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Selective cyclohexane oxidation catalyzed by manganese porphyrins and co-catalysts

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ABSTRACT

Several polar molecules, such as alcohols, ketones, esters and acids, were used as co-catalysts for the cyclohexane oxidation catalyzed by manganese porphyrins, and the catalytic activity was found to be closely related to polarity of co-catalysts. The results indicated that the total selectivity of products was as high as 96.3% and glutaric acid selectivity was up to 50.9%. Thus, the proposed method provides a new approach for preparing glutaric acid.

1. Introduction

Cyclohexane is an important hydrocarbon and bulk chemicals [1]. The oxidation products of cyclohexane include cyclohexanol, cyclohexanone, adipic acid, and glutaric acid etc. Selective cyclohexane oxidation is a significant process in the chemical industry because the products of this reaction may be utilized in a number of ways [2–4]. Cyclohexanol and cyclohexanone are valuable chemical intermediates for preparing adipic acid and caprolactam [5–8]. Adipic acid is an important intermediate used for manufacturing nylon-6,6 and nylon-6 polymers, urethane foams, plasticizers, and lubricants etc. [9–12]. Therefore, the direct oxidation of cyclohexane into adipic acid under mild reaction conditions is a worthwhile endeavor.

The generation of dicarboxylic acids was considered in two approaches: cyclohexanone oxidation and beta bond-breaking of epoxy radicals. Lusztyk et al. [13] reported that the solvents exert an important effect on epoxy radical dehydrogenation and beta bond-breaking. Increases in solvent polarity gradually increase the beta-bond breaking ability of epoxy radicals. Sheldon et al. [14] observed the same phenomenon during catalytic cyclododecane oxidation. While no acids were generated when benzotrifluoride was used as a solvent, acetic acid exerted opposite effects. Hermans and Peeters et al. [15,16] reported that cyclohexanone presents good effects on cyclohexane oxidation, as verified by experimental and computational methods. Weng et al. [17,18] studied the liquid-phase cooxidation of cyclohexane and cyclohexanone, and proposed possible routes to obtain glutaric and succinic acids. Ishii et al. [19] reported the cyclohexane oxidation in air under mild condition without the use of any solvent by employing the lipophilic NHPI derivatives, which are easily dissolved in alkanes. Simonato et al. [20] reported one-step process for obtaining adipic acid from cyclohexane using a very stable lipophilic carboxylic acid and very low manganese and cobalt salts loadings. This new approach to produce adipic acid avoids the final nitric oxidation step, which generates a strong greenhouse gas, and thus provides an environmentally benign alternative to an important industrial reaction. Miyake et al. [9] reported the cyclohexane oxidation with molecular oxygen using a novel system composed of isoamyl nitrite, $Co(acac)_3$ and $Mn(acac)_3$. In this reaction, the nitrite contributed to the rate-determining step, which involves the initial dissociation of C–H bond of cyclohexane, and the Co and Mn promoters contributed to the succeeding oxidation steps; a high adipic acid selectivity of about 40% was also attained. Xu et al. [21]

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reported the hydrocarbons oxidation catalyzed by a $MgCl_2$/NHPI system and found that $MgCl_2$ remarkably promotes effect on NHPI-catalyzed aerobic oxidation of cyclohexane. Li et al [22] investigated the cyclohexane oxidation catalyzed by several small organic molecules including ketones, aldehydes, esters, alcohols and amines. The catalytic activity was found to be closely related to polarity, α-H activity, the strength of the hydrogen bond formed with cyclohexane and the radical scavenging capability of these molecules. Hwang et al [11] reported a N_2O-free process for adipic acid synthesis. Treatment of neat cyclohexane, cyclohexanol, or cyclohexanone with ozone at room temperature and 1 atm affords adipic acid as a solid precipitate. Zhong and Lin et al. [23] reported one-step oxidation of cyclohexane into adipic acid over manganese-doped titanium silicalite with hollow structure (HTS) using oxygen as oxidant without any initiator or solvent. Here, the catalyst exhibited high conversion (13.4%) and reasonable adipic acid selectivity (57.5%). Bal et al. [24] prepared a $CuCr_2O_4$ spinel nanoparticle catalyst that was speculated to be highly active for selective oxidation of cyclohexane into cyclohexanone with H_2O_2. A cyclohexane conversion rate of 70% and cyclohexanone selectivity of 85% was achieved at 50 °C.

