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Progress in the Preparation and Catalytic Performance Research of Encapsulated Polyoxometalate-based POMs@MOFs Materials

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Abstract: *The composition, structure and size of the polyoxometalates are easy to be controlled in their synthetic process, and they have good electronic storage and redox capabilities. They are favored by chemists due to their broad application prospects in the development of clean, green and environmentally efficient catalysts. Encapsulating polyoxometalates into metal-organic framework materials can solve some problems such as deactivation due to agglomeration during the catalytic reaction process, difficulty in catalysts recycling in homogeneous system, and their low specific surface area. In this paper, the preparation methods of polyoxometalate-based metal-organic framework materials, namely, in-situ synthesis, immersion synthesis and mechanical grinding synthesis, are summarized, and the advantages and disadvantages of each method are discussed respectively. We further summarized the research progress of polyoxometalate-based metal-organic framework materials in the field of catalysis, and looked forward to their development trends in future.*

Keywords: *Polyoxometalate-based metal-organic framework materials, Preparation, Catalytic properties*

1. Introduction

Polyoxometalates (POMs) are a kind of transition metal oxygen clusters with nano size and clear structure, showing high thermal stability and acid-base stability[1-4]. As an important research field in inorganic chemistry, POMs chemistry has a history of more than 200 years and its research object is the polyoxometalate compounds containing Mo, W, V, Nb, Ta and other elements. In the catalytic field, POMs have achieved large-scale industrial applications as green catalysts for several important industrial processes due to their excellent electronic storage and redox capabilities.[5-7]. In recent years, great progress has been made in the research of photo/electric driven water decomposition to produce H_2 or O_2[8-10], petroleum desulfurization[11,12], chemical warfare agent decomposition/degradation[13-15], and the preparation of high value-added chemicals catalyzed by POMs-based materials[16-20].

POMs show good solubility in homogeneous catalytic reaction systems, which result in that they are difficult to be recycled. While in heterogeneous systems, POMs often have low specific surface area and poor stability, which affect their catalytic activity. All the above problems greatly limit their industrial application. POMs immobilization provides an effective way to realize large-scale industrial application of such catalyst materials. Metal-organic frameworks (MOFs) materials have been extensively studied by chemists since Yaghi's group first reported them in 1999[21]. As a kind of crystalline porous materials with clear structure, MOFs show broad application prospects in heterogeneous catalysis, acting as the support of homogeneous catalysts, gas storage, molecular separation and many other fields[22-24]. When MOFs are used as the catalyst support, they can selectively combine different functional guest molecules to optimize the structure and improve their performance. Recently, introducing POMs as active guest molecules into MOFs to construct POMs@MOFs materials have become an important research direction of POMs-based catalysts.

2. Preparation of POMs@MOFs Materials

In recent years, the synthesis methods of POMs@MOFs materials include in-situ synthesis, immersion synthesis and mechanical grinding synthesis. These three synthesis methods have their own advantages and limitations, which are described in detail in the following categories.

2.1. In-Situ Synthesis Method

In-situ synthesis, also known as "shipbuilding in bottle", refers to adding POMs or the initial raw materials for synthesizing POMs in the preparation process of MOFs. Then, POMs are encapsulated into the pore structure of MOFs in one step by adjusting the reaction conditions, such as the pH value of the solution, the amount of POMs added, and the selection of appropriate modifiers. This method has the advantage of simple operation and is suitable for the preparation of POMs encapsulated by MOFs with small window size and large cavity volume. However, the disadvantage is that the synthesis of some MOFs requires higher temperature, and even some organic solvents are used. These harsh conditions required in their synthetic process make it difficult for some POMs to maintain structural stability. Moreover, the load of the prepared material POMs is often uneven. All the above factors result in that the in-situ synthesis method is only suitable for preparing the POMs@MOFs materials with stable structures[25-33,35,36,39,42].

2.2. Immersion Synthesis Method

The impregnation synthesis method refers to dissolve the POMs in deionized water or organic solvent in advance to prepare a solution, then add a certain amount of MOFs as a support, stir at a certain temperature and then stand it still. During the immersion process, the POMs are loaded into the channels of MOFs via electrostatic adsorption of MOFs and intermolecular diffusion. The advantage of this method is that it avoids the destruction of POMs structure by the harsh conditions required for MOFs synthesis in the in-situ synthesis method. The dispersion of POMs in the POMs@MOFs materials is relatively uniform. The disadvantage of this method is that MOFs materials with appropriate window and channel structures need to be selected according to the size of POMs. If the window of MOFs is too small and the size of POMs is too large, POMs can not enter the cavity of MOFs. If the window of MOFs is too large, POMs are easy to lose and are difficult to disperse stably[34, 37, 38, 43].

