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Mixed matrix membranes incorporated with amine-functionalized titanium-based metal-organic framework for CO_2/CH_4 separation

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ABSTRACT

High performance mixed matrix membranes arise from a targeted selection of constituent materials, especially the choice of fillers. An amine-functionalized metal-organic framework (MOF), NH_2-MIL-125(Ti), was used in this work to prepare polysulfone-based mixed matrix membranes (MMMs). Permeation measurements on CO_2/CH_4 gas mixture demonstrate that the incorporation of NH_2-MIL-125(Ti) particles can significantly improve the CO_2 permeability compared to the pure polymer membrane, along with slightly enhanced CO_2/CH_4 separation factor. This work also shows that the separation factor at high pressures can remain almost unchanged for the prepared MMMs with the MOF loadings up to 20 wt%. The obtained results may provide useful information in facilitating the applications of promising MOF-containing MMMs for the practical membrane-based natural gas purification.

1. Introduction

Despite the significant progress in the development of new renewable energy in recent years, fossil fuels likely still occupy a dominant position in the worldwide energy supply for the foreseeable future [1]. Along with the shale gas revolution, natural gas is one of the fastest growing fossil fuels during the past decades. Natural gas has a relatively large storage capacity around the world and is much cleaner than petroleum oil and coal. However, before being transported into pipelines or used as vehicle fuel, natural gas must meet strict specifications for the undesired components. As the major impurity in natural gas, CO_2 will decrease the energy content and lead to pipeline corrosion [2–6]. So far, pre-consumption removal of CO_2 from natural gas was usually realized by cryogenic distillation, amine absorption and pressure swing adsorption (PSA) processes [7,8]. Compare with these traditional methods, the membrane-based separation process has advantages in energy efficient and environmentally friendly aspects and has been recognized as an important technology for CO_2 capture and gas separation [9–12].

Due to the excellent mechanical strength, chemical and creep resistances and thermal stability [13–15], polysulfone (PSF) is one of the most popular amorphous polymers and has been widely used in preparing membranes for gas separation, acting as selective layer on rigid porous substrate or being as the supported membranes. The first commercial membrane system for industrial gas separation is the PRISM™ membrane separator designed by Monsanto Company. In this system, thin PSF membrane is used as the selective layer with the surfaces coated using silicon to eliminate the nonselective voids. The separator has been applied to remove the acid gases in natural gas, as well as recycle H_2 from purge gas during ammonia synthesis. However, PSF membrane has a disadvantage in gas permeability, which affects its wide application in the field of membrane-based gas separation. Great efforts have been devoted to improving the performance of PSF membranes; one of which is to incorporate fillers into the PSF matrices to fabricate mixed matrix membranes (MMMs) [4,10,16–18]. For this purpose, various kinds of fillers have been considered, including porous silica [19–22], zeolite [23–26], carbon nanotube [27], graphite [28] and metal oxide [29]. However, the particles of these traditional inorganic additives often exhibit poor affinities with the polymer chains, which may induce nonselective defects in the resulting MMMs. Thus, it remains a challenge to improve gas permeability of the membranes without a sacrifice of selectivity.

Metal-organic frameworks (MOFs) are a new class of nanoporous crystalline materials that are built up from inorganic metal-ion subunits connected by polytropic organic ligands [30,31]. The regular micropores with tunable surface chemical properties at the molecular level make MOFs ideal candidates for gas separation [32], as well as potential additives for the fabrication of MMMs [16,33–42]. During the past several years, MOFs-containing MMMs

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have attracted tremendous interest in the membrane-based gas separation. For example, Zornoza et al. [43] fabricated MMMs based on PSF and ZIF-8, HKUST-1, Silicate-1 as well as the mixture of MOF and Silicate-1. They found that incorporation of all these porous fillers can increase the gas permeabilities at the cost of decreasing CO_2/CH_4 separation factor in different degrees. Gascon et al. [44] investigated the CO_2/CH_4 separation performance of NH_2-MIL-53(Al)/PSF MMMs and found an increase of the separation factor with the addition of the MOF. Sorribas et al. [45] studied the effect of incorporating meso-microporous silica (MSS)/ZIF-8 composite into PSF matrix on CO_2/CH_4 separation. They showed that the gas permeability of the fabricated MMMs was significantly improved and the selectivity remains almost unchanged even at a filler loading of 32 wt%. For the two MMMs prepared by Car et al. [46] using PSF with $Cu_3(BTC)_2$ and Mn$(HCOO)_2$ as fillers at the loading of 10 wt%, the CO_2/CH_4 ideal selectivities decrease by factors of 58% and 50%, respectively. Rodenas et al. [47] found that the CO_2 permeability and the CO_2/CH_4 separation factor of NH_2-MIL-101(Al)/PSF MMMs with a filler loading of 25 wt% can be enhanced by factors of 63% and 22%, respectively. Musselman et al. investigated the gas separation performance of the Matrimid-based MMMs with embedded MOF-5 [48] and ZIF-8 [49]. Compared to the pure polymer membrane, they found that the CO_2 permeability increases with the addition of MOF-5 particles, while the influence on the CO_2/CH_4 ideal selectivity is negligible. In contrast, the selectivity is significantly enhanced due to molecular sieve effect existing in the ZIF-8-containing MMMs. Zhang et al. [50] reported that the addition of Cu–BPY–HFS into Matrimid can increase the CO_2 permeability but slightly decline the CO_2/CH_4 ideal selectivity. Fe(BTC) was also studied by Shahid et al. [51] as fillers for Matrimid membranes, showing that both the permeability and selectivity are slightly enhanced.

