

# Green Oxidation of Cyclohexanone to Adipic Acid over Phosphotungstic Acid Encapsulated in UiO-66

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#### Abstract

A very stable catalyst, phosphotungstic acid (PTA) encapsulated in metal–organic framework UiO-66, was prepared by a simple one-pot solvothermal method. Characterization results show that UiO-66 is quite stable in the catalyst preparation process, and PTA is encapsulated in the cavities of UiO-66 with good dispersity. The as-synthesized composite material exhibited good catalytic activity and excellent reusability for the green oxidation of cyclohexanone to adipic acid (AA). Under mild reaction conditions, the isolated yield of AA was as high as 80.3% without the introduction of any organic solvent or phase transfer agent. The excellent immobilization effect of UiO-66 for PTA is mainly because UiO-66 has a well matched window size to confine PTA molecule in its nanocages.

#### **Graphical Abstract**



Keywords Phosphotungstic acid · Metal-organic frameworks · Cyclohexanone · Adipic acid

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# Abbreviations

AA	Adipic acid				
DMF	N,N-dimethylformamide				
FT-IR	Fourier transform infrared spectroscopy				
ICP-AES	Inductively coupled plasma-atomic emission				
	spectroscopy				
MOFs	Metal-organic frameworks				
PTA	Phosphotungstic acid				
SEM	Scanning electron microscope				
TEM	Transmission electron microscopy				
TGA	Thermogravimetric analysis				

TOF Turnover frequency

XRD X-ray diffraction

# 1 Introduction

Adipic acid (AA) is an important commodity chemical with huge demand worldwide. The primary use of AA is served as a precursor for the synthesis of Nylon-6,6. At present, the industrial process for the production of AA involves the oxidation of cyclohexanone and/or cyclohexanol using excess HNO<sub>3</sub> [1, 2]. A serious problem of the current oxidation process is the generation of nitrogen oxides, especially N<sub>2</sub>O, which is generally considered as a nuisance causing global warming and ozone depletion [3]. Therefore, it is in urgent need to explore an environmental friendly oxidant to replace HNO<sub>3</sub>.

Hydrogen peroxide is one of the most promising green oxidants because the only byproduct from it is water. In particular, the oxidation of cyclohexanone to AA by  $H_2O_2$ can be achieved in the presence of various catalysts [3-15]. Among the reported catalysts, phosphotungstic acid (PTA) exhibits very high activity, but the application of PTA is limited due to its low stability under the catalytic condition and high solubility in the reaction mixture [16, 17]. These properties of PTA will bring many troubles to the product separation and catalyst recycling. A feasible strategy to improve the performance of PTA as well as other heteropolyacids is loading them onto solid supports like silica [18, 19], molecular sieves [20, 21], and metal oxides [22]. Nevertheless, the use of conventional support materials shows several disadvantages such as PTA leaching, PTA agglomeration, and deactivation by water [22]. Hence the stabilization of PTA using a suitable new-type support is highly desirable.

Metal-organic frameworks (MOFs), emerging as a new class of crystalline porous materials, have been regarded as potential and eminent candidates for the catalyst supports [23–25]. MOFs possess a series of unique properties such as high surface area, well-defined and tunable pore structure, and intriguing functionality [23, 26]. In recent years, the encapsulation of PTA in the pore of MOFs has attracted much attention because MOFs can act as hosts to confine and stabilize PTA in their cavity, thereby facilitating the product separation and catalyst recycling. For example, PTA was successfully encapsulated in the nanocages of MIL-101, and this composite material showed good catalytic activity in the oxidative desulfurization, although PTA leaching was observed in the catalyst recycling test [27]. MIL-100(Fe) was also used as a host to confine PTA, which exhibited satisfying performances for the oxidative desulfurization of gasoline [17] or the acetalization of benzaldehyde [28].

