

Aerobic oxidation of *p*-xylene over metalloporphyrin and cobalt acetate: Their synergy and mechanism

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Abstract

The aerobic liquid-phase oxidation of *p*-xylene (PX) over metalloporphyrin and $\text{Co}(\text{OAc})_2$ was studied, and the co-catalysis between metalloporphyrin and $\text{Co}(\text{OAc})_2$ for the oxidation of PX was discovered for the first time. The results showed that both the PX conversion and terephthalic acid yield could be increased significantly despite the fact that only a minute amount of metalloporphyrin was added to the reaction mixture in addition to the $\text{Co}(\text{OAc})_2$ catalyst. The effects of the structure of metalloporphyrin and reaction conditions such as temperature, air pressure and catalyst concentration on the overall reaction performance were also studied. A possible mechanism for the observed synergy between metalloporphyrin and $\text{Co}(\text{OAc})_2$ as co-catalysts for the aerobic liquid-phase oxidation of PX was proposed based on some experimental observations. The results suggested that the PX oxidation was improved because of the acceleration of the chain initiation of PX oxidation by metalloporphyrin, and the acceleration of the chain initiation itself was due to the ease of peroxide formation over metalloporphyrin.

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1. Introduction

Aerobic liquid-phase oxidation of *p*-xylene (PX) into terephthalic acid (TPA) is a very important reaction in the contemporary chemical industry [1–5]. The catalyst system of $\text{Co}(\text{AcO})_2/\text{Mn}(\text{AcO})_2/\text{HBr}$ is widely used in the large scale PX oxidation with air because high PX conversion and TPA selectivity (>95%) could be achieved [6–8]. Since the highly corrosive bromide is employed as a component of the catalyst system, a titanium reactor is required and it is very costly to build and maintain. Moreover, the corrosive bromide poses a serious environmental threat. Many scientists have attempted to develop new catalytic routes to avoid or reduce the use of bromide. One representative work in this field is the aerobic oxidation of PX with the catalyst system of NHPI/Co developed by Ishii and co-workers [9–11]. Though a yield of TPA as high as 82% could be obtained, there are several major shortcomings associated with this method such as low PX concentration (4%) and long reaction time (14 h) as well as the need for high catalyst loading (20% NHPI, 0.5%

$\text{Co}(\text{AcO})_2$, 0.5% $\text{Mn}(\text{AcO})_2$). Consequently it is not suitable for industrial application.

Metalloporphyrins have been shown to be effective catalysts in the selective oxidation of hydrocarbons under mild conditions [12–18]. As catalysts, they are environmentally benign and, for selected cases, high turnover numbers could be achieved with very low catalyst loading. The process of aerobic liquid-phase oxidation of cyclohexane to produce KA oil over metalloporphyrins is such an example and it is being industrialized in SINOPEC CORP with the annual capacity of 124 kt [19]. Recently aerobic oxidations of aromatic hydrocarbons such as toluene [20], PX [21], ethyl benzene [22,23] by metalloporphyrins have also been reported.

In this paper, a novel bimetallic catalyst system based on simple metalloporphyrin and $\text{Co}(\text{OAc})_2$ was tested for the first time in the aerobic liquid-phase oxidation of PX. The results obtained with the catalyst system of metalloporphyrin– $\text{Co}(\text{OAc})_2$ were not only much better than those results obtained with either metalloporphyrin or $\text{Co}(\text{OAc})_2$ alone but also better than the two results combined, clearly showing the effect of co-catalysis [24]. The effects of catalyst components and reaction conditions such as temperature, air pressure and catalyst concentration on the aerobic liquid-phase oxidation of PX were further investigated.

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A possible mechanism for the observed co-catalysis between metalloporphyrin and $\text{Co}(\text{OAc})_2$ for the PX oxidation was also proposed.

2. Experimental

2.1. Instruments and reagents

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. ^1H NMR spectra were determined using a Bruker-400. IR spectra were obtained on a PE-783 Spectrometer. UV–vis spectra were recorded on a PE L-17 spectrometer. A PerkinElmer 2400 elementary analyzer was used for elemental analysis. The high-pressure autoclave with high speed magnetic agitating and CYS-1 automatic oxygen-measuring instrument was similar to those reported previously [19].

Pyrrole was redistilled before use. PX was purified and analyzed by GC to ensure the absence of impurities before use. Other reagents were all of analytical grade and used as received.

