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Metal organic framework membranes for separation applications

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Microprous metal organic framework materials possess unique properties as membrane materials for gas and liquid separation. An increasing number of metal organic framework membranes have been synthesized. Most studies were focused on more stable zeolitic imidazolate framework membranes for gas separation. Thin metal organic framework membranes are synthesized on porous inorganic or polymer supports by seeded secondary growth or *in situ* (counter-diffusion) synthesis methods. These membranes exhibit unique gas separation properties, such as high H_2/CO_2 selectivity, unattainable to other microporous inorganic or polymer membranes. However, much less studies have been reported on the liquid separation properties and stability of metal organic framework membranes. To make metal organic framework membranes a viable separation technology requires understanding of the thermal and chemical stability of metal organic framework materials and membranes, and development of cost-effective synthesis of metal organic membranes with high permeance or on more easily scalable supports.

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Introduction

Metal organic frameworks (MOFs) represent an extensive class of crystalline materials including three series of microporous materials attractive as membrane materials: IRMOFs (isoreticular metal-organic framework), ZIFs (zeolitic imidazolate frameworks), and MIL-53(Fe) (Material Institut Lavoisier). These materials can have a large variety of ordered structures, functional groups, pore sizes and porosity. Among these materials, ZIFs consist of tetrahedral transition metal ions (zinc, cobalt, or copper, etc.) bridged by imidazole or imidazolate type linkers. ZIFs hold permanent porosity and more topology structures and coordination factors than zeolites [1]. Their structural complexity, versatility of imidazolate linkers, and the tunable pore size and surface property make them promising membrane materials for different applications. The last five years have seen an increasing number of papers on MOF, especially ZIF membranes. The progress on MOF membranes is reviewed in at least four recent review papers [2–5]. The objective of this communication is to provide a concise summary of the progress in pure MOF, especially ZIF, membrane research with focus on properties important to industrial separation applications. The paper will suggest several important issues that should be addressed in order to make metal organic membranes a viable separation technology.

MOF membranes studied

A MOF membrane consists of a continuous film of a MOF material formed on a porous substrate which provides mechanical strength and allows gas or liquid to permeate with minimum resistance. The research groups of Caro and Kapteijn were among the first to report synthesis of MOF membranes: oriented microporous manganese formate $Mn(HCO_2)_2$ [6] and Cu-BTC [7] on porous graphite and alumina supports, respectively. Later on, Lai and Jeong and their co-workers [8,9] reported *in situ* synthesis by conventional and microwave heating of IRMOF-1 membranes of 25–50 μm thick on alumina supports. Zhu and coworkers [10] reported synthesis of Cu-BTC membranes in a copper-net support. IRMOF-1 and Cu-BTC have pores larger than 12-ring FAU type zeolites (>0.7 nm) so these membranes are not expected to show molecular sieving characteristics for separation of small molecules such as H_2 and CO_2. Smaller pore MOF membranes might be more effective for gas separation by molecular sieving effects. The groups of Tsapatsis and Ranjan [11], Caro *et al.* [12,13], and Carreon and Venna [14] reported earlier studies on synthesis of microporous MOF membranes with a pore diameter smaller than 0.4 nm. Qiu *et al.* [4••] provided a comprehensive review of MOF membranes studied by different research groups in the past few years. The list of MOF membrane materials includes the following materials, with increasing pore size, ZIF-7, ZIF-22, ZIF-8, ZIF-90, ZIF-95, ZIF-71, ZIF-78, CAU-1, MIL-53, MOF-5, ZIF-69, HKUST-1, SIM-1, IFMOF-3 and IRMOF-74.

So far MOF membranes have been studied mainly for gas separation applications. The separation by microporous membranes is governed by the molecular sieving or adsorption–diffusion mechanism [15,16]. Therefore, all the researchers have selected a MOF material to make a membrane for separation of a given mixture by considering either (1) aperture size of MOF respective to the molecule sizes of the mixture to be separated to introduce diffusive-based selectivity or (2) surface chemical properties of the MOF material to provide adsorption-based selectivity. The stability of the materials and simplicity/ease of material synthesis are other factors to consider in selecting a MOF material to make membrane. Table 1 lists MOF membranes studied by our laboratory and the structure (pore sizes) of these MOF materials to illustrate the selection of MOF material for membranes for separation of different mixtures. ZIF-7 and ZIF-8 membranes are studied for separation of the gas mixtures based on the diffusion-controlled separation mechanism. However, ZIF-71, ZIF-68 and IRMOF-1 show preferential adsorption of CH_3OH over H_2O, or CO_2 over CH_4 or N_2. These membranes are studied to explore adsorption-controlled separation of these mixtures.

