

# Oxidation of cyclohexane with a new catalyst $(\text{TPPFe}^{\text{III}})_2\text{O}$ supported on chitosan

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## Abstract

The chitosan-supported  $\mu$ -oxo dimeric iron tetraphenylporphyrin  $((\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS})$  was prepared and its ability to catalyze aerobic oxidation of cyclohexane into the corresponding ketone and alcohol in the absence of any co-reductants and solvents was investigated. Under the optimum reaction conditions of 398 K and 0.6 MPa, the heterogeneous catalytic system gave about 90% selectivity of ketone and alcohol at 13.0% yield and a catalyst turnover number of  $1.03 \times 10^5$ . The supported catalyst can be efficiently reused at least six times. The changes in various catalytic parameters with reaction temperature, pressure and the amount of catalyst were investigated. Compared with the corresponding unsupported catalyst,  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  was more robust towards destruction by oxygen and provided better catalysis for cyclohexane oxidation.

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**Keywords:** Chitosan;  $\mu$ -Oxo dimeric iron tetraphenylporphyrin; Cyclohexane oxidation; Air

## 1. Introduction

Metalloporphyrins have been successfully used as models for the cytochrome P-450 enzyme with respect to the oxidation and hydroxylation of hydrocarbons [1–3]. In order to understand the mechanism of cytochrome P-450 monooxygenase and apply metalloporphyrins in industrial processes in practice, much work has been devoted to the homogenous and heterogenous catalytic system of metalloporphyrins, especially the chemical modification of the metalloporphyrin microenvironment in studies of cytochrome P-450 models [4–14]. One of the important ways is to anchor the metalloporphyrins onto solid supports. The supported metalloporphyrins can overcome the disadvantages of the homogenous catalytic system, which is easily deactivated and is recovered only with difficulty from the reaction mixture which leads to many restrictions in large-scale practical processes [15]. In addition, metalloporphyrins are often expensive. In models of the metalloporphyrin microenvironment that employ polysaccharides such as chi-

tosan, chitin and cellulose as supports [16–18], we found that the supports exerted different effects on the catalytic activity and selectivity of the metalloporphyrins, because they can provide various microenvironments for the metalloporphyrin catalyst.

Studies of a catalytic system consisting of mono-/bis-metalloporphyrin and molecular oxygen [19–23] have suggested the worth of further research on polysaccharide-supported metalloporphyrins as catalysts for aerobic oxidation of hydrocarbons. It is generally accepted that  $\mu$ -oxo dimer metalloporphyrins are catalytically inactive [24,25]. However, these  $\mu$ -oxo metallocomplexes have been used to catalyze hydroxylation of isobutene and propane [9,26]. Poltowicz et al. [23] and Guo et al. [27,28] have observed the catalytic activity of the  $\mu$ -oxo manganese (or iron) porphyrins with (or without) electron-donating/-withdrawing substituents in the oxidation of cyclooctane, ethylbenzene and cyclohexane with air. In the present study, we have used chitosan-supported  $\mu$ -oxo dimeric iron tetraphenylporphyrin  $(\text{TPPFe}^{\text{III}})_2\text{O}$  as catalyst for oxidation of cyclohexane with air in the absence of co-reductants and solvents to gain a better understanding of the possibility of hydrocarbon oxidation catalyzed by the supported catalyst.

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## 2. Experimental

### 2.1. Instruments and reagents

UV–vis spectra were recorded on a Perkin-Elmer L-17 spectrometer. GC analysis of catalytic oxidation products was accomplished with a Shimadzu GC-16A chromatograph equipped with a 0.5 mm i.d.  $\times$  25 m PEG20000 capillary column and a flame ionization detector. The reactor was a KCF-10 500-ml autoclave fitted with a magnetic stirrer and a CYS-1 digital oxygen meter.

All reagents and solvents were of analytical grade and were obtained commercially.  $\text{TPPFe}^{\text{III}}\text{Cl}$  and  $(\text{TPPFe}^{\text{III}})_2\text{O}$  were synthesized according to published procedures [29–31]. No impurities were found in the cyclohexane by GC analysis before use.

