



Catalytic oxidation of cyclohexane with dioxygen over boehmite supported trans-A₂B₂ type metalloporphyrins catalyst

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ABSTRACT

Metalloporphyrin-catalysed direct functionalization of saturated C–H bonds is one among the topical and challenging areas within the chemical industry. In this work, three types of unsupported and boehmite supported trans-A₂B₂-metalloporphyrin chloride complexes (Co-D(*p*-Cl)PPCl, Fe-D(*p*-Cl)PPCl, Mn-D(*p*-Cl)PPCl) were prepared and characterized. It has been found that these trans-A₂B₂-metalloporphyrins have high catalytic activity in cyclohexane oxidation under dioxygen. The boehmite supported metalloporphyrins show better catalytic performance and are more stable than unsupported metalloporphyrins. Among these supported metalloporphyrin catalysts, Co-D(*p*-Cl)PPCl/BM was better than Fe-D(*p*-Cl)PPCl/BM and Mn-D(*p*-Cl)PPCl/BM, the cyclohexane conversion and selectivity to KA oil are 6.83% and 83.30%, respectively, and the turnover number is 1.05×10^7 . The Co-D(*p*-Cl)PPCl/BM catalyst can be facily recovered and was recycled up to six times without significant decrease in catalytic performance.

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1. Introduction

Although many types of metalloporphyrins (MPs) have been largely studied for their catalytic performance in oxidation reactions, the application of metalloporphyrins in synthetic chemistry and chemical industry is not popular because of its economic problem. Therefore, the selective oxidation of hydrocarbons and other organic compounds is still a challenging and promising subject. Cyclohexane oxidation with air or dioxygen in the absence of additives and solvents is one of the most important industrial process to produce KA oil (cyclohexanol/cyclohexanone) or adipic acid, which are key intermediates used principally for the production of caprolactam, nylon-6,6 and nylon-6 [1,2].

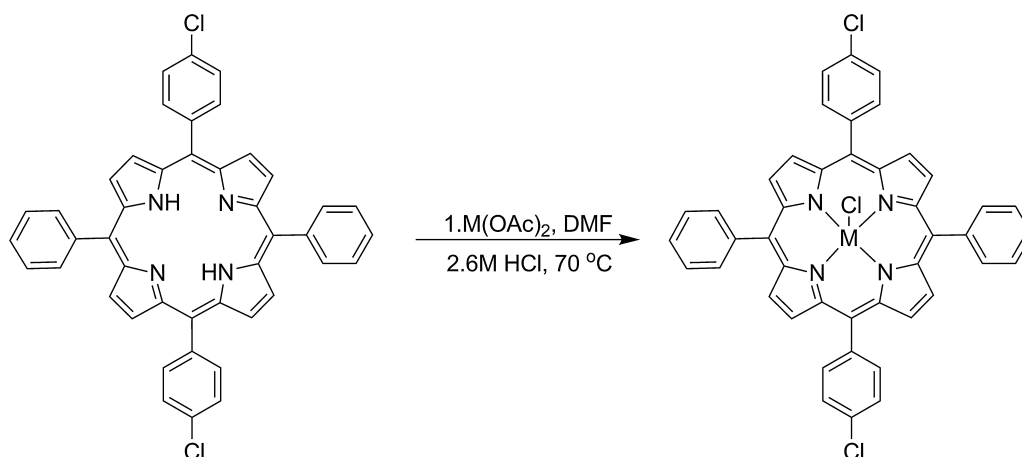
Like cytochrome P-450, metalloporphyrins have been proven to be efficient oxidation catalysts, which are known to activate O₂ and perform hydrocarbon oxidation into the corresponding oxygenic compounds under mild condition [3–6]. Homogeneous systems based on metalloporphyrins have achieved good activities and high selectivities in catalytic oxidation of hydrocarbons. However, the metalloporphyrins are inclined to aggregation through π – π interactions or decompose during the catalytic oxidation process [7–10]. Furthermore, it is hard to recover and recycle

from the homogeneous media at the end of the first reaction [11]. Immobilization of the metalloporphyrins on inert and stable inorganic supports is one of the most effective ways to overcome the above drawbacks. In addition, much efforts have been devoted to develop heterogeneous metalloporphyrin catalysts on various supports [12–16], which referred that the turnover number (TON) is 18.92, 1.54×10^5 and 7.91×10^4 .