Synthesis of MOF membranes

Similar to zeolite membrane synthesis, MOF membranes are synthesized mainly by *in situ* and seeded-secondary growth methods. Most studies reported MOF membranes on macroporous alumina supports because of the ready availability of disk or tubular supports made of this material. In the *in situ* synthesis of MOF membranes, porous support is brought in contact with synthesis solution of metal salt, organic ligand in an organic solvent such as dimethylformamide (DMF) or methanol. Lai and Jeong and co-workers [8] were the first to report *in situ* synthesis of IRMOF-1 membranes. Successful *in situ* synthesis procedures have also been reported for ZIF-8 and ZIF-69 [23,24]. Liu *et al.* [23] found that immersing an alumina support in a DMF solution containing the needed imidazole linkers and zinc source, then allowing the mixture to solvothermally react for 72 hours created a continuous, high quality ZIF-69 membrane. Synthesis of ZIF-8 membranes by the *in situ method* was not as successful until Cravillon *et al.* [24] found that in addition to the needed zinc source and the imidazole precursor, ZIF-8 membranes required the incorporation of sodium formate into the synthesis solution before solvothermal reaction. Further work by Jeong and coworkers [25] concluded that the sodium formate was necessary, not so much to maintain a certain hydrogen activity level within the solution, as was initially speculated, but rather so it would react with the zinc source, $ZnCl_2$, to create a ZnO layer that almost immediately reacted with the imidazole precursors to create a securely anchored membrane layer.

The *in situ* synthesis includes nucleation and crystal growth steps. Synthesis should be conducted under conditions to create local supersaturation near the support surface to facilitate nucleation of MOF crystals on the support surface. Thus, it was difficult to prepare high quality MOF membranes by the *in situ* solvothermal methods. This difficulty has motivated improvement of the *in situ* synthesis methods by two approaches. The first approach is the covalent functionalization of the alumina surface by a covalent linker such as propyltriethoxysilane (APTES) [26••,27,28] or dopamine [29]. With the alumina surface grafted with an organic linker, it become easier for nucleation of the MOF on the support surface followed by the crystal growth. The second approach is the counter-diffusion *in situ* growth of the MOF membranes [30••,31,32••,33••]. This approach is similar to counter-diffusion chemical vapor deposition method to prepare microporous or dense metal oxide membranes [15]. In this approach, the support separates the solution containing metal source precursor and that containing the organic linker. The metal precursor and organic linker counter-diffuse in the support and react in the support (near the support surface) to form crystals deposited in (or on the surface of) the support. Though the membranes synthesized by these approaches show good separation properties, the synthesis methods remain to be optimized and the quality of the membranes, such as stability and bonding to the support, has not been studied. The counter-diffusion method also is more difficult to scale up because it requires the support to be sealed during synthesis.

MOF (mostly ZIF) membranes are also synthesized by the seeded-secondary growth method [17••,20,21•,22,34–36]. In this method, a MOF crystallite seed layer is formed on macroporous alumina support by the dip-coating method using sol or suspension containing the MOF crystallites of size about a few hundred nanometers to a few microns. The support with the seed layer is then brought in contact with synthesis solution containing metal precursor and organic linker. Secondary solvothermal (or hydrothermal) growth leads to the formation of

Table 1

Sample MOF membranes studied for separation of gas or liquid mixtures

MOF	Organic linkers	$d_{\text{Aperture (A)}}$	$d_{\text{Pore (A)}}$	Topology	Sample mixture to separate	References
ZIF-8	Methylimidazole	3.4	11.6	SOD	C_3H_6/C_3H_8	[17••]
ZIF-71	Dichloro imidazole	4.8	16.8	RHO	CH_3OH/H_2O	[18]
ZIF-68	Nitroimidazole benzimidazole	7.5	10.3	GME	CO_2/CH_4	[19]
IRMOF-1	Benzenedicarboxylate	8	12		CO_2/N_2	[20,21•,22]