In conclusion, there were some disadvantages in the above methods of cyclohexane oxidation. For example, reaction conditions were harsh and use of solvent, reaction system was complex, and catalyst was difficult to prepare. Therefore, the cost of cyclohexane oxidation was high.

Metalloporphyrins have recently been recognized as valuable biomimetic catalysts for oxidation of hydrocarbons because of their high selectivity and efficiency [12,25–32], in particular, cyclohexane oxidation with metalloporphyrins has been extensively studied [33,34]. The direct aerobic oxidation of cyclohexane into adipic acid catalyzed by $Fe^{III}T(o\text{-}Cl)PP$ was firstly reported by our group; in this method, molecular oxygen was used as an oxidant without any solvents and promoters [33].

In this present paper, we employed co-catalysts during the selective oxidation of cyclohexane catalyzed by manganese porphyrins to increase product selectivity.

2. Experimental

2.1. Instruments and reagents

Preliminary materials purchased from commercial sources were of analytical grade and used without further treatment unless indicated. The metalloporphyrins catalysts were prepared according to previously published procedures [35–37], and their structures were characterized by UV–vis, IR, and elementary analysis.

2.2. General procedures for cyclohexane oxidation

The cyclohexane oxidation with oxygen as an oxidant catalyzed by manganese porphyrins and co-catalysts was conducted as follows: Cyclohexane, manganese porphyrins and co-catalysts were charged into a 100 mL autoclave equipped with an electromagnetic stirrer and a temperature-controlling device. The mixture was heated to 3 °C below the set value (120/140 °C). The reactor was then charged with O_2 once, or the reaction system pressure was maintained at the set value. The mixture was stirred with the stirring rate of 800 rpm for certain time. The reactor was cooled to room temperature and the mixture was dissolve with acetone after completion of the reaction. The remaining reactants were analyzed by GC (Agilent HP-5MS) with methylbenzene as an internal standard. The oxidized products were derived through silylation (BSTFA: TMCS = 99:1) and monitored through GC (Agilent HP-5ms) and GC/MS; here, 2-ethylhexanoic acid was used as an internal standard [38].

3. Results and discussion

3.1. Cyclohexane oxidation catalyzed by $[Mn^{III}T(p\text{-}Cl)PP]Cl$ and co-catalysts

First, the aerobic oxidation of cyclohexane with O_2 catalyzed by $[Mn^{III}T(p\text{-}Cl)PP]Cl$ and co-catalysts was investigated, and the relevant results are summarized in Table 1. The main oxidation products (Scheme 1) were adipic acid (AA, 1), cyclohexanol (2), and cyclohexanone (3).

Table 1 shows that the cyclohexane oxidation without co-catalysts hardly occurs (Entry 1). The same observation holds true for oxidation of cyclopentanol and cyclooctanol (Entries 2–3), which present fairly low polarity. The reaction was achieved and showed good effects with cycloalkanones (Entries 4–7). Molecular polarity decreased with increasing number of cycloalkanone rings, and total selectivity decreased. Cycloalkanones were utilized completely during the reaction. Thus, they could not be recovered as catalyst. Considering these results, cycloalkanones were not taken into account in subsequent studies. N-Hydroxyphthalimide (NHPI) and N,N-Dimethylformamide (DMF) (Entries 13–14), which present high polarity, showed fairly extensive cyclohexane conversion. Product selectivity was very low because of the increased occurrence of side reactions. Cyclohexane conversion and product selectivity increased when organic acids, namely acetic acid (CH_3COOH) and benzoic acid (PhCOOH), were reacted. Benzoic acid also showed good effects on the catalytic reaction.