2.3. Mechanical Grinding Synthesis Method

The mechanical grinding synthesis method refers to convert the mechanical energy of mechanical grinding into chemical energy without solvent (pure solid phase) or with the aid of a small amount of solvent, so that the solid phase chemical reaction can occur quickly. It has the advantages of green, energy saving, simple and efficient. The disadvantage is that the reaction activation energy is required to be not too high. The yield and crystallinity of the product synthesized by this method are not so satisfactory, and it is difficult to explain the reaction mechanism at the micro molecular level[40,41].

3. Catalytic Performance of POMs@MOFs Materials

The POMs@MOFs material not only has a beautiful topological structure, but also has the rich dual functions of POMs and MOFs. It also has the characteristics of open channels, large specific surface area and high dispersion rate. The catalytic properties of the POMs@MOFs materials are classified and summarized and briefly introduced as follows.

3.1. Photocatalytic Performance

Lin et al. used POMs@MOFs materials formed by Wells Dawson type polyanion $[P_2W_{18}O_{62}]^{6-}$ and UiO-MOFs as photocatalysts for water photolysis. This type of material catalyst is the first example of hydrogen production from water decomposition driven by visible light [25]. In 2017, He et al. used the synthesized $\{(PW_9)_2M_7\}$@TTF-F-COFs (M = Co, Ni) material as the electroreduction catalyst for oxygen production, showing comparable catalytic activity and higher stability than Pt/C electrode in neutral medium [26]. In 2018, Zhang et al. used encapsulation materials prepared from Wells Dawson type polyanions $[P_2W_{15}V_3O_{62}]^{9-}$, $[P_2W_{17}(NiOH_2)O_{61}]^{8-}$ and $[P_2W_{17}(CoOH_2)O_{61}]^{8-}$ with MIL-101(Cr) to catalyze photo-driven water decomposition reaction, with hydrogen production efficiency up to 25578 $\mu mol\ h^{-1}\ g^{-1}$[27].

In 2018, Nadeem et al. used $[Co^{II}Co^{III}W_{11}O_{39}(H_2O)]$@MIL-100(Fe) and $[Co_4(PW_9O_{34})_2(H_2O)_2]$@MIL-100(Fe) materials as water oxidation catalysts, which have better photo-driven catalytic oxygen production performance compared with pure POMs catalysts under visible light irradiation[28].

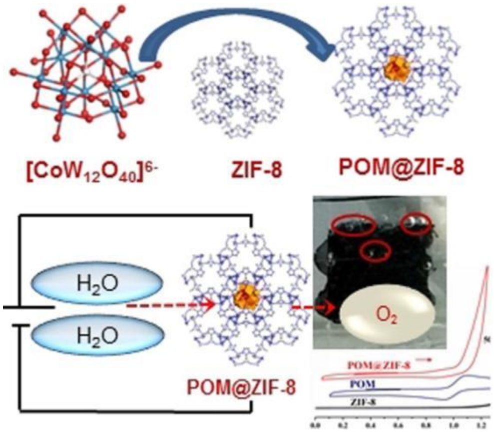

Figure 1: Schematic representation for the synthesis of encapsulated $[CoW_{12}O_{40}]$@ZIF-8 and electrocatalytic water oxidation. Reprinted with permission from ref. [29]. Copyright 2018 John Wiley & Sons Ltd.

As shown in Figure 1, Das et al. used $[CoW_{12}O_{40}]$@ZIF-8 as an efficient electrodecomposition water oxidation catalyst to achieve the electrocatalytic oxygen generation by saturated POMs. The turnover frequency (TOF) of the catalyst under neutral pH condition is 10.8mol O_2 (mol Co)$^{-1}$s^{-1}, and the catalyst show highly efficient electrocatalytic water oxidation activity, and there is no significant decrease in activity after 1000 cycles of use [29].

