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Metal organic framework membranes for carbon dioxide separation

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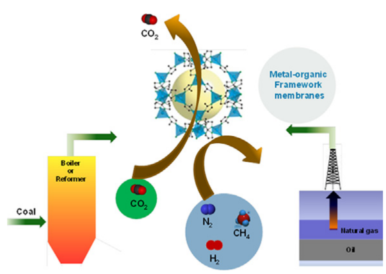
HIGHLIGHTS

- Progress on metal organic framework membranes for CO_2 separation is reviewed.
- The paper focuses mainly on CO_2/N_2, CO_2/CH_4, and CO_2/H_2 gas separations.
- Strategies for the continuous defect-free MOF membrane fabrication are discussed.
- Advantages of using MOFs in mixed matrix membranes are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we review research progress on metal organic framework membranes which have demonstrated ability to separate carbon dioxide from different light gases. More specifically, we focus mainly on CO_2/N_2, CO_2/CH_4, and CO_2/H_2, gas separations which are highly relevant compositions in flue gas treatment, natural gas purification, and hydrogen purification, respectively.

We also discuss several conventional and novel strategies developed by several research groups for the continuous defect-free MOF membrane fabrication. Finally, the advantages of using MOFs in mixed matrix membranes and improvements in gas separation performances with the MOF based mixed matrix membranes are presented.

1. Introduction

From the environmental and energy perspective, the purification and recovery of carbon dioxide from power generation, industrial operation and natural gas are of great interest. CO_2 is the main component of greenhouse gases, and its accumulation in the environment is leading to severe global warming issues. It has been estimated that the total CO_2 emissions in the U.S. grew to 6022 million metric tons (MMT) in 2007 which represents more than 80% of the total greenhouse emissions (DOE/EIA, 2007). World CO_2 emissions in 2005 were estimated at 28,051 MMT and projected to be 42,325 MMT in 2030 (DOE/EIA, 2008). To alleviate CO_2 accumulation it is important to separate and recycle carbon dioxide before it is released in to air. From the energy point of view, CO_2 is an undesirable impurity in natural gas wells, with concentrations as high as 70%. About 17% of all domestic natural gas in the U.S. is treated to remove CO_2 before it is passed to the pipeline (Baker, 2002). Pipeline specifications for natural gas require a CO_2 concentration below 2–3%. CO_2 must be separated from CH_4 because it reduces the energy content of the gas; CO_2 is also acidic and corrosive in the presence of water. Furthermore, removing CO_2 without large energy expenditures is also desirable,

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and thus membranes that preferentially permeate CO_2 at high selectivities can significantly impact utilization of these gas wells by reducing the costs of natural gas purification (Lin et al., 2006a). Another relevant technology related to CO_2 capture involves the reaction of a fuel with oxygen or air to produce H_2 and CO (syngas). In the pre-combustion process the formed CO reacts with steam producing a mixture of CO_2 and H_2 which is desirable to be separated to obtain pure hydrogen which can be used directly as a fuel source.

The benchmark technology used for CO_2 removal is amine adsorption, but amine plants suffer from several problems (Baker, 2002). First, capital costs are high. Second, operation of these plants is complex, and third maintenance is expensive and labor intensive. The capture of CO_2 from flue gas and natural gas wells and from pre-combustion involves treating enormous gas volumes. In this respect, membrane technology could play a key role in making this process economically feasible. Membrane separation processes have several advantages over conventional amine adsorption (Alexander Stern, 1994); for instance, it is a viable energy-saving method, since it does not involve any phase transformation, furthermore, the required membrane process equipment is simple, easy to operate, control and scale-up.

Metal organic frameworks (Park et al., 2006; Yaghi et al., 2003) in membrane form, have emerged as an appealing type of crystalline microporous materials which combine highly desirable properties, such as uniform micropores, high surface areas, and exceptional thermal and chemical stability, making them ideal candidates for CO_2 gas separations.

In this paper we review research progress on metal organic framework membranes which have demonstrated ability to separate carbon dioxide from different light gases. More specifically, we focus mainly on CO_2/N_2, CO_2/CH_4, and CO_2/H_2, gas separations which are highly relevant compositions in flue gas treatment, natural gas purification, and hydrogen purification, respectively. We also discuss several conventional and novel strategies developed by several research groups for the continuous defect-free MOF membrane fabrication. Finally, the advantages of using MOFs in mixed matrix membranes and improvements in gas separation performances with the MOF based mixed matrix membranes are presented.

