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Recent progresses in the size and structure control of MOF supported noble metal catalysts

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ABSTRACT

The preparation, characterization and application of metal organic framework (MOF) supported noble metal catalysts have drawn a great interest with the rapid progresses in the syntheses of MOFs and MOF based composites. There are several principal objectives for the investigation of MOF supported catalysts, including (1) the designable frameworks provide us a very clear model for the fundamental catalytic studies; (2) the extremely large surface area and the extremely high porosity of MOFs are always attractive for the catalytic applications; (3) the designable or the controllable porous structure with uniform pore size is excellent for the preparation of designable catalyst, a dream of chemists and chemical engineers worldwide; (4) the MOFs can be easily modified by various functional groups; (5) MOF based composites (with graphene and other materials) can be easily fabricated; (6) the needs for novel catalysts keep growing; (7) the member of the MOF family increases remarkably recently with the improvement of thermal and chemical stability of MOFs; (8) the hybrid of noble metal catalysts and MOFs is leading to many unusual catalytic properties. In this perspective, we summarize the recent advances in the preparation and application of MOF supported noble metal catalysts. To prepare this kind of new catalysts, two general methods have been reported: the precursor way and the metal nanoparticle way. The former is based on metal ions or metal precursors like inorganic salt (nitrate or chloride) or metallorganic compound. The metal ions or metal precursors have to be loaded into the MOF framework *via* chemical vapor infiltration, solution impregnation and incipient wetness infiltration or to be pre-incorporated on the organic linkers before the synthesis of MOF. The second way is based on the pre-synthesized metal nanoparticles. To do so, the pre-synthesized metal nanoparticles have to be directly involved in the synthesis of MOFs from the beginning. The characteristics of two ways have been discussed. Because of the unique properties and the structure of MOFs, the loading of metal or metal ion with the assistance of organic solvent is very helpful for the confinement of nanoparticles within the cavities of MOF frameworks or for control of size and location of nanoparticles. The structure control of catalyst together with size and location control still remains a significant challenge.

1. Introduction

Catalyst has been extensively applied in various processing industries. With the depleting petroleum resource and with the increasing concerns on the renewable energy, environmental protection and others, catalyst will play even more important role. The development of new catalysts has therefore become a hot topic. However, the catalyst preparation in a controllable way remains a big challenge worldwide. In this regard, metal organic frameworks (MOFs), combined with metal ions and organic ligands, can be precisely designed and have attracted a great attention for potential applications as catalysts or supporting materials of catalysts,[1–12] with their designable highly porous structure and large internal surface areas. A significantly increasing publication can be found in the literature with topics of MOF and catalyst. These publications have received an unusual high citation. This means the use of MOFs for catalysts have drawn a lot of interests. According to the reported works [2–16], the advantages of MOFs as the catalyst support include: (1) the much larger surface area (compared to zeolites and other conventional catalyst supports) is the most interesting property of MOFs. This would lead to unusual chemistry if this large surface could be fully covered by active sites;

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(2) the extremely high porosity is very useful to expose the active sites completely to reactant(s) and to enhance the reactivity remarkably; (3) the designable or the controllable porous structure with uniform pore size is excellent for the preparation of designable catalyst, a dream of chemists and chemical engineers worldwide; (4) the MOFs can be easily modified by various functional groups; (5) MOF based composites (with graphene and other materials) can be easily fabricated [13,14]; (6) MOFs can be used as the catalyst precursors to improve the selectivity or yield of objective products or to enhance the catalytic activity [15,16]. However, because MOFs (also called porous coordination polymers (PCPs) or coordination polymer networks (CPNs)) are formed by connection of metal ions and multi-dentate organic building blocks, the unique structural characteristics lead to some drawbacks that may limit the use of MOFs as the catalyst (1) the thermal stability is not impressed and needs to be enhanced; (2) the chemical stability is not good. Some MOFs are sensitive to water or to organic solvent or to acid or to base; (3) the lack intrinsically of defects or catalytically active functional group or active sites leads a poor activity. To solve these problems, new MOFs with high thermal and chemical stability are being synthesized [17]. Functionalization and loading of nano metallic particles (with MOFs as the catalyst supporting materials) are creating a significantly high content of active sites. One can find the summary of these promising progresses in several review articles published in the literature [2–7]. In this perspective, we attempt to summarize the recent advances in the preparation of MOF supported catalysts. The discussions are limited with supported noble metal catalysts but the methods can be helpful for other catalysts. Attentions have been paid to the size and structure control of nano particles loaded or formed, which are special requirements for the catalytic applications. Future development will be discussed too at the end of this article.

