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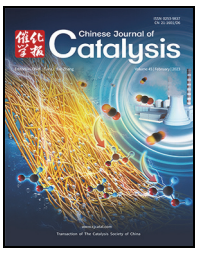

Comment

Metal-organic frameworks for catalysis: Fundamentals and future prospects

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ABSTRACT

The past three decades have witnessed significant development of metal-organic frameworks (MOFs) for heterogeneous catalysis. At the crossroads of development, the fundamentals on the design of MOF-based catalysts along with the specific uniqueness of MOFs for catalysis are summarized in this Comment. Moreover, the bottlenecks limiting the further development and opportunities moving this field forwards are further discussed.

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1. Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), constructed by metal clusters and organic linkers *via* coordination interactions, have attracted wide attention and have achieved great progress in catalytic field over the last 30 years [1–6]. Due to the highly porous structure and large surface area, MOFs can realize the spatial separation of catalytic sites and benefit the transport of molecules, resulting in enhanced activity. Similar to homogenous catalysts, MOFs is structurally tailorable with atomic precision, meanwhile MOFs are readily recyclable from the reaction system. By combining the merits of both homogeneous and heterogeneous catalysts, MOFs present many unique features superior to traditional inorganic or organic materials. Particularly, MOFs integrate metal nodes and organic linkers in periodic structures, providing an ideal model for the accurate understanding of structure-property relationship. In view of these, MOF-based catalysis has been widely investigated in various catalytic applications including thermocatalysis, photocatalysis and electrocatalysis, and has witnessed enormous success within a relatively short period of development [1–6].

In this comment, the fundamentals on the design of MOF-based catalysts along with the uniqueness of MOFs are briefly introduced. After that, the limitations on future development of MOF catalysis are critically evaluated. Finally, our personal views on the promising niches of MOFs that are unlikely replaced by other catalysts are further discussed.

2. Fundamentals on the design of MOFs for catalysis

Catalysis is one of the earliest and most intensively studied

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applications of MOFs. In 1994, Fujita and coworkers [7] employed a Cd-based MOF for Lewis acid catalysis, illustrating a proof of concept of MOF catalysis. Since then, MOF catalysis begins its glorious journey.

2.1. Classical catalytic site within MOFs

Generally, there are three parts in MOFs that can be functionalized as catalytic sites, namely, metal nodes, organic linkers and pore space (Fig. 1).

On metal nodes, the coordination unsaturated sites (CUSs) existed in pristine MOFs or created by defect engineering can be employed as Lewis acid sites [8,9]. Diverse organic functional groups and metal-complex units have been linked to organic units, serving as catalytic sties [10–12]. Moreover, the metal nodes and organic linkers can also be functionalized by grafting external catalytic sites, further extending their functions [13–15]. More importantly, MOFs can serve as porous matrices to incorporate and stabilize diverse guest catalytic species such as metal complexes, inorganic nanoparticles and enzymes, largely extending the origin of catalytic sites [16,17]. In addition, MOFs are also promising precursors to obtain porous carbons, nanostructured metal-based compounds and related composites *via* chemical transformation [18,19]. Many structural advantages of MOFs, such as high porosity and uniform elemental distribution, are largely preserved during the transformation, enabling the MOF derivatives to outperform conventional catalyst counterparts.

2.2. Uniqueness of MOFs for catalysis

The multiple sources of active sites in MOFs as indicated above, together with unique structural features, once being fully exploited and integrated, are able to afford fantastic opportunities in heterogeneous catalysis.

2.2.1. Inhibit deactivation of catalytic sites

Molecular-based catalytic sites immobilized in the porous skeletons of MOFs can be isolated and stabilized as active monomers, perfectly bypassing deactivation induced by molecular aggregation (Fig. 2(a)) [20]. Similarly, it is also feasible for MOFs to introduce multifunctional active sites that are chemically incompatible, such as acid and base sites, and make them cooperate with each other [21].

2.2.2. Spatial location control of adjacent catalytic sites

The well-defined structure of MOFs facilitates the accurate control of adjacent active sites in terms of relative distance and orientation (Fig. 2(b)). This would achieve unusual cooperative effect, such as C–C coupling, that cannot be observed by the physical mixtures [22].

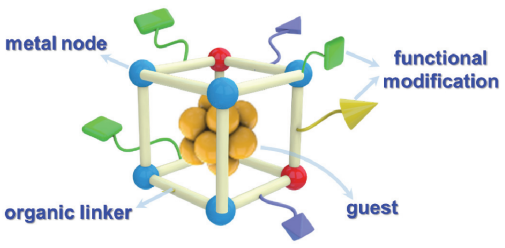

Fig. 1. The catalytic site origins inside a MOF.