According to the reported literatures and our experimental phenomena, the oxidation of cyclohexane was a free radical reaction. Firstly, high-valence porphyrin intermediates captured α-H from cyclohexane to form the free radical $R^\bullet$. Then $R^\bullet$ trapped O_2 to generated peroxide free radicals which could initiate crossly more free radicals from cyclohexane. The rapidly increase of free radical concentration promoted the propagation of free-radical reactions. The oxidation of cyclohexane produced ROOH as the intermediates which could be immediately decomposed to ketone and alcohol by manganese porphyrins. Meanwhile, this reaction also produced $RO^\bullet$ which could react with cyclohexane and ring-open via β C–C cleavage. These radicals were further oxidized to produce AA and other decarboxylated by-products.

From the above results we could know that the polarity of co-catalysts was important for the cyclohexane oxidation catalyzed by manganese porphyrins. Because of the addition of co-catalyst, such as PhCOOH, the a-H was more easily to be captured from cyclohexane at lower temperature. Thus, the conversion rate of cyclohexane was increased.

3.2. Cyclohexane oxidation with dioxygen catalyzed by $[Mn^{III}T(p\text{-}Cl)PP]Cl$ and PhCOOH

The aerobic oxidation of cyclohexane with O_2 catalyzed by $[Mn^{III}T(p\text{-}Cl)PP]Cl$ and PhCOOH was subsequently investigated. The main oxidation products (Scheme 2) were adipic acid (AA, 1), cyclohexanol (2), cyclohexanone (3) and glutaric acid (GA, 4).

3.2.1. Effect of benzoic acid amounts on cyclohexane oxidation

The results in Table 2 reveal that cyclohexane conversion gradually increases with increasing PhCOOH content. The system with 5 mol% PhCOOH performed well during the reaction. Product yield increased with further increases in PhCOOH content, but the selectivity gradually decreased. Therefore, the appropriate PhCOOH dosage is 5 mol%.

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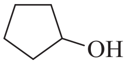
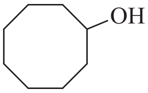
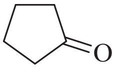
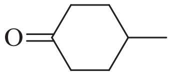
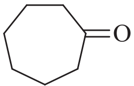
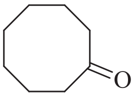
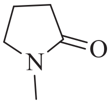
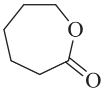
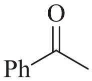
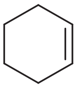
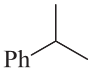
Table 1
Cyclohexane oxidation catalyzed by [Mn^{III}T(*p*-Cl)PP]Cl and co-catalysts.[a]

Entry	Co-catalysts	Conversion [%]	Yield [%]				Selectivity [%]			
			1	2	3	Total	1	2	3	Total
1	Blank	N.R.								
2	 Cyclopentanol	N.R.								
3	 Cyclooctanol	N.R.								
4	 Cyclopentanone	12.4	3.9	3.1	3.9	10.9	31.5	25.0	31.5	88.0
5	 4-Methylcyclohexanone	13.6	3.6	3.2	3.8	10.6	26.5	23.5	27.9	77.9
6	 Cycloheptanone	12.7	3.0	3.1	3.9	10.0	23.6	24.4	30.7	78.7
7	 Cyclooctanone	13.1	2.5	3.2	4.0	9.7	19.1	24.4	30.5	74.0
8	 NMP, 1-Methyl-2-pyrrolidinone	6.6	3.2	1.4	1.2	5.8	48.5	21.2	18.2	87.9
9	 ε-Caprolactone	N.R.								
10	 Acetophenone	N.R.								
11	DMSO	5.9	1.6	–	–		27.1	–	–	
12	 Cyclohexene	5.3	1	1.3	1.4	3.7	18.9	24.5	26.4	69.8
13	NHPI	12.0	0.9	0.7	2.0	3.6	7.5	5.8	16.7	30.0
14	DMF	27.6	0.6	–	–		2.2	–	–	
15	DMA	N.R.								
16	 Isopropylbenzene	N.R.								
17	CH_3COOH	9.6	2.4	2.4	2.5	7.3	25.0	25.0	26.0	76.0
18	PhCOOH	14.2	2.4	1.2	4.1	7.7	16.9	8.5	28.9	54.3

[a] *Reaction conditions*: [Mn^{III}T(*p*-Cl)PP]Cl (7×10^{-4} mol%), co-catalyst (30 mol%), 120 °C, O_2 pressure 1.4 MPa (continuous) for 3 h, 800 rpm.

