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Catalytic oxidation of cycloalkanes by porphyrin cobalt(II) through efficient utilization of oxidation intermediates

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ABSTRACT: The catalytic oxidation of cycloalkanes using molecular oxygen employing porphyrin cobalt (II) as catalyst was enhanced through utilizing cycloalkyl hydroperoxides that are the primary intermediates in oxidation of cycloalkanes, as additional oxidants to further oxidize cycloalkanes in the presence of porphyrin copper (II), especially for the cyclohexane, for which the selectivity was enhanced from 88.6% to 97.2% to the KA oil, at the same time, the conversion of cyclohexane was enhanced from 3.88% to 4.41%. The enhanced efficiency and selectivity were mainly attributed to the avoided autoxidation of cycloalkanes and efficient utilization of oxidation intermediates cycloalkyl hydroperoxides as additional oxidants instead of the conventional thermal decomposition. Besides the cyclohexane, the protocol presented in this research is also very applicable in the oxidation of other cycloalkanes, such as cyclooctane, cycloheptane and cyclopentane, and can serve as a applicable and efficient strategy to boost the conversion and selectivity simultaneously in oxidation of alkanes. And this work also is a very important reference for the extensive application of metalloporphyrins in catalysis chemistry.

KEYWORDS: metalloporphyrin, oxidation, oxygen, cycloalkane, cycloalkyl hydroperoxide.

INTRODUCTION

The efficient, selective and practical oxidation of cycloalkanes is still of great urgency and challenge in chemical industry for the extensive application of their oxygenated products and the high inertness of the C-H bond in cycloalkanes, especially for cyclohexane, which has captured a continuous and significant interest from scientists in both theory researches and application researches [1-5]. The oxygenated products of cyclohexane, which mainly refer to KA oil (a mixture of cyclohexanol and cyclohexanone), are the indispensable raw materials in production of the intermediates for a series of polymers, for example nylon-6 and nylon-66 [6-9]. In the oxidative functionalization of cycloalkanes, molecular oxygen (O_2) is regarded as the most promising oxidant for its readily availability, low cost and environmental harmlessness [9-13], compared with others such as hydrogen peroxide [14,15], *tert*-butyl hydroperoxide [16,17], 3-chloroperbenzoic acid [18,19], iodosylbenzene [20-23], iodosylbenzene diacetate [24,25] and so on [26], considering the demands of green chemistry. Thus, the oxidation of cyclohexane in industry is carried out employing O_2 as oxidant at present catalyzed by the

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homogeneous cobalt salt with the conversion of 3%~8% and selectivity of 80%~85% to KA oil, and in order to activate O_2, the industrial process is usually conducted at 150~170 ºC under the oxygen pressure of 1.0~2.0 MPa [8,27,28]. It is obvious that the current process of cyclohexane oxidation suffers from low conversion, low selectivity and high temperature seriously. And the low selectivity could be mainly ascribed to the high reaction temperature to some extent, since the autoxidation of cyclohexane without selectivity would occur at high temperature, accompanied by the undesired thermal decomposition of oxidation intermediate cyclohexyl hydroperoxide which is the primary intermediate product in oxidation of cyclohexane [8,29-31]. Both of them can product a lot of undesired oxygenated products, such as hexanedioic acid, which is a troublesome component to be separated from the obtained oxygenated mixtures. Therefore, it is a great urgency to develop the process of cycloalkane oxidation with high conversion and selectivity under mild conditions.