Boehmite (BM) has attracted much attention because of their unique structure, high surface energy and easy preparation [17–19]. Some of them referred that the turnover number (TON) is 1.14×10^5 and 2.3×10^5 . Boehmite, a principal oxo-hydroxide of aluminum, which is also the topological precursor for synthesizing γ -Al₂O₃, is widely used as adsorbent, catalyst, catalyst support, and composite material. Boehmite can be easily prepared in nanoparticle form of high surface energy and good thermal stability. It also possesses an oxygen atom acting as an electron pair donor, thus providing an opportunity of coordination to the metal ion of the metalloporphyrin. Furthermore, metalloporphyrin can be firmly adsorbed onto its surface. Boehmite supported A₄-type metalloporphyrin (Mn TPP) has been utilized in cyclohexane oxidation by Huang [20], the single-pass yield of KA oil is around 5% and the turnover number (TON) is 1.49×10^5 .

In this paper, several trans-A₂B₂ types metalloporphyrin chloride complexes (Co-D(*p*-Cl)PPCl, Fe-D(*p*-Cl)PPCl, Mn-D(*p*-Cl)PPCl) were synthesized (Scheme 1) and immobilized on boehmite. The relationship between the central metal ion of trans-A₂B₂ type

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Scheme 1. Synthesis of trans-A₂B₂-metalloporphyrins.

metalloporphyrins and their catalytic performance in cyclohexane oxidation was studied.

2. Experimental

2.1. Reagents

Aluminum nitrate nonahydrate (98%), NH₃ aqueous (NH₃ 27%) and absolute ethanol were all obtained from Aladdin Reagent. No impurities were found in the cyclohexane by GC analysis before use.

2.2. Trans-A₂B₂-metalloporphyrin chloride complexes (MsDCIPPCl)

All reagents and solvents used for the synthesis of porphyrin were of analytical grade and were obtained commercially. MsDCIPPCl (CoDCIPPCl, FeDCIPPCl, MnDCIPPCl) was prepared by referring to the following procedures [21,22]. D-(*p*-Cl)PP (0.25 mol) was dissolved in DMF (50 mL). The solution was heated to reflux with stirring. Then, cobalt acetate, ferrous chloride or manganous acetate (1.50 mmol) was added in three portions within 30 min. When the thin-layer chromatography (silica) indicated no free base porphyrin, the solution was cooled to 70 °C, and 40 mL of 6 M HCl was added and stirred for 4 h. The solution was cooled and the appeared solid was filtrated and washed with 3 M HCl until the filtrate no longer appeared red. The obtained solid was vacuum-dried, and gave 89–98% yield of MsDCIPPCl (CoDCIPPCl, FeDCIPPCl, MnDCIPPCl).

2.3. Preparation of trans-A₂B₂-metalloporphyrin chloride/BM catalyst

The trans-A₂B₂-metalloporphyrin chloride/BM (MsDCIPPCl/BM) catalysts were prepared by referring to the following procedures [20]. Aluminum nitrate nonahydrate (0.25 mol) was dissolved in distilled water (500 mL) for 30 min under vigorous stirring at room temperature, and 1.45 mol of NH₃ aqueous was slowly added into the solution. After the white aluminum hydroxide precipitate was formed for 1 h, the mixture was filtrated and washed with distilled water until no NH₃ aqueous or NH₄Cl was detected. Then, the precipitate was added to 250 mL of ethanol in a three-necked flask with high stirring for 1 h. Subsequently, 0.015 mmol of MsDCIPPCl ethanol solution were slowly added into the above suspension and stirred for another 40 min, and the mixture was heated to 50 °C with rapid stirring for 6 h. The

light-brown suspension was filtrated and washed with distilled water, and the cake was vacuum-dried at 170 °C for 10 h.

