



Review

The role of the counter-ion in metal-organic frameworks' chemistry and applications

Huacheng He^{a,1}, Lida Hashemi^{b,1}, Mao-Lin Hu^{a,*}, Ali Morsali^{b,*}^a College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, China^b Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-4838, Tehran, Islamic Republic of Iran

ARTICLE INFO

Article history:

Received 26 May 2018

Accepted 14 August 2018

ABSTRACT

A review of the synthesis, structure and specifically the effect of counter-ions on the properties of ionic metal organic frameworks (ionic-MOFs) is presented, highlighting the important advances in this regard over the past decade. Most focus is on ionic porous metal-organic frameworks (MOFs) materials consisting of porous anionic or cationic frameworks and cationic or anionic guests. The structure and performance of cationic and anionic MOFs are influenced by several factors, such as organic ligands, metal ions and charge-balancing anions. These types of anionic and cationic materials have distinct advantages in comparison with neutral MOFs in the design of functional materials and their synthesis affords several distinct advantages over that for routine neutral frameworks by virtue of the isolated charged species in confined nano-spaces. The nanosized and charged pores in these ionic structures generate a strong interaction between the host and guest molecules, including enhanced adsorption towards small gases and solvent molecules. Ionic-MOFs can be easily modified via ion exchange and accommodate other charged guest molecules, making them an ideal platform for different applications, such as functional materials. The development of synthesis methods by ion exchange and the potential applications of such cationic or anionic structures have been discussed thoroughly in this review.

© 2018 Elsevier B.V. All rights reserved.

Contents

1. Introduction	320
2. Tuning of the MOFs properties by counter-ion exchange process	322
2.1. Anion-exchange	322
2.2. Cation-exchange	324
3. Effect of counter-ions on the stability of porous MOFs	325

Abbreviations: Tempt, 2,4,6-tris[4-(imidazole-1-ylmethyl)phenyl]-1,3,5-triazine; 1,3,5-tris, 1,3,5-tris(pyrazol-1-yl)benzene; 4-bpdh, 2,5-bis(4-pyridyl)-3,4-diaza-2,4-hexadiene; HL, 1H-1,2,4-triazole-3-carboxylic acid; HDMA, dimethyl ammonium; BDC, benzene dicarboxylic acid; DMA, *N,N*-dimethyl amide; TMA, tetra methyl ammonium; TEA, tetra ethyl ammonium; TPA, tetra propyl ammonium; H₄mdip, 5,5'-methylenediisophthalic acid; ad, adeninate; BPDC, biphenyl dicarboxylate; L1, 2-amino-4,6-dimethylpyrimidine; L2, 2-amino-4-methoxy-6-methylpyrimidine; L3, 2-amino-4,6-dimethoxypyrimidine; NDC, 2,6-naphthalene dicarboxylate; dma, *N,N'*-dimethyl acetamide; bpdc, 4,4'-biphenyldicarboxylate; NH₂bdc, 2-amino-1,4 benzene dicarboxylate; HCOO, formate; H₂PPZ, tetracarboxylate isophthalate; btr, 4,4'-bis(1,2,4-triazole); Tipa, tris(4-(1Himidazol-1-yl)phenyl)amine; 1,4-H₂bda, 1,4-H₂benzenediacetate; mtrb, 1,3-bis(1,2,4-triazol-4-ylmethyl)benzene; BPDC, 4,4'-dicarboxylate-2,2'-dipyridine anion; H₄mtb, 4-[tris(4 carboxyphenyl)methyl]benzoic acid; L, 4,4'-dicarboxylate-2,2'-dipyridine anion; BTB, 1,3,5-benzene(tris)benzoate; H₆dpa, 3,4-di(3,5-dicarboxyphenyl)phthalic acid; DMF, dimethyl formamide; dobd⁴⁻, 2,5-dioxido-1,4-benzene dicarboxylate; pbdc, 5-phosphonobenzene-1,3-dicarboxylic acid; bmbi, 1,4-bis(2-methylimidazol-1'-yl)butane; H₃btc, 1,3,5-benzenetricarboxylic acid; H₃cpip, 5-(4-carboxyphenoxy)isophthalic acid; NMP, *N*-methyl-2-pyrrolidone; H₄L, 4,8-disulfo naphthalene-2,6-dicarboxylic acid; bpy, 4,4'-bipyridine; H₂L, pyridine-3,5-bis(phenyl-4-carboxylic acid); tata, melamine, 2,4,6-triamino-1,3,5-triazine; bped, *meso*-1,2-bis(4-pyridyl)-1,2-ethanediol; BBPTZ, 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl; H₂thb, 2,5-thiophenedicarboxylate; H₃BTB, 4,4',4''-benzene-1,3,5-triyl-tribenzoic acid; IDC³⁻, imidazole-4,5-dicarboxylate; L1, (N-phenyl-N0-phenyl bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxydiimide tetracarboxylic acid; H₄-DHBDC, 2,5-dihydroxy-1,4-benzene dicarboxylic acid; H₆dpa, 3,4-di(3,5-dicarboxyphenyl)phthalic acid; TATB, 4,4',4''-s-triazine-2,4,6-triyltribenzoate; MOF, Metal Organic Framework; H₅hpdia, 5,5'-(hydroxy phosphoryl)diisophthalic acid; NDC, 2,6-naphthalene dicarboxylate; H₆dpa, 3,4-di(3,5-dicarboxyphenyl)phthalic acid; DDS, drug delivery systems; AEMFC, Alkaline polymer Electrolyte Membrane Fuel Cells; AEM, Alkaline polymer Electrolyte Membrane; DPT, 3,6-di(pyridin-4-yl)-1,2,4,5-tetrazine; H₃IDC, imidazole-4,5-dicarboxylic acid.

