A Polyoxometalate Composite Based on Hierarchical MIL-101 with Enhanced Catalytic Activity in Methanolysis of Styrene Oxide

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Abstract: A new efficient polyoxometalate composite catalyst of hierarchical MIL-101 and phosphotungstic acid (PTA) was facilely prepared by the immersion method. The material was thoroughly characterized by powder x-ray diffraction (PXRD), scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDX) and inductively coupled plasma-optical emission spectrometry (ICP-OES). Compared to the pristine nonhierarchical MIL-101 composite, the hierarchical composite demonstrated much higher catalytic performance in methanolysis of styrene oxide, such as catalytic activity and reusability.

Keywords: hierarchical MIL-101; higher catalytic activity; phosphotungstic acid; styrene oxide

1. Introduction

Metal organic frameworks (MOFs) have attracted keen interest in the past decades, attributed to their unique porous structures [1–4]. However, most of them suffered from framework collapse when they were exposed in water/moisture environment; thus, their applications were greatly limited [5].

MIL-101, a famous chromium-benzenedicarboxylate MOF, possesses ultrahigh porosity and stability and hence has received great attention since it was reported [5–8]. The application fields of this material refer to gas adsorption/separation [9,10], magnetism [11,12], catalysis [13] and water adsorption [14], etc.

Polyoxometalates (POMS), which are formed by oxygen bonding with transition metal ions, are widely utilized in many areas such as pesticides detection [15], catalysis [16–19], batteries [20,21] and so on [22,23]. Phosphotungstic acid (PTA), one of the strongest heteropolyacids with high thermal stability, can be used as an efficient catalyst in many redox reactions and has received continuous attention [24–27]. Nevertheless, pure PTA can be dissolved in various organic solvents such as alcohols and ethers, which leads to difficulty in recovering catalysts. An efficient strategy was loading PTA into the pores of MIL-101 to yield a composite catalyst for heterogeneous catalysis applications [7,28]. The composite catalyst was reusable.

In previous research, we proposed a simple synthetic approach to the obtained hierarchically porous MIL-101 with larger mesopores width around ~8 nanometer (nm) by involving a specific amount of phenylphosphonic acid [29]. The additional large mesopores of hierarchically MIL-101 accelerated the diffusion rate and exposed more active sites of the material, and hence exhibited better catalytic capability than those nonhierarchical MIL-101s in the oxidation of indene and 1-dodecene [30]. Thus, it would be interesting to see whether hierarchical MIL-101 shows better performance than that of nonhierarchical pristine MIL-101 when using MIL-101 as carrier for PTA.

In this work, a composite catalyst (PTA@S1) comprised of hierarchical MIL-101 (S1) and PTA was prepared with immersion method. The loaded PTA was an efficient catalyst component, and had...
hierarchical MIL-101 as support. Nonhierarchical pristine MIL-101 (S2) and PTA were also employed to form a composite as a control group (PTA@S2). The results revealed that, with the same weight of the PTA component, PTA@S1 disclosed much better catalytic activity and reusability than that of PTA@S2 in the ring-opening reaction of styrene oxide with methanol.

2. Results and Discussion

Hierarchical MIL-101 was prepared according to the report [29] by using phenylphosphonic acid as a modulator, and the product was named as S1. Nonhierarchical MIL-101 was synthesized following the literature [6] by involving hydrofluoric acid as mineralizing agent, and the sample was called S2. The corresponding composite catalysts were obtained by soaking MIL-101s in the methanol solution of PTA for 24 hours. For the preparation details, please see Exp. Part.

Phosphotungstic acid (PTA) is a new multifunctional green catalyst with a molecule diameter around 13 Å. MIL-101 has two kinds of natural aperture windows: pentagonal window (~12 × 12 Å) and hexagonal window (~14.7 × 16 Å). Thus, for nonhierarchical pristine MIL-101 (S2), the loading of PTA via immersion method was quite limited (Scheme 1). On the contrary, hierarchical MIL-101 (S1) had much larger pores, which allowed PTA molecules to enter inside of S1 much easier. The larger pores of S1 were also connected with the its natural pores. Once PTA molecules diffused into the mesopores, they likely blocked inside the pores and made it difficult to escape from the caves (Scheme 1).

