Solvent-Free Aerobic Oxidation of Toluene over Metalloporphyrin/NHPI/CTAB: Synergy and Mechanism

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Abstract The solvent-free catalytic oxidation of toluene using molecular oxygen over metalloporphyrin/*N*-hydroxyphthalimide (NHPI)/cetyl trimethyl ammonium bromide (CTAB) has been developed. The results showed that the type of metalloporphyrin used, catalyst loading, reaction temperature, and the flow rate of oxygen all influenced the conversion of toluene and the selectivities of the products. Furthermore, a co-catalysis was observed between metalloporphyrin, NHPI, and CTAB. The toluene conversion was significantly improved from 10.74 to 40.95 mol% after adding CTAB to the reaction mixture. Based upon experimental observations, a possible mechanism was also proposed for the present oxidation.

Keywords Toluene oxidation · Co-catalysis · Metalloporphyrin · NHPI · CTAB

1 Introduction

Aerobic oxidation of toluene is a very important industrial process because its main products, benzyl alcohol (BAL) and benzaldehyde (BA), as well as benzoic acid (BAC), are widely used to synthesize a large variety of fine chemicals such as pharmaceuticals, foodstuff, dyes, perfume, and resins [1]. Currently, BAC is mainly obtained from the aerobic oxidation of toluene with cobalt carboxylate as catalyst and bromides as initiators in the presence of acetic acid as solvent [2, 3], while BA and BAL are synthesized

by the chlorination of toluene followed by hydrolysis, which have obvious drawbacks such as the danger associated with the use of Cl₂ [4]. Recently, great effort has been made to develop environmental friendly strategies for the aerobic oxidation of toluene. For example, several catalyst systems including metalloporphyrins [5, 6], Au–Pd nanoparticles [7], Cu-Mn oxides [8], and g-C₃N₄ nanocomposite [9] have been developed as effective catalysts for the solvent-free aerobic oxidation of toluene. However, most of these reactions suffered from harsh conditions such as high temperature and pressure. More recently, N-hydroxyphthalimide (NHPI) has been reported as an effective mediator for the oxidation of toluene in the presence of cobalt salt [10], manganese dioxide [11], under mild conditions. However, these processes also have some shortcomings including high catalyst loading, low toluene concentration, and using acetic acid as solvent, thus limiting their application in industry.

Metalloporphyrins, which are widely recognized as environmentally benign catalysts, have been shown to be able to catalyze the oxidation of hydrocarbons under mild conditions [12–15]. Our group have shown that simple metalloporphyrin catalyzed toluene oxidation using dioxygen as oxidant with the selectivity of BA and BAL upto 60 % at the conversion of toluene upto 8.9 % [5]. Aiming to further improve the catalytic efficiency of metalloporphyrin catalysts, we tried to use other additives to co-catalyze the aerobic oxidation of hydrocarbons and we found that NHPI was an effective co-catalyst [10, 11]. We recently reported a (T(p-Cl)PP)MnF/NHPI catalyzed the aerobic oxidation of toluene toward BA and BAL at atmospheric pressure in acetic acid [16]. However, under solvent free conditions which are preferred in industrial processes, we found that the catalytic activity of (T(p-Cl)PP)MnF/NHPI for the oxidation of toluene was much

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lower. As a continuation of our research involving metalloporphyrin-catalyzed oxidations with dioxygen, we now report the aerobic oxidation of toluene over metalloporphyrins/NHPI under solvent-free conditions can be significantly improved after adding CTAB as the co-catalyst. The effects of various reaction parameters such as catalyst components, catalyst concentration, reaction temperature and the flow rate of oxygen on the conversion of the toluene aerobic oxidation and selectivities of products were also investigated. The results obtained with the catalyst system of metalloporphyrin/NHPI/CTAB were not only much better than those results with metalloporphyrin/ NHPI, metalloporphyrin/CTAB or NHPI/CTAB but also better than the three results combined, thus clearly showing the effect of co-catalysis. A possible mechanism for the synergy of metalloporphyrin/NHPI/CTAB in the toluene oxidation was also proposed.