2.2. Preparation of metalloporphyrin catalysts

Tetra[*p*-chlorophenyl]porphin ($\text{T}(p\text{-Cl})\text{PPH}_2$) was prepared by the direct condensation of pyrrole and *p*-chlorobenzaldehyde according to the following procedures [25]: 250 mL of propionic acid was placed in a 0.5-L three-neck round-bottom flask fitted with a mechanical stirrer and a reflux condenser and the acid was heated to reflux. After the addition of 1:1 ratio of *p*-chlorobenzaldehyde (75 mmol) and freshly distilled pyrrole (75 mmol), the color of reaction mixture darkened and eventually turned black. The reaction mixture was refluxed for another 30–40 min, and then approximately 100 mL of propionic acid was distilled off. The flask was cooled to room temperature and 200 mL of water was added. The flask was placed in the refrigerator overnight and the solid formed was collected via filtration, which was subsequently washed with warm water, ethanol, then dried in vacua. The crude product was purified by column chromatography (neutral Al_2O_3 , CHCl_3) to afford $\text{T}(p\text{-Cl})\text{PPH}_2$ in 22% yield. Analytical data: MS m/z : 750.9 ($\text{M}^+ + 1$, 77.7); UV–vis (CHCl_3 , nm) λ_{max} : 415, 511, 545, 585, 643; IR (KBr, cm^{-1}): 3313 (N–H), 3027 (C–H, Ar–H), 2972 (C–H, pyrrole), 1598, 1488 (C=C, Ar); ^1H NMR (CDCl_3 , 400 MHz) δ –2.84 (s, 2H, N–H), 7.74–7.96 (d, 8H, *m*-Ar–H), 8.11–8.33 (d, 8H, *o*-Ar–H), 8.83 (s, 8H, pyrrole) ppm.

Metalloporphyrins including $\text{T}(p\text{-Cl})\text{PPMnCl}$, $\text{T}(p\text{-Cl})\text{PPFeCl}$ and $\text{T}(p\text{-Cl})\text{PPCo}$ were synthesized by the reaction of the $\text{T}(p\text{-Cl})\text{PPH}_2$ with the corresponding metal salts, and purified according to the following procedure [25]: 100 mL of DMF and 1.0 g of $\text{T}(p\text{-Cl})\text{PPH}_2$ were placed in a 250-mL three-neck round-bottom flask equipped with a thermometer, a reflux condenser, and a mechanical stirrer, and heated to reflux. Then 2.0–3.0 g of the salts (MnCl_2 , FeCl_2 , CoCl_2) were added. The metallation of $\text{T}(p\text{-Cl})\text{PPH}_2$ was monitored by TLC analysis. The reaction was stopped when the

complete disappearance of the starting material $\text{T}(p\text{-Cl})\text{PPH}_2$, and the mixture was cooled to room temperature. Then 100 mL of deionized water was added into the reaction mixture to precipitate out the desired product. The product was collected by filtration and washed with warm deionized water, absolute ethanol and dried in vacua. The crude product was purified by column chromatography (200–300 mesh silica gel, petroleum ether/chloroform = 3:1) to give the desired products in 90–95% yield.

$\text{T}(p\text{-Cl})\text{PPMnCl}$, MS m/z : 805.4 ($\text{M}^+ - \text{Cl}$); UV–vis (CHCl_3 , nm) λ_{max} : 477.6, 532.0, 585.6, 621.2; IR (KBr, cm^{-1}): 320 ($\text{Mn}-\text{Cl}$); anal. calcd. (%): C 62.85, H 2.88, N 6.66; found: C 62.81, H 2.72, N 6.63.

$\text{T}(p\text{-Cl})\text{PPFeCl}$, MS m/z : 806.2 ($\text{M}^+ - \text{Cl}$); UV–vis (CHCl_3 , nm) λ_{max} : 420.7, 509.0, 574.8, 652.1; IR (KBr, cm^{-1}): 384 ($\text{Fe}-\text{Cl}$); anal. calcd. (%): C 62.78, H 2.87, N 6.66; found: C 62.74, H 2.80, N 6.72.

$\text{T}(p\text{-Cl})\text{PPCo}$, MS m/z : 808.7 (M^+); UV–vis (CHCl_3 , nm) λ_{max} : 407.0, 524.0; anal. calcd. (%): C 65.29, H 2.99, N 6.92; found: C 65.32, H 3.17, N 6.82.

