Metal-Organic Framework Catalytic Membranes for Environmental Management

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Abstract. Metal-organic frameworks (MOFs) materials have been widely used in environmental protection due to the unique characteristics such as high surface area, adjustable pore size and abundant functionalization. Recently, various methods have been applied to prepare continuous MOF catalytic membranes with active catalytic sites and uniform apertures to realize the effective separation and catalysis at the same time. This paper briefly introduces and compares the preparation methods of MOF catalytic membrane and analyses catalytic site on the related membranes. The applications of MOF catalytic membrane in environmental management are summarized and the expectations about future development way are made as well.

1. Introduction

Over the past decades, catalytic membranes have been developed to deal with multiple pollutants and have attracted more and more interests at the same time (Fig. 1a) [1]. These membranes use catalytic materials to prepare membrane reactors or implant the catalysts into the membrane, in which the reactants can selectively penetrate the membrane for the catalytic reaction or the reaction products can selectively penetrate the membranes. Compared with the traditional methods for water and gas treatment such as membrane bioreactor (MBR), the catalytic membrane, coupled with the membrane separation and chemical oxidation, can not only reduce the operational procedure and time, but also eliminate the interaction between the contaminants [2]. In terms of green chemistry, membrane catalysis as an innovative technology is more efficient and environmentally friendly than traditional physical and chemical methods [3].

Hybrid membranes composed of porous materials such as zeolite, carbon nanotube (CNT) and metal-organic framework (MOFs) are considered to hold a great potential in preparation of catalytic membranes, which possess the dual ability of molecular sieving and selective catalysis. Recently, MOFs as a new porous material prepared by the connection of metal ions and organic ligands, have attracted intensive interests in various applications including gas separation [4], drug delivery [5] and catalysis [6, 7] due to the high surface area, adjustable pore size and abundant functionalization (Fig.

1b). Researchers including our group have applied various methods to prepare the MOF membrane with excellent performance [8-12]. Generally, there are mainly two types of MOF membrane: mixed-matrix membranes and MOF layer membranes. For the mixed-matrix MOF membranes, MOF nanoparticles were incorporated into the polymer matrix to not only overcome the inherent fragile of MOF membrane in practical applications, but also improve the membrane performance. For the MOF layer membranes, various methods such as in-situ growth and chemical modification method have been developed to grow the continuous MOF layer on porous supports (Fig. 1c) [13].

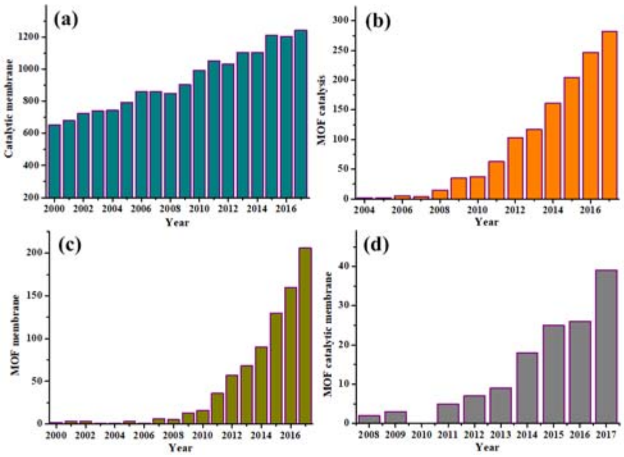

Figure 1. The number of publications per year: (a) catalytic membrane, (b) MOF catalysis, (c) MOF membrane and (d) MOF catalytic membrane. Data obtained from the Web of Science until Dec 31st, 2017.

The MOF catalytic membranes, consisting the base and MOFs layer, can be considered as a good combination of MOF membrane and catalyst. The advantages of MOF catalytic membranes are mainly listed in the following aspects: 1) many MOF membranes have their own catalytic sites without the need for reloading catalyst. 2) MOF membranes with adjustable pore size have the sieve ability for highly purified product. In the last decade, despite being in its infancy, the research on MOF catalytic membrane presents a steadily growth trend (Fig. 1d). The application of MOF catalytic membranes has gained extensive attention and the MOF catalytic membrane will be a new hot research direction [14].

2. Preparation of MOF Catalytic Membranes

Generally, there are mainly two types of MOF catalytic membrane: mixed-matrix membranes and MOF layer membranes. For the improvement of the membrane performance, it is necessary to control the membrane thickness, continuity, compactness and the compatibility of MOF layer with the substrate. In addition, the hydrothermal stability and mechanical stability of MOF layer make a great contribution to the preparation of continuous MOF catalytic membrane. The synthetic methods of MOF catalytic membranes can be mainly divided into in-situ growth, chemical modification, layer growth method and doping method.