3.2.2. *Effect of reaction pressure on cyclohexane oxidation*

The results listed in Table 3 demonstrate that oxygen pressure exerts a certain influence on cyclohexane oxidation. Cyclohexane conversion increased when the oxygen was sustained by 1.4 MPa. When the oxygen pressure was charged once, reaction conversion increased as the initial oxygen pressure increased. However, selectivity did not increase significantly. Thus, in subsequent experiments, an oxygen pressure of 2.5 MPa was adopted.

3.2.3. *Effect of different catalysts on cyclohexane oxidation*

The results in Table 4 reveal that the reaction is influenced by the type of manganese porphyrins applied. Mn^{III}T(*p*-Cl)PP showed

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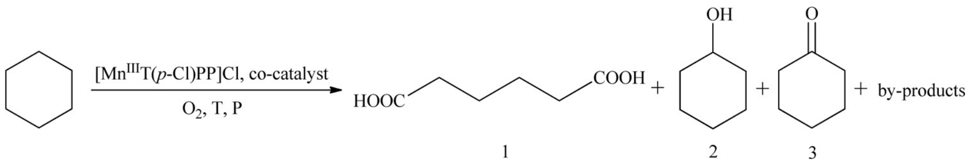
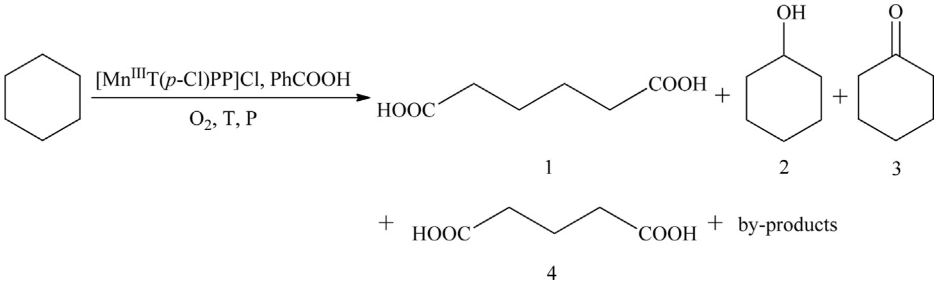


Scheme 1. Cyclohexane oxidation with dioxygen catalyzed by [Mn^{III}T(*p*-Cl)PP]Cl and co-catalysts.

Table 2
Effect of PhCOOH amount on cyclohexane oxidation[a].

Entry	PhCOOH amount [mol%]	Conversion [%]	Yield [%]					Selectivity [%]				
			1	2	3	4	Total	1	2	3	4	Total
1	0	12.9	1.7	2.1	3.1	1.1	8.0	13.2	16.3	24.0	8.5	62.0
2	5	23.6	6.3	1.7	5.0	5.8	18.8	26.7	7.2	21.2	24.6	79.7
3	10	29.3	9.1	2.1	5.4	5.1	21.7	31.1	7.2	18.4	17.4	74.1
4	15	39.3	11.0	2.4	6.4	5.1	24.9	28.0	6.1	16.3	13.0	63.4

[a] *Reaction conditions*: [Mn^{III}T(*p*-Cl)PP]Cl (7×10^{-4} mol%), 140 °C, O_2 pressure 1.4 MPa (continuous) for 3 h, 800 rpm.



Scheme 2. Cyclohexane oxidation with dioxygen catalyzed by [Mn^{III}T(*p*-Cl)PP]Cl and PhCOOH.

Table 3
Effect of reaction pressure on cyclohexane oxidation.[a]

Entry	Pressure [MPa]	Conversion [%]	Yield [%]					Selectivity [%]				
			1	2	3	4	Total	1	2	3	4	Total
1	1.4[b]	23.6	6.3	1.7	5.0	5.8	18.8	26.7	7.2	21.2	24.6	79.7
2	2.5[c]	19.3	6.4	2.3	4.7	3.2	16.6	33.2	11.9	24.4	16.6	86.0
3	3.0[c]	20.7	7.1	2.0	5.2	3.4	17.7	34.3	9.7	25.1	16.4	85.5

[a] *Reaction conditions*: [Mn^{III}T(*p*-Cl)PP]Cl (7×10^{-4} mol%), PhCOOH (5 mol%),140 °C for 3 h, 800 rpm.
[b] O_2 pressure 1.4 MPa (continuous).
[c] Initial O_2 pressure (one time).

