NRC Research Press

ARTICLE

Synthesis and catalytic properties of trans-A_2B_2-type metalloporphyrins in cyclohexane oxidation

Yujia Xie, Fengyong Zhang, Pingle Liu, Fang Hao, and He'an Luo

Abstract: A new efficient and mild protocol for synthesizing a series of trans-A_2B_2-porphyrins through a TFA-catalyzed condensation reaction between various aldehydes and dipyrromethanes has been developed. Several trans-A_2B_2-metalloporphyrins (cobalt, nickel) were synthesized and used to catalyze cyclohexane oxidation C–H bonds with dioxygen in the absence of additives and solvents. The results show that the catalytic activities were relative to the nature of the substituted groups and the central metal ions of trans-A_2B_2-metalloporphyrin. Cobalt metalloporphyrin presents better catalytic performance in the conversion of cyclohexane than the nickel metalloporphyrin under the same reaction conditions.

Key words: trans-A_2B_2-porphyrin, trans-A_2B_2-metalloporphyrin, cyclohexane oxidation, cyclohexanol, cyclohexanone.

Résumé : Nous avons établi un nouveau protocole efficace et doux pour la synthèse d'une série de porphyrines de type trans-A_2B_2 par une réaction de condensation de divers aldéhydes et dipyrrométhanes en présence de TFA comme catalyseur. Nous avons synthétisé plusieurs métalloporphyrines (cobalt, nickel) de type trans-A_2B_2 dont nous nous sommes servi pour catalyser l'oxydation des liaisons carbone–hydrogène du cyclohexane par du dioxygène en l'absence d'additifs et de solvants. Les résultats montrent que l'activité catalytique dépend de la nature des groupes substitués et de l'ion métallique central de la métalloporphyrine de type trans-A_2B_2. La métalloporphyrine contenant du cobalt est un meilleur catalyseur de la conversion du cyclohexane que celle contenant du nickel dans les mêmes conditions de réaction. [Traduit par la Rédaction]

Mots-clés : porphyrine trans-A_2B_2, métalloporphyrine trans-A_2B_2, oxydation du cyclohexane, cyclohexanol, cyclohexanone.

Introduction

Functionalization of inert alkanes to more valuable products (e.g., carboxylic acids, alcohols, ketones) has attracted much attention.[1] Generally speaking, the oxidation of alkane is problematic because of the inactivity of C–H bonds of alkane chemically. Although catalytic oxidation of C–H bond in saturated hydrocarbons under mild conditions is a key step in the oxyfunctionalization of organic compounds, much progress has been achieved in the selective cleavage and functionalization of C–H bonds of alkanes.[2–7] The cytochrome P-450 monooxygenase enzyme, which can catalyze the oxidation of the inert C–H bonds under mild conditions in organisms, is able to effectively and stereospecially catalyze the hydroxylation and epoxidation of hydrocarbon in the metabolic system. There has been significant interest in modeling of the P-450 enzyme active sites and developing the biomimetic oxidation catalysts. Therefore, progress has been made in the preparation of metalloporphyrin and subsequent application in catalytic reaction of C–H bonds.

Oxidation of cyclohexane with air or dioxygen in the absence of additives and solvents to ketone–alcohol (KA) oil (cyclohexanol–cyclohexanone) or adipic acid is a very crucial industrial process with regard to economic viability and from environmental points of view.[8] For instance, KA oil is used to make adipic acid, which is required for the production of nylon-6.6, and cyclohexanone is the building block in the large industrial scale manufacture of ε-caprolactam, which is the intermediate for the production of nylon-6. Currently, cyclohexane oxidation is carried out by using the cobalt salt as the catalyst with a poor cyclohexane conversion of 3%–6% and unfavorable selectivity of KA oil.[9] People have made much effort to discover better ways to increase the conversion of cyclohexane and have obtained some achievements by using metalloporphyrins as catalysts.[5,10–11] However, the technology in which cyclohexane was oxidized by air or dioxygen to produce cyclohexanol and cyclohexanone has not been improved much up to now.

