Catalysis Communications 132 (2019) 105809

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Enhanced catalytic performance of porphyrin cobalt(II) in the solvent-free oxidation of cycloalkanes (C5~C8) with molecular oxygen promoted by porphyrin zinc(II)

Hai-Min Shen, Long Zhang, Jin-Hui Deng, Jing Sun, Yuan-Bin She*

College of Chemical Engineering, State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310014, China

ARTICLE INFO

Keywords:
Cycloalkane
Oxidation
Metalloporphyrin
Oxygen
Catalysis

ABSTRACT

Dual-metalloporphyrins catalytic system based on T(*p*-Cl)PPCo and T(*p*-Cl)PPZn was presented to enhance the oxidation of cycloalkanes, especially for cyclohexane, the selectivity towards KA oil increasing from 90.7% to nearly 100.0%, meanwhile the conversion increasing from 3.42% to 4.29%. Enhancement on conversion and selectivity was realized simultaneously. In the dual-metalloporphyrins system, T(*p*-Cl)PPCo served the role to activate molecular oxygen and promote the decomposition of cyclohexyl hydroperoxide, and T(*p*-Cl)PPZn catalyzed the decomposition of cyclohexyl hydroperoxide to avoid unselective thermal decomposition. This protocol is also very applicable to other cycloalkanes and will provide a applicable strategy to enhance the oxidation of alkanes.

1. Introduction

The selective oxidation of alkanes to corresponding alcohols, aldehydes, ketones and carboxylic acids is an extremely important and challenging transformation in both chemical industry and academic research, in which the abundant and inexpensive alkanes in petroleum and natural gas are converted to high-value chemical intermediates and fine chemicals [1,2]. Among these significant reactions, the oxidation of cycloalkanes to cycloalkanols and cycloalkanones has gained a continuous and considerable interest, especially for the cyclohexane [3,4], since the obtained cyclohexanol and cyclohexanone (KA oil) can be further converted to caprolactam and hexanedioic acid which are the irreplaceable intermediates in the production of various polymers such as nylon-6 and nylon-66 [5,6]. And the oxygenated products from other cycloalkanes, such as cyclopentane, cycloheptane and cyclooctane, not only are important precursors of a series of macromolecule polymers [7], but also are building blocks in several valuable chemicals [8]. In order to realize these essential transformations, several oxidants have been explored, including iodosylbenzene [9], *m*-chloroperoxybenzoic acid [10], *tert*-butyl hydroperoxide [11], hydrogen peroxide [12], molecular oxygen [13], and so on. It is obvious that molecular oxygen is the most promising one according to the requirements of green chemistry, which possesses low cost, readily availability and environmental harmlessness with innocuous water as the only by-product. But compared with other oxidants, the activation of molecular oxygen in the oxidation of cycloalkanes is very difficult. Thus the industrial oxidation of cyclohexane is conducted at 150–170 °C and 1.0–2.0 MPa oxygen pressure employing homogeneous cobalt salt as catalyst with conversion of 3%–8% for cyclohexane and selectivity of 80%–85% towards KA oil [14,15], which suffers from the low selectivity seriously. To some extent, the low selectivity in oxidation of cycloalkanes can be attributed to the high reaction temperature, because the autoxidation of cycloalkanes and thermal decomposition of cycloalkyl hydroperoxides which are the main intermediate products in the oxidation of cycloalkanes [16], would occur at high temperature. Both of them process through unselective free radical chain reaction pathway, and give rise to a lot of undesired oxydates, including hexanedioic acid which is very difficult to separate from the oxidation products. Despite the fact that most of the KA oil is employed as intermediate to produce hexanedioic acid, the formation of hexanedioic acid in the production of KA oil is a troublesome issue. Hence, it is highly urgent to develop the selective oxidation of cycloalkanes to cycloalkanols and cycloalkanones under mild conditions.

To smooth the oxidation of cycloalkanes to their corresponding alcohols and ketones using molecular oxygen, various catalytic systems have been explored, including transition metal complex catalysis [17], metal nanoparticle catalysis [18], molecular sieve catalysis [19], photocatalysis [20], biocatalysis [21], and so on. Synthetic

---

* Corresponding author.
E-mail address: haimshen@zjut.edu.cn (Y.-B. She).

https://doi.org/10.1016/j.catcom.2019.105809
Received 3 July 2019; Received in revised form 30 August 2019; Accepted 1 September 2019
Available online 02 September 2019
1566-7367/ © 2019 Elsevier B.V. All rights reserved.