2 Experimental

2.1 Instruments and Materials

GC analysis was performed on a Shimadzu GC-2010 equipped with a 0.5 mm i.d. 25 m PEG 20 M capillary column and a flame ionization detector. MS spectra were measured on a Class-5000 GC–MS spectrometer and an Agilent 1100 LC–MS. UV–Vis absorption spectra were recorded on a PEL-17 spectrometer. Toluene was purified and analyzed by GC to ensure the absence of impurities before use. Pyrrole was redistilled before use. Other reagents were all analytical grade and used as received. Porphyrin and their metal complexes were synthesized and purified according to documented procedures [17, 18].

2.2 Toluene Oxidation over Metalloporphyrins/NHPI/ CTAB

The catalytic oxidation of toluene with dioxygen at atmospheric pressure under the temperature range from 60 to 100 °C was performed according to the following typical procedure: 10 g of toluene and precisely weighted catalysts were added into a 50 mL three-neck flask equipped with a reflux condenser and a magnetic stirrer. Then while being stirred, the flask was heated to reaction temperature. Upon reaching the reaction temperature, oxygen was continuously introduced into the flask through a flowmeter. The mixture of toluene oxidation was sampled, characterized by GC–MS and LC–MS in comparison with the authentic sample, respectively, and quantified with GC using bromobenzene as the internal standard [16]. The contents of benzyl hydrogen peroxide (BHPO) were determined by iodometric method and analyzed with GC according to the literature [18].

3 Results and Discussion

3.1 Toluene Oxidation over Metalloporphyrins/NHPI/ CTAB

The oxidation of toluene catalyzed by Metalloporphyrins/ NHPI/CTAB with molecular oxygen was investigated. The products of toluene aerobic oxidation were identified by GC–MS and LC–MS, and compared with authentic samples. The oxidation products are mainly BA, BAL and BAC, as shown in Scheme 1. The results of toluene oxidation with dioxygen catalyzed by T(p-Cl)PPMnCl/CTAB, NHPI/CTAB or T(p-Cl)PPMnCl/NHPI/CTAB are shown in Table 1. When T(p-Cl)PPMnCl/NHPI (20 mL acetic

Scheme 1Metalloporphyrins/
NHPI/CTAB catalyzed toluene
oxidation CH_3
+ CH_3
Metalloporphyrin-NHPI-CTBA
T, 1atm.CHO
+ CH_2OH
+COOH
+++02T, 1atm.+++++other products

Table 1 Oxidation of toluene catalyzed by T(p-Cl)PPMnCl/NHPI/CTAB

Entries	Catalysts			Solvent	Yield (mol%)		Conv. (mol%)	
					BA	BAL	BAC	
1	T(p-Cl)PPMnCl	NHPI	CTAB	_	10.22	1.44	28.93	40.95
2	T(p-Cl)PPMnCl	NHPI	CTAB	AcOH ^a	7.02	2.18	20.68	30.15
3	T(p-Cl)PPMnCl	NHPI	_	AcOH ^a	6.14	1.12	3.31	10.74
4	T(p-Cl)PPMnCl	_	CTAB	_	0.31	0.11	0	0.44
5	_	NHPI	CTAB	_	2.57	0.82	3.30	6.79

