

# Catalysis of cyclohexane oxidation with air using various chitosan-supported metallotetraphenylporphyrin complexes

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## Abstract

Three types of chitosan-supported metallotetraphenylporphyrins were prepared at room temperature by loading iron, cobalt and manganese tetraphenylporphyrins (TPP) onto chitosan. These were employed as catalysts for the aerobic oxidation of cyclohexane in the absence of additives and solvents. Three chitosan-supported and three simple metallotetraphenylporphyrins (MTTPs) showed different catalytic activity for the oxidation of cyclohexane. Under optimum reaction conditions of 418 K and 0.8 MPa, both the cobalt TPP and the corresponding chitosan-supported complex showed the highest catalytic activity, but lower ketone and alcohol selectivity. The reverse situation was observed for the iron TPP and the corresponding chitosan-supported complex. For cyclohexane oxidation, there was a difference in catalytic activity and ketone and alcohol selectivity between the simple MTTPs or the corresponding chitosan-supported complexes. These differences in catalysis probably result from two factors: the potential for O<sub>2</sub> activation of the different bivalent metal ions, which affects the activity of the corresponding chitosan-supported MTTPs and chitosan assistance of the MTTP catalysis.

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**Keywords:** Chitosan; Metallotetraphenylporphyrins; Cyclohexane; Oxidation; Air

## 1. Introduction

Immobilization of metalloporphyrins onto various supports, which can be inorganic, organic or hybrid materials, not only facilitates catalyst recovery and reuse but also improve catalytic activity and selectivity because of the influence of the microenvironment of the support [1–4]. In recent years, many studies have focused on exploring the relationship between the structure of porphyrin and the corresponding catalytic efficiency [5,6]. In particular, the effect of the support's microenvironment on the catalytic properties of metalloporphyrins has been investigated [7,8]. In fact, when metalloporphyrins are anchored on solid materials, their resistance to oxidation, redox potential and ambience are different from those of the original. This results

in important changes in catalysis of hydrocarbon oxidation and influences the distribution of products.

We previously prepared chitosan-supported iron and cobalt tetraphenylporphyrins (TPPs) by the method of physical adsorption at room temperature and used them as catalysts for cyclohexane oxidation with air [9,10]. The catalytic activity of metallotetraphenylporphyrins (MTTPs) and their selectivity for the main cyclohexane oxidation products can be greatly enhanced by using a chitosan support. However, there are distinct differences in the catalytic activity of different chitosan-supported MTTPs. This paper reports a recent study on differences in catalysis among chitosan-supported iron, manganese and cobalt TPPs used as catalysts for the aerobic oxidation of cyclohexane in the absence of additives and solvents. The differences were investigated in terms of the selectivity, catalyst turnover and cyclohexane conversion. The catalytic activity of the supported catalysts and the selectivity for ketone and alcohol appear to be dependent on the microenvironment of chitosan and the character of the catalytic center of the MTTPs.

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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 performed on a Shimadzu GC-16A chromatograph. The reactor was a model KCF-10 500-ml high-pressure tank fitted with a magnetic stirrer and a model CYS-1 digital oxygen detector.

All reagents and solvents used were of analytical grade and were obtained commercially. Iron, cobalt and manganese TPPs were synthesized according to published procedures [11,12]. No impurities were found in the cyclohexane by GC analysis before use.

### 2.2. Preparation and analysis of chitosan-supported TPPs

A mixture of 100 ml of 0.01 mol/l hydrochloric acid and 2 g of 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 1% NaCO<sub>3</sub> was slowly added to neutralize the reaction solution (pH 6.5–7.0). Then 0.1000 g of chloro (tetraphenylporphyrinato) manganese dissolved in 100 ml of chloroform was slowly added to the reaction vessel. After stirring for 2 h, the reaction was stopped and the solution was filtered. The filter cake was washed with distilled water and then alcohol, and was extracted using chloroform in a Soxhlet apparatus until no manganese TPP could be detected in the chloroform, as measured on a UV–vis spectrophotometer. A green solid (1.978 g) was obtained after drying the filter cake at 333 K, which was analyzed to determine the amount of chloro (tetraphenylporphyrinato) manganese in the solid product. Chitosan-supported chloro (tetraphenylporphyrinato) iron (III) and (tetraphenylporphyrinato) cobalt (II) were prepared according to a literature method [10,13]. The amount of chloro (tetraphenylporphyrinato) iron (III) and manganese (III), and (tetraphenylporphyrinato) cobalt (II) supported per 1 g of chitosan was 4.47, 4.35 and 4.26 × 10<sup>-5</sup> mol, respectively, as determined by UV–vis spectrophotometry [14].

