



Intermediate gel coating on macroporous Al₂O₃ substrate for fabrication of thin carbon membranes

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Abstract

To fabricate carbon membranes based on a low-cost macroporous Al₂O₃ substrate, a pretreatment called “intermediate gel coating” on the substrate was introduced. It can be carried out simply by coating the substrate with an AlOOH sol and drying to form a gel layer. The PFA (polyfurfuryl alcohol) was synthesized and coated on the gel-modified Al₂O₃ substrate, and the carbon membranes were obtained after a carbonization treatment. Scanning electron microscopy (SEM), thermogravimetry (TG), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and pore-size analysis were conducted in material characterization, and the permeation performances of the carbon membranes were tested with H₂, N₂, O₂ and CO₂. Upon the substrate surface modification for fabrication of carbon membranes, such an intermediate gel coating method is superior to the traditional sol–gel treatment because the intermediate gel layer effectively prevented the PFA from penetrating into the macroporous substrate during coating and carbonization treatments so that a thin and uniform carbon layer can be created. The resulting carbon membranes exhibited promising gas permeability and permselectivity.

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1. Introduction

Membrane technology has attracted considerable attention in gas separation industries such as hydrogen recovery, air separation, olefin/paraffin separation, CO₂ capture, nature gas dehydration, etc. [1,2]. Organic membranes are most popular so far, but in many cases, their poor temperature and chemical stabilities greatly limit their applications, and the demands for inorganic gas-permeable membranes are increasing [3]. Through adsorption and molecular sieving mechanism, the carbon membranes (i.e. nanoporous carbon molecular sieve membranes) are particularly useful in gas separation, and excellent separation may be achieved even between gases with almost similar molecular size [4–6]. However, they suffer greatly from low permeability and poor mechanical strength in

industrial applications [7], and therefore the concept of composite membrane has been introduced, which consists of a thin layer of carbon molecular sieve on a porous substrate [8–14].

During membrane fabrication, it is important to avoid membrane defects (e.g., cracks and pinholes) so as to maintain the membrane selectivity. For this purpose, not only the fabrication process but also the substrate material plays a key role. An ideal substrate should have a defect-free surface with low roughness, high porosity and small pore size apart from the other required properties such as physical strength, gas diffusivity and temperature stability (i.e., resistance to the high-temperature carbonization treatment during membrane fabrication). The porous ceramics are most common substrate materials, so far, because of their outstanding stability and abundant market availability. In general, most of the micro- and nano-porous ceramics are manufactured by depositing one or more fine porous ceramic layers on a macroporous ceramic base through sol–gel approach, forming an asymmetric structure [11,15].

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The routine sol–gel process is the dip coating with a sol of ceramic precursor, followed by drying and heating treatments. In order to narrow the pore size distribution, more ceramic layers with gradient pore sizes are necessary, making the whole process extremely time-consuming and complicated.

Although the high quality of the substrate material helps to suppress the membrane defects and ease the membrane fabrication difficulty, their high cost will eventually hold back the perspective of membrane applications. Such a situation motivates the development of substrate materials that are low in cost but good enough for carbon membrane fabrication. In this paper, we introduced an intermediate gel coating to modify the low-cost macroporous Al_2O_3 material, and the permeable and selective carbon membranes were then created.

2. Experimental details

2.1. Substrate preparation

Some Al_2O_3 tubes (o.d., 13 mm; i.d., 8 mm; length, 70 mm) were cut from a tubular macroporous $\alpha\text{-Al}_2\text{O}_3$ filter, with mean and largest pore sizes of 3.0 and 9.4 μm , respectively. After being cleaned with water, they were heated at 600 °C for 2 h to get rid of the possible organic contaminants. An AIOOH sol was prepared similar to that reported in [16]. About 3.2 g $\gamma\text{-AlOOH}$ (pseudo-boehmite, purchased from PURAL SB, Condea Chemie GmbH) was mixed with 100 mL deionized water and 2.8 mL 1.6 mol/L nitric acid solution, followed by a peptization at 85 °C under refluxing for 5 h. Then, 31.8 g 5% PVA (polyvinyl alcohol, polymerization degree, 1750) and 0.8 g PEG (polyethylene glycol; average molecular weight, 400) were added under stirring, to obtain a translucent homogeneous sol. The Al_2O_3 tubes were coated with the AIOOH sol through an intermediate gel coating and a sol–gel coating as schemed in Fig. 1.