The PXRD patterns of all samples, including pure PTA, were shown in Figure 1. Both synthesized MIL-101 samples S1 and S2 were well matched for the simulated pattern, which confirmed the structure of MIL-101 (Figure 1a). For PTA@S1 and PTA@S2, the main peaks of MIL-101 still can be found in the PXRD patterns, which proved that the immersion process did not affect the framework of MIL-101s (Figure 1b). However, three new strong peaks came out in the region of 6–8° 2θ compared with MIL-101, and they did not match the pattern of PTA (Figure 1b). In fact, those new peaks had arisen
from the highly loaded PTA molecules in the pores of MIL-101s, and this result was in line with the literature reported [7]. The stronger reflection peaks in PTA@S1 may suggest a higher loading of PTA component than that of PTA@S2.

Figure 1. (a) The powder x-ray diffraction (PXRD) patterns of S1 and S2 compared with simulated pattern of MIL-101, which was generated from the deposited x-ray data file at the Cambridge Structure Database (CSD-Refcode OCUNAK) [6]. (b) The PXRD patterns of S1, S2, PTA@S1, PTA@S2 and pure PTA.

SEM images of MIL-101s and composites were presented in Figure 2; the morphology of S1 and S2 had significant differences. S1 showed obviously smaller particle sizes than that of S2, and most particles of S1 were irregular, while the particles of S2 displayed regular octahedral morphology that was consistent with other reports [6,10]. After immersion, PTA@S1 and PTA@S2 possessed the same appearance with their corresponding MIL-101, and no PTA crystals were found, which suggested that the PTA residuals outside the pores of MIL-101s were removed during the washing procedure.

Figure 2. Scanning electron microscopy (SEM) images of S1, S2, PTA@S1 and PTA@S2.
Since the PTA molecules were loaded into the pores of MIL-101s, their porosity was largely decreased compared to the blank host MIL-101s. The nitrogen physical-sorption results proclaimed that both PTA@S1 and PTA@S2 had much lower porosity than their corresponding blank MIL-101s (Figure 3, for detailed porous information, please see Table 1). The Brunauer–Emmett–Tiller (BET) surface area of PTA@S1 had decreased to 780 m$^2$/g, which was only 33.5% of value of S1 (Table 1). Additionally, the hysteresis loop between adsorption curve and desorption curve of S1, which is characteristic of hierarchical structure, cannot be found in PTA@S1 (Figure 3a). This result indicated that after loading PTA in S1, the larger pores were completely occupied by PTA molecules. The calculated pore size distribution (PSD) curves, which were based on nonlocal density functional theory (NL-DFT) model, demonstrated that only small pores (<3 nm) were in the system, while blank S1 contained extra larger pores (average diameter ~8 nm) (Figure 3c). S2 possessed excellent porosity with BET surface of 3500 m$^2$/g and total pore volume of 1.73 cm$^3$/g (Figure 3b, Table 1). After loading PTA by immersion method, the surface area of PTA@S2 had also decreased considerably (2530 m$^2$/g) but still remained at 72.3% of the value of S2 (Table 1). In PSD curves, both S2 and PTA@S2 only possessed the natural pores of MIL-101 (Figure 3d).

![Figure 3. N$^2$ adsorption-desorption isotherms of (a) S1, PTA@S1, (b) S2 and PTA@S2. Pore size distributions of (c) S1, PTA@S1, (d) S2 and PTA@S2.](image_url)

| Sample  | $S_{BET}$ (m$^2$/g) $^a$ | $S_{Langmuir}$ (m$^2$/g) | $V_{pore}$ (cm$^3$/g) $^b$ |
|---------|------------------------|-------------------------|-------------------------|
| S1      | 2330                   | 3350                    | 1.49                    |
| PTA@S1  | 780                    | 1130                    | 0.45                    |
| S2      | 3500                   | 4780                    | 1.73                    |
| PTA@S2  | 2530                   | 3600                    | 1.32                    |

$^a$ $S_{BET}$ were calculated in the pressure range 0.05 < $p/p_0$ < 0.2 from N$^2$ sorption isotherm at 77 K with an estimated standard deviation of ±50 m$^2$/g. $^b$ Calculated from N$^2$ sorption isotherm at 77 K ($p/p_0 = 0.95$) for pores ≤ 20 nm.
The PTA content in the composites was determined by EDX and ICP-OES measurement. W content in PTA, H$_3$PW$_{12}$O$_{40}$ is 76.6%, while Cr content in MIL-101, [Cr$_3$(O)·X(bdc)$_3$(H$_2$O)$_2$] (bdc = benzene-1,4-dicarboxylate, X = OH or F) is 21.76%. The EDX analysis results displayed that, in PTA@S1 and PTA@S2, the ratio of Cr:W = 1:2.46 and 1:0.74, respectively. Thus, according to these results the calculated PTA loading of PTA@S1 and PTA@S2 were 41.1 wt% and 17.4 wt%, respectively. However, in the ICP-OES measurement, ratio of Cr:W for PTA@S1 and PTA@S2 were only 1:1.67 and 1:0.31; hence, the corresponding calculated PTA loading were 32.2 wt% and 8.1 wt%, respectively. The significant discrepancy of these two methods may be caused by the enrichment of PTA near the surface of the PTA@S composites, which led to a higher fraction of PTA in EDX analysis. Based on the above discussion, the ICP-OES results may be more reliable.

