Composites of metal–organic frameworks: Preparation and application in adsorption

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Metal–organic frameworks (MOFs) are one of the most discussed materials of the last decade. Their extraordinary porosity and functionality from metals and organic linkers make them one of the most promising materials for a vast array of applications. The easy tunability of their pore size and shape from the micro- to meso-scale, by changing the connectivity of the inorganic moiety and the nature of the organic linkers, makes these materials special. Moreover, by combining with other suitable materials, the properties of MOFs can be improved further for enhanced functionality/stability, ease of preparation and selectivity of operation. In this review, various methods and paths for the preparation of composites are discussed, especially for those which have been successfully applied to gas and liquid phase adsorptions. In the second part of this paper, several applications in adsorptive processes are discussed.

Introduction

Remarkable progress on porous materials has been achieved because of developments in mesoporous materials [1,2] and metal–organic frameworks (MOFs) [3–5], which are one of the most important and rapidly growing groups of porous materials. MOF materials are composed of metal ions (or clusters) and coordinating linkers which impart high porosity to the MOF structures. The particular interest in MOF materials is due to the easy tunability of their pore size and shape from a microporous to a mesoporous scale, by changing the connectivity of the inorganic moiety and the nature of the organic linkers. Recently, MOF materials have been used in many applications including gas adsorption/storage, separation, catalysis, adsorption of organic molecules, drug delivery, luminescence, electrode materials, carriers for nanomaterials, magnetism, polymerization, imaging, membranes and so on [3–11]. Their potential increases every year due to the easy modification of MOFs, which make them a prominent group of materials in a vast number of published reports.

As mentioned, MOFs show very promising physical and chemical properties for various applications; moreover, their properties can be further improved by several means. Some of these are grafting active groups [12], changing organic linkers [13], impregnating suitable active materials [14], postsynthetic ligand and ion exchange [15], making composites with suitable materials [16–20], and so on. A composite is a multi-component material with multiple phases which has at least one continuous phase [21]. Recently, MOF composites have been receiving tremendous interest due to their various applications, including adsorption. This is a relatively new concept and several reports have been published recently with successful syntheses and promising applications of MOF composites. By composing MOFs with suitable materials, the synthesis kinetics [22], morphology [15,23], physicochemical properties [24,25], stability [26–28] and potential applications [24,25] can be largely improved.

Adsorption receives more attention every year for its superiority to other techniques in the removal of hazardous materials, purification of fuels or water and storage of gases such as hydrogen and methane. Because adsorption can be carried out at low temperatures, it is less energy intensive and hence of comparatively low cost. It also has the advantages of a wide range of applications, simplicity of design, easy operation, and low harmful secondary products. MOF-type materials are very well known for their applicability in adsorption processes due to their high surface area with adequate pore openings [29,30]. Additionally, MOFs contain special and specific chemical functionalities which are useful to selectively adsorb some species, and these functionalities are one of the great properties of MOFs. Recently MOF composite

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materials have been used to improve functionality and porosity and, hence, improve the performance of adsorbents for their selectivity or adsorption capacity. These materials have been applied to both gas/vapor phase and liquid phase adsorptions.

Gas phase adsorptions are carried out mainly to remove toxic gases. There are a large number of reports showing high adsorption capacity for the adsorption of gases over MOFs. Recently, MOF composites have also been used for gas phase adsorption to improve the capacity and selectivity of adsorbents [30]. A large number of studies have shown promising gas storage capabilities with MOF composites which are also based on the adsorptive phenomenon [31–33]. By imparting special functionality, selective adsorption of specific gases can be achieved. Therefore, it is very important to improve the selectivity of MOF materials by combining them with suitable materials for removal, storage and separation of gaseous materials. Several toxic gases such as H_2S, NH_3 and NO_2 could be adsorbed and hence separated by, for example, graphite oxide/MOF composites [24,25,34,35]. MOF composites have also been used for gas storage. A few reports have been published for hydrogen storage using carbon nanotube (CNT)/MOF composites, and in some cases, metals were also loaded to these composites to improve the storage capacity [16,36].

