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Preparation of C/CMS composite membranes derived from Poly(furfuryl alcohol) polymerized by iodine catalyst

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ABSTRACT

C/CMS composite membranes derived from poly(furfuryl alcohol) (PFA) polymerized by iodine catalyst were prepared. Gas separation performance was investigated by molecular probe study with pure gases (H_2, CO_2, O_2, N_2, and CH_4) at 25 °C. The pyrolysis behaviour of PFA was studied by TG and DTG. The surface morphology of C/CMS composite membranes was observed by SEM and HRTEM. The results show a C/CMS composite membrane with uniform and defect-free thin top layer can be prepared by the PFA liquid in only one coating step. The C/CMS composite membranes have excellent gas separation properties for the gas pairs such as H_2/N_2, CO_2/N_2, O_2/N_2 and CO_2/CH_4, the permselectivities for above gas pairs in same sequence were 124.72, 12.74, 9.12 and 15.91 respectively. Compared to carbon membranes derived from PFA polymerized by acid catalyst, the carbon membranes obtained from PFA polymerized by iodine catalyst have slightly lower permselectivity, but higher permeance.

1. Introduction

Carbon molecular sieve (CMS) membranes have received much attention as advanced materials for gas separation because of their superior gas permeation performance, as well as their thermal and chemical stability compared to polymeric membranes [1–4]. In general, CMS membranes are prepared by pyrolysis of various polymers such as polyimide and derivatives [5,6], polyacrylonitrile (PAN) [7,8], phenol formaldehyde (PF) [9–11], polyvinylidene chloride–acrylate terpolymer (PVDC–AC) [12] and poly(furfuryl alcohol) (PFA) [13–16]. Of these polymeric materials, the poly (furfuryl alcohol) (PFA), a cheap thermosetting resin with high carbon content, has been regarded as a potential precursor for making CMS composite membranes with high performance. As mentioned in our previous paper [17–21], the PFA has poor mechanics and elasticity properties that are not favorable for forming a thin film. In addition, the commercial products of PFA featuring high viscosity are mostly chosen in preparation of CMS composite membranes. The commercial PFA needs to be dissolved in solvents to obtain a dilute solution with appropriate viscosity before coating onto the support, and because of this, the coating/carbonization procedures are usually needed to be repeated many times in order to obtain a CMS composite membrane with good gas separation performance. This makes the preparation technology more complex and costly, and often results in poor reproducible results. To tackle this problem, we propose that a poly (furfuryl alcohol) liquid made by polymerization of furfuryl alcohol is used as the dip-coating liquid to prepare the C/CMS composite membrane, which is different from the commercial PFA process that needs to be conducted in solvents. In the polymerization of PFA, a traditional acid is generally chosen as catalyst, and we also prepared high performance gas separation carbon membranes successfully with the acid catalyst [21]. Recently, we find that iodine catalyst can also initialize the polymerization of furfuryl alcohol, and the PFA polymerized by iodine catalyst has a different chemical structure compared to the PFA polymerized by acid catalyst. This may give us a hint that the PFA obtained by unique cross-linking style should contribute another characteristic to separation performance of carbon membranes. In this paper, we will adopt the PFA polymerized by iodine catalyst as precursor to prepare carbon membranes and investigate the performance of PFA-based carbon membranes.

2. Experimental

2.1. Preparation and characterization of support

The coal-based carbon tubular supports were prepared by mixing the coal particles with binder, and the mixture was extruded into a tube with a 10 mm external diameter by a hydraulic extruder at 2.5–3.0 MPa. After drying at room atmosphere, the tubes were carbonized up to 900 °C at a rate of 3 °C/min following Ar and were held for 1 h at 900 °C before cooling back to room temperature naturally, which leads to the final products, coal-based tubes that will be used as the membrane support.

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The pore structure which is a characteristic of support were studied at room temperature by bubble–pressure method with isopropanol as a wetting liquid and nitrogen as porometry gas. The average pore size and pore size distribution were calculated according to the method recommended by Venkataraman [22]. The porosity was measured following the criterion method of the China National Standards. The surface morphology of support was examined using scanning electron microscopy (KYKY2800B).

2.2. The preparation procedure of C/CMS composite membrane

2.2.1. Synthesis of poly(furfuryl alcohol)

The polymeric reaction of furfuryl alcohol was carried out in a reactive vessel, in which the mixture of furfuryl alcohol and iodine catalyst was added and stirred for 11 h at 35 °C to make a viscous poly(furfuryl alcohol) liquid. The polymerization reaction of poly(furfuryl alcohol) is shown in Fig. 1.

2.2.2. Preparation and characterization of C/CMS composite membrane

The viscous poly(furfuryl alcohol) liquid obtained was directly used as a dip-coating liquid to prepare C/CMS composite membrane. A coal-based carbon tubular support dried at 90 °C for 2 h was dipped into the poly(furfuryl alcohol) liquid for 5 min and removed from the coating liquid at 10 cm/min. The coated membrane was first dried at 40 °C for 12 h, and then dried at 80 °C for 24 h. The dried PFA-based polymeric membrane was carbonized in Ar up to 600 °C–900 °C at the rate of 1 °C/min and held for 4 h.

