

Communication



# Synthesis of Stable Hierarchical MIL-101(Cr) with Enhanced Catalytic Activity in the Oxidation of Indene

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Received: 18 August 2018; Accepted: 11 September 2018; Published: 13 September 2018



**Abstract:** Nowadays, the controllable synthesis of stable hierarchical metal–organic frameworks (MOFs) is very important for practical applications, especially in catalysis. Herein, a well-known chromium–benzenedicarboxylate metal–organic framework, MIL-101(Cr), with a stable hierarchical structure, was produced by using phenylphosphonic acid (PPOA) as a modulator via the hydrothermal method. The presence of phenylphosphonic acid could create structural defects and generate larger mesopores. The synthesized hierarchical MIL-101(Cr) possesses relatively good porosity, and the larger mesopores had widths of 4–10 nm. The hierarchical MIL-101(Cr) showed significant improvement for catalytic activity in the oxidation of indene. Further, the presence of a hierarchical structure could largely enhance large dye molecule uptake properties by impregnating.

**Keywords:** MIL-101(Cr); phenylphosphonic acid; hierarchical; enhanced catalytic activity; large molecule uptake

## 1. Introduction

Metal–organic frameworks (MOFs) are a class of porous materials which consist of metal ions or their clusters interconnected by organic ligands [1,2]. Over the last decades, they have attracted much interest [3,4] and have been used in gas storage [5,6], separations [7,8], catalysis [9,10], heat transformation [11], drug delivery [12], etc. However, the narrow pores inside the MOF structure impose restrictions on their applications, such as large molecule adsorption and anchoring molecular catalysts. Thus, the stable hierarchical MOF possesses micro-mesopores that become a heating field due to the fast diffusion rate resulting from the mesopores and the more exposed coordination metal sites [13,14].

Many research groups have contributed to the preparation of hierarchical MOFs by developing various strategies for them. Dai et al. [15,16] reported a perturbation-assisted nanofusion method to prepare room-temperature synthesized MOFs, including Zn-MOF-74, IRMOF-3, Cu-BDC, and Cu-BTEC. Jiang et al. [17] demonstrated that monocarboxylic acid can be used as a modulator to obtain hierarchical MOFs, and the size of the mesopores can be adjusted by choosing modulators with different chains. Nevertheless, the investigation of micro-mesostructured MOFs is still in its infancy.

MIL-101(Cr) [18], one of the most hydrochemically stable MOFs, has not yet been prepared with a hierarchical structure. The addition of a modifier is commonly used to improve the properties of MIL-101(Cr), for instance, by adding nitric acid to improve yield (>80%) and processability while retaining high surface areas [19]. Also, acetic acid decreases the temperature of the synthesis and/or yield of nanosized MIL-101(Cr), with an average particle diameter of ~90 nm [20]. Herein, we propose a simple method to synthesize micro-mesohierarchically structured MIL-101(Cr) by using

phenylphosphonic acid as a modulator. In the selected condition, the obtained hierarchical MIL-101(Cr) retained its classical microporous skeletons and showed relatively good porosity.

#### 2. Results and Discussion

To obtain stable hierarchical MIL-101(Cr), phenylphosphonic acid (PPOA) was used as the modulator in the synthesis. In order to get the optimal synthetic conditions, a series of experiments with varying amounts of PPOA were carried out. During the experimentation, we found that with a specific ratio of PPOA associated with 1:1:0.25 for Cr:H<sub>2</sub>BDC:PPOA, a hierarchical MIL-101(Cr) product was formed. The experiment, without any additive, would generate larger separated MIL-101(Cr) particles, while an excessively high concentration of PPOA would affect the structure of MIL-101(Cr) and yield unknown phase products.