Reaction conditions: toluene 10 g, NHPI 2.0 mol%, T(p-Cl)PPMnCl 20 ppm, CTAB 1 mmol, 100 °C, O₂ 0.05 L/min, reaction time 10 h ^a AcHO 20 mL added

acid is used as solvent) was employed as the catalyst, the toluene conversion is 10.74 % and the yields of BA, BAL, and BAC are 6.14, 1.12, and 3.31 %, respectively (Table 1, entry 3). On the other hand, when NHPI/CTAB was used as the catalyst, the toluene conversion is 6.79 % and the yields of BA, BAL, and BAC are 2.57, 0.82, and 3.30 %, respectively (Table 1, entry 5). Interestingly, the toluene conversion was significantly increased to 30.15 % if the oxidation was carried out using T(p-Cl)PPMnCl in combination with NHPI and CTAB as the catalyst in acetic acid (Table 1, entry 2). Even more surprising is that the toluene conversion can be elevated to 40.95 % and the yields of BA, BAL, and BAC were 10.22, 1.44, and 28.93 % (Table 1, entry 1), respectively, when the oxidation was carried out in solvent free condition. The toluene conversion over T(p-Cl)PPMnCl/NHPI/CTAB are much higher than those over T(p-Cl)PPMnCl/NHPI and NHPI/CTAB, and even better than the two results combined. This marked improvement of catalytic efficiency suggested co-catalysis for the T(p-Cl)PPMnCl/NHPI/CTAB catalyst system in the aerobic oxidation of toluene.

3.2 Effect of the Catalyst Composition on the Toluene Oxidation

It has been reported that the catalytic activity of metalloporphyrin could be greatly affected by the type of metal ions of the metalloporphyrin catalysts in the aerobic oxidation of toluene [16] or *p*-xylene [19]. As a result, we investigated the influence of different metalloporphyrins on the aerobic toluene oxidation using NHPI and CTAB as cocatalysts and the results are summarized in Table 2. Four types of metalloporphyrins, i.e., (T(*p*-Cl)PPMnCl, T(*p*-Cl)PPCo, T(*p*-Cl)PPFeCl, T(*p*-Cl)PPCu) combined with NHPI and CTAB, are chosen as catalysts, and the conversions of toluene are 8.32, 7.87, 7.17, and 6.49 % respectively. The highest toluene conversion was obtained using T(*p*-Cl)PPMnCl/NHPI/CTAB as the catalyst. So T(*p*-Cl)PPMnCl was chosen as the standard catalyst to examine

 Table 2
 Oxidation of toluene over different metallporphyrins/NHPI/ CTAB

Metallporphyrins	Select.	Conv. (mol%)		
	BA	BAL	BAC	
T(p-Cl)PPMnCl	28.61	4.93	65.14	8.32
T(p-Cl)PPCo	28.33	5.59	66.58	7.87
T(p-Cl)PPFeCl	34.45	6.69	57.04	7.17
T(p-Cl)PPCu	31.12	4.93	61.94	6.49

Reaction conditions: toluene 10 g, NHPI 2.0 mol%, 100 °C, metallporphyrins 20 ppm, CTAB 1 mmol, O_2 0.05 L/min, reaction time 6 h the solvent-free aerobic oxidation of toluene in the presence of NHPI and CTAB.

3.3 Effect of Catalyst Concentration on the Toluene Oxidation

3.3.1 Effect of T(p-Cl)PPMnCl Concentration on Toluene Oxidation

The catalyst concentration is a very important factor influencing the conversion and product yields in metalloporphyrin-catalyzed alkane oxidations [15, 16]. In order to understand the effect of catalyst on toluene oxidation, we examined the effect of T(p-Cl)PPMnCl concentration on the toluene conversion and the selectivities of products in the presence of 2.0 mol% NHPI and 1.0 mmol CTAB at 90 °C for 8 h. The results are shown in Table 3. When T(p-Cl)PPMnCl was absent, the conversion of toluene is 5.31 %, the yields of BA, BAL, and BAC were 2.48, 0.68, 2.10 % respectively, and the total selectivity to BA and BAL reached 59.6 %. This suggested that NHPI and CTAB could catalyze the toluene aerobic oxidation even without T(p-Cl)PPMnCl. The toluene conversion increased with the increase of T(p-Cl)PPMnCl concentration. However the toluene conversion decreased with further increase of T(p-Cl)PPMnCl concentration. This observation is consistent with our earlier results that the oxidation reaction can be inhibited at high concentration of metalloporphyrin [5, 14, 19, 20]. A possible reason could be that high concentration of metalloporphyrins can actually increase the selfoxidation rate of metalloporphyrin catalyst, which leads to metalloporphyrin decomposition, thus reducing effective catalyst concentration [21].