2. Metal organic frameworks (MOFs) and MOF membranes

2.1. MOF structure

MOFs consist of metal cations or metal-based-clusters linked by organic molecules forming a crystalline network, which after removal of guest species may result in three dimensional structures with permanent porosity (Yaghi et al., 2003; Férey, 2008; MacGillivray, 2010). Metal organic frameworks are crystalline

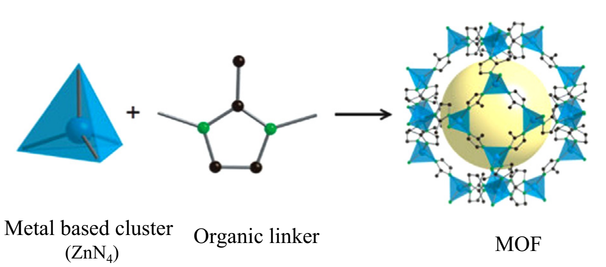

Fig. 1. A typical MOF structure composed of a metal based cluster and an organic linker. The yellow sphere denotes "open space". (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

materials that can be tailored to specific applications through varying the metals, ligands, and linkers making up the MOF and the number of potential MOFs are virtually limitless (Mueller et al., 2006). They can be synthesized inexpensively, relatively easily, in high purity, and in a highly crystalline form. These materials cover a much wider range of pore sizes than zeolites, even bridging micro and mesoporous materials. The combination of organic and inorganic building blocks offers an almost infinite number of variations, enormous flexibility in pore size, shape, and structure, and myriad opportunities for functionalization and grafting. Fig. 1 shows a typical representation of the components and final structure of a MOF.

2.2. Generalities of MOF membranes

From the membrane viewpoint, the highly accessible porosity of MOFs (inferring high fluxes) its wide range of pore sizes, and its unique surface chemistry properties would make it possible to tackle classical, and relevant industrial separations (Gascon and Kapteijn, 2010) such as the separation of hydrogen from other gases, the removal of CO_2, the separation of alkanes from alkenes, linear from branched alkanes, and mixtures of aromatic isomers, as well as the separation of larger molecular isomers. MOF membranes for molecular gas separations is an emerging research area that is rapidly evolving (Bohrman and Carreon, 2012; Bux et al., 2009, 2011; Dong et al., 2012; Guerrero et al., 2010; Guo et al., 2009; Huang et al., 2010a, 2010b, 2013b; Huang and Caro, 2011; Li et al., 2010b; Y. Li et al., 2010; Liu et al., 2010, 2011; McCarthy et al., 2010; Pan and Lai, 2011; Ranjan and Tsapatsis, 2009; Takamizawa et al., 2010; Tzialla et al., 2013; Venna and Carreon, 2010; Xie et al., 2014; Yoo et al., 2009). Nevertheless, the development of continuous MOF membranes displaying high separation performance is challenging. The main challenges include poor intergrowth at the membrane-support interface, moisture limited stability, and limited control over "non-porous pathways" resulting typically in poor separation performance membranes. In addition, the high framework flexibility due to the presence of the organic linker imposes limits on the molecular sieving. Another challenging aspect of MOF membranes (similar to zeolite membranes) is the reproducibility of the synthesis methods to prepare membranes with similar separation performance (reproducible membranes).

Similar synthesis methods employed for zeolite membrane synthesis have been used to prepare MOF membranes. In general these methods involve direct synthesis of the MOF membrane on porous supports (in-situ approach), or employing "seeds" as crystals in the surface of the porous support to promote membrane growth (secondary seeded approach). The latter is in general the preferred method since it allows better microstructural control on the resultant membrane. Different MOF membrane fabrication methods are discussed in detail in Section 3.

2.3. Why MOF membranes for CO_2 separation?

Due to its remarkable high CO_2 uptakes, open porous framework structure with large accessible pore volumes, chemical stability in the presence of hydrocarbons and water (some of them), and limiting pore apertures in the range of the kinetic diameters of several relevant gas molecules, MOFs are highly appealing materials for CO_2 capture. CO_2 adsorption capacities of several potential MOFs compared to zeolites was shown in Table 1. In particular, zeolitic imidazolate frameworks (ZIFs), a subclass of MOFs, have emerged as a novel type of crystalline porous materials which combine highly desirable properties from both zeolites and MOFs, such as microporosity, high surface areas, and exceptional thermal, chemical stability, making them ideal