μ -Oxo-bis[*meso*-tetra(*p*-chlorophenyl)porphyrinatoiron(III)] ($[\text{T}(p\text{-Cl})\text{PPFe}]_2\text{O}$) was synthesized according to the following procedure [26]: a 100-mL three-neck round-bottom flask equipped with a thermometer, a reflux condenser, and a mechanical stirrer were charged with 35 mL of DMF and 1.0 g of $\text{T}(p\text{-Cl})\text{PPH}_2$. After the mixture was heated to reflux, 0.3 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ was added in batches followed by 0.35 g of NaOH in batches 30 min later. The mixture was stirred under reflux for 40 min. And then the reaction was worked up as above to obtain the crude product. The pure product $[\text{T}(p\text{-Cl})\text{PPFe}]_2\text{O}$ was obtained by recrystallizing the crude product in benzene and cyclohexane. Yield: 85%. Analytical data: UV–vis (benzene, nm) λ_{max} : 408.0, 570.8, 611.2; IR (KBr, cm^{-1}): 870 ($\text{Fe}-\text{O}-\text{Fe}$), 895 ($\text{Fe}-\text{O}-\text{Fe}$); anal. calcd. (%): C 64.90, H 2.97, N 6.88; found: C 64.73, H 2.88, N 7.11.

μ -Oxo-bis[*meso*-tetra(*p*-chlorophenyl)porphyrinatomanganese(III)] ($[\text{T}(p\text{-Cl})\text{PPMn}]_2\text{O}$) was synthesized according to the following procedure [26]: 1.0 g of $\text{T}(p\text{-Cl})\text{PPMnCl}$ was placed in a reactor filled with 250 mL of benzene, and then 50 mL of 5% aqueous NaOH was added. After vigorously stirring for 3 h, 300 mL of water was added. The crude product $[\text{T}(p\text{-Cl})\text{PPMn}]_2\text{O}$ was obtained by evaporation of the benzene, filtration and washing with water until the filtrate liquor became neutral. $[\text{T}(p\text{-Cl})\text{PPMn}]_2\text{O}$ was dried in air and recrystallized with benzene and cyclohexane. Yield: 80%. Analytical data: UV–vis (benzene, nm) λ_{max} : 420.4, 470.2, 578.4, 616.0; IR (KBr, cm^{-1}): 850 ($\text{Mn}-\text{O}-\text{Mn}$), 883 ($\text{Mn}-\text{O}-\text{Mn}$); anal. calcd. (%): C 64.97, H 2.97, N 6.89; found: C 64.42, H 3.05, N 6.74.

2.3. PX oxidation with air

2.3.1. Oxidation of PX at elevated pressure

Oxidation of PX at elevated pressure was carried out using the following typical procedure: 300 mL of PX, 125 mL of acetic acid, 5 mg of $\text{T}(p\text{-Cl})\text{PPMnCl}$ and 400 mg of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ were placed into a 500-mL steel autoclave pressurized with

nitrogen at 2.0 MPa. When the desired temperature was reached, nitrogen was released and air was injected continuously at a flow rate of 160 L h⁻¹. A digital gas detector was used to measure the concentration of oxygen and carbon dioxide in the tail gas. The reaction mixture was stirred for 3 h before it was cooled to room temperature.

2.3.2. Oxidation of PX at atmospheric pressure

Oxidation of PX at atmospheric pressure was carried out according to the following procedure: 20 mL of PX and precisely weighed catalyst were added into a 100-mL three-neck flask (in dark) with magnetic stirring. Oxygen (0.1 MPa) was continuously introduced into the flask at flow rate of 0.1 L min⁻¹ while the temperature was kept at 411 K (the boiling point of PX).

2.4. Analysis of PX oxidation products

The oxidation products of PX were identified by GC–MS, LC–MS, by HPLC co-injection of commercially available authentic samples, and quantified with an Agilent 1100 HPLC with UV (254 nm) detector and a Zorbax SB-C₁₈ (4.5 × 250 mm) column. Eluent consisting of 25% CH₃OH, 20% CH₃CN and 55% H₃PO₄ buffer solvent (0.5%) with a flow rate of 1.0 mL min⁻¹ was used.

The contents of hydroperoxides were determined by iodometric method. A weighed amount (about 1 g) of oxidation products was dissolved in 10 mL of isopropyl alcohol and treated with 5 mL of saturated KI solution at room temperature. After 60 min, the in situ generated iodine was titrated with 0.02 M Na₂S₂O₃ solution until the brown color of the iodine disappeared.

