

Covalently Immobilized Mn(III)deuteroporphyrin on Chitosan: An Efficient and Recyclable Catalyst for Aerobic Oxidation of Cyclohexane

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ABSTRACT: Chitosan-supported Mn(III)deuteroporphyrin chlorine [Mn(III)DFCl-CTS] catalyst was prepared by covalent binding of Mn(III)deuteroporphyrin-bearing carboxyl groups on the side chain of the macrocycle ring to chitosan. The supported catalyst was found to efficiently catalyze the hydroxylation of cyclohexane with air as oxygen source. The effect of various reaction parameters, such as reaction time, temperature, and pressure on the catalytic performances, was in detail investigated and the designed installed oxidation equipment was convenient for on-line sampling during the reaction every time. Under an optimum temperature of 140°C and a pressure

of 0.7 MPa, the obtained cyclohexane conversion (16.9%) and chemoselectivity (88.7%) for cyclohexanol and cyclohexanone were much better than those observed with unsupported Mn(III)deuteroporphyrin and synthetic Mn(III) tetraphenylporphyrin. An intermolecular interaction between amino moieties in chitosan and dipropionic groups in Mn(III)deuteroporphyrin was suggested to play a role in the high conversion of this system. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: chitosan; deuteroporphyrin; catalytic oxidation; supported Mn(III)porphyrin; biocatalyst

INTRODUCTION

Metalloporphyrin catalysts for selective functionalization of saturated C–H bonds have attracted a great deal more research attention. A survey of the literature revealed that these catalysts, as bioinspired model compounds of cytochrome P450, are most efficient in hydroxylation of high-energy C–H bonds to give alcohol products.¹ In recent years, a variety of solid-supported metalloporphyrin catalysts have been developed by immobilizing metalloporphyrins on various supports, such as natural mineral clays, silica, polymers, and hybrid materials.^{2–7} After immobilization, metalloporphyrins exhibit higher catalytic efficiency and larger resistance to degradation than their homogeneous counterparts, not to mention their possible separation and recovery of the catalyst from the reaction media, thereby envisaging a future technological application for these catalysts.⁸ In most instances, the way of supported metalloporphyrins can either be achieved by a coor-

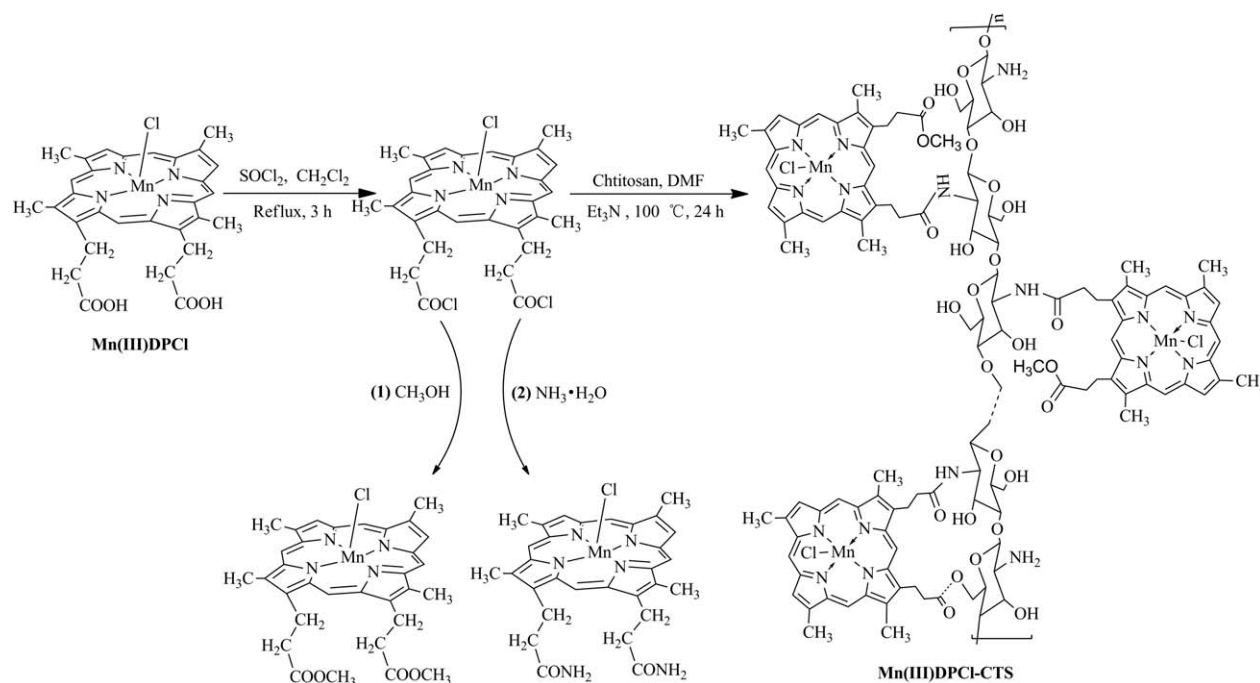
dination bond linkage or via physical adsorption. By these methods of supported metalloporphyrins are usually limited to unstability under thermal condition^{9,10} and prone to lose their activities after many cycles of reuse.¹¹ In contrast, the methods of covalently immobilized metalloporphyrins on supports are the best technology to synthesize recyclable catalysts that are commonly applied to the field of organic synthesis under conditions of high temperature and pressure.