With the purpose to boost the efficiency and selectivity in cycloalkane oxidation employing O_2, and smooth the process, a variety of catalytic systems have been developed, for example employing metal nanoparticles as catalysts [32,33], metal oxides as catalysts [34,35], transition metal complexes as catalysts [36,37], molecular sieves as catalysts [38], biocatalysis [39], photocatalysis [10,40], and so on. Among them, metalloporphyrins as transition metal complexes and chemical structural analogues of cytochrome P-450, have been employed in the oxidation of cycloalkanes widely, which could activate O_2 efficiently and functionalize C-H bond selectively [13,22,23,41]. The conversion reached up to 39.8% reported by Huang and co-workers in the oxidation of cyclohexane employing heterogeneous metalloporphyrins as catalysts, but the selectivity was just 56.5% to the KA oil, and the reaction temperature range was 150~165 ºC [36,37,42,43]. In the report of Liu and co-workers, the selectivity obtained was 72.1% to the KA oil in the conversion of 13.1% for cyclohexane catalyzed by heterogeneous metalloporphyrins too [44]. And in the work of Yang and co-workers, the selectivity was 72.2% in the conversion of 29.9% using porous polymeric metalloporphyrins as catalysts at 150 ºC [41]. Although the conversion of cyclohexane was enhanced with the aid of metalloporphyrins, to boost the conversion and selectivity simultaneously in catalytic oxidation of cycloalkanes has not been achieved, even in the presence of metalloporphyrins as catalysts, because of the unselective autoxidation and thermal decomposition of oxidation intermediates cycloalkyl hydroperoxides at so high reaction temperature. Therefore, it is still a very challenging task to realize the catalytic oxidation of cycloalkanes with high selectivity and acceptable conversion employing molecular oxygen (O_2) as oxidant under mild conditions.

In the exploration to boost the efficiency and selectivity in oxidative functionalization of cycloalkanes with O_2 employing metalloporphyrins as catalysts [45-50], we focus on the catalytic transformation of cycloalkyl hydroperoxides and the lower reaction temperature in order to avoid the unselective thermal decomposition of the oxidation intermediates cycloalkyl hydroperoxides and autoxidation of cycloalkanes. Inspired by the high selectivity and low reaction temperature in catalytic oxidation of cyclohexane using *tert*-butyl hydroperoxide as oxidant and copper (II) complexes as catalysts [51-54], a strategy emerged in our minds to enhance the catalytic oxidation of cycloalkanes through efficient utilization of the oxidation intermediates cycloalkyl hydroperoxides as additional oxidants to oxidize cycloalkanes employing porphyrin copper (II) as catalyst. In order to activate O_2, porphyrin cobalt (II) was introduced to this catalytic system, which was a kind of very efficient catalyst in oxidation of various C-H bonds in hydrocarbon compounds [55,56]. Employed in the oxidation of cyclohexane, this dual-metalloporphyrins catalytic system exhibited encouraging outcomes as expected. Not only the selectivity was enhanced from 88.6% to 97.2% towards the KA oil, but also the conversion was improved from 3.88% to 4.41% simultaneously for cyclohexane. And for other cycloalkanes, this method was also very practical with satisfying selectivity and conversion. Hence, herein we reported the efficient and selective oxidative functionalization of cycloalkanes using O_2 catalyzed by porphyrin cobalt (II) employing oxidation intermediates cycloalkyl hydroperoxides as

additional oxidants in the presence of porphyrin copper (II) (Equation 1). This work not only presented a practical strategy to enhance the process of cycloalkanes oxidation, but also demonstrated a significant protocol for other alkanes' selective oxidation. To the best of our knowledge, the research demonstrated in this paper is a very rare and significant documentation for catalytic oxidation of alkanes, in which oxidation intermediates cycloalkyl hydroperoxides were utilized as additional oxidants instead of the conventional thermal decomposition to increase the selectivity of target products and the conversion of cycloalkanes substrates simultaneously in the presence of dual-metalloporphyrins catalytic system. And this work also is a very important reference for the extensive application of metalloporphyrins in catalysis chemistry.

<Equation 1>

EXPERIMENTAL

Chemical reagents and materials

Cyclopentane (98%), cyclohexane (99%), cycloheptane (98%) and cyclooctane (99%) were purchased from Shanghai Energy Chemical Co. Ltd., China, TCI Co. Ltd., Alfa Aesar Co. Ltd. respectively, and redistilled in the presence of sodium before use. All of the oxygenated products employed as standard samples were analytical grade and purchased from TCI Co. Ltd. All of the metalloporphyrins were synthesized as illustrated in supporting information. All of the other common chemical reagents employed in this work were in analytical-grade and used as received without any further purification unless noted otherwise.

