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Metal–organic framework composite membranes: Synthesis and separation applications

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HIGHLIGHTS

- We present a review on MOF-based membranes for separation.
- Potential applications of different types of MOF membranes are discussed.
- Inorganic/polymer substrates and strategies for continuous membranes are focused.
- The characters of MOF-based mixed matrix membranes are presented.
- Scopes for future research of MOF-based membranes are outlined.

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ABSTRACT

Metal–organic framework (MOF) materials, which are built of metal ions or metal ion clusters bridged organic linkers, possess the well-defined pore structures, large surface area and extraordinary adsorption affinities. In recent years, MOF-based membranes have attracted large attention in separation applications due to their excellent performance. In respect to practical applications, the substrates and construction will greatly influence the industrial promotion and separation performance of the MOF-based membranes. Inorganic materials are the earliest substrates for continuous MOF membranes. Both the bare and modified substrates can be used for supporting the MOF membranes by changing the synthesis preparation process, such as solvothermal synthesis, interfacial synthesis and liquid phase epitaxy approach. In order to reduce the cost and enhance the processability of the MOF membrane, the polymer substrates can also be employed to obtain the continuous MOF membranes. Moreover, the hollow fiber substrates can provide the large membrane areas per volume. Since there is good compatibility between the MOFs and polymers, MOFs can also be employed as fillers to fabricate mixed matrix membranes. Those MOF-based membranes exhibit good performance in gas separation, pervaporation and nanofiltration. Therefore, this review gives an overview of the continuous MOF membranes supported by inorganic substrates and polymer substrates and the MOF-based mixed matrix membranes.

1. Introduction

Traditional separation processes, such as distillation, condensation and crystallization, are highly energy intensive (Linnhoff et al., 1983; Gupta and Verma, 2002; Choong and Smith, 2003). As an environmentally friendly and energy efficient separation method, membrane-based separation have attracted more and more attention and been applied in many fields successfully (Zhang and Cussler, 2003a, 2003b). Among the investigations in membrane separation, one of the most active fields is focused on membrane materials. Polymers as earliest membrane materials possess many irreplaceable advantages, such as low cost, rich category and high processing (Baker, 2002). However, polymer membranes in general have short membrane lifetimes, low thermal and chemical stabilities, and low selectivity (Koonaphapdeelert et al., 2008; Robeson, 2008). Because of the high regularity, well-defined pore structure and excellent stability, zeolites have been introduced in membrane separations (Lai et al., 2003; Choi et al., 2009; Caro and Noack, 2010; Tung et al., 2011;

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Varoon et al., 2011). However, zeolite membranes also have their bottlenecks such as limited range of available pore sizes, limited chemical tailorability, high cost of production and others (Caro and Noack, 2010).

As a relatively new class of porous hybrid materials, metal–organic frameworks (MOFs) that are consisted of inorganic metal centers and organic linkers by coordinate bonds have been developed in recently years (Li et al., 1999; Chui et al., 1999; Eddaoudi et al., 2002; Rosi et al., 2003; Ferey, 2008). Because of the diverse ranges of metal ions and linkers, MOFs usually possess a series of unique characteristics, such as structure diversity, large surface area, extraordinary adsorption affinities, tunable pore sizes and facilely tailorable functionality (James, 2003; Li et al., 2012). These features make them very attractive for various applications including gas adsorption and storage, separation, catalysis and delivery (Li et al., 2012; Furukawa et al., 2013). Like the zeolites, it can also be used for membrane fabrications. Because of the relatively poor mechanical stability (Tan and Cheetham, 2011), MOFs are usually grown on the substrates to obtain continuous membranes or exploited as filler to form mixed matrix membranes (MMMs) (Shah et al., 2012; Tanh Jeazet et al., 2012a; Erucar et al., 2013; Yao and Wang, 2014; Qiu et al., 2014). Generally, the separation of mixture materials depends on the shape and size of the molecules to be separated, or the interaction between the molecules and the membrane materials. So the complete continuity and defect free are very important for the preparation of MOFs based membrane. For continuous MOF membranes, the physicochemical properties of the substrates determine the quality of crystal heterogeneous growth, so some special synthesis or modification methods of the substrates are used to improve the heterogeneous nucleation sites (Bradshaw et al., 2012). Different from the zeolite membranes, the high temperature sintering process is vital for removing the surfactant to obtain their pore structure, the activation for MOF membranes can be carried out at a relatively lower temperature, so the MOF membranes are also usually deposited on the polymer substrates (Bradshaw et al., 2012). Moreover, the linkers of the MOFs are organic molecules, so MOFs can interact with the polymer phase without microgaps, which often cause losses in selectivity (Erucar et al., 2013).

