



# Hierarchically micro- and mesoporous metal–organic framework-supported alloy nanocrystals as bifunctional catalysts: Toward cooperative catalysis



Yuan-Biao Huang, Min Shen, Xusheng Wang, Peng-Chao Shi, Hongfang Li, Rong Cao\*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, 155, Yangqiao Road West, Fuzhou 350002, China

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## ABSTRACT

Metal–organic frameworks (MOFs) in most metal nanoparticles (NPs)/MOFs composite catalysis systems serve only as supports to protect NPs from agglomeration. Up to now, most MOFs have still been largely restricted to the microporous regime, which limits the diffusion and mass transfer of substrates and products. Here, we use hierarchically micro- and mesoporous MOFs for the first time to immobilize highly dispersed PtPd bimetallic alloy nanoparticles (NPs). The obtained composites as bifunctional catalysts based on the combination of MOFs and alloy NPs show synergistic enhanced catalysis of oxidant-free dehydrogenation of alcohols. The mesopores facilitate diffusion and accessibility of substrates and products, while the micropores provide large pore volumes and high surface areas to create more active sites to enhance the catalytic activity.

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## 1. Introduction

The oxidation of alcohols to carbonyl compounds is an important organic transformation. Although homogeneous catalysts have been extensively studied as effective systems [1], they often suffer from drawbacks such as difficulties in expensive catalyst recovery and separation from the products. To circumvent these problems, heterogeneous catalysts have been developed because of their sustainability and economical acceptability. In addition, most of the oxidation of alcohols needs oxygen to produce carbonyl compounds [2]. However, for the safety of the catalysis and atom efficiency, oxidant-free catalytic dehydrogenation of alcohols is a green way [3–14].

Metal nanoparticles (M NPs) generally show high catalytic activity, due to their high surface-area-to-volume ratios [15]. Especially, bimetallic alloy NPs usually exhibit synergistic enhancement catalysis because of their interplay of electronic and lattice effects [16,17]. However, those highly unstable metal NPs should be dispersed on suitable supports and/or stabilizers to prevent agglomeration leading to loss of catalytic activity [18]. Moreover, the cooperative catalysis of M NPs with supports is generally needed to realize the target of oxidant-free dehydrogenation of alcohols [3–6].

\* Corresponding author.

E-mail address: [rcao@fjirsm.ac.cn](mailto:rcao@fjirsm.ac.cn) (R. Cao).

Metal–organic frameworks (MOFs), constructed from metal nodes with organic ligands, have emerged as a new class of porous materials to support metal NPs due to their high surface area, their fine-tunable pores/cages to confine NPs, and the presence of organic functional groups to stabilize NPs [19–22]. However, to date, using MOFs to immobilize bimetallic alloy NPs for heterogeneous catalysis has been rare because it is difficult to control the morphology and composition of alloy NPs [23–26]. In addition, MOFs in most of the reported MOFs–imbedded metal NPs catalyst systems serve only as supports to protect NPs from agglomeration [27–30]. Bifunctional catalysts based on the combination of MOFs and metal NPs for cooperative catalysis are less reported [31–34]. Moreover, most MOFs are still largely restricted to microporous regimes, which limit the diffusion and mass transfer of the substrates and products [27–30,35,36]. Fortunately, a few hierarchically micro- and mesoporous MOFs have recently been prepared using a supramolecular template strategy [37–45]. These hierarchical pore systems are advantageous in adsorption and catalysis, because they commonly facilitate diffusion and accessibility of guest molecules through the larger pores, while smaller pores provide large pore volumes and high surface areas. To the best of our knowledge, so far, there have been no reports of using hierarchically micro- and mesoporous MOFs as supports to wrap metal NPs [46].

In this work, we focus on the hierarchically micro- and mesoporous MOFs MIL-53(Al), denoted as MM-MIL-53(Al) (the formula of MIL-53(Al) is  $\text{Al}(\text{OH})[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$ ) [37–39]. The frameworks

of microporous MIL-53(Al) are built up by the interconnection of infinite trans chains of corner-sharing  $\text{AlO}_4(\text{OH})_2$  octahedra (Figs. S1, S2) [47], which may serve as acid–base active sites to enhance the oxidant-free dehydrogenation of alcohols [3–6,48,49]. Microporous MIL-53(Al) crystals form the walls of the mesoporous MM-MIL-53(Al) (Fig. 1). Herein, we choose MM-MIL-53(Al) to support PtPd alloy NPs as a bifunctional catalyst for synergistic catalysis of oxidant-free dehydrogenation of alcohols, which was enhanced by cooperation between MM-MIL-53(Al) and alloy NPs.

## 2. Experimental

### 2.1. Materials and instrumentation

All chemicals were obtained from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Miniflex 600 diffractometer using Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm). The morphologies of catalysts were studied using a FEIT 20 transmission electron microscope (TEM) working at 200 kV. The samples were prepared by placing a drop of product in ethanol onto a continuous carbon-coated copper TEM grid. Noble metal content was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Ultima 2 analyzer (Jobin Yvon). BET surface area measurements were performed on a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of  $10^{-9}$  Torr. GC-MS measurements were performed on a Varian 450-GC/240-MS.