Procedure of cycloalkane oxidation

The catalytic oxidation of cycloalkanes with O_2 in the presence of metalloporphyrins as catalysts was conducted in an autoclave reactor (100 mL) possessing an inner Teflon liner. In the typical procedure, cycloalkane (200 mmol) and metalloporphyrin (1.2×10^{-3}%, mol/mol) were sealed in the reactor, and heated with stirring to the set reaction temperature. Then, molecular oxygen (O_2) was introduced to reach up to the set pressure. The catalytic oxidation reaction was conducted with stirring for 8.0 h under the set temperature and pressure. When the reaction finished, the reactor was transferred to ice water to be cooled to room temperature. When the autoclave reactor was opened, triphenylphosphine (25 mmol, 6.5573 g) was added to the obtained solution and stirred for 30 min at room temperature to reduce the residual oxidation intermediates cycloalkyl hydroperoxides to alcohols quantitatively. Then the reaction mixture was shifted totally to a 100 mL volumetric flask using acetone as solvent to calculate the yields of oxygenated products. The yields of alcohols and ketones were calculated through GC analyses with toluene as internal standard. A small amount of residual hydroperoxides was obtained based on the amount of O=PPh$_3$ in GC analyses. The quantities of aliphatic diacids were calculated based on HPLC analyses using benzoic acid as internal standard and employing a Amethyst C18-H liquid chromatography column (250 mm × 4.6 mm × 0.25 μm). All of the substances in GC and HPLC analyses were identified through comparison with the authentic samples purchased from TCI Co. Ltd.

RESULTS AND DISCUSSION

Catalytic oxidation of cyclohexane employing dual-metalloporphyrins system

In this work, considering the importance of oxygenated products in chemical industry, cyclohexane was selected as the representative to carry out the catalytic oxidation of cycloalkanes to verify our design and expectation. In order to avoid the autoxidation of cyclohexane without selectivity, the reaction temperature was set at 120 ℃, at which the autoxidation would not occur as illustrated in our previous work [49]. T(4-Cl)PPFe (5, 10, 15, 20-tetrakis(4-chlorophenyl)porphyrin iron(II)), T(4-Cl)PPMn, T(4-Cl)PPCo, T(3-Cl)PPCo, T(2-Cl)PPCo were selected to activate O_2, and T(4-Cl)PPCu (5, 10, 15, 20-tetrakis(4-chlorophenyl)porphyrin copper(II)) was prepared to enhance the oxidizing ability of cyclohexyl hydroperoxide. The catalytic test was carried out under solvent-free conditions using O_2 as oxidant. And in this work, the amount of cyclohexyl hydroperoxide was calculated into the selectivity of KA oil for cyclohexyl hydroperoxide in a small amount could be transformed to KA oil smoothly when the reaction was completed. It was demonstrated in Table 1 and Table S1 in the supporting information that, the autoxidation of cyclohexane could not happen at 120 ℃ without the presence of metalloporphyrins (Table 1, Entry 1). When metalloporphyrins were employed as catalysts, the conversion reached up to 3.88% for T(2-Cl)PPCo as catalyst under the same reaction conditions with an acceptable selectivity of 88.6% towards KA oil. Other metalloporphyrins involved also exhibited obvious catalytic activity expect for T(4-Cl)PPCu in oxidation of cyclohexane, which meant that T(4-Cl)PPCu could not activate molecular oxygen under current reaction conditions. However, when T(4-Cl)PPCu was introduced to the cyclohexane oxidation employing other metalloporphyrins mentioned above as catalysts to form dual-metalloporphyrins system, the efficiency and selectivity were enhanced obviously for most metalloporphyrins involved, especially for T(2-Cl)PPCo. The conversion was boosted from 3.88% to 4.41% for cyclohexane, and more importantly the selectivity of KA oil was enhanced from 88.6% to 97.2% (Entry 2, Entry 6) owing to the introduction of T(4-Cl)PPCu. The simultaneous increase in selectivity and conversion were realized as expected, especially in the dual-metalloporphyrins catalytic system constituted by T(4-Cl)PPCu and T(2-Cl)PPCo. In above dual-metalloporphyrins catalytic system constituted by T(4-Cl)PPCu and T(2-Cl)PPCo, the oxidation intermediate cyclohexyl hydroperoxide was employed as secondary oxidant to transform cyclohexane to cyclohexanol and cyclohexanone catalyzed by T(4-Cl)PPCu, in which not only the thermal decomposition of cyclohexyl hydroperoxide was avoided, resulted in the higher selectivity towards KA oil, but also the conversion of cyclohexane was boosted obviously, resulted in the simultaneous enhancement in conversion and selectivity. As for the catalytic system composed by T(4-Cl)PPCu and T(4-Cl)PPMn, the unsatisfying catalytic efficiency and selectivity could be attributed to the adverse intermolecular interactions between two metalloporphyrins, which had been illustrated as dimerization of two metalloporphyrins and intermolecular redox [57,58].