2. Preparation methods in general

To prepare the MOF supported catalysts, two ways have been employed in reported works. The first way is based on metal ions or metal precursors like inorganic salt (like nitrate or chloride) or metallorganic compound (the precursor way). To do so, metal ions or metal precursors have to be loaded into the MOF framework *via* chemical vapor infiltration [4–7], solution impregnation [4–7] and incipient wetness infiltration [4–7] or to be pre-incorporated on the organic linkers before the synthesis of MOF (*in situ* metal precursor incorporation) [18,19]. Inorganic salt is cheaper than metallorganic compound but sometimes have some problems to get it well dispersed within the framework. Organic solvent is mostly used to assist with the loading of metal precursor(s). After the loading of metal precursor(s), the subsequent decomposition or reduction of metal precursor(s) has to be conducted to convert metal ions into metal nanoparticles. The second way is based on the pre-synthesized metal nanoparticles (the metal nanoparticle way) [20–22]. To do so, the pre-synthesized metal nanoparticles have to be directly involved in the synthesis of MOFs from the beginning. Since surfactant or protecting agent or stabilizer is normally required with the pre-synthesized metal nanoparticles [21,22], it may induce a complex chemistry with the formed catalysts or composites [21].

Fig. 1 presents a schematically representative of the precursor way (*ex situ* metal precursor incorporation [18]). For the comparison purpose, *in situ* metal precursor incorporation is illustrated in Fig. 2. The metal nanoparticle way is almost the same with *in situ* metal precursor incorporation. One just needs to use pre-synthesized metal nanoparticles instead metal ions.

Based on the preparation conditions, different distributions of metal nanoparticles have been observed. Fig. 1 shows three typical cases. In case A, nanoparticles are preferentially deposited at the external surface of the MOF crystal with particle size larger than the accessible pore dimension. This case normally occurs when the metal precursor exceeds the size of the available pore aperture. In case B, nanoparticles can be distributed throughout the bulk of the MOF. However, they are still larger in size than the characteristic pore dimension. In this case, especially, the formation of metal nanoparticles can be accompanied by a partial or full decomposition of the framework. The supposed mechanism of degradation

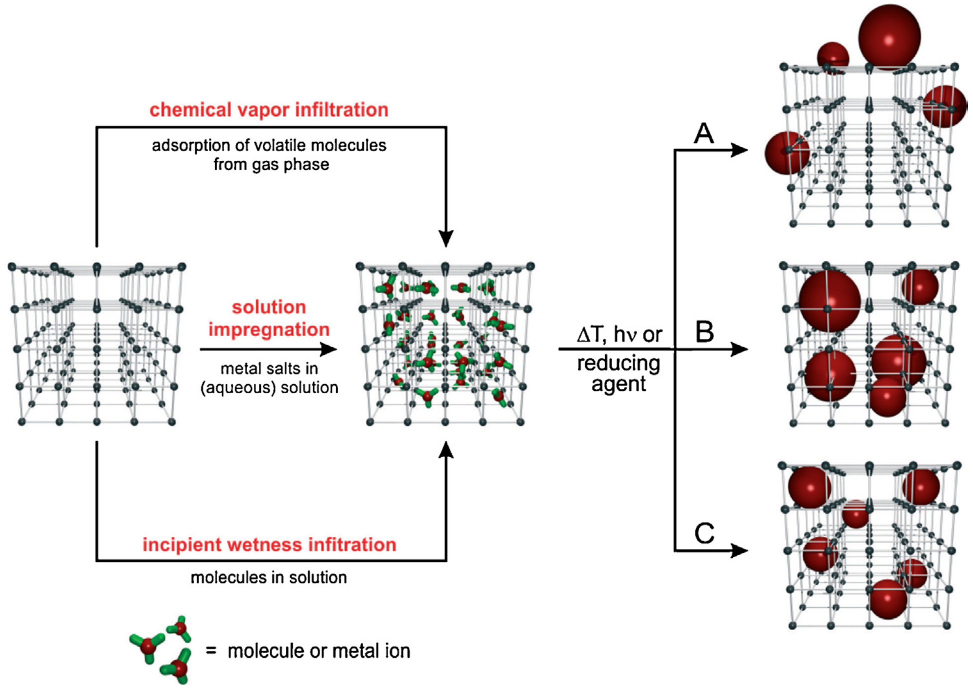

Fig. 1. Schematic representative of the precursor way with three different cases of distribution of metal nanoparticles. Reproduced with permission from Ref. [4] Copyright 2015, RSC.