The porous Co_3O_4/$CoMoO_4$ nano cage obtained from calcination of the $H_3PMo_{12}O_{40}$@ZIF-67 material is used as a catalyst by Wang et al., and its electrodecomposition water oxidation activity under alkaline conditions has been significantly improved. Its performance is comparable to that of commercial precious metal IrO_2, and it is an excellent electrodecomposition water oxidation catalyst derived from POMs based MOFs materials [30].

3.2. Thermal Catalytic Performance

The POMs@MOFs materials used in the field of thermal catalytic reactions are mainly reflected in the acid-base catalytic performance and oxidation catalytic performance.

3.2.1. Acid-base Catalytic Performance

Liu et al. obtained tetragonal and octahedral crystals respectively via the regulation of POMs@MOFs materials (NENU-3). They have enhanced the crystal plane catalytic active sites and adsorption properties for reaction substrates in the process of catalytic preparation of biodiesel, which proves that $H_3PW_{12}O_{40}$ exposes much more on the {100} crystal plane (tetragonal crystal) than on the {111} crystal plane (octahedral crystal), greatly improving its Brønst acid catalytic activity. The problem that the reaction substrate molecule is too large to fully contact with the active site of the catalyst has been solved. The conversion of long-chain fatty acids (C12-C22) in the process of preparing biodiesel exceeds 90%[31].

In 2018, the $H_3PW_{12}O_{40}$@ZIF-8 material was applied to the acid catalyzed esterification of benzoic anhydride and cinnamyl alcohol by Yadav et al.[32]. In 2019, Xie et al. used AILs/POMs/UiO-66-2COOH materials (POMs = $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) for transesterification of acid vegetable oil to prepare biodiesel[33]. Shul et al. developed an acid-base dual function heterogeneous catalyst $H_3PW_{12}O_{40}$@ZIF-8 with core shell structure. Then, it was used as an environment-friendly heterogeneous catalyst for transesterification of rapeseed oil and methanol to produce high-quality biodiesel[34].

3.2.2. Oxidation Catalytic Performance

A series of $H_3PM_{12}O_{40}$@rht-MOF-1 (M = Mo, Si, W) encapsulating materials (HLJU1-3) were used as adsorption materials and catalysts by Yan et al. The porous structure of the material improved the absorption efficiency of rhodamine B (RhB) and crystal violet dyes. The materials were further used as catalysts in the reaction of selective oxidation of benzyl alkanes with TBHP as oxidant to corresponding ketones with high conversion and selectivity[35].

In 2016, Fazaeli et al. used $H_3PW_{12}O_{40}$@ZIF-8 to catalyze the selective oxidation of sulfide. By regulating the solvent type and the amount of H_2O_2, sulfoxide and sulfone can be prepared by catalytic oxidation of sulfide, and the activity of the catalyst has not been significantly reduced after three times of recycling[36].

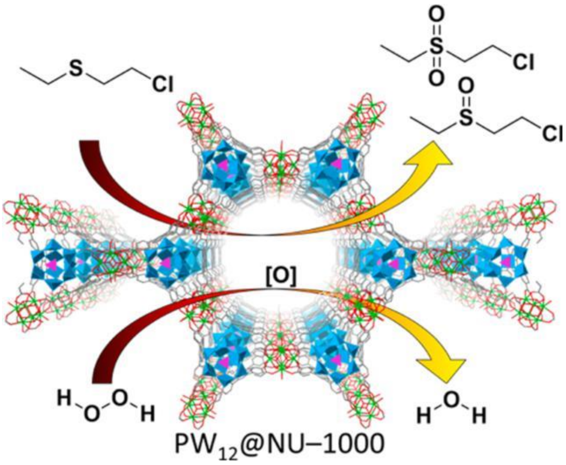

Figure 2: The oxidative decontamination of CEES catalyzed by PW_{12}@NU-1000. Reprinted with permission from ref. [37]. Copyright 2017 American Chemical Society.

As shown in Figure 2, the PW_{12}@NU-1000 material was used as a catalyst for the oxidative degradation of 2-chloroethyl ethyl sulfide (CEES, mustard gas analogue) with H_2O_2 as oxidant by Farha et al. When $H_3PW_{12}O_{40}$ was used as homogeneous catalyst alone, the reaction time is very long (about 90 min), but the partial oxidation product 2-chloroethyl ethyl sulfoxide (CEESO) was the only product. When NU-1000 was used as catalyst alone, the product was mainly 2-chloroethyl sulfone peroxide ($CEESO_2$). If the amount of H_2O_2 was increased, $CEESO_2$ became the only product. When using PW_{12}@NU-1000 as a heterogeneous catalyst, CEES can be completely converted in a very short time (about 20 min), and CEESO is the main product. The above experimental results fully proved the synergistic catalysis of POMs and MOFs in the PW_{12}@NU-1000 materials[37].