### 2.3. Cyclohexane oxidation catalyzed by chitosan-supported Fe, Co and Mn TPPs

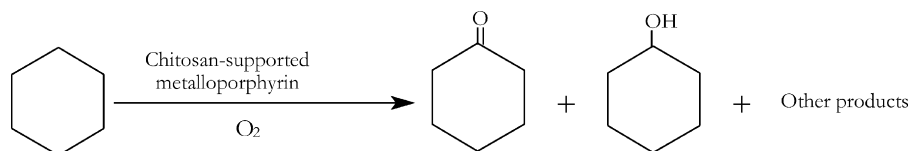
Into a 500-ml autoclave reactor were added chitosan-supported MTPP (containing 7.1 × 10<sup>-6</sup> mol of MTPP) and 350 ml of cyclohexane. The mixture was stirred and heated to 418 K. Then air was continuously pumped into the reaction system and the pressure was kept at 0.8 MPa. The flow of air was

measured using a rotameter, and the oxygen concentration of the tail gas was determined using a model CYS-1 digital oxygen detector. Samples of the reaction mixture were identified using GC–MS and were quantified by GC using chlorobenzene as the internal standard [15]. After oxidation was complete, the solid catalysts were simply recovered by separating them from the reaction mixture. The catalysts were then washed with alcohol and dried in air, and were used in subsequent cyclohexane oxidation reactions.

## 3. Results and discussion

### 3.1. Chitosan-supported MTPP catalysis of cyclohexane oxidation

The cyclohexane oxidation reaction catalyzed by chitosan-supported chloro (tetraphenylporphyrinato) iron or manganese and (tetraphenylporphyrinato) cobalt with air was as follows:



When cyclohexane oxidation was catalyzed using unsupported MTPPs, the main oxidation products were also cyclohexanone and cyclohexanol, and the other products were cyclohexyl hydrogen peroxide, hexanedioic acid and esters, as confirmed by GC–MS analysis. The experimental results indicate that the catalysis of aerobic oxidation of cyclohexane was independent of the catalysts, but their catalytic activity and selectivity were quite different.

### 3.2. Differences in catalysis by Fe, Co and Mn TPPs for cyclohexane oxidation

To investigate the influence of chitosan on the catalytic activity and selectivity for cyclohexane oxidation catalyzed by chloro (tetraphenylporphyrinato) iron or manganese, and (tetraphenylporphyrinato) cobalt, the simple MTPPs were used as catalysts under the same reaction conditions for catalytic oxidation of cyclohexane with air. Fig. 1 displays the changes in mole percent of cyclohexanone and cyclohexanol with reaction time. First, it is evident that between 0.5 and 1.5 h, the total mole percent (ketone + alcohol) for cyclohexane oxidation catalyzed by cobalt TPP was greater than that catalyzed by iron or manganese TPP. Second, because cobalt TPP activated oxygen molecules more quickly than the other two catalysts, the time required to achieve a high mole percent of ketone and alcohol was shorter. Third, the rate constant for cyclohexanone production ( $k_{\text{cyclohexanone}}$ ) was greatest for cobalt TPP, as shown in Table 1. Although the corresponding  $k_{\text{cyclohexanol}}$  was the lowest value (0.010 h<sup>-1</sup>), cobalt TPP had the highest cyclohexane conversion and the largest turnover number of 1.96% and 0.86 × 10<sup>4</sup>, respectively (Table 1). Fig. 2 shows changes in cyclohexane conversion and