TG analysis (TGA, TGA/SDTA851^e Mettler-Toledo, Switzerland) in flowing nitrogen was conducted with a heating rate of 10 °C/min and at temperatures ranging from 100 °C to 800 °C to evaluate the thermal stability of poly(furfuryl alcohol) samples. The surface morphologies of C/CMS composite membranes were observed by scanning electron microscopy (KYKY2800B). The microstructures of carbon membranes were examined by high resolution transmission electron microscopy (HRTEM, JEM-2000EX operated at 100 kV).

2.3. Molecular probe study of C/CMS composite membrane

To evaluate the capability of C/CMS composite membranes for gas separation, molecular probe studies were respectively conducted at 25 °C with a variable volume–constant pressure method to measure the permeability of single component gas through the membranes. Tested gases included H_2 (2.89 Å), CO_2 (3.3 Å), O_2 (3.46 Å), N_2 (3.64 Å), and CH_4 (3.8 Å). To ensure good reproducibility, all of the results reported here are averaged based on the measurements of at least 3 membranes prepared and tested under the same conditions.

3. Result and discussion

3.1. Thermal decomposition behavior of poly(furfuryl alcohol)

TG is used to ascertain the thermal decomposition behavior of PFA (Fig. 2). It was found that the thermal decomposition temperature of PFA is about 180 °C, and then PFA showed rapid thermal decomposition. The remaining weight is nearly 37.2% of its initial weight up to a temperature of 900 °C. DTG curves were also integrated to investigate thermal decomposition behavior of PFA. As observed, the decomposition process of PFA can be divided into three steps. The first step takes place at 180–250 °C. Elimination of oxygen atoms from furan rings gives dominant contribution to this weight loss [23]. The major thermal degradation occurred from 250 to 700 °C, the mass loss of 48.5% is ascribed to the transformation from furan rings to condensed aromatic ring [24]. It is meaningful to investigate the thermal behavior and reactive dynamics for the second stage. After 700 °C, the phenomenon of weight loss is not obvious and 7.6% weight loss takes place in this stage.

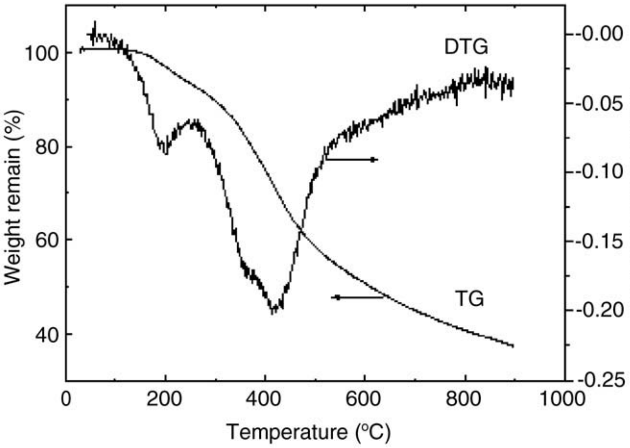

Fig. 2. TG and DTG curves of PFA.

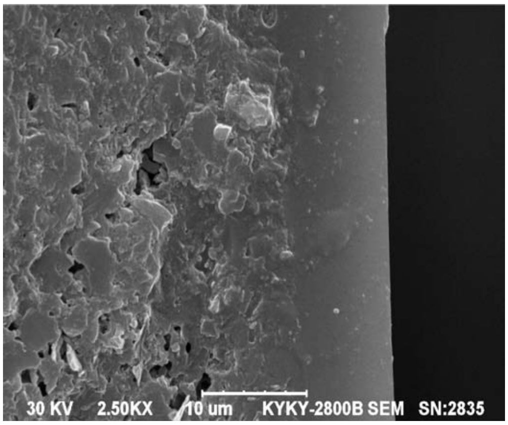

Fig. 3. SEM of C/CMS composite membrane.

3.2. Morphology and microstructure of PFA-based carbon membrane

Fig. 3 shows the SEM microphotograph of the cross section of the C/CMS composite membrane. The resulting carbon membrane processes an asymmetric structure that consists of the top thin layer and the macroporous support. The top thin layer with a thickness of around 10 μm is very smooth and almost defect-free, which determines the separation properties of carbon membrane, whereas the macroporous support provides high mechanical strength of carbon membrane. A close adherence between the top thin layer and the support can be clearly seen. This evidences that a defect-free thin top layer over the C/CMS composite membrane can be prepared by coating the coal-based support using the viscous poly(furfuryl alcohol) liquid polymerized by iodine catalyst in one single step.

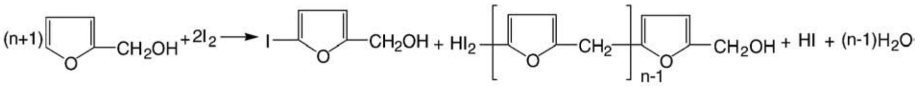

Fig. 1. Polymerization reactions of poly(furfuryl alcohol) polymerized by iodine catalyst.