### 2.2. Preparation and analysis of chitosan-supported $(\text{TPPFe}^{\text{III}})_2\text{O}$

A mixture of 100 ml of 2% acetic acid and 2 g chitosan in a three-neck flask was stirred electromagnetically at 298 K for 15 min. Then 100 ml distilled water was added to form a colloidal solution. A solution of 2.5% NaOH was slowly added to neutralize the reaction solution (pH 8.5). Then 0.0600 g  $(\text{TPPFe}^{\text{III}})_2\text{O}$  dissolved in 100 ml benzene was slowly added to the reaction vessel. This was stirred for 2 h, then the reaction was stopped and the solution was filtered. The filter cake was washed with distilled water and then with alcohol, and was extracted with benzene in a Soxhlet apparatus until no  $(\text{TPPFe}^{\text{III}})_2\text{O}$  could be detected in benzene, as measured on a UV–vis spectrophotometer. The filter cake was dried at 333 K and the light-green solid (1.899 g) obtained was analyzed to determine the amount of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  in the solid product. The amount of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  supported per 1 g of chitosan was  $4.43 \times 10^{-6}$  mol, as determined by UV–vis spectrophotometry [32].

### 2.3. Cyclohexane oxidation catalyzed by chitosan-supported $(\text{TPPFe}^{\text{III}})_2\text{O}$

Except where special explanation is given, all cyclohexane oxidations were performed according to the following procedures. Into a 500-ml autoclave reactor were added a measured amount of chitosan-supported  $(\text{TPPFe}^{\text{III}})_2\text{O}$  and 350 ml of cyclohexane. The mixture was stirred and heated to 398 K. Then air was continuously pumped into the reaction system and the pressure was kept at 0.6 MPa. The flow of air was measured with a rotameter, and the oxygen concentration of the tail gas was determined with a CYS-1 digital oxygen detector. Samples of the reaction mixture were identified by GC–MS and were quantified by GC using chlorobenzene as the internal standard [33]. After the oxidation was terminated, i.e., when the reduction of oxygen content in the tail gases ceased, the supported catalyst was recovered by simple separation from the reaction mixture followed by washing with ethanol and drying in air, and used in subsequent cyclohexane oxidation reactions.

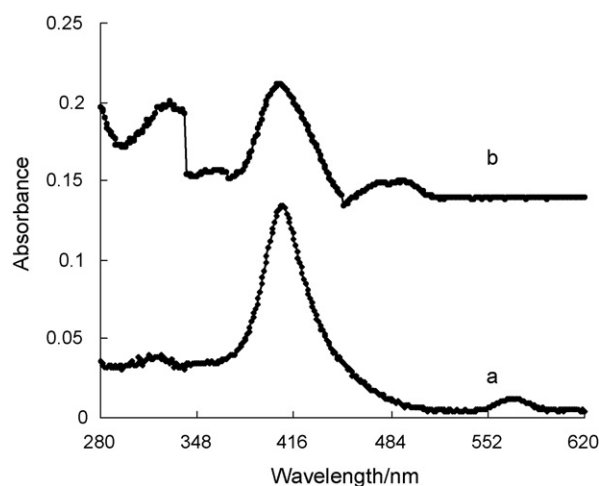


Fig. 1. UV–vis spectra at room temperature. (a) Chloroform solution of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  and (b) in glycerol mull  $(\text{TPPFe}^{\text{III}})_2\text{O}$  on chitosan.

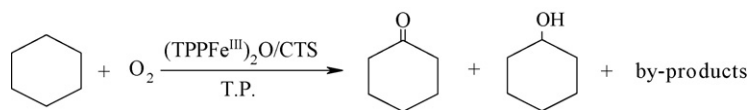
## 3. Results and discussion

### 3.1. Characterization of the supported catalyst

When  $(\text{TPPFe}^{\text{III}})_2\text{O}$  was immobilized on white chitosan, a light-green solid was obtained. It indicates the presence of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  on the support. This was also confirmed by UV–vis spectroscopy for the supported catalyst. The spectra for  $(\text{TPPFe}^{\text{III}})_2\text{O}$  in chloroform solution and  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  in glycerol mull are shown in Fig. 1. In the chloroform solution of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  (Fig. 1a) a Soret band was visible at 407 nm. After immobilization of  $(\text{TPPFe}^{\text{III}})_2\text{O}$  on chitosan, no significant red shift in the Soret band position was observed in the UV–vis spectrum (Fig. 1b), indicating that the porphyrin ring was not modified during the anchoring procedure. There were two bands present at 479 and 489 nm which are different from the two Q bands at 572 and 612 nm for the  $(\text{TPPFe}^{\text{III}})_2\text{O}$  (Fig. 1a). In addition, the chloroform extractions from the powder of the supported catalysts showed the same absorption bands as those shown in Fig. 1a. These indicate that the electronic absorption spectra for  $(\text{TPPFe}^{\text{III}})_2\text{O}$  in the supported catalyst were only interfered by chitosan. Hence, the macrocyclic complex is still retained after immobilization on the support.