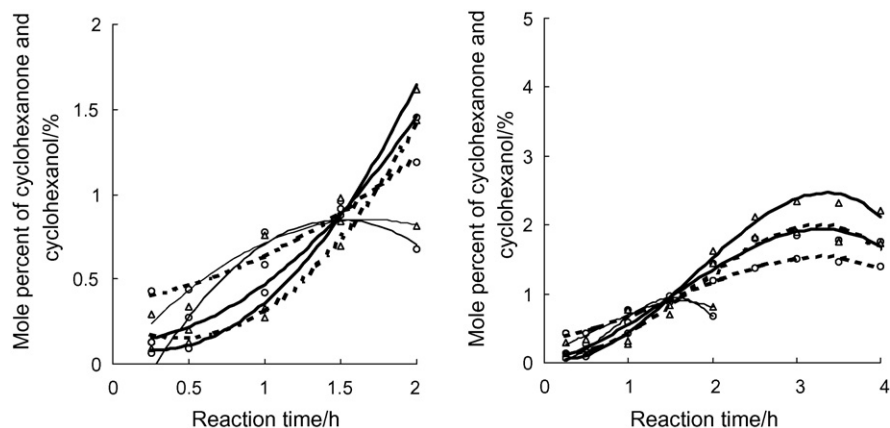


Fig. 1. Changes in mole percent of cyclohexanone (○) and cyclohexanol (△) with reaction time for cyclohexane oxidation catalyzed by iron (---), manganese (—) and cobalt (···) TPPs, respectively.

Table 1  
Data for catalytic activity and selectivity of unsupported metalloporphyrins

Catalysts	Selectivity (%)	Conversion (%)	Turnover number ( $\times 10^4$ )	$k_{\text{cyclohexanone}}$ ( $\text{h}^{-1}$ )	$k_{\text{cyclohexanol}}$ ( $\text{h}^{-1}$ )
PFe	92.2	1.39	0.63	0.006	0.011
PMn	81.5	1.56	0.66	0.010	0.013
PCo	82.9	1.96	0.86	0.014	0.010

$k$  stands for the rate constants of production of cyclohexanone and cyclohexanol, and their values are obtained according to Ref. [13]. Reaction conditions: see Fig. 1.

turnover number with reaction time for cyclohexane oxidation catalyzed by iron, cobalt and manganese TPPs. It is evident that from 0.5 to 1.5 h, the cyclohexane conversion and turnover number for catalysis by cobalt TPP was higher than those for manganese and iron TPPs.

All the above evidence indicates that cobalt TPP had the best catalytic activity for aerobic oxidation of cyclohexane of the three simple MTPPs.

From Fig. 1 it is evident that the total mole percent (ketone + alcohol) for cyclohexane oxidation catalyzed by iron TPP was greater than that for manganese TPP before 1 h; in contrast, the latter gradually increased compared to the former

after a reaction time of 1 h. Between 1 and 3 h, manganese TPP catalyzed aerobic oxidation of cyclohexane to form cyclohexanone and cyclohexanol at rates of  $0.010$  and  $0.013 \text{ h}^{-1}$ , respectively, which were higher than the corresponding rates ( $0.006$  and  $0.011 \text{ h}^{-1}$ ) for iron TPP (Table 1). Fig. 2 shows that the cyclohexane conversion and turnover number catalyzed by manganese TPP were also higher than those for iron TPP after 1 h. All these experimental results indicate that manganese TPP was more active than iron TPP in catalyzing cyclohexane oxidation with air under our reaction conditions. In summary, under reaction conditions of 418 K and 0.8 MPa of air, the catalytic activity of the three simple MTPPs for oxidation of cyclohexane increases in the order: iron < manganese < cobalt TPP. This sequence is in agreement with the literature [16].