Despite the fact that MOFs have many advantages as catalyst supports, most MOFs show low stability owing to the reversible nature of coordination bonds [23]. The regeneration and reuse of MOFs-based catalysts is still far from that of the more robust and stable inorganic zeolites [26]. Considerable effort has been devoted to preparing MOFs with improved stability [29]. Gratifyingly, a very stable Zr-based MOF, UiO-66, was constructed by Cavka et al. and coworkers [30]. The structure of UiO-66 exhibits exceptional thermal, chemical and mechanical stability beyond most of other present MOFs. It has been reported to be stable up to 540 °C, and also stable to water and many organic solvents [30]. To the best of our knowledge, there are no reports on the oxidation of cyclohexanone to AA over a catalyst derived from UiO-66. Considering the high activity of PTA for the target reaction, we envisage using UiO-66 to encapsulate PTA for improved performances. In this paper, we report the encapsulation of PTA in the pore of UiO-66 by a onepot solvothermal method. The composite material (PTA@ UiO-66) was used as a catalyst for the oxidation of cyclohexanone to AA, which exhibited good AA yield and excellent reusability.

# 2 Experimental

# 2.1 Catalyst Preparation

UiO-66 samples were prepared following a recipe described previously [31] with some modifications. Briefly,  $ZrCl_4$  (0.7 g) and terephthalic acid (0.5 g) were dissolved in 60 mL *N*,*N*-dimethylformamide (DMF) by using ultrasound for 20 min. Then, the modulator acetic acid (3 mL) was added into the solution and dispersed by ultrasound for 1 min. The mixture was sealed in a Teflon-lined autoclave and kept in an oven at 120 °C under static conditions for 24 h. White precipitates were produced, and were isolated by centrifugation after cooled down to room temperature. The solids were successively washed with DMF and methanol to remove unreacted precursors and residual solvent. Finally, the obtained samples were dried at 160 °C overnight.

The encapsulation of PTA in UiO-66 was performed by a one-pot solvothermal method following the same procedure as that for pure UiO-66, besides PTA was added to the DMF solution during the synthesis process. The PTA weight content was 28.7% based on the measurement using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo iCAP 6300). The resulting catalyst was denoted as PTA@UiO-66.

#### 2.2 Characterization

The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-7000 diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =0.1541 nm), which operated at 40 kV and

60 mA. Fourier transform infrared spectroscopy (FT-IR) characterization was performed on a Bruker Tensor-37 spectrometer in the range of  $4000-400 \text{ cm}^{-1}$ . The spectra of samples were collected with diluting by KBr. The nitrogen adsorption and desorption were performed on a Quantachrome Autosorb-IQ-C apparatus. The samples were degassed under vacuum at 150 °C for 6 h before the adsorption measurements. The specific surface areas were evaluated 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 images were taken on a JEOL JSM-7800F scanning electron microscope (SEM). All the samples were mounted on a carbon tape and coated with a thin film of gold prior to measurement. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM-2100F microscope operating at 200 kV. The samples were ultrasonically suspended in ethanol and deposited on carbon-coated copper grids. The thermogravimetric analysis (TGA) measurements were carried out on a Hengjiu HCT-4 thermoanalyzer in air atmosphere with a flow rate of 50 mL min<sup>-1</sup>.

#### 2.3 Catalytic Reaction

The oxidation of cyclohexanone was carried out in a roundbottom flask fitted with a water condenser and a magnetic stirrer. In a typical reaction procedure, required amounts of catalyst and hydrogen peroxide (30 wt%) were mixed. After vigorous stirring for 10 min, cyclohexanone (5.9 g, 60 mmol) was introduced. The mixture in the flask was placed in a preheated oil bath at the reaction temperature, and stirred for 2 to 16 h. Then, the catalyst was separated by filtration. The filtrate was allowed to stand at 4 °C for 12 h, and the resulting precipitate was separated by suction filtration and washed with a small amount of cold water. Generally, the product was isolated as pure white crystals, whose FT-IR spectroscopy and melting point (152 °C) were consistent with the standard sample [6, 7]. In some cases, the product can be purified by recrystallization if necessary. The AA yield is calculated as the ratio of the isolated AA mass to the theoretical AA mass.

To test if further conversion occurs by the leached PTA from the catalyst, a hot filtration experiment was carried out. After reaction for 4 h, the catalyst was removed by a syringe filter, and the obtained reaction solution was stirred for another 6 h. In the recycling experiment, the catalyst obtained from filtration was washed thoroughly with methanol and dried in air overnight before the reusability test.

