Review

Ionic liquid transported into metal–organic frameworks

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ABSTRACT

Ionic liquids (ILs) show promise as new green solvents for chemical reactions, extractions, catalysis, gas absorption, and electrolytes in electrochemical devices. For the widespread use of ILs, the concept of ILs impregnated with porous supports has recently been established. Metal–organic frameworks (MOFs) have great potential as new host materials for ILs; they are able to decrease the amounts of ILs and tune the properties of ILs via host–guest interactions. In this review, we will present an overview of the studies carried out to date on MOF-supported IL systems, and their possible applications, such as in gas absorption, catalysis, templates for synthesis of nanoporous carbons, and ionic conductors.

1. Introduction

Solvents called molten salts or ionic liquids (ILs) consist of liquid phase ions and are free from any electrically neutral molecular solvents. The melting points of ILs are significantly lower than those of classical salts as a result of the many efforts that have been made to design the structures of component ions [1,2]. ILs whose melting points are as low as ambient temperature are specifically referred to as room-temperature ionic liquids (RTILs). Many RTILs have been reported to date. Since the 1980s, research into ILs has attracted

much interest, largely due to their suitable properties for various applications, such as their negligible volatility, nonflammability, high thermal and chemical stability, and high ionic conductivity. ILs therefore show promise as new green solvents for chemical reactions [3–5], extractions [6,7], catalysis [8–12], and gas absorption [13,14]. Moreover, ILs are promising candidate materials for electrolytes in electrochemical devices, such as lithium ion batteries [15–17], electric double layer capacitors (EDLCs) [18,19], fuel cells [20], and dye-sensitized solar cells [21]. For the widespread use of ILs, the structures of component ions have been modified to tune the physical or chemical properties of ILs to suit the various intended purposes. Because of their high designability, ILs are called "designer solvents." Despite the advantages of ILs, their actual applications are limited due to their drawbacks, such as high cost, high viscosity, water absorbability, and strong interaction with

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other ions. Over the past decade, the concept of ILs impregnated with porous supports, referred to as "supported ionic liquid phase (SILP)," has been established [22–27]. Various porous materials have been used as supports in SILPs, such as silica gels, mesoporous silica, activated carbons, or porous glasses. SILPs have potential to suppress the costs of ILs because SILPs can decrease the amount of ILs per surface area. Moreover, the properties of ILs can be tuned or enhanced because of the nanosizing of ILs or interactions between ILs and host materials.

Metal–organic frameworks (MOFs), which are also called porous coordination polymers (PCPs), comprise a new group of porous materials. MOFs are crystalline materials composed of metal centers and organic ligands, infinitely connected by coordinative bonds. MOFs have numerous uniformly sized micropores or mesopores originating from the crystal structures of MOFs. A large variety of MOFs have been reported, and various properties of MOFs have been studied, such as gas adsorption [28–30], catalysis [31,32], and ionic conductivity [33–35]. The extraordinary advantage of MOFs as host materials is the ability to create tunable host–guest interactions. We can tune the properties of MOFs, such as pore size, surface area, framework topology, and polarity of the inner surface, by appropriate selection of the metal centers and organic ligands. Because this high designability of MOFs enables tunable host–guest interactions, MOFs have great potential as new host materials for SILPs, which, in turn, could tune or enhance the properties of ILs.

ILs incorporated within MOFs (symbolized as IL@MOFs) were first obtained by ionothermal synthesis [5,36–38]. Ionothermal synthesis is a form of solvothermal synthesis, where ILs are used as solvents. Ionothermally synthesized MOFs usually have negatively charged frameworks, and the cations of ILs are left in the MOFs as counterions to maintain electric neutrality. The cations are embedded in the MOFs with ordered structure because of strong host–guest interactions. However, the cations in ionothermally synthesized MOFs are considered not to exhibit the same useful properties as bulk ILs, because the cations of ILs are strongly bound to the MOFs. Moreover, there are a limited number of options for ILs and MOFs in ionothermal synthesis. This may be a disadvantage for the widespread application of IL@MOFs.

Recently, several groups have reported IL@MOFs obtained by a postimpregnation strategy—ILs are incorporated in MOFs after the synthesis of the MOFs. The postimpregnation strategy maximally utilizes the advantage of the IL@MOF system, because a large number of ILs and MOFs can be selected as the components of the IL@MOFs. Here, we present an overview of the studies of IL@MOF systems obtained by the postimpregnation method and their possible applications, such as in gas absorption, catalysis, templates for synthesis of nanoporous carbons, and ionic conductors.