2.1. In-situ growth method

The in-situ growth, the most commonly used method, needs to constantly heat the synthetic solution which consists the metal compound and organic ligand (Fig. 2a). Microwave-assisted thermal deposition is a fast in-situ growth method for the preparation of continuous MOF membrane on porous substrate. This method provides the higher temperature for the growth of the MOF layer [15]. Some conductor materials such as amorphous carbon, graphene and metal nets, can be used as the substrate to strengthen the heterogeneous nucleation and growth of the MOF crystals.

2.2. Chemical modification method

Without any pretreatment of substrate, in-situ growth method is difficult to obtain a dense continuous MOFs layer because of the few nucleation sites. Therefore, it is necessary for the substrate to be functionalized for the preparation of continuous MOF membranes (Fig. 2b) [16]. The substrates of MOF membranes are usually divided into organic and inorganic substrates. The inorganic substrates including Al2O3 and TiO2, possessing excellent chemical stability. But the high cost and the difficulty in fabrication restricts their further development. Compared with the inorganic substrates, organic substrates such as PS, PVDF and PAN, have many advantages such as low cost and high processing ability. The organic substrates possess many functional groups, which are beneficial to the chemical modification of the substrate to increase the nucleation sites. Sun and co-workers fabricated the Re-SURMOF catalytic membrane by modifying the substrates with plasma to generate a surface with hydroxyl groups [17].

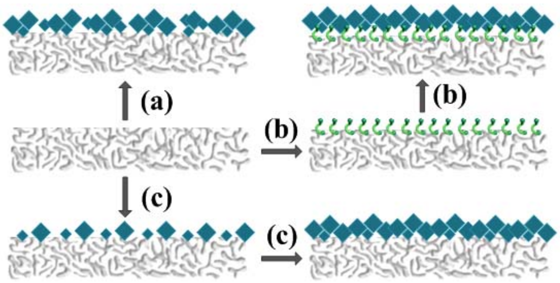

Figure 2. Different preparation of MOF Catalytic Membrane: (a) in-situ growth method, (b) chemical modification method and (c) layer-by-layer growth.

2.3. In-situ growth method

For the layer-by-layer growth method, the substrates are placed into the solution of metal compounds and organic ligands for thermostatic reaction to obtain the MOF layer with the thickness down to nanometer (Fig. 2c) [18]. Ultimately, MOF membranes can be prepared by repeating the process several times, which have the advantage of controllable thickness. Huo and co-workers control the thickness of the Pt/ZIF-8 hybrid thin membranes from one layer to five layers by this method [19].

2.4. Doping method

To date, the preparation of MOF catalytic membranes by doping method has been interestingly studied. The MOFs or metal nanoparticles with catalytic ability are doped into polymer matrix to prepare the MOF mixed-matrix membrane. The key of doping method to prepare catalytic membranes is the compatibility between catalyst and polymer matrix. The poor compatibility may result in the uneven distribution of MOF catalyst in the membrane, ultimately affecting the catalytic membrane performance. For example, Ho et al. incorporated MOF-525 nanocrystals into the graphene nanoribbons to conduct the electrocatalytic oxidation of nitrite [20].

3. Analysis of Catalytic Sites on MOF Catalytic Membrane

The catalytic site of MOF catalytic membranes can be divided into two types. First, the sandwich structure which encapsulates the catalyst between the MOF layer and substrate (Fig. 3a)[21]. Another type is that the catalytic sites are inserted inside the MOF particles (Fig. 3b) [22].

3.1. Between MOF layer and Substrate

This sandwich structure can cover all metal nanoparticles below the MOF layer, whose adjustable pore structure is beneficial to the selective separation and catalysis. This structure not only helps to improve the catalytic activity, stability and utilization of metal nanoparticles, but also makes full use of high surface area and pore structure of MOF to improve product selectivity. For example, ZIF-8 layer was grown on the substrate with hydroxy functional groups, and then metal nanoparticles were coated to obtain ZIF-8 composite membrane by repeating the above process [23]. The modification of nanoparticles by PVP not only contributes the stronger adsorption but also makes the ZIF-8 layers easier to grow continuously. The ZIF-8 catalytic membrane loading with Pt nanoparticles had a good selectivity for the catalytic hydrogenation of chain olefins.