3.3.2 Effect of NHPI Concentration on Toluene Oxidation

The aerobic oxidation of toluene catalyzed by NHPI with $Co(OAc)_2$ as co-catalyst using acetic acid as solvent has been reported in literature [10]. In this reaction process, a

Table 3 Effect of T(p-Cl)PPMnCl concentration on tolueneoxidation

T(p-Cl)PPMnCl (ppm)	Yield	(mol%)	Conv. (mol%)	
	BA	BAL	BAC	
0	2.48	0.68	2.10	5.31
10	3.51	0.92	2.84	7.37
20	2.52	0.92	8.68	12.12
30	2.42	0.81	6.94	10.25
40	2.12	0.72	6.64	9.77

Reaction conditions: toluene 10 g, NHPI 2.0 mol%, CTAB 1 mmol, 90 °C, O_2 0.05 L/min, reaction time 8 h

Table 4 Effect of NHPI dosages on toluene oxidation

NHPI (mol%)	Yield (1	nol%)	Select. (mol%)	Conv. (mol%)	
	BA	BAL	BAC	BA and BAL	. ,
0	0.31	0.11	0	95.45	0.44
0.5	3.26	0.67	2.34	61.02	6.44
1.0	5.76	1.61	7.21	49.73	14.82
1.5	7.44	2.15	15.12	38.61	24.84
2.0	10.22	1.44	28.93	28.47	40.95
2.5	9.68	1.30	29.31	27.12	40.45

Reaction conditions: toluene 10 g, T(*p*-Cl)PPMnCl 20 ppm, CTAB 1 mmol, 100 °C, O₂ 0.05 L/min, reaction time 10 h

vield of 81 % of BAC was obtained in the presence of 10 mol% NHPI. In our study, by fixing the T(p-Cl)PPMnCl concentration and the amount of CTAB at 20 ppm, 1 mmol respectively, the influence of NHPI concentration on the toluene conversion and product yields was investigated (Table 4). From Table 4, it was observed that the conversion of toluene was only 0.44 % in the absence of NHPI, which showed that NHPI is essential for the toluene aerobic oxidation to proceed efficiently. It was found that the conversion of toluene and the yields of BA and BAL increased significantly with the concentration of NHPI increasing. When the concentration of NHPI reached 2.0 mol%, the conversion of toluene was 40.95 %, and the yields of BA, BAL, and BAC were 10.22, 1.44, 28.93 %, respectively. Moreover, the change of the toluene conversion and the selectivities to BA and BAL with reaction time in the reaction catalyzed by T(p-Cl)PPMnCl/NHPI/CTAB in the presence of different NHPI concentration are shown in Fig. 1. It was found that the conversion of toluene increased and the selectivity to BA and BAL decreased



Fig. 1 Changes of toluene conversion and selectivities to BA and BAL with time at different concentration of NHPI. Reaction conditions: toluene 10 g, T(p-Cl)PPMnCl 20 ppm, CTAB 1 mmol, 100 °C, O2 0.05 L/min

with the reaction time. However, when NHPI concentration was 0.5 mol%, the toluene conversion and the selectivities to BA and BAL changed slowly with reaction time, while the toluene conversion and the selectivities to BA and BAL changed drastically with reaction time when NHPI concentration was 2.0 mol%. In addition, using 0.5 mol% NHPI, the maximum conversion of toluene was up to 8.48 mol%, and the total selectivity of BA and BAL was 58.40 % whereas with 2.0 mol% NHPI, the maximum conversion of toluene reached 33.11 mol%, and the total selectivity of BA and BAL was 30.4 %. However, when the concentration of NHPI was increased further to 2.5 mol%, the conversion of toluene was almost unchanged. This behavior might be due to the low solubility of NHPI in toluene.