metalloporphyrins which are the chemical models of cytochrome P-450 enzymes, are a type of transition metal complexes and have been widely applied in the oxidation of cycloalkanes as biomimetic catalysts for their high efficiency in activation of molecular oxygen and satisfying selectivity in oxidation of C—H bond [9,13,17,22,23]. A number of satisfying results were achieved. For example, Huang and co-workers reported tetrakis(4-carboxylphenyl)porphyrin iron(III) chloride, tetrakis(pentafluorophenyl) porphyrin iron(III) chloride, tetrakis(4-sulfonatophenyl)porphyrin iron(III) chloride and tetrakis(4-carboxylphenyl) porphyrin iron(II), cobalt(II), manganese(II), which were immobilized onto zinc oxide(ZnO), zinc sulfide(ZnS) and chitosan respectively to boost their stability and catalytic performance, were employed as catalysts in the oxidation of cyclohexane at the temperature range of 150–165 °C, and the most satisfying selectivity towards KA oil was 56.5% with the conversion of 39.8% [17,22,24]. Liu and co-workers reported 5,15-di(4-chlorophenyl)-10,20 -diphenylporphyrin cobalt(III) chloride immobilized onto zinc oxide(ZnO) catalyzed oxidation of cyclohexane with molecular oxygen at 155 °C, and the selectivity towards KA oil reached up to 72.1% with the conversion of 13.1% [25]. Yang and *co*-workers reported the synthesis of porous polymeric metalloporphyrins using tetrakis(4-bromophenyl)porphyrin iron(III) chloride, tetrakis(4-bromophenyl) porphyrin manganese(III) chloride and 1, 4-phenyldiboronic acid as building blocks, which were applied in the oxidation of cyclohexane at 150 °C, and the selectivity was up to 72.2% with the conversion of 29.9% [26]. Pamin and co-workers investigated the performance of three generations of porphyrin cobalt(II) in the oxidation of cycloalkanes with molecular oxygen systematically, and found that the generation II porphyrin cobalt(II) showed higher activity [13]. Evidently, the oxidation of cyclohexane with molecular oxygen was promoted by metalloporphyrins, especially for the conversion and yield, but still suffered from the high temperature and low selectivity, which would lead to a lot of undesired by-products and pollute the environment. Thus, how to increase the selectivity and lower the reaction temperature is still an enormous challenge lied in the progress of cycloalkanes oxidation.

In our attempt to increase the selectivity in oxidation of cycloalkanes catalyzed by metalloporphyrins with molecular oxygen [27–29], the formation of carboxylic acid and other undesired by-products from unselective free radical reaction occurred at higher temperature, became the primary issue to consider. To solve this problem, an idea to conduct the oxidation of cycloalkanes at lower-temperature and decompose the cycloalkyl hydroperoxides through catalytic pathway emerged in our minds. After systematic investigation on the autoxidation temperature of cycloalkanes(C5-C8) [30], the catalytic oxidation of cycloalkanes was conducted at the temperature not higher than their autoxidation temperature in our following work. Meanwhile, in order to realize the catalytic decomposition of cycloalkyl hydroperoxides, dual-metalloporphyrins system was introduced to the catalytic oxidation of cycloalkanes, in which one metalloporphyrin mainly served the decomposition of cycloalkyl hydroperoxides. Encouraging outcomes were obtained, especially for the selectivity towards KA oil. The selectivity towards KA oil was increased from 90.7% to nearly 100.0%, meanwhile the conversion of cyclohexane was also increased from 3.42% to 4.29%. Thus, in this work we reported the enhanced performance of porphyrin cobalt(II) in the solvent-free oxidation of cycloalkanes (C5~C8) with molecular oxygen promoted by porphyrin zinc(II), which not only reveals a strategy to enhance the conversion and selectivity in the oxidation of cycloalkanes, but also act as an important reference in the selective oxidation of other alkanes. To the best of our knowledge, our work is a very scarce example in the oxidation of alkanes, in which the conversion and selectivity is enhanced simultaneously through the delicate cooperation of two different metalloporphyrins.

2. Experimental

2.1. Materials and reagents

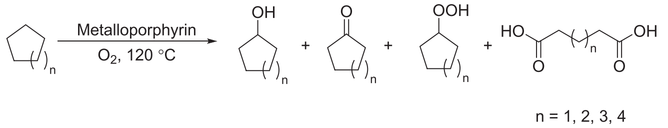
Cyclohexane in 99% purity was purchased from Hangzhou Shuanglin Chemical Reagent Co. Ltd., China. Cyclopentane and cycloheptane in 98% purity were purchased from TCI Co. Ltd. Cyclooctane in 99% purity was purchased from Alfa Aesar Co. Ltd. All of the above cycloalkanes were dried over sodium and redistilled before use. All the other common reactants and reagents were analytical grade, and all of them were used as received without further purification unless otherwise noted.