2.4. Catalysts characterization

2.4.1. UV-vis

UV-vis spectra was obtained by UV-2550 spectrophotometry with a scan range of 300–800 nm for trans-A₂B₂-metalloporphyrin chloride complexes using 1 cm quartz cuvette. MsDCIPPCl/BM was characterized by using barium sulphate as reference, a small amount of BaSO₄ was pressed into thin pellets, and some samples were put on the pellets and pressed again, then it was placed in the sample holder to assay their spectra.

2.4.2. FTIR

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 380 spectrometer. The spectra of the samples were acquired in the wave number range of 400–4000 cm⁻¹. The samples were ground to fine powders, mixed with KBr, and then were pressed into thin pellets and placed in the sample holder of the spectrometer to assay their spectra.

2.4.3. Thermal analysis

TG/DTG curves were carried out on a TGA Q50 using air as purge gas (80 mL min⁻¹). The temperature is between 30 and 800 °C with a heating rate of 10 °C min⁻¹.

2.4.4. X-ray diffraction analysis

X-ray diffraction (XRD) patterns were collected on a Japan Rigaku D/Max 2550 VB+ 18 kW X-ray diffractometer under the conditions of 40 kV, 30 mA, Cu Kα radiation, with a scanning rate of 2°/min in the range of 2θ = 20–80°.

2.4.5. Inductively coupled plasma (ICP)

The amount of MsDCIPPCl/BM (Co, Fe and Mn) per gram of boehmite was determined by Inductively Coupled Plasma Atomic Emission Spectrometer (IRIS Intrepid II XSP ICP-AES) (Thermo Electron Co.) under a microwave pressure digestion (MDS 200; CEM) with hydrofluoric and aquaregia. The samples were digested by a traditional acid method (HF, HNO₃, HClO₄ and HCl), diluted adequately and analyzed for Co, Fe and Mn.

2.5. Procedures for the catalytic test

Cyclohexane oxidation was carried out in a 50 mL autoclave reactor with a magnetic stirrer in the absence of solvent. Typically,

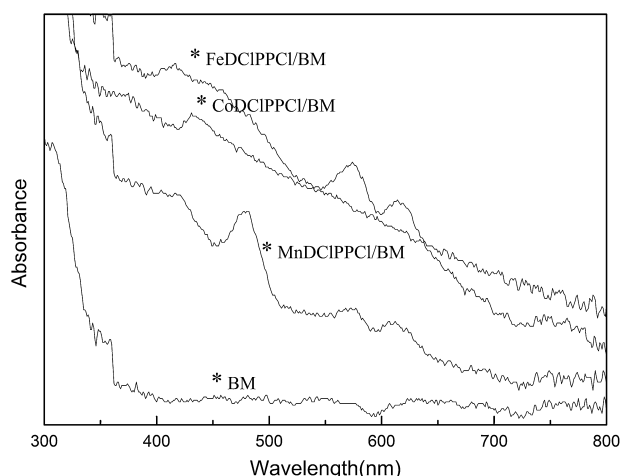


Fig. 1. UV-vis spectra of BM and BM supported metalloporphyrin.

catalysts and cyclohexane (15.6 g) were added into the autoclave reactor. And the reactor was sealed and heated to the setting temperature. Then it was pressurized to the setting pressure with the molecular oxygen under stirring. After the reaction, the reactor was cooled to the ambient temperature. The mixture was dissolved in ethanol and the catalysts were removed by filtration. And the catalysts were washed in alcohol and dried, and then recycled in the next reaction. The samples of the reaction mixture were identified by GC-MS and LC-MS. The acid in the product can mainly be attributed to the succinic acid, glutaric acid and adipic acid. The cyclohexanol and cyclohexanone in the product were analyzed by gas chromatography with the internal standard method using chlorobenzene as the internal standard. The total acid in the product was analyzed by the chemical titration method. The total ester in the product was analyzed by the chemical titration method with a solution of hydrochloric acid.