3. Results and discussion

3.1. Co-catalysis of metalloporphyrin and Co(OAc)₂ for the aerobic oxidation of PX

It has been shown that Co(OAc)₂ can efficiently catalyze the PX oxidation with air in acetic acid (acetic acid/PX, 4/1 by

volume) [5]. On the other hand, metalloporphyrins have been shown to be effective catalysts for the PX oxidation with air with much less acetic acid (acetic acid/PX, 1/4 by volume) [21]. Aiming to further improve the efficiency of the aerobic oxidation of PX, we carried out the oxidation using metalloporphyrin in combination with Co(OAc)₂ as catalyst. The oxidation products consisted mainly of *p*-toluic aldehyde (TALD), *p*-toluic acid (*p*-TA) and TPA, as shown in Fig. 1. These products were also the major products when the oxidation was catalyzed by either metalloporphyrin or Co(OAc)₂.

The aerobic oxidation of PX oxidation was carried out using three different catalyst systems, i.e., T(*p*-Cl)PPMnCl, Co(OAc)₂, and T(*p*-Cl)PPMnCl-Co(OAc)₂, and the results were summarized in Table 1. When T(*p*-Cl)PPMnCl was used as the catalyst, less than 1% TPA was produced while 12% of the PX reacted. When the catalyst was switched to Co(OAc)₂, the yield of TPA increased to 8% while the reaction conversion reached 47%. Much to our delight, when T(*p*-Cl)PPMnCl and Co(OAc)₂ were used together, the PX conversion increased to 67% and the TPA yield almost doubled (17%). It is understandable that the PX conversion and TPA yield by T(*p*-Cl)PPMnCl-Co(OAc)₂ are higher than those by either T(*p*-Cl)PPMnCl or Co(OAc)₂ alone, however, the fact that the results obtained with T(*p*-Cl)PPMnCl-Co(OAc)₂ system are much better than the combined results of T(*p*-Cl)PPMnCl and Co(OAc)₂ may not be so easy to explain. The results strongly suggest there is synergy between the two components of the catalyst system, i.e., T(*p*-Cl)PPMnCl and Co(OAc)₂, which means that co-catalysis between the two may be operative in the aerobic oxidation of PX. This discovery could be significant due to the fact that (a) higher PX conversion and TPA yield could be obtained with the catalyst system of T(*p*-Cl)PPMnCl-Co(OAc)₂ than Co(OAc)₂ alone; (b) it did not require the use of highly corrosive bromide; (c) the amount of acetic acid used was also cut down from 80% to 38% (by volume). Above advantages could make the catalyst system of T(*p*-Cl)PPMnCl-Co(OAc)₂ potentially industrially applicable for the PX oxidation with air.

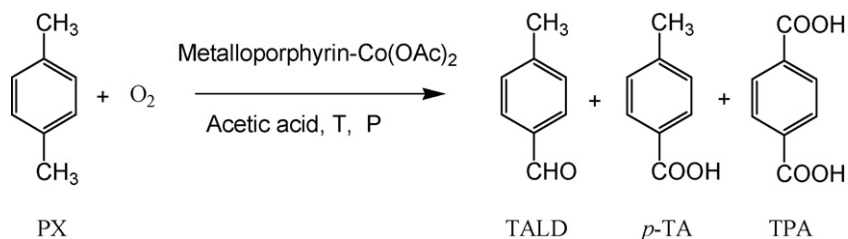


Fig. 1. Metalloporphyrin-Co(OAc)₂ catalyzed PX oxidation.

Table 1
Effect of Co(OAc)₂ on PX oxidation catalyzed by T(*p*-Cl)PPMnCl^a

Catalyst (mg)		Selectivity (mol%)			PX conversion (mol%)	TPA yield (mol%)
Co(OAc) ₂ ·4H ₂ O	T(<i>p</i> -Cl)PPMnCl	TPA	<i>p</i> -TA	TALD		
	5	2	73	24	12	<1
400		18	79	3	47	8
400	5	25	73	2	67	17

^a Reaction conditions: PX, 200 mL; HOAc, 125 mL; temperature, 453 K; air pressure, 2.0 MPa; air flow, 160 L h⁻¹; reaction time, 3 h.