In 1979, the first metalloporphyrin (iron tetraphenylporphyrin) catalyzed oxidation was discovered by Groves[12] in which cyclohexane was oxidized to cyclohexanol by using iodosobenzene as the oxidant. Subsequently, oxygenation of alkanes has been observed with a number of metalloporphyrin systems. In general, the metalloporphyrin catalytic activity is related to its substituent group and central metal ion (ionization potential and dioxygen-binding ability). Research has shown that the adsorption of dioxygen is the first step for oxygen reduction;[13–14] then the interaction between the catalyst and oxygen molecule and its effect of dissociation of the O–O bond is important in understanding the reaction mechanism. These processes are considered to proceed by a mechanism similar to the enzymatic systems. Hence, higher ionization potential and larger dioxygen-binding energy are associated with better catalytic activity.

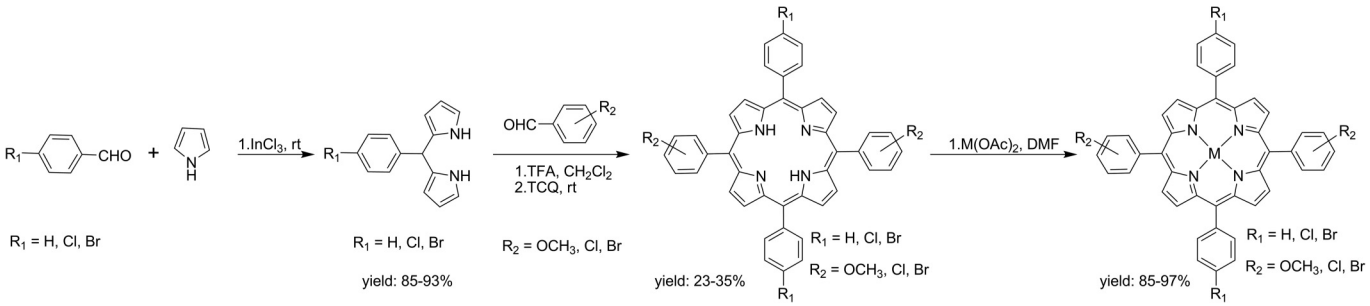
Most of the previous research only focused on the synthesis of A_4-type porphyrins and their catalytic activity studied. In this work, trans-A_2B_2-metalloporphyrins (cobalt, nickel) were synthesized and applied to the oxidation of cyclohexane inert hydrocarbon bonds. Several trans-A_2B_2-porphyrins and cobalt- and nickel-trans-A_2B_2-porphyrins with different substituents on the porphyrin rings were synthesized and are described in Scheme 1, and their catalytic activity for cyclohexane oxidation with dioxygen, the relationship between the substituent structures and the central metal ion of trans-A_2B_2-metalloporphyrins, and their

Received 3 September 2013. Accepted 5 November 2013.

Y. Xie, F. Zhang, P. Liu, F. Hao, and H. Luo. College of Chemical Engineering, Xiangtan University, Xiangtan 411105, China.
Corresponding author: Pingle Liu (e-mail: liupingle@xtu.edu.cn).

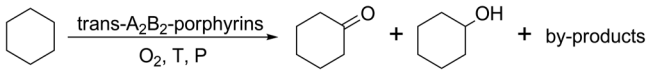
Published at www.nrcresearchpress.com/cjc on 7 November 2013.

Scheme 1. Synthesis of trans-A_2B_2-porphyrins and trans-A_2B_2-metalloporphyrins.



catalytic selectivity were studied. The structures of different trans-A_2B_2-metalloporphyrin catalysts and the dioxygen oxidation of cyclohexane to the KA oil catalyzed by these metalloporphyrins are shown in Scheme 2.

Scheme 2. Cyclohexane oxidation catalyzed by the given catalysts with dioxygen.



Experimental method

General

^{1}H spectra were recorded on a Bruker Avance (400 MHz). Neutral aluminum oxide (100–200 mm average particle size) and silica gel (40 mm average particle size) were used for column chromatography. Thin-layer chromatography was performed using SiliCycle silica gel 60 F254 TLC plates and visualized with ultraviolet light. All compounds were purchased from Alfa-Aesar and used without further purification unless otherwise noted. Pyrrole was distilled from CaH_2 before use.