Selective oxidation of cyclohexane (Cy-ane) to yield cyclohexanol (Cy-nol) and cyclohexanone (Cy-one) is the center piece of the commercial production of Nylon. Industrially, the process for Cy-ane oxidation is carried out at a pressure of about 1.0–1.6 MPa and a temperature of 150–180°C without catalyst or using a cobalt salt catalyst. The relatively low conversion (less than 10%) and selectivity (less than 80%) were distinctly limited. Therefore, it is of great interest to develop a more efficient, easily separable catalyst for the oxidation process. Recently, we have successfully used metallodeuteroporphyrin dimethyl esters, where M = Co(II), Ni(II), Cu(II), Zn(II), as catalysts for the selective oxidation of Cy-ane with air in the absence of any cocatalyst or reductant, to give Cy-nol and Cy-one with a total yield of about 15%.^{12,13} During the study, we discovered important compatibility issues between the nature of the linker groups, and catalyst activities and

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Scheme 1 Preparation of Mn(III)DPCL-CTS.

stabilities. These homogeneous catalysts, derived from the naturally occurring heme, have demonstrated to be robust, and exhibited higher catalytic activities than synthetic metallo-tetraphenylporphyrins. So, selecting an applicable support to immobilize the metallodeuteroporphyrin chlorine (MDPCL) is of importance. Especially, one advantage of the natural deuteroporphyrin possesses double propionic groups that can be immobilized on the polymer through forming the covalent bond.

Chitosan (CTS), in this study, was chosen as the precursor support for synthesis of the supported metallodeuteroporphyrin because its $-\text{NH}_2$ and $-\text{OH}$ groups are capable of forming amide bonds or ester groups after reaction with propionic groups in MDPCL.¹⁴ Moreover, its low price and clean are some of the advantages of CTS as a support over inorganic oxides.^{15,16} On the other hand, CTS was also the best cocatalyst. Guo et al.^{17–19} have reported the method for synthesis of CTS-supported metallo-tetraphenylporphyrins (MTPP/CTS) by the physical adsorption, in oxidation of Cy-ane which greatly enhanced the catalytic activities of catalysts. Hence, the objective of this article was to synthesize highly active and stable Mn(III)DPCL catalyst on CTS through forming the covalent bond (Scheme 1) and examine the effect of reaction conditions such as reaction time, temperature, and pressure, on the activity and selectivity of supported catalyst in the catalytic oxidation with air of Cy-ane. The CTS was found to be not only the best support but also an analog of protein, which is helpful in the formation

of high-valent metal-oxo species and enhancing the catalytic activity of the metalloporphyrin catalysts.

EXPERIMENTAL

Materials and apparatus

Chitosan (CTS) was finely purified to a deacetyl degree of 80–95% and purchased from Sinopharm Chemical Reagent (China). Deuteroporphyrin (DP) was prepared according to our recently reported procedures.²⁰ The Mn(III)DPCL was prepared from the reaction with metal salt according to documented procedures.²¹ Cyclohexane (Cy-ane) was analyzed by GC-MS analysis before use, and no impurity was found. Other reagents and solvent used were of analytical grade.

IR spectra were obtained using a Nicolet iS10 FTIR spectrophotometer, and the UV-vis spectroscopy of MnDPCL and supported catalyst was recorded on a Shimadzu UV-240 spectrophotometer using a method similar to that previously described.²² The diffuse reflectance UV-vis spectra were measured on a Shimadzu UV-2550 spectrophotometer in the region 300–700 nm. Thermal stability (TG-DTA) studies were carried out on a Mettler Toledo TG-DTA 851e instrument with a heating rate of $20^\circ\text{C min}^{-1}$ in nitrogen atmosphere. Transmission electron microscopy (TEM) observation of the composite was performed with a JEOL JEM-2100 instrument operated under an acceleration voltage of 200 kV. Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a