2.2. Catalytic oxidation of cycloalkanes

The catalytic oxidation of cycloalkanes employing metalloporphyrins as catalysts and molecular oxygen as oxidant was conducted in a 100 mL autoclave reactor equipped with an inner Teflon liner and a magnetic stirrer. In a typical procedure, metalloporphyrin (1.2×10^{-3}%, mol/mol) was suspended in cycloalkane (200 mmol) in the 100 mL autoclave reactor, and the reactor was heated to the desired reaction temperature after sealing. When the reaction temperature reached, oxygen was fed into the autoclave to obtain a desired pressure. The resultant reaction mixture was stirred at the desired temperature and desired pressure for 8.0 h, then cooled to room temperature. Triphenylphosphine (25 mmol, 6.5573 g) was added into the reaction mixture to reduce the cycloalkyl hydroperoxide to corresponding cycloalkanol quantitatively. After stirring for 30 min, the reaction mixture was dissolved in acetone and transferred into a 100 mL volumetric flask totally. Then the GC and HPLC analyses were performed to determine the yields of the oxidized products. The oxidized products were determined by comparison with the authentic samples. The yields of cycloalkanol and cycloalkanone were determined by GC employing toluene as internal standard, and the yield of cycloalkyl hydroperoxide was determined through the amount of $O=PPh_3$ obtained from reduction of cycloalkyl hydroperoxide with PPh_3 using GC. GC analyses were performed on a Thermo Scientific Trace 1300 instrument using a TG-5MS column (30 m × 0.32 mm × 0.25 μm). The yields of aliphatic diacids were determined by HPLC with benzoic acid as internal standard. HPLC analyses were performed on a Thermo Scientific Ultimate 3000 chromatography equipped with a Ultimate 3000 Photodiode Array Detector using a Amethyst C18—H column (250 mm × 4.6 mm × 0.25 μm).

3. Results and discussion

In this work, the catalytic oxidation of cycloalkanes was carried out in a 100-mL stainless steel autoclave reactor equipped with an Teflon liner and a magnetic stirrer under solvent-free condition with metalloporphyrins as catalysts and molecular oxygen as oxidant as shown in Scheme 1. The representative metalloporphyrins employed in this work were tetrakis(2-chlorophenyl)porphyrin cobalt(II) (T(*o*-Cl) PPCo), tetrakis(3-chlorophenyl)porphyrin cobalt (II) (T(*m*-Cl)PPCo), tetrakis(4 -chlorophenyl)porphyrin cobalt(II) (T(*p*-Cl)PPCo), tetrakis(4-chlorophenyl) porphyrin iron(II) (T(*p*-Cl)PPFe), tetrakis(4-chlorophenyl) porphyrin manganese(II) (T(*p*-Cl)PPMn), tetrakis(4-chlorophenyl)porphyrin zinc(II) (T(*p*-Cl)PPZn), which were synthesized through the



Scheme 1. Selective oxidation of cycloalkanes (C5-C8) with molecular oxygen catalyzed by metalloporphyrins

Table 1
Catalytic oxidation of cyclohexane with O_2 catalyzed by various metalloporphyrins.[a]

Entry	Catalyst	Conversion[b] (%)	Selectivity[b] (%)			
			Alcohol	Ketone	Hydroperoxide	Total
1	/	N. D.	N. D.	N. D.	N. D.	N. D.[c]
2	T(*o*-Cl)PPCo	3.88	39.9	44.3	4.4	88.6
3	T(*m*-Cl)PPCo	3.72	45.2	41.1	4.0	90.3
4	T(*p*-Cl)PPCo	3.43	42.3	43.4	5.0	90.7
5	T(*p*-Cl)PPMn	3.54	43.8	29.4	23.4	96.6
6	T(*p*-Cl)PPFe	1.08	19.4	31.5	49.1	100.0
7	T(*p*-Cl)PPZn	N. D.	N. D.	N. D.	N. D.	N. D.
8[d]	T(*o*-Cl)PPCo T(*p*-Cl)PPZn	3.48	41.7	41.1	11.8	94.6
9	T(*m*-Cl)PPCo T(*p*-Cl)PPZn	3.01	44.2	45.2	5.3	94.7
10	T(*p*-Cl)PPCo T(*p*-Cl)PPZn	4.18	42.6	33.0	20.8	96.4
11	T(*p*-Cl)PPMn T(*p*-Cl)PPZn	1.25	28.8	20.8	46.4	96.0
12	T(*p*-Cl)PPFe T(*p*-Cl)PPZn	1.09	6.4	24.8	60.6	91.8

[a] Reaction condition: cyclohexane (200 mmol, 16.83 g), metalloporphyrin (1.2×10^{-3}%, mol/mol), O_2 (1.40 MPa), 120 °C, 8.0 h.
[b] The conversion and selectivity of cyclohexanol and cyclohexanone were determined by GC after treatment with PPh_3 employing toluene as internal standard, and the selectivity of cyclohexyl hydroperoxide was determined through the amount of $O{=}PPh_3$ obtained from reduction of cyclohexyl hydroperoxide with PPh_3. The products were determined by comparison with the authentic samples.
[c] No obvious reaction was detected.
[d] The molar ratio of two metalloporphyrins was 1:1, and the total concentration of metalloporphyrins was kept at 1.2×10^{-3}%, mol/mol.

Table 2
Effect of molar ratios between T(*p*-Cl)PPCo and T(*p*-Cl)PPZn on the catalytic oxidation of cyclohexane[a].

