Functionalized metal organic framework-polyimide mixed matrix membranes for CO_2/CH_4 separation

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ABSTRACT

This work describes the preparation, characterization and CO_2/CH_4 gas separation properties of mixed matrix membranes (MMMs) made from five different as-synthesised metal organic frameworks (MOFs): UiO-66 (Zr-BDC), NH_2-UiO-66 (Zr-ABDC), UiO-67 (Zr-BPDC), MOF-199 (Cu-BTC), and NH_2-MOF-199 (containing 25% ABDC and 75% BTC mixed-linker) fillers and as-synthesized 6FDA–ODA polyimide as the polymeric matrix in order to investigate the ligand functionalization effect ($-NH_2$) on MOF's adsorption properties and on the CO_2/CH_4 gas separation performance of the MMMs.

The as-synthesized MOFs were carefully characterized by XRD, SEM, ATR-FTIR, and N_2 adsorption at 77 K. MMMs were also characterized using ATR-FTIR, and SEM and CO_2/CH_4 pure and mixed gas separation measurements were carried out. Incorporation of the fillers in the MMMs resulted in an increase in perm-selectivity except for the UiO-67 filler. The presence of amine-functional groups in as-synthesized MOFs increased both the ideal selectivity and CO_2 permeability. On the other hand, MMM made with UiO-66 increased significantly the CO_2 permeability compared to the neat 6FDA–ODA membrane without any loss in ideal selectivity. Using mixed-linker NH_2-MOF-199 enhanced the perm-selectivity of the MMM maybe because of the presence of some whisker-like roughness on their crystal surface as observed in SEM.

1. Introduction

Nowadays in natural gas refining, the gas phase separation of carbon dioxide (CO_2, kinetic diameter 3.3 Å) from methane (CH_4, kinetic diameter 3.8 Å) is an important research topic. Mixed matrix membrane (MMM) is one of the promising candidates with significant potential to overcome the Robeson's upper bound trade-off for polymeric membranes in gas separation applications. According to the Robeson upper bound, the membranes more permeable are generally less selective and vice versa [1]. Therefore, the idea of incorporating some selective inorganic fillers such as zeolites [2–6] or carbon molecular sieves [7–9] in a polymer matrix to enhance the perm-selectivity of the membranes has been explored over the last 15 years. However, the use of novel materials such as metal organic frameworks (MOFs) in MMM has not been extensively studied [10–20] in this area.

MOFs are a relatively new class of hybrid materials built from metal ions as connectors and organic bridging ligands as linkers. The strong bonds between connectors and linkers allow building up one-, two-, or three-dimensional porous frameworks. MOFs are extended structures with extremely high surface area and pore volume having precisely sized cavities that can adsorb and store gas molecules. By carefully selecting the metal and organic linkers, it is possible to produce a variety of topologies and structures. Furthermore, the pore sizes can be systematically tuned and the pore walls could be functionalized. Over 600 chemically and structurally diverse MOFs have been developed over the past several years. In contrast to zeolitic fillers, MOFs have high surface areas, and high flexibility in terms of crystal structures and chemical composition which make them allowing the addition of functional groups in selected linkers that could change the pore size as well as chemical properties of the MOFs [21].

The interface morphology in MMMs is one of the important factors which can control the perm-selectivity of as-synthesized membranes. There are several drawbacks to fabricate MMMs using inorganic fillers (for example zeolites) such as the formation of non-selective voids at the inorganic–polymer interface, the partial pore blockage of microporous inorganic fillers by polymer chains, and the limited number of possible structures and compositions [2,22]. However, using MOFs as filler, controlling the interface morphology between filler and polymer matrix is easier due to the presence of organic linkers into the MOF structure. These have better affinity and compatibility with polymer chains, and their surface can be easily functionalized by choosing the functional linkers. The benefits of the inclusion of amines in MOFs for the separation of CO_2/CH_4

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mixtures have been experimentally demonstrated [23–25], while the use of amine-modified MOFs in MMMs and the effect of the amine functionality over polymer–filler matching has been already reported [20].

UiO-66 (Zr-BDC) (BDC = 1,4-benzenedicarboxylate) (UiO for University of Oslo [26]), a new zirconium-based porous MOF attracts much attention owing to its very promising properties for CO_2/CH_4 gas separation including a good selectivity, high adsorption capacity and low cost [27–29]. It is built up from inorganic nodes $Zr_6O_4(OH)_4(CO_2)_{12}$ linked with terephthalate ligands and has a 3-dimensional porous lattice having close to 11 and 8 Å free diameters for the two types of cages, and narrow triangular windows with a free diameter close to 6 Å [27]. This MOF shows high thermal stability (up to 500 °C) due to the presence of the $Zr_6O_4(OH)_4$ inorganic building blocks and remains unaltered towards a wide class of solvents such as water, acetone, benzene and DMF in contrast to the majority of the MOFs reported so far [26]. The amino-substituted analogue NH_2-UiO-66 can be synthesized by using ABDC (2-amino-1,4-benzenedicarboxylate) linker instead of BDC. This amine-functional MOF has been used as high yields base catalyst for the cross-aldol reaction [30].

Very recently, Yang et al. [31] reported a computational exploration of the effect of functionalizing porous UiO-66 for CO_2/CH_4 separation. Their results showed an increase in CO_2/CH_4 adsorption selectivity of the amine-functionalized UiO-66 (NH_2-UiO-66) at both the lower (1 bar) and higher (10 bar) pressure.