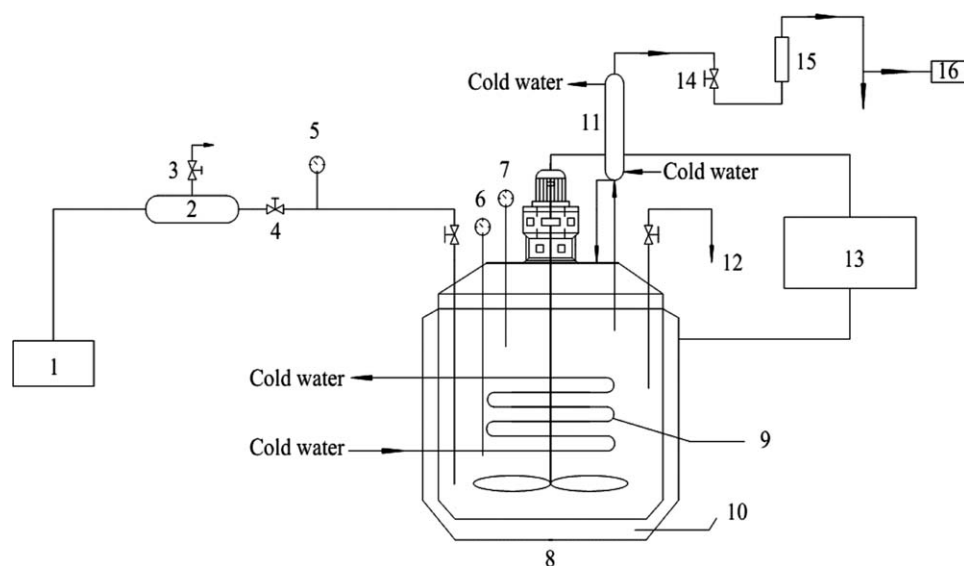


Figure 1 Experimental equipment diagram of oxidation of Cy-ane by air. (1) Air compressor, (2) gas tank, (3) bleeder valve, (4) admission valve, (5) pressure gauge, (6) digital thermometer, (7) pressure gauge, (8) high-pressure reactor, (9) cooling coil, (10) electric heating jacket, (11) condenser, (12) sampling valve, (13) high-pressure reactor control meter, (14) needle valve, (15) gas rotor flow meter, and (16) oxygen detector.

Thermo Trace DSQ GC-MS mass spectrometer. Atomic absorption spectroscopy analysis was recorded on a Perkin-Elmer ICP-5000 apparatus.

Two methods of preparation of the catalyst [Mn(III)DPCI-CTS]

To a stirred solution of 50 mL dry CH_2Cl_2 containing 0.3 g of Mn(III)DPCI, 0.5 mL of SOCl_2 was added. The resulting mixture was refluxed for 3 h. After evaporation, 30 mL *N,N*-dimethylformamide (DMF), 1 mL Et_3N , and 3.0 g CTS were added and heated at 100°C for 48 h. At the end of the reaction, the catalyst was filtered, washed thoroughly with CH_3OH and DMF, and dried in vacuum.

The Mn(III)DPCI (0.3 g) was dissolved in anhydrous DMF (50 mL) at the room temperature under nitrogen atmosphere. The solution was cooled to 0°C . Dicyclohexylcarbodiimide (DCC; 4 mmol) and 4-dimethylaminoipyridine (DMAP; 2 mmol) were added, the mixture was stirred in an ethanol/ice bath for 30 min. The CTS (3.0 g) was then added, and the reaction mixture was allowed to warm room temperature and stirred for additional 48 h. Subsequently, CH_3OH (5 mL) was added, and stirring was continued for 10 min. At the end of the reaction, the catalyst was filtered, washed thoroughly with CH_3OH and DMF, and dried in vacuum.

General procedure for hydroxylation of Cy-ane by [Mn(III)DPCI-CTS]

In order to effectively monitor the reaction process, we have designed and installed the oxidation equip-

ment as indicated in Figure 1. The catalytic oxidation of Cy-ane has been carried out in a stainless steel reactor of 1 L volume equipped with mechanical stirrer, internal cooling coils, and external electric heating jacket. Air was continuously pumped into the reaction system by the air compressor. In a typical experiment, the amounts of Cy-ane and nitrobenzene were 400 and 50 mL, respectively. The optimum temperature was set at 140°C , the air pressure was 0.7 MPa, and the metalloporphyrin catalyst was 0.035 mmol. The reaction mixture was sampled by an on-line means every 30 min until the yield decreased markedly. The samples and the final products were analyzed by GC-MS. In a comparative experiment, Mn(III)DPCI (0.035) was also used as catalyst for comparison with Mn(III)DPCI-CTS under an optimum temperature of 140°C and a pressure of 0.7 MPa.

RESULTS AND DISCUSSION

Preparation and characterization of the catalyst [Mn(III)DPCI-CTS]

Initially, Mn(III)DPCI was made to react with CTS in the presence of DCC and DMAP in DMF solution. As expected, the reaction rate was very slow, after 48 h, the solution contained a amount of unreacted Mn(III)DPCI by UV-vis analysis. In order to increase the reactivity of Mn(III)DPCI, the carboxylic acid groups were first converted to acyl chloride by reaction with SOCl_2 . In our experiments, the Mn(III)porphyrin acyl chloride was also detected via reaction with CH_3OH and $\text{NH}_3\cdot\text{H}_2\text{O}$, and the products were confirmed by mass spectroscopy. It was found that Mn(III)DPCI was completely converted into the corresponding

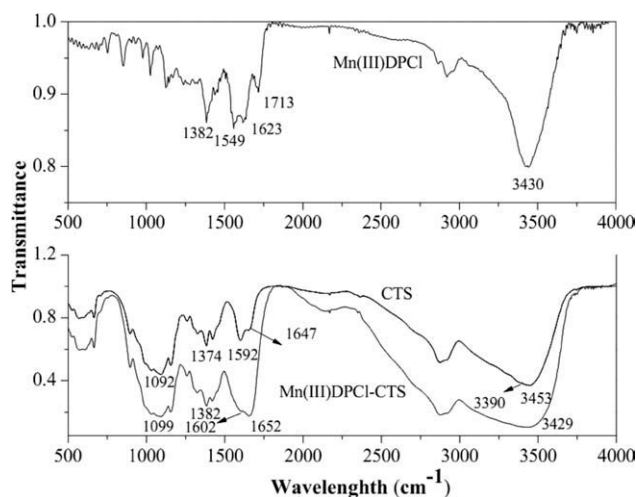


Figure 2 FTIR spectra of Mn(III)DPCI, CTS, and Mn(III)DPCI-CTS.

esters or amides (Scheme 1), which suggested that the conversion of Mn(III)DPCI to acyl chloride proceeded well. Then, the Mn(III)DPCI-CTS was obtained by the reaction of Mn(III)porphyrin acyl chloride reaction with CTS in DMF in the presence of triethylamine (Scheme 1).