Entry	Molar ratio[b]	Conversion[c] (%)	Selectivity[c] (%)			
			Alcohol	Ketone	Hydroperoxide	Total
1	1.0:1.0	4.18	42.6	33.0	20.8	96.4
2	1.0:1.5	4.28	52.6	37.4	8.6	98.6
3	1.0:2.0	4.29	49.7	31.7	18.6	100.0[d]
4	1.0:2.5	3.90	55.6	33.4	11.0	100.0
5	1.0:3.0	3.55	45.6	29.9	24.5	100.0

[a] Reaction condition: cyclohexane (200 mmol, 16.83 g), T(*p*-Cl)PPCo (6.0×10^{-4}%, mol/mol), T(*p*-Cl)PPZn as shown in table, O_2 (1.40 MPa), 120 °C, 8.0 h.
[b] $m_{[T(p\text{-Cl})PPCo]}$: $m_{[T(p\text{-Cl})PPZn]}$.
[c] Same with Table 1.
[d] No obvious by-product was detected.

Table 3
Decomposition of *tert*-butyl hydroperoxide in the presence or absence of metalloporphyrins.[a]

Entry	Metalloporphyrin	Decomposition ratio[b] (%)	Yield[c] (%)	Selectivity[c] (%)
1	/	5.2	N. D.	N. D.
2	T(*p*-Cl)PPZn	36.9	30.0	81.3
3	T(*p*-Cl)PPCo	59.0	39.3	66.6
4	T(*p*-Cl)PPCo T(*p*-Cl)PPZn	21.7	16.9	77.9

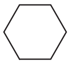
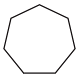
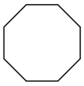
[a] Reaction condition: *t*-BuOOH (5.0 mmol, 70% aqueous solution, 0.6437 g) in cyclohexane (20 mmol, 1.6832 g), metalloporphyrin (2.5×10^{-3} mmol), 80 °C, 4.0 h.
[b] Determined by GC employing toluene as internal standard through the amount of $O{=}PPh_3$ obtained from reduction of the residual *t*-BuOOH with PPh_3. The products were determined by comparison with the authentic samples.
[c] Yield and selectivity of *tert*-butanol, determined by GC employing toluene as internal standard.

condensation of freshly distilled pyrrole with corresponding chlorobenzaldehyde in propionic acid followed by the metallation in DMF [31]. All the metalloporphyrins were purified by silica column chromatography and characterized through ^{1}H NMR, ^{13}C NMR and ESI-MS. With metalloporphyrins in hand, the catalytic oxidation of cyclohexane was selected as probe reaction to test and verify our ideas at the reaction temperature of 120 °C, at which the autoxidation would not happen. And the major products were KA oil, cyclohexyl hydroperoxide and a little of carboxylic acids which were analyzed by GC and HPLC to determine the conversion and selectivity. Because a small amount of cyclohexyl hydroperoxide could be converted to KA oil smoothly after reaction, the selectivity towards cyclohexyl hydroperoxide was considered as a part of KA oil. As shown in Table 1, no oxidation occurred in the absence of metalloporphyrins (Entry 1). When the metalloporphyrins were introduced to the reaction, the conversion of cyclohexane reached up to 3.43%–3.88% for porphyrin cobalt and porphyrin manganese with an acceptable selectivity of 88.7%–96.6% towards KA oil. But there are still some hexanedioic acid and undesired by-products formed, especially for the porphyrin cobalt. As for T(*p*-Cl)PPFe, a lower catalytic performance was observed, and T(*p*-Cl)PPZn did not exhibit any catalytic activity in the oxidation of cyclohexane at all. However, when dual-metalloporphyrins systems were applied to the oxidation of cyclohexane, the catalytic performance of T(*p*-Cl)PPCo was enhanced considerably by T(*p*-Cl)PPZn. The conversion of cyclohexane increased from 3.43% to 4.18% meanwhile the selectivity towards KA oil increased from 90.7% to 96.4% (Entry 3, Entry 10). The increase in the conversion did not consume the selectivity. Increase in both of the conversion and selectivity were realized as a result of the promotion of porphyrin znic. Thus, T(*p*-Cl)PPCo employed as catalyst combined with T(*p*-Cl)PPZn as promoter was considered as the most successful dual-metalloporphyrins system in this work. For other dual-metalloporphyrins systems, the unsatisfying catalytic performance might be ascribed to the undesired interactions between two metalloporphyrins such as the formation of dimmers and the intermolecular redox [32,33].

With the optimized dual-metalloporphyrins system established, the molar composition of T(*p*-Cl)PPCo and T(*p*-Cl)PPZn was investigated deeply, in which the loading of T(*p*-Cl)PPCo was set as 6.0×10^{-4}% (mol/mol), and the molar ratios between T(*p*-Cl)PPCo and T(*p*-Cl)PPZn varied from 1: 1.0 to 1: 3.0. It was illustrated in Table 2 that, when the

Table 4

Oxidation of cycloalkanes (C5-C8) catalyzed by dual-metalloporphyrins system based on T(*p*-Cl)PPCo and T(*p*-Cl)PPZn.[a]

Entry	Cycloalkane	Conversion[b] (%)	Selectivity (%)[b]			
			Alcohol	Ketone	Hydroperoxide	Total
1[c]		1.84	11.4	35.3	7.5	54.2
2[c]		4.29	49.7	31.7	18.6	100.0[f]
3[d]		2.20	N. D.[g]	18.2	81.8	100.0
4[e]		2.29	N. D.	16.2	83.8	100.0

[a] Reaction condition: cycloalkane (200 mmol), T(*p*-Cl)PPCo (6.0×10^{-4}%, mol/mol), T(*p*-Cl)PPZn (1.2×10^{-3}%, mol/mol), O_2 (1.40 MPa), 8.0 h.