In 2018, Farha et al. further studied the influence of PW_{12}@NU-1000 materials on their catalytic performance under different activation conditions. It is found that PW_{12}@NU-1000-$scCO_2$ shows higher catalytic activity and selectivity in the selective oxidative degradation reaction of CEES compared with PW_{12}@NU-1000-120°C[38].

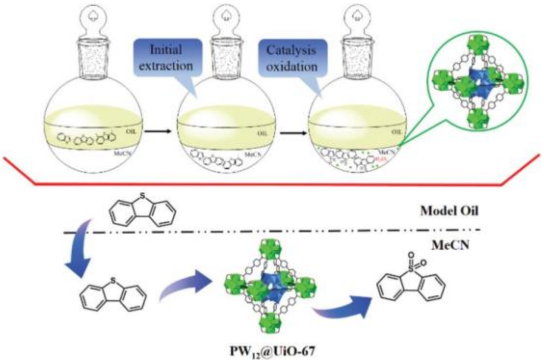

Figure 3: Schematic representation of ODS using PW_{12}@UiO-67 as catalyst. Reprinted with permission from ref. [39]. Copyright 2018 Royal Society of Chemistry.

In 2018, Li et al. prepared PW_{12}@UiO-67 materials and they were further used as catalysts for deep oxidative desulfurization (ODS) of petroleum. In the simulated petroleum with sulfur content of 1000 ppm, the removal rate of dibenzothiophene can reach 99.5% within 1 hour, and the reaction activity of the catalyst has not been significantly reduced after 8 cycles of experiments (Figure 3)[39].

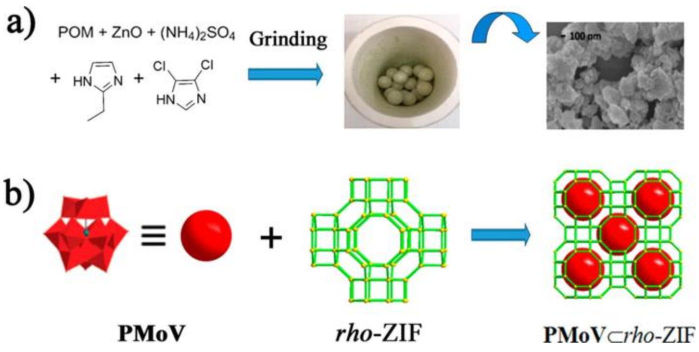

Figure 4: Schematic representation for the mechanochemical synthesis of encapsulated PMoV@rho-ZIF.Reprinted with permission from ref. [40]. Copyright 2017 American Chemical Society.

As shown in Figure 4, the PMoV@rho-ZIF (PMoV = $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$) materials were used as catalysts for highly selective catalytic oxidation of sulfides by Hu et al. The results showed that the selectivity of sulfoxide was low when PMoV was used as homogeneous catalyst alone, and the catalytic activity was poor when rho ZIF was used as catalyst alone. As the synergistic heterogeneous catalyst of POMs and MOFs, the PMoV@rho-ZIF materials can solve the above problems well, maintaining the high activity and selectivity of the catalyst. The catalyst can be recycled for at least 4 times without significant decrease in activity. This research is of great significance for developing more active and selective POMs based MOFs nano catalysts[40].