Liquid phase adsorptions have also been widely discussed and applied to the various fields of MOF composites. Presently, fuel processing is an important area of research, and every year MOFs are being used to purify fuels or to remove harmful components from fuels. In most cases, organic compounds are removed or separated through MOFs using their selective interaction behavior. One of the most discussed adsorption processes is the adsorptive removal of sulfur or nitrogen containing compounds from fossil fuels as shown by a few recent review articles [37,38]. Besides these, water purification using MOFs is also gaining interest every year. Understanding their true potential, researchers are turning their interests to the adsorptive nature of MOF materials, and a vast number of publications related to MOFs have been published in the last decade. The opportunity to study pure MOFs has become narrower due to the broadening field, and hence, researchers now are experimenting with modified MOF materials with plenty of room for studies on MOF composites.

In this review, we will discuss various methods and aspects for the synthesis of MOF composites. The improvements in MOFs made by combining with different materials will also be discussed. Applications of MOF composites in adsorption will be explained through the enhancement of porosity (surface area and pore volume) or improved interaction between adsorbents and adsorbates (by acid–base interaction or π-complexation, and so on).

Discussion

Preparation of MOF composites

Several methods and approaches have been applied for the synthesis of MOF composites. In general, there are two basic types of MOF composites according to the formation of the composite [39]. In MOF composites, MOFs can be in both the discontinuous phase and the continuous phase. However, the first type of composites (discontinuous MOFs) is not commonly used for application in adsorption and are prepared mainly for purposes such as composites that require different sizes/shapes and that demand easy handling. These include monoliths, beads, fibers, membranes/films, and so on. Examples of these materials are HKUST-1 monoliths [40], ZIF-8/PVP (polyvinylpyrrolidone) fiber mats [41], composite membranes of MOF-5 and ZIF-8 [42,43], and HKUST-1/PAM (polyacrylamide) beads [27]. The second type of MOF composites is the well-known MOF composites with continuous MOFs for applications such as adsorption, and our discussion will be focused on these materials.

For the preparation of MOF composites where MOFs are in a continuous phase, a wide variety of methods have been applied. The methods can be generally categorized into a few major classes. In one of these methods, MOF precursors are mixed with presynthesized composing materials and then the synthesis procedure is carried out. Graphite oxide/MOF (GO/MOF) is one of these types of materials that has been widely reported for various applications [25,35,44,45]. Bandosz et al. published several reports on GO/MOF composites prepared using this procedure and successfully applied them in gas phase adsorptive removal of toxic gases such as NH_3, H_2S, NO_2, and so on [25,35,44,45]. In these composites, the GO layers are somewhat separated and stacked in-between the planar cage structure of the MOFs (Fig. 1). In some cases, for this type of synthesis, the particles of the composing materials can be trapped in the pores of the MOF and hence can be stabilized or immobilized. This concept is known as 'bottle around ship' (BAS) and is shown in Fig. 2(a). In the BAS method, large particles of the composing materials are immobilized inside the cage of the MOF, which is only possible by in situ synthesis of the MOF. The MOF is built from the precursors around the composing materials, and after complete formation of the MOF, the composing materials are trapped inside the pores. Several reports about the encapsulation of polyoxometalates (POM) in MOFs have also been published [22,46,47].

Liu, Su and coworkers also prepared several MOF composites (the preparation method was very similar to the BAS method), named NENU-*n*, from the in situ synthesis of MOFs (HKUST-1) in the presence of POMs. Fig. 3 shows the structure of two pores of NENU-*n*, which was unambiguously obtained by single crystal X-ray analysis [48]. It was later demonstrated that the NENU-11 (a sodalite-type porous MOF with a POM template as shown in Fig. 3(c)) possessed a good adsorption/decomposition capability for dimethyl methyl phosphonate (from 6 molecules in MOF-5 to 15.5 molecules in NENU-11 per unit formula) [49].

In the other preparation method, the MOF composite is supposed to form from the precursors of the composing materials and the preformed MOF. This method is called sometimes the 'ship in a bottle' (SIB) method, as explained by Gascon et al. [19] (Fig. 2(b)). In this case, the composing material forms inside the cages of the MOF and the diffusion of the precursors is usually carried out in the cages by a solvent system. Due to the increased size, the particles stay stable inside of the cages. In most cases, the precursors of the composing materials are added through solutions and diffused into the pores. Then the composite is formed by stabilizing the composing moiety inside the pores (of the MOFs) by means of chemical or thermal methods. One of the best examples of this, shown in Fig. 4, is direct encapsulation of different porphyrines into ZMOFs, and this composite was successfully applied in catalytic oxidation [50]. Although SIB techniques are widely known for zeolite composites [51], their study within the MOF