Compared to UiO-66, UiO-67 (Zr-BPDC) (BPDC = biphenyl-4,4′-dicarboxylate) is another Zr-MOF containing extended linker with two benzene ring dicarboxylic acid, BPDC instead of BDC. This increases both the surface area and pore diameter of the MOF without affecting the stability of the structure [26]. The pore diameter of UiO-67 is 8 Å which is more than UiO-66 (6 Å) as expected. These new three MOFs, UiO-66, NH_2-UiO-66, and UiO-67 have not been used as filler in MMMs yet.

On the other hand, MOF-199 or $Cu_3(BTC)_2$ (BTC = benzene-1,3,5-tricarboxylate) is a 3-dimensional porous MOF composed of a copper dimeric paddlewheel unit with the main pore diameter of ca. 9 Å surrounded by tetrahedral pockets of ca. 5 Å diameter. These pockets are connected to the main channels by triangular windows of ca. 3.5 Å diameter [32]. MOF-199 exhibits unsaturated metal sites after activation. It has a high CO_2 storage capacity and a pore size suitable for natural gas separation [33] yielding a 5–9 selectivity for 50:50 bulk composition and 7–10 for 75:25 composition [34]. This MOF has been used as filler in making MMMs for gas separation applications [13,19,35,36], however not in 6FDA–ODA polymer matrix.

For the preparation of the amine-functionalized MOF-199, it was not possible to provide the corresponding amine-linker (NH_2-BTC), therefore we tried to partially substitute the NH_2-BDC (ABDC) with BTC linker. The resulting material is designated hereafter as NH_2-MOF-199.

Car et al. [36] used MOF-199 with two polymer matrices, polydimethylsiloxane (PDMS) and polysulfone (PSf) to make MMMs for gas separation. Their results showed an increase in permeability of CO_2 without any changes in the CO_2/CH_4 selectivity in PDMS-based MMMs compared to a neat polymer membrane. Both the CO_2 permeability and CO_2/CH_4 selectivity increased in PSf-based MMMs at 5 wt.% filler loading. By increasing the filler loading to 10 wt.%, the selectivity decreased significantly. The authors described this effect to the presence of voids at the interface of MOF particles and polymers.

Liu et al. [35] in their patent reported the fabrication of 30 wt.% MOF-199/Matrimid MMMs. Their results showed an increase in CO_2 permeability without any loss of CO_2/CH_4 selectivity compared to a neat Matrimid membrane.

In another work, Basu et al. [13] synthesized MOF-199/Matrimid and MOF-199/Matimid-polysulphone blends MMMs via the phase inversion method. Their results showed that CO_2/CH_4 selectivity increased with filler loading depending on CO_2 concentration at 10 bar and 35 °C. Also the CO_2 permeability of MMMs increased upon adding the filler.

Recently, Hu et al. [19] synthesized hollow fibers of MOF-199/polyimide MMMs for gas separation and adsorption. However, their results showed a reduction in CO_2 permeation without any change in CO_2/CH_4 selectivity at both the 3 and 6 wt.% filler loadings compared to the neat polymeric membrane.

The 6FDA–ODA (4,4′-(hexafluoroisopropylidene)diphthalic anhydride-4,4′-oxydianiline) polyimide was chosen in this work because numerous studies had shown that fluorinated polyimides containing 6FDA exhibit good combination of gas separation factors and permeability coefficients for CO_2/CH_4 separation application [37,38].

In our previous works [2,22,39], we have reported synthesis and characterization of FAU/EMT zeolite functionalized with different aminosilanes. The grafting reaction conditions were optimized via Taguchi method. The new fillers were incorporated in as-synthesized 6FDA–ODA polyimide to make MMMs for CO_2/CH_4 gas separation. In the present work, we prepared several MOFs, some of which being functionalized with amine-functional ligands. These materials have similarities with the amine-functionalized zeolites. They are however prepared in a simpler manner. They were then incorporated in the same polyimide (6FDA–ODA) as in our previous work, which allows comparing both series of fillers. The aim of the present work is therefore, to study the effect of amine-functionalization of the MOFs on performance of the MMMs as well as to compare the resulting membranes with amine-functionalized zeolite-MMMs made with the same polyimide matrix.

2. Experimental

2.1. Materials

For polyimide synthesis, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA, mp 246 °C, >99%) was provided by Chriskey Co. 4,4′-Oxydianiline (ODA, mp 188–192 °C, 97%) was purchased from Sigma–Aldrich and purified by vacuum sublimation. 1-Methyl-2-pyrrolidone (NMP, bp 204 °C, >99.0%) was purchased from TCI America and purified by vacuum distillation. Acetic anhydride (bp 138–140 °C, 99.5%) and triethylamine (bp 88.1 °C, ≥99.5%) were received from Sigma–Aldrich. Methanol was obtained from Fisher Scientific. Starting materials and solvents for synthesis of MOFs were purchased from commercial suppliers (Sigma–Aldrich, EMD, and others) and used without further purification.

Gas permeation measurements were conducted using 99.99% pure CO_2 and 99.5% pure CH_4 (Praxair Co.).

2.2. Polymer synthesis

6FDA–ODA polyimide was synthesized by a two-step method in accordance with our previously published procedure (Fig. 1) [2]. In the first step, polyamic acid (PAA) derived from equimolar amounts of solid 6FDA and diamine (ODA) was prepared by solution condensation in purified NMP. The reaction mixture was stirred under argon in an ice-water bath for 15 h. In the second step, PAA was imidized to form polyimide. The cyclization was achieved by chemical imidization under argon at RT for 24 h through the addition of acetic anhydride (dehydrating agent) and triethylamine (catalyst). The polyimide solution was precipitated with methanol, then washed several times by methanol and dried at 220 °C in vacuum oven for 24 h. Imidization was confirmed by ATR-FTIR analysis.