Table 2
Effect of types of metalloporphyrins on PX oxidation over Co(OAc)₂–metalloporphyrin^a

Metalloporphyrin	Selectivity (mol%)			PX conversion (mol%)	TPA yield (mol%)
	TPA	<i>p</i> -TA	TALD		
T(<i>p</i> -Cl)PPMnCl	25	73	2	67	17
T(<i>p</i> -Cl)PPCo	18	80	2	57	10
T(<i>p</i> -Cl)PPFeCl	15	81	4	54	8
[T(<i>p</i> -Cl)PPMn] ₂ O	12	82	6	52	6
[T(<i>p</i> -Cl)PPFe] ₂ O	10	82	7	50	5

^a Reaction conditions: PX, 200 mL; HOAc, 125 mL; metalloporphyrin, 5 mg; Co(OAc)₂·4H₂O, 400 mg; temperature, 453 K; air pressure, 2.0 MPa; air flow, 160 L h⁻¹; reaction time, 3 h.

3.2. The effect of the catalyst structure on the PX oxidation

When different metalloporphyrins were tested as co-catalysts together with Co(OAc)₂, different PX conversions and product selectivities were obtained for the aerobic oxidation of PX (Table 2). Overall, five different metalloporphyrins were tried, namely, T(*p*-Cl)PPMnCl, T(*p*-Cl)PPCo, T(*p*-Cl)PPFeCl, [T(*p*-Cl)PPMn]₂O and [T(*p*-Cl)PPFe]₂O. Out of the five, the performance of T(*p*-Cl)PPMnCl–Co(OAc)₂ was clearly the best in terms of both the PX conversion and the yield of TPA. The catalytic reactivity differences between catalyst systems might be related to the rate of peroxide formation by different metalloporphyrin complexes, and this will be elaborated further in Section 3.5.

The catalyst concentration can be one of the key factors influencing the conversion and product selectivity in metalloporphyrin catalyzed alkane oxidations [19–21]. To understand the effect of the concentration of metalloporphyrin and Co(OAc)₂ on the PX oxidation, we investigated the changes of the PX conversion and product selectivities with respect to the change of catalyst concentration, and the results were shown in Table 3. When 400 mg of Co(OAc)₂ was used in combination with 1, 3, and 5 mg of T(*p*-Cl)PPMnCl, the PX conversions were 46%, 49%, 67%, respectively, and their corresponding yields of TPA were 6%, 7%, 17%, respectively. In other words, the PX conversion and TPA yield both increased when the concentration of metalloporphyrin was increased. Surprisingly, further increase of the catalyst amount led to lower PX conversion (47% when 10 mg of T(*p*-Cl)PPMnCl was used, 35% when 15 mg of T(*p*-Cl)PPMnCl was used), and the yield of TPA also dropped (6% when 10 mg of T(*p*-Cl)PPMnCl was used, 5%

when 15 mg of T(*p*-Cl)PPMnCl was used). This observation is consistent with our earlier results that the oxidation reaction can be inhibited at high concentration of metalloporphyrin [19,21]. One possible reason could be that the self-oxidation rate of metalloporphyrins increased when a higher amount of metalloporphyrin was employed, which in turn could facilitate the deactivation of catalyst. PX oxidation was also investigated with different amount of Co(OAc)₂, while keeping the amount of T(*p*-Cl)PPMnCl constant. It was found that 400 mg of Co(OAc)₂ was optimal. Both the PX conversion and the TPA yield suffered when more Co(OAc)₂ was used. Similar results were obtained when lesser amount of Co(OAc)₂ was used. Previous results already indicated that the PX oxidation could be inhibited when high concentration of cobalt salt was employed [27].

It has been reported that the efficiency of PX oxidation catalyzed by Co(OAc)₂ could be improved by employing Mn(OAc)₂ as the co-catalyst. For example, the reaction rate and TPA yield increased when Mn(OAc)₂ was added in the NHPI/Co(OAc)₂ catalyzed oxidation of PX [10,11], and similar results were obtained when part of Co(OAc)₂ was substituted by Mn(OAc)₂ in the Co/Br catalyzed PX oxidation system [6,28]. To probe whether or not the same phenomenon can be repeated with the T(*p*-Cl)PPMnCl–Co(OAc)₂ catalyst system, various amounts of Mn(OAc)₂ were added to the reaction mixture in addition to the T(*p*-Cl)PPMnCl and Co(OAc)₂ catalysts, and the results were shown in Table 4. The addition of Mn(OAc)₂ did not lead to any improvement at all. In fact both the PX conversion and TPA yield suffered greatly. A possible reason responsible for these significant drops will be discussed in detail in Section 3.5.