<Table 1>

Effect of proportion between two metalloporphyrins and the function of T(4-Cl)PPCu

With the optimized catalytic system obtained, the molar proportion of two metalloporphyrins in dual-metalloporphyrins system was explored thoroughly. Firstly the amount of T(2-Cl)PPCo was set at 6.0×10^{-4}% (mol/mol), then the proportion between T(2-Cl)PPCo and T(4-Cl)PPCu was changed from 1.0 : 1.0 to 1.0 : 3.0, and the reaction time was set as 8.0 h based on our previous exploratory experiments in which no obvious induction period was observed because the oxidation of cycloalkanes in this work was mainly conducted through the catalytic route, not the non-selective free

radical path. As illustrated in Table 2 that, satisfying selectivity (97.2%) towards KA oil in acceptable conversion of cyclohexane (4.41%) was achieved when the proportion between T(2-Cl)PPCo and T(4-Cl)PPCu was 1.0 : 1.0. Further raising the amount of T(4-Cl)PPCu, no enhanced efficiency and selectivity was obtained and the conversion of cyclohexane exhibited some decrease because of the adverse intermolecular interactions between metalloporphyrins. Thus, the satisfying proportion between T(2-Cl)PPCo and T(4-Cl)PPCu was set as 1.0 : 1.0. As mentioned above, the enhanced efficiency and selectivity in catalytic oxidation of cyclohexane could be mostly ascribed to the avoided autoxidation of cyclohexane and efficient transformation of cyclohexyl hydroperoxide, which was realized through utilization of cyclohexyl hydroperoxide as an additional oxidant to oxidize cyclohexane employing T(4-Cl)PPCu as catalyst. The autoxidation of cyclohexane under current conditions has been inhibited as demonstrated in Table 1. The performance of cyclohexyl hydroperoxide in oxidation of cyclohexane employing T(4-Cl)PPCu as catalyst was confirmed through using *tert*-butyl hydroperoxide as the analogue of cyclohexyl hydroperoxide in our work. As demonstrated in Table 3, when the oxidation of cyclohexane was conducted at 60 ℃ for 4.0 h with *tert*-butyl hydroperoxide, no oxygenated product was produced without the presence of metalloporphyrins (Table 3, Entry 1). But as T(4-Cl)PPCu, T(2-Cl)PPCo or their physical mixture were applied as catalysts, obvious cyclohexanol and cyclohexanone were detected, which illustrated that all of T(4-Cl)PPCu, T(2-Cl)PPCo and their physical mixture could enhance the oxidizing ability of cyclohexyl hydroperoxide, and T(4-Cl)PPCu exhibited higher performance than T(2-Cl)PPCo. Obviously, the existence of T(4-Cl)PPCu promoted the efficient utilization of cyclohexyl hydroperoxide as oxidant and decreased the unselective thermal decomposition, resulting in the enhanced efficiency and selectivity.