### 3.2. Chitosan-supported $(\text{TPPFe}^{\text{III}})_2\text{O}$ catalysis of cyclohexane oxidation

$(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  was able to catalyze oxidation of cyclohexane into cyclohexanone and cyclohexanol (Scheme 1). The by-products were dicyclohexyl, cyclohexyl hydrogen peroxide, hexanedioic acid and esters. GC–MS and chemical analysis data showed that there were very small amounts of dicyclohexyl and cyclohexyl hydrogen peroxide, all products being the same as those of cyclohexane oxidation catalyzed by  $(\text{TPPFe}^{\text{III}})_2\text{O}$ . In contrast, cyclohexanone and cyclohexanol were not produced after aerobic oxidation for 24 h either in the absence of  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  or in the presence of CTS alone. Therefore, we consider that the  $(\text{TPPFe}^{\text{III}})_2\text{O}$  component



Scheme 1.

in the supported catalyst plays a catalytic role in cyclohexane oxidation. (TPPFe<sup>III</sup>)<sub>2</sub>O can generate [TPPFe<sup>IV</sup>=O]<sup>•+</sup> when under illumination and can accomplish the photocatalytic reaction [34]. The catalytic mechanism of the metalloporphyrins is known to include electrocatalysis and photocatalysis, and [TPPFe<sup>IV</sup>=O]<sup>•+</sup> is held to be a key catalytic intermediate in hydrocarbon oxidation catalyzed by iron tetraphenylporphyrin [28,35–40].

### 3.3. Effect of reaction time on cyclohexane oxidation

The amount of main product and the selectivity for ketone and alcohol were determined in the oxidation catalyzed by (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS. In general, the yields of cyclohexanone and cyclohexanol increased with reaction time (Fig. 2): from 0 to 2 h, the increment of ketone and alcohol was slight, because the supported catalyst was in the induction and activation period and cyclohexane was not oxidized into the main products; after 2 h, the amount of the main products sharply increased; it reached the maximum, more than 15 mol%, after about 4 h. The yields and the selectivity for ketone and alcohol gradually decreased as the oxidation proceeded further, probably as a result of over-oxidation of cyclohexanone and cyclohexanol into by-products. Hence, a reaction time of 4 h gave the best results (15.5% yield and 90% selectivity for ketone and alcohol) in the catalysis by (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS of aerobic oxidation of cyclohexane into the corresponding cyclohexanone and cyclohexanol.

### 3.4. Effect of reaction pressure on cyclohexane oxidation

Table 1 lists the effect of reaction pressure on the catalytic activity, yields and catalyst turnover in cyclohexane oxidation

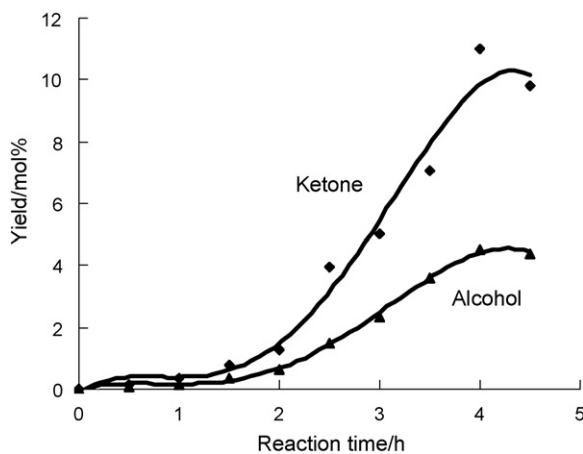


Fig. 2. Changes in main product yields with reaction time for cyclohexane oxidation catalyzed by (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS. Catalyst: 1 g; cyclohexane: 350 ml; temperature: 398 K; pressure: 0.6 MPa.

catalyzed by (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS. When the air pressure was 0.6 MPa, the supported catalyst had the highest activity ( $1.60 \times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ ), the largest turnover number ( $8.6 \times 10^4$ ) and the highest yield for the main products (14.2%). In general, the higher the air pressure, the higher the dioxygen solubility in the liquid phase. Hence, at a lower air pressure, the concentration of O<sub>2</sub> in cyclohexane was so low that little oxygen could be activated by (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS; this resulted in the lower catalytic activity, yield and catalyst turnover number (Table 1). However, excessive air pressure could have two consequences: excess soluble oxygen directly destroyed (TPPFe<sup>III</sup>)<sub>2</sub>O and even the support; for example, the recovered solid catalyst was found to be darkened on its surface, or (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS activated too much oxygen to oxidize ketone and alcohol deeply into by-products. Therefore, air pressure in the gas–liquid–solid phase reaction system indirectly influenced the activation of O<sub>2</sub> and further the distribution of products.