It has been well-recognized that the water-insensitive property of MOFs is one of the vital prerequisites related to their practical utility [52]. Recently, Zlotea et al. [53] reported a novel amine-functionalized MOF named NH_2-MIL-125(Ti) (MIL= Material Institut Lavoisier), which exhibits excellent water and thermal stabilities as well as high porosity. As shown in Fig. 1, this material is built up from the octameric $Ti_8O_4(OH)_4$ oxoclusters bounded to 12 2-amino-terephthalate ligands [53–55], leading to a quasi-cubic tetragonal structure in which the octahedral (10.7 Å) and tetrahedral (4.7 Å) cages are accessible through a window of about 5–7 Å. With a combination of experimental and computational methods, Vaesen et al. [56] recently investigated the adsorption behaviors of CO_2 and CH_4 in NH_2-MIL-125(Ti). They found that this material exhibits an almost constant difference of adsorption heat between CO_2 and CH_4 in a wide range of pressure up to 20 bar ($\sim$12 kJ/mol), which was attributed to the presence of accessible –OH and –NH_2 sites in the framework. Considering these facts, it would be expected to improve the gas permeability as well as the CO_2/CH_4 selectivity of polymeric membranes after incorporation of NH_2-MIL-125(Ti). Therefore, in the present work, this MOF was for the first time used as porous filler to fabricate PSF/MOF composite membranes. By surveying the literature, many studies available so far have used single-component gas permeation data to characterize the separation properties of polymer/MOF composite membranes. Such a treatment is helpful in primarily screening the promising MMMs for a targeted separation system. However, out of the consideration for practical applications, it is more useful to provide the information of the permeation properties toward real mixtures. Thus, the permeation experiments were directly performed on CO_2/CH_4 gas mixture to characterize the separation performance of the MMMs prepared in this work.

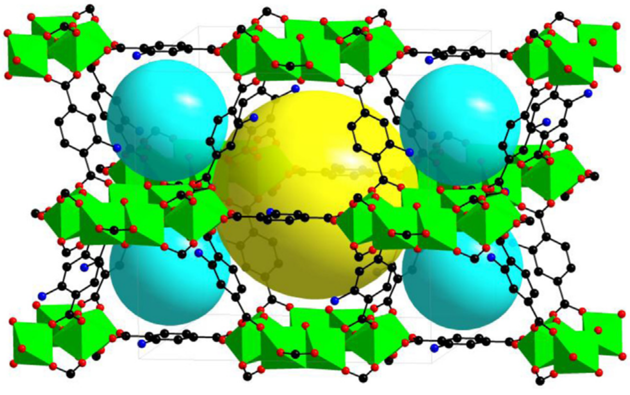

Fig. 1. Illustration of the NH_2-MIL-125(Ti) structure. Hydrogen atoms were omitted for clarity. The large yellow and cyan spheres represent the void regions inside the octahedral and tetrahedral cages, respectively (Ti, green polyhedral; O, red; C, black; N, blue). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2. Experimental

2.1. Materials

Titanium(IV) isopropoxide was purchased from J&K Scientific (China), and 2-aminoterephthalic acid (NH_2-BDC) was obtained from Alfa Aesar (China). Dimethylformamide (DMF) was supplied by Sinopharm Chemical Reagent Co., Ltd. and methanol (CH_3OH) and acetic acid (HAc) were purchased from Beijing Chemical Works. The received solvent was further purified to remove the containing water. The PSF pellet (Ultrason® S 6010, see Fig. 2) was provided by BASF (China) and was thermal treated at 393 K in a vacuum oven overnight before the use.

2.2. Synthesis of NH_2-MIL-125(Ti)

NH_2-MIL-125(Ti) was synthesized using the method of Zlotea et al. [53] with slight modifications. Typically, 6 mmol NH_2-BDC, 25 ml CH_3OH and 25 ml DMF were mixed and 10 ml HAc was added as the modulator for the purpose of retarding the hydrolysis of titanium isopropoxide and tuning the MOF particle sizes [55]. Then, 3 mmol titanium isopropoxide was further added under agitation. The slurry was introduced into a 125 ml Teflon liner within a stainless-steel autoclave. The reactor was heated at 433 K for 48 h. The resulting light yellow product was filtered off and washed with DMF to remove the excess of unreacted ligands, followed by using methanol to exchange the DMF. Finally, the sample was activated at 393 K under vacuum overnight, and the obtained powder was reserved for further characterization.

2.3. Membrane fabrication

The membrane samples were fabricated through a mixing-casting process. Specifically, for pure PSF membrane fabrication, the polymer was dissolved into chloroform portion-wise to form a 25 wt% solution. For MMMs preparation, the NH_2-MIL-125(Ti) powder after activation was ground sufficiently in an agate mortar to reduce the particle sizes, and was then dispersed in chloroform. The suspension was placed in ultrasonic bath for 30 min before adding PSF pellets. The proportion of the MOF in the MMMs was

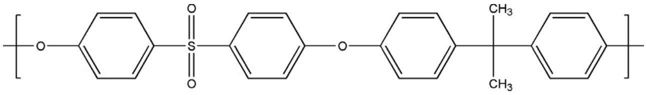

Fig. 2. Chemical structure of PSF (Ultrason® S 6010).