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Fabrication of triazine-based Porous Aromatic Framework (PAF) membrane with structural flexibility for gas mixtures separation

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A B S T R A C T

A transparent, freestanding Porous Aromatic Framework-97 (PAF-97) membrane was successfully synthesized via a one-step acid-catalyzed reaction. Due to the introduction of ether groups, the obtained PAF-97 membrane possesses enhanced structural flexibility, thus increasing the flexibility of the resulting membrane. This is proofed by the fact that the feeding pressure of the membrane reaches as high as 5.5 bar during the separation of gas mixtures. The Young's moduli of the membrane were 6.615 GPa and 11.11 GPa, either in a dry or hydrated state respectively. To be highlighted, under a feeding pressure of 3.6 bar, the PAF-97 membrane rendered the permeance values of 2.90×10^{-7}, 1.29×10^{-8} mol m^{-2} s^{-1} Pa^{-1} for CO_2 and CH_4, respectively, with a CO_2/CH_4 permselectivity of 22.48.

Introduction

Membrane separation, an economical and efficient technology, is considered as a suitable modern technology for separation objective compared with the conventional, intensely energy-consuming cryogenic method [1–5]. According to the compositions, gas separating membranes can generally be divided into three categories: inorganic membranes [6–8], organic membranes [9–11], and organic-inorganic hybrid membranes [12,13]. The inorganic membranes are thermally and chemically stable and can sustain of high temperature or corrosive gases. However, inorganic membranes have difficulties in preparing and processing and the membranes are usually fragile. Hybrid membranes such as Metal-Organic Framework (MOF) membranes have been studied for gas separation recently [14]; however their low chemical and thermal stabilities kind of limit their wide utilization in the industry. The concept of using polymeric membranes for gas separation was proposed in a century ago. It becomes attractive for industrial applications in the recent two decades since membranes with commercially interested permeability and selectivity for gas separation were developed [15].

Various polymeric film materials have been prepared such as cellulose derivatives, polyimides, polyesters, ethylene-based polyolefin, etc. and their separation performances for different gases have been investigated. A main limitation of polymeric membrane is the trade-off relationship between permeability and selectivity. The relationship is shown as a Robeson's upper bound [16]. The separation factor of a polymeric membrane would normally decrease with the increasing permeability of each gas component. To achieve the high permeability which is demanded in industrial applications, the general method is increasing the feed pressure. Thus the membranes' mechanical strength should be high enough to withstand the feeding pressure. However, many of the report membranes are not strong enough to survive under elevated pressure [17]. For the purpose of improving the membrane separation performance, tremendous works have been developed.

Recently, Dai et al. have reported a polymerization reaction of aromatic nitriles using a super acid of trifluoromethanesulfonic acid (CF_3SO_3H) as catalyst [17,18]. The pore size of the membrane obtained by the polymerization reaction is either blocked, or very large. Besides that these membranes have poor mechanical strength because of the usage of rigid ditopic monomers. On the basis of this reaction, we used a flexible monomer and adjusted the procedure to directly obtain the triazine based Porous Aromatic Framework-97 (PAF-97) membrane. Specially, the PAF-97 membrane is not only transparent and freestanding, but also flexible and because of the introduction of the ether bond which can increase the membrane's applications (e.g. windscreens, impact protection). Characterizations of FT-IR and NMR indicate the formation of triazine from nitrile groups. The film possesses CO_2/

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N_2 and CO_2/CH_4 selectivity of 1.49 and 22.5, respectively. That the high selectivity of CO_2 over other gas components may due to the nitrogen-rich characteristics of triazine rings which result in the strong affinity of framework for CO_2 and the lone pair-pi interaction between oxygen of CO_2 and the plane of triazine probably accelerating the accessibility of CO_2 through the membrane. In addition, the flexible ether groups in the film increase the flexibility of the film, which can be proofed by the fact that the membrane can separate gas mixtures at pressure as high as 5.5 bar. This feed pressure is over any other previously reported pressure of a triazine-based membrane.

Results and discussion

Similar to most of other PAF materials, PAF-97 membrane is of amorphous nature, indicated by the PXRD patterns (Fig. 1).

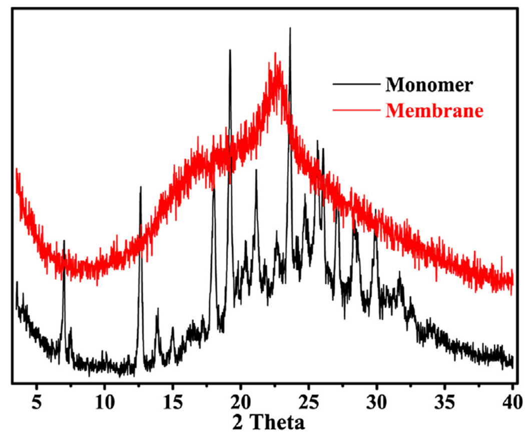

Fig. 1. Powder X-ray diffraction pattern of the monomer and membrane.