In this review, we first give a brief introduction to the chemistry and structure of MOFs that are most used in separation membranes. We then focus on the synthesis and applications of continuous MOF membranes on inorganic substrates, continuous MOF membranes on polymer substrates, and the MOF-based mixed matrix membranes (MMMs). The applications only refer to gas separation, pervaporation and nanofiltration. Those who are interested in MOF structures and MOF films are recommended to read some excellent extensive review articles (Stock and Biswas, 2012; Furukawa et al., 2013; Zacher et al., 2009; Shekhah et al., 2011; Bradshaw et al., 2012). This review is organized by the following sections: (1) Introduction; (2) Materials and synthesis of MOF membranes; (3) Continuous MOF membranes on inorganic substrates; (4) Continuous MOF membranes on polymer substrates; (5) MOF-based mixed matrix membranes; (6) Conclusions and outlook.

2. Materials and synthesis of MOF membranes

2.1. MOF materials

In past decade, more than 20,000 MOF materials have been reported and studied, which typically possess the larger surface area values range from 1000 to 10,000 $m^2\,g^{-1}$ (Furukawa et al., 2013).

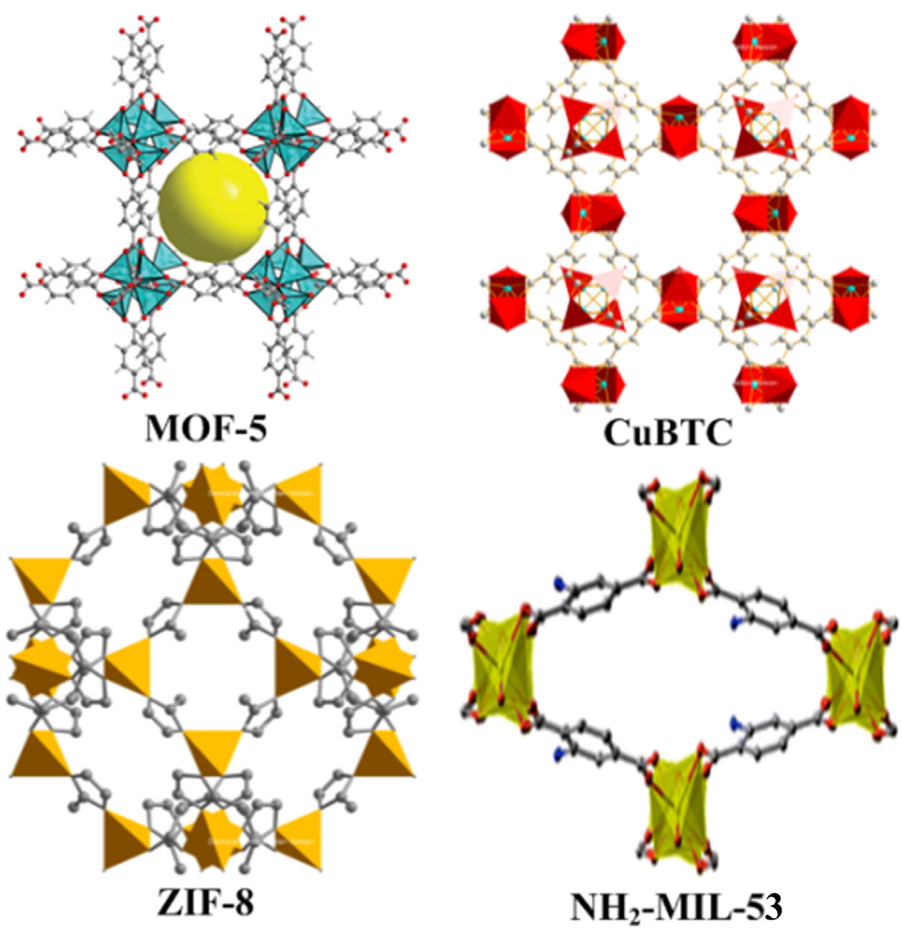

Fig. 1. Crystalline structure for some of the MOFs.