Table 3
Effect of T(*p*-Cl)PPMnCl concentration on PX oxidation over Co(OAc)₂–T(*p*-Cl)PPMnCl^a

Catalyst (mg)	T(<i>p</i> -Cl)PPMnCl	Selectivity (mol%)			PX conversion (mol%)	TPA yield (mol%)
		TPA	<i>p</i> -TA	TALD		
400	1	13	85	2	46	6
400	3	14	83	3	49	7
400	5	25	73	2	67	17
400	10	13	84	2	47	6
400	15	14	83	3	35	5
200	5	9	87	4	34	3
600	5	12	84	3	42	5

^a Reaction conditions: PX, 200 mL; HOAc, 125 mL; temperature, 453 K; air pressure, 2.0 MPa; air flow, 160 L h⁻¹; reaction time, 3 h.

Table 4
Effect of $\text{Mn}(\text{OAc})_2$ on PX oxidation over $\text{Co}(\text{OAc})_2\text{-T}(p\text{-Cl})\text{PPMnCl}^{\text{a}}$

Catalyst (mg)			Selectivity (mol%)			PX conversion (mol%)	TPA yield (mol%)
$\text{Co}(\text{OAc})_2^{\text{b}}$	$\text{Mn}(\text{OAc})_2^{\text{c}}$	$\text{T}(p\text{-Cl})\text{PPMnCl}$	TPA	<i>p</i> -TA	TALD		
400		5	25	73	2	67	17
300	100	5	14	79	6	39	5
200	200	5	17	77	5	45	8
100	300	5	11	71	17	37	4

^a Reaction conditions: PX, 200 mL; HOAc, 125 mL; temperature, 453 K; air pressure, 2.0 MPa; air flow, 160 L h⁻¹; reaction time, 3 h.

^b $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$.

^c $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$.

Table 5
Effect of temperature and air pressure on PX oxidation^a

Temperature (K)	Air pressure (MPa)	Selectivity (mol%)			PX conversion (mol%)	TPA yield (mol%)
		TPA	<i>p</i> -TA	TALD		
423	2.0	9	80	11	30	3
433	2.0	11	83	6	40	5
443	2.0	16	82	2	52	8
453	2.0	25	73	2	67	17
453	1.2	13	85	2	55	7
453	3.0	25	74	1	70	18

^a Reaction conditions: PX, 200 mL; HOAc, 125 mL; $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, 400 mg; $\text{T}(p\text{-Cl})\text{PPMnCl}$, 5 mg; air flow, 160 L h⁻¹; reaction time, 3 h.

3.3. The effect of reaction temperature and pressure on the PX oxidation

Reaction temperature and air pressure could also affect the conversion and the product selectivities of the PX oxidation profoundly. A series of studies were carried out to investigate the effects of reaction temperature and air pressure on the aerobic oxidation of PX (Table 5). As it could be seen from Table 5, the PX conversion increased steadily as the reaction temperature was increased. On the other hand, the TPA yield almost doubled each time as the temperature was raised by 10°. The effect of air pressure is more complex. There was a sharp increase on the PX conversion and the TPA yield (55–67% for conversion, 7–17% for the TPA yield) when the air pressure was changed from 1.2 to 2.0 MPa. Further increase of the air pres-

sure did not lead to any significant change on the overall reaction performance.

3.4. Investigation of the concentration of peroxides in the PX oxidation over metalloporphyrin and $\text{Co}(\text{OAc})_2$

It is known that peroxides, formed in the hydrocarbon oxidation, play an important role for the initiation of the chain reaction of the hydrocarbon oxidation [27]. To understand the effect of peroxides on the PX oxidation over the metalloporphyrin– $\text{Co}(\text{OAc})_2$ catalyst system, we decided to measure the content of peroxides in the reaction system. Typically, reactions were carried out at 411 K and under 0.1 MPa of oxygen using $\text{T}(p\text{-Cl})\text{PPMnCl}$, $\text{Co}(\text{OAc})_2$ and $\text{T}(p\text{-Cl})\text{PPMnCl}\text{-Co}(\text{OAc})_2$ as catalysts, and the concentration of peroxides and