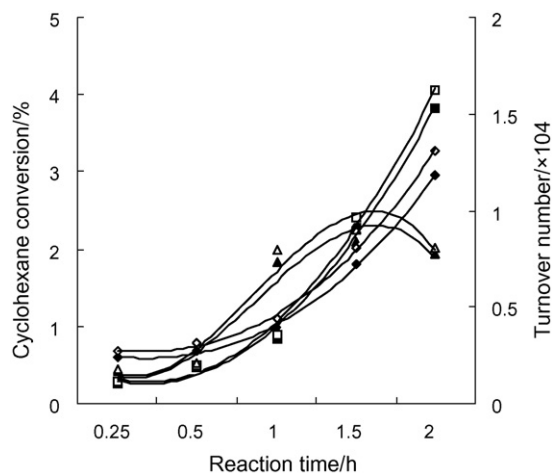


Fig. 2. Changes in cyclohexane conversion (◆, ■, ▲) and turnover number (◇, □, △) with reaction time for cyclohexane oxidation catalyzed by iron (◆, ◇), manganese (■, □) and cobalt (▲, △) TPPs, respectively.

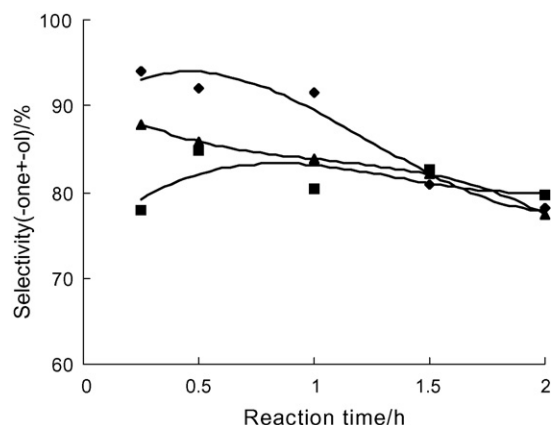


Fig. 3. Changes in selectivity with reaction time for cyclohexane oxidation catalyzed by iron (◆), manganese (■) and cobalt (▲) TPPs, respectively.

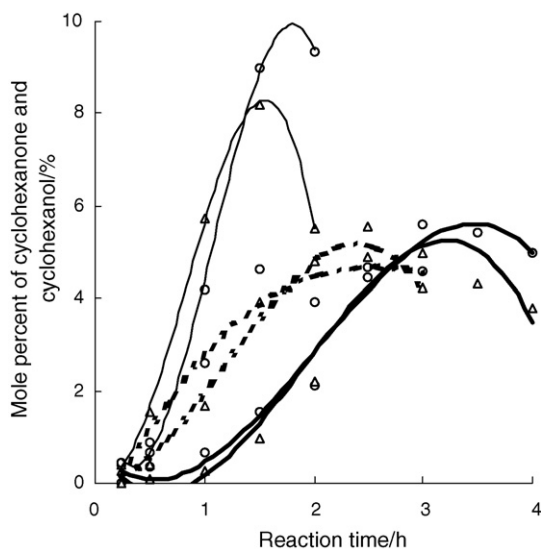


Fig. 4. Changes in mole percent of cyclohexanone (○) and cyclohexanol (△) with reaction time for cyclohexane oxidation catalyzed by chitosan-supported iron (---), manganese (—) and cobalt (—) TPPs, respectively.

Fig. 3 shows the changes in selectivity with reaction time for aerobic oxidation of cyclohexane catalyzed by the simple MTPPs. The selectivity of iron TPP was higher than that of the other MTPPs between 0.25 and 1.5 h. This indicates that iron TPP exhibited the best selectivity for ketone and alcohol in cyclohexane oxidation. At the same time, it showed the lowest catalytic activity. Although cobalt TPP displayed the highest catalytic activity, the selectivity was only intermediate and was close to that of manganese TPP, and thus it is likely that more cyclohexanone and cyclohexanol were turned into by-products during cyclohexane oxidation. Therefore, the ketone and alcohol selectivity was in the order: iron > cobalt > manganese for the three simple MTPPs.

To sum up, cobalt TPP catalytic activity was very high and led to over-oxidation of the predominant products into by-products, with intermediate ketone and alcohol selectivity. However, iron TPP with moderate activity catalyzed aerobic oxidation of cyclohexane with the best selectivity.