General procedure for the preparation of dipyrromethanes

***Data for 5-(4-bromophenyl)dipyrromethane* (1c)**

By modifying a literature procedure,[15–16] a mixture of 4-bromobenzaldehyde (3.7 g, 20 mmol) and pyrrole (60 mL, 0.87 mol) was treated with $InCl_3$ (0.2 g, 1.0 mmol) at room temperature under argon. After stirring for 6 h, powdered NaOH (4.0 g, 0.1 mol) was added and the reaction mixture was stirred for 45 min. The mixture was filtered. Excess pyrrole was removed by distillation under reduced pressure and the resulting yellow solid was treated with hexanes. The solvent was removed under reduced pressure, affording a precipitate. Recrystallization (CH_3CH_2OH–H_2O) gave a light-yellow solid (5.62 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (br, 2H, NH), 7.42–7.44 (d, 2H, ArH), 7.07–7.09 (d, 2H, ArH), 6.70 (s, 2H, pyrrole-H), 6.15–6.16 (d, 2H, pyrole-H), 5.88 (s, 2H, pyrole-H), 5.43 (s, 1H, meso-H).

***Data for phenyldipyrromethane* (1a)**

A sample of benzaldehyde (2.12 g. 20 mmol) was treated identically as for 5-(4-bromophenyl)dipyrromethane, affording a tan solid (4.0 g, 90%). ^{1}H NMR ($CDC1_3$) δ: 7.89 (br, 2H, NH), 7.35–7.19 (m, 5H, ArH), 6.69 (q, 2H, pyrole-H), 6.15 (q, 2H, pyrole-H), 5.91 (m. 2H, pyrole-H), 5.47 (s, 1H, meso-H).

***Data for 5-(4-Chlorophenyl)dipyrromethane* (1b)**

A sample of *p*-chlorobenzaldehyde (2.8 g. 20 mmol) was treated identically as for 5-(4-bromophenyl)dipyrromethane, affording a light-yellow solid (4.35 g, 85%). ^{1}H NMR ($CDC1_3$) δ: 7.97 (br, 2H, NH). 7.35–7.15 (m, 4H, ArH), 6.82 (m, 2H, pyrole-H), 6.20 (m, 2H, pyrole-H), 5.87 (m. 2H, pyrole-H), 5.47 (s, 1H, meso-H).

General procedure for the synthesis of trans-A_2B_2-porphyrin derivatives

By modifying a literature procedure,[17] dipyrromethane (2 mmol) and the appropriate aldehyde (2 mmol) was dissolved in CH_2Cl_2 (200 mL) under argon at room temperature. After a homogenous solution was obtained, TFA (0.3 mL, 4.0 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. Chloranil (750 mg, 3.06 mmol) was added and stirring was continued for 3 h. The reaction was terminated by addition of triethylamine (1 mL). The mixture was passed through column chromatography (alumina, CH_2Cl_2) and eluted with CH_2Cl_2 until the eluant was no longer dark. The collected eluant was concentrated. The resulting crude product was purified by column chromatography on silica gel (CH_2Cl_2–hexanes = 3:1). Recrystallization ($CHCl_3$–CH_3OH) gave a purplish black solid. The main products of trans-A_2B_2-porphyrin were obtained in yields between 23% and 35%.

Data for D(p-Cl)PP

Condensation of 5-(4-chlorophenyl)dipyrromethane (0.51 g, 2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0 mmol) following the procedure described for the general procedure gave a purple solid with a yield of 27%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (m, 8H, pyrole-H), 8.20 (m, 4H, ArH), 8.16 – 8.05 (m, 4H, ArH), 7.74 (t, *J* = 7.8 Hz, 10H, ArH), –2.80 (s, 2H, NH). UV/Vis ($CHCl_3$): 419, 515, 551, 591, 647 nm.