The supported catalyst was characterized by FTIR spectroscopy, UV-vis spectrophotometry, TG-DTA analysis, and TEM instrument. The Mn³⁺ content of the catalyst was determined by atomic absorption spectroscopy analysis, which showed a value of 1.4 mg/L. Based on this value, the Mn(III)deuteroporphyrin chlorine content of the catalyst obtained was about 0.0528 mmol per gram of the catalyst.

The most informative spectroscopic data, which confirmed the covalent anchoring of Mn(III)DPCI on CTS, were obtained by comparison of the FTIR spectra of CTS and Mn(III)DPCI-CTS (Fig. 2). In the IR spectrum of the CTS, the absorption band at ~ 1647 and ~ 1590 cm^{-1} , which correspond to the O=C-NHR stretch of the secondary amide and the N-H bending of the primary amine, respectively.²³ The absorption band of -NH₂ in Mn(III)DPCI-CTS almost disappeared and the intensity of absorption band at ~ 1652 cm^{-1} was dramatically increased, suggesting that N-acylations in CTS occurred. The IR spectrum of the CTS has strong peak around ~ 3390 and ~ 3453 cm^{-1} , due to the stretching vibration of O-H, the extension vibration of N-H and inter hydrogen bonds of the polysaccharide.²⁴ In supported Mn(III)DPCI-CTS, the peak at ~ 3429 cm^{-1} is of quite reduced broad, possible due to part of -OH reaction with acyl chloride. Additionally, we can also see from the Figure 2, the key bands assigned to CTS in the Mn(III)DPCI-CTS complex shifted to longer wave numbers, which indicate that there is a strong interaction between the CTS and Mn(III)DPCI.

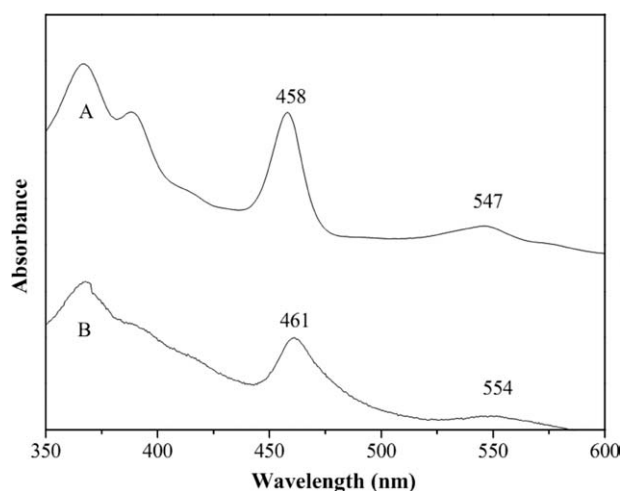


Figure 3 UV-vis spectra at room temperature; (A) Chloroform and glycerol mull solution of Mn(III)DPCI and (B) in glycerol mull of Mn(III)DPCI-CTS.

The immobilization process was characterized by the color change of the white CTS to dark brown, with a final color of brown in the case of the dry solid. Covalently bonding the Mn(III)DPCI on the CTS was also characterized by the UV-vis analyses. The results are shown in Figure 3. The Soret peak for Mn(III)DPCI appeared at 458 nm, and Q band peaks appeared at 547 nm in the region of 500–600 nm. When compared with the absorption band of Mn(III)DPCI, the supported catalyst have the 461 and 554 nm absorption bands, which are seen in longer wavelength regions than Mn(III)DPCI as a result of the interactions between CTS and porphyrin. As the CTS shows no absorption peak in its UV-Vis spectrum, it is confirmed that Mn(III)DPCI has been supported on the CTS.

Furthermore, Figure 4 shows the TG-DTA curves of the Mn(III)DPCI-CTS catalyst traced under

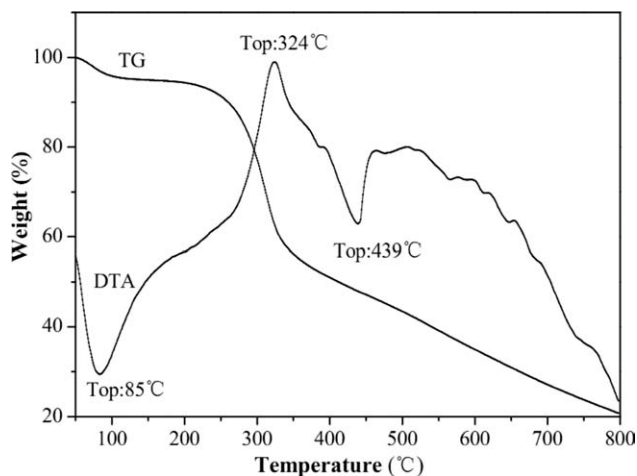


Figure 4 TG-DTA diagram of Mn(III)DPCI-CTS, the TGA curve is extrapolated to 800°C, assuming that no Mn(III)DPCI is involved in the weight decrease.