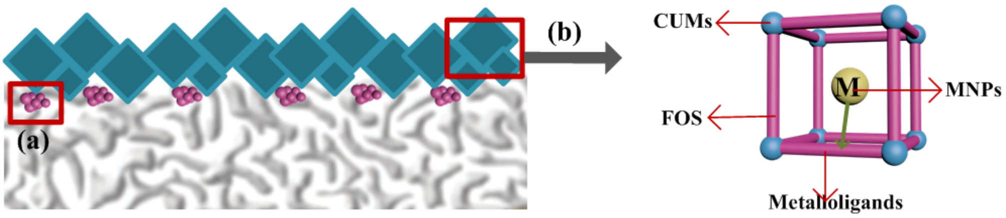

Figure 3. Different catalytic sites on MOF catalytic membrane.

3.2. Between MOF layer and Substrate

There are four types of catalytic sites for the second type of MOFs: functional organic sites (FOS), coordinatively unsaturated metal sites (CUMs), metal nanoparticals (NMPs@MOF) and metalloligands (Fig. 3b) [22]. FOS, the functional groups with catalytic properties on MOF structure. The CUMs can be obtained by the following two methods. First, the failure to cooperate with the weak bond of metal ions helps to expose the metal ions. Second, in the preparation process of MOFs, unstable compounds can be combined with metal ions, and the metal ions are exposed by the heat treatment. NMPs@MOF is the most commonly used MOF catalyst, which can be obtained by the encapsulation of metal nanoparticles into different kinds of MOF to achieve excellent catalytic performance.

4. Applications of MOF Catalytic Membrane

Along with the rapid development of preparation process, MOF catalytic membrane has been explored in gas separation catalysis and liquid separation catalysis. As shown in Fig.4, the reactant and product can be gas or liquid phase. k and k' are the reaction rate constant for the reversible reaction, and Sm is membrane selectivity. The high efficient separation of the product will accelerate the reaction, which results in the high catalytic performance.

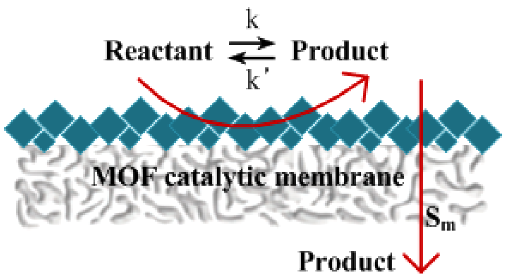

Figure 4. Schematic diagram of catalysis and separation performance for MOF catalytic membrane.

4.1. Liquid Separation and Catalysis

Zhang and co-workers synthesized a MOF-based composite membrane through in-situ growth of MIL-53-NH_2 by coordination of Al^{3+} and BDC-NH_2 inside the channels and on the surface of anodized aluminum oxide (AAO) membrane [14]. This study not only solved the problem of channel blocking, but also exhibited high catalytic performance and stability in the Knoevenagel condensation reaction due to the intrinsic structure of MOF-based composite membranes. The prepared MOF-based composite membrane can remove the products from the reaction zone quickly and prevent the aggregation and loss of catalysts during reaction and recycling process. Ma et al. prepared the thin UiO-66 membrane with high water flux and salt rejection due to the molecular sieving and superhydrophilic nature of UiO-66 particles [24]. Farha and co-workers prepared NU-1000 on conducting glass substrates with promising electrocatalytic activity for water oxidation [25].

4.2. Liquid Separation and Catalysis

Hu and co-workers prepared the copper(II)-based MOF membrane (MOF-199/Ni) with an exceptionally high photocatalytic hydrogen production and separation performance, and the triethanolamine can be easily recycled and reused after photocatalytic hydrogen production [26]. Xu and co-workers fabricated metal/MOF hybrid thin membrane with well-defined sandwich structures which exhibited excellent size selectivity and catalytic performance in olefin hydrogenation [19].

5. Conclusion and outlook

MOF catalytic membranes have great advantages in high efficient separation and catalysis due to large specific surface area and uniform pore size. The catalytic process does not require the separation of additional reactants and products. Although progress has been achieved, there are still problems existed in preparation process, such as the coordination of thickness and continuity for MOF layer, the compatibility of MOF layer to substrate and the dispersibility of catalyst. The multi-level structure of catalytic membranes has not been controlled precisely. With the development of preparation technology and the continuous exploration of new methods, these bottlenecks will be broken and novel MOF catalytic membranes will be very promising in future industrial production process.

Acknowledgments

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