# **3** Results and Discussion

#### 3.1 Catalyst Characterization

The XRD patterns of pure UiO-66 and PTA@UiO-66 are shown in Fig. 1. The diffraction pattern of the as-synthesized UiO-66 is fairly consistent with the reported standard patterns [30, 31], indicating that the crystalline structure of UiO-66 is well constructed by the preparation method in this work. The diffraction pattern of PTA@UiO-66 is almost the same as that of pure UiO-66, suggesting that UiO-66 has a robust structure as a host for PTA nanoparticles. It should be noted that the characteristic diffraction peaks of PTA are not observed after the encapsulation, which indicates that PTA is evenly dispersed in the nanocages of UiO-66 [17]. The XRD pattern of the recycled catalyst is also presented in Fig. 1, and this will discuss in the section of catalyst reusability.

The FT-IR spectra of the catalyst samples are illustrated in Fig. 2. For UiO-66, the broad band centered at  $3420 \text{ cm}^{-1}$ can be ascribed to physisorbed water condensed inside the crystal cavities [32]. A small band around 1658 cm<sup>-1</sup> is associated with the C=O asymmetric stretch of the residual DMF within the pores of UiO-66, indicating that DMF is very difficult to completely eliminated [32]. The two intense bands around 1585 and 1395 cm<sup>-1</sup> represents the in- and out-of-phase stretching modes of the carboxylate group in terephthalic acid. A sharp band at 1508 cm<sup>-1</sup> corresponds to the vibration of C=C in the benzene ring. At lower frequencies, the bands (mainly around 820, 746, 659, 555 and 478 cm<sup>-1</sup>) due to OH and C–H bending are mixed with Zr–O modes. The spectra of PTA@UiO-66 and PTA@UiO-66 after the reaction cycles show similar bands to the UiO-66



**Fig. 1** XRD patterns of (*a*) UiO-66, (*b*) PTA@UiO-66, and (*c*) PTA@UiO-66 after the reaction cycles



**Fig.2** FT-IR spectra of (*a*) UiO-66, (*b*) PTA@UiO-66, and (*c*) PTA@UiO-66 after the reaction cycles

support, suggesting that the crystalline structure of UiO-66 is stably retained after the treatments. These FT-IR results are in good agreement with the XRD results. The successful incorporation of PTA can be verified from the four typical infrared bands of PTA with Keggin structures. As labeled in Fig. 2, the band at 1080 cm<sup>-1</sup> is attributed to the asymmetric vibrations of the P–O bond in PTA, while the bands at 982, 890, and 825 cm<sup>-1</sup> are ascribed to the terminal W=O<sub>a</sub>, edge-sharing W–O<sub>b</sub>–W, and corner-sharing W–O<sub>c</sub>–W, respectively [17]. For the PTA@UiO-66 sample, although the two bands at 890 and 825 cm<sup>-1</sup> are overlapped with the skeletal modes of pure UiO-66, the bands at 1080 and 982 cm<sup>-1</sup> are very obvious, indicating that PTA is definitely encapsulated in UiO-66.

The N<sub>2</sub> adsorption–desorption isotherms of UiO-66 and PTA@UiO-66 are presented in Fig. 3, and the corresponding textural properties are listed in Table 1. The UiO-66 sample basically exhibits a type-I isotherm, demonstrating the microporous feature of this material. The isotherm of PTA@UiO-66 is similar to that of UiO-66, but the volume of N<sub>2</sub> adsorbed decreased, further indicating the entry of PTA into the pores of UiO-66 reaches 1054 m<sup>2</sup> g<sup>-1</sup>, and the pore volume is 0.83 cm<sup>3</sup> g<sup>-1</sup>, which are in accord with the preparation method we consulted [31]. After PTA loading, a decrease of the BET surface area and pore volume are observed, which can be attributed to the occupation of nanocages by PTA nanoparticles.

Figure 4 provides the SEM and TEM images of PTA@ UiO-66. As can be seen from the SEM picture in Fig. 4a, the morphology of the composite catalyst is not very regular, showing near octahedral shapes with passivated edges. The obtained PTA@UiO-66 catalyst is composed



Fig.3  $N_2$  adsorption-desorption isotherms of (a) UiO-66 and (b) PTA@UiO-66

of intergrown aggregates rather than individual nanocrystals, which is in line with the result of a previous study [16]. Similar SEM micrograph was observed for the pure UiO-66 support, suggesting that the crystalline framework can be retained after PTA incorporation. The TEM images show the morphology more clearly (Fig. 4b, c). No conglomeration of PTA particles was observed, further verifying the good dispersity of PTA on the support as that has been demonstrated by XRD.

