedded chitosan (CS) hybrid membranes. Chitosan is chosen as the polymer matrix for its good film-forming property as well as the reactive amino and hydroxyl groups, which can facilitate the preferential sorption and diffusion of water molecules through the membranes. Titanate nanotubes (TNTs)-embedded chitosan hybrid membranes (CS-TNTs) were prepared by physical blending, and their physicochemical properties were investigated through SEM, FTIR, contact angle, XRD, TG, PALS. To obtain high permeation flux and selectivity, the composite membranes using CS-TNTs hybrid membrane as the active layer and PAN microporous membrane as the support layer were prepared and their IPA dehydration performance was evaluated.

2. Experimental

2.1. Materials

Chitosan with a viscosity-average molecular weight of 450 kDa (90.2% N-deacetylation degree) was obtained from Jinan Haidebei Marine Bioengineering Co. Ltd. (Jinan, China). The flat-sheet ultrafiltration membrane combining PAN porous layer with polyethylene terephthalate nonwoven fabric substrate was purchased from the Shanghai Mega Vision Membrane Engineering & Technology Co. Ltd. (Shanghai, China) and had a molecular weight cut-off of 100 kDa. Poly(aspartic acid) (PASP) was kindly supplied by the Shandong Taihe Water Treatment Co. Ltd. (Shandong, China). Absolute IPA was received from the Tianjin Jiangtian Chemical Engineering & Technology Co. Ltd. (Tianjin, China). All the reagents were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

2.2. Preparation and modification of TNTs

TNTs were synthesized by a hydrothermal method as described by Geng et al. (2008). The modified TNTs were prepared as follows: after ultrasonication for 30 min, 0.6 g of TNTs were immersed into 80 ml 0.4 wt% aqueous solution of PASP under stirring for 3 h at room temperature. Then, the resulting suspension was centrifuged, and the precipitate was washed with water. PASP-modified titanate nanotubes (MTNTs) were finally obtained after dried at 60 °C in an oven overnight.

2.3. Preparation of CS-MTNTs/PAN membranes

The CS solution containing MTNTs and crosslinking agent-glutaraldehyde, was cast onto the PAN substrate to fabricate CS-MTNTs/PAN composite membranes. Firstly, 1.5 g of chitosan was dissolved in 40 ml 2 wt% aqueous solution of acetic acid at 80 °C; while a certain amount of MTNTs was ultrasonicated in 35 ml 2 wt% aqueous solution of acetic acid at room temperature. The above two solutions were mixed and stirred vigorously overnight at room temperature, and then a given amount of glutaraldehyde (2.5 wt%) and HCl (1 M) were directly added into the mixed solution to crosslink for 1 h. Afterwards, the resulting suspension was thoroughly degassed and cast onto the PAN flat-sheet membrane (10 cm × 10 cm), which had been pretreated with deionized water in order to remove the glycerin on the surface of PAN. The cast membrane did not need to be washed thoroughly and just dried in air at room temperature for 1 day. At last, a desirable composite membrane was obtained. The CS nanocomposite membranes with different MTNTs contents are designated as CS-MTNTs(X)/PAN, where X (X=2, 4, 6, 8 or 10) is the weight percentage of MTNTs to chitosan. For characterization purpose, the CS-MTNTs(X) hybrid membranes without the PAN support were fabricated using the same procedure. Moreover, pure CS and CS-TNTs(X)/PAN hybrid membranes were also fabricated using the same procedure for comparison purpose. All of the as-prepared membranes are 50–90 μm in thickness.

2.4. Characterization

The microstructure of CS-MTNTs hybrid membranes were explored by the scanning electron microscope (SEM) using a Philips XL30ESEM instrument. To study the crystallinity of hybrid membranes, a Rigaku D/max 2500v/pc X-ray diffractometer in the range of 5–40° at the speed of 5°/min (CuKα, 40 kV, 200 mA) was adopted. Fourier transform infrared spectroscopy (FTIR, 4000–400 cm^{-1}) was performed on a Nicolet MAGNA-IR 560 instrument to characterize the function groups of (M)TNTs and CS-(M)TNTs hybrid membranes. The surface hydrophilicity of acquired hybrid membranes was evaluated by the static contact angle tests using distilled water as indicator on a goniometer (ERMA Contact Angle Meter, Japan). The thermogravimetric analysis (TGA, PerkinElmer Pyris) of the membranes was carried out from room temperature to 800 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. X-ray photoelectron spectroscopy (XPS) was conducted to examine elemental composition of TNTs surface before and after modification, for which a PHI 1600 spectrometer with an Mg Kα radiation for excitation was used.

2.5. Positron annihilation lifetime spectroscopy (PALS) analysis

To investigate the changing trend of the free-volume in the CS-MTNTs hybrid membranes, the positron annihilation lifetime spectroscopy (PALS) was conducted on an EG&GORTEC fast-fast coincidence system (resolution, 201 ps) at room temperature. The positron source (^{22}Na) was sandwiched between two pieces of membranes each about 1.0 mm in thickness. There were more than a million counts recorded on every spectrum, which were then analyzed by an LT-v9 program. In this technique, the o-positronium (o-Ps) lifetime τ_3 and intensity I_3 were measured, which could be directly correlated to the size and number of the free-volume holes (V), respectively. Assuming that the o-Ps was localized in a spherical potential well surrounded by an electron layer whose thickness Δr is equal to 0.1656 nm, the radius of free-volume holes (r) could be calculated according to the quantum-mechanical model by a semi-empirical equation (Nakanishi et al., 1988; Tao, 1972)

$$\tau = \frac{1}{2}\left[1-\frac{r}{r+\Delta r}+\left(\frac{1}{2\pi}\right)\sin\left(\frac{2\pi r}{r+\Delta r}\right)\right]^{-1} \quad (1)$$

The volume of the equivalent sphere could be calculated by the following equation:

$$V_f = \frac{4\pi}{3}r^3 \quad (2)$$

Finally, the fractional free-volume (FFV) can be considered as the result from the following equation:

$$FFV = V_f I_3 \quad (3)$$

where V_f and I are the free-volume of the sphere and intensity of o-Ps, respectively.