3. Results and discussion

3.1. Characterization of the catalysts

UV-vis and FTIR spectroscopies were used to confirm the cobalt, iron and manganese MsDCIPPCl. The results of UV-vis absorption measurements of MsDCIPPCl are shown in Table 1. It is well known that porphyrin has one Soret band and four Q band absorption peaks in the ultraviolet visible region. The number of Q band usually reduces to one or two owing to the increase of symmetry of the molecular structure when metalloporphyrins form. The results of UV-vis absorption in Table 1 show that MsDCIPPCl forms. Furthermore, IR spectra of these metallic complexes shows some characteristic bands; the strong absorption band appeared at 1000 cm^{-1} , an increased intensity of the band at 1350 cm^{-1} , corresponding to C=N stretching, and the absence of the band at 3300 cm^{-1} indicates that the metalloporphyrins form, that is, N-H stretching of the intramolecular hydrogen bonds usually presents in the free base porphyrin. These contributions directly argue for the formation of the corresponding metallic complexes [23].

CoDCIPPCl/BM shows bright red in color. FeDCIPPCl/BM and MnDCIPPCl/BM show light green in color, which indicates that metalloporphyrins are successfully supported on boehmite.

UV-vis spectra of the boehmite supported metalloporphyrins are shown in Fig. 1. CoDCIPPCl/BM, FeDCIPPCl/BM and MnDCIPPCl/BM show the Soret peak at 432 nm, 417 nm and 480 nm respectively. Besides, FeDCIPPCl/BM and MnDCIPPCl/BM present absorption peaks at 574 nm and 614 nm. The UV-vis spectra confirm that these supported materials contain metalloporphyrin species.

FTIR spectra were obtained in order to observe the interactions between OH groups on the surface of boehmite and metalloporphyrin complexes. However, the main characteristic peak of the immobilized metalloporphyrin complexes could not be observed due to the very low amount of metalloporphyrins on the surface of boehmite.

Thermal analysis was used to verify the stability of the supported catalysts designed for oxidation reactions. For all samples, there is a rapid weight loss between 60 and 140°C . The weight loss of the supported catalysts reduced during $140\text{--}240^\circ\text{C}$ indicating that the weight loss of MsDCIPPCl/BM was too small to change the structure of the complexes. This can also be seen from the corresponding DTG curves. Thus, the structure of the supported catalysts will not lead to decomposition since the cyclohexane oxidation was carried out at $150\text{--}160^\circ\text{C}$.

The XRD patterns of boehmite, CoDCIPPCl/BM, FeDCIPPCl/BM and MnDCIPPCl/BM exhibit characteristic broad peaks of the boehmite phase. The easy formation of nanoparticles enhances the dispersion and adsorption of the metalloporphyrin. And the typical peaks pattern at $2\theta = 28, 38, 49$ and 65° for all the samples of boehmite and boehmite supported metalloporphyrins were in agreement with the literature [24].

The amount of metalloporphyrin on the support was determined by Inductively Coupled Plasma Atomic Emission Spectrometer (IRIS Intrepid II XSP ICP-AES). The results show that the amount of CoDCIPPCl, FeDCIPPCl and MnDCIPPCl was 0.276, 0.284 and 0.056 mg g^{-1} of boehmite respectively.

