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journal homepage: www.elsevier.com/locate/memsciFacile synthesis of highly permeable CAU-1 tubular membranes for separation of CO₂/N₂ mixturesYuan Jian^{a,b,c}, Huimin Yin^d, Fengyu Chang^d, Linjuan Cheng^d, Jianhua Yang^{d,*},
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ABSTRACT

Facile synthesis of a thin tubular CAU-1 membrane was carried by simple in-situ solvothermal growth method through the use of the asymmetric α -Al₂O₃ tube support with the same metal centre as the CAU-1 framework. The solvent ratio, reactant concentration and support property were found significant for the formation of a dense and continuous pure CAU-1 membrane with highly permeable and selective CO₂ towards N₂ and CH₄. A high CO₂ permeance of $0.80 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with separation factor of 14.8 was achieved for the M3 for 1:1 CO₂/N₂ binary mixtures at room temperature. Both the increase of ethanol in the solvent mixture and reactant concentration were favourable for the formation of a dense and well intergrown pure CAU-1 membrane while their excessive increase led to impure NH₂-MIL-53 formation. The composition and pore size of the support contributed to high permeance and selectivity of CAU-1 membrane for CO₂/N₂ separation.

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1. Introduction

CO₂ emission from flue or natural gas has been assigned to be a major factor in global warming. CO₂ separation by membranes has attracted great interest due to its high energy efficiency. Because the crystallization of nanoporous metal-organic frameworks (MOFs) possessing the striking features of fine-tuned size, shape, and chemical functionality of cavities and internal surfaces on the surface of organic ligand [1–4], MOF materials [5–9] as separation membranes have received enormous attentions. It has been shown that MOF based membranes and thin films synthesized on organic and inorganic supports have been extensively studied for the separation of industrial gases [10–18] and liquids [19–26] including CO₂ capture. Due to the strong interactions of CO₂ molecules with the unsaturated metal sites or the ligands of the frameworks, many MOFs materials from MOF-5 and its isostructural frameworks [27–35], zeolite frameworks (ZIFs) [36–40] to Al containing MOFs [41–44] show remarkably high CO₂ adsorption capacity and selectivity over the non-polar gases such as CH₄ and N₂. In particular, amino-functionalized MOFs such as NH₂-MIL-53 [45], bio-

MOF-11 [46–48] and CAU-1 [49], are particularly attractive for CO₂ capture because of the preferential acid-base interaction between CO₂ molecules and amino groups, which can facilitate the CO₂ adsorption prominently. However, despite of the high adsorption capacity and selectivity of CO₂ over N₂ or CH₄ of MOF materials, only MOF-5 and CAU-1 membranes were shown to have good CO₂ separation efficiency. The strong interaction between MOFs and CO₂ has two edges. The strong interaction of CO₂ with MOFs can largely enhance the CO₂ adsorption capacity but probably reduce the mobility of CO₂ simultaneously.

The amino-decorated 12-connected [Al₄(OH)₂(OCH₃)₄(H₂N-BDC)₃] · xH₂O CAU-1 reported by Stock's group [50] is an appealing membrane candidate for molecular gas applications. CAU-1 is built from unprecedented aluminium-based octameric building units, which are connected through twelve amino-terephthalate linkers to form a three-dimensional microporous framework that involves distorted octahedral and tetrahedral cages as shown in Fig. 1. Access to the cages is only possible through small triangular windows with a free aperture of 0.3–0.4 nm. In addition, CAU-1 shows a relatively rigid framework and high thermal stability up to 573 K. The framework functionality with unprecedentedly high CO₂ adsorption capacity in combination with the small pore aperture and rigid framework prompted us to study the CAU-1 membrane for CO₂ separation from flue gas.

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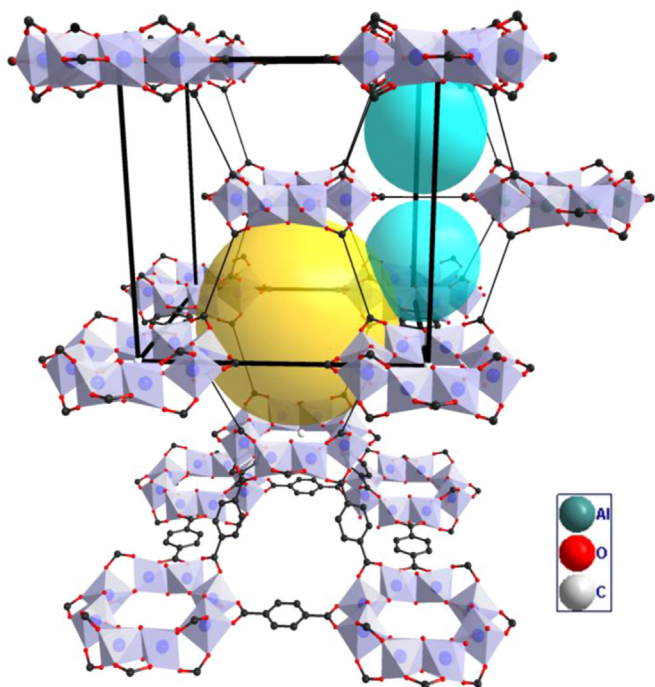


Fig. 1. The crystal structure of CAU-1 [50], the yellow and blue sphere illustrates the distorted octahedral and tetrahedral cages with effective diameters of approximately 1 nm and 0.5 nm formed by the brick $\{Al_8(OH)_4(OCH_3)_8\}^{12+}$ respectively.

