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Optimizing the synthesis of composite polyvinylidene dichloride-based selective surface flow carbon membranes for gas separation

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ABSTRACT

Selective surface flow (SSF) carbon membranes were fabricated by pyrolysis of polyvinylidene dichloride (PVDC) layer deposited on macroporous ceramic supports. The pore properties of PVDC carbons were examined by physical adsorption of nitrogen and subsequent micropore analysis. The measured average pore sizes range from 1.23 to 1.42 nm for PVDC carbons with the pyrolysis temperature range of 873–1273 K respectively. The advantage of PVDC-based SSF carbon membranes is their low transport resistance with typical gas permeances of 10^{-6}–10^{-7} mol/m^2 s Pa, 2–4 orders of magnitude higher than those of carbon molecular sieve membranes. They are suitable for separation of feed streams containing strongly adsorbing species such as hydrocarbons from non/weakly adsorbing components. In this study, gas molecules of similar kinetic diameter but disparate adsorption ability like ethane and nitrogen were chosen to evaluate the membrane separation performance and the reverse-selectivity characteristic of SSF carbon membranes. Commercial PVDC solutions were used and the preparation factors like concentration of polymer precursor, carbonization temperature and coating conditions were taken into account to optimize the SSF carbon membranes performance for hydrocarbons–nitrogen separations.

1. Introduction

The development of inorganic membranes for gas separation has exhibited remarkable progresses during the past two decades. Research impetuses on inorganic membranes are rooted in their anticipated better selectivity, thermal and chemical stability under harsh operating conditions than polymeric membranes. Meanwhile, microporous inorganic membranes also demonstrate the possibility to push the “upper bound” of the permeability–selectivity tradeoff relationship that limits the separation performance of processable polymeric materials [1].

Carbon membranes, one of the microporous inorganic membranes, are promising candidates for gas separation both in terms of separation ability, higher temperature operation and corrosion resistance [2]. Carbon membranes may be divided into two subcategories according to the micropore size: carbon molecular sieve (CMS) and selective surface flow (SSF) membranes. CMS membranes possess molecular discrimination effect by allowing smaller molecules to transport through the pores and hindering the passage of larger molecules. These membranes have high selectivity for separation of gas mixtures containing small gas species and certainly require a precise control of pore sizes near the threshold of molecular sieving size. For the nanoporous SSF membranes, the pores are much larger than the dimensions of the molecules and the separation is based on the preferential adsorption of certain components in gas mixture followed by surface diffusion in the carbon matrix [3].

The gas transport mechanism through porous membranes is affected by the pore size distribution and the chemistry of the pores. The mechanism of transport basically changes when membrane pore size decreases, in the micropore region, from Knudsen’s diffusion where gas molecules collide more often with the pore walls than with other gas molecules to molecular sieving where only small enough molecules could penetrate through. Gas molecules may adsorb on the pore walls and then diffuse through by a surface diffusion mechanism. When this adsorption is physical, the adsorbed solutes are highly mobile and diffuse along the pore walls at a faster rate than they move in the bulk [4]. The adsorbed species can also significantly reduce the void space of the membrane pores that limits the entry and passage of the non- or weak-adsorbing molecules, which leads to an adsorption selective membrane transport mechanism. The gas transport through CMS carbon membranes is mainly based on molecular sieving [2], while surface diffusion mechanism typically fits gas permeation in SSF carbon membrane. Therefore, for SSF membranes, it is reasonable to expect the separation selectivity not as high as their CMS counterparts, but with much higher gas fluxes, due to the larger pore size.

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Polyvinylidene chloride (PVDC) is a polymeric precursor starting with the monomer, vinylidene chloride. PVDC comes in three basic forms: latex (aqueous emulsion), solvent soluble resin, and extrudable or blown resin. The typical commercially available PVDC is the latex form. PVDC latex can provide excellent barrier to flavors, oils, greases, many common solvents, and odor as well as giving abrasion resistance and heat sealability. For the application as precursor for carbon membranes, PVDC is very attractive since it can create a porous structure only by carbonization at high temperature without any additional activation process. PVDC-based SSF membranes were first developed by Air Products and Chemicals, Inc. and were applied to separations of gas mixtures of C_2^+ hydrocarbon–hydrogen [5,6], hydrogen sulfide–hydrogen [7], carbon dioxide–hydrogen [8] and hydrogen sulfide–methane [9]. However, little membrane preparation information was disclosed and the rejection–recovery relationship was applied in evaluating membrane performance. In this study, commercial PVDC solutions were used as the polymeric precursor and the preparation factors like concentration of PVDC solution, carbonization temperature and coating conditions are discussed in detail. Ethane and nitrogen were chosen as permeating gases to evaluate the membrane separation performance and to demonstrate the reverse selectivity mechanism of SSF carbon membranes because of their similar kinetic diameters but different adsorption affinities on the carbon matrix.