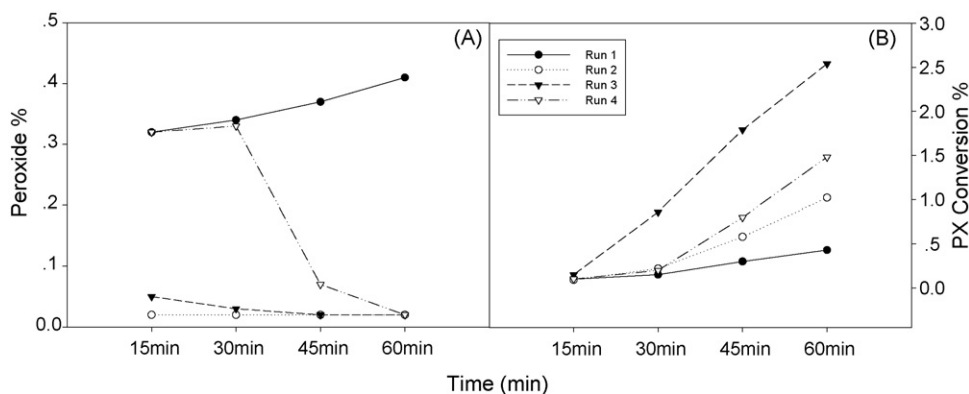


Fig. 2. Change of content of peroxides (A) and PX conversion (B) with reaction time. Reaction conditions (in dark): PX 20 mL, temperature 411 K, O₂ pressure 0.1 MPa, O₂ flow rate 0.1 L min⁻¹, catalyst: run 1, 1 mg of $\text{T}(p\text{-Cl})\text{PPMnCl}$; run 2, 10 mg of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; run 3, 1 mg of $\text{T}(p\text{-Cl})\text{PPMnCl}$ and 10 mg of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$; run 4, 1 mg of $\text{T}(p\text{-Cl})\text{PPMnCl}$ and 10 mg of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was added at 30 min.

Table 6
Amount of peroxide produced with different metalloporphyrins^a

Metalloporphyrin	Peroxide content (mol%)	
	30 min	60 min
T(<i>p</i> -Cl)PPMnCl	0.34	0.42
T(<i>p</i> -Cl)PPCo	0.04	0.11
T(<i>p</i> -Cl)PPFeCl	0.07	0.14
[T(<i>p</i> -Cl)PPMn] ₂ O	0.02	0.07
[T(<i>p</i> -Cl)PPFe] ₂ O	0.01	0.03

^a Reaction conditions (in dark): PX, 20 mL; metalloporphyrin, 1 mg; temperature, 411 K; O₂ pressure, 0.1 MPa; O₂ flow rate, 0.1 L min⁻¹.

the PX conversions over time are shown in Fig. 2. With T(*p*-Cl)PPMnCl as catalyst, the peroxide concentration was kept around 0.34% through out the reaction, and the PX conversion only increased slowly. However, when Co(OAc)₂ was employed, the peroxide concentration was about 0.02%, and the PX conversion increased slowly for the first 30 min, then increased quickly. For the T(*p*-Cl)PPMnCl-Co(OAc)₂ system, only a low concentration of peroxide was detected (0.02%), whereas the PX conversion increased rapidly from the very beginning. It is interesting to note that addition of Co(OAc)₂ after the PX oxidation has been run for 30 min over catalyst T(*p*-Cl)PPMnCl could make the concentration of peroxide drop rapidly from 0.33% to 0.07% within 15 min. At the same time the PX conversion increased rapidly from 0.2% to 0.8% (see Fig. 2).

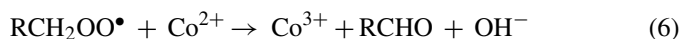
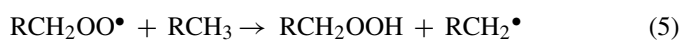
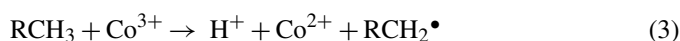
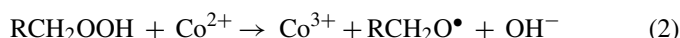
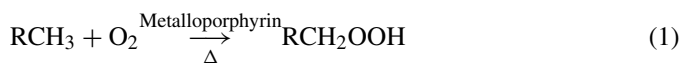
Different metalloporphyrins have different reactivity for the formation of peroxide in the PX oxidation, and the concentrations of peroxide in the PX oxidation catalyzed by five different metalloporphyrins, i.e., T(*p*-Cl)PPMnCl, T(*p*-Cl)PPFeCl, T(*p*-Cl)PPCo, [T(*p*-Cl)PPMn]₂O and [T(*p*-Cl)PPFe]₂O under otherwise same conditions were shown in Table 6. From it we can tell that the order of the ability to produce peroxide by different metalloporphyrins is: T(*p*-Cl)PPMnCl > T(*p*-Cl)PPFeCl > T(*p*-Cl)PPCo > [T(*p*-Cl)PPMn]₂O > [T(*p*-Cl)PPFe]₂O. This trend correlated well with their respective catalytic activity in the PX oxidation with air when used in combination with Co(OAc)₂ (shown in Table 2 in preceding sections).

