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Biomimetic Oxidation of Hydrocarbons with Air over Metalloporphyrins

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1. Introduction

The oxidation of C-H, C-C and C=C of hydrocarbons, from the syntheses of many fine chemicals to the manufacture of various commodities in large scale, plays great important role in transformation of basic materials to useful synthetic building in organic chemistry and in conversion of hydrocarbon to oxygen-containing industrial production especially the hydroxylation, epoxidation, degradation of hydrocarbon derivatives[1-6]. Conventional oxidation methodologies often suffer low chemo- and/or regio-selectivity with low conversion and low turnover number (TON) in an unfriendly way from both economical and environmental aspects which the catalyst is very expensive and generates amounts of hazardous waste. Oxidation reactions catalyzed by both non-metal[7-8] and metal[9-14] catalysts have been receiving increasing attention, particularly for the highly selective aerobic oxidations catalyzed by metal complexes[15-17]. In nature, aerobic oxidation processes are carried out in a highly selective manner by mono- or dioxygenases under mild conditions[18-19]. A well-known type of monooxygenase is cytochrome P-450(CP-450)[20-23], which features an iron porphyrin core, and can catalyze a wide variety of oxidation reactions including epoxidation, hydroxylation, dealkylation, degradation, dehydrogenation, and oxidation of amines, sulfides, alcohols and aldehydes, even for unreactive substrates such as unactivated hydrocarbons. This stimulates numerous efforts in developing biomimetic oxidation systems[24-26].

Metalloporphyrins, with a core structure closely resembling that of the iron porphyrin core of CP-450, have been extensively studied as catalysts to oxidate a series kind of reactions mimic the natural style[24,27]. In 1979, Groves and co-workers[28] reported the first oxidation system with synthetic metalloporphyrin as a catalyst. They developed the oxidation system of terminal oxidant iodosylbenzene(PhIO) and ironporphyrin catalyst [Fe^{III}(por)Cl], which can effect both epoxidation of styrene and cyclohexene, and hydroxylation of cyclohexane and adamantane. Subsequently, many reports focusing on metalloporphyrin-catalyzed oxidation systems have appeared in the literature, as described in previous reviews[29-34]. As documented in the literature, the hydroxylation of alkanes and epoxidation of alkenes catalyzed by iron, manganese and ruthenium porphyrins with the traditional terminal oxidants PhIO, NaOCl and 2,6-dichloropyridine-*N*-oxide, including enantioselective oxidations are the most extensively studied systems.

It has been well documented that the active species in the oxidation reactions catalyzed by CP-450 are high-valent iron-oxo species. High-valent oxometalloporphyrins have been observed in the reactions of synthetic metalloporphyrins with PhIO, *m*-CPBA and O_2, and have been reported to be able to oxidize alkanes, alkenes, phosphines, amines and sulfides by oxygen atom transfer and/or insertion reactions[31,35].

In the past several decades, oxyfunctionalization of hydrocarbons in biomimetic systems with molecular oxygen in the presence of metalloporpyrins as catalysts is one of the most attractive transformations in synthetic organic chemistry and manufacture of hydrocarbon derivatives. The behavior of metalloporphyrin-catalyzed hydrocarbon oxidation under mild conditions has been systematically studied as a model of CP-450 monooxygenase by many researchers[21,24,36,37] with the ultimate goal of searching for the most effective metalloporphyrin catalysts for hydrocarbon oxidation. Chemoselective oxidation process of hydrocarbons is of great importance in fine chemicals industry and oil product industry. Aerobic oxidation of alkanes, alkenes and aromatic hydrocarbons, an extremely important reaction in chemical industries, has attracted more and more attention during recent decade due to the oxidation products are widely used in pharmaceutical, dyestuff, perfume, resin and textile fiber industries, such as the very important Nylon-6 and Nylon-66. Investigation of the mechanism, industrial procedure and the pertinent fields for biomimetic oxidation of hydrocarbons with air over metalloporphyrins attracts more and more attentions.

This chapter mainly summarized the systematic researches of our group focusing on biomimetic oxidation of hydrocarbon with air over simple metalloporphyrins, μ-oxo-metalloporphyrins including oxidation of alkanes, alkenes, aromatic hydrocarbons, mechanism study and industrial-scale biomimetic oxidation of hydrocarbons.

2. Biomimetic oxidation of C-H of alkanes

Recent work on catalytic hydroxylation using metalloporphyrin-based oxidation systems is mainly focused on C–H bonds of alkane. A few research groups reported a catalytic system consisting of monometalloporphyrin and molecular oxygen[38-39]. Unfortunately, this system needs to use the reducers. To improve this system, Lyons et al. synthesize the perhalogenated metalloporphyrin complexes and use the complexes as catalysts for isobutane and propane hydroxylation with molecular oxygen[40]. These results open a door for the biomimetic oxidation of hydrocarbons with molecular oxygen over metalloporphyrins in which coreductants are not required, but more and more researching work must to be investigated because perhalogenated metalloporphyrin complexes is very expensive and in high catalyst loading with low turn over number(TON), which makes it difficult for industrialization.

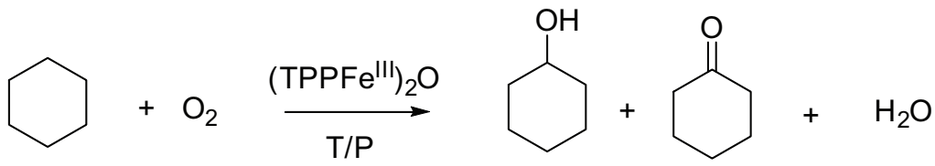
2.1 Biomimetic oxidation of C-H of cyclohexane

The liquid-phase aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone (the so-called KA oil) has always been an area of intensive research[41-42] because it is one of the key steps in the industrial production of ε-caprolactam and Nylon[43-44]. For this particular transformation, current industrial methods either employ cobalt salts as catalysts or use no catalyst at all (autoxidation at higher temperature). However, there are several major shortcomings associated with the current technology, such as low conversion (~4%) and low selectivity for the desired product KA oil(<80%). Based on above unsolved problems, many scientists regarded that the industrial production of KA oil from cyclohexane has been

considered as the least efficient procedure of all major industrial processes. The development of a more efficient and chemo-selective process is highly desirable. Lately, particularly in the last 10 years, scientists have developed many new heterogeneous or homogeneous catalytic processes for the aerobic oxidation of cyclohexane, such as *N*-hydroxyphthalimide(NHPI)[45-47], metalloaluminophosphates [58-50], Zeolite Y[51-52], etc., to overcome these shortcomings, and much progress has been made.

For the purpose of solving the bottle-neck problem in oxidation of hydrocarbons, our group has been engaging development novel biomimetic and more efficient method using porphyrin complexes as catalysts during the last two decades. After systematical investigation, till now, our research and development results have not only improved the reaction conversion to >7%, but also increased the selectivity of KA oil to >85% in industrial scale. The aerobic oxidation of cyclohexane over tetraphenylporphinatocobalt(TPPCo) is currently employed by the Sina-Petro Chemical-Baling Petro chemical Company to produce more than 124,000 tons of KA oil annually.

In 2003, inspired by the success of the work of Lyons et al., we tried to use the simple μ-oxo-bismetalloporphyrin $(TPPFe^{III})_2O$ to catalyze hydroxylation of hydrocarbons using air as the terminal oxidant to gain a better understanding of the possibility of using simple μ-oxo dimeric metalloporphyrin to catalyze the hydrocarbon oxidation directly by air. We developed a new reaction system for the aerobic oxidation of the inactive C-H bond of cyclohexane catalyzed by a very small amount of simple μ-oxo-ironporphyrin $(TPPFe^{III})_2O$[53](Scheme 1).



Scheme 1. Aerobic oxidation of cyclohexane by μ-oxo-ironporphyrin

Cyclohexane was oxidized into cyclohexanol and cyclohexanone with air catalyzed by a very small amount of $(TPPFe^{III})_2O$ in the absence of solvent and cocatalyst. The results showed that the selectivity to cyclohexanol and cyclohexanone is 90% with a conversion of 12.55% and catalyst turnover numbers of 90,000 (based on the metal) under the optimum conditions. The reaction of cyclohexane oxidation catalyzed by μ-oxo-bisironporphyrin was carried out in a 500 ml of autoclave with 3mg of catalyst, 350ml of cyclohexane under the temperature of 398K and pressure of 0.6MPa.

The μ-oxo-bisironporphyrin is synthesized from the corresponding simple metalloporphyrin, we wanted to know that whether the simple tetraphenylporphyrins could catalyzed the cyclohexane hydroxylation or not in the absence of any cocatalysts or reductants. After further investigation, we developed a catalysis system for the cyclohexane oxidation into KA oil with air catalyzed by some simple tetraphenylporphyrins in the absence of any cocatalysts or reductants[37]. After systematical researches on this catalytic oxidation at different temperatures and pressures in the presence of different catalysts, we obtained the optimum reaction conditions and found that cyclohexane conversion was up to 16.2%, general yields of cyclohexanol and cyclohexanone was 82%, catalyst turnover number reached 400,000.

Also the catalysis of chitosan-supported iron(III) tetraphenylporphyrin for cyclohexane oxidation with air in the absences of solvent, reductant and co-catalyst became true[54]. The

research result showed 10.48% conversion of cyclohexane, 79.20% cyclohexanol and cyclohexanone selectivity and 1.40×10^5 catalyst turnover number, respectively under the relatively moderate conditions of 418K and 0.8MPa. We found that the coordination between partly deacetylated chitosan and ironporphyrin increased the yields and selectivity of the aerobic oxidation of cyclohexane catalyzed by ironporphyrin.

In order to investigate the reason why the nitrogenous biopolymers can enhance the catalytic ability of metalloporphyrins, both chitin-supported ironporphyrin and completely deacetylated chitosan-supported ironporphyrin were used to study the Fe–N coordinate behavior between ironporphyrin and the nitrogenous group of polysaccharides[55]. The corresponding coordinate constants of the ironporphyrin with different nitrogenous polysaccharides by means of Langmuir's adsorption isotherm equation were determined, and then the effects of the coordination on the cyclohexane oxidation catalyzed by polysaccharide-supported ironporphyrin were investigated. It is shown that the coordination of the nitrogenous polysaccharide to ironporphyrin had an important influence on both the conversion and selectivity of the aerobic oxidation of cyclohexane catalyzed by ironporphyrin. The selectivity to the cyclohexanone and cyclohexanol production, the catalyst turnover, and the rate constants of cyclohexane oxidation increased with increasing coordination constant as compared in table 1.

	Conversion, %	TON **
Chitosan-ironporphyrin	8.76	39328
Chitin-ironporphyrin	5.01	21760
Ironporphyrin	1.81	8076
Chitin	0	-
Chitosan	0	-

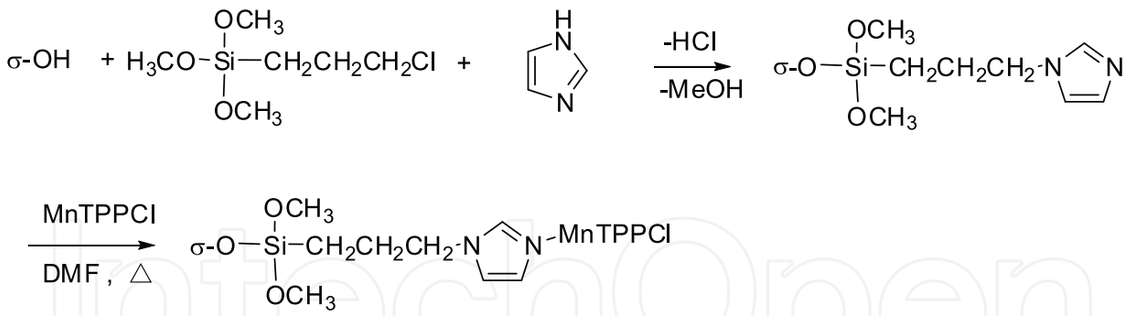
Notes: * Reaction conditions: TPPFeCl, 0.0071 mmol; cyclohexane, 350 ml; temperature, 418K; pressure, 0.8 MPa; reaction time, 1.5 h.
** Referred to one mole of iron atom.

Table 1. The results of cyclohexane oxidations catalyzed by chitosan- and chitin-supported ironporphyrin and ironporphyrin with air*

Also the chitosan-supported cobalt tetraphenylporphyrin can catalyzed the aerobic oxidation of cyclohexane under the relatively moderate conditions of 418K and 0.8Mpa with 11% conversion of cyclohexane, 87% selectivity for the main product cyclohexanol and cyclohexanone and 2.9×10^5 catalyst turnover number[56]. Chitosan-supported iron(III)/or cobalt tetraphenylporphyrin can be prepared easily. Chitosan is cheap and plentiful, and possesses particular microstructure and excellent function; the preparation technology of catalyst is simple also. Chitosan-supported iron(III)/or cobalt tetraphenylporphyrin will have a bright future in industrial applications.

Manganeseporphyrin supported on imidazole-modified silica gel(Scheme 2) can highly catalyze the oxidation of cyclohexane efficiently with yield of 7.1% and selectivity above 90% to cyclohexanol and cyclohexanone, and the catalyst can be reused several times[57].

A systematic study on the effect of a catalyst on the aerobic oxidation of cyclohexane was carried out using cobalt isooctanoate, metalloporphyrin *p*-ClTPPCo and $[p\text{-ClTPPFe}]_2O$ as catalysts[58]. The results showed that the metalloporphyrin-catalyzed system performed better than the traditional cobalt salt (Co isooctanoate) in terms of both the reaction



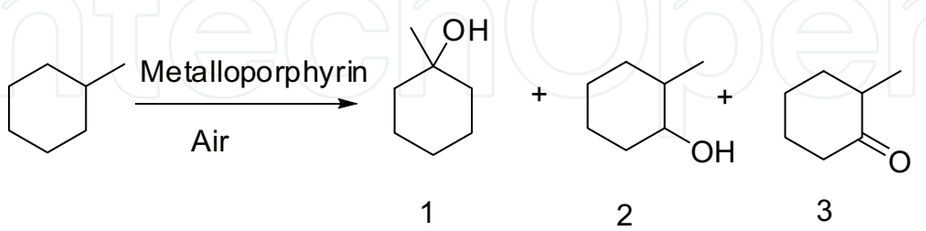
Scheme 2. Synthetic route to manganeseporphyrin supported on imidazole-modified silica gel

conversion and the selectivity of cyclohexanol and cyclohexanone. More importantly, bisironporphyrin complex, which was traditionally considered to be either non-active or not-so-active for hydrocarbon oxidation, excelled at 155°C, achieving high selectivity for KA oil (80%) and good reaction conversion (13.8%). Meanwhile, the production of adipic acid was also increased and good selectivity of adipic acid among the by-products was also obtained. The study suggested that [*p*-ClTPPFe]$_2$O catalyzed aerobic oxidation could be used to produce adipic acid in addition to KA oil. Some mechanistic rationales were proposed to explain the superior performance of the [*p*-ClTPPFe]$_2$O catalyst based on its unique structural and chemical properties.

Biomimetic oxidation of cyclohexane via air catalyzed by metalloporphyrins has already been the subject of a Chinese patent application[59] and had successfully achieved industrial scale production.

2.2 Biomimetic oxidation of C-H of methylcyclohexane

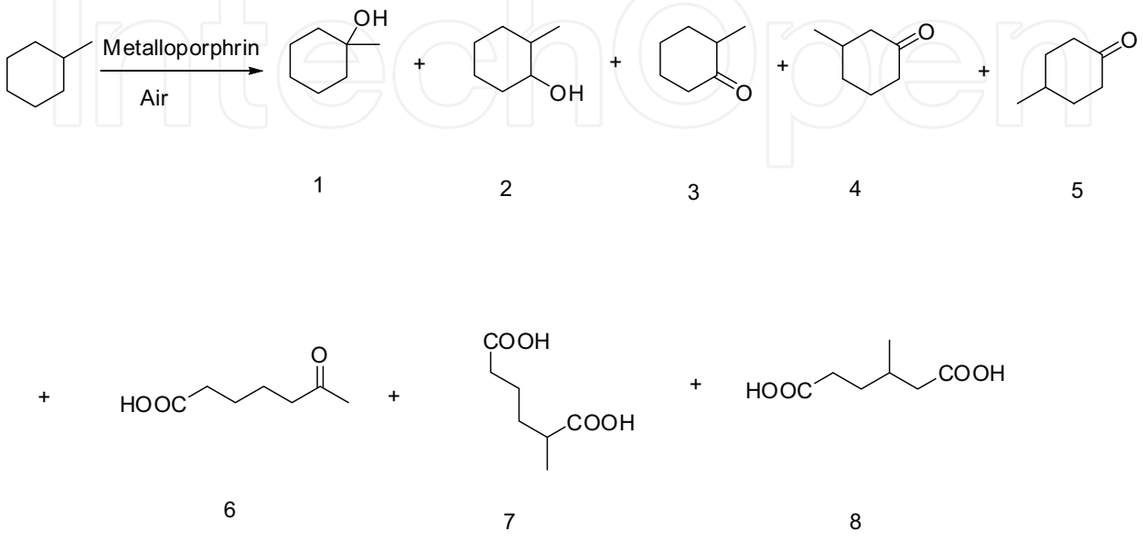
Methylcyclohexanol and methylcyclohexanone also play an important role in fine chemicals and in relative fields. Our group had been engaged in preparation of methylcyclohexanone and methylcyclohexanol via selective aerobic oxidation of methylcyclohexane catalyzed by metalloporphyrin encouraged by the success of biomimetic oxidation of cyclohexane. We reported first[60] that catalyzed by Mn(III)porphyrin, methylcyclohexane could be oxidized by air(Scheme 3).



Scheme 3. Aerobic oxidation of methylcyclohexane by metalloporphyrin

The main products were 1-methylcyclohexanol, 2-methylcyclohexanol and 2-methylcyclohexanone. The effect on the conversion and selectivity was investigated when reaction conditions or porphyrin structure were changed. With the alkoxylsubstituting metalloporphyrins as catalysts, the selectivity of methylcyclohexanone and methylcyclohexanol was better than using TPPMnOAc. Moreover, the larger the substitute's

volume, the higher the conversion, and selectivity still remained satisfactory. Using 5,10,15,20-tetra(*p*-2-heptanoxylphenyl)porphyrinatomanganese as catalyst, the conversion was up to 20 % and the overall selectivity of methylcyclohexanone and methylcyclohexanol was 76 %.
Further researching for the selective catalysis of metalloporphyrins for the aerobic oxidation of different C-H bonds of hydrocarbons in the system of manganeseporphyrin–methylcyclohexane–air was investigated in detail in our group(Scheme 4)[61].



Scheme 4. Biomimetic aerobic oxidation of methylcyclohexane

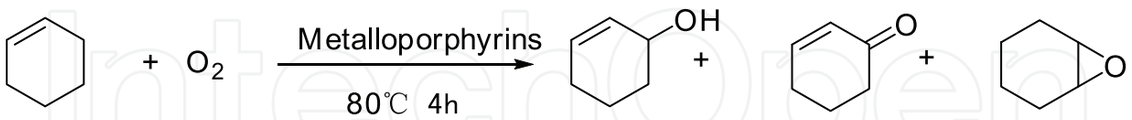
After systematic investigation, it showed that the oxidation reaction of alkanes catalyzed by metalloporphyrin is kept to the classic radical chain mechanism [62-64]. While at the initial stage of methylcyclohexane aerobic oxidation, metalloporphyrin turns into high-valent oxo-metal radical cation $[PM^{IV}=O]^{\bullet+}$, which is responsible for the velocity of the reaction. The selective oxidation of different C-H bond is mainly affected by two factors: activation energy and regioselectivity of different C-H bond. Obviously, the activation energy of secondary C-H bond is greater than that of tertiary C-H bond, so the factors such as temperature, catalyst activity can affect the activation energy. For the selective oxidation of secondary C-H bond, higher temperature and stronger catalyst activity is preferred. Though the pressure in the reaction system does not affect the two factors, it can shift the equilibrium of the reaction. Therefore, it can change the oxidation selectivity of different C-H bonds.

3. Biomimetic oxidation of alkenes

In the field of olefin oxidations with molecular oxygen catalyzed by metalloporphyrins, the catalytic system metalloporphyrins-O_2-BH_4^- were developed[65]. In this catalytic system, sodium borohydride ($NaBH_4$) used as reductant was essential for oxygenation of olefins[66]. Lately, some papers reported the aerobic oxidation of olefins catalyzed by perhalogenated metalloporphyrins or multisubstituent dioxoruthenium porphyrins catalysts [67-69]. Recently, the catalysis of simple porphyrins for oxidation of cyclohexene and the carbon-carbon double bond oxidation with air in the absence of cocatalysts or reductants using the styrene-manganeseporphyrin-air system were reported by our group. The selectivities among epoxidation of C=C, oxidation of allyl C-H, C=C breaking were investigated in detail.

3.1 Biomimetic oxidation of C-H of cyclohexene

The selective oxidation of C-H of olefins is one of the paramount reactions in organic chemistry. Many hydroxyl, carbonyl, unsaturated ketone and other compounds could be synthesized by this methodologies[70-73]. We reported a selective oxidation of allylic C-H of cyclohexene catalyzed by simple porphyrin over air (Scheme 5)[74].



Scheme 5. Aerobic oxidation of cyclohexene

The simple cobalt tetraphenylporphyrins can catalyze cyclohexene oxidation into cyclohexenone with air in the absence of additives and solvents. The temperature, air velocity, catalyst concentration and pressure influenced the yield and conversion of cyclohexene oxidation with air. The result of effect of temperature, air velocity, pressure and catalyst concentration were summarized in the table 2-5 respectively.

Temperature/°C	Cyclohexene Conv./%（mol）	Select.of Cyclohexenone/%（mol）	Time at maximum yield/h	TON
60	5.2	80	8.0	2.1×10^4
70	12	78	6.0	5.0×10^4
80	21	75	4.0	8.7×10^4
90	23	63	3.5	9.5×10^4

Table 2. Effect of temperature on cyclohexeneoxidation reaction

Air velocity /$m^3{\cdot}h^{-1}$	Cyclohexene Conv. /%（mol）	Select.of Cyclohexenone /%（mol）	Time at maximum yield/h	TON
0.04	12	58	5.0	5.0×10^4
0.06	18	69	4.5	7.4×10^4
0.08	21	75	4.0	8.7×10^4
0.10	21	74	4.0	8.7×10^4

Table 3. Effect of air velocity on cyclohexene oxidation reaction

Pressure /MPa	Cyclohexene Conv. /%（mol）	Select.of Cyclohexenone /%（mol）	Time at maximum yield/h	TON
0.2	20	71	4.0	8.25×10^4
0.4	21	75	4.0	8.7×10^4
0.6	20	76	4.0	8.25×10^4

Table 4. Effect of pressure on cyclohexene oxidation reaction

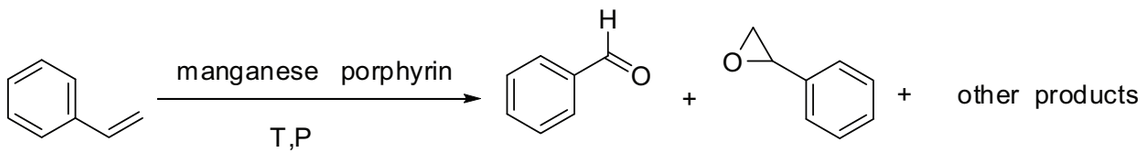
Catalyst Concentration ×10^5/(mol/L)	Cyclohexene Conv. /%（mol）	Select.of Cyclohexenone /%（mol）	Time at maximum yield/h	TON
57	14	56	2.0	2.3×10^3
23	17	63	2.5	7.0×10^3
4.5	19	69	3.5	3.9×10^4
2.3	21	75	4.0	8.7×10^4

Table 5. Effect of catalyst concentration on cyclohexene oxidation reaction

The conversion of cyclohexene was up to 21 %, the selectivity of cyclohexenone reached 75% under the optimum conditions of 0.4 MPa, 80 °C and 2.3×10^{-5}mol/L cobalt tetraphenylporphyrin.

3.2 Biomimetic oxidation of C=C of styrene

In 2006, We[75] reported a novel aerobic oxidative cleavage of C=C double bonds of styrene catalyzed by simple manganese porphyrin(Scheme 6).



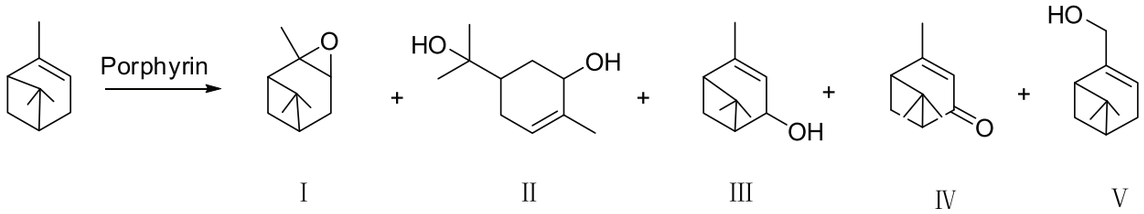
Scheme 6. Aerobic oxidation of styrene by metalloporphyrin

Under the catalysis of chloro(tetraphenylporphinato)manganese, the oxidative cleavage of the carbon-carbon double bond of the styrene with air yields the main product benzaldehyde. The results show that the oxidative cleavage and the epoxidation of the styrene double bond are the competition reactions in the styrene-manganese porphyrin-air system. The reaction temperature decided the product distribution. Under the conditions of 0.4 MPa air and 30 ppm of chloro(tetraphenylporphinato)- manganese, the styrene conversion was 20.0% and the selectivity of benzaldehyde and styrene oxide was 81.7% and 12.7% respectively when the reaction temperature was 110 °C. Styrene conversion was 92.5% and the selectivity of benzaldehyde and styrene oxide was 48.1% and 41.2% respectively when the reaction temperature was 120 °C.

3.3 Biomimetic oxidation of C=C and allylic C–H bonds in α-pinene

α-pinene is the single largest renewable terpene in nature and an important industrial raw material in the terpene industry. With oxidation, isomerization, and hydrogenation, α-pinene can produce a variety of important products. The α-pinene epoxide has great industrial value. We[76] reported simple metalloporphyrins(TPPMnCl, TPPCoCl, TPPFeCl, TPPNi, TPPCu or TPPZn) catalyzed the aerobic oxidation of α-pinene in the absence of co-catalyst and solvents, and the catalytic selectivity of metalloporphyrins for aerobic oxidation of C=C double bond and allylic C-H of α-pinene was investigated(Scheme 7).

When TPPMnCl loaded as the catalyst with a concentration of 6×10^{-5} mol/L, 16 L/h of the air flow rate at ambient pressure and 5h of reaction time, the results are summarized in table 6.



I II III IV V

2,3-epoxypinane (I) sobrerol (II) verbenol (III) verbenone (IV) myrtenol (V)

Scheme 7. Aerobic oxidation of α-pinene by metalloporphyrin

Temperature(°C)	Conversion(%)	Selectivity(%)[a]		
		Products I and II	Products III and IV	Product V
80	23.02	60.19	36.58	3.23
70	19.87	60.45	35.86	3.69
60	16.22	60.99	35.67	3.33
50	14.78	62.00	34.55	3.45
40	8.77	66.86	30.12	3.23

Table 6. Effect of temperature on aerobic oxidation of α-pinene

Different metal core in TPPMCl got the different conversion and selectivity(Table 7).

Catalysts	Conversion(%)	Selectivity(%)[a]		
		Products I and II	Products III and IV	Product V
TPPMnCl	16.22	60.99	35.67	3.33
TPPCoCl	13.84	59.11	37.05	3.84
TPPFeCl	12.40	51.30	43.83	4.87

Conditions: the concentration of the catalyst, 6×10^{-5} mol/L; the temperature, 60 ◦C; ambient pressure; the flow rate of air, 16 L/h; reaction time, 5 h.

Table 7. Effect of metal core of porphyrin on aerobic oxidation of α-pinene

Over TPPMnCl catalyst, the selectivity regarding the oxidation of C=C bond increased with decreasing temperature. Among various metalloporphyrins, TPPMnCl presented the largest selectivity regarding the oxidation of C=C bond and TPPFeCl the largest selectivity regarding the oxidation of allylic C-H bonds. With increasing the electron-donating abilities of the peripheral substituents in (*p*-X)PPMnCl (*X*=-Cl, -CH_3, -OCH_3, -OH), the selectivities regarding the oxidation of C=C bond decreased. Manganese tetraphenylporphyrin supported on nano-TiO_2 has been used as catalyst for the aerobic oxidation of α-pinene[77]. Experimental results showed that this much enhanced activity could arise from possible co-catalysis between metalloporphyrin and the nano-TiO_2 support. The catalyst can be reused several times with minor loss to its catalytic activity. Table 8 summarized the results of different catalysts catalyzed aerobic oxidation of α-pinene.

4. Biomimetic oxidation of C-H of aromatic hydrocarbons

The aerobic liquid-phase oxidation of toluene, *p*-xylene (PX), *p*-toluic acid over metalloporphyrin, metalloporphyrin/ $Co(OAc)_2$, metalloporphyrin/NHPI and other systems were studied in our group.

Catalyst	pinene epoxide,%	Sobrerol, %	Verbenol, %	Verbenone, %	Myrtenol, %	Others, %	Conversion, %	Epoxide selectivity, %
No catalyst	1.63	2.12	1.04	1.34	0.29	0.45	6.87	23.72
TiO_2	7.13	3.59	1.71	0.51	0.48	0.24	13.66	52.20
Ti-Si	4.38	1.83	0.53	1.34	0.58	0.34	9.00	48.67
T(*p*-Cl)PPMnCl[a]	3.85	3.26	2.71	1.56	0.41	0.81	12.60	30.56
TiO_2+(*p*-Cl)PPMnCl[b]	5.84	3.39	1.61	2.39	0.93	2.01	16.17	36.11
TiO_2+(*p*-Cl)PPMnCl+imidazole[c]	6.52	3.96	1.84	2.50	0.85	1.93	17.50	37.25
Ti-Si-PMn	12.88	8.20	11.45	4.48	1.01	1.24	39.26	32.81

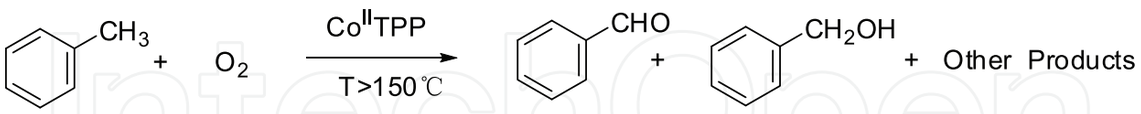
a Concentration, 3.56×10^{-5} M; the amount of T(*p*-Cl)PPMnCl is the same as Ti-Si-PMn.
b Mixture of nano-TiO_2 and T(*p*-Cl)PPMnCl ((1.55 mg T(*p*-Cl)PPMnCl)/(100 mg TiO2)).
c Mixture of "b" and imidazole, mol ratio of imidazole/T(*p*-Cl)PPMnCl = 5/1

Table 8. Results of α-pinene oxidation in the presence of different catalysts

4.1 Biomimetic oxidation of C-H of toluene

Toluene is the most important aromatic hydrocarbon. Scientists have been interested in the selective oxidation of toluene with air to synthesize benzaldehyde and benzyl alcohol, which are versatile intermediates in the chemical industry[78]. But the present oxidation of toluene with air could not produce benzaldehyde and benzyl alcohol because it was difficult to effectively prevent the over-oxidation of benzaldehyde into benzoic acid during the oxidation of toluene. So far, the oxidation of toluene with air is mainly used to synthesize benzyl acid, and benzaldehyde and benzyl alcohol are synthesized by the chlorination of toluene followed by hydrolysis, a serious polluting process[79]. Some researchers tried the selective aerobic oxidation of toluene catalyzed by the transition metal salts. But these technologies are companied by drawbacks such as low selectivity and use of large amounts of solvents and bromides [80].

We[81] firstly reported catalysis of simple cobalt tetraphenylporphyrin for selective liquid phase oxidation of toluene with air in the absence of any solvents or promoters to produce benzaldehyde and benzyl alcohol(Scheme 8).



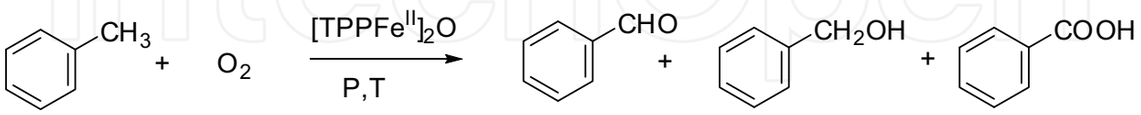
Scheme 8. Aerobic oxidation of toluene by metalloporphyrin

Compared with the present synthetic method of benzaldehyde and benzyl alcohol by the chlorination of toluene followed by hydrolysis, which has been used in the world industry, our new method has the advantage of friendly environmental effects. We found that the reaction time, temperature, air pressure, the amount of catalyst and the flowing rates of air influenced the toluene conversion and the selectivity of benzaldehyde and benzyl alcohol. By the use of 3.2×10^{-5} M cobalt tetraphenylporphyrin as catalyst, toluene oxidation with air under the optimum conditions of 160°C and 0.8 MPa and 0.04 m^3/h air flow produced benzaldehyde and benzyl alcohol at 60% selectivity and 8.9% conversion of toluene. The mole turnover numbers of the catalyst was about 25,000. Compared with the $Co(OAc)_2$ catalyst, Cobalt tetraphenylporphyrin is effective both in conversion and selectivity (Table 9).

Catalyst	Selectivity(mol %)			Conversion（mol%）	Turnover number（mol/mol）
	Benzaldehyde	Benzyl alcohol	Benzoic acid		
Co(II)TPP	33	27	39	8.9	24275
$Co(OAc)_2$	29	20	50	2.9	3125

Table 9. Comparison of aerobic oxidation of toluene catalyzed by Co(II)TPP and $Co(OAc)_2$

The further investigationresulted that μ-oxo-bis[porphyriniron(III)] is another effective catalyst for aerobic oxidation of toluene(Scheme 9)[82].



Scheme 9. Aerobic oxidation of toluene by μ-oxo-bis metalloporphyrin

Catalyzed by μ-oxo-bis[porphyriniron(III)] under the reaction conditions of 438 K and 0.8 MPa, the molar total yields for the products benzaldehyde and benzyl alcohol and the turnover number of the catalyst are 4.35% and 21,830 (based on the metal ion), respectively. Compared with the reaction catalyzed by the corresponding monometalloporphyrin $TPPFe^{III}Cl$, the total yields of the oxidation products and the catalyst turnover number by the dimeric ironporphyrin were almost twice those by the former(Table 10).

Catalyst	Turnover number	Toluene convension,%	Selectivity (-aldehyde +-ol), %	-aldehyde /-ol
$[TPPFe]_2O$	21830	7.36	59.06	1.15
$TPPFe^{III}Cl$	12593	4.08	60.94	0.84

Oxidation carried out by the reaction of 7.5 mg catalyst with toluene (350 mL) at 438 K, 0.8 MPa for 225 min.

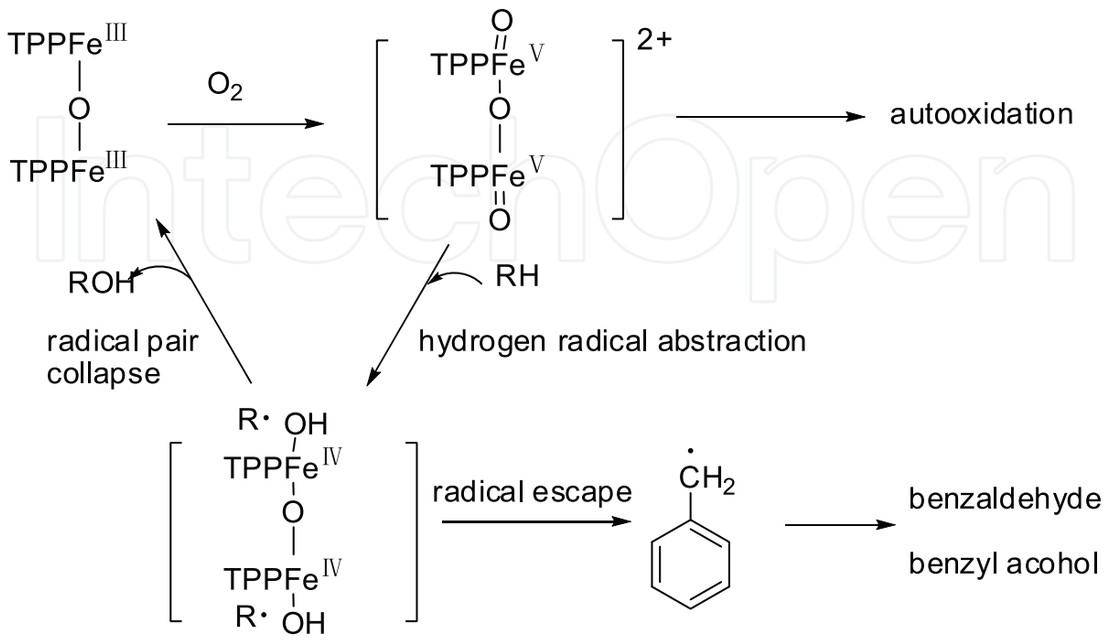
Table 10. Comparison of catalytic property of $[TPPFe^{III}]_2O$ and $TPPFe^{III}Cl$ in toluene oxidation

Possible mechanism of toluene oxidation catalyzed by μ-oxo-bis[porphyriniron(III)] is proposed as bellowing(Scheme 10).

After systematical investigation, it showed that toluene oxidation catalyzed by μ-oxo-bis[porphyriniron(III)] may proceed via a mechanism similar to the hydrocarbon oxidation with molecular oxygen over monometalloporphyrins.

Meanwhile, we[83] got the optimized reaction condition for toluene oxyfunctionalization with air over metalloporphyrins. The effects of different central metal ions in metalloporphyrins [T(p-C1)PPMCl(M=Fe,Co,Mn,Cu)] on the reaction course had been examined and it was found that T(p-C1)PPCu presented the highest catalytic activity in the reaction. The reaction conditions of toluene oxidation were optimized by using orthogonal experiment design. Five relevant factors were investigated: temperature, air pressure, catalyst loading, air flow rate and reaction time. The effects of the five factors on both toluene conversion and total yield of benzaldehyde and benzyl alcohol were discussed. The research results showed that the reaction temperature was the most significant factor influencing toluene oxidation. On the basis of the margin analysis, the optimum conditions for the toluene conversion and the total yield of benzaldehyde and benzyl alcohol respectively were achieved, under which the toluene conversion was up to 14.67% and the total yield of benzaldehyde and benzyl alcohol reached 5.89%.The aerobic oxidation of

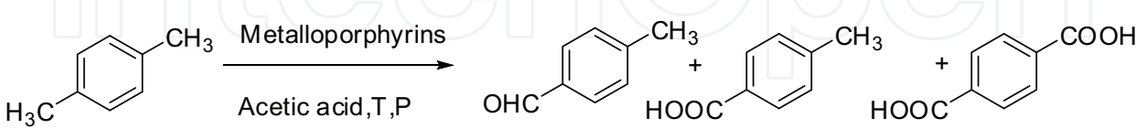
toluene over metalloporphyrin is currently employed by Balaji Amines LTD in India to produce more than 10,000 tons of benzaldehyde annually.



Scheme 10. Possible mechanism for aerobic oxidation of toluene by μ-oxo-bis metalloporphyrin

4.2 Biomimetic oxidation of C-H of *p*-xylene

Liquid-phase aerobic oxidation of *p*-xylene is an important process for the production of terephthalic acid, which is widely used in the commercial production of polyesters. So far, *p*-xylene oxidation with air has been carried out in acetic acid, using $Co(OAc)_2/Mn(OAc)_2/HBr$ as catalysts in industry. However, the high environmental impact of the catalysts, corrosion of reactors due to the halides, low space-time yield and the oxidative combustion of acetic acid present in the process of *p*-xylene oxidation, are the major shortcomings. We reported the aerobic liquid-phase oxidation of *p*-xylene over metalloporphyrins(Scheme 11)[84].



Scheme 11. Aerobic oxidation of *p*-xylene by metalloporphyrin in acetic acid

The oxidation was carried out in 20% acetic acid with 10 ppm metalloporphyrins as catalyst, and corrosive bromide was omitted. Effect of different metalloporphyrins on the oxidation reaction was investigated and got the result below.

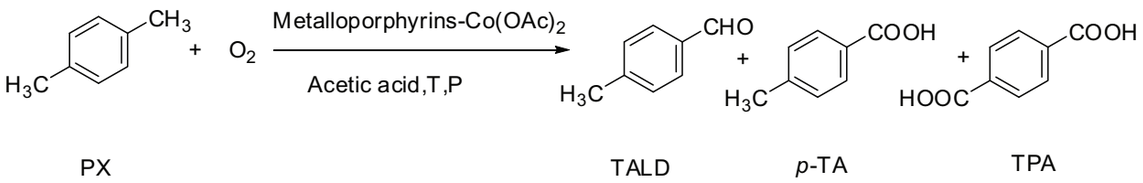
T(*p*-Cl)PPMnCl was the most efficient catalyst for the oxidation of *p*-xylene with air under the chosen conditions. It gave the highest *p*-xylene conversion and yield of *p*-toluic acid and terephthalic acid. A possible reason was related to its stability and the higher oxidation-

reduction potential of T(*p*-Cl)PPMnCl. Under the conditions of 180 °C and 2.0 MPa, 44% conversion of *p*-xylene and 85% selectivity of *p*-toluic acid were obtained. The oxidation of *p*-xylene with air to terephthalic acid was a series of reactions, and some intermediate products such as the *p*-toluic alcohol, *p*-toluic aldehyde and *p*-toluic acid were formed during the oxidation. The formation, accumulation and conversion of these products all affected the overall *p*-xylene oxidation. The catalytic oxidation of *p*-xylene with air over metalloporphyrins was a "green" reaction with potential industrial applications.

Recently, We reported an aerobic liquid-phase oxidation of *p*-xylene(PX) over metalloporphyrin and $Co(OAc)_2$[85].

Catalyst	*p*-toluic aldehyde, %		*p*-toluic acid, %		Terephthalic acid, %		Conversion, %
	Yield	Selectivity	Yield	Selectivity	Yield	Selectivity	
T(*p*-Cl)PPMnCl	1.76	5.7	27.09	86.9	2.31	7.4	32.05
T(*p*-Cl)PPCo	2.07	7.4	25.08	89.3	0.92	3.4	28.54
T(*p*-Cl)PPFeCl	2.31	8.8	22.77	86.9	1.12	4.3	26.76
T(*p*-Cl)PPCu	1.94	36.6	3.08	58.1	0.28	5.3	5.36
T(*p*-Cl)PPZn	2.44	59.2	1.51	36.7	0.17	4.1	4.19

Table 11. Comparison of catalytic property of different porphyrin in *p*-xylene oxidation



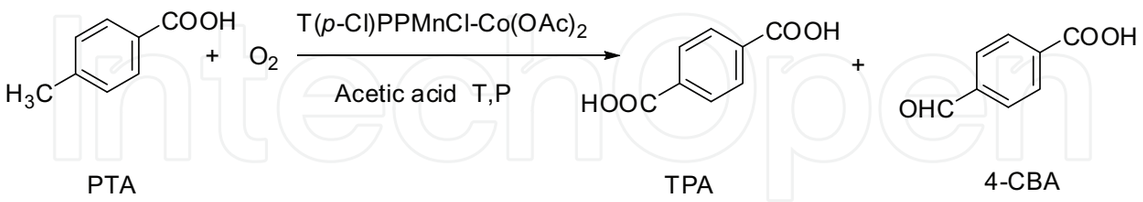
Scheme 12. Aerobic oxidation of *p*-xylene by metalloporphyrin-$Co(OAc)_2$ in acetic acid

When T(*p*-Cl)PPMnCl was used as the catalyst, less then 1% TPA was produced while 12% of the PX reacted. When the catalyst was switched to $Co(OAc)_2$, the yield of TPA increased to 8% while the reaction conversion reached 47%. Much to our delight, when T(*p*-Cl)PPMnCl and $Co(OAc)_2$ were used together, the PX conversion increased to 67% and the TPA yield almost doubled (17%). It is understandable that the PX conversion and TPA yield by T(*p*-Cl)PPMnCl-$Co(OAc)_2$ are higher than those by either T(*p*-Cl)PPMnCl or $Co(OAc)_2$ alone. The results showed that both the PX conversion and TPA yield could be increased significantly even though only a minute amount of metalloporphyrin is added to the reaction mixture besides the cobalt catalyst. The results suggested that the PX oxidation was improved because of the acceleration of the chain initiation of PX oxidation by metalloporphyrin catalyst, and the acceleration of the chain initiation itself was due to the ease of peroxide formation over metalloporphyrin.

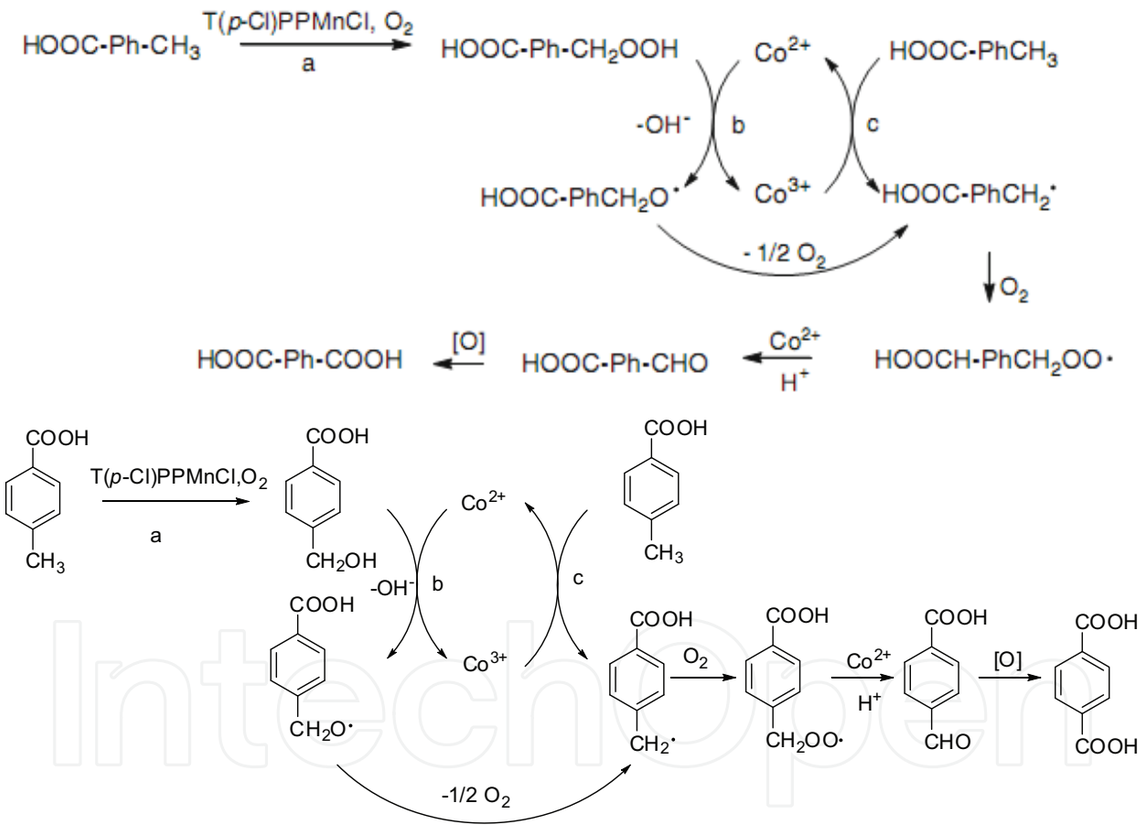
4.3 Biomimetic oxidation of *p*-toluic acid

The preparation of terephthalic acid (TPA) via the aerobic oxidation of *p*-xylene (PX) is a very important industrial process from both economical and environmental aspects. But the difficulty of the aerobic oxidation of PX to TPA lies in the oxidation of *p*-toluic acid (PTA) with

air to TPA. Our previous work has solved the step of the oxidation of PX to PTA, however, the oxidation of PTA to TPA still remains a challenge to the oxidation of PX to TPA. For the purpose of exploring how to oxidize PTA to TPA effectively under moderate conditions, we reported for the first time the aerobic oxidation of *p*-toluic acid to terephthalic acid over tetra(*p*-chlorophenylporphinato)-manganese (T(*p*-Cl)PPMnCl)/cobalt acetate(Scheme 13)[86].



Scheme 13. Aerobic oxidation of *p*-toluic acid by metalloporphyrin-Co(OAc)$_2$ in acetic acid



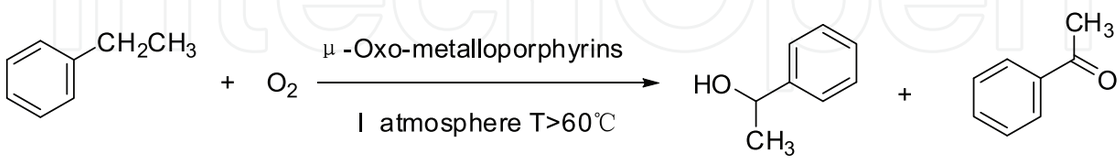
Scheme 14. Preliminary mechanism of co-catalysis between T(*p*-Cl)PPMnCl and Co(OAc)2 in the aerobic oxidation of PTA to TPA

The studies indicated that the PTA oxidation was influenced by the catalyst composition, catalyst concentrations and reaction conditions. The co-catalysis of T(*p*-Cl)PPMnCl/Co(OAc)$_2$ was also studied. Both the PTA conversion and TPA yield increased significantly when the a small amount of T(*p*-Cl)PPMnCl was added to the PTA-O_2-Co(OAc)$_2$ system. By the use of 548 ppm Co(OAc)$_2$ and 16 ppm T(*p*-Cl)PPMnCl as the catalysts, PTA oxidation under the optimum conditions of 190°C, 1.2 MPa and 160 L/ h airflow produced TPA at 96.8% selectivity

and 62.9% conversion of PTA in 5 h. For the co-catalysis between metalloporphyrin and cobalt acetate, the function of T(*p*-Cl)PPMnCl might be to produce more peroxides from the PTA, and then more Co^{3+} was formed from the oxidation of the Co^{2+} with peroxides. Moreover, Co^{3+} promoted the PTA oxidation due to the ease of the free radicals' formation.

4.4 Biomimetic oxidation of C-H of ethylbenzene

We reported selective oxidation of ethylbenzene with air catalyzed by simple μ-oxo-metalloporphyrins under mild conditions in the absence of additives(Scheme 15)[87].



Scheme 15. Aerobic oxidation of ethylbenzene by μ-oxo-metalloporphyrins

Two simple μ-oxo dimeric metalloporphyrins, μ-oxo-bis(tetraphenylporphinato)iron $[TPPFe]_2O$ and μ-oxo-bis(tetraphenylporphinato)manganese $[TPPMn]_2O$ were used as catalyst in the oxidation of ethylbenzene with air under mild condition. The results showed that the products of ethylbenzene oxidation catalyzed by $[TPPFe]_2O$ or $[TPPMn]_2O$ with air are acetophenone and α-phenylethanol exclusively under T> 60 °C and atmospheric pressure in absence of any additives. $[TPPMn]_2O$ is an active catalyst with high selectivity and turnover number of 2134 for oxidation of ethylbenzene by air when temperature reacts at 70 °C. The kinetic study shows that the ethylbenzene oxidation is zero-order for oxygen and first-order for ethylbenzene. The activation energy of the reaction is 72.7 kJ/mol. Comparing with the corresponding monometalloporphyrins TPPFeCl and TPPMnCl, $[TPPFe]_2O$ and $[TPPMn]_2O$ have the better catalytic activity for ethylbenzene oxidation with air without any additive under mild conditions.

Metalloporphyrin	$(TPPMn)_2O$	TPPMnCl	$(TPPFe)_2O$	TPPFeCl
Maximum yield(h)	20	23	5	6
Ethylbenzene conversion	8.08	6.48	3.73	5.41
Maximum yield of acetophenone(%)	4.89	3.62	1.97	2.91
Maximum yield of Phenylethanol(%)	3.19	2.86	1.76	2.50
Ketone/alcohol (mol/mol)	3.76	3.10	2.74	2.85
Total turnover number (mol/mol)	2024	783	878	642
Total yields at 2h(mmol)	3.33	2.30	7.68	5.61

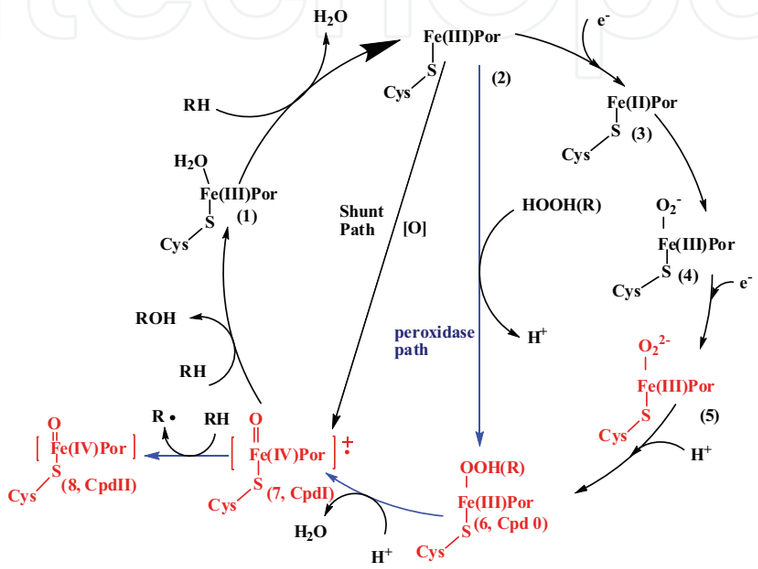
Reaction temperature is 85°C. The flow rate of air is 0.06m^3/h. Ethylbenzene is 30ml. Catalysts are 10mg.

Table 12. Effects of metalloporphyrins on oxidation products of ethylbenzene

5. Mechanism of biomimetic oxidation of hydrocarbons over metalloporphyrins

The oxygenation mechanism operating in CP-450 and in synthetic metalloporphyrin models has received much attention in recent decades [21,88-90]. However, the putative character of

the active oxidants recently remains a controversial matter in the catalytic cycles of reductive oxygen activation and reaction by CP-450[35,91] (Scheme 16), three different species have been considered as possible active oxidants[2]: one presenting a nucleophilic character, a peroxy species (d), one with electrophilic character, a iron(IV) oxo porphyrin p-cation radical intermediate (7) similar to the Compound I (Cpd I) of horseradish peroxidase, and the last with both nucleophilic and electrophilic character, a hydroperoxy species (Fe^{III}-OOH(R), 6) known as Compound 0 (Cpd 0). Recently, iron (IV) oxo-porphyrin complexes(Fe^{IV}=O, (8)), a model of a peroxidase Compound II(CpdII), is believed to participate in hydroxylation of hydrocarbon[35].



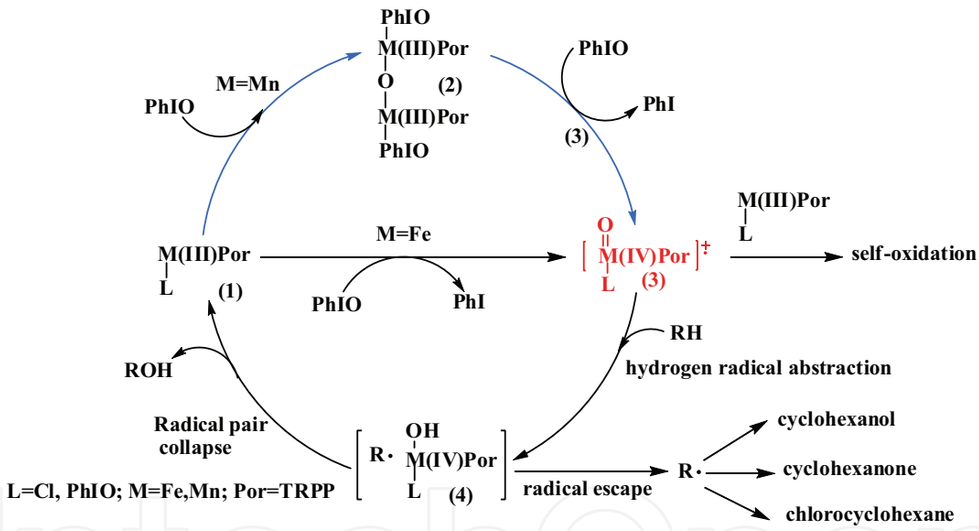
Scheme 16. Proposed catalytic cycle of CP- 450(Black) and Peroxidase(Blue).

To synthesize and distinguish the reactivity of these active oxidants, many oxygen-atom-transfer reactions catalyzed by synthetic metalloporphyrin complexes as CP-450 models have been extensively studied[92-93].

5.1 Mechanism of oxidation reactions with oxygen donors catalyzed by metalloporphyrins

Since the pioneering work of Groves *et.al.* on the synthesis and characterization of metal-oxo porphyrin π-cation radicals[31,94], a number of metal-oxo porphyrin complexes, especially iron(IV)-oxo porphyrin complexes have been synthesized and characterized with various spectroscopic techniques and isotopically labeled experiments, and their reactivities have been extensively investigated in oxygenation reactions.[35,92,95] Similarly to CP-450 catalytic cycle mechanism, the metal-oxo porphyrin π-cation radicals formed via shunt path (Scheme 16, (7)) have been proposed as ultimate reactive species under different oxidation reactions with single oxygen atom donors such as PhIO, NaClO, $KHSO_5$, *m*-CPBA, ^{t}-BuOOH, H_2O_2 etc. However, iron (III)–hydroperoxo species (analogous to (6) in Scheme 16) was postulated recently as the second electrophilic oxidant in biomimetic oxidation reaction with H_2O_2 and alkyl peroxide as oxygen donor[35]. The action of these metal-oxo porphyrin species seems to be dependent on the nature of the porphyrin ligand, the axial ligand, the solvent and the oxygen donor [35, 92].

Our research group has also been involved in elucidating the formation mechanisms of metal-oxo porphyrin π-cation radicals. We attempted to apply the linear free-energy relationships to metalloporphyrin-catalyzed biomimetic oxidation of hydrocarbon. Forty metalloporphyrins with different substituents (R) on the porphyrin ring, RTPPM^{III}Cl and (RTPPM^{III})$_2$O(M=Fe, Mn) were synthesized and were used to catalyze cyclohexane hydroxylation with PhIO under mild conditions[96-98]. A Hammett relationship, log$k$=ρσ+c, was shown to exist between the rate constants k of the cyclohexane hydroxylation and Hammett constants σ of substituents on the porphyrin rings. The value of the reaction constant ρ changed from 0.3 to 0.5 for the cyclohexane oxidation catalyzed by metalloporphyrins, and electron-withdrawing substituents increased the reaction rates. This means that the active oxidant was a radical cation species analogue with the high-valent oxo–metal π-cation radicals intermediate (Scheme 17,(3)). Further quantitative structure-activity relationship (QSAR) studies[99] on ironporphyrin-catalyzed cyclohexane oxidation with PhIO indicate that the electron withdrawing substituents could lower E_{LUMO-b} and disperse the electron density of around the centro-metal core of porphyrin better, they can facilitate ironporphyrin binding with the oxidant and increase the catalytic activity of ironporphyrin consequently.



Scheme 17. Proposed reaction mechanism of metalloporphyrin biomimetic catalytic of alkane hydroxylation with oxygen donors

Although high value metal–oxo porphyrin complexes exhibit a versatile reactivity to catalyze the epoxidation of alkenes and the hydroxylation of alkane under different circumstances, many metalloporphyrin-based catalysts suffer from limited lifetime activity due to the oxidative self-destruction of porphyrin ligands[100]. However, the self-oxidation of metalloporphyrins is less studied. Our group's further study[35] on the linear free-energy relationships of self-oxidation of metalloporphyrins show that high value metal–oxo porphyrin complexes as active oxidants are ascribed to the oxidative destruction of porphyrin ring, and the self-oxidation of metalloporphyrins and hydrogen radical abstraction in the system of the cyclohexane hydroxylation are two competition reactions via the same active oxidant. The reaction rates depend on the porphyrin ligands, axial ligands and oxidants. The oxidation of monometalloporphyrins is highly sensitive to

substituents of porphyrin rings, both electron-withdrawing substituents and electron-donating substituents of porphyrin ligands could accelerate the self-oxidation reaction rate. On the contrary, the oxidation of μ-oxo bismetalloporphyrin is not sensitive to substituents of porphyrin rings. Electron-withdrawing substituents slightly favor the oxidation reaction. In addition of the porphyrin ligand effect, the catalytic hydroxlation of cyclohexane was also markedly affected by the axial ligands of metalloporphyrins, different oxygen donors and solvents[101], indicating that the neutral organic axial ligands, strong polarity of solvent and the oxidation ability are important factors in the oxidation ability of high value metal–oxo porphyrin complexs.

5.2 Mechanism of oxidation reactions using molecular oxygen without a reductant catalyzed by metalloporphyrins

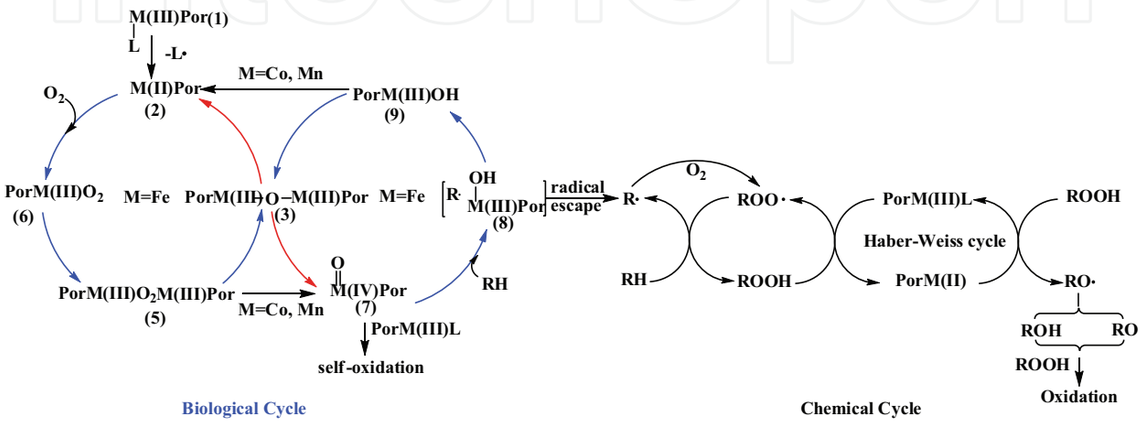
Although metalloporphyrin-catalyzed biomimetic oxidation of hydrocarbon with O_2 without reductants is analogue with the catalytic cycle of CP-450 systems, this catalytic system named as Lyons system do not require reductants or photochemical and electrochemical technical assistance. In order to search after more evidence of the mechanism in Lyons catalyst system, Lyons [44,102-103], Labinger [68,104-105], Therien [106-107], and Harber [108-109] have made many ground-breaking work. There are three main reaction mechanisms in Lyons catalytic system. One is a high-value metal-oxo species mechanism, one is metal-bound alkylperoxide mechanism, and the last is a radical-chain autoxidation mechanism.

Lyons[44,102] and Therien[107] have found that an iron (IV)-oxo porphyrin complex (PFe^{IV}=O, Cpd II) generated by μ-oxo iron porphyrin thermal disproportionation (Scheme 18, marked by blue line), is involved in polyhalogenated ironporphyrins oxidation of isobutane through the UV-vis and high pressure NMR measurements. Haber *et al*[109] proposed that homolytic cleavage of alkyl peroxide manganese(III)porphyrin complexes $PMn^{III}OOR$ result in ketone as the main reaction product in the study of manganeseporphyrin-catalyzed oxidation of cyclooctane. Takeuchi [110] and Mansuy [111] have also found a similar alkylperoxide-bound porphyrin complexs in metalloporphyrin-O_2-$NaBH_4$ system and a metalloporphyrin-O_2-photocatalytic system. However, by means of alkyl hydroperoxide characterization[107], products comparition[73], and a simple kinetic model calculation[105], a radical-chain autoxidation mechanism proposed by Labinger et.al[104] is likely operative in isobutane oxidation where the role of metalloporphyrin is to generate radicals by catalyzing the decomposition of alkyl hydroperoxides via Haber-Weiss cycle[103]. (Shceme 18, chemical cycle)This cycle is also present in cycloalkane[109] and alkylaromatics oxidation[112].

Reductive conversion of ferric complexs to ferrous complex in CP-450 catalytic cycle needs for co-reductants, which plays a key role in activation of molecular oxygen. In general, polyhalogenation[113], photochemical reduction, and electrochemical reduction of metalloporphyrin[114] can facilitate the ferric complexs reduction. Through the temperature effect research of different metalloporphyrin catalytic oxidation of hydrocarbons[41], our group found that trivalent metal porphyrins (such as PorFe(III) and PorMn(III)) at low temperature cannot be converted to divalent metalloporphyrin, but increase of reaction temperature facilitate the thermal decomposition of PorM(III) to divalent PorM(II).

Our group always found that a small amount of cyclohexanone was obtained in the hydroxidation of cyclohexane with metalloporphyrins and PhIO. However, the

hydroxylation of hydrocarbon in CP-450 only obtains alcohol via high value metal–oxo complexs(Scheme 16). Cyclohexanol is the product formed by the cage collapse of radical pairs(Scheme 17,(4)), and where the cyclohexanone comes from? By means of studying the effects of the structure of metalloporphyrins[98] and the reaction conditions on the kinetics of ketones formation[115], our group founded that cyclohexanone is the product formed by the reaction of the escaped radical R · (Scheme 17) and oxidants. The experiments showed that cyclohexanone yield increased when the above reaction was carried out in air [104] at elevated temperature [115]. Moreover, alky radicals could escape more easily from the solvent cage at the higher temperature to participate in the radical-chain autoxidation[112].



Scheme 18. Biological-chemical-cycle coupling mechanism of metalloporphyrin biomimetic catalytic of hydrocarbon oxygenation with O_2 without a reductant

We thus propose a novel mechanism referred to as the biological-chemical-cycle coupling mechanism (Scheme 18). The main function of the biological cycle is to initiate the radical species and further amplify them through a cycle in analogous with CP-450 catalytic cycle. After escaping from the CP-450 catalytic cycle, the alkyl radical may then enter the chemical cycle to be further amplified and oxidized through a Haber-Weiss cycle to afford the products. Therefore, one molecule of metalloporphyrin catalyst could catalyze several hundred thousands of molecules of cyclohexane through coupling of the biological and chemical cycles. The total turnover number should be geometric growth in the biological-chemical-cycle coupling cycle.

6. Industrial-scale biomimetic oxidation of hydrocarbons

The ultimate goal for basic researching of aerobic oxidation of hydrocarbons is to find their application for the green environment. As the selectivity and activity for oxidation of C-H bond of alkane, alkene and aromatic hydrocarbon is poor, biomimetic oxidation using porphyrin as catalyst now surmounted above shortcomings and realized the industrial application.

Current industrial hydrocarbon oxidation methods generally suffer from extremely low efficiency and environment-unfriendly problems. For example, aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone mixture (KA oil), a key step in polyamide nylon production, is a very significant industrial process not only because KA oil is an extremely important commercial raw material of nylon-6 and nylon-66, but also because the

reaction is among the least efficient of major industrial chemical processes. So far, general industrial cyclohexane oxidation has a 4% conversion rate with no higher than 80% yield of cyclohexanone, using a two-step process without catalyst, or with a soluble cobalt salt catalyst[47].

In the past 40 years, the discovery of novel methods aiming to solve the reciprocal inhibition relationship between the reaction conversion and the cyclohexanol and cyclohexanone yield in aerobic oxidation of cyclohexane remain a daunting task for the cyclohexane oxidation industry[46,116], and significant efforts have been made to develop the technology for selective oxidation of alkane with air [16].

The oxidation of hydrocarbon catalyzed by metalloporphyrins has been known for several decades[117] , and aerobic oxidation of hydrocarbon by polyhalogenated metalloporphyrins has also been reported[44]. However, the catalytic activity of the metalloporphyrins was generally poor, the catalyst life was short, and catalysts were extremely expensive. Due to these seemingly insurmountable shortcomings, it was widely believed that profitable industrial-scale oxidation of hydrocarbon catalyzed by metalloporphyrins was impossible [118].

Our group reported firstly all over the world [119] a novel industrial approach of hydrocarbon oxidation with air based on a metalloporphyrins as CP-450 monooxygenase model and its industrial application to cyclohexane oxidation. Upon addition of extremely low concentrations (1–5 ppm) of simple cobalt porphyrin (tetraphenylporphinatocobalt, TPPCo) to the commercial cyclohexane oxidation system, and decrease of the reaction temperature and pressure about 20 °C and 0.4 MPa respectively, the conversion of the cyclohexane increased from 4.8% to 7.1%, the yield of cyclohexanol and cyclohexanone increased from 77% to 87%. The aerobic oxidation of cyclohexane was carried out using a 70,000-ton cyclohexanone equipment set comprised of five series-wound stirring reactors using extremely low concentrations (2 ppm) of simple cobaltporphyrin TPPCo as catalyst, under 145 °C and 0.8 MPa air pressure. The industrial-scale oxidation results are shown in table 13.

Catalyst	Cobalt porphyrin	No Catalyst
Production output, kt/a	125	70
Conversion,mol, %	≥ 7.1	4.8
Turnover number, mol/mol	308800	-
Cyclohexanone yield, %	≥ 87	77
Cyclohexanol; Cyclohexanone	1.2:1	0.9:1
Temperature, °C	145	165
Pressure, MPa	0.8	1.2

Table 13. Comparison of cyclohexane aerobic oxidation over 70,000-ton cyclohexanone equipment set

The advantages of this industrial procedure includes: (1) no need to modify the cyclohexanone equipment currently used in industry, (2) lower reaction temperature and pressure, (3) extremely low (1–5 ppm) concentrations of simple metalloporphyrin catalysts used, (4) cyclohexane conversion increasing from 4.8% to 7.1%, (5) cyclohexanone yield elevating from 77% to 87%, and (6) no catalyst reclaimed process and setups.. Therefore, this procedure significantly improves the low conversion rate and low yield the cyclohexane oxidation industry has been facing for the past 40 years.

7. Conclusion

Metalloporphyrin-based oxidation systems not only hold great importance in biomimetic studies but also, as bioinspired oxidation systems, provide a useful tool for organic oxidation reactions. A highly important reaction is the aerobic oxidation catalyzed by metalloporphyrins. Such reactions will have an impact if further increases in product turnovers are realized.

Progress is still required to further improve these metalloporphyrin-based oxidation systems, mainly in two directions. Improvement of the selectivity of substrate recognition by the catalyst or the support of the catalyst, which is performed by the protein in CP-450, should lead to more regio-, stereo- and enantioselective oxygenations. Major improvements are also necessary for the construction of efficient systems for substrate hydroxylation by O_2 itself, because of the difficulty to mimic the catalytic cycle of O_2 activation by CP-450 that involves a tight coupling between the electron-and proton-transfer steps.

8. Reference

[1] J. E. Backvall, Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004

[2] M. Hudlicky, Oxidations in Organic Chemistry, American Chemical Society, Washington, DC, 1990

[3] E. T. Denisov and I. B. Afanas'ev, Oxidation and Antioxidants in Organic Chemistry and Biology, CRC Taylor&Francis, Boca Raton, 2005

[4] S. Bhaduri and D. Mukesh, Homogeneous Catalysis: Mechanisms and Industrial Applications, John Wiley&Sons, New York, USA, 2000

[5] S. M. Roberts and G. Poignant, Catalysts for Fine Chemical Synthesis, Hydrolysis Oxidation and Reduction, John Wiley&Sons Ltd, Chichester, UK, 2002, 1

[6] S. Caron, R. W. Dugger, S. G. Ruggeri, J. A. Raganand, D. H. B. Ripin, Large-Scale Oxidations in the Pharmaceutical Industry,Chem. Rev, 2006, 106, 2943

[7] W. Adam, C. R. Saha-Moller and P. A. Ganeshpure, Synthetic Applications of Nonmetal Catalysts for Homogeneous Oxidations, Chem. Rev, 2001, 101, 3499

[8] A. Wong and Y. Shi, Organocatalytic Oxidation. Asymmetric Epoxidation of Olefins Catalyzed by Chiral Ketones and Iminium Salts,Chem. Rev, 2008, 108, 3958

[9] R. A. Sheldon and J. K. Kochi, Metal Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981

[10] K. A. Jørgensen, Transition-Metal-Catalyzed Epoxidations, Chem. Rev, 1989, 89, 431

[11] S. S. Stahl, J. A. Labinger and J. E. Bercaw, Homogeneous Oxidation of Alkanes by Electrophilic Late Transition Metals, Angew Chem. Int. Ed, 1998, 37, 2180

[12] A. Corma and H. Garcıa, Lewis Acids as Catalysts in Oxidation Reactions: From Homogeneous to Heterogeneous Systems, Chem Rev, 2002, 102, 3837

[13] B. Limberg, The Role of Radicals in Metal-Assisted Oxygenation Reactions, Angew. Chem. Int. Ed, 2003, 42, 5932

[14] Q. H. Xia, H. Q. Ge, C. Ye, Z. M. Liu and K. X. Su, Advances in Homogeneous and Heterogeneous Catalytic Asymmetric Epoxidation, Chem. Rev, 2005, 105, 1603

[15] E. Marko, P. R. Giles, M. Tsukazaki, S. M. Brown and C. J. Urch, Copper-Catalyzed Oxidation of Alcohols to Aldehydes and Ketones: An Efficient, Aerobic Alternative, Science, 1996, 274, 2044
[16] I. M. Thomas, R. Raja, G. Sankar and R. G. Bell, Molecular-sieve Catalysts for the Selective Oxidation of Linear Alkanes by Molecular Oxygen, Nature, 1999, 398, 227
[17] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, Solvent-Free Oxidation of Primary Alcohols to Aldehydes Using Au-Pd/TiO_2 Catalysts, Science, 2006, 311, 362
[18] E. I. Solomon, U. M. Sundaram and T. E. Machonkin, Multicopper Oxidases and Oxygenases, Chem. Rev, 1996, 96, 2563
[19] T. D. H. Bugg, Dioxygenase Enzymes: Catalytic Mechanisms and Chemical Models, Tetrahedron, 2003, 59, 7075
[20] M. Sono, M. P. Roach, E. D. Coulter and J. H. Dawson, Heme-Containing Oxygenases, Chem. Rev, 1996, 96, 2841
[21] B. Meunier, S. P. de Visser and S. Shaik, Mechanism of Oxidation Reactions Catalyzed by Cytochrome P450 Enzymes, Chem. Rev, 2004, 104, 3947
[22] V. B. Urlacher and S. Eiben, Cytochrome P450 Monooxygenases: Perspectives for Synthetic Application, Trends. Biotechnol, 2006, 24, 324
[23] D. Mansuy, Biocatalysis and Substrate Chemodiversity: Adaptation of Aerobic Living Organisms to Their Chemical Environment, Catal. Today, 2008, 138, 2
[24] B. Meunier, Biomimetic Oxidations Catalyzed by Transition Metal Complexes, Imperial College Press, London, 2000
[25] R. V. Eldik and J. Reedijk, Homogeneous Biomimetic Oxidation Catalysis, Adv. Inorg. Chem, Elsevier, Amsterdam, 2006, 58
[26] P. Gamez, P. G. Aubel, W. L. Driessen and J. Reedijk, Homogeneous Bio-inspired Copper-Catalyzed Oxidation Reactions, Chem. Soc. Rev, 2001, 30, 376
[27] R. A. Sheldon, D. Marcel, Metalloporphyrins in Catalytic Oxidations, New York, 1994
[28] I. T. Groves, T. E. Nemo and R. S. Myers, Hydroxylation and Epoxidation Catalyzed by Iron-Porphine Complexes. Oxygen Transfer from Iodosylbenzene, J. Am. Chem. Soc, 1979, 101, 1032
[29] T. J. McMurry and J. T. Groves, Cytochrome P-450: Structure, Mechanism, and Biochemistry, Plenum Publishers, New York, 1986,
[30] J. T. Groves, K. Shalyaev and J. Lee, The Porphyrin Handbook, Academic Press, 2000, 4, 17
[31] J. T. Groves, Cytochrome P-450: Structure, Mechanism, and Biochemistry, Kluwer Academic/Plenum Publishers, New York, 2005, 3, 1
[32] D. Ostovic and T. C. Bruice, Mechanism of Alkene Epoxidation by Iron, Chromium, and Manganese Higher Valent Oxo-Metalloporphyrins, Acc. Chem. Res, 1992, 25, 314
[33] I. M. Smith and R. Guilard, The Porphyrin Handbook, Academic Press, 2000, 4, 41
[34] W. Nam, High-Valent Iron(IV)–Oxo Complexes of Heme and Non-Heme Ligands in Oxygenation Reactions, Acc. Chem. Res, 2007, 40, 522

[35] D. Ostovic and T. C. Bruice, Mechanism of Alkene Epoxidation by Iron, Chromium, and Manganese Higher Valent Oxo-Metalloporphyrins,Acc. Chem. Res, 1992, 25, 314

[36] H. B. Ji, Y. B. She, Green Oxidation and Reduction, China Petrochemical Press, Beijing, 2005

[37] C. C. Guo, M. F. Chu, Q. Liu, Y. Liu, D. C. Guo, X. Q. Liu, Effective Catalysis of Simple Metalloporphyrins for Cyclohexane Oxidation with Air in the Absence of Additives and Solvents, App1. Cata1. A, 2003, 246, 303

[38] D. Mansuy, M. Fontecave, J.F. Bartoli, Mono-Oxigenase-Like Dioxygen Activation Leading to Alkane Hydroxylation and Olefin Epoxidation by an Mn^{III}(porphyrin)–Ascorbate Biphasic System, J. Chem. Soc. Chem. Commun, 1983,1, 253

[39] I. Fontecave, D. Mansuy, Monooxygenase-Like Oxidations of Olefins and Alkanes Catalyzed by Manganese Porphyrins : Comparison of Systems Involving either O_2 and Ascorbate or Iodosylbenzene, Tetrahedron, 1984, 40, 4297

[40] J. E. Lyons, P. E. Ellis, H. K. Mayers, Halogenated Metalloporphyrin Complexes as Catalysts for Selective Reactions of Acyclic Alkanes with Molecular Oxygen, J. Catal, 1995, 155, 59

[41] U. Schuchardt, W. A. Carvalho, and E. V. Spinacé, Why Is It Interesting to Study Cyclohexane Oxidation?, Synlett, 1993, 10, 713

[42] U. Schuchardt, D. Cardoso, R Sercheli, R. D. Pereira, R. S. Cruz, M. C. Guerreiro, D. Mandelli, E. V. Spinacé and E. L. Pires, Cyclohexane Oxidation Continues to Be a Challenge, App1. Cata1. A, 2001, 211, 1.

[43] K. Suresh, M. M. Sharma and T. Sridhar, Engineering Aspects of Industrial Liquid-Phase Air Oxidation of Hydrocarbons, Ind. Eng.Chem. Res, 2000, 39, 3958.

[44] A. Castellan, J. C. J. Bart and S. Cavallaro, Industrial Production and Use of Adipic Acid, Catal. Today, 1991, 9, 237

[45] Y. Ishii, A Novel Catalysis of *N*-Hydroxyphthalimide (NHPI) Combined with $Co(acac)_n$ (n = 2 or 3) in the Oxidation of Organic Substrates with Molecular Oxygen, J. Mol. Catal. A: Chem. 1997, 117, 123

[46] T. Iwahama, K. Syojyo, S. Sakaguchi and Y. Ishii, Direct Conversion of Cyclohexane into Adipic Acid with Molecular Oxygen Catalyzed by *N*-Hydroxyphthalimide Combined with $Mn(acac)_2$ and $Co(OAc)_2$, Org. Process Res. Dev, 1998, 2, 255

[47] I. Sawatari, T. Yokota, S. Sakaguchi and Y. Ishii, Alkane Oxidation with Air Catalyzed by Lipophilic *N*-Hydroxyphthalimides without Any Solvent, J. Org. Chem, 2001, 66, 7889

[48] J. M. Thomas, R Raja, G. Sankar and R. G. Bell, Redox Molecular Sieve Catalysts for the Aerobic Selective Oxidation of Hydrocarbons, Stud. Surf. Sci. Catal,2000, 130, 887

[49] M. Dugal, G. Sankar, R. Raja and J. M. Thomas, Designing a Heterogeneous Catalysts for the Production of Adipic Acid by Aerial Oxidation of Cyclohexane, Angew. Chem. Int. Ed. Engl, 2000, 39, 2310

[50] R. Raja, G. Sankar and J. M. Thomas, Powerful Redox Molecular Sieve Catalysts for the Selective Oxidation of Cyclohexane in Air, J. Am. Chem.Soc, 1999, 121, 11926

[51] E. L. Pires, M. Wallau and U. Schuchardt, Selective Oxidation of Cyclohexane over Rare Earth Exchanged Zeolite Y, Stud. Surf. Sci. Catal, 1997, 110, 1025

[52] E. L. Pires, M. Wallau and U. Schuchardt, Cyclohexane Oxidation over Rare Earth Exchanged Zeolite Y, J. Mol. Chem. A: Chem, 1998, 136, 69

[53] C. C. Guo, X. Q. Liu, Y. Liu, Q. Liu, M. F. Chu, X. B. Zhang, Studies of Simple μ-Oxo-Bisiron(III)porphyrin as Catalyst of Cyclohexane Oxidation with Air in Absence of Cocatalysts or Coreductants, J. Mol. Chem. A: Chem,2003, 192, 289

[54] C. C. Guo, G. Huang, X. B. Zhang, D. C. Guo, Catalysis of Chitosan-Supported Iron Tetraphenylporphyrin for Aerobic Oxidation of Cyclohexane in Absence of Reductants and Solvents, App1. Cata1. A, Gene, 2003, 247, 261

[55] C. C. Guo, G. Huang, D. C. Guo, Preparation of Nitrogenous Polysaccharide-Supported Ironporphyrins and Their Catalysis for the Aerobic Oxidation of Cyclohexane, Kinet. Catal, 2006, 47(1), 93

[56] G. Huang, X. J. Li, C. C. Guo, Aerobic Oxidation of Cyclohexane Catalyzed by Chitosansupported Cobalt Tetraphenylporphyrin, Chin J. Catal, 2005, 26(9), 765

[57] X. T. Wang, M. F. Chu, C. C. Guo, Catalysis of Manganeseporphyrin Supported on Imidazole-modified Silica Gel for Cyclohexane Oxidation with Air, Chem. J. Chin. Univ., 2005, 26(1), 64

[58] B. Y. Hu, Y. J. Yuan, J. Xiao, C. C. Guo, Q. Liu, Z. Tan and Q. H. Li, Rational Oxidation of Cyclohexane to Cyclohexanol, Cyclohexanone and Adipic Acid with Air over Metalloporphyrin and Cobalt Salt, J. Porphyrins Phthalocyanines, 2008, 12, 27

[59] C. C. Guo, Q. Liu, X. B. Zhang, Method for Oxidation of Alkanes and Cycloalkane Useing Air, CN 1269343A, 2000

[60] J. M. Ma, C. C. Guo, Preparation of Methylcyclohexanol and Methylcyclohexanone from Aerobic Oxidation of Methylcyclohexane Catalyzed by Metalloporphyrins, J. Chem. Indu. Eng, (China), 2005, 56(5), 835

[61] K. W. Xu, J. Y. Ma, Q. Jiang, H. Y. Hu, C. C. Guo, Selective Catalysis of Manganeseporphyrins on Aerobic Oxidation of Different Carbon–Hydrogen Bonds of Methylcyclohexane, J. Mol. Catal. A: Chem., 2006, 243, 194

[62] K.T. Moore, I. T. Horvath, M. J. Therien, Mechanistic Studies of (Porphinato)Iron-Catalyzed Isobutane Oxidation. Comparative Studies of Three Classes of Electron-Deficient Porphyrin Catalysts, Inorg. Chem, 2000, 39, 3125

[63] R. B. Brown Jr, C. L. Hill, Catalytic Homogeneous Functionalization of Adamantane. Influence of Electronic and Structural Features of the Metalloporphyrin Catalyst on Atom Transfer Selectivity (Oxygenation versus Acidification/Halogenation), J. Org. Chem, 1988, 53, 5762

[64] C. C. Guo, Q. Liu, X. T. Wang, H. Y. Hu, Selective Liquid Phase Oxidation of Toluene with Air, App1. Cata1. A, 2005, 282, 55

[65] I, Tabushi and N. Koga, P-450 Type Oxygen Activation by Porphyrin-Manganese Complex, J. Am. Chem.Soc,1979, 101, 6456

[66] K. Kano, H. Takagi, M. Takeuchi, S. Hashimoto and Z. Yoshida, Porphinatoiron-Catalyzed Oxygenation of Styrene in Aqueous Solution, Chem. Lett, 1991,519

[67] J. T. Groves, and R. Quinn, Aerobic Epoxidation of Olefins with Ruthenium Porphyrin Catalysts, J. Am. Chem.Soc,1985, 107, 5790

[68] E. R. Birnbaum, M. W. Grinstaff, J. A. Labinger, J. E. Bercaw and H. B. Gray, On the Mechanism of Catalytic Alkene Oxidation by Molecular Oxygen and Halogenated Iron Porphyrins, J. Mol. Catal. A: Chem., 1995, 104, 119

[69] E. R. Birnbaum, J. A. Labinger, J. E. Bercaw and H. B. Gray, Catalysis of Aerobic Olefin Oxidation by a Ruthenium Perhaloporphyrin Complex, Inorg. Chim. Acta, 1998, 270, 433

[70] E. N. Jacobsen, L. Deng, Y. Furukawa and L. E. Martinez, Enantioselective Catalytic Epoxidation of Cinnamate Esters, Tetrahedron 1994, 50, 4323

[71] T. Katasuki, Catalytic Asymmetric Oxidations Using Optically Active (Salen)manganese(III) Complexes as Catalysts, Coord. Chem. Rev, 1995, 140, 189

[72] T. Takemori, A. Inagaki and H. Suzuki, A Novel Type of Carbon−Carbon Double Bond Cleavage of 1,1-Disubstituted Alkenes on a Triruthenium Polyhydrido Cluster, J. Am. Chem. Soc, 2001, 123, 1762

[73] D. Yang and C. Zhang, Ruthenium-Catalyzed Oxidative Cleavage of Olefins to Aldehydes, J. Org. Chem, 2001, 66, 4814

[74] W. Liu, Q. Liu and C. C. Guo, Catalysis of Simple Cobaltporphyrin for Aerial Oxidation of Cyclohexene to Cyclohexenone, J. Chem. Indus. Eng. (China), 2005, 59(5), 1537

[75] Y. F. Li, C. C. Guo, X. H. Yan and Q. Liu, Aerobic Oxidative Cleavage of C=C Double Bond of Styrene Catalyzed by Simple Manganese Porphyrin, J. Porphyrins Phthalocyanines, 2006, 10, 942

[76] C. C. Guo, W. J. Yang, Y. L. Ming, Selectively Aerobic Oxidation of C=C and Allylic C-H Bonds in α-Pinene over Simple Metalloporphyrins, J. Mol. Catal. A: Chemical, 2005, 226, 279

[77] W. J. Yang, C. C. Guo, Z. Y. Li and N. Y. Tao, Aerobic Oxidation of α-Pinene Catalyzed by Nano-Titania-Supported Manganese Tetraphenylporphyrin, J. Porphyrins Phthalocyanines 2009; 13, 973

[78] R. A. Sheldon, Fine Chemicals by Catalytic-oxidation, Chemtech, 1991, 556

[79] W. Partenheimer, Methodology and Scope of Metal/Bromide Autoxidation of Hydrocarbons, Catal. Today, 1995, 23, 69

[80] R. A. Sheldon, J. K. Kochi, Metal Catalysed Oxidation of Organic Compounds, Academic Press, New York, 1981

[81] C. C. Guo, Q. Liu, X. T. Wang, H. Y. Hu, Selective Liquid Phase Oxidation of Toluene with Air, App1. Cata1. A, 2005, 282, 55

[82] H. Y. Hu, Q. Jiang, Q. Liu, J. X. Song, W. Y. Lin and C. C. Guo, Catalysis of μ-Oxo-Bis[porphyriniron(III)] for Toluene Oxidation with Molecular Oxygen, J. Porphyrins Phthalocyanines 2006, 10, 948

[83] L. Y. Li, X. H. Yang, G. F. Jiang, Q. Liu, J. X. Song and C. C. Guo, Toluene Oxyfunctionalization with Air over Metalloporphyrins and Reaction Condition Optimization, Chin. J. Chem. Eng., 2007, 15(3), 453

[84] Q. Jiang, H. Y. Hu, C. C. Guo, Q. Liu, J. X. Song and Q. H. Li, Aerobic Liquid-Phase Oxidation of *p*-Xylene over Metalloporphyrins, J. Porphyrins Phthalocyanines 2007, 11, 524

[85] Q Jiang, Y. Xiao, Z. Tan, Q. H. Li, C. C. Guo, Aerobic Oxidation of *p*-Xylene over Metalloporphyrin and Cobalt Acetate: Their Synergy and Mechanism, J. Mol. Catal. A: Chem, 2008, 285, 162

[86] Y. Xiao, W. P. Luo, X. Y. Zhang, C. C. Guo, Q. Liu, G. F. Jiang, Q. H. Li, Aerobic Oxidation of *p*-Toluic Acid to Terephthalic Acid over T(*p*-Cl)PPMnCl/$Co(OAc)_2$ Under Moderate Conditions, Catal. Lett, 2010, 134, 155

[87] C. C. Guo, Q. J. Peng, Q Liu, G. F. Jiang, Selective Oxidation of Ethylbenzene with Air Catalyzed by Simple μ-Oxo Dimeric Metalloporphyrins Under Mild Conditions in the Absence of Additives, J. Mol. Catal. A: Chem, 2003, 192, 295

[88] P.R. Ortiz de Montellano (Ed.), Cytochrome P450: Structure, Mechanism and Biochemistry, third ed., Kluwer Academic/ Plenum Publisher, New York, 2005.

[89] K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 3, Academic Press, 2000.

[90] S.shaik, W. Z. Lai, H. Chen, Y. Wang, The Valence Bond Way: Reactivity Patterns of Cytochrome P450 Enzymes and Synthetic Analogs, Acc. Chem. Res. 2010, 43(8), 1154.

[91] T.M. Makris, I. Denisov, I. Schlichting, S.G. Sligar, in: P.R. Ortiz de Montellano (Ed.), Cytochrome P450: Structure, Mechanism and Biochemistry, third ed., Kluwer Academic/ Plenum Publisher, New York, 2005, p. 149.

[92] B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 4, 2000, p. 119.

[93] D. Mansuy, A Brief History of the Contribution of Metalloporphyrin Models to Cytochrome P450 Chemistry and Oxidation Catalysis, C. R. Chimie. 2007, 10, 392.

[94] J.T. Groves, in: P.R. Ortiz de Montellano (Ed.), Cytochrome P450: Structure, Mechanism and Biochemistry, third ed., Kluwer Academic/Plenum Publisher, New York, 2005, p. 1.

[95] Y.Watanabe, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 4, 2000, p. 97.

[96] C. C. Guo, Synthesis of μ-Oxo-bisiron(III)Porphyrin Compounds and Their Catalysis for Cyclohexane Hydroxylation, J.Catal.1998, 178(1): 182.

[97] C. C. Guo, H. P. Li, J. B. Xu, Study of Synthesis of μ-Oxo-bismanganese(III)Porphyrin Compounds and Their Catalysis of Cyclohexane Oxidation by PhIO, J. Catal. 1999, 185(2): 345.

[98] C.C. Guo, J. X.Song, X. B Chen, G. F Jiang, A New Evidence of the High-Valent Oxo–Metal Radical Cation Intermediate and Hydrogen Radical Abstract Mechanism in Hydrocarbon Hydroxylation Catalyzed by Metalloporphyrins, J. Mol. Catal. A: Chem. 2000, 157, 31.

[99] N. Liu, G. F. Jiang, C. C. Guo, Z. Tan, Quantitative Structure–Activity Relationship Studies on Ironporphyrin-Catalyzed Cyclohexane Oxidation with PhIO, J. Mol. Catal. A: Chem. 2009, 304, 40.

[100