A Novel Class of Nanomaterials Derived from Metalorganic Frameworks

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Metal-organic frameworks (MOFs), an emerging novel class of materials created from supramolecular assembly of inorganic components (metal ions or metal clusters) with organic components (organic or organometallic complexes), have attracted increasing attention in the last two decades. Owning to their diverse structural topologies through careful selection of metal centers and different functional linkers, the development of multi-functional applications of MOFs has been realized in recent years. The most intriguing characteristic advantage of MOFs is their exceptionally high porosity and surface area, which are widely used in applications such as heterogeneous catalysis, biomedical imaging, drug delivery, gas separation and storage. MOFs prepared in high yield through cheap starting materials can also be used as self-templates to generate porous metal oxides and carbon materials with unique properties, which provide an approach to prepare novel nanostructured inorganic materials.

Storage and Separation

As porous materials with well-defined pore sizes and high surface areas, MOFs exhibit great promise for applications in gas storage and separation. Since the first report of hydrogen adsorption in a porous MOF in 2003, lots of MOFs with functional groups have been designed for hydrogen storage applications (**DOI**: 10.1021/ja101541s). The gas separation is one of hot research topics in chemical industries. For example, the separation of CO₂ from CH₄ is an important process in natural gas upgrading because CO₂ significantly lowers the energy density of natural gas and induces pipeline corrosion (DOI: 10.1039/C0CC05419D). Additionally, MOFs can also be used in chromatographic separation of larger molecules.

Heterogeneous Catalysis

Porous MOFs have many interesting potential applications in catalysis: (1) MOFs with a large specific surface area and well defined

pore size can act as carriers for supporting catalysts (Ag, Au, Pd and so on) on their surface or in their pores (DOI: 10.1038/NCHEM.1272). Notably, MOF carriers could effectively avoid agglomeration of small metal particles in the catalytic process. (2) A MOF itself can act as a catalyst, where its catalytic activity may be originated from metal centers, organic linkers and other groups from post-synthetic modification. The centered metal ions (M) are connected with Oor N-containing linkers to form M-O or M-N clusters in MOFs, providing active sites for catalysis (DOI: 10.1021/cs1000625). (3) The metal ions in MOFs can be partially replaced to generate a novel class material such as catalysts. For example, metal ions (Ag⁺, Au⁺, Pd⁺, Pt²⁺, Ce²⁺, et al.) can partially replace metal centers of MOFs, forming catalysts in the reduction of p-nitrophenol to p-aminophenol, Suzuki cross-coupling reactions and so on. (4) MOFs act as catalyst precursors. In specific conditions, MOFs can be converted to metal oxides, metals, heteroatom-doped carbon materials and even their composites serving as catalysts.

Biomedical Imaging and Drug Delivery

MOFs have also attracted increasing interest in biomedical applications because they can be used as delivery vehicles for imaging contrasts and molecular therapeutics. Recently, they have been explored as contrast agents of magnetic resonance imaging (MRI) through using paramagnetic ions as metal centers of MOFs. For example, as contrast agents Gd³⁺ or Mn²⁺ bearing MOFs exhibit excellent T₁-weight MRI with large per metal- and per particle-based MR relaxivities (DOI: 10.1021/ar200028a). Nevertheless, MOFs containing Fe3+ have demonstrated excellent T2-weight contrast enhancement. In addition, MOFs have also served as viable contrast agents for optical imaging through the incorporation of luminescent building blocks in MOFs (DOI: 10.1038/NMAT2608). Owning to their large specific surface area and large internal pore volumes, MOFs have also been used as carriers for the delivery of anticancer drugs and other chemotherapeutics. Therefore, MOFs have great potential as novel and effective platforms for drug delivery.

Template or Precursor for Preparing Porous inorganic Materials

Because of their permanent nanoscale cavities and open channels similar to those of mesoporous silica's and zeolites, MOFs show a potential for large-scale application as templates to prepare nanoporous carbon materials. Since Xu et al. employed MOF-5 framework $(Zn_4O(OOCC_6H_4COO)_3)$ as a template for preparing porous carbon materials with furfuryl alcohol (FA) as a carbon precursor, several other kinds of MOFs have been used as templates for the fabrication of porous carbon materials (**DOI**: 10.1021/ ja7106146). MOFs that include diverse C-containing linkers and metal centers can also be used as precursors to prepare carbon materials or metal oxides through a process called pyrolysis. The as-prepared carbon materials or metal oxides can inherit the excellent structure

Citation: Zheng F, Yang Y and Chen Q. A Novel Class of Nanomaterials Derived from Metal-organic Frameworks. Ann J Materials Sci Eng. 2014;1(2): 2. features of MOFs with a large specific surface area and uniform pore size, which demonstrated potential applications in energy storage, catalysis, gas sensor and so on. Interestingly, binary-metal oxides can also be produced by calcination of binary-metal-containing MOFs. In recent years, researchers show interest in high-level heteroatomdoped carbon materials through direct pyrolysis of MOFs with heteroatoms in their organic components, such as phosphorus, boron, sulfur and nitrogen (DOI: 10.1002/chem.201300054). In addition, the direct pyrolysis of MOFs in an inert atmosphere provides an efficient route to avoid generation of hydroxyl groups or epoxy groups in the resulting carbon materials, which can lead to modifications of the surface structure and surface properties of resulted materials.

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