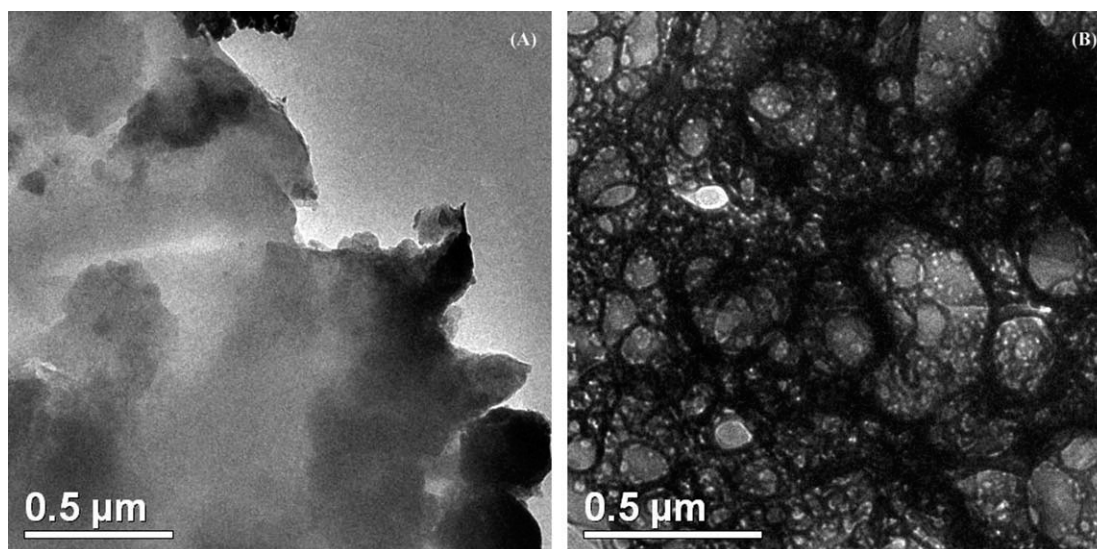


Figure 5 TEM images: (A) CTS; (B) Mn(III)DPCI-CTS.

nitrogen stream. The TG curve indicates an initial weight loss of 4.0% up to 115°C due to the adsorbed water in Mn(III)DPCI-CTS. An abrupt weight loss occurs from 205 to 800°C. This weight loss is caused by the decomposition of CTS, the amount of which was about 74.1% against the total solid catalyst. The DTA curve shows one exothermic peak, with maximum situated in the 250–390°C temperature range and the top temperature at 324°C. Based on the temperature range of weight loss, the exothermic peak can be ascribed to the combustion of CTS in Mn(III)DPCI-CTS. Meantime, the TEM image of Mn(III)DPCI-CTS (Fig. 5), clearly indicates that the structure of the CTS has been modified by the reaction of metalloporphyrin acyl chloride with CTS.

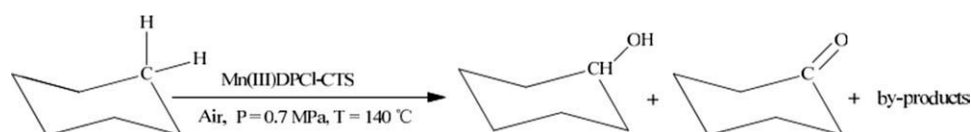
Hydroxylation of Cy-ane catalyzed by Mn(III)DPCI-CTS with air

The liquid-phase oxidation of Cy-ane catalyzed by Mn(III)DPCI-CTS was performed at temperature between 130 and 170°C and air pressures between 0.5 and 0.9 MPa without any cocatalyst and solvent. The reaction mixtures were analyzed by means of GC-MS using nitrobenzene as the internal standard, which indicates Cy-nol and Cy-one were the main products. The catalytic aerobic oxidation of Cy-ane is described in Scheme 2. Quantification of the products was carried out by comparison with authentic commercial samples. Besides, in order to investigate

the CTS on the catalytic activity of metalloporphyrin, the influences of reaction time, temperature, and pressure on the catalytic behavior of Mn(III)DPCI-CTS were evaluated as following.

Effect of reaction time

Figure 6 illustrates the changes of selectivity, yields of Cy-nol and Cy-one and molar ratio of Cy-nol to Cy-one under an optimum temperature of 140°C and a pressure of 0.7 MPa catalyzed by Mn(III)DPCI-CTS with air. Generally, the yield increased with reaction time. From 0 to 1 h, the increment of Cy-nol to Cy-one was slight. This phenomenon is attributed to the fact that the supported catalyst was in the induction and activation period. Subsequently, the amount of Cy-nol to Cy-one sharply increased until the time reached 4.5 h, at which the maximum yield was more than 14%. However, after about 4.5 h, the selectivity for Cy-nol and Cy-one gradually decreased with a prolonged time, possibly because the Cy-nol to Cy-one were more readily oxidizable than Cy-ane, and even with the limited conversion a whole range of further oxidation products were formed such as adipic acid and ester. Besides, the value of molar ratio of Cy-nol to Cy-one reached the maximum at 2.5 h and basically kept the same trend. Although it is worthwhile to note that at the beginning of the reaction time, the oxidation of Cy-ane was easy to produce Cy-nol. In a word, the



Scheme 2 Aerobic oxidation of Cy-ane over Mn(III)DPCI-CTS.