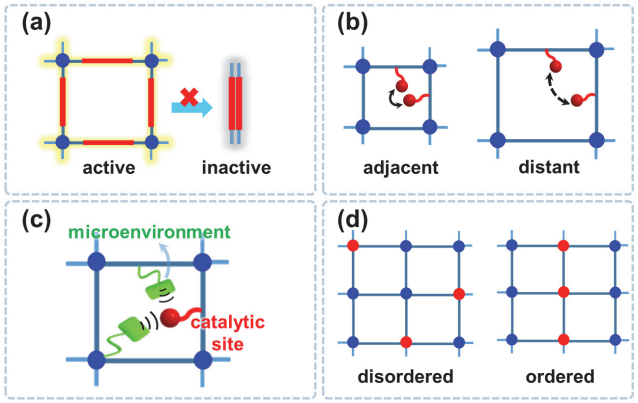

Fig. 2. Illustrations of the uniqueness of MOFs for catalysis. (a) Deactivation suppression of catalytic sites; (b) Spatial location control of adjacent catalytic sites; (c) Microenvironment modulation around catalytic sites; (d) Heterogeneity in order.

2.2.3. Microenvironment modulation (MEM)

Learned from enzymes, the surrounding microenvironments created by the amino acid residue around catalytic sites, in which secondary interactions preconcentrate substrates and facilitate selective conversion, play central roles in the catalytic processes. It is believed that MOFs would be the most ideal candidates to mimic the complex microenvironment in enzymes to some level [23]. By dangling diverse functional species onto MOF pore walls (mimicking binding pockets) that can regulate the electronic states of catalytic sites or interact with particular reactive group or "transition state" species for improved catalysis (Fig. 2(c)) [23–25]. In addition to the chemical microenvironments, the self-adaptive dynamic microenvironment and precisely tailored pore geometry created by MOFs are favorable to optimized selectivity [23,26].

2.2.4. Multivariate characteristic and heterogeneity in order

The introduction of diverse constituents within one material is intriguing for performance optimization, while the control over their order and arrangement remains a grand challenge. The emergency of multivariate MOFs achieves the introduction of multiple components in specific sequences, demonstrating their great superiorities on precise synthesis (Fig. 2(d)) [27,28].

2.2.5. Single crystal structure

Thanks to the crystalline structure of MOFs, the exact location of each atom, such as catalytic sites and surrounding microenvironment, can be precisely determined. Moreover, the host-guest (catalyst-substrate) interactions within MOFs and the structural evolution of active sites are possibly traced *via in situ* single-crystal structural determination, providing a valuable solution to understand the catalytic mechanism.

3. Limitations of MOFs for catalysis

Although tremendous progresses have been achieved in fundamental catalysis, we still have some way to go for pushing MOFs to commercial applications.

3.1. Stability

The coordination bonding and organic constituent of MOFs lead to their relatively weak chemical and thermal stability [29,30]. Moreover, for large-scale applications, the powders of catalysts are usually pressed into desired shapes. So far, very limited studies have been reported and indicate relatively inferior mechanical stability; the compression of MOFs over certain pressures may lead to the collapse of crystalline structure [31].

3.2. Regeneration

Heterogeneous catalysts usually become deactivated after long-term operation due to the adsorption of reactants or products, and regeneration is necessary. Unfortunately, the common calcination method for traditional inorganic catalysts is not suitable for MOFs due to their inferior thermal stability. Methods applicable to MOFs in practice are under development.

3.3. Costs and large-scale production

The synthesis of specific MOFs might require relatively expensive organic linkers and solvents or complex process. The question remains whether MOFs could be synthesized under more economic and efficient conditions while maintaining high yield and purity.

3.4. Mass transfer

The pore size of most MOFs reported to date still in the range of micropore (pore sizes of < 2 nm) or small mesopores close to 2 nm. The limited pore sizes will cause substantial resistance in terms of mass transfer and restrict catalytic efficiency. Mesoporous MOFs with large pore sizes or hierarchically porous MOFs are highly desired.

4. Where to go

MOFs are undoubtedly a class of ideal materials in fundamental catalysis, due to their atomically precise structure and tailorability as well as high surface area and compatibility. For future application in industry, MOF catalysis might be less likely to follow the route of traditional catalysts. More efforts would be directed on investigating killer application scenarios where MOFs are irreplaceable.

4.1. High value added reactions

The reactions affording high value added products would be promising to compensate the potential weakness of MOF catalysts in cost and stability. Due to the structural superiorities of MOFs, it is possible to afford fine chemical products with high chemo-, stereo- and regioselectivity.

4.2. Enzyme-mimicking catalysis

MOFs are very promising candidates to construct enzyme-like catalytic pockets in terms of both catalytic sites and modulated biomimetic microenvironments. This make it possible for MOF-based catalysts to achieve challenging catalytic processes in efficient and selective way under mild conditions like enzymes, offering unprecedented opportunities for large-scale applications.

4.3. External field-assisted MOF catalysis

The external field (light, electric and magnetic field, etc.) assisted catalysis is also a promising way to overcome the high reaction energy barriers (e.g. high temperature and pressure) and pave a new way to bypass harsh reaction conditions.