### 3.3. Differences in catalysis for chitosan-supported Fe, Co and Mn TPP

When chitosan-supported metallotetraphenylporphyrins (CTSPMs) were used as catalysts for cyclohexane oxidation, it was found that chitosan had a significant effect on the catalytic activity of the MTPPs, leading to very large differences in catalytic activity and selectivity. Fig. 4 shows the changes in

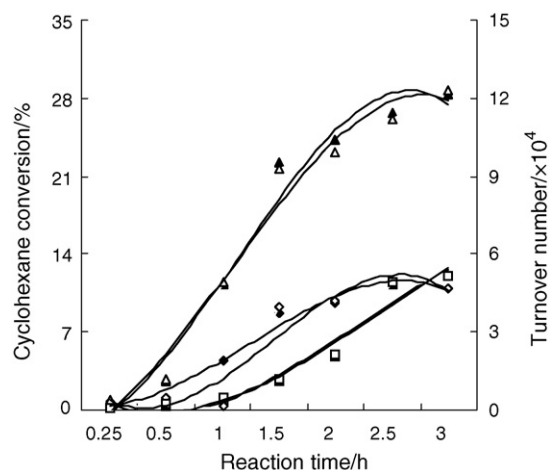


Fig. 5. Changes in cyclohexane conversion (◆, ■, ▲) and turnover number (◇, □, △) with reaction time for cyclohexane oxidation catalyzed by chitosan-supported iron (◆, ◇), manganese (■, □) and cobalt (▲, △) TPPs, respectively.

mole percent cyclohexanone and cyclohexanol with reaction time for cyclohexane oxidation catalyzed by iron, cobalt and manganese CTSPMs. First, the ketone and alcohol formation curves for CTSPCo are steeper than those for CTSPFe, which are steeper than those for CTSPMn. These phenomena imply that the concentration of the main products was in the order: CTSPCo > CTSPFe > CTSPMn between 0.5 and 2 h. Second, there were different rates for converting cyclohexane into the main products. The concentration of cyclohexanone and cyclohexanol changed very quickly for CTSPCo-catalyzed aerobic oxidation of cyclohexane. The rate constants for the production of ketone and alcohol were 0.081 and 0.067 h<sup>-1</sup>, respectively, which were almost two-fold greater than the rates for CTSPFe. The  $k_{\text{cyclohexanone}}$  and  $k_{\text{cyclohexanol}}$  values for cyclohexane oxidation catalyzed by CTSPMn were the lowest. Table 2 lists data for the catalytic activity and selectivity of the CTSPMs. For CTSPCo-catalyzed aerobic cyclohexane oxidation, the cyclohexane conversion and turnover number reached 16.31% and  $6.92 \times 10^4$ , respectively, when the oxidation reaction ran for 1.25 h. At this time, the values for CTSPMn were only 1.81% and  $0.82 \times 10^4$ , respectively. The values for CTSPFe were three-fold greater than for the latter. Thus, the catalytic activity was quite different. Fig. 5 shows that the changes in conversion and turnover number with reaction time were also quite different for the three CTSPMs throughout the oxidation process. Catalysis by CTSPCo showed the highest conversion and turnover number, whereas CTSPMn showed the lowest values. In summary, under reaction conditions of 418 K and 0.8 MPa air, there were large differences in catalytic activity

Table 2  
Data for catalytic activity and selectivity of chitosan-supported metalloporphyrins

Catalysts	Selectivity (%)	Conversion (%)	Turnover number ( $\times 10^4$ )	$k_{\text{cyclohexanone}}$ (h <sup>-1</sup> )	$k_{\text{cyclohexanol}}$ (h <sup>-1</sup> )
CTSPFe	97.8	6.56	2.95	0.041	0.036
CTSPMn	95.1	1.81	0.82	0.029	0.034
CTSPCo	83.7	16.31	6.92	0.081	0.067

$k$  stands for the rate constants of production of cyclohexanone and cyclohexanol, and their values are obtained according to Ref. [13]. Reaction conditions: see Fig. 4.