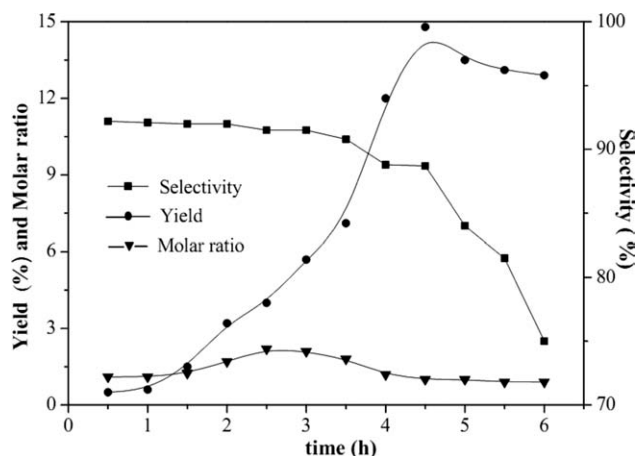


Figure 6 Changes of conversion and selectivity with reaction time in Cy-ane oxidation catalyzed by Mn(III)DPCI-CTS; Selectivity = $[n(\text{Cy-nol}) + n(\text{Cy-one})]/n(\text{conversion})$. Molar ratio = $n(\text{Cy-nol})/n(\text{Cy-one})$. Turnover number is based on the mol of product per mol of catalyst used.

Mn(III)DPCI-CTS systems catalyzed the oxidation of Cy-ane by using air at 4.5 h under optimal conditions to give Cy-nol and Cy-one with a modest yield of more than 14% and selectivity of 88.7%.

Effect of reaction temperature

The effect of the reaction temperature on Cy-ane conversion and its selectivity is presented in Table I, where the Mn(III)DPCI-CTS was used as a catalyst. When the temperature was below 130°C, no product was formed in the control reactions. Concerning the differences among the varieties in the four value of temperature it may be evident that a higher temperature was required to achieve a higher conversion, despite the fact that too high a temperature resulted in very low selectivity, as shown by the Cy-ane oxidation at 170 °C. One explanation can be offered for this observation, based on the Arrhenius equation, by increasing the reaction temperature increases the energy of the collisions and thus gets a greater prob-

ability that the sufficient energy will promote faster reaction rate, resulting in a high conversion. However, the decreased selectivity might in principle have two causes. From the point of view of the catalyst stability, part of the catalysts may be demolished and lose their activities at elevated temperature, leading to the selectivity decline. This conclusion is in coordinate with the result obtained by using MTPP/CTS catalysts. Another reason for the decrease in selectivity lies in the fact that the Cy-nol and Cy-one are easily over-oxidized to other oxidation products. Under the conditions of this experiment, the latter is emphasized. Because the catalytic circulation could persist and the catalyst would not loss of its initial activity in the second run when the recyclable Mn(III)DPCI-CTS was used to catalyze oxidation of Cy-ane. The most effective evidence can be gained from the TG-DTA curves. It was indicated that the supported Mn(III)DPCI-CTS would not be decomposed before 200°C. From another point of view, the covalent link of the supported Mn(III)DPCI-CTS could enhance the stability of catalyst compared to the supported MTPP/CTS by the physical adsorption. In addition, as shown in Table I, the value of molar ratio of was no big difference affected by change of the temperature. Therefore, the most appropriate reaction temperature for the aerobic oxidation of Cy-ane catalyzed by Mn(III)DPCI-CTS was about 140°C.

Effect of reaction pressure

To determine whether higher pressure operation was advantageous, the effect of increasing the pressure from 0.5 to 0.9 MPa was investigated at 140°C using Mn(III)DPCI-CTS as a catalyst. The results are shown in Table II. Conversion of Cy-ane was observed to increase on increasing reaction pressure and then it changed slightly after the oxygen pressure reached a certain level under the reaction conditions. For example at 0.5 MPa, slow in reaction with only 10.8% conversion of Cy-ane was observed

TABLE I
Effect of Temperature on the Oxidation Reaction

Temperature (°C)	Conversion (%) ^a	Time (h) ^b	Selectivity (%)	$n(\text{Cy-nol})/n(\text{Cy-one})$	Turnover numbers ^c
130	11.4	6.0	90.1	1.3	11,986
140	16.9	4.5	88.7	1.0	17,769
150	17.0	4.0	72.1	0.9	17,874
170	17.4	3.5	61.5	0.9	18,295

Reaction conditions: Cy-ane 400 mL, Mn(III)DPCI-CTS (containing Mn(III)DPCI 0.035 mmol), pressure 0.7 MPa.