Figure 5 shows the TGA curves of UiO-66 and PTA@ UiO-66. The two curves display a similar profile, mainly including two stages of weight loss. The first weight loss between 50 and 350 °C is due to the release of adsorbed water and residual DMF solvent. The second weight loss in the range of 450 to 540 °C can be attributed to the thermal decomposition of organic ligand, leading to the formation of  $ZrO_2$  [30]. For PTA@UiO-66, the decomposition of the PTA Keggin structure into simple oxides may be accompanied with the decomposition of organic ligand [16]. When the temperature is above 550 °C, no weight loss was observed. According to the TGA results, the UiO-66 support is really thermal stable as reported [30], and the incorporation of PTA has no obvious influence on the thermal stability.

Table 1 Some textural properties of the catalyst samples

Catalysts	BET surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )
UiO-66	1054	0.83
PTA@UiO-66	952	0.80





Fig. 5 TGA curves of (a) UiO-66 and (b) PTA@UiO-66

# UiO-66 PTA@UiO-66 PTA Fig. 6 Catalytic performances of various catalysts for the oxidation of cyclohexanone with H2O2. Reaction conditions: catalyst 0.9 g,

cyclohexanone 60 mmol, H<sub>2</sub>O<sub>2</sub> (30 wt%) 270 mmol, 90 °C, 8 h

result confirms that the encapsulation of PTA by UiO-66 is a feasible strategy to seek advantages and avoid disadvantages of PTA. Interestingly, the pristine UiO-66 also showed a little catalytic activity, giving a yield of AA to 12.9%. This is probably owing to the formation of  $Zr^{IV}$ -peroxo groups on the surface of the MOF material by the interaction with

# 3.2 Catalytic Performance

The catalytic performances of UiO-66, PTA@UiO-66, and PTA are illustrated in Fig. 6. Notably, a high yield of AA (80.3%) was achieved by PTA@UiO-66, which was comparable to the yield of AA (88.7%) using PTA as catalyst. This



 $H_2O_2$  [33]. Oxygen from the Zr<sup>IV</sup>-peroxo groups can act as active species to participate in the oxidation reactions [17, 33]. In the light of the high activity of PTA@UiO-66, PTA is undoubtedly the main active centers for the oxidation of cyclohexanone to AA.

The reaction temperature significantly influenced the catalytic performance of PTA@UiO-66 (Fig. 7). As the temperature increased from 70 to 90 °C, the yield of AA increased rapidly, after which the yield began to decrease. It is well reported that  $H_2O_2$  will decompose into water and oxygen at high temperature [3, 11]. Hence the decrease of AA yield at a temperature above 90 °C is probably related to the rapid decomposition of  $H_2O_2$ . In addition, excessively high temperature may lead to the formation of byproducts such as succinic acid and glutaric acid, which can also account for the decrease of AA yield.

The theoretical molar ratio of  $H_2O_2$  to cyclohexanone is 3 for the target reaction, but the practical dosage of  $H_2O_2$ exceeded the theoretical value. This phenomenon can also be explained by the undesirable decomposition of  $H_2O_2$  as we discussed above. It can be seen in Fig. 8 that the optimal molar ratio of  $H_2O_2$  to cyclohexanone is 4.5. Too much of  $H_2O_2$  may cause side reactions, resulting in the decrease of AA yield.

The effect of reaction time on the catalytic performance of PTA@UiO-66 is presented in Fig. 9. Initially, the reaction rate rapidly increased within 6 h, after which it proceeded slowly. The highest yield of AA was achieved after 8 h of reaction. The further extension of reaction time led to reducing of AA yield, which is probably due to the formation of more byproducts [8]. In fact, the product obtained after reaction for 16 h was impure based on the melting point, and it had to be further purified by recrystallization.



Fig.7 Effect of reaction temperature on the oxidation of cyclohexanone with  $H_2O_2$  over PTA@UiO-66. Reaction conditions are the same as that in Fig. 6 but varied with reaction temperature



**Fig. 8** Effect of molar ratio of  $H_2O_2$  to cyclohexanone on the oxidation of cyclohexanone with  $H_2O_2$  over PTA@UiO-66. Reaction conditions are the same as that in Fig. 6 but varied with molar ratio of  $H_2O_2$  to cyclohexanone

The PTA loading also influences the catalytic performance of PTA@UiO-66, and the results are shown in Table S1. Initially, the yield of AA increased with increasing PTA loadings (from 10.2 to 28.7 wt%) because of more available active centers. However, keeping on increasing the PTA loading resulted in the decrease of AA yield. A reasonable explanation for this is that excessive amount of PTA can intensify the decomposition of  $H_2O_2$  [1, 2], leading to a part of  $H_2O_2$  consumed without participating in the oxidation of cyclohexanone.