Table 4
Effect of manganese porphyrins on cyclohexane oxidation.[a]

Entry	Manganese porphyrins	Conversion [%]	Yield [%]					Selectivity [%]					
			1	2	3	4	Total	1	2	3	4	Total	1 + 4
1	[Mn^{III}T(*p*-Cl)PP]Cl	19.3	6.4	2.3	4.7	3.2	16.6	33.2	11.9	24.4	16.6	86.0	49.7
2	[Mn^{III}T(*p*-OCH_3)PP]Cl	20.0	4.8	2.0	4.4	4.8	16.0	24.0	10.0	22.0	24.0	80.0	48.0
3	[Mn^{III}T(*p*-NO_2)PP]Cl	16.4	5.3	2.0	4.5	3.6	15.4	32.3	12.2	27.4	22.0	93.9	54.3
4	[Mn^{III}T(*o*-Cl)PP]Cl	17.1	5.9	2.0	4.4	2.9	15.2	34.5	11.7	25.7	17.0	88.9	51.5
5	Mn^{III}T(*p*-Cl)PP	16.4	6.3	2.0	4.5	3.0	15.8	38.4	12.2	27.4	18.3	96.3	56.7

[a] *Reaction conditions*: [Mn^{III}T(*p*-Cl)PP]Cl (7×10^{-4} mol%), PhCOOH (5 mol%), 140 °C for 3 h, initial O_2 pressure 2.5 MPa, 800 rpm.

good results with a total selectivity of products up to 96.3%, and the total selectivity of adipic acid and glutaric acid up to 56.7%.

3.3. Cyclohexane oxidation catalyzed by manganese porphyrins and organic acids

The aerobic oxidation of cyclohexane with O_2 catalyzed by Mn^{III}T(*p*-Cl)PP and organic acids was investigated. The main oxidation products (Scheme 3) were adipic acid (AA, 1), cyclohexanol (2), cyclohexanone (3) and glutaric acid (GA, 4).

The results in Table 5 reveal that organic acids exert an important influence on the conversion reaction. Cyclohexane conversion gradually decreased among the substituted benzoic acids (Entries 1–5). Benzoic acid showed better effects than other acids. A yield and selectivity of 6.3% and 38.4%, respectively, were obtained with benzoic acid, and total product selectivity was as high as 96.3%.

The use of dicarboxylic acids (Entries 6–9) caused gradual decreases in the total selectivity of adipic acid and glutaric acid. As malonic acid is broken down at 140 °C, the reaction temperature was not excessively high. With the conditions of malonic acid

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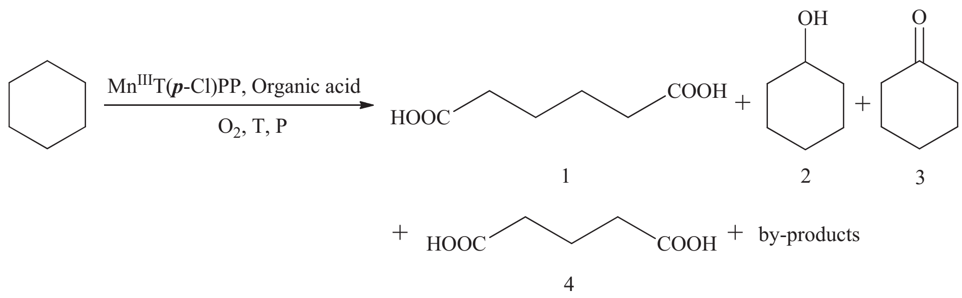

Scheme 3. Oxidation of cyclohexane with dioxygen catalyzed by Mn^{III}T(*p*-Cl)PP and organic acids.