For the synthesis of MOF membranes, there are several synthetic strategies to fabricate MOF membranes and films including secondary growth, in-situ growth, chemical modification, use of polymer substrate and exfoliation of MOFs for ultrathin nanosheet MOFs layers [18,24,51–61]. The key process for the secondary growth is to produce a thin seed layer adhesive well with the surface of the substrate. Many strategies such as reactive seeding and thermal seeding [24,51] were developed to improve the weak interaction between the MOF seeds and the inorganic substrate. As for chemical modification, covalent linkers [52–55] or metal oxides [18,56] with the same metal source as the MOF materials, through which the heterogeneous nucleation sites of MOF crystals on support surface can be enhanced, are deposited on the support surface. The use of polymer materials [57–59] as substrates is another effective approach because the polymer materials provide a good interaction with the MOF materials that is significant for formation of high quality MOF membranes. In the case of in-situ growth, the membrane directly grows on the

substrate. Compared to the relative complex secondary growth and chemical modification approach, despite its simplicity it is often difficult to prepare MOF membranes by the in-situ growth owing to the absence of interaction between MOF materials and support surface that results in the low heterogeneous nucleation sites. Therefore, only a few MOF membranes have been successfully prepared by this method. For instance, Liu and co-workers [62,63] prepared MOF-5 and ZIF-69 membranes on α -alumina discs, while Bux et al. [64] grew ZIF-8 membranes on bare titania under microwave irradiation.

In our previous work [15], a CAU-1 membrane was demonstrated to possess high potential in separating CO_2 from flue gas with high CO_2 permeability and CO_2/N_2 selectivity in a wide CO_2 feed range. This CAU-1 membrane was achieved by secondary growth. In this work, the possibility of preparation of CAU-1 membrane by simple in-situ growth was explored. The asymmetric porous α - Al_2O_3 tubes with α - Al_2O_3 buffer layers of a nominal pore size of 0.2 μm without further modification were used as substrates. The same metal centre of the buffer layer as the CAU-1 framework is expected to enhance the heterogeneous nucleation sites of CAU-1 on the support surface. The effects of solvent and reactant concentration together with the support materials on the formation and separation performance of the CAU-1 membranes for CO_2/N_2 mixtures were investigated.

2. Experimental

2.1. Materials

Chemicals were used as received: 2-amino-1,4-benzenedicarboxylic acid (H_2N - H_2BDC) (> 99%, J&K Scientific Ltd.), Aluminium chloride hexahydrate (> 99%, J&K Scientific Ltd.), Methanol (MeOH), ethanol (EtOH) (> 99%, Tianjin Kermel reagent Co., Ltd.). Asymmetric porous α - Al_2O_3 tubes with an α - Al_2O_3 buffer layer of a nominal pore size of 200 nm and porosity of 30–35% and pore size of 2–3 μm (13 mm outside diameter, 9 mm inside diameter, and 8 cm length) (Foshan Ceramics Research Institute of China) were used as supports.

2.2. Pretreatment of the α - Al_2O_3 tubes

Prior to the synthesis, α - Al_2O_3 tubes with α - Al_2O_3 buffer layers were firstly washed with acid solution, alkaline solution, distilled water and ethanol in an ultrasonic bath in turn for 10 min several times to remove organic impurities. Subsequently, the supports were dried overnight at 373 K and then calcined in air at 823 K for 6 h with a heating rate of 1 K/min⁻¹. All the tubes were stored in the dryer for use. The morphology of α - Al_2O_3 tubes after

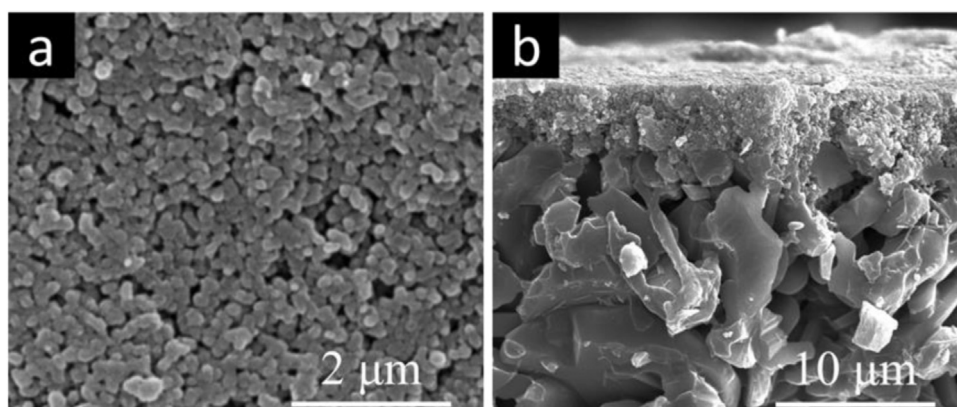


Fig. 2. SEM images of bare α - Al_2O_3 tube: surface (a), cross section (b).

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