[b] Same with Table 1.

[c] 120 °C.

[d] 110 °C.

[e] 100 °C.

[f] No obvious by-product was detected.

[g] No obvious cycloalkanol was detected.

Table 5

Catalytic performance of some metalloporphyrins in the oxidation of cyclohexane with molecular oxygen under solvent-free condition.

Entry	Catalyst	Temperature (°C)	Conversion (%)	Selectivity[a] (%)	Ref.
1	T(penta-F)PPCo immobilized onto chitosan	165	38.5	62.8	[34]
2	T(*p*-COOH)PPCo immobilized onto ZnS	165	67.8	34.2	[17]
3	T(*p*-COOH)PPMn immobilized onto ZnS	160	46.1	46.1	[17]
4	T(*p*-COOH)PPFe immobilized onto ZnS	160	51.8	42.3	[17]
5	T(*p*-COOH)PPMnCl immobilized onto chitosan	155	14.7	76.9	[35]
6	T(*p*-COOH)PPFeCl immobilized onto chitosan	155	17.3	75.3	[35]
7	T(*p*-SO_3H)PPFeCl immobilized onto chitosan	155	51.4	55.8	[24]
8	T(*p*-COOH)PPMn	150	9.76	74.7	[23]
9	T(*p*-COOH)PPMn immobilized onto ZnO	150	7.98	91.0	[23]
10	T(penta-F)PPFeCl	150	23.4	64.0	[22]
11	T(penta-F)PPFeCl immobilized onto ZnO	150	39.8	56.5	[22]
12	Porous polymeric T(*p*-Br)PPMnCl	150	29.9	72.3	[26]
13	Porous polymeric T(*p*-Br)PPFeCl	150	27.5	69.8	[26]
14	Porous polymeric T(*p*-Br)PPMnCl	135	12.5	84.8	[26]
15	T(*p*-Cl)PPCo	120	3.43	90.7	This work
16	T(*p*-Cl)PPCo & T(*p*-Cl)PPZn	120	4.29	100.0	This work

[a] Selectivity towards KA oil.

molar ratio of T(*p*-Cl)PPCo to T(*p*-Cl)PPZn was changed from 1.0:1.0 to 1.0:1.5, the selectivity towards KA oil increased from 96.4% to 98.6%. Further increasing the ratio of T(*p*-Cl)PPZn to 1.0: 2.0, no obvious by-product was detected with satisfying conversion of 4.29%. Thus, with the promotion of T(*p*-Cl)PPZn, it was achieved to enhanced the conversion and selectivity in the oxidation of cyclohexane catalyzed by T(*p*-Cl)PPCo. With the acceptable conversion of 4.29%, nearly 100% selectivity towards KA oil was obtained, which would simplify the separation process and reduce the production costs remarkably in the industrial oxidation of cyclohexane. As mentioned above, the exciting conversion and selectivity in our work was mainly attributed the low-temperature oxidation and the catalytic decomposition of cyclohexyl hydroperoxide promoted by T(*p*-Cl)PPZn. At lower reaction temperature, the unselective autoxidation of cyclohexane, cyclohexanol and cyclohexanone, and the unselective thermal decomposition of cyclohexyl hydroperoxide were inhibited. On the other hand, the cyclohexyl hydroperoxide was decomposed to cyclohexanol catalyzed by T(*p*-Cl)PPZn. Both of them reduced the formation of undesired by-products and improved the selectivity in the oxidation cyclohexane. The catalytic performance of T(*p*-Cl)PPZn in the decomposition of cyclohexyl hydroperoxide was verified in our work employing *tert*-butyl hydroperoxide as representative. It was demonstrated in Table 3 that when *tert*-butyl hydroperoxide was stirred in cyclohexane at 80 °C for 4.0 h, the decomposition ratio was just 5.2%, but when T(*p*-Cl)PPCo or T(*p*-Cl)PPZn was added, the decomposition reached up to 59.0% and 36.9% respectively with *tert*-butanol as major product. Both of T(*p*-Cl)PPCo and T(*p*-Cl)PPZn can catalyze the decomposition of *tert*-butyl hydroperoxide and T(*p*-Cl)PPZn possesses better selectivity towards *tert*-butanol. With the results obtained in Table 1 that T(*p*-Cl)PPCo was an effective catalyst in the oxidation of cyclohexane with molecular oxygen and T(*p*-Cl)PPZn did not exhibit any catalytic activity, and the catalytic mechanism in the oxidation of cyclohexane with molecular oxygen catalyzed by metalloporphyrins that molecular oxygen was activated by metalloporphyrins [17,24,25], it could be concluded that in this dual-metalloporphyrins catalytic system, T(*p*-Cl)PPCo not only served the role to activate molecular oxygen, but also possessed the function to promote the decomposition of cyclohexyl hydroperoxide, and T(*p*-Cl)PPZn served the decomposition of cyclohexyl hydroperoxide exclusively. Their delicate cooperation made the high selective oxidation of cyclohexane realized. As for the optimized molar ratio of T(*p*-Cl)PPCo to T(*p*-Cl)PPZn was 1.0: 2.0, it should be attributed to the high efficiency of T(*p*-Cl)PPCo in activation of molecular oxygen and formation of cyclohexyl hydroperoxide, and the lower transformation rate of cyclohexyl hydroperoxide to cyclohexanol and cyclohexanone. More catalytic active centers were needed to enhanced the transformation of cyclohexyl hydroperoxide to cyclohexanol and cyclohexanone. What should be mentioned additionally is that cyclohexanol and cyclohexanone at negligible levels compared with *tert*-butanol were also detected in the decomposition of *tert*-butyl hydroperoxide in cyclohexane.