### 2.2. Preparation of MM-MIL-53(Al)

MM-MIL-53(Al) was synthesized according to the literature [37,38]. A 1.0 g quantity of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.3 g of  $\text{H}_2\text{BDC}$  were dissolved in a mixed solvent of 13 mL DMF, 3.6 mL absolute  $\text{C}_2\text{H}_5\text{OH}$ , and 4.9 mL  $\text{H}_2\text{O}$ . After mixing, 3.34 g Pluronic F-127 was added under stirring. Then the mixture was stirred at room temperature for 2 h and transferred into a Teflon-lined steel autoclave to react at 130 °C for 48 h. The products were centrifuged and washed with deionized water and ethanol. Then a mixture of the products and ethanol was refluxed at 70 °C for 48 h to extract surfactant Pluronic F-127. Finally, the residual BDC was extracted by immersing the samples in DMF for 24 h and DMF was removed by heating it in an air oven at 150 °C for 12 h.

### 2.3. Preparation of MIL-53(Al)

MIL-53(Al) was synthesized according to the literature [47]. A 0.85 g quantity of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and 0.25 g  $\text{H}_2\text{BDC}$  were added

into a mixed solvent of 4 mL water and 11 mL DMF ( $\text{H}_2\text{BDC}$  = terephthalic acid, DMF = dimethylformamide) to prepare MIL-53(Al). After magnetic stirring at 25 °C, the mixture was transferred into a Teflon-lined steel autoclave and heated in an oven at 130 °C for 48 h. The product was centrifuged and washed with deionized water several times to remove the nitric acid formed during the synthesis. The unreacted BDC was extracted by immersing it in DMF for 24 h. Then the white powder was filtered from the DMF and dried in an air oven at 150 °C for 12 h.

### 2.4. Preparation of $\text{Pt}_m\text{Pd}_n/\text{MM-MIL-53(Al)}$

Typically, a mixture of potassium tetrachloroplatinate (20 mM, 1.0 mL, aqueous solution) and sodium tetrachloropalladate (20 mM, 1.0 mL, aqueous solution) at different ratios, sodium iodide (75 mg), and MM-MIL-53(Al) (150 mg) was added to 10 mL DMF. After being stirred for 12 h at room temperature, the mixture was heated at 130 °C for 5 h before it was cooled to room temperature. The resulting black products were collected by centrifugation, washed several times with ethanol, and dried at 80 °C under vacuum.  $\text{Pt}_{13}\text{Pd}_{12}/\text{MIL-53(Al)}$  was synthesized by a similar method except using MIL-53(Al).

### 2.5. Typical catalysis for the dehydrogenation of alcohols

Before a reaction,  $\text{Pt}_{16}\text{Pd}_{15}/\text{MM-MIL-53(Al)}$  was dried at 150 °C under vacuum for 12 h.  $\text{Pt}_{16}\text{Pd}_{15}/\text{MM-MIL-53(Al)}$  (30.8 mg, 0.5 mol% Pt) was added to a mixture of *o*-xylene (0.5 mL) and 2-octanol (0.130 g, 1 mmol) in a Schlenk tube under  $\text{N}_2$ . The mixture was stirred at 144 °C. After workup, the reaction mixtures were analyzed by GC-MS.

To study the catalysis of PtPd leaching during the reaction, after reaction the mixture was hot filtered under vacuum, and the liquid phase was analyzed by ICP-AES. For the recyclability experiment, the catalyst was recovered at the end of the catalytic reaction and washed with ethanol and acetone, respectively, followed by drying at 150 °C under vacuum. The dried catalyst was then reused in the next run.

### 2.6. Adsorption of 2-hexanol and 2-hexanone by MM-MIL-53(Al) and MIL-53(Al)

A liquid-phase adsorption experiment was carried out at 298 K in 2 mL glass vials filled with MM-MIL-53(Al) or MIL-53(Al) (0.025 g) and a solution of *o*-xylene (1.2 mL), including 2-hexanol or 2-hexanone (0.60 mmol). Then the vials were agitated on a shaker for 48 h. The final *o*-xylene solution, after the solid adsorbents were removed, was analyzed by GC.

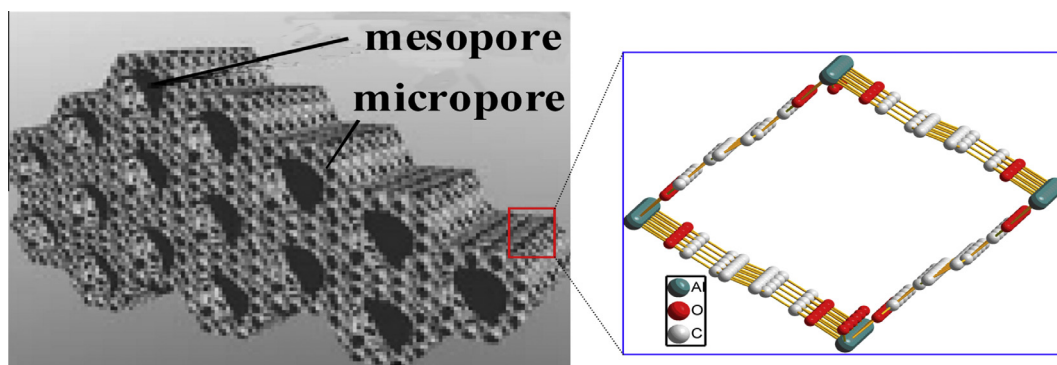


Fig. 1. The walls of hierarchically micro- and mesoporous MM-MIL-53(Al) were formed by microporous MIL-53(Al) crystals.

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