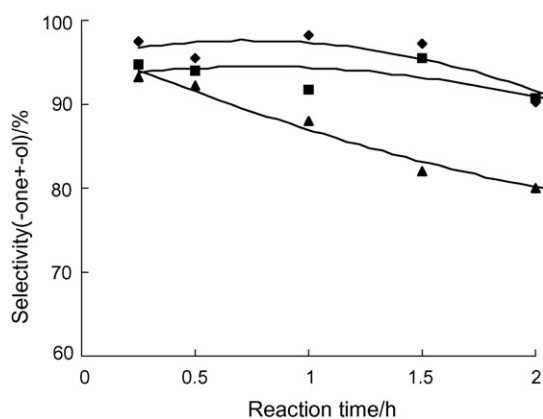


Fig. 6. Changes in selectivity with reaction time for cyclohexane oxidation catalyzed by chitosan-supported iron (♦), manganese (■) and cobalt (▲) TPPs, respectively.

between the three CTSPMs, with the following sequence for activity: CTSPCo > CTSPFe > CTSPMn.

The selectivity for cyclohexanone and cyclohexanol was also changed by immobilization of the MTPPs on chitosan. For the aerobic oxidation of cyclohexane catalyzed by CTSPMs, the changes in selectivity with reaction time are shown in Fig. 6. From the discussion above, it is clear that CTSPCo had the highest catalytic activity, but the selectivity for cyclohexanone and cyclohexanol was poor and decreased rapidly with reaction time (Fig. 6). This indicates that the immobilization of Co TPP on chitosan had little effect on the selectivity. However, CTSPFe, which had moderate catalytic activity, had the highest selectivity for cyclohexane oxidation. It is likely that chitosan greatly contributed to the catalytic activity of Fe TPP by appropriately influencing the rate of production of the main products and avoiding high concentrations of ketone and alcohol. The rapid production of cyclohexanone and cyclohexanol is not beneficial for the selectivity. CTSPMn had better selectivity, which was close to that of Fe TPP supported on chitosan, and the selectivity of these two supported catalysts decreased very slowly with reaction time. When the oxidation ran for 1.25 h, the selectivity of iron, manganese and cobalt TPPs supported on chitosan was 97.8%, 95.1% and 83.7%, respectively (Table 2). In terms of selectivity, CTSPFe was the best catalyst, while the poorest was CTSPCo.

#### 3.4. Relationship between catalytic activity and selectivity

In general, the higher the catalytic activity, the lower was the catalyst selectivity for cyclohexanone and cyclohexanol, as shown by the data for PMn, PCo and CTSPCo in Tables 1 and 2; exceptions to this trend were shown by PFe, CTSPFe and CTSPMn. In the same way, the selectivity was closely related to the production rates for ketone and alcohol, with a similar relationship as for the examples above. The changes in selectivity with the activity and/or the rate constants depended on the nature of the MTPP and chitosan. The selectivity of Fe TPP was originally the highest of the three MTPPs; when supported on chitosan, the corresponding Fe catalyst was even better. Indeed,

Table 3

Data for catalytic activity and selectivity of reused chitosan-supported metalloporphyrins

Catalysts	Run	Selectivity (%)	Conversion (%)	Turnover number ( $\times 10^4$ )
CTSPFe	1	97.3	8.76	3.93
	2	95.3	1.05	0.48
	3	95.5	1.61	0.73
	4	92.5	2.37	1.07
	5	92.9	1.87	0.85
	6	92.9	1.75	0.80
Average		94.5	2.54	1.15
CTSPMn	1	94.4	6.09	2.75
	2	93.6	5.85	2.46
	3	92.9	4.92	2.03
	4	92.0	4.93	1.98
Average		93.2	5.45	2.31
CTSPCo	1	87.9	11.21	4.93
	2	86.0	10.92	4.80
	3	87.3	11.02	4.85
	4	86.9	11.00	4.90
	5	87.0	10.98	4.88
Average		87.0	11.03	4.87

Reaction conditions: see Fig. 4.

both PFe and CTSPFe showed the highest selectivity in the corresponding experimental groups. The selectivity of PMn and PCo catalysts were very close; chitosan enhanced the selectivity of CTSPMn by approximately 13% under the promotion of chitosan, but CTSPCo was only improved by 0.8%. This shows that chitosan had specificity in assisting MTPP catalysis.