<Table 2>

<Table 3>

Substrate scope

In order to check the applicability of the dual-metalloporphyrins catalytic system investigated here, cyclopentane (C5), cycloheptane (C7) and cyclooctane (C8) besides cyclohexane (C6) were selected as cycloalkanes substrates, and the oxidative conversion were carried out at the temperature at which autoxidation would not happen. It was illustrated in Table 4, except for the cyclopentane, all the other cycloalkanes could be transformed to corresponding alcohols, ketones and hydroperoxides with satisfying selectivity above 97% in acceptable conversion. The poor selectivity in cyclopentane oxidation could be primarily ascribed to the higher strain in cyclopentane. As demonstrated in Table S2 and Table S5, in the oxidation of cycloheptane, the main oxygenated product is pentanedioic acid. Based on the satisfying substrate tolerance, it is considered as a practical and efficient strategy to promote the catalytic oxidation of cycloalkanes through utilizing oxidation intermediates cycloalkyl hydroperoxides as additional oxidants catalyzed by dual-metalloporphyrins system, which will be a helpful reference in the enhancement of catalytic oxidation of other alkanes too.

<Table 4>

Comparison with existing cyclohexane oxidation systems

At last, for the importance of oxygenated products in chemical industry, the dual-metalloporphyrins catalysis system presented herein was compared with a number of existing oxidation systems for cyclohexane catalyzed by metalloporphyrins or others with O_2 as oxidant. The results were listed in Table 5. It is obvious that, the major superiorities of our protocol were the lower reaction temperature, higher selectivity for the KA oil, solvent-free and additive-free conditions, and simpler catalysts. The strategy was proven to be very effective to boost the catalytic oxidation of cyclohexane through employing oxidation intermediate cyclohexyl hydroperoxide as additional oxidant and dual-metalloporphyrins as catalysts, with satisfying selectivity of 97.2% towards KA oil and acceptable conversion of 4.41%, which was very comparable to the level of cyclohexane conversion in industry. Although the conversion in other catalytic systems was higher than ours, the higher conversion consumed the selectivity, resulting in lower selectivity of 34.2%~91.0% towards KA oil. The lower selectivity will not only bring enormous difficulty to the separation process in industry, but also increase the amount of chemical waste discharged to the environment, which is incompatible with the urgent requirements of green chemistry. Therefore, taking the requirements of chemical process and green chemistry into account, our reported procedure is a very promising and competitive choice to enhance the oxidation of cycloalkane through efficient utilization of oxidation intermediates cycloalkyl hydroperoxides as additional oxidants under the catalysis of dual-metalloporphyrins system. At last, the endeavor to simultaneously boost the selectivity and conversion in cycloalkanes oxidation further is still being conducted in our group.

<Table 5>

In summary, a practical and efficient strategy to simultaneously increase the efficiency and selectivity in cycloalkanes oxidation with metalloporphyrins as catalysts was provided in this research, in which the oxidation intermediates cycloalkyl hydroperoxides were employed as additional oxidants to oxidize cycloalkanes further under the catalysis of T(4-Cl)PPCu. Both of the conversion and selectivity were boosted, especially for cyclohexane, and in the catalytic oxidation of cyclohexane, the selectivity was enhanced from 88.6% to 97.2% for the KA oil, at the same time the conversion was enhanced from 3.88% to 4.41%. The enhanced efficiency and selectivity were mainly ascribed to the suppressed autoxidation of cycloalkanes and the efficient utilization of oxidation intermediates cycloalkyl hydroperoxides as additional oxidants. To the best of our knowledge, the protocol demonstrated in this research is a very rare and significant example in catalytic oxidation of C-H bond in various alkanes through efficient utilization of their intermediate products as additional oxidants to promote the conversion and selectivity, and will serve as an important reference not only for industrial oxidation of alkanes, but also for the efficient construction of other catalytic oxidation systems employing metalloporphyrins. And this work also is a very important reference for the extensive application of metalloporphyrins in catalysis chemistry.