3.2. Catalytic performance

The results of catalytic performance of cobalt, iron and manganese metalloporphyrins are described in Table 2. Under the same reaction conditions (entries 1–3 and 5–7), Co-D(p-Cl)PPCl presents the highest selectivity to KA oil, and Mn-D(p-Cl)PPCl exhibits the highest cyclohexane conversion. Comparing the consequences of entry 4 and 5, we could find that the cyclohexane conversion decreases in a certain degree while the selectivity to KA oil increases by 21.61%. During the cyclohexane oxidation process, we observe that the induction period varies with the different metalloporphyrin catalysts, Co-D(p-Cl)PPCl may activate oxygen molecules more quickly than the other two metalloporphyrin catalysts. The reason may be that different central metal ions changed the original electric potential of the MsDCIPPCl.

Table 3 shows the results of cyclohexane oxidation catalyzed by MsDCIPPCl/BM. It was found that boehmite supported metalloporphyrin catalysts show better catalytic performance than unsupported catalysts. When the reaction was catalyzed by boehmite supported metalloporphyrins under 1 MPa in the absence of solvent, the selectivity to KA oil increases 12–17% at almost the same cyclohexane conversion. Similarly, compared with the results of supported and unsupported catalysts, the selectivity to KA oil increases 6–10% at the cyclohexane conversion of around 15% under 2 MPa in the absence of solvent. And the TON is more than one order of magnitude higher than that of unsupported catalyst. Among these boehmite supported metalloporphyrin catalysts, Co-D(p-Cl)PPCl/BM presents the best catalytic performance in cyclohexane oxidation. This is in accordance with the known differences in chemistry of the concerned metalloporphyrins [25,26]. The cobalt porphyrins are active in one-electron redox processes, such as the activation of dioxygen, while iron and manganese porphyrins are more likely to activate single oxygen donors, such as PhIO, H_2O_2 , t-BuOOH, or NaOCl in a two-electron redox reaction.

It can be seen from Tables 2 and 3 that MsDCIPPCl/BM presents better catalytic performance in cyclohexane oxidation. At the same time, MsDCIPPCl/BM catalysts show a longer induction period than that of MsDCIPPCl. In metalloporphyrins/ O_2 system [27,28],

Table 1
Results of UV–vis absorption measurements of MsDCIPPCI.^a

Metalloporphyrin	Soret band (nm), ϵ (L mol ⁻¹ cm ⁻¹)	Q band (nm), ϵ (L mol ⁻¹ cm ⁻¹)
CoDCIPPCI	428(2.24 × 10 ⁵)	544(0.24 × 10 ⁵)
FeDCIPPCI	417(1.69 × 10 ⁵)	509(0.20 × 10 ⁵)
MnDCIPPCI	480(1.39 × 10 ⁵)	584(0.13 × 10 ⁵)
DCIPP	419(2.97 × 10 ⁵)	515(1.39 × 10 ⁴)
		551(0.60 × 10 ⁴)
		591(0.44 × 10 ⁴)
		647(0.32 × 10 ⁴)

^a The absorption spectra were measured in chloroform solution.

Table 2
Results of cyclohexane oxidation catalyzed by MsDCIPPCI.

Entry	Catalysts	Conversion (%)	Selectivity (%) K–A	K/A (mol ratio)	TON (× 10 ⁶) ^d	Yield of KA oil (%)
1 ^a	Co-D(<i>p</i> -Cl)PPCI	6.95	68.77	0.49	0.55	4.78
2 ^a	Fe-D(<i>p</i> -Cl)PPCI	7.71	68.22	0.74	0.61	5.26
3 ^a	Mn-D(<i>p</i> -Cl)PPCI	8.41	65.40	0.65	0.67	5.50
4 ^b	Co-D(<i>p</i> -Cl)PPCI	23.44	40.15	1.12	0.93	9.41
5 ^c	Co-D(<i>p</i> -Cl)PPCI	15.14	61.76	0.76	1.21	9.35
6 ^c	Fe-D(<i>p</i> -Cl)PPCI	15.13	58.83	0.92	1.20	8.90
7 ^c	Mn-D(<i>p</i> -Cl)PPCI	16.31	55.91	0.86	1.29	9.12

^a Reaction conditions: cyclohexane (20 mL), catalysts (1.8 mg), 155 °C for 2 h, oxygen pressure (1 MPa).