3.4 Effect of other Reaction Parameters on the Toluene Oxidation

3.4.1 Effect of Reaction Temperatures on the Toluene Oxidation

Reaction temperature is a very important factor in the aerobic hydrocarbon oxidation reactions catalyzed by metalloporphyrin. Increasing reaction temperature can shorten the induction period and accelerate the reaction rate [16, 22]. In this paper, the influence of reaction temperature on the toluene aerobic oxidation catalyzed by T(p-Cl)PPMnCl/NHPI/CTAB in the temperature range of

Table 5 Effect of temperature on toluene oxidation

Temp. (°C)	Yield (1	Conv. (mol%)		
	BA	BAL	BAC	
60	0	0	0	0
70	2.12	0.41	1.30	3.85
80	3.59	0.89	2.93	7.48
90	3.62	0.95	3.11	7.71
100	3.77	1.14	3.52	8.48

Reaction conditions: toluene 10 g, NHPI 0.5 mol%, T(p-Cl)PPMnCl 20 ppm, CTAB 1 mmol, O₂ 0.05 L/min, reaction time 8 h

Table 6 Effect of O2 flows on toluene oxidation

O ₂ flows (L/min)	Yield (mol%)	Conv. (mol%)	
	BA	BAL	BAC	
0.03	2.71	0.48	2.30	5.51
0.05	3.62	0.95	3.11	7.37
0.07	2.96	0.89	2.97	6.83

Reaction conditions: toluene 10 g, NHPI 0.5 mol%, 90 °C, T(*p*-Cl)PPMnCl 20 ppm, reaction time 8 h

60–100 °C was investigated. As illustrated in Table 5, we found that the conversion of toluene was indeed influenced significantly by the reaction temperature. The rate of toluene oxidation was so slow and no products were detected when the reaction was conducted at 60 °C for 8 h in the presence of 10 ppm of T(*p*-Cl)PPMnCl, 0.5 mol% of NHPI, and 1 mmol of CTAB. With the increase of reaction temperature, the conversion of toluene and the yield of products increased rapidly. However, though the yields of BA and BAL increased at higher temperature, the selectivity of them decreased somewhat. This could be due to the fact that BA and BAL could be further oxidized to BAC at higher temperature.

3.4.2 Effect of O₂ Flow on the Toluene Oxidation

The influence of the O_2 flow on the toluene oxidation was also investigated and the results are shown in Table 6. With the increase of O_2 flow from 0.03 L/min to 0.05 L/min in the reaction system, the toluene conversion increased from 5.51 to 7.37 %. When the O_2 flow was further increased to 0.07 L/min, the toluene conversion and the yields of products remained almost unchanged. One possible explanation is that when the O_2 flow was too high, the rate of toluene oxidation with O_2 is slower than that of O_2 mass transfer in toluene, thus making the excess amount of O_2 useless [5].



Fig. 2 Concentration of benzyl peroxide and conversion of toluene versus reaction time in the oxidation of toluene. Reaction conditions: (*a*) toluene 10 g, NHPI 2.0 %, T(p-Cl)PPMnCl 20 ppm, CTAB 1 mmol, 100 °C, O2 0.05 L/min; (*b*) HOAc 20 ml added; (*c*) without CTAB

Scheme 2 Preliminary mechanism of toluene oxidation over T(*p*-Cl)PPMnCl/NHPI/ CTAB

3.5 Preliminary Mechanism of Co-catalysis for T(*p*-Cl)PPMnCl/NHPI/CTAB in the Aerobic Oxidation of Toluene

The aerobic oxidation of hydrocarbons over metalloporphyrins is a biomimetic model of C–H activation by cytochrome P450 monoxygenase [1, 12, 23]. The mechanisms of hydrocarbon oxidations with dioxygen catalyzed by metalloporphyrins have been extensively investigated [24, 25]. All previous literatures have suggested that the aerobic oxidations of hydrocarbons catalyzed by metalloporphyrins involve free radical reactions [5, 16]. For the aerobic oxidation of toluene over T(p-Cl)PPMnCl/NHPI/ CTAB, when 2,6-di-tertbutyl-p-cresol, a free radical inhibitor, was added into toluene oxidation system, the reaction was substantially quenched. The result suggested that the toluene aerobic oxidation catalyzed by T(p-Cl)PPMnCl/NHPI/CTAB indeed proceeded via a radical process.