Acknowledgements

Supporting information

A full list of experimental procedure, supplementary experimental data and characterization spectra are given in the supplementary material. This material is available at http://www.u-bourgogne.fr/jpp/.

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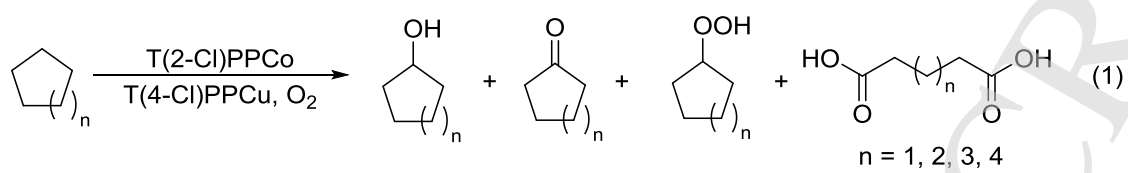
Equation 1:

$$n = 1, 2, 3, 4 \quad (1)$$

Table 1. Oxidation of cyclohexane using metalloporphyrins as catalysts with O_2[a].

Entry	Catalysts	Conversion, %	Selectivity, %			
			Alcohol	Ketone	Hydroperoxide	Total
1	/	N. D.	N. D.	N. D.	N. D.	N. D.[b]
2	T(2-Cl)PPCo	3.88	39.9	44.3	4.4	88.6
3	T(3-Cl)PPCo	3.72	45.2	41.1	4.0	90.3
4	T(4-Cl)PPCo	3.43	42.3	43.4	5.0	90.7
5	T(4-Cl)PPCu	N. D.	N. D.	N. D.	N. D.	N. D.
6[c]	T(2-Cl)PPCo T(4-Cl)PPCu	4.41	46.6	43.0	7.6	97.2
7	T(3-Cl)PPCo T(4-Cl)PPCu	3.74	50.9	41.2	6.1	98.2
8	T(4-Cl)PPCo T(4-Cl)PPCu	3.52	46.5	44.6	3.6	94.7

[a] Reaction conditions: cyclohexane (200 mmol, 16.83 g), metalloporphyrin (1.2×10^{-3}%, mol/mol), 1.40 MPa, 120 ºC, 8.0 h.

[b] No obvious reaction.

[c] The molar proportion of two metalloporphyrins, 1:1.

Table 2. Effect of proportion between two metalloporphyrins[a].

Entry	Molar proportion[b]	Conversion, %	Selectivity, %			
			Alcohol	Ketone	Hydroperoxide	Total
1	1.0 : 1.0	4.41	46.6	43.0	7.6	97.2
2	1.0 : 1.5	4.21	35.1	54.4	7.5	97.0
3	1.0 : 2.0	3.52	39.0	50.9	7.3	97.2
4	1.0 : 2.5	3.70	40.4	50.0	9.2	99.6
5	1.0 : 3.0	3.18	43.1	49.7	6.0	98.8

[a] Reaction conditions: cyclohexane (200 mmol, 16.83 g), T(4-Cl)PPCu as shown in table,

T(2-Cl)PPCo (6.0×10^{-4}%, mol/mol), O_2 (1.40 MPa), 120 ºC, 8.0 h.
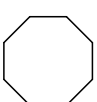
[b] Molar proportion of T(2-Cl)PPCo to T(4-Cl)PPCu.

Table 3. Oxidation of cyclohexane by *tert*-butyl hydroperoxide[a].