Data for D(p-Br)PP

Condensation of 5-(4-bromophenyl)dipyrromethane (0.60 g, 2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0 mmol) following the procedure described for the general procedure gave a purple solid with a yield of 25%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (m, 8H, pyrole-H), 8.20 (d, *J* = 5.8 Hz, 4H, ArH), 8.06 (d, *J* = 8.1, 4H, ArH), 7.88 (d, *J* = 8.1 Hz, 4H, ArH), 7.75 (d, *J* = 6.2 Hz, 6H, ArH), –2.81 (s, 2H, NH). UV/Vis ($CHCl_3$): 419, 516, 551, 592, 648 nm.

Data for D(p-Cl)PD(p-Br)P

Condensation of 5-(4-chlorophenyl)dipyrromethane (0.51 g, 2.0 mmol) and 4-bromobenzaldehyde (0.37 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0vmmol) following the procedure described for the general procedure gave a purple solid with a yield of 30%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.83 (s, 8H, pyrole-H), 8.12 (d, *J* = 8.1 Hz, 4H, ArH), 8.06 (d, *J* = 8.1 Hz, 4H, ArH), 7.89 (d, *J* = 8.1 Hz, 4H, ArH), 7.74 (d, *J* = 8.1 Hz, 4H, ArH), –2.85 (s, 2H, NH). UV/Vis ($CHCl_3$): 420, 516, 550, 590, 647 nm.

Data for D(p-Cl)PD(p-OCH_3)P

Condensation of 5-(4-chlorophenyl)dipyrromethane (0.51 g, 2.0 mmol) and *p*-methoxybenzaldehyde (0.27 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0 mmol) following the procedure described for the general procedure gave a purple solid with a yield of 26%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.85 (s, 8H, pyrole-H), 8.12 (t, *J* = 7.6 Hz, 8H, ArH), 7.87–7.61 (m, 4H, ArH), 7.42–7.13 (m, 4H, ArH), 4.09 (s, 6H, OCH_3), –2.80 (d, 2H, NH). UV/Vis ($CHCl_3$): 419, 516, 551, 590, 648 nm.

Data for D(p-OCH_3)PP

Condensation of phenyldipyrromethane (0.44 g, 2.0 mmol) and *p*-methoxybenzaldehyde (0.27 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0 mmol) following the procedure described for the general procedure gave a purple solid with a yield of 35%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58 (s, 8H, pyrole-H), 7.97 (m, 8H, ArH), 7.51–7.55 (m, 6H, ArH), 7.25 (m, 4H, ArH), 4.16 (s, 6H, OCH_3), –2.59 (s, 2H, NH). UV/Vis ($CHCl_3$): 419, 516, 552, 591, 648 nm.

Data for D(p-Br)PD(o-Br)P

Condensation of 5-(4-bromophenyl)dipyrromethane (0.60 g, 2.0 mmol) and 2-bromobenzaldehyde (0.37 g, 2.0 mmol) in CH_2Cl_2 (200 mL) with TFA (0.3 mL, 4.0 mmol) following the procedure described for the general procedure gave a purple solid with a yield of 23%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.82 (s, 4H), 8.70 (s, 4H), 8.25–7.95 (m, 8H), 7.89 (s, 4H), 7.69 (s, 4H), –2.75 (s, 2H). UV/Vis ($CHCl_3$): 420, 516, 551, 590, 647 nm.

General procedure for the synthesis of trans-A_2B_2-metalloporphyrin derivatives

A standard reaction was performed using a 100 mL round-bottom flask in which trans-A_2B_2-diphenylporphyrin (0.25 mmol) was dissolved in DMF (50 mL). Then, cobalt acetate or nickel acetate (1.5 mmol) was predissolved in MeOH (5 mL) and was added to the reaction mixture at room temperature. The reaction mixture was refluxed and the evolution of the reaction was monitored by thin-layer chromatography. Once no further progress of the reaction was detectable, the solvents were placed into water. The mixture was filtered and washed with water. The resulting solid was vacuum-dried. The titled compound was obtained in yields between 85% and 97%.