The material was thus investigated by Fourier-transform IR (FT-IR) spectroscopy to identify the spectral changes between the monomer and PAF-97 membrane. (Fig. 2A) Two strong absorption bands were found at 1503 and 1361 cm^{-1} representing the aromatic C—N stretching and breathing vibrations in the triazine unit, respectively [17,18]. Absorption at 2230 cm^{-1} of PAF-97 membrane indicates the existence of the unreacted terminal nitrile [17,18]. It is obvious that the intensity of the nitrile adsorption decreases after polymerization. These results support that the PAF-97 membrane was formed by trimerization of nitrile groups.

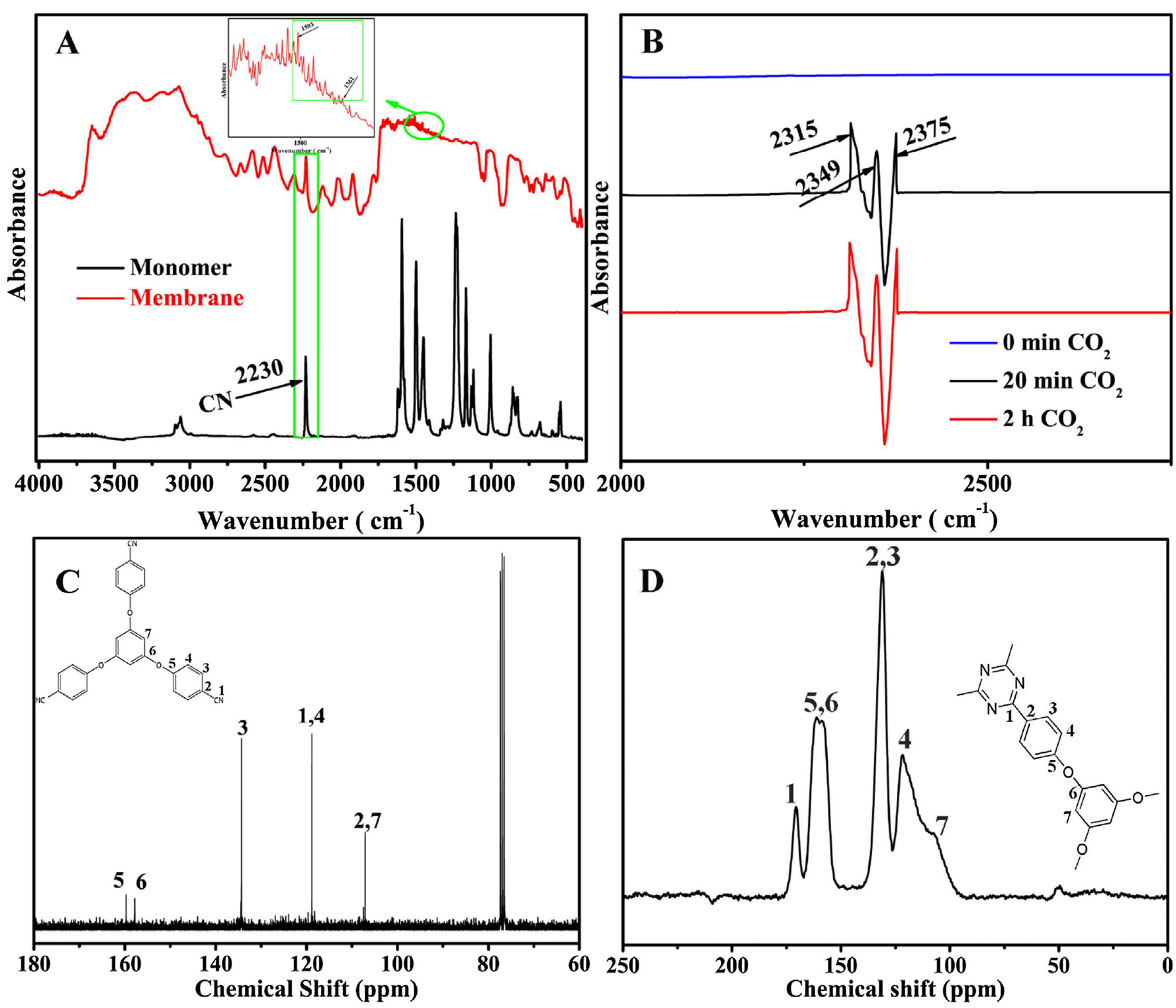

Fig. 2. (A) FT-IR spectra of monomer and PAF-97 membrane prepared at 100 °C. (B) FT-IR spectra of the PAF-97 membrane without CO_2 (top) and with pure CO_2 in the cell after 20 min and 2 h (middle and bottom). (C) The solution NMR spectrum of the monomer. (D) The solid-state NMR spectrum of PAF-97 membrane.

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