#### 3.5. Catalytic activity of reused CTSPMs

To investigate the catalytic activity of reused CTSPMs, the supported catalyst used in each catalytic oxidation was isolated from the reaction mixture for reuse later. The experimental results listed in Table 3 show that CTSP iron, cobalt and manganese could be reused six, five and four times, respectively, with average selectivity of 94.5%, 87.0% and 93.2%, average cyclohexane conversion of 2.54%, 11.03% and 5.45%, and average turnover number of  $1.15$ ,  $4.87$  and  $2.31 \times 10^4$ , respectively. These data indicate that the supported catalysts are highly reusable. The catalytic variables with reaction time presented similar features to the various curves above. However, because the individual MTPPs were different, the supported catalysts showed quite different catalysis for cyclohexane oxidation.

#### 3.6. Reason for the differences in CTSPM catalysis of cyclohexane oxidation

The experimental results reveal that both the MTPPs and the corresponding CTSPMs showed differences in catalytic activity or selectivity existed for cyclohexane oxidation. First, the catalytic centers of the MTPPs were different. According to the mechanism of oxygen activation by MTPPs [17–19], chloro (tetraphenylporphyrinato) metal (III) [ $\text{PM}^{\text{III}}\text{Cl}$ ] loses a



chlorine radical to form (tetraphenylporphyrinato) metal (II) [ $\text{PM}^{\text{II}}$ ], which then combines with an oxygen molecule at high temperature to form an activated radical species ( $\text{PM}^{\text{III}}\text{O}^\bullet$ ). (Tetraphenylporphyrinato) metal (II) is a key intermediate in the reaction with  $\text{O}_2$ . Usually, cobalt TPP exists in the form of  $\text{PCo}^{\text{II}}$ , which favors the activation of oxygen. However, under the same reaction conditions at 418 K, chloro (tetraphenylporphyrinato) iron (III) and manganese (III) are probably first changed to the forms  $\text{PFe}^{\text{II}}\text{Cl}$  and  $\text{PMn}^{\text{II}}\text{Cl}$ , in contrast to Co, for which  $\text{PCo}^{\text{II}}$  is not needed. It is probable that the more slowly  $\text{PMn}^{\text{III}}\text{Cl}$  and  $\text{PFe}^{\text{III}}\text{Cl}$  change into the form  $\text{PM}^{\text{II}}$ , the more slowly they activate the oxygen molecule. Hence, the catalytic activity of  $\text{PCo}^{\text{II}}$  was greater than that of  $\text{PMn}^{\text{III}}\text{Cl}$  or  $\text{PFe}^{\text{III}}\text{Cl}$ . The corresponding chitosan-supported catalysts probably had a similar mechanism of activation. Second, chitosan provided some assistance to the MTPPs for the catalytic oxidation of cyclohexane. It is possible that chitosan had a greater effect on Fe TPP than on Mn TPP or that it changed their original potential by the action of amino or hydroxyl groups, which conferred better activity and selectivity on CTSPFe than on CTSPMn.

#### 4. Conclusion

Simple MTPPs were supported on chitosan to mimic cytochrome P 450 monooxygenase for the catalysis of cyclohexane oxidation. Some very interesting phenomena were observed. Under the influence of the chitosan microenvironment, CTSPMs showed remarkably enhanced rate constants for the production of ketone and alcohol, as well as increases in cyclohexane conversion and turnover number, thus showing higher catalytic activity and selectivity than the corresponding unsupported catalysts. Of the three chitosan-supported catalysts, CTSPCo had the best catalytic activity and CTSPFe showed the best selectivity. The catalytic activity for aerobic oxidation of cyclohexane was influenced by two factors. The first is the potential for  $\text{O}_2$  activation of the different bivalent metal ions, which affects the

activity of the corresponding CTSPMs. The second is the assistance provided by chitosan, especially by some key functional groups, such as amino and hydroxyl groups, to the MTPPs.

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