



# Phosphotungstic acid encapsulated in metal-organic framework UiO-66: An effective catalyst for the selective oxidation of cyclopentene to glutaraldehyde



Xin-Li Yang<sup>a,\*</sup>, Li-Ming Qiao<sup>a</sup>, Wei-Lin Dai<sup>b,\*</sup>

<sup>a</sup> School of Chemistry & Chemical Engineering, Henan University of Technology, Henan 450001, PR China

<sup>b</sup> Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, PR China

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## ABSTRACT

A heterogenous Zr-based metal organic framework (UiO-66) encapsulating phosphotungstic acid (HPWs) catalyst (HPWs@UiO-66), was prepared by a simple direct hydrothermal reaction of ZrCl<sub>4</sub>, terephthalic acid, and HPWs in DMF. The as-prepared novel material was very active as the catalyst for the selective oxidation of cyclopentene (CPE) to glutaraldehyde (GA) with environmentally benign hydrogen peroxide as the oxidant. The crystal structure and morphology of UiO-66 were well preserved after the incorporation of HPWs, as confirmed by X-ray diffraction (XRD), SEM, and TEM. Moreover, the XRD, N<sub>2</sub> adsorption, and FT-IR analyses reveal that HPW components could stably exist in the nanocages of UiO-66. FT-IR-CO adsorption experiments indicated that additional Lewis acid sites were present in the HPWs@UiO-66 sample, which were essential to catalyze the selective oxidation of CPE to GA. A proper amount of HPWs and their high dispersion accounted for high catalytic activity. Almost complete conversion of CPE (~94.8%) and high yield of GA (~78.3%) were obtained using the 35 wt% HPWs@UiO-66 catalyst. Furthermore, HPW components hardly leached in the reaction solution, enabling the catalyst to be used for three reaction cycles without obvious deactivation.

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## 1. Introduction

In recent years, Metal Organic Frameworks (MOFs) have received an increased attention as they are considered as the newest generation porous materials [1–3]. This type of crystalline materials is self-assembled by linking organic ligands with metal ions or metal clusters to form infinite network structures. The porosity, structure, and functionality of MOFs can be adjusted by varying the bridging ligands and/or the metal centers. In addition to their “classic” applications in gas storage [4,5] and separation [6], MOFs have attracted the interest of researchers in the field of catalysis owing to their unique properties such as high surface area, crystalline open structures, tunable pore size, and functionality [7]. Hitherto, mainly three different types of catalytic activities are reported for the catalysts based on MOFs. First, the catalytic activity observed for these materials is directly related to their metallic

components either as isolated metal centers or clusters; second, MOFs structure can contain catalytically active centers at the organic linker molecules of the framework; third, none of the components of the MOFs are directly involved in the catalysis. MOFs simply play the role of a support material, and their porous system provides the physical space for catalysis or functions as a cage where the catalytic centers are encapsulated [8]. Although MOFs have been studied as the catalysts in the hydrogenation, oxidation, enantioselective, photocatalytic, carbonyl cyanosilylation, hydrodesulfurization, and esterification reactions, their catalytic applications are still quite limited because of their low thermal and hydrolytic stability apart from often completely blocked metal sites by the organic linker or solvent, leaving no free positions available for substrate chemisorption. Recently, new synthesis strategies have been proposed to overcome the drawbacks including post-synthetic modification [9], the use of specific synthesis modulators [10–13], and ultrasonication and microwave-assisted methods [14,15]. The zirconium (IV) terephthalate UiO-66(Zr), (UiO = University of Oslo), first reported by Lillerud and coworkers, has a rigid 3D cubic close packed structure based on the hexamers of eight-coordinated ZrO<sub>6</sub>(OH)<sub>2</sub> polyhedra and 12

\* Corresponding authors. Fax: +86 371 67756718.

E-mail addresses: [xlyang@haut.edu.cn](mailto:xlyang@haut.edu.cn) (X.-L. Yang), [wldai@fudan.edu.cn](mailto:wldai@fudan.edu.cn) (W.-L. Dai).

terephthalate linkers [16]. UiO-66(Zr) solid with tetrahedral and octahedral cages of 8 and 11 Å, respectively, is accessible through microporous triangular windows in the range 5–7 Å, leading to a high porosity combined with high thermal, chemical, and mechanical stability. Furthermore, the textural and physicochemical properties of UiO-66(Zr) solid can be easily tuned by functionalized terephthalate linkers (NH<sub>2</sub>, Br, NO<sub>2</sub>, etc.) or extended organic ligands [17–19]. Owing to these interesting properties, UiO-66(Zr) solid appears to be a good candidate in catalysis. De Vos et al. [20] reported the catalytic performances of UiO-66 and UiO-66-NH<sub>2</sub> for the synthesis of jasminaldehyde via the cross-aldol condensation of benzaldehyde and heptanal. UiO-66 was less active in comparison to UiO-66-NH<sub>2</sub> which acted as a bi-functional catalyst and suppressed the formation of byproduct. They also studied the effect of functionalized terephthalate linkers on the catalytic properties of UiO-66 in the cyclization of citronellal [21]. A combination of catalytic and computational molecular modeling indicated that the type of functional groups present in the linker units could alter the Lewis acidic properties and induce additional stabilizing/destabilizing effects on the reactants depending on their electronic properties. Recently, they reported that the use of specific synthesis modulators (trifluoroacetic acid and HCl) allowed a high level of control on the number and nature of the defect sites in the well-studied zirconium terephthalate, UiO-66, and thereby influenced the catalytic activity of the material [11]. The study of Ahn et al. indicated that the catalytic activities of UiO-66 and UiO-66-NH<sub>2</sub> correlated to their Lewis acid–base properties in the cycloaddition of CO<sub>2</sub> to styrene oxide [22]. Jhung et al. investigated the effects of linker substitutions on the catalytic properties of porous zirconium terephthalate, UiO-66, in the acetalization of benzaldehyde with methanol. The results showed that the insertion of electron-donating NH<sub>2</sub>-groups into the linker ligand increased the strength of basic sites in contrast to electron-withdrawing NO<sub>2</sub>-groups. The strength of Lewis acid sites decreased in the order of UiO-66-NO<sub>2</sub> > UiO-66 > UiO-66-NH<sub>2</sub>, thus their catalytic activities for the acetalization of benzaldehyde with methanol decreased in the same order [23].