Table 5
Cyclohexane oxidation catalyzed by manganese porphyrins and organic acids.[a]

Entry	Organic acids	Conversion [%]	Yield [%]					Selectivity [%]					
			1	2	3	4	Total	1	2	3	4	Total	1 + 4
1	(*p*-tBu)PhCOOH	21.9	3.9	2.2	5.5	4.4	16.0	17.8	10.0	25.1	20.1	73.1	37.9
2	(*p*-Cl)PhCOOH	20.0	5.5	2.6	5.0	0.0	13.1	27.5	13.0	25.0	0.0	65.5	27.5
3	PhCOOH	16.4	6.3	2.0	4.5	3.0	15.8	38.4	12.2	27.4	18.3	96.3	56.7
4	(*p*-C_2H_5)PhCOOH	14.3	4.5	2.1	3.8	2.0	12.4	31.5	14.7	26.6	14.0	86.7	45.5
5	(p-OMe)PhCOOH	7.1	2.2	1.2	1.2	0.0	4.6	31.0	16.9	16.9	0.0	64.8	31.0
6[b]	Malonic acid	5.7	1.8	0.0	0.0	2.9	4.7	31.6	0.0	0.0	50.9	82.5	82.5
7	Succinic Acid	10.0	3.4	1.2	2.1	2.9	9.6	34.0	12.0	21.0	29.0	96.0	63.0
8	Glutaric acid	9.0	2.0	1.2	1.3	2.2	6.7	22.1	13.3	14.5	24.5	74.4	46.6
9	Adipic acid	8.6	0.9	0.7	1.4	2.9	5.9	10.5	8.1	16.3	33.7	68.6	44.2
10	Isonicotinic acid	15.0	1.1	2.1	2.5	3.4	9.1	7.3	14.0	16.7	22.7	60.7	30.0
11	Acetic acid	15.7	3.5	1.6	4.1	4.9	14.1	22.3	10.2	26.1	31.2	89.8	53.5
12	Pentanoic acid	17.9	6.0	2.6	5.7	2.4	16.7	33.5	14.5	31.8	13.4	93.3	46.9
13	Hexanoic acid	19.3	5.7	2.4	4.9	2.1	15.1	29.5	12.4	25.4	10.9	78.2	40.4

[a] *Reaction conditions*: organic acids (5 mol%), Mn^{III}T(*p*-Cl)PP (7×10^{-4} mol%), 140 °C for 3 h, initial O_2 pressure 2.5 MPa, 800 rpm.
[b] 120 °C.

(5 mol%), Mn^{III}T(*p*-Cl)PP (7×10^{-4} mol%), 120 °C for 3 h, initial O_2 pressure 2.5 MPa, and 800 rpm, glutaric acid selectivity reached 50.9% and the total selectivity of adipic acid and glutaric acid were as high as 82.5%. These results demonstrate that the proposed method provides a new approach for preparing glutaric acid.

4. Conclusions

In summary, several polar molecules such as alcohols, ketones, esters, and acids were used as co-catalysts for the cyclohexane oxidation catalyzed by manganese porphyrins. The results indicated that the catalytic activity was closely related to polarity.

During cyclohexane oxidation catalyzed by Mn^{III}T(*p*-Cl)PP and PhCOOH with under reaction conditions of PhCOOH (5 mol%), Mn^{III}T(*p*-Cl)PP (7×10^{-4} mol%), 140 °C for 3 h, initial O_2 pressure 2.5 MPa, and 800 rpm, the yield and selectivity of adipic acid were 6.3% and 38.4%, respectively, and the total selectivity of products was as high as 96.3%.

During cyclohexane oxidation catalyzed by Mn^{III}T(*p*-Cl)PP and malonic acid with under the reaction conditions of malonic acid (5 mol%), Mn^{III}T(*p*-Cl)PP (7×10^{-4} mol%), 120 °C for 3 h, initial O_2 pressure 2.5 MPa, and 800 rpm, the selectivity of glutaric acid was up to 50.9%. Thus, the proposed method provides a new approach for preparing glutaric acid.

This method employed simple manganese porphyrins and co-catalysts in the catalytic selective oxidation of cyclohexane, the reaction conditions were relatively mild, the reaction system was solvent-free and simple, and the selectivity of main products was high. All of those were in conformity with the principles of green chemistry. Therefore, this method had a good prospect of industrial application in the future.

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