2. Strategies for impregnation of ILs into MOFs

Three strategies have been reported to prepare the IL@MOFs by the postimpregnation. In the first strategy, the solution of ILs were used [39–42]. Amino-functionalized basic ionic liquid (ABIL-OH) was introduced into a MOF, HKUST-1 (Cu$_3$(BTC)$_2$, H$_3$(BTC) = 1,3,5-benzenetricarboxylic acid) by this strategy shown in Fig. 1 [39]. The powder of HKUST-1 was dispersed in the ethanol solution of ABIL-OH, and the mixture was stirred at ambient temperature. HKUST-1 has coordinatively unsaturated sites (CUSs), which can lead to pinning of the ABIL-OH ions by their Lewis acidity. The solvent was separated by filtration and the excess ABIL-OH was removed by washing with solvents. After the solvents were removed by drying under vacuum, ABIL-OH@HKUST-1 was obtained. This strategy is the most widely used to introduce the ILs into the MOFs with CUSs.

The second strategy is the tandem postsynthetic modification. A Brönsted acidic IL (BAIL) was confined in the mesopores of Cr-MIL-101 (Cr$_3$O(F, OH)(H$_2$O)$_2$(BDC)$_2$) by this strategy (Fig. 2) [43]. Cr-MIL-101 was first modified by N–Cr coordinate covalent bonds between the CUSs and the *N*-heterocyclic compounds (triethylene diamine or imidazole) that contain two nitrogen atoms. Subsequently, 1,4-butane sultone was added and reacted with the *N*-heterocyclic compounds to construct ILs. Finally, the anions of ILs were exchanged with HSO$_4^-$ by the addition of H$_2$SO$_4$. The tandem postsynthetic modification strategy makes it possible to incorporate the ILs with larger ions than pore aperture diameter into the pores of MOFs. This ship-in-bottle process can effectively confine the ILs inside the pores of MOFs.

In the third strategy, the ILs are introduced into the pores of MOFs through capillary action [44–46]. An IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (EMI-TFSA; Fig. 3a) was introduced into the micropores of a MOF, ZIF-8 (Zn(MeIM)$_2$, H(MeIM) = 2-methylimidazole; Fig. 3b) by this strategy [45,46]. The ZIF-8 powder was dried to remove guest molecules from the micropores, and was mixed with EMI-TFSA. The mixture was heated and stored to enhance the diffusion of EMI-TFSA through capillary action. The advantage of the capillary action is that this strategy can widely be applied to various types of ILs and MOFs such as ZIF-8, which has no CUSs.

After the impregnation of ILs into MOFs by the strategies described above, nitrogen gas adsorption or infrared absorption (IR) measurements have been conducted to confirm the existence of ILs inside the pores of MOFs [39–43,45,46]. For example, the impregnation of 1-butyl-3-methylimidazolium chloride (BMI-Cl; Fig. 4) into Cr-MIL-101 was confirmed by these measurements [40]. As shown in Fig. 5a, there is no change in the crystal structure of Cr-MIL-101 after the loading of the BMI-Cl. The nitrogen gas
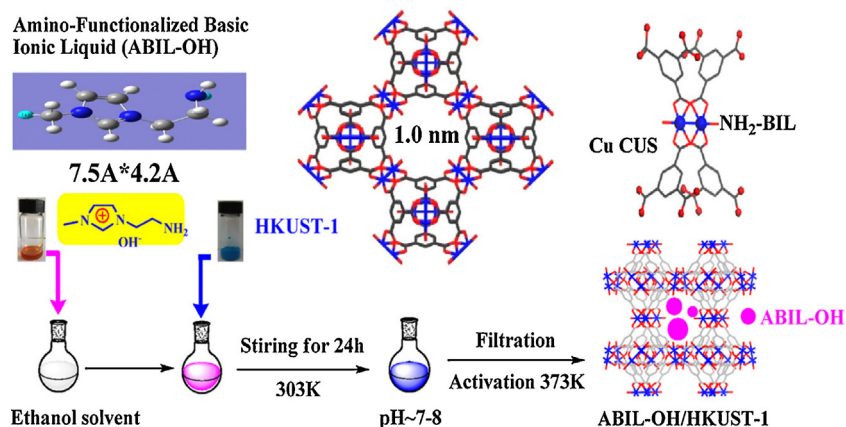

Fig. 1. The schematic illustration for synthesizing ABIL-OH@HKUST-1.

Source: Adapted from Ref. [39].