Data for Co-D(p-Cl)PP

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 97%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.70 (s, 8H, pyrrole-H), 12.97 (s, 8H, ArH), 9.87 (s, 8H, ArH), 9.70 (s, 2H, ArH). UV/Vis ($CHCl_3$): 411, 528 nm.

Data for Co-D(p-Br)PP

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.74 (s, 8H, pyrrole-H), 12.96 (d, 8H, ArH), 10.01 (s, 4H, ArH), 9.90 (s, 4H, ArH), 9.70 (s, 2H, ArH). UV/Vis ($CHCl_3$): 411, 529 nm.

Data for Co-D(p-Cl)PD(p-Br)P

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 95%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.74 (s, 8H, pyrrole-H), 12.90 (s, 8H, ArH), 9.96 (m, 8H, ArH). UV/Vis ($CHCl_3$): 419, 520 nm.

Data for Co-D(p-Cl)PD(p-OCH_3)P

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.79 (s, 8H, pyrrole-H), 13.03 (s, 8H, ArH), 9.89 (s, 4H, ArH), 9.46 (s, 4H, ArH), 5.28 (s, 6H, OCH_3). UV/Vis ($CHCl_3$): 413, 531 nm.

Data for Co-D(p-OCH_3)PP

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.93 (s, 8H, pyrrole-H), 13.13 (s, 8H, ArH), 9.92 (s, 6H, ArH), 9.71 (s, 2H, ArH), 9.43 (s, 2H, ArH), 5.24 (s, 6H, OCH_3). UV/Vis ($CHCl_3$): 411, 528 nm.

Data for Co-D(p-Br)PD(o-Br)P

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 15.24 (s, 8H, pyrrole-H), 12.89 (s, 8H, ArH), 9.96–9.53 (m, 8H, ArH). UV/Vis ($CHCl_3$): 419, 518 nm.

Data for Ni-D(p-Cl)PP

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (d, J = 11.6 Hz, 8H, pyrrole-H), 7.99 (s, 4H, ArH), 7.93 (d, J = 6.7 Hz, 4H, ArH), 7.67 (s, 10H, ArH). UV/Vis ($CHCl_3$): 415, 528 nm.

Data for Ni-D(p-Cl)PD(p-Br)P

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.73 (s, 8H, pyrrole-H), 7.89 (m, 12H, ArH), 7.67 (s, 4H, ArH). UV/Vis ($CHCl_3$): 416, 529, 617 nm.

Data for Ni-D(p-Br)PD(o-Br)P

The compound was prepared using the general procedure as described above; a brick-red solid was obtained with a yield of 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.71 (d, J = 4.0 Hz, 4H, pyrrole-H), 8.61 (s, 4H, ArH), 7.91 (m, 6H, ArH), 7.82 (s, 4H, ArH), 7.67 (d, J = 7.2 Hz, 2H, ArH), 7.61 (s, 4H, ArH). UV/Vis ($CHCl_3$): 415, 529, 620 nm.

Cyclohexane oxidation catalyzed by trans-A_2B_2-metalloporphyrin with dioxygen

Except where a special explanation is given, cyclohexane oxidation was performed according to the following procedures. It was conducted in a 50 mL autoclave reactor with a magnetic stirrer in the absence of solvent. Catalysts (1.8 mg) and cyclohexane (15.6 g) were added. Then the reactor was sealed and heated to the setting temperature. Molecular oxygen was then pumped into the autoclave until the system pressure reached the setting pressure. Then the mixture was stirred. After the reaction, the reactor was cooled to ambient temperature. The catalysts were removed by filtration. The products of cyclohexanol and cyclohexanone were analyzed by gas chromatography with the internal standard method using chlorobenzene as an internal standard. The total acid in the product was analyzed with a sodium hydroxide solution with the chemical titration method. The total ester in the product was analyzed with a solution of hydrochloric acid with the chemical titration method.