^a Conversion = $[n(\text{cyclohexane feed}) - n(\text{nonreacted cyclohexane})]/n(\text{cyclohexane feed})$.

^b Time is defined as the reaction time until the yield reaches the maximum.

^c Turnover number is based on the mol of product per mol of catalyst used.

TABLE II
Effect of Pressure on the Oxidation Reaction

Pressure (MPa)	Conversion (%)	Time (h)	Selectivity (%)	$n(\text{Cy-nol})/$ $n(\text{Cy-one})$	Turnover numbers
0.5	10.8	6.0	62.6	1.1	11,355
0.6	16.7	5.5	78.6	1.1	17,559
0.7	16.9	4.5	88.7	1.0	17,769
0.9	17.2	4.0	59.5	0.9	18,085

Reaction conditions: Cy-ane 400 mL, Mn(III)DPCI-CTS (containing Mn(III)DPCI 0.035 mmol), temperature 140°C.

in 6 h. The conversion of Cy-ane was found to be 16.9 and 17.2% at reaction pressure of 0.7 and 0.9 MPa, respectively. However, the selectivity of Cy-nol and Cy-one was observed to decrease on increasing the reaction pressure. This change is associated with operational pressure. Higher oxygen saturation pressure means higher initial dissolved oxygen concentration in the liquid phase. After a certain concentration of oxygen was reached at a temperature of 140°C, further increasing air pressure did not markedly accelerate the reaction rate and the conversion of Cy-ane almost reached a flat value, whereas higher air pressure in the reaction system could promote the formation of byproducts, which is responsible for the low selectivity of the catalyst. From the above, it can be concluded that air pressure is also an important parameter for the oxidation of Cy-ane and 0.7 MPa might be a better operation pressure both for activity and selectivity.

Catalyst reuse and stability

The reusability of a supported catalyst is of great importance from the economical and application of practical chemical industry points of view. The reusability of catalyst in the oxidation of Cy-ane were performed under the optimum condition of 140°C and 0.7 MPa. After a Cy-ane oxidation run, the supported catalysts were separated by simple filtration, washed with methanol, and dried carefully before using it in the subsequent run. The catalyst was consecutively reused five times. As shown in Figure 7, Mn(III)DPCI-CTS retained its activity and selectivity. Compared with unsupported catalyst [Mn(III)DPCI], which could be exhausted one time for oxidation Cy-ane, the Mn(III)DPCI-CTS was used as a catalyst for aerobic oxidation of Cy-ane with average conversion of 16.2%, average selectivity of 88.1%, respectively. Figure 8 showed that the recycled catalyst was studied by diffuse reflectance UV-vis spectroscopy. Based on a comparison with CTS, Mn(III)DPCI, and Mn(III)DPCI-CTS, the presence of Soret and Q bands of manganese porphyrin in the recovered catalyst clearly indicated the presence of Mn(III)porphyrin on the surface of the CTS. The

Mn(III)DPCI-CTS was not destroyed and kept its activity after consecutively reused five times.

A reason for the difference of catalytic activities of the metalloporphyrins

To investigated the effect of CTS on catalytic activities of metalloporphyrins, the Mn(III)DPCI-CTS and unsupported Mn(III)DPCI were studied under the same conditions of pressure and temperature, and the results were listed in Table III, from which it can be found that the supported Mn(III)DPCI-CTS has much more notable activities in conversion and selectivity than unsupported Mn(III)DPCI. When compared with MnTPP/CTS, the natural porphyrin exhibited its best catalytic performance in conversion. However, there is a common character in relation to the supported catalysts that the interaction between CTS and metalloporphyrins is able to enhance their catalytic activities in the oxidation process. The difference in conversion of MnTPP/CTS and Mn(III)DPCI-CTS increased our attention to take into consideration structure of porphyrin and may be explained by the following causes.

First, we need to have a look at structure-activity relationships in cytochrome P450-dependent monooxygenases. It is well documented in the literature

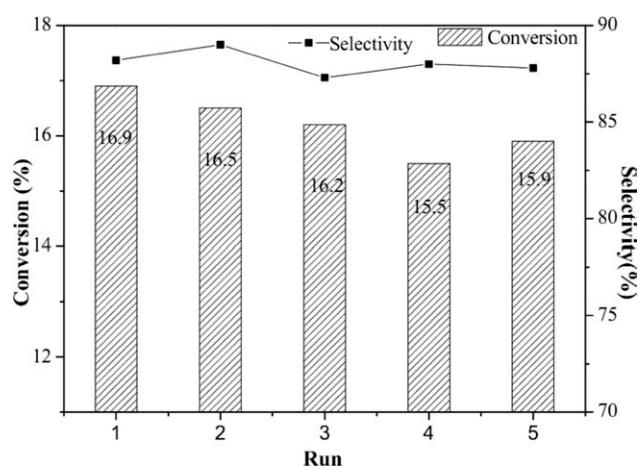


Figure 7 The study of conversion and selectivity on reused Mn(III)DPCI-CTS.