* Corresponding authors.

E-mail addresses: maolin_hu@yahoo.com (M.-L. Hu), morsali_a@modares.ac.ir (A. Morsali).¹ The authors contributed equally to this work.

4.	Templating effects of counter-ions on the structure of MOFs	326
5.	Organic counter-ions versus inorganic counter-ions	327
6.	Synthesis strategies of ionic MOFs	328
6.1.	Anion stripping method	328
6.2.	Post-synthetic modification method	328
6.3.	Ionothermal synthesis method	328
6.4.	Selection of building blocks method	329
6.5.	Interpenetrating porous structure with independent cationic and anionic frameworks	329
6.6.	Counter-ions exchange: a useful route for the preparation of ionic-MOFs	330
7.	MOFs containing counter-ions for organic and inorganic ion removal, extraction and sensing	332
7.1.	Dichromate ($\text{Cr}_2\text{O}_7^{2-}$)	332
7.2.	Chromate (CrO_4^{2-})	332
7.3.	Iodide (I^-)	333
7.4.	Metal ions	333
8.	Effect of counter-ions on MOFs' properties and applications	334
8.1.	Counter-ions' role in MOFs application as a nanocarrier for drug delivery	334
8.2.	Counter-ions' role in membrane and proton transferring systems in MOFs	335
8.3.	Counter-ions' role in dye removal in MOFs	335
8.4.	Counter-ions' role in MOFs catalysis	337
8.4.1.	Effect of counter-anions on the catalysis of cationic MOFs	338
8.4.2.	Effect of counter-cations on the catalysis of anionic MOFs	339
8.5.	Effect of counter-ions on gas sorption in MOFs	339
8.6.	Effect of counter-ions on the luminescence properties of MOFs	341
8.7.	Effect of counter-ions on MOFs sensors	343
8.8.	Effect of counter-ions on hydrocarbon separation by MOFs	344
9.	Conclusion	344
	Acknowledgements	344
	Appendix A. Supplementary data	344
	References	344

1. Introduction

Advances in new materials for any targeted application require the ability to make progressive changes through an iterative cycle of design, execution and assessment. Metal-Organic Frameworks (MOFs) are a class of compounds consisting of metal clusters or nodes linked by organic moieties. MOFs are highly crystalline, which allows for easy structural determination [1], so they are garnering ever increasing attention in research laboratories worldwide [2–20]. Rational design and the diversity of possible topologies and useful properties allow for the possible application of MOFs in areas such as gas adsorption [2], hydrogen storage [3], molecular sieves [4], catalysis [5], molecular magnets [6], nonlinear optical devices [7], luminescence [8], sensors [9] and drug delivery [10]. Today, there are over several thousand examples of MOF materials in the literature due to the flexibility in metal charge, coordination number and the choice of organic linking agent. Therefore, using different synthesis routes and crystal engineering is an effective method for growing crystals of MOFs and extended materials, in general, allowing a great deal of structural diversity and varying dimensionality [21,22].

Among the various MOFs, those having cations and anions in their structures are very interesting and applicable in comparison with neutral ones in the design of functional materials. They include anionic structures in which the compound is anionic, thereby resulting in the existence of a counter cation to balance their overall charge, and cationic structures where the cationic nature of the backbone results in the necessity of anions to neutralize the charge in order to maintain the electrical neutrality. Cationic structures can serve as promising anion exchange materials through selective exchange of charge balancing anions in the compound with other anions, leading to tunable change in physical properties. Besides, cationic structures can serve as ionic hosts to accommodate different guest molecules by electrostatic interactions, which can cooperatively result in specific functions.

Ion-exchange chromatography and ion-exchange solid phase extraction based on ion-exchange resins are known as the first generation of powerful tools for the separation of charged molecules, so researchers are interested in finding new materials with higher performance in their ability for ion separation. Another separation method, size-exclusion chromatography, is based on the size or molecular weight of the analytes. Although these methods are especially useful, they are used only for separation of very large species, such as proteins and polymers. In another way, by mixing the unique structure of MOFs, especially their porous structures, with the efficiency of ion chromatography, it is possible to develop a novel separation system in which charged MOFs replace conventional ion-exchange resins (Fig. 1). The structural characteristics of porous MOFs, such as precisely defined pores, can result in useful properties, including a size-exclusion effect for guest molecules in a size regime that cannot be achieved by conventional ion-exchange resins [23].

Hence, increasing interest has recently shifted to the design and synthesis of ionic MOFs. As we know, the structure and performance of cationic and anionic porous MOFs are influenced by several factors, such as the organic ligands, metal ions, and charge-balancing anions. The ions inside these polarized MOFs are often exchanged with other exogenous ions, making them promising candidates to be used in ion exchange resins. Moreover, the presence of charged species inside the structure may cause specific interactions which can be effectively used for diverse applications; therefore, research on ionic MOFs has considerably advanced over the last decade. Considering just metal-organic frameworks (MOFs) and reviewing the articles in ionic structures and searching in web of science with the keywords “Anionic MOFs”, “Cationic MOFs” and “Ionic MOFs” the following chart was drawn up. Scheme 1a and b shows the increase in the number of articles published in this area (Cationic and Anionic MOFs) and also the importance of discussion in this field. Scheme 1c compares articles with keywords “Anionic MOFs”, “Cationic MOFs” and “Ionic MOFs”.

Download English Version:

<https://daneshyari.com/en/article/11005966>

Download Persian Version:

<https://daneshyari.com/article/11005966>

[Daneshyari.com](https://daneshyari.com)