### 3.5. Effect of reaction temperature on cyclohexane oxidation

The effects of the reaction temperatures on the catalytic activity of the supported catalyst, the yield of main products and the catalyst turnover number in the cyclohexane oxidation are shown in Table 2. The catalytic activity at 398 K was almost five times as high as that at 393 K, and almost four times that at 403 K. The reason is probably that at the lowest temperature the energy was not sufficient for the activation of oxygen molecules or the catalytic circulation, and that at the highest temperature some of the (TPPFe<sup>III</sup>)<sub>2</sub>O, and even of the chitosan, was burned out and the main products were oxidized in excess. Consequently, at a high temperature, (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS easily lost activity and the catalytic circulation did not persist. At the optimum reaction temperature (398 K) for cyclohexane oxidation catalyzed by the supported catalyst, the yield for cyclohexanone and cyclohexanol was 14.2% and the mole turnover number of the catalyst reached  $8.6 \times 10^4$ .

Table 1  
Effect of pressure on the cyclohexane oxidation<sup>a</sup>

Pressure (MPa)	Catalytic activity ( $\times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ )	Yield (mol%)	Cyclohexanone (%)	Turnover numbers ( $\times 10^5$ )
0.5	0.93	7.21	49.34	0.61
0.6	1.60	14.20	51.85	0.86
0.7	1.29	10.06	49.20	0.75

Yield is total yield of cyclohexanone and cyclohexanol. Turnover number is based on the mmol of catalyst used.

<sup>a</sup> Experimental conditions: chitosan-supported catalyst (containing 3 mg (TPPFe<sup>III</sup>)<sub>2</sub>O); cyclohexane: 350 ml; temperature: 398 K; reaction time: 4 h.

Table 2  
Effect of temperature on the cyclohexane oxidation<sup>a</sup>

Temperature (K)	Catalytic activity ( $\times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ )	Yield (mol%)	Cyclohexanone (%)	Turnover numbers ( $\times 10^5$ )
393	0.30	2.36	34.53	0.43
398	1.60	14.20	51.85	0.86
403	0.43	3.31	38.43	0.57

Yield is total yield of cyclohexanone and cyclohexanol. Turnover number is based on the mmol of products per mmol of catalyst used.

<sup>a</sup> Experimental conditions: chitosan-supported catalyst (containing 3 mg  $(\text{TPPFe}^{\text{III}})_2\text{O}$ ); cyclohexane: 350 ml; pressure: 0.6 MPa; reaction time: 4 h.

Table 3  
Effect of the amount of catalyst on the cyclohexane oxidation<sup>a</sup>

$(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$ (g)	Catalytic activity ( $\times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ )	Yield (mol%)	Cyclohexanone (%)	Turnover numbers ( $\times 10^5$ )
0.5	1.60	14.20	51.85	0.86
1.0	0.87	15.50	71.13	0.96
1.5	0.39	9.10	68.02	0.88

Yield is total yield of cyclohexanone and cyclohexanol. Turnover number is based on the mmol of products per mmol of catalyst used.

<sup>a</sup> Experimental conditions: cyclohexane: 350 ml; pressure: 0.6 MPa; reaction time: 4 h.

### 3.6. Effect of the amount of catalyst on cyclohexane oxidation

The amount of catalyst influenced cyclohexane oxidation at optimum temperature and air pressure. The use of 1 g of  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$ , which contained 6 mg of  $(\text{TPPFe}^{\text{III}})_2\text{O}$ , brought about the best results, with 15.5% yield, 71.1% cyclohexanone selectivity and  $9.6 \times 10^4$  in turnover number (Table 3). The lowest amount of catalyst gave the highest catalytic activity and a lower yields of ketone and alcohol, whereas a suitable amount of catalyst adequately and efficiently catalyzed the oxidation of cyclohexane into the main products, enhancing the yields and the proportion of ketone, because more amount of which was transformed from the oxidation of ethanol under the condition (i.e., 1.0 g catalyst) than the others (see Table 3 and Fig. 2). Using more amount of catalyst results in lower yield. We still found that the use of more and more catalyst did not lead to the increase in cyclohexane conversion, and inversely, the decrease in the corresponding conversion, yield of main products and catalyst turnover number. The catalytic behavior is similar to the so-called ‘catalyst inhibitor conversion’ phenomenon reported by Black [41]. Recently, Guo et al. has also discovered a similar phenomenon [42].