In order to compare the catalytic capability of the PTA@S composites, the catalytic methanolysis of styrene oxide was tested, and the intermediate was monitored periodically by gas chromatography (GC) analysis (Figure 4, Table 2). The product was identified by comparing it the stand pure 2-methoxy-2-phenylethanol methanol solution. No other products were found. So as to keep each catalytic test with the same amount of PTA in catalysts, 10 mg of PTA@S1 and 40 mg of PTA@S2 were used in the experiments (based on ICP-OES results). PTA was the efficient catalyst in this reaction, and the pure MOF samples S1 and S2 had no activity (Figure 4a). PTA@S1 produced much higher catalytic activity than PTA@S2, even when they contained same amount of PTA (Figure 4a). For instance, in the 1st run after 20 min, the conversion of styrene oxide with PTA@S1 sample was 79.3%, while the conversion with the PTA@S2 sample was only 45.1% (Table 2). The turnover number (TON) value of PTA@S1 was 177.32, which was near a pure PTA system with TON of 194.81. While for PTA@S2, the TON value was only 100.22, which was much lower than the case of PTA@S1. The turnover frequency (TOF) values of PTA@S1 (3.07 mmol·g$^{-1}$·min$^{-1}$) were 1.77 times greater than that of the PTA@S2 sample (1.74 mmol·g$^{-1}$·min$^{-1}$). Moreover, PTA@S1 exhibited superior catalytic performance to PTA@S2 and was recyclable without large activity drop, indicating excellent stability (Figure 4b). After five cycles, the conversion of styrene oxide with the PTA@S1 was still 63.7% (Figure 4c), while for PTA@S2 sample the conversion dropped to 15.7% (Figure 4d). Hence, in the 5th run, PTA@S1 still possessed over 80% of catalytic activity of 1st run, while for PTA@S2 the catalytic activity was less than 35% of 1st run (Table 2). It is worthy to notice that, for the homogenous PTA catalysis, the TOF value was 3.38 mmol·g$^{-1}$·min$^{-1}$, which was only 10% higher than that of PTA@S1. In order to figure out the reason for catalyst deactivation, the content of element W in filtrate of catalyst after each run was also tested (Table 3). The results revealed that, after every reaction, the PTA leaching in both cases were quite limited, and over 90% of PTA component remained in the composite. Thus, one possible explanation of such catalyst deactivation was the blocking of active sites by reaction product. PTA@S1 had hierarchical larger mesopores, which allowed for faster mass transport than that of PTA@S2, and exhibited better reusability. Thus, in addition to an advantage in terms of their encapsulation of large active components, the hierarchical pores facilitated the transport of large substrates/products, revealing the advantage of hierarchical MOF.
was synthesized according to the literature [6]. All chemicals were purchased from commercial sources (Aladdin or Sinopharm chemical reagent Co., Ltd., Beijing, China) without any further treatments.

### 3. Experimental Section

#### 3.1. The Preparation of MIL-101s

The hierarchical MIL-101 (S1) was prepared according to the literature [29]. The pristine MIL-101 (S2) was synthesized according to the literature [6]. All chemicals were purchased from commercial sources (Aladdin or Sinopharm chemical reagent Co., Ltd., Beijing, China) without any further treatments.

![Figure 4](image_url)

Figure 4. (a) Time-variable conversion of the ring opening of styrene oxide with methanol over S1, S2, PTA@S1 and PTA@S2; the insert image is the reaction scheme. (b) Comparison of the conversion for PTA@S1 and PTA@S2 over five reaction runs; the reaction time is 20 min. The kinetic plot (conversion versus time) of (c) PTA@S1 and (d) PTA@S2 for each run.

| Table 2. Summary of catalytic reactions of the ring opening of styrene oxide with methanol. |
|---------------------------------|---|---|---|---|
| Sample | Catalyst Weight (mg) | TON | TOF (mmol g⁻¹·min⁻¹ | Conversion (%) |
| S1 | 40 | - | - | <3/- |
| S2 | 40 | - | - | <3/- |
| PTA@S1 | 10 | 177.32 | 3.07 | 79.3/63.7 |
| PTA@S2 | 40 | 100.22 | 1.74 | 45.1/15.7 |
| PTA | 3.5 | 194.81 | 3.38 | 94.7/- |