^b Reaction conditions: cyclohexane (10 mL), acetonitrile (10 mL), catalysts (1.8 mg), 155 °C for 2 h, oxygen pressure (2 MPa).

^c Reaction conditions: cyclohexane (20 mL), catalysts (1.8 mg), 155 °C for 2 h, oxygen pressure (2 MPa).

^d The turnover number (TON) is the value of 2 h reaction time, calculated by mol product (ketone + alcohol + acid + ester)/mol trans-A₂B₂-metalloporphyrin.

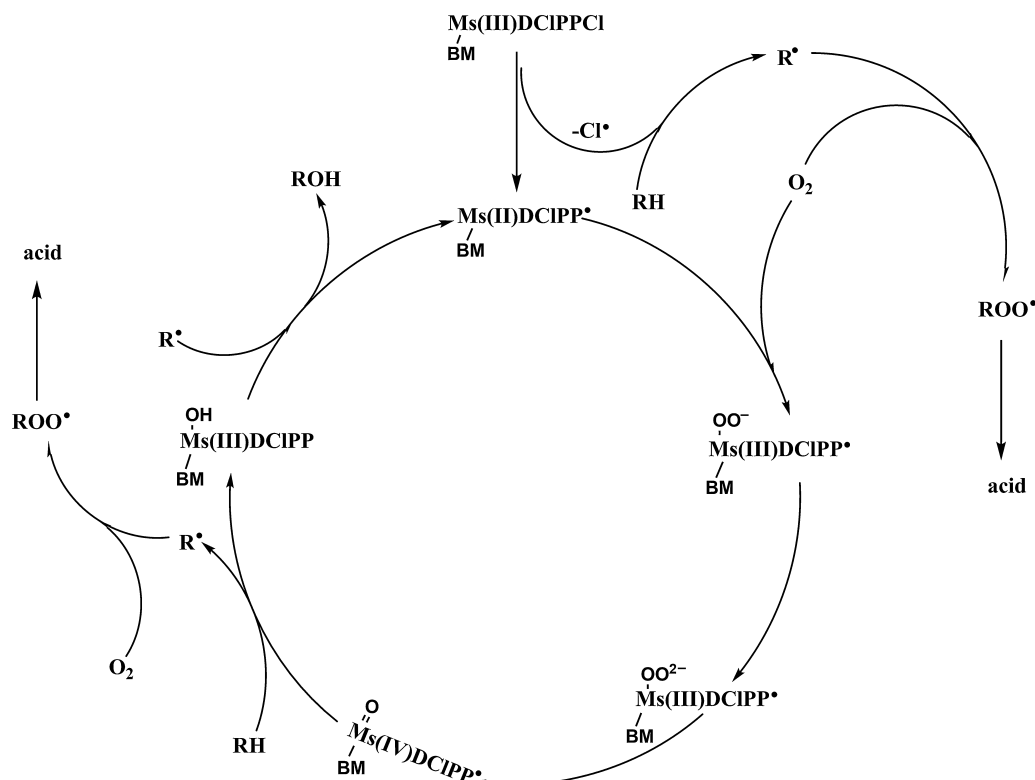
Table 3
Results of cyclohexane oxidation catalyzed by MsDCIPPCI/BM.