Entry	Metalloporphyrins	Yield, %	
		Cyclohexanol	Cyclohexanone
1	/	N. D.	0.08
2	T(4-Cl)PPCu	1.65	1.16
3	T(2-Cl)PPCo	1.25	0.48
4	T(2-Cl)PPCo T(4-Cl)PPCu	2.81	2.03

[a] Reaction conditions: cyclohexane (20 mmol, 16.83 g), 5 mol/L *t*-BuOOH in decane (4.0 mmol, 0.80 mL), metalloporphyrin (1.2×10^{-2}%, mol/mol), 60 ºC, 4.0 h.

Table 4. Catalytic oxidation of cycloalkanes with O_2 in the presence of T(2-Cl)PPCo and T(4-Cl)PPCu[a].

Entry	Cycloalkanes	Conversion, %	Selectivity, %			
			Alcohol	Ketone	Hydroperoxide	Total
1[b]		2.29	11.8	32.7	3.1	47.6
2[b]		4.41	46.6	43.0	7.6	97.2
3[c]		5.17	7.7	25.7	65.6	99.0
4[c]		23.99	N. D.	46.0	51.9	97.9

[a] Reaction conditions: cycloalkane (200 mmol), 1.40 MPa, 8.0 h.

[b] T(2-Cl)PPCo (6.0×10^{-4}%, mol/mol), T(4-Cl)PPCu (6.0×10^{-4}%, mol/mol), 120 ºC.

[c] T(2-Cl)PPCo (6.0×10^{-4}%, mol/mol), T(4-Cl)PPCu (6.0×10^{-4}%, mol/mol), 110 ºC.

Table 5. Comparison with some reported systems in cyclohexane oxidation employing O_2 as oxidant.

Entry	Conditions	Conversion, %	Selectivity[a], %	References
1	Annealed carbon nanotubes, 130 ºC, 1.50 MPa, Acetone	8.57	76.2	[59]
2	Porous cobalt silica materials, 120 ºC, 1.00 MPa, Acetonitrile	14.3	94.2	[60]
3	NHPI/Co(II)/Fe(II), 150 ºC, O_2 0.50 MPa, $scCO_2$ 9.50 MPa	10.2	94.1	[61]
4	Partially graphitic carbon, 125 ºC, 1.50 MPa, Cyclohexanone, Acetonitrile	54.8	44.4	[62]
5	Copper nanoparticles on N-doped Grapheme, 115 ºC, 0.40 MPa, NHPI, Acetone	34.5	89.2	[63]
6	Co-based spinel nanocrystals in Laponite cages, 150 ºC, 2.00 MPa	17.2	95.3	[64]
7	Ionic liquid-modified cobalt-containing ZSM-5 zeolites, 150 ºC, 1.50 MPa air	9.7	92.2	[65]
8	Hydrotalcite-derived Co-MgAlO, 150 ºC, 0.60 MPa	9.1	82.0	[66]
9	V_{16} based MOF, 150 ºC, 1.00 MPa	24.6	99.0	[67]
10	Cobalt molybdenum oxide supported on mesoporous silica,150 ºC, 1.00 MPa	8.3	85.5	[35]
11	TPFPPCo, 165 ºC, 0.80 MPa	25.7	72.0	[68]
12	TPFPPCo on nanoporous chitosan, 165 ºC, 0.80 MPa	38.5	62.8	[68]
13	T(4-COOH)PPMnCl, 155 ºC,	14.6	73.5	[69]