Based on the results obtained from the selective oxidation of cyclohexane catalyzed by the dual-metalloporphyrins system, the substrates were extended from cyclohexane to cyclopentane, cycloheptane and cyclooctane. All the catalytic transformations were conducted at the temperature no autoxidation would occur. As shown in Table 4, nearly 100% selectivity towards alcohol, ketone and hydroperoxide was achieved for the cycloalkanes involved, except for the cyclopentane. The lower selectivity in cyclopentane oxidation was mainly attributed the higher strain in cyclopentane molecule. And the major product in the oxidation of cyclopentane is pentanedioic acid illustrated in Tables S1 and S2. For the satisfying substrate tolerance, the dual-metalloporphyrins catalytic system presented in this work has enormous potential application in the selective oxidation of cycloalkanes, and will serve as a applicable strategy in the enhancement of various alkanes oxidation.

At last, the catalytic oxidation of cyclohexane in this work was compared with some reported cyclohexane oxidation systems employing metalloporphyrins as catalysts and molecular oxygen as oxidant under solvent-free condition, as shown in Table 5. It is clear that, in the term of conversion, the dual-metalloporphyrins catalytic system in this work is not so competitive, but in the aspects of reaction temperature and selectivity towards KA oil, our protocol in the oxidation of cyclohexane is very promising without any obvious by-product produced, which will not only simplify the separation process remarkably in the industrial oxidation of cyclohexane, but also cut down the chemical waste discharged to the environment. Although the conversion in this work is comparable to the industrial level, the attempt to further improve the conversion of cyclohexane with high selectivity is still in process in our group at present.

4. Conclusion

In conclusion, a strategy to enhance the selectivity in the catalytic oxidation of cycloalkanes was presented in this work, especially for the cyclohexane, the selectivity towards KA oil was increased from 90.7% to nearly 100.0%, meanwhile the conversion of cyclohexane was increased from 3.42% to 4.29%. The increase in the conversion and selectivity was achieved simultaneously. The encouraging results in the oxidation of cyclohexane were mainly attributed to the low temperature reaction and the delicate cooperation between T(*p*-Cl)PPCo and T(*p*-Cl)PPZn in the dual-metalloporphyrins catalytic system, in which T(*p*-Cl)PPCo served the role to activate molecular oxygen and promote the decomposition of cyclohexyl hydroperoxide, and T(*p*-Cl)PPZn could catalyze the decomposition of cyclohexyl hydroperoxide selectively. For the low temperature reaction and the delicate cooperation of T(*p*-Cl)PPCo and T(*p*-Cl)PPZn, the unselective autoxidation of cyclohexane and the unselective thermal decomposition of cyclohexyl hydroperoxide were inhibited, resulting in the higher selectivity. This protocol to enhance the oxidation of cyclohexane is also very applicable to other cycloalkanes, such as cyclopentane, cycloheptane and cyclooctane. To the best of our knowledge, this work is a very scarce example in the oxidation of alkanes, in which the conversion and selectivity is enhanced simultaneously, and will provide a applicable strategy to increase the conversion and selectivity in the oxidation of alkanes. And the attempt to further improve the conversion of cycloalkane with high selectivity is still in process in our group at present.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 21878275, 21476270, 21776259, 21306176).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.105809.

References

[1] J.T. Grant, J.M. Venegas, W.P. McDermott, I. Hermans, Aerobic oxidations of light alkanes over solid metal oxide catalysts, Chem. Rev. 118 (2018) 2769–2815.

[2] L.Y. Wang, Y.B. Zhang, R.F. Du, H.R. Yuan, Y.T. Wang, J. Yao, H.R. Li, Selective one-step aerobic oxidation of cyclohexane to ε-caprolactone mediated by N-hydroxyphthalimide(NHPI), ChemCatChem 11 (2019) 2260–2264.

[3] S. Kal, A. Draksharapu, L. Que, Sc^{3+} (or HClO$_4$) activation of a nonheme Fe^{III}-OOH intermediate for the rapid hydroxylation of cyclohexane and benzene, J. Am. Chem. Soc. 140 (2018) 5798–5804.