3.5. The mechanism of co-catalysis between metalloporphyrin and Co(OAc)₂ in the aerobic oxidation of PX

The oxidation of PX with oxygen over cobalt salts is generally considered as a free radical autoxidation reaction [27,29]. The primary products, hydroperoxides produced in the autoxidation process could oxidize Co(II) into Co(III) [6,30] and Co(III) reacting with PX to form alkyl free radicals is the key initiation step of cobalt catalyzed PX oxidation reaction [31,32]. So making the initial formation of hydroperoxides easier can facilitate the formation of Co(III) ions which in turn will also facilitate the cobalt catalyzed oxidation of PX with air.

The selective oxidation of hydrocarbons with oxygen catalyzed by metalloporphyrins is a biomimetic process, whose mode of action is closely related to that of the important enzyme cytochrome P450 monooxygenase [33–35]. With metallopor-

phyrin catalysis, hydroperoxides can be produced under much milder conditions [23] in the hydrocarbon oxidation with O₂. For the metalloporphyrin-Co(OAc)₂ catalyzed oxidation of PX, we believe that hydroperoxide is first generated by the catalysis of metalloporphyrin, then they can be decomposed immediately by Co(OAc)₂ (as indicated by Fig. 2 in preceding sections), and at the same time, Co(II) is oxidized to Co(III). Subsequent reaction of Co(III) with PX initiate the chain reaction by generating free radical RCH₂• which will react further with oxygen to generate more peroxides. Then the reaction pathway follows the typical autoxidation sequences and the whole reaction process might be as follows:



It is reasonable to conclude that the observed co-catalysis between T(*p*-Cl)PPMnCl and Co(OAc)₂ is largely due to the acceleration of peroxide formed by T(*p*-Cl)PPMnCl in the reaction system.

It is interesting that co-catalysis between the Mn(OAc)₂ and Co(OAc)₂ exists in the Mn(OAc)₂-Co(OAc)₂-NaBr catalyst system, but not in Mn(OAc)₂-Co(OAc)₂-T(*p*-Cl)PPMnCl catalyst system. When Mn(II) was added in the Co/Br catalyst system, it could be oxidized into Mn(III) by Co(III), and the steady-state concentration of Co(III) was decreased. This reduced the extent of the decarboxylation of aromatic acids. In addition Mn(III) could oxidize the bromide ions to dibromine, which could react with PX to generate more free radicals. So synergistic effect was observed and both PX conversion and TPA selectivity were increased when Mn(II) was added in the Co/Br catalyst system [6,28]. In contrast, similar phenomenon could not be observed in the T(*p*-Cl)PPMnCl-Co(OAc)₂ catalyst system. One possible reason could be that when Mn(II) was added in the T(*p*-Cl)PPMnCl-Co(OAc)₂ catalyst system, the effective concentration of Co(III) is decreased. Since Mn(III) has lower reactivity for PX oxidation [28], less amount of Co(III) resulted in lower PX conversion when part of Co(OAc)₂ was substituted by Mn(OAc)₂.

4. Conclusions

The aerobic liquid-phase oxidation of PX over metalloporphyrin and Co(OAc)₂ was studied, and the co-catalysis between metalloporphyrin and Co(OAc)₂ for the oxidation of PX was discovered for the first time. The results showed that both the PX conversion and TPA yield could be increased significantly even though only a minute amount of metalloporphyrin is added to the reaction mixture besides the cobalt catalyst. The effects of the structure of metalloporphyrin and reaction conditions such as

temperature, air pressure and catalyst concentration on the overall reaction performance were also studied. A possible reason for the observed synergy between catalysts metalloporphyrin and cobalt acetate for the aerobic liquid-phase oxidation of PX was proposed based on experiment observations. The results suggested that the PX oxidation was improved because of the acceleration of the chain initiation of PX oxidation by metalloporphyrin catalyst, and the acceleration of the chain initiation itself was due to the ease of peroxide formation over metalloporphyrin. This paper could be helpful in the future development of biomimetic oxidation of hydrocarbons by metalloporphyrins. It can also have significant impact on the development of new approaches for the oxidation of PX and other hydrocarbons with oxygen. Further studies into the scope and mechanism of this co-catalyzed oxidation reactions are being carried out in our laboratory.

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