Hydroperoxides can be produced as intermediates in the hydrocarbon aerobic oxidation catalyzed by metalloporphyrins [18] under mild conditions, and they play an important role in the initiation of the aerobic oxidation of hydrocarbon [19]. In metalloporphyrin catalyzed aerobic oxidation of toluene, BHPO could come from the reaction of molecular oxygen with toluene catalyzed by metalloporphyrin [26-28]. NHPI can be an excellent radical catalyst promoter for the aerobic oxidation of toluene through an active intermediate PINO to produce benzyl radical [10, 16], which was then trapped by O_2 to generate BHPO. The change of BHPO concentration and the conversion of toluene with the reaction time over T(p-Cl)PPMnCl/NHPI and T(p-Cl)PPMnCl/NHPI/CTAB were investigated and the results were shown in Fig. 2. When the reaction was carried out at 100 °C and 0.05 L/min flow of oxygen with T(p-Cl)PPMnCl/NHPI as the catalyst, the BHPO concentration increased rapidly, while the conversion of toluene increased slowly. The toluene conversion was about 8 % when the reaction time was 8 h. However, it is interesting to find that when 1 mmol of CTAB was added to the reaction system under the same conditions, the BHPO concentration was kept at below 0.05 % during the oxidation of toluene and the toluene conversion increased rapidly with the reaction time. When the reaction time was 8 h, the conversion of toluene was 33 %. One possible reason could be that the highly volume of R₄N cation of CTAB could be in favor of interacting with the BHPO, facilitating its decomposition [29, 30]. When 20 mL acetic acid was added to the reaction system under the same conditions, the concentration of BHPO was lower than that when acetic acid was absent. It could be due to that the coordinating solvent effect of acetic acid reduced the catalytic activity of CTAB to decompose benzyl peroxide [29]. So for the aerobic oxidation of toluene over T(p-Cl)PPMnCl/NHPI/CTAB, the toluene oxidation process might be as follows (Scheme 2): BHPO is first generated by the catalysis of T(p-Cl)PPMnCl and NHPI, and then it can be decomposed immediately by CTAB or T(p-Cl)PPMn(III)Cl. And T(p-Cl)PPMn(III)Cl was oxidized to high valent T(p-Cl)PPMn(IV)(OH)Cl [14]. The more active T(p-Cl)PPMn(IV)(OH)Cl then can react with toluene to produce a benzyl radical.

4 Conclusions

The synergy of metalloporphyrin/NHPI/CTAB catalyst in the aerobic liquid phase oxidation of toluene has been reported. The toluene conversion with metalloporphyrin, NHPI and CTAB was higher than those when each catalyst component was used alone or two of them combined together. Experimental results indicated that T(p-Cl)PPMnCl was the best metalloporphyrin catalyst, affording higher toluene conversion than other metalloporphyrin catalyst. The concentration of catalyst, O₂ flow, reaction temperature, and reaction time influenced the toluene aerobic oxidation significantly. Best results were obtained at 100 °C with 0.05 L/min O₂ flow, 20 ppm T(p-Cl)PPMnCl, 2.0 mol% NHPI, and 1 mmol CTAB as catalyst, the toluene conversion can be as high as 40.95 %. And we believe that the improvement after adding CTAB might be due to the fact CTAB could efficiently decompose BHPOs which are generated from the toluene oxidation. Further studies of this catalytic oxidation reaction are underway in our laboratory.

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