2. Experimental methods

2.1. Membrane formation

A commercial DARAN 8550 PVDC suspension (Owensboro Specialty Polymers) was used as the polymer precursor. A polymeric solution with appropriate concentration was coated inside the macroporous, tubular, CoorsTek symmetric 0.2 μm pore size α-alumina substrate (GTC-998). As a cleaning step, the GTC ceramic supports were sonicated in distilled water for 5 min. The ends of the support tubes were glazed by brushing commercial glaze (DUNCAN Pure Brilliance^{TM}) at both ends to prevent gas bypass. The glazing was completed by heating in air to 880 °C with a ramp rate of 180 °C/h. The DARAN PVDC suspension (~50 wt% of PVDC) was diluted by deionized water to certain concentrations for membrane preparation. The coated polymeric membranes were dried in inert atmosphere in a tubular furnace at 50 °C for 8–10 h and then subjected to a carbonization process during which the temperature was heated up between 600 °C and 1000 °C in flowing nitrogen with the ramp rate of 100 °C/h and kept for 1 h before cooling down to room temperature.

2.2. Characterization and permeation testing

The membranes were characterized to determine the film thickness using scanning electron microscopy (FEI SEM). The microstructure of the PVDC carbons was characterized using a Micrometrics ASAP 2020 adsorption porosimeter equipped with micropore analysis function at the liquid nitrogen temperature of 77 K. Their specific Langmuir area and Brunauer–Emmet–Teller (BET) surface area, pore volume and pore size distribution were obtained from N_2 isotherm measured. The apparatus was also used for the adsorption isotherm of nitrogen and ethane at room temperature.

Single-gas permeation experiments with industrial-grade (99.9+% purity) N_2 and C_2H_6 were performed at room temperature with a pressure gradient of 137.8 kPa and the permeate flows were measured by a soap film meter. The permeate side was kept at local atmospheric pressure, approximately 82 kPa. N_2 was introduced to the module first followed by switching to C_2H_6, and then N_2 was fed again to the system. The C_2H_6/N_2 selectivity is designated as the ratio of C_2H_6 flux to the lowest transient N_2 flux of the second feed. Methane flux was tested at room temperature for calculating its diffusivity and estimating average pore size of SSF membranes. Krypton, argon and helium permeation measurements were also carried out for comparison of the transport mechanism through the membranes.

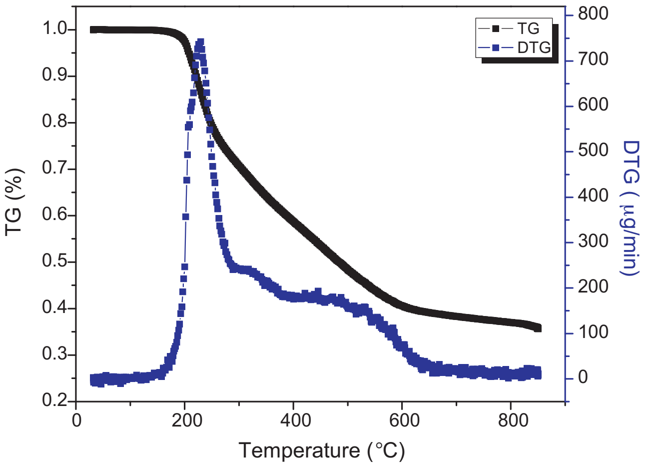

Fig. 1. Thermogravimetric analysis of PVDC under flowing nitrogen gas.

3. Results and discussion

3.1. Characteristics of PVDC carbons

Fig. 1 shows the results of thermogravimetric analysis of PVDC solution (dried at 110 °C before testing) under flowing nitrogen gas. The main and drastic weight loss occurs at 230 °C due to the release of chlorine and hydrogen chloride. This extensive gas release is thought to induce the formation of an open microporous structure in the resultant carbon matrix. Another weight loss, taking place at around 500 °C, should originate from the evolution of hydrogen that creates the nanopores. This is consistent with the results in the literature that the evolution from polymer to carbonaceous materials for PVDC occurs via two weight variations when being carbonized [10,11]. After carbonization at 850 °C, the weight loss is about 65% of the original sample mass. Since the weight loss at temperatures higher than 600 °C is very small, a temperature range of 600–1000 °C was applied in this work to measure the pore properties of PVDC carbons.

Fig. 2 shows the nitrogen adsorption isotherm of PVDC carbon pyrolysed at 600–1000 °C. According to the classification of IUPAC, this N_2 isotherm exhibits a typical type I isotherm with an initial steep increase in the N_2 uptake followed by a plateau at high pressures. This isotherm type usually reflects the micropore filling phenomena on microporous adsorbents, with the saturated sorption amounts being the volume of micropore filling. Similar results were obtained for all PVDC carbons pyrolysed at 600–1000 °C. Nearly all of the pore volumes are filled at relatively low relative partial pressures ($P/Po \leq 0.1$), indicating the highly microporous structure of these samples. Table 1 lists the surface area and pore volume information for different PVDC carbon materials. For carbonization temperatures higher than 800 °C, both specific surface area and pore volume decrease compared to those for samples carbonized at temperatures lower than 800 °C. The porous structure is developed during the carbonization process, in which the release of the chlorine and hydrogen creates the pores that finally form the carbon matrix. So the specific surface area and pore volume should