[4] Y.L. Wan, Q. Guo, K. Wang, X.T. Wang, Efficient and selective photocatalytic oxidation of cyclohexane using O$_2$ as oxidant in VOCl$_2$ solution and mechanism insight, Chem. Eng. Sci. 203 (2019) 163–172.

[5] A.A. Alshehri, A.M. Alhanash, M. Eissa, M.S. Hamdy, New catalysts with dual-functionality for cyclohexane selective oxidation, Appl. Catal. A-Gen. 554 (2018) 71–79.

[6] A.P. Unnarkat, T. Sridhar, H.T. Wang, S.M. Mahajani, A.K. Suresh, Study of cobalt molybdenum oxide supported on mesoporous silica for liquid phase cyclohexane oxidation, Catal. Today 310 (2018) 116–129.

[7] Y. Yu, Z.Y. Wei, C. Zhou, L.C. Zheng, X.F. Leng, Y. Li, Miscibility and competition of cocrystallization behavior of poly (hexamethylene dicarboxylate)s aliphatic copolyesters: effect of chain length of aliphatic diacids, Eur. Polym. J. 92 (2017) 71–85.

[8] P.L. Rivas, I. Randelovic, A.R.M. Dias, A. Pina, D. Arosio, J. Tovari, G. Mezo, A. Dal Corso, L. Pignataro, C. Gennari, Synthesis and biological evaluation of paclitaxel conjugates involving linkers cleavable by lysosomal enzymes and $\alpha_V\beta_3$-integrin ligands for tumor targeting, Eur. J. Org. Chem. (2018) 2902–2909.

[9] A.R. Antonangelo, C.G. Bezzu, N.B. McKeown, S. Nakagaki, Highly active manganese porphyrin-based microporous network polymers for selective oxidation reactions, J. Catal. 369 (2019) 133–142.

[10] M. Sankaralingam, P. Vadivelu, M. Palaniandavar, Novel nickel(II) complexes of sterically modified linear N4 ligands: effect of ligand stereoelectronic factors and solvent of coordination on nickel(II) spin-state and catalytic alkane hydroxylation, Dalton Trans. 46 (2017) 7181–7193.

[11] A.P.C. Ribeiro, L.M.D.R.S. Martins, S.A.C. Carabineiro, J.G. Buijnsters, J.L. Figueiredo, A.J.L. Pombeiro, Heterogenized C-scorpionate iron(II) complex on nanostructured carbon materials as recyclable catalysts for microwave-assisted oxidation reactions, ChemCatChem 10 (2018) 1821–1828.

[12] Q.H. Wei, H.L. Fan, F.F. Qin, Q.X. Ma, W.Z. Shen, Metal-free honeycomb-like porous carbon as catalyst for direct oxidation of benzene to phenol, Carbon 133 (2018) 6–13.

[13] K. Pamin, E. Tabor, S. Gorecka, W.W. Kubiak, D. Rutkowska-Zbik, J. Poltowicz, Three generations of cobalt porphyrins as catalysts in the oxidation of cycloalkanes, ChemSusChem 12 (2019) 684–691.

[14] L.M.D.R.D. Martins, S.A.C. Carabineiro, J.W. Wang, B.G.M. Rocha, F.J. Maldonado-Hodar, A.J.L.D. Pombeiro, Supported gold nanoparticles as reusable catalysts for oxidation reactions of industrial significance, ChemCatChem 9 (2017) 1211–1221.

[15] S.A.C. Carabineiro, L.M.D.R.S. Martins, A.J.L. Pombeiro, J.L. Figueiredo, Commercial gold(I) and gold(III) compounds supported on carbon materials as greener catalysts for the oxidation of alkanes and alcohols, ChemCatChem 10 (2018) 1804–1813.

[16] X. Zheng, J.P. Ma, M. Wang, S. Shi, Z.Q. Sun, J. Xu, Coupling reaction in catalytic decomposition of cyclohexyl hydroperoxide, Catal. Commun. 101 (2017) 77–80.

[17] G. Huang, W.L. Wang, X.X. Ning, Y. Liu, S.K. Zhao, Y.A. Guo, S.J. Wei, H. Zhou, Interesting green catalysis of cyclohexane oxidation over metal tetrakis(4-carboxyphenyl)porphyrins promoted by zinc sulfide, Ind. Eng. Chem. Res. 55 (2016) 2959–2969.

[18] L.F. Chen, Y.Y. Zhou, Z.Y. Gui, H.Y. Cheng, Z.W. Qi, Au nanoparticles confined in hybrid shells of silica nanospheres for solvent-free aerobic cyclohexane oxidation, J. Mater. Sci. 52 (2017) 7186–7198.

[19] X.G. Duan, W.M. Liu, L.M. Yue, W. Fu, M.N. Ha, J. Li, G.Z. Lu, Selective oxidation of cyclohexane on a novel catalyst Mg-Cu/SBA-15 by molecular oxygen, Dalton Trans. 44 (2015) 17381–17388.