Results and discussion

The catalytic activities of different cobalt- and nickel-trans-A_2B_2-metalloporphyrins in liquid-phase oxidation of cyclohexane was investigated under 1 MPa for 1 h; the experimental results are shown in Table 1. From Table 1, we could find that the structure of cobalt- and nickel-metalloporphyrins affected their catalytic performance. In other words, the catalytic activities of cobalt- and nickel-metalloporphyrins in the oxidation of cyclohexane to cyclohexanol and cyclohexanone are related to the variety of peripheral substituents on the metalloporphyrin ring. For the cobalt-trans-A_2B_2-metalloporphyrin catalyst, the different substituents in the phenyl ring of metalloporphyrin (Table 1, entries 1, 2, 3, and 6) showed that these trans-metalloporphyrin catalysts with an electron-withdrawing group such as *o*/*p*-Cl or *o*/*p*-Br exhibit higher conversions than those with an electron-donating group such as *p*-OCH_3 (Table 1, entries 4 and 5). This result is similar to the reported result.[18] Namely, the existence of electron-withdrawing groups could also accelerate the reaction rate of cyclohexane hydroxylation with the metalloporphyrin catalysts. The reasons might be that the electronic density of cobalt ions in metalloporphyrins decreased with an increase of the electron-withdrawing degree of substituents from *p*-OCH_3 to *o*/*p*-Cl or *o*/*p*-Br, thus leading to the enhancement of the Co(III)–Co(II) reduction potential, and Co(III) could be easily reduced to Co(II) and the catalytic cycle of metalloporphyrins could proceed successfully.

Table 1. Results of oxidation of cyclohexane catalyzed by trans-A_2B_2-metalloporphyrins at 1 MPa.

Entry	Catalyst	Conversion (%)	Selectivity (%)			Ketone/alcohol (mol ratio)	Turnover number (×10^5)[a]
			KA	Acid	Ester		
1	Co-D(*p*-Cl)PP	7.93	76.16	8.20	15.64	0.51	6.04
2	Co-D(*p*-Br)PP	7.64	78.67	8.25	13.08	0.54	6.51
3	Co-D(*p*-Cl)PD(*p*-Br)P	9.23	74.54	8.15	17.31	0.61	8.52
4	Co-D(*p*-Cl)PD(*p*-OCH_3)P	7.20	78.05	9.22	12.13	0.64	5.92
5	Co-D(*p*-OCH_3)PP	7.12	72.19	7.58	20.23	0.48	5.35
6	Co-D(*p*-Br)PD(*o*-Br)P	8.85	75.93	8.93	15.14	0.63	8.98
7	Co-TPP	10.65	74.27	10.89	14.84	0.61	7.35
8	Co-T(*p*-Cl)PP	9.61	73.26	9.68	17.06	0.60	7.99
9	Ni-D(*p*-Cl)PP	5.57	68.76	11.13	20.11	0.78	4.24
10	Ni-D(*p*-Cl)PD(*p*-Br)P	5.70	72.63	10.53	16.84	0.78	5.26
11	Ni-D(*p*-Br)PD(*o*-Br)P	3.54	57.06	6.21	36.73	1.00	3.59

Note: Reaction conditions: cyclohexane 185 mmol, catalysts 1.8 mg, 155 °C for 1 h, oxygen pressure 1 MPa.
[a]The turnover number is the value at 1 h of reaction time calculated by mole product (ketone + alcohol + acid + ester)/mol trans-A_2B_2-metalloporphyrin.

Table 2. Results of oxidation of cyclohexane catalyzed by trans-A_2B_2-metalloporphyrins at 2 MPa.

Entry	Catalyst	Conversion (%)	Selectivity (%)			Ketone/alcohol (mol ratio)	Turnover number (×10^5)[a]
			KA	Acid	Ester		
1	Co-D(*p*-Cl)PP	17.43	67.24	14.74	18.02	0.81	13.27
2	Co-D(*p*-Br)PP	17.30	60.92	14.68	24.40	0.84	14.75
3	Co-D(*p*-Cl)PD(*p*-Br)P	18.57	57.21	17.63	25.16	0.85	17.15
4	Co-D(*p*-Cl)PD(*p*-OCH_3)P	14.10	57.81	18.77	23.42	1.26	11.60
5	Co-D(*p*-OCH_3)PP	14.10	57.81	15.43	22.87	1.26	10.60
6	Co-D(*p*-Br)PD(*o*-Br)P	17.49	58.15	15.32	26.53	0.90	17.75
7	Co-TPP	18.99	55.98	17.59	26.43	0.94	13.11
8	Co-T(*p*-Cl)PP	19.64	56.36	18.28	25.36	0.99	16.34
9	Ni-D(*p*-Cl)PP	10.51	61.94	14.65	23.41	0.63	8.00
10	Ni-D(*p*-Cl)PD(*p*-Br)P	14.06	60.60	15.93	24.47	0.82	12.98
11	Ni-D(*p*-Br)PD(*o*-Br)P	2.10	45.24	5.23	49.53	0.98	2.13