Entry	Catalysts	Conversion (%)	Selectivity (%) K–A	K/A (mol ratio)	TON (× 10 ⁷) ^c	Yield of KA oil (%)
1 ^a	CoDCIPPCI/BM	6.17	84.27	0.38	0.64	5.20
2 ^a	FeDCIPPCI/BM	7.05	80.43	0.37	0.69	5.67
3 ^a	MnDCIPPCI/BM	6.20	82.26	0.38	3.16	5.10
4 ^b	CoDCIPPCI/BM	14.02	68.12	0.59	1.45	9.55
5 ^b	FeDCIPPCI/BM	14.77	63.98	0.55	1.45	9.45
6 ^b	MnDCIPPCI/BM	14.97	64.80	0.57	7.64	9.70

^a Reaction conditions: cyclohexane (20 mL), MsDCIPPCI/BM (CoDCIPPCI 0.138 mg, FeDCIPPCI 0.142 mg, MnDCIPPCI 0.028 mg), 155 °C for 2 h, oxygen pressure (1 MPa).

^b Reaction conditions: cyclohexane (20 mL), MsDCIPPCI/BM (CoDCIPPCI 0.138 mg, FeDCIPPCI 0.142 mg, MnDCIPPCI 0.028 mg), 155 °C for 2 h, oxygen pressure (2 MPa).

^c The turnover number (TON) is the value of 2 h reaction time, calculated by mol product (ketone + alcohol + acid + ester)/mol MsDCIPPCI.



Scheme 2. Proposed mechanisms of the supported catalyst.

Table 4

Results of cyclohexane oxidation catalyzed by CoDCIPPCl/BM.

Entry	CoDCIPPCl catalysts (mg)	Conversion (%)	Selectivity (%) K–A	K/A (mol ratio)	TON ($\times 10^7$) ^d	Yield of KA oil (%)
1 ^a	0.22	5.73	83.77	0.35	0.38	4.80
2 ^a	0.14	6.17	84.27	0.38	0.64	5.20
3 ^a	0.12	6.26	82.10	0.37	0.76	5.14
4 ^{a,c}	0.10	7.29	71.19	0.38	1.05	5.19
5 ^b	0.44	14.58	68.58	0.61	0.48	10.00
6 ^b	0.22	14.67	67.22	0.62	0.97	9.86
7 ^b	0.14	14.02	68.12	0.59	1.46	9.55
8 ^b	0.04	16.33	61.18	0.70	5.33	9.99
9 ^{b,c}	0.10	15.00	57.60	0.72	21.53	8.64

^a Reaction conditions: cyclohexane (20 mL), CoDCIPPCl/BM catalysts, 155 °C for 2 h, oxygen pressure (1 MPa).^b Reaction conditions: cyclohexane (20 mL), CoDCIPPCl/BM catalysts, 155 °C for 2 h, oxygen pressure (2 MPa).^c Reaction conditions: unsupported catalysts.^d The turnover number (TON) is the value of 2 h reaction time, calculated by mol product (ketone + alcohol + acid + ester)/mol CoDCIPPCl.**Table 5**

Recycle of CoDCIPPCl/BM catalyst.

Catalysts	Entry	Conversion (%)	Selectivity (%) K–A	K/A (mol ratio)	TON ($\times 10^7$) ^b	Yield of KA oil (%)
CoDCIPPCl/BM	1 ^a	6.17	84.27	0.38	0.64	5.20
	2	6.52	83.27	0.46	0.77	5.43
	3	6.93	82.25	0.50	0.94	5.70
	4	6.87	83.26	0.49	1.19	5.72
	5	7.54	82.76	0.45	1.39	6.24
	6	6.94	84.01	0.45	1.38	5.83
	Average	6.83	83.30	0.46	1.05	5.69

^a Reaction conditions: cyclohexane (20 mL), CoDCIPPCl/BM catalysts (CoDCIPPCl 0.138 mg), 155 °C for 2 h, oxygen pressure (1 MPa).^b The turnover number (TON) is the value of 2 h reaction time, calculated by mol product (ketone + alcohol + acid + ester)/mol CoDCIPPCl.