Fig. 9 Effect of reaction time on the oxidation of cyclohexanone with  $H_2O_2$  over PTA@UiO-66. Reaction conditions are the same as that in Fig. 6 but varied with reaction time

# 3.3 Comparison of Catalytic Performance Between PTA@UiO-66 and Reported Solid Catalysts

The catalytic performance of PTA@UiO-66 is compared with other reported solid catalysts, and the corresponding results are summarized in Table 2. The turnover frequency (TOF) of the catalysts cannot be calculated because the specific active species are unknown in the literature. However, all the AA yield values presented in Table 2 are the highest one as reported in the corresponding references. Therefore, the catalytic performance can be compared as far as the AA yield is concerned. The optimal yield of AA in the present work was 80.3%, which was much higher than most of the reported values using zeolites, TIPO-1, Al<sub>2</sub>O<sub>3</sub>@Fe<sub>2</sub>O<sub>3</sub>, and polyoxometalates as catalysts. Although 75.5% AA yield was achieved over  $H_1Co_1PMo_{12}O_{40}$ , the reaction time was much longer (20 h). Moreover, this polyoxometalate could not be separated by a simple filtration because of the formation of a homogeneous mixture after the reaction [6]. It is worth mentioning that, besides TOF and the AA yield, the average AA productivity can be also used to compare the catalytic activity. In this case, we just need to take the weight of PTA in the PTA@UiO-66 catalyst into account. The AA productivity in the present work is 23.2 mmol  $g^{-1} h^{-1}$  as calculated, which is also the highest value for all the catalysts listed in Table 2. Accordingly, PTA@UiO-66 shows a better function as compared with other heterogeneous solid catalytic systems under the investigated reaction conditions.

## 3.4 Catalyst Reusability

To evaluate the stability of the PTA@UiO-66 catalyst, the reusability test was performed under the optimized reaction conditions. After each run of the reaction, the catalyst was recovered according to the procedure described in the Sect. 2. It can be observed from Fig. 10 that there is no



Fig. 10 Catalytic reusability of PTA@UiO-66 for the oxidation of cyclohexanone with  $H_2O_2$ . Reaction conditions are the same as that in Fig. 6

significant decrease of AA yield after fifth successive reaction cycles. Thus, PTA@UiO-66 exhibited good catalytic stability for the oxidation of cyclohexanone to AA using H<sub>2</sub>O<sub>2</sub> as oxidant. What's more, the characterization results demonstrate that PTA@UiO-66 can maintain its skeleton structure after the oxidation reaction. The XRD pattern of the recycled PTA@UiO-66 catalyst in Fig. 1 shows that all the crystalline phases are matched well with that of the fresh catalyst. The FT-IR spectrum of the recycled catalyst is almost identical to that of the fresh catalyst (Fig. 2). In addition, besides the bands of PTA with Keggin structures, the FT-IR spectra of UiO-66 and PTA@UiO-66 after the reaction cycles seems to differ slightly. This indicates that H<sub>2</sub>O<sub>2</sub> doesn't show obvious damage to the UiO-66 material surface sites along the reaction despite the formation of Zr<sup>IV</sup>–peroxo groups as discussed above.

Catalysts	Conditions				Yield of AA (%)	References
	Catalyst amount (g)	CHO amount (mmol)	Tempera- ture (°C)	Time (h)		
PTA@UiO-66	0.9 <sup>a</sup>	60	90	8	80.3	This work
HTS-1	0.05	10	90	8	16.8	[4]
TIPO-1	0.04	10	80	8	60.7	[5]
$H_1Co_1PMo_{12}O_{40}$	0.0625	15	90	20	75.5	[6]
(NH <sub>4</sub> ) <sub>0.5</sub> Ni <sub>1.25</sub> PMo <sub>12</sub> O <sub>40</sub>	0.0625	30	90	20	45.0	[7]
Al <sub>2</sub> O <sub>3</sub> @Fe <sub>2</sub> O <sub>3</sub>	0.015	5	80	24	59.3	[8]
HTS	0.5	100	80	6	17.0	[10]
$K_6 P_2 M o_6 W_{12} O_{62}$	0.125	15	90	20	58.8	[11]