	0.90 MPa			
14	T(4-COOH)PPMnCl immobilized onto porous chitosan, 155 ℃, 0.90 MPa	14.7	76.9	[69]
15	T(4-COOH)PPFeCl, 155 ℃, 0.80 MPa	16.5	75.8	[69]
16	T(4-COOH)PPFeCl immobilized onto porous chitosan, 155 ℃, 0.80 MPa	17.3	75.3	[69]
17	T(4-NO$_2$)PPMn, 150 ℃, 1.00 MPa	9.76	74.7	[70]
18	T(4-NO$_2$)PPMn immobilized onto ZnO, 150 ℃, 1.00 MPa	7.98	91.0	[70]
19	T(4-COOH)PPFeCl immobilized onto ZnS, 160 ℃, 0.80 MPa	64.9	37.6	[42]
20	TPFPPFeCl, 150 ℃, 0.70 MPa	23.4	64.0	[43]
21	TPFPPFeCl immobilized onto ZnO, 150 ℃, 0.70 MPa	39.8	56.5	[43]
22	D(4-Cl)PPCoCl immobilized onto ZnO, 155 ℃, 1.00 MPa	6.23	89.4	[44]
23	T(4-COOH)PPMn, 160 ℃, 0.80 MPa	21.9	62.1	[36]
24	T(4-COOH)PPMn immobilized onto ZnS, 160 ℃, 0.80 MPa	46.1	46.1	[36]
25	T(4-COOH)PPCo, 165 ℃, 0.90 MPa	38.9	51.7	[36]
26	T(4-COOH)PPCo immobilized onto ZnS, 165 ℃, 0.90 MPa	67.8	34.2	[36]
27	Porous organic framework T(4-Br)PPMnCl, 135 ℃, 0.80 MPa	12.5	84.8	[41]
28	Porous organic framework T(4-Br)PPMnCl, 150 ℃, 0.80 MPa	29.9	72.3	[41]

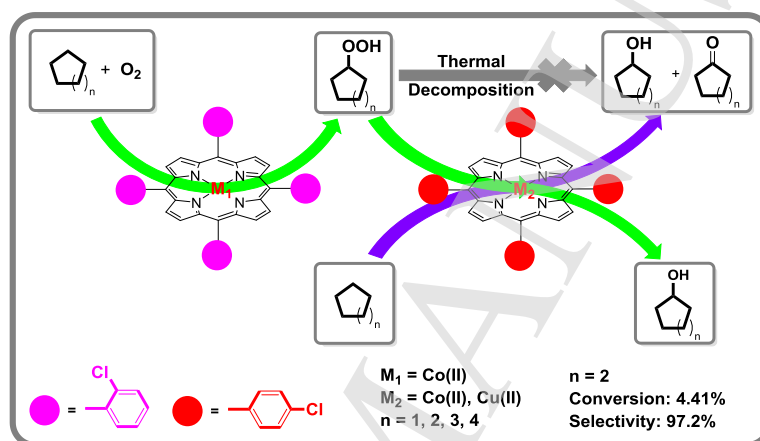| 29	Porous organic framework T(4-Br)PPFeCl, 150 ºC, 0.80 MPa	27.5	69.8	[41]
30	T(4-SO$_3$H)PPFeCl, 155 ºC, 0.80 MPa	29.2	32.5	[37]
31	T(4-SO$_3$H)PPFeCl immobilized onto chitosan, 155 ºC, 0.80 MPa	51.4	55.8	[37]
32	T(4-Cl)PPCo & T(4-Cl)PPZn, 120 ºC, 1.40 MPa	4.18	96.4	[71]
33	T(3-Cl)PPCo, 120 ºC, 1.40 MPa	3.72	90.3	This work
34	T(2-Cl)PPCo, 120 ºC, 1.40 MPa	3.88	88.6	This work
35	T(2-Cl)PPCo & T(4-Cl)PPCu, 120 ºC, 1.40 MPa	4.41	97.2	This work

[a] Selectivity towards the KA oil.

Catalytic oxidation of cycloalkanes by porphyrin cobalt(II) through efficient utilization of oxidation intermediates

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The oxidative functionalization of cycloalkanes using O_2 catalyzed by porphyrin cobalt (II) was enhanced through employing oxidation intermediates cycloalkyl hydroperoxides as additional oxidants to further oxidize cycloalkanes in the presence of porphyrin copper (II), especially for cyclohexane with the selectivity of 97.2% towards KA oil in the conversion of 4.41%.

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