Note: Reaction conditions: cyclohexane 185 mmol, catalysts 1.8 mg, 155 °C for 1 h, oxygen pressure 2 MPa.
[a]The turnover number is the value at 1 h of reaction time calculated by mole product (ketone + alcohol + acid + ester)/mol trans-A_2B_2-metalloporphyrin.

Table 2 demonstrates the results of cyclohexane oxidation catalyzed by cobalt- and nickel-trans-A_2B_2-metalloporphyrins; the consequence of the various substituents of the cobalt- and nickel-metalloporphyrins is similar to that of the cobalt-metalloporphyrin. Obviously, the conversion of cyclohexane increased with an increase of pressure; on the contrary, the selectivity of KA oil decreased significantly. More cyclohexanone and cyclohexanol was oxidized into by-products (acid and ester) in the course of cyclohexane oxidation catalyzed by trans-A_2B_2-metalloporphyrin.

The conversion of cyclohexane was compared with cobalt-metalloporphyrin and nickel-metalloporphyrin in the same parent under the same reaction conditions. From Table 1 (entries 1, 3, 6, and 9–11) and Table 2 (entries 1, 3, 6, and 9–11), we could find that the different central metal ion influenced their catalytic performance. Under the same reaction conditions, the catalytic activity of cobalt-metalloporphyrin in the conversion of cyclohexane was higher than that of the nickel-metalloporphyrin. It is generally known that cyclohexane oxidation undergoes two steps: the adsorption and desorption of oxygen from the catalyst. Thus, the interaction between catalyst and oxygen molecule and its effect on dissociation of the O–O bond can cause the unique conversion of cyclohexane.

Tables 1 and 2 show the differences in cyclohexane conversion and turnover number with reaction pressure for cyclohexane oxidation catalyzed by cobalt- and nickel-trans-A_2B_2-metalloporphyrins. It is obvious that the cyclohexane conversion and turnover number catalyzed by cobalt-trans-A_2B_2-metalloporphyrin was higher than that of nickel-trans-A_2B_2-metalloporphyrin under the same reaction conditions. The more quickly the activated species comes into being, the more cyclohexane is oxidized, indicating that the corresponding turnover number is higher. We also find that it is about a 3–10 min inducing period for cobalt-trans-A_2B_2-metalloporphyrin, but a 30–50 min inducing period for nickel-trans-A_2B_2-metalloporphyrin, and that they had different turnover numbers. The phenomenon may explain that different central metal ions had a different influence on the cyclohexane oxidation process.

The significant differences in the ratio of the ketone to alcohol may be attributed to the redox property of trans-A_2B_2-metalloporphyrin. That is, the difference of the substituents between trans-A_2B_2-metalloporphyrin (Table 1, Entry 1–6) and A_4-mettalloporphyrin (Table 1, entries 7 and 8) led to those results under the oxidation conditions. Possibly the substituent changes the adsorption and desorption behavior of cyclohexane and oxygen toward the catalyst.

Conclusion

The catalytic activities of trans-A_2B_2-metalloporphyrins in the oxidation of cyclohexane to cyclohexanol and cyclohexanone not only change with the variety of metal atom ions in trans-A_2B_2-metalloporphyrins but also change with the variety of peripheral substituents on the trans-A_2B_2-metalloporphyrin ring. Trans-A_2B_2-metalloporphyrins with electron-withdrawing groups were more efficient catalysts than those with electron-donating groups while using the same center metal ions. The cobalt-trans-A_2B_2-metalloporphyrins show better catalytic performance than the nickel-trans-A_2B_2-metalloporphyrins under the same reaction conditions. Further studies on the synthesis of trans-A_2B_2-metalloporphyrins and even supported catalysts are in progress in our laboratory.