To carry out the intermediate gel coating, each Al_2O_3 tube was sealed with silicone plugs and immersed into the AIOOH sol for 5 min, and it was pulled out vertically at a velocity of 1 cm/min with an electric motor through a nylon string fastened to the upper silicone plug. After drying at 10 °C for 2 d in a refrigerator, a gel film forms on Al_2O_3 , and the resulting gel-coated Al_2O_3 material is denoted as Gel– Al_2O_3 . For reference, conventional sol–gel coating was also

performed, which included three intermediate gel coatings and three calcinations at 600 °C for 5 h. The resulting material is denoted as SG– Al_2O_3 .

2.2. Carbon membrane fabrication

The precursor of the carbon membrane was polyfurfuryl alcohol (PFA), which was synthesized by polymerization of furfuryl alcohol at 70 °C under stirring and refluxing for 12 h with 5 g/L oxalic acid as a catalyst. The PFA was cooled in an ice bath for 1 h, and dip-coating was carried out on SG– Al_2O_3 and Gel– Al_2O_3 . After aging at 40 °C for 12 h and then at 80 °C for 24 h, the PFA/SG– Al_2O_3 and PFA/Gel– Al_2O_3 were heated under argon atmosphere at 700 °C for 4 h with a ramp of 1 °C/min, followed by a cooling to room temperature under argon. The resulting carbon membranes are correspondingly denoted as C/SG– Al_2O_3 and C/Gel– Al_2O_3 .

2.3. Characterization

Pore size was measured by a bubble-point (or the so-called capillary flow) method with a GaoQ PSDA–20 porometer [17]. The TG (thermogravimetry) analysis was conducted on a NETZSCH STA 409PC with a heating ramp of 5 °C/min from 30 up to 900 °C in nitrogen (50 mL/min). The FT-IR (Fourier transform infrared spectroscopy) spectra were recorded in 4000–400 cm^{-1} with a Nicolet-20DXB spectrometer. Before analysis, the synthesized PFA was directly smeared on a KBr plate by thin-film method, while the carbon layer of the membranes was scratched, mixed with KBr, ground and finally pressed into a disk. The surface and cross-sectional morphologies were observed with a field-emission scanning electron microscope (FEI Siron 200), but before the cross-sectional analysis all the specimens were encapsulated with epoxy resin and treated on a grinder-polisher (BUEHLER Phoenix Beta).

2.4. Gas permeation tests

Each carbon membrane was assembled in a testing cell described in [18,19] and was sealed with rubber O-rings, giving an effective membrane length of 5 cm. The permeation test was carried out in single-gas mode at room temperature.

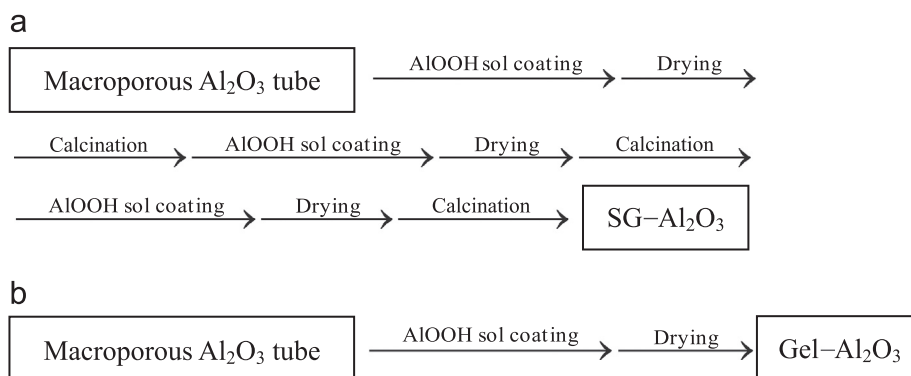


Fig. 1. Preparation of substrate materials: (a) SG– Al_2O_3 and (b) Gel– Al_2O_3 .

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