*CHO* cyclohexanone, *HTS* hollow titanium silicate zeolite, *TIPO-1* oxyfluorinated titanium phosphate <sup>a</sup>PTA content=0.26 g

Table 2Comparison of<br/>catalytic performance betweenPTA@UiO-66 and reported<br/>solid catalysts



A hot filtration experiment was carried out to see if further conversion occurs by the leached PTA from the catalyst, and the results are shown in Fig. 9. The catalytic reaction almost stopped after the removal of the catalyst, indicating that the oxidation of cyclohexanone occurred on the surface of the PTA@UiO-66 catalyst rather than in the solution.

The excellent immobilization effect of the UiO-66 support for PTA is worthy of further comment. The pore system of UiO-66 is constructed by two types of cages with different sizes (free apertures of ~ 1.4 nm and ~ 1.0 nm for the octahedral and tetrahedral cages, respectively), which are joined together through triangular windows with a size of ~ 0.6 nm [17]. PTA has a molecular size of ~ 1.2 nm [34]. Accordingly, PTA can be encapsulated in the larger cages of UiO-66 but cannot leak out from the windows. That is to say, UiO-66 has a well matched window size to confine PTA molecule in its nanocages, which can be responsible for its excellent immobilization effect for PTA.

To verify the window size of UiO-66 is important for its good catalytic stability, a well-established MOF (MIL-101) with larger window size was employed as support for comparison. PTA@MIL-101 with a same PTA loading (29.1 wt%) was prepared according to previous works [17, 27], and its catalytic reusability was evaluated under the same conditions using for PTA@UiO-66 (Fig. S1). Obviously, the catalytic stability of PTA@MIL-101 for the oxidation of cyclohexanone to AA was inferior, leading to low AA yield (42.5%) only after three recycling runs. The ICP-AES tests showed that the leaching of PTA into the reaction solution was about 45%. This poor immobilization effect of MIL-101 for PTA is mainly due to its larger window size  $(1.6 \times 1.6 \text{ nm}^2)$ , which results in a serious leaching of PTA during the reaction process [17]. For PTA@UiO-66, the leaching of PTA can be effectively avoided because of its well matched window size as discussed earlier.

In short, all the above results have confirmed the good structural stability of PTA@UiO-66, which is especially important for its practical uses.

#### 3.5 Plausible Reaction Mechanism

As discussed above, the oxidation of cyclohexanone to AA over PTA@UiO-66 is really heterogeneous which occurs on the catalyst surface. To investigate the possible reaction mechanism, the mixture after the reaction was detected by GC–MS. Besides AA, 6-hydroxyhexanoic acid and a small

amount of ε-caprolactone were found. Combining the established reaction pathway for the oxidation of cyclohexanone to AA over other tungsten compounds [2, 3, 13], a plausible reaction mechanism is proposed and shown in Fig. 11. The first step is a typical Baeyer–Villiger oxidation process, which occurs on the oxidation active sites of PTA@UiO-66. These oxidation active sites may exist as peroxo species of tungsten such as  $[WO(O_2)_2(OH)_2]^{2-}$ , originating from the oxidation of PTA in the presence of  $H_2O_2$  [2, 3, 13]. The  $\varepsilon$ -caprolactone obtained in the first step is successively hydrolyzed to 6-hydroxyhexanoic acid. This hydrolysis step can readily take place on the acid sites of PTA@UiO-66 (including both Brønsted and Lewis acid sites). Finally, AA is formed by the oxidation of hydroxyl group in 6-hydroxyhexanoic acid, which can also proceed on the oxidation active sites.

# **4** Conclusions

The encapsulation of PTA in a stable MOF UiO-66 was achieved by a one-pot solvothermal method. The as-synthesized PTA@UiO-66 composite material demonstrated to be an efficient catalyst for the green oxidation of cyclohexanone to AA using  $H_2O_2$  as oxidant. High isolated yield of AA was obtained under mild reaction conditions without the addition of organic solvent or phase transfer agent. PTA@UiO-66 exhibited high stability and excellent reusability in the oxidation process, which provides the possibility to its further industrial applications.

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#### **Compliance with Ethical Standards**

Conflict of interest The authors declare no conflict of interest.

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