Acknowledgements

This work was supported by the NSFC (21276218), the program for New Century Excellent Talents in University (NCET-10-0168), SRFDP (20124301110007), and the Scientific Research Fund of the Hunan Provincial Education Department (13k043, CX2012B253).

References

(1) Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28* (3), 154. doi:10.1021/ar00051a009.
(2) Połtowicz, J.; Haber, J. *J. Mol. Catal. A: Chem.* **2004**, *220* (1), 43. doi:10.1016/j.molcata.2004.03.050.
(3) Biswas, A. N.; Das, P.; Agarwala, A.; Bandyopadhyay, D.; Bandyopadhyay, P. *J. Mol. Catal. A: Chem.* **2010**, *326* (1–2), 94. doi:10.1016/j.molcata.2010.04.014.
(4) Riley, C. R.; Montgomery, N. E.; Megally, N. N.; Gunn, J. A.; Davis, L. S. *The Open Catalysis Journal* **2012**, *5*, 8.
(5) Staudt, S.; Burda, E.; Giese, C.; Müller, C. A.; Marienhagen, J.; Schwaneberg, U.; Hummel, W.; Drauz, K.; Gröger, H. *Angew. Chem. Int. Ed.* **2013**, *52* (8), 2359. doi:10.1002/anie.201204464.
(6) Silva, A. R.; Mourão, T.; Rocha, J. *Catal. Today* **2013**, *203* (0), 81. doi:10.1016/j.cattod.2012.07.043.
(7) Alavi, S.; Hosseini-Monfared, H.; Siczek, M. *J. Mol. Catal. A: Chem.* **2013**, *377* (0), 16. doi:10.1016/j.molcata.2013.04.013.
(8) Suresh, A. K.; Sharma, M. M.; Sridhar, T. *Ind. Eng. Chem. Res.* **2000**, *39* (11), 3958. doi:10.1021/ie0002733.
(9) Pocutsa, A. P.; Bras, J.; Muzart, J. *Russ. Chem. Bull.* **2005**, *54* (2), 312. doi:10.1007/s11172-005-0253-0.
(10) Guimarães, C. A.; de Moraes, M. *Appl. Catal. A: Gen.* **2004**, *258* (1), 73. doi:10.1016/j.apcata.2003.08.013.
(11) Choi, B. G.; Ko, S. Y.; Nam, W.; Jeong, B. *Bull. Korean Chem. Soc.* **2005**, *26* (11), 1819. doi:10.5012/bkcs.2005.26.11.1819.
(12) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101* (4), 1032. doi:10.1021/ja00498a040.
(13) Shi, Z.; Zhang, J. *J. Phys. Chem. C* **2007**, *111* (19), 7084. doi:10.1021/jp0671749.
(14) He, H.; Lei, Y.; Xiao, C.; Chu, D.; Chen, R.; Wang, G. *J. Phys. Chem. C* **2012**, *116* (30), 16038. doi:10.1021/jp303312r.
(15) Littler, B. J.; Miller, M. A.; Hung, C.-H.; Wagner, R. W.; O'Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64* (4), 1391. doi:10.1021/jo982015+.
(16) Krüger, R. A.; Terpstra, A. S.; Sutherland, T. C. *Can. J. Chem.* **2011**, *89* (2), 214. doi:10.1139/V10-098.
(17) Senge, M. O.; Fazekas, M.; Pintea, M.; Zawadzka, M.; Blau, W. J. *Eur. J. Org. Chem.* **2011**, *2011* (29), 5797. doi:10.1002/ejoc.201100641.
(18) Guo, C.-C.; Song, J.-X.; Chen, X.-B.; Jiang, G.-F. *J. Mol. Catal. A: Chem.* **2000**, *157* (1–2), 31. doi:10.1016/S1381-1169(99)00444-6.