[20] L.P. Xiang, J.J. Fan, W.Z. Zhong, L.Q. Mao, K.Y. You, D.L. Yin, Heteroatom-induced band-reconstruction of metal vanadates for photocatalytic cyclohexane oxidation towards KA oil selectivity, Appl. Catal. A-Gen. 575 (2019) 120–131.

[21] A. Hoschek, I. Heuschkel, A. Schmid, B. Buhler, R. Karande, K. Buhler, Mixed-species biofilms for high-cell-density application of Synechocystis sp. PCC 6803 in capillary reactors for continuous cyclohexane oxidation to cyclohexanol, Bioresour. Technol. 282 (2019) 171–178.

[22] G. Huang, L.Q. Mo, J.L. Cai, X. Cao, Y. Peng, Y.A. Guo, S.J. Wei, Environmentally friendly and efficient catalysis of cyclohexane oxidation by iron meso-tetrakis (pentafluorophenyl)porphyrin immobilized on zinc oxide, Appl. Catal. B-Environ. 162 (2015) 364–371.

[23] Z. Feng, Y.J. Xie, F. Hao, P.L. Liu, H.A. Luo, Catalytic oxidation of cyclohexane to KA oil by zinc oxide supported manganese 5, 10, 15, 20-tetrakis (4-nitrophenyl) porphyrin, J. Mol. Catal. A Chem. 410 (2015) 221–225.

[24] G. Huang, Y. Liu, J.L. Cai, X.F. Chen, S.K. Zhao, Y.A. Guo, S.J. Wei, X. Li, Heterogeneous biomimetic catalysis using iron porphyrin for cyclohexane oxidation promoted by chitosan, Appl. Surf. Sci. 402 (2017) 436–443.

[25] Y.J. Xie, F.Y. Zhang, P.L. Liu, F. Hao, H.A. Luo, Zinc oxide supported trans-CoD(p-Cl)PPCl-type metalloporphyrins catalyst for cyclohexane oxidation to cyclohexanol and cyclohexanone with high yield, Ind. Eng. Chem. Res. 54 (2015) 2425–2430.

[26] Y.J. Li, C.R. Liu, W.J. Yang, Synthesis of porous polymeric metalloporphyrins for highly efficient oxidation of cyclohexane in heterogeneous systems, New J. Chem. 41 (2017) 8214–8221.

[27] H. Li, Y. She, T. Wang, Advances and perspectives in catalysts for liquid-phase oxidation of cyclohexane, Front. Chem. Sci. Eng. 6 (2012) 356–368.

[28] H. Li, Y.B. She, H.Y. Fu, M.J. Cao, J. Wang, T. Wang, Synergistic effect of co-reactant promotes one-step oxidation of cyclohexane into adipic acid catalyzed by manganese porphyrins, Can. J. Chem. 93 (2015) 696–701.

[29] T. Wang, Y.B. She, H.Y. Fu, H. Li, Selective cyclohexane oxidation catalyzed by manganese porphyrins and co-catalysts, Catal. Today 264 (2016) 185–190.

[30] H.M. Shen, Y. Wang, J.H. Deng, L. Zhang, Y.B. She, Catalyst-free and solvent-free oxidation of cycloalkanes (C5-C8) with molecular oxygen: determination of autoxidation temperature and product distribution, Chin. J. Chem. Eng. 26 (2018) 1064–1070.

[31] N. Sheng, B. Gu, B.X. Ren, J. Zhang, Y.Y. Wang, J.X. Wang, J.Q. Sha, A series of polycyclic aromatic hydrocarbon-substituted metal-free porphyrins: substituent effect on two-photon absorption property, Dyes Pigments 142 (2017) 116–120.

[32] K.A.D.F. Castro, F.H.C. de Lima, M.M.Q. Simoes, M.G.P.M.S. Neves, F.A.A. Paz, R.F. Mendes, S. Nakagaki, J.A.S. Cavaleiro, Synthesis, characterization and catalytic activity under homogeneous conditions of ethylene glycol substituted porphyrin manganese(III) complexes, Inorg. Chim. Acta 455 (2017) 575–583.

[33] A.R. Antonangelo, C.G. Bezzu, S.S. Mughal, T. Malewschik, N.B. McKeown, S. Nakagaki, A porphyrin-based microporous network polymer that acts as an efficient catalyst for cyclooctene and cyclohexane oxidation under mild conditions, Catal. Commun. 99 (2017) 100–104.

[34] L.Q. Mo, X.F. Huang, G. Huang, G.P. Yuan, S.J. Wei, Highly active catalysis of cobalt tetrakis(pentafluorophenyl)porphyrin promoted by chitosan for cyclohexane oxidation in response-surface-methodology-optimized reaction conditions, ChemistryOpen 8 (2019) 104–113.

[35] G. Huang, P. Wang, L. Shen, Y.X. Wei, K. Zeng, S.J. Wei, Porous chitosan-supported metal tetra(4-carboxyphenyl) porphyrin as a practical model for the hydrophobic pocket/cavity of cytochrome P-450 enzyme, Mat. Sci. Eng. C-Mater. 49 (2015) 844–850.