### 3.7. Reuse of $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$ for catalysis of cyclohexane oxidation

The performance of the reused supported catalyst was studied in repeated cyclohexane oxidations. The reaction was carried out as described above. At the end of the oxidation,  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  was recovered by filtration, washed with alcohol, and reused. After used six consecutive times, the supported catalyst retained its catalytic activity at around  $0.73 \times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ .  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  was an efficient catalyst for each run of the cyclohexane oxidation, with 13% yield,  $1.03 \times 10^5$  in turnover number and a 2/1 yield ratio of

ketone/alcohol (Table 4). Hence,  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  performed well as a reusable catalyst.

### 3.8. Differences between $(\text{TPPFe}^{\text{III}})_2\text{O}$ and $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$ in catalysis

$(\text{TPPFe}^{\text{III}})_2\text{O}$  and  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  differed in their catalysis of the oxidation of cyclohexane (Table 5). The higher the catalytic activity, the better the yield and the turnover numbers; these were  $0.73 \times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ , 13.0 mol% and  $1.03 \times 10^5$  for the supported catalyst, respectively, higher than those of the unsupported catalyst. We suggest that since chitosan provided the nitrogenous and oxygenous microenvironment for the  $(\text{TPPFe}^{\text{III}})_2\text{O}$  catalyst, resulted in the different catalysis for cyclohexane oxidation between the two catalysts, and that chitosan with the polar groups, such as amido and hydroxyl, physically adsorbed  $\mu$ -oxo dimeric iron porphyrin, thereby allowing recovery and reuse of  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$  for six repeated oxidations, in contrast to unsupported  $(\text{TPPFe}^{\text{III}})_2\text{O}$  which could be used as a catalyst only once and was then exhausted.

Table 4  
The results of cyclohexane oxidation catalyzed by reused  $(\text{TPPFe}^{\text{III}})_2\text{O}/\text{CTS}$ <sup>a</sup>

Runs	Catalytic activity ( $\times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ )	Yield (mol%)	Cyclohexanone (%)	Turnover numbers ( $\times 10^5$ )
1	0.87	15.50	71.13	0.96
2	0.67	11.94	71.22	1.01
3	0.68	12.01	71.12	1.01
4	0.74	13.19	62.20	1.10
5	0.69	12.26	68.54	1.03
6	0.72	12.78	66.97	1.07
Average	0.73	12.95	68.53	1.03

Yield is total yield of cyclohexanone and cyclohexanol. Turnover number is based on the mmol of products per mmol of catalyst used.

<sup>a</sup> Experimental conditions: catalyst (containing 6 mg  $(\text{TPPFe}^{\text{III}})_2\text{O}$ ); cyclohexane: 350 ml; temperature: 398 K; pressure: 0.6 MPa; reaction time: 4 h.

Table 5  
Comparison (TPPFe<sup>III</sup>)<sub>2</sub>O with (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS in catalysis for cyclohexane oxidation

Catalyst (mg)	Catalytic activity ( $\times 10^4 \text{ mol}^{-1} \text{ h}^{-1}$ )	Yield (mol%)	Cyclohexanone (%)	Turnover numbers ( $\times 10^5$ )
(TPPFe <sup>III</sup> ) <sub>2</sub> O <sup>a</sup>	0.61	8.10	67.85	0.31
(TPPFe <sup>III</sup> ) <sub>2</sub> O/CTS <sup>b</sup>	0.73	12.95	68.53	1.03

Experimental conditions: cyclohexane: 350 ml; temperature: 398 K; pressure: 0.6 MPa; reaction time: 4 h.

<sup>a</sup> Amount of catalyst is 6 mg.

<sup>b</sup> Average values for six times reuse.

#### 4. Conclusions

We have shown that a new supported catalyst, (TPPFe<sup>III</sup>)<sub>2</sub>O/CTS, which is very easily prepared from commercially available compounds, can efficiently catalyze aerobic oxidation of cyclohexane into ketone and alcohol, and can be recycled several times. The catalyst resists destructive oxidation and is easily recovered by simple isolation from the reaction mixture. It is probably more suitable for industrial use than the corresponding unsupported catalyst.

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