- Molar ratio: styrene oxide/methanol = 1/200, ambient temperature, get 2-phenyl-2-methoxyethanol.
- Sample was dried in the vacuum oven overnight.
- TON of the catalyst = (moles of substrate consumed)/moles of PTA for 1st run.
- TOF of the catalyst = (moles of substrate consumed)/(mass of PTA × reaction time) for 1st run.

| Table 3. The phosphotungstic acid (PTA) content of filtrate of catalyst for each run. |
|---------------------------------|---|---|---|---|
| Sample | Run | W conc. (mg/L) | PTA conc. (mg/L) | PTA Leaching (mg) |
| PTA@S1 | 1 | 3.672 | 4.794 | 0.0479 |
| | 2 | 2.098 | 2.739 | 0.0274 |
| | 3 | 2.583 | 3.372 | 0.0337 |
| | 4 | 2.272 | 2.966 | 0.0297 |
| | 5 | 2.478 | 3.235 | 0.0324 |
| PTA@S2 | 1 | 3.353 | 4.377 | 0.0438 |
| | 2 | 2.764 | 3.608 | 0.0361 |
| | 3 | 3.347 | 4.369 | 0.0437 |
| | 4 | 2.341 | 3.056 | 0.0306 |
| | 5 | 2.253 | 2.941 | 0.0294 |

- The content of PTA was calculated based on the W, which was obtained from inductively coupled plasma-optical emission spectrometry (ICP-OES) measurement of the filtrate. W content in PTA, H₃PW₁₂O₄₀ (2880.05 mol/g) is 76.6%. The weight of PTA leaching = concentration of PTA × 10 mL.

3. Experimental Section

#### 3.1. The Preparation of MIL-101s

The hierarchical MIL-101 (S1) was prepared according to the literature [29]. The pristine MIL-101 (S2) was synthesized according to the literature [6]. All chemicals were purchased from commercial sources (Aladdin or Sinopharm chemical reagent Co., Ltd., Beijing, China) without any further treatments.
3.2. The Preparation of S@PTA Composites

One hundred mg of S1 or S2 was soaked in 10 mL of phosphotungstic acid methanol solution (PTA, H₃PW₁₂O₄₀·nH₂O, concentration: 20 mg/mL) for 24 h at room temperature. The soaked solid was collected by centrifugation and washed with methanol over 10 times. Finally, the obtained product was dried at 85 °C for 12 h, and they were named PTA@S1 and PTA@S2, respectively.

3.3. Characterization

PXRD measurements were conducted at RT via an Ultima IV instrument (Rigaku, Tokyo, Japan). N₂-sorption measurements were carried out in a NOVA-4000e instrument (Quantachrome, Boynton, FL, USA). SEM characterizations were performed on a Nova NanoSEM230 instrument (Thermo Fisher Scientific, New York, USA). The elemental analysis was performed by the ICP-OES on a Prodigy 7 instrument. The conversion of reactants was analyzed via an Agilent Technologies 7890A GC system (Agilent, Palo Alto, CA, USA) with capillary column at room temperature.

3.4. Catalysis Reaction

The catalyst (40 mg of S1, S2, PTA@S2, or 10 mg of PTA@S1, 3.5 mg of PTA) and styrene oxide (0.25 mmol) were mixed in with 10 mL of methanol and the reaction started. The intermediate was monitored periodically by GC. Because of high dissolubility of PTA in methanol, when using PTA as catalyst, the reaction became a homogeneous catalysis system, and the PTA catalyst could not be reused.

3.5. ICP-OES Analysis

A few precisely weighted milligrams of PTA@S1 and PTA@S2 were completely dissolved in 2 mL HNO₃ (65%) solution. Then, the solutions were thoroughly transferred into 20 mL volumetric flasks and ready for measurement. The W and Cr content of each sample was determined by comparison to standard solution.

4. Conclusions

In summary, the large molecular catalyst PTA can be facilely loaded in hierarchical MIL-101 using the soaking method. Due to its unique hierarchical structure, S1 could load more PTA molecules in its hierarchical pores, though pristine MIL-101 S2 possessed much higher porosity. The composite PTA@S1 also exhibited much better catalytic activity and reusability than that of PTA@S2. Thus, compared to the parent MIL-101, hierarchical MIL-101 demonstrated better performance when large-size active guests were involved to get porous functional composites, which are highly valuable for miscellaneous real-life applications.

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