4.4. Unveiling the key elements in catalyst design

The infinite advantages on structural and component tunability of MOFs make them a powerful platform to understand the key elements in catalyst structures for optimized catalysis. In this regard, MOFs indeed play a role of “coaches” rather than “athletes”, providing customized solutions to guide the design of non-MOF-based catalysts toward industrial application, and the related limitations above are no longer a problem.

In the past 30 years, tremendous progress has been achieved in MOF catalysis, and the blueprint of development is better identified. The unrivalled superiority of MOFs in fundamental research of catalysis has been well recognized and acknowledged. With sustained research efforts, MOFs will also make reasonable contributions in a certain ways toward industrial catalysis. We have good grounds to believe that MOF catalysis would possess a bright future.

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Graphical Abstract

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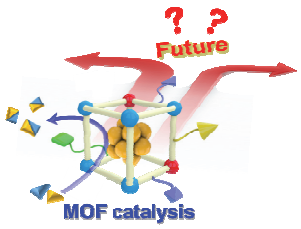

This comment introduces the fundamentals on the design of MOF-based catalysts along with the specific advantages of MOFs for catalysis. Moreover, the potential limitations and further prospects on MOF catalysis are briefly discussed.

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金属有机框架材料在催化领域的研究现状与展望

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摘要: 金属有机骨架材料(MOF)又称多孔配位聚合物(PCP), 是一类由金属团簇和有机配体通过配位作用形成的新型晶态多孔材料. 近30年, MOF材料在催化领域受到了广泛的关注和研究. MOF的多孔结构和高比表面积可以实现催化位点的空间分离并促进物质传输, 从而提高催化活性. MOF可以像均相催化剂一样在原子精度进行灵活剪裁和调控, 同时具有非均相催化剂易分离回收的优势. 通过结合均相和非均相催化剂的优点, MOF表现出了诸多优于传统催化材料的独特性质. 本文首先简要介绍了MOF基催化材料设计的基本原理和MOF应用于催化的独特性, 其次对MOF在催化中面临的瓶颈和局限进行了论述, 最后指出了MOF在未来催化领域中潜在的独特应用前景.

MOF材料中金属节点、有机配体和孔空间都可以进行灵活功能化, 从而赋予催化活性. 金属节点上的不饱和配位点可作为路易斯酸催化中心. 配体可以通过修饰不同功能基团从而赋予催化活性. 此外, 金属节点和有机配体还可以通过接枝外来催化位点进行功能化. 更重要的是, MOF孔空间可以限域客体活性单元, 极大扩展了活性位的来源. MOF还可以作为前驱体通过化学转化获得多孔碳、金属化合物及其复合材料. MOF的高孔隙率、均匀掺杂等特性可以很好地继承到MOF衍生材料中, 使其表现出优异的催化性能.

MOF既有广泛的活性位来源, 同时表现出独特的结构和成分优势, 为催化的发展带来了新的重要机遇. 首先, MOF可以实现催化位点空间分离, 有效抑制其聚集失活, 同时可以稳定均相体系中不兼容的活性位点, 实现多位点协同催化. 其次, MOF结构的明确性可以精准控制相邻活性位的空间位置, 从而实现调控催化行为. 第三, MOF孔壁上可以悬挂不同功能基团, 实现催化中心微环境调控, 显著优化催化性能. 此外, 多变量MOF实现了在MOF中同时引入多种组分并精准控制

其空间序列, 进而有效改善催化效果. MOF的单晶结构还可以精准的确定催化位点和微环境组分中每个原子的位置, 为理解催化机制提供了新的研究手段.

虽然MOF在催化领域已经取得了极大进展, 但其化学稳定性、热稳定性和机械稳定性往往相对较差, 制约了其大规模应用. 此外, 多相催化剂在长期运行过程中通常面临失活问题, 因而需要再生处理. 但是MOF热稳定性相对较差, 传统常用的煅烧方法不再适用于MOF, 亟待开发适用于MOF的再生方法. 另外, MOF合成用到的有机配体和溶剂成本较高, 合成过程相对较为复杂, 经济性上面临较大挑战. 此外, 多数MOF的孔径相对较小, 传质阻力较大, 限制了催化效率.

由于上述限制的存在, 在未来的工业应用中MOF催化剂的出路是寻找其在催化领域的独特应用场景. 例如催化高附加值反应, 当产品附加值足够高时, 才有望弥补MOF催化剂在成本和稳定性方面的不足. 此外, MOF是构建类酶催化材料的理想选择. 因而MOF基催化剂有望像酶一样在温和条件下高效、高选择性催化挑战性反应, 为其大规模应用提供了重要机遇. 而外场(光、电、磁等)辅助催化也可以克服高的反应能垒, 有效降低反应条件的苛刻性, 为MOF的应用推广创造了机会. 在催化机制研究方面, MOF在探究催化剂结构中关键要素以及优化催化性能方面具有显著优势, 基于MOF获得的催化关键信息, 可以进一步指导非MOF体系下催化剂的设计和工业应用.

关键词: 金属有机框架材料; 多相催化; 催化位点设计; 微环境调控; 催化材料

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