The syntheses were conducted with 0.25, 0.5, and 1 equivalents of phenylphosphonic acid and the related products were named as PPOA-0.25, PPOA-0.5, and PPOA-1, respectively. The experiment, without any additive, was labeled as PPOA-0. All these experiments were conducted on 1.0 mmol of both  $Cr(NO_3)_3 \cdot 9H_2O$  and  $H_2BDC$  in a PTFE-lined autoclave at 220 °C for 8 h followed by thorough washing with dimethylformamide and ethanol (see Experimental Section for further details).

The X-ray diffraction (XRD) patterns were performed for all samples (Figure 1). The patterns of PPOA-0 and PPOA-0.25, which corresponded to lower concentrations of phenylphosphonic acid, matched the simulated pattern for MIL-101(Cr) very well. The simulated pattern of MIL-101(Cr) was generated from the known crystal structure (CSD-Refcode: OCUNAK) using the program MERCURY (Figure 1) [21]. the samples PPOA-0.5 and PPOA-1, which were prepared with higher concentrations of phenylphosphonic acid, were confirmed to contain other unknown phase products (Figure 1). The characteristic peaks of MIL-101(Cr) were not found in the patterns of PPOA-0.5 and PPOA-1. Hence, higher dose of phenylphosphonic acid would not be helpful for the synthesis of MIL-101(Cr).



Figure 1. The XRD patterns of PPOA-0, PPOA-0.25, PPOA-0.5, and PPOA-1 samples with simulated patterns of MIL-101(Cr) (CSD-refcodes: OCUNAK) [18].

Figure 2 shows the nitrogen sorption isotherms of all samples and the pore size distribution curves of PPOA-0 and PPOA-0.25, and the porosity results are listed in Table 1. PPOA-0 and PPOA-0.25 possessed the typical type I(b) sorption isotherms [22] of MIL-101(Cr), which has been reported in the literature [18]. The only difference is that PPOA-0.25 had a hysteresis loop between adsorption and desorption isotherms (Figure 2a), which is typical for mesopores > 4 nm [22]. The pore size distribution curves of PPOA-0 and PPOA-0.25, which were analyzed by the nonlocaldensity functional theory (NL-DFT) model, showed mesopores in PPOA-0.25 with the widths 4–10 nm, but for PPOA-0, there were no such mesopores detected (Figure 2b). Due to excessive unknown phase byproducts in PPOA-0.5 and PPOA-1, they had much lower porosity, so it is not necessary to show their pore size distributions here.

**PPOA-0.25** 

PPOA-0.5

PPOA-1

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Phenylphosphonic Acid	MOFtype	S <sub>BET</sub>	S <sub>Langmuir</sub>	V <sub>pore</sub>	N <sub>2</sub> Uptake
(PPOA)-(Equivalents) <sup>a</sup>		(m <sup>2</sup> /g) <sup>b</sup>	(m²/g)	(cm <sup>3</sup> /g) <sup>c</sup>	(cm <sup>3</sup> /g) <sup>c</sup>
PPOA-0	MIL-101	2487	3621	1.34	890

2329

729

693

**MIL-101** 

Unknown

Unknown

3350

1039

1020

1.49

0.69

0.58

**Table 1.** Yield, surface area, and pore volume for MIL-101(Cr) with various amounts of phenylphosphonic acid (PPOA) as additive.

<sup>a</sup> PPOA equivalents with respect to chromium and H<sub>2</sub>BDC. The Cr:BDC ratio is always 1:1. <sup>b</sup> S<sub>BET</sub> was calculated using data points in the range of  $0.05 < p/p_0 < 0.2$  from N<sub>2</sub> sorption isotherm at 77 K, with an estimated standard deviation of  $\pm$  50 m<sup>2</sup>/g. <sup>c</sup> Calculated from N<sub>2</sub> sorption isotherm at 77 K ( $p/p_0 = 0.95$ ) for pores with diameters  $\leq 20$  nm.