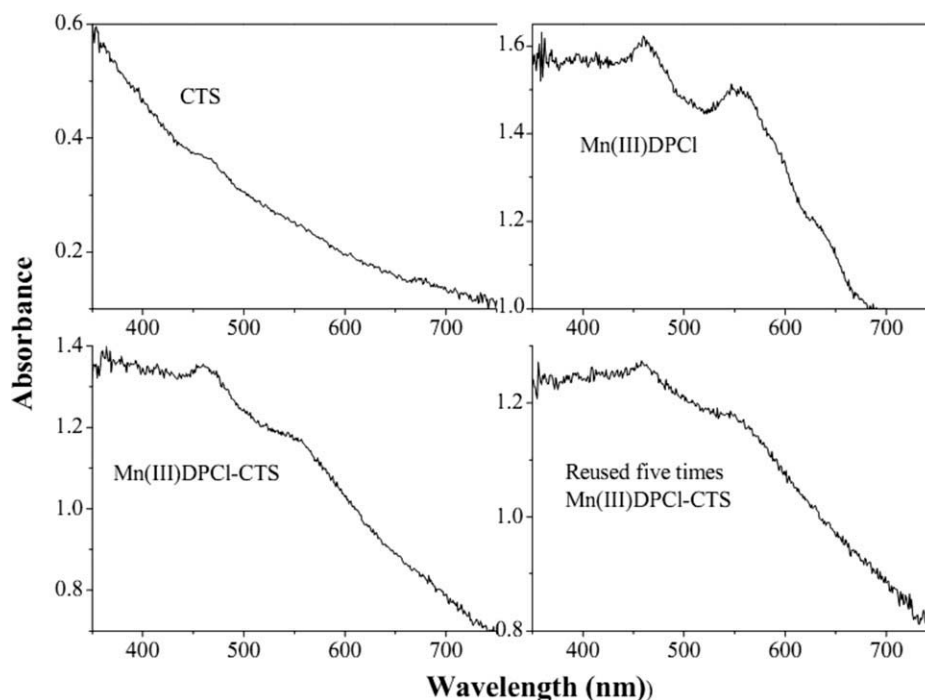


Figure 8 Solid state UV spectra of CTS, Mn(III)DPCI, Mn(III)DPCI-CTS, and reused Mn(III)DPCI-CTS.

that the heme propionate side chains have been regarded as anchors for connecting the heme prosthetic group to the protein matrix.^{25–30} The propionate peripheral side chain can form hydrogen bonding interactions with amino acid residues, which is known to contribute to the thermostability of the protein and cytochrome P450. In this study, CTS was chosen as a support and provided notable assistance to the Mn(III)DPCI for the catalytic oxidation of Cy-ane. Both the CTS and amino acid residues contain amounts of amine groups ($-\text{NH}_2$). The strong donation of electron of the $-\text{NH}_2$ groups on the CTS were bonded to MnCl, resulting in the high stability of catalyst. Meanwhile, the CTS can provide a similar exterior environment for imitating cytochrome P450 *in vivo*.

Second, the propionate side chain has also been proposed to participate in an electron-transfer and help to form the intermediates in the enzyme cycle

of P450, although there is no experimental evidence that demonstrates a functional role of the propionate side chain in the protein interior. Taking into consideration our experimental results, we suggested that Mn(III)DPCI immobilized on CTS was capable to facilitate the cleavage of the O—O bond of the active species $[(\text{por})\text{Mn}^{\text{III}}\text{O}—\text{O}—\text{H}]$ and stabilize the high-valent manganese-oxo species $[(\text{por})\text{Mn}^{\text{V}}=\text{O}]^+$ by the help of the dipropionate side chains linking CTS. In subsequent, the active species can transfer the oxygen atom to Cy-ane more easily, leading to the fact that the catalytic efficiency for Mn(III)DPCI-CTS was higher than these for MnTPP, Mn(III)DPCI, and MnTPP/CTS, respectively. In conclusion, CTS has been found to be the best support in our study on the supported metallodeuteroporphyrin and provides vital assistance for metalloporphyrins catalyzing oxidation of Cy-ane.

TABLE III
Results of the Oxidation Catalyzed by Different Metalloporphyrin Complexes

Catalyst	Conversion (%)	Selectivity (%)	$n(\text{Cy-nol})/$ $n(\text{Cy-one})$
MnTPP ^a	1.6	81.5	—
MnTPP/CTS ¹⁷	6.1	94.4	—
MnDPCI	9.6	80.7	1.2
MnDPCI-CTS	16.9	88.7	1.0

Reaction conditions: Cy-ane 400 mL, Mn(III)DPCI-CTS (containing Mn(III)DPCI 0.035 mmol), pressure 0.7 MPa, Temperature 140°C.

CONCLUSIONS

We have successfully immobilized the Mn(III)deuteroporphyrin on CTS by the covalent linkage and have investigated its performance as a catalyst in the oxidation reaction of cyclohexene. It was suggested that CTS was responsible for the highlight of the catalytic activity for Mn(III)DPCI-CTS. The supported catalyst was highly reusable and recycled five times without loss its initial activity. Therefore, Mn(III)DPCI-CTS may be a promising catalyst in industrial applications. This research will help us to further develop

the heterogeneous metallodeuteroporphyrin catalysts used in the oxidation of hydrocarbons.

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