Heteropolyacids (HPAs), as a unique class of anionic metal-oxygen clusters of early transition metals, have many properties that make them suitable candidates for applications in catalysis. They have been extensively used as acidic and oxidation catalysts in many reactions because their acid–base and redox properties can be tuned easily by changing polyanion chemical composition [24]. Phosphotungstic acid (HPW) with the strongest Brønsted acidity in the HPAs series is a promising heterogeneous catalyst for many organic reactions such as esterification, alkylation, hydrolysis, and oxidation [24,25]. The industrial applications of pure HPAs have been hindered notably because of their low surface area (1–10 m<sup>2</sup>/g). Considerable efforts have been directed to their heterogenization onto various solid supports such as silica [26,27], activated carbon [28,29], ion-exchange resin [30], and mesoporous molecular sieves [31–33]. However, the supported HPAs catalysts usually show low activities because of low HPA loading, HPA leaching, the conglomeration and nonuniform distribution of HPAs particles, and the deactivation of acid sites by water. Therefore, the immobilization of HPAs in a suitable solid matrix, which can overcome these drawbacks, is a step toward the challenging goal of catalysis.

The hydrothermal, chemical, and mechanical stabilities, together with its high porosity, make UiO-66 an ideal candidate for host matrices to encapsulate HPAs. The heterogenization of HPAs in the host matrices of a MOF offers many advantages such as the isolation of the Keggin units improving molecular accessibility, simple recovery of catalysts by filtration, and convenient reuse. Therefore, the encapsulation of HPAs in MOFs such as MIL-101 and

HKUST-1 prepared by the impregnation or direct synthesis method, has attracted considerable attentions [34–43]. To the best of our knowledge, there are no reports on the synthesis of HPA incorporated into UiO-66. Herein, for the first time, we report the encapsulation of active HPW species in UiO-66 material via the direct synthesis method and the investigation of its catalytic performance for the selective oxidation of cyclopentene (CPE) to glutaraldehyde (GA) with environmentally benign aqueous H<sub>2</sub>O<sub>2</sub> as the green oxidant. GA is extensively used in the fields of disinfection and sterilization. An important method to produce GA is the selective oxidation of CPE, because a significant quantity of CPE could be easily obtained by the selective hydrogenation of cyclopentadiene, which in turn is easily obtained from the decomposition of dicyclopentadiene, a main byproduct from the C-5 fraction in the petrochemical or coke industry [44,45]. We found that HPWs were highly dispersed into the matrices of the support UiO-66, and the as-prepared heterogeneous catalysts showed much higher activity and selectivity for this oxidation reaction. The recyclability and reusability of the catalysts were also investigated.

## 2. Experimental

### 2.1. Catalyst preparation

All the chemicals were obtained commercially and used without further purification.

UiO-66 was synthesized according to the hydrothermal method described in the literature [16,46].

The encapsulation of HPWs in UiO-66 denoted as HPWs@UiO-66 was prepared following the same procedure as for the pure UiO-66, besides HPWs were being added to the mixture during the synthesis. In a typical preparation procedure, 1.45 g zirconium chloride (ZrCl<sub>4</sub>), 1.06 g terephthalic acid (H<sub>2</sub>BDC), 0.5 mL condensed HCl, and the required amount of HPWs were added in DMF (40 mL). The resulting reaction mixture was ultrasonicated for ~5 min at room temperature. Then, the obtained mixtures were sealed in a Teflon-lined autoclave and kept in an oven at 393 K for 24 h. The crystallization was carried out under static conditions. Then, the autoclave used for the synthesis was cooled to room temperature in air. The resulting white product was filtered off, washed with DMF to remove excess H<sub>2</sub>BDC, repeatedly washed with methanol, and finally dried at room temperature. The as-prepared catalyst was dried at 453 K for 10 h before catalytic test.

### 2.2. Characterizations

The powdered X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-rB spectrometer with Cu K $\alpha$  radiation, which was operated at 60 mA and 40 kV. The FT-IR measurements were carried out with an IR Prestige-21 spectrometer (SHIMADZU) using KBr pellet technique. The *in situ* FT-IR spectra using CO as a probe molecule were collected on a BRUKER (Tensor 27) spectrophotometer equipped with a DTGS detector at 4 cm<sup>-1</sup> resolution on a thin self-supported wafer. The sample was activated in a home-made cell under high vacuum (residual pressure 10<sup>-4</sup> mbar) at 473 K for 2 h. CO gas (*P*<sub>eq</sub> = 50 torr) was dosed on the sample for 20 min at RT. Nitrogen adsorption and desorption at 77 K were measured by using a Micromeritics ASAP 2020 instrument after the samples were degassed (1.33 × 10<sup>-2</sup> Pa) at 423 K overnight. The specific surface area was calculated using the BET method. The total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.99. Scanning electron micrographs were obtained using JSM-6510LV scanning electron microscope (JEOL). The samples were deposited on a sample holder with a piece of adhesive carbon tape and were then sputtered with a thin film of

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