Ms(III)DCIPPCl loses a chlorine radical to form Ms(II)DCIPP•, which combines with an oxygen molecule to form an activated radical species Ms(III)OODCIPP•, and then form the high-valent metal-oxo active species. And the intermediate Ms(IV)=ODCIPP• can easily capture a hydrogen atom from cyclohexane to afford an alkyl radical and then form the products [29]. The chlorine radical can also easily capture a hydrogen atom from cyclohexane to afford an alkyl radical, which combines with an oxygen molecule to form the activated peroxoradicals species (ROO•), then it may form organic acids. The corresponding active species for the supported catalyst [20] were mainly Ms(IV)=ODCIPP•/BM (Scheme 2). The longer induction period of Ms(III)DCIPPCl/BM may be that the formation of Ms(IV)=ODCIPP• is faster than Ms(IV)=ODCIPP•/BM. The existence of BM hindered the supported catalysts and dioxygen to form the active species Ms(IV)=ODCIPP•/BM, which can capture a hydrogen atom from cyclohexane to afford an alkyl radical and then form the products. The chlorine radical and Ms(IV)=ODCIPP•/BM can also easily capture a hydrogen atom from cyclohexane to afford an alkyl radical, and then it combines with an oxygen molecule to form the activated peroxoradicals species (ROO•) which may form organic acids. That is, the steric hindrance of BM decreases the oxygen activation ability of the supported metalloporphyrin catalysts. This steric hindrance leads to increase the selectivity to KA oil and prevents from further oxidation of KA oil to byproducts. It may be the reason why the supported catalyst shows better catalytic performance than the unsupported catalyst, which is consistent with the results of Tables 2 and 3.

In general, the electron-withdrawing metalloporphyrins are very strong for activating O₂ because the electron deficiency of the central metal ion is willing to accept a pair of electrons donated by O₂. The potential order of metal ions is different. The synergistic effect on the potential and the formation of active species could give rise to the long induction period and different catalytic performance. This may be the reason why cobalt metalloporphyrin shows better results than that of iron and manganese metalloporphyrin.

3.3. Effect of the catalyst amount

The effect of the amount of CoDCIPPCl/BM catalyst was investigated and the results are shown in Table 4. The cyclohexane conversion and selectivity to KA oil change very little when the amount of CoDCIPPCl/BM catalyst increases from 0.12 to 0.22 mg under 1 MPa or increase from 0.14 to 0.44 mg under 2 MPa. However, the selectivity to KA oil decreases significantly when the catalyst amount declines from 0.14 to 0.04 mg under 2 MPa. Similarly, the boehmite supported Co-DCIPPCl catalyst show better catalytic performance than the unsupported catalyst, the selectivity to KA oil increases by more than 11%.

3.4. Recycle of the CoDCIPPCl/BM catalyst

Recycling tests with repeated use of CoDCIPPCl/BM catalyst in six consecutive reactions were carried out under the typical reaction conditions, the recycled catalysts were washed with alcohol, dried and then used for the next reaction. The results are shown in Table 5. It can be seen from Table 5 that the change of catalytic activity and selectivity could be ignored. However, the cyclohexane oxidation catalyzed by the unsupported catalysts gives lower selectivity to KA oil (65.40–68.77%) and lower TON (0.55–0.67 $\times 10^6$). Furthermore, unsupported catalysts are difficult to recover and reused. Thus, the advantages of the boehmite supported CoDCIPPCl catalyst were obvious.

4. Conclusion

Unsupported and boehmite supported metalloporphyrin catalysts were prepared and characterized. The prepared catalysts were used to mimic cytochrome P-450 in cyclohexane oxidation process. In general, boehmite supported metalloporphyrin catalysts show better catalytic performance than unsupported metalloporphyrins, the selectivity to KA oil is improved 12–17% under the cyclohexane

conversion of 6–8%. And CoDCIPPCl/BM presents the best results, it gives the selectivity to KA oil of 83.30% at the cyclohexane conversion of 6.83% and TON reaches 1.05×10^7 . This complex may prove to be an active and reusable catalyst for industrial cyclohexane oxidation process.

Acknowledgments

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