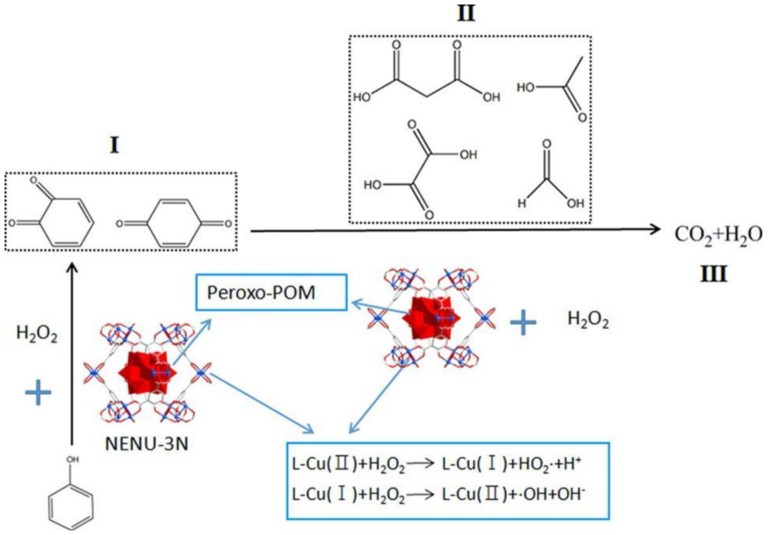

Figure 5: Schematic representation of the catalytic degradation process of phenol. Reprinted with permission from ref. [41]. Copyright 2018 John Wiley & Sons Ltd.

As shown in Figure 5, Liu et al. synthesized a microcrystalline material $H_3PW_{12}O_{40}$@HKUST (NENU-3N) and further used it to catalyze the degradation of phenol. Under the synergistic catalysis of POMs and MOFs, 97% of the conversion rate and 88% of the mineralization rate were achieved. In addition, comparative experiments show that the size reduction of NENU-3N catalyst can improve its catalytic performance, and the catalyst has high stability, which is easy to be recovered and recycled for 5 times without loss of catalytic activity[41].

In 2019, Liu et al. used the material $[V_7^{IV}V_9^{V}Cl]$@Ni-MOFs with ultra-thin nano sheet (about 5 nm) (NENU-MV-1a) as the catalyst for olefin epoxidation reaction with air as oxidant and isobutyraldehyde as sacrificial agent. The catalyst showed better catalytic performance (conversion rate 95%) than the block crystal (conversion rate 35%). The relationship between catalyst structure and performance was also discussed, and the mechanism of POMs and MOFs synergistic catalytic reaction was proposed. This research is of great significance for developing MOFs nano catalysts with more active and selective mixed valence metal oxygen clusters[42].

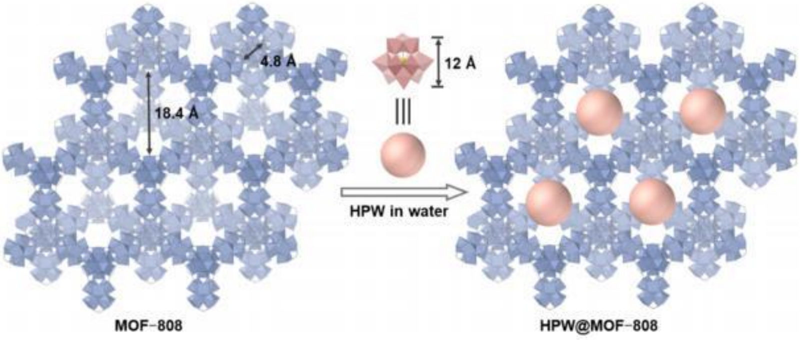

Figure 6: Synthesis of HPW@MOF-808 by a direct impregnation method. Reprinted with permission from ref. [43]. Copyright 2021 American Chemical Society.

In 2021, Hu et al. prepared a HPW@MOF-808 (HPW = $H_3PW_{12}O_{40}$) material, and then applied it to the preparation of levulinic acid γ-double acid catalytic system of pentolactone. The catalyst can be recycled for at least 5 times while maintaining its structural stability without significantly reducing its catalytic activity (Figure 6)[43].

4. Conclusions and Prospects

In recent years, POMs chemists have successfully encapsulated POMs into porous MOFs materials by in-situ synthesis, immersion synthesis and mechanical grinding synthesis, and prepared a series of POMs@MOFs materials. In this kind of materials, POMs are evenly distributed in MOFs materials as active guest molecules, which not only improve the stability of MOFs materials, but also endow them with excellent performance, and have broad application prospects in the fields of photo/electric catalytic water decomposition to prepare clean energy, preparation of biodiesel, fuel desulfurization, chemical warfare agent decomposition, etc. Among the currently prepared POMs@MOFs materials, POMs are mainly saturated Keggin type structure, which is mainly due to their high stability, while the research on the loading of other types of POMs including vacancy in frame materials is obviously insufficient. It is expected that the synthesis and catalytic application of POMs based MOFs materials will continue to make new progress.

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