**Figure 2.** N<sub>2</sub> adsorption–desorption isotherms for PPOA-0, PPOA-0.25, PPOA-0.5, and PPOA-1 (**a**), and the pore size distribution curves for PPOA-0 and PPOA-0.25, which were analyzed by the NL-DFT method (**b**).

Scanning electron microscopy (SEM) (Figure 3) results showed the morphologies of PPOA-varied products. PPOA-0 chiefly exhibited particles with an octahedral morphology, which is characteristic of MIL-101(Cr). PPOA-0.25 showed smaller particles which were partly fused together that contained larger structural defects and generated large mesopores. Considering its XRD positively matched the simulated pattern, these smaller fused particles were still MIL-101(Cr) without a crystal structure change. However, for PPOA-0.5 and PPOA-1, the small particles were totally fused together and also created structural defects. However, a too high concentration of phenylphosphonic acid had already affected the reaction and generated unknown phase byproducts. Hence, under SEM, PPOA-0.5 and PPOA-1 presented caking morphology. This result is in line with the abovementioned XRD and N<sub>2</sub> adsorption–desorption characterizations.

In order to compare PPOA-0 and PPOA-0.25, the large dye molecule Congo red (around  $3 \times 0.25 \times 0.73$  nm in size) was involved in adsorption via impregnating. Congo red, which is larger in size than the aperture windows of MIL-101(Cr), usually has difficulty accessing the pores of MIL-101(Cr). As visual evidence, the uptake experiment confirmed that the solution of Congo red with PPOA-0.25 gradually faded, while the solution with PPOA-0 still showed a dark red color (Figure 4). The UV–Vis absorption spectra of the filtrate were in line with the observation (Figure 4).

Both PPOA-0 and PPOA-0.25 were effective catalysts for the indene oxidation reaction (Figure 5a, Table 2). Further, PPOA-0.25 presented obviously higher catalytic activity in the oxidation of indene than that of PPOA-0 (Figure 5a, Table 2). In order to optimize the reaction condition, a series of standard reactions with different amounts of catalysts (0–15 mg) were conducted. The results show that the use of 10 mg of PPOA-0.25 as a catalyst was the optimal condition. After 60 min of the reaction, the conversion of indene for PPOA-0.25 (10 mg) could reach up to 92.3%, which was much higher than that of PPOA-0 (10 mg) (Figure 5 and Table 2). Although the continued increase of the use of catalysts (15 mg) could still slightly raise the conversion of indene, this increase was extremely limited (Table 2).

970

448

442

Thus, 10 mg of catalyst was enough and highly efficient for this reaction. Considering that PPOA-0 possessed slightly higher porosity than PPOA-0.25, the enhanced catalytic activity of PPOA-0.25 contributed to its hierarchically porous structure, which eventually accelerated the diffusion rate and increasingly exposed the coordination metal sites [13,14]. In our case, the turnover frequency (TOF) value of PPOA-0.25 (10 mg, 60 min) was 46.2 mmol g<sup>-1</sup> h<sup>-1</sup>, which is much higher than that of PPOA-0 (35.2 mmol g<sup>-1</sup> h<sup>-1</sup>). TOF of the catalyst = (molar conversion of substrate)/(mass of MIL-101Cr × reaction time).



Figure 3. SEM images of PPOA-0, PPOA-0.25, PPOA-0.5, and PPOA-1; the scale bar is 1 µm.

Moreover, the catalytic stability of MIL-101(Cr) with a hierarchically porous structure was significantly improved. After three runs, the conversion of indene with PPOA-0.25 was 76%, while the conversion with PPOA-0 was only 48% (Figure 5b). One possible explanation may be that, after the first run, the produced products are trapped in the pores of MIL-101(Cr) and cover the active sites, which decreases catalytic activity. PPOA-0.25 with a hierarchically porous structure had much larger mesopores, allowing product molecules to diffuse more easily and retain relatively more active sites, thus exhibiting better catalytic stability.

Recently, Ying et. al. [23] reported that mesoporous-silica-encapsulated MIL-101(Cr) possessed higher catalytic activity in the oxidation of indene compared with normal MIL-101(Cr). The mesoporous silica coating had a hierarchically porous structure, accelerating the diffusion speed of the reactants and solvent molecules and promoting effective contact with the active sites of catalysts, which benefited the oxidation of indene. For our work, the synthesized hierarchically porous MIL-101(Cr) revealed the same dynamic progress; thus, PPOA-0.25 presented better catalytic performance.



**Figure 4.** UV–Vis absorption spectra for filtrate of PPOA-0 and PPOA-0.25. The left insert image is the structural formula of Congo red, and the right insert image is the color of the filtrate of the Congo red solution with PPOA-0 and PPOA-0.25.

**Table 2.** The conversion of indene by PPOA-0 and PPOA-0.25 with different weights after 60 min of the reaction.

Catalysts/Weight	0 mg (Conversion)	5 mg (Conversion)	10 mg (Conversion)	15 mg (Conversion)
PPOA-0	0%	69.2%	70.4%	71.9%
PPOA-0.25	0%	82.1%	92.3%	92.7%



**Figure 5.** Time-variable conversion of indene by PPOA-0 and PPOA-0.25 (**a**). Comparison of the conversion for PPOA-0 and PPOA-0.25 over three reaction runs. The reaction time is 120 min (**b**). The weight of catalysts is 10 mg.

It has been reported that with the presence of monocarboxylic acids in the synthesis of MOFs would create structural defects and form a hierarchical structure [17]. In our case, phenylphosphonic acid played a similar role in a certain concentration. Hierarchical MIL-101(Cr) forms when a 1:1:0.25 ratio of Cr:H<sub>2</sub>BDC:PPOA is used and the concentration of PPOA is 50 mmol L<sup>-1</sup>. If phenylphosphonic acid had been added to the MIL-101(Cr) reaction system to pre-coordinate to Cr-oxo clusters, the ligand H<sub>2</sub>BDC with lower pKa than phenylphosphonic acid would have readily replaced the modulator, and this incomplete exchange would cause structural defects (Scheme 1) [24]. Thus, stable hierarchical MIL-101(Cr) could be prepared simply by introducing a specific concentration of phenylphosphonic acid into the hydrothermal reaction system. Our results also suggest that an overly high concentration of phenylphosphonic acid would affect the formation of hierarchical MIL-101(Cr) and generate unknown phase byproducts.



Scheme 1. Schematic illustration of the synthesis of hierarchical MIL-101(Cr) with phenylphosphonic acid.

#### 3. Experimental Section

#### 3.1. Materials

 $Cr(NO_3)_3$ ·9H<sub>2</sub>O (AR, 99%, Aladdin, Shanghai, China), terephthalic acid (H<sub>2</sub>BDC, 99%, Aladdin, Shanghai, China), phenylphosphonic acid (AR, 99%, Aladdin, Shanghai, China), Congo red (98%, Aladdin, Shanghai, China), acetonitrile (CH<sub>3</sub>CN, 99.8%, Aladdin, Shanghai, China), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt% in H<sub>2</sub>O, Aladdin, Shanghai, China), N,N-dimethylformamide (DMF, AR, 99%, Aladdin), and ethanol (AR, 99.7 + %, Sinopharm chemical reagent Co., Ltd., Beijing, China) were used as obtained from commercial sources without further purification.

#### 3.2. Instrumentation

X-ray diffraction (XRD) patterns were obtained at ambient temperature by using an Ultima IV instrument (Rigaku, Tokyo, Japan). Nitrogen physisorption measurements were carried out by using a NOVA-4000e instrument (Quantachrome, Boynton, FL, USA). Scanning electron microscopy (SEM) images were recorded with an EVO MA 10 instrument (ZEISS, Jena, Germany). The catalytic reaction products were identified and analyzed by using the Agilent Technologies 7890A GC system (Agilent, Palo Alto, CA, USA). UV–visible spectra measurements were performed on a UV-2550 spectrophotometer (Shimadzu, Kyoto, Japan).

#### 3.3. Synthesis of Hierarchical MIL-101(Cr)

400 mg of  $Cr(NO_3)_3 \cdot 9H_2O$  (1 mmol), 166 mg of  $H_2BDC$  (1 mmol), and 39.5 mg of phenylphosphonic acid were mixed in 5 mL of deionized water, and the mixture was transferred to a PTFE/Teflon-lined autoclave which was heated to 220 °C for 8 h. After cooling down to room temperature, the content was separated by centrifugation, and then the solid in the tube was washed with DMF (15 mL) in a hot (80 °C) ultrasonic bath for 1 h. Centrifugation was used again for separation and the precipitate was dispersed in 15 mL of ethanol with a clean glass tube. The tube was placed in the hot (70 °C) ultrasonic bath for another 2 h. The washing procedure with ethanol was repeated once more at the same temperature. The final products were collected after drying the sample in a vacuum oven (120 °C, 12 mbar) for 2 h.

All the other experiments were conducted under the same conditions and the washing procedure was the same as described above.

#### 3.4. The Uptake of Large Molecules

The PPOA-0.25 and PPOA-0 were used for large sizes of molecule/compound uptakes.

The uptake of Congo red molecules: 20 mg of PPOA-0 or PPOA-0.25 was immersed in 2 mL of Congo red ( $\sim 3 \times 0.25 \times 0.73$  nm in size, concentration: 4 mg mL<sup>-1</sup>) aqueous under ambient conditions

for 4 h. Then, the solid was filtered by filter paper, and the filtrate measured by a UV-visible spectra instrument (Shimadzu, Kyoto, Japan).

## 3.5. Catalytic Activity Evaluation

Indene oxidation reaction: The catalyst (PPOA-0 or PPOA-0.25, 0–15.0 mg), indene (0.5 mmol), and CH<sub>3</sub>CN were mixed in a glass vessel at 70 °C with stirring for 10 min. Then, 500  $\mu$ L of H<sub>2</sub>O<sub>2</sub> (30 wt %, 5 mmol) was injected into the mixture. The aliquots of the reaction mixture were collected at different reaction times and monitored by gas chromatography (GC).

## 4. Conclusions

In summary, a certain concentration of phenylphosphonic acid induced the controllable synthesis of MIL-101(Cr) with a hierarchical structure. The obtained MIL-101(Cr) possessed large mesopores with widths of 4–10 nm and exhibited a good micro-meso hierarchical structure. Further, the hierarchical MIL-101(Cr) exhibited significant improvement in large molecule adsorption and demonstrated the enhancement of catalytic activity in the oxidation of indene. Hence, the results are an interesting continuation of the research focussing on facile hierarchically structured chromium MOF syntheses. We hope that this work will promote the further application of hierarchical MOFs, such as macromolecule delivery/catalysis, etc.

Author Contributions: Conceptualization and Methodology, T.Z.; Formal Analysis, T.Z., M.D. and Y.L.; Resources, Y.L.; Writing-Original Draft Preparation, T.Z.; Writing-Review & Editing, T.Z. and M.D.; Funding Acquisition, T.Z. and Y.L.

**Funding:** This research was funded by National Natural Science Foundation of China (No. 51802094) and Hunan Provincial Natural Science Foundation of China (2018JJ3122).

**Acknowledgments:** L.Y. thanks the Hunan Provincial Innovation Foundation for Postgraduate (CX2017B679). Y.L. thanks the National Natural Science Foundation of China (No. 11872179). We thank X.Y. for fruitful discussions regarding the synthesis and characterization of hierarchical structured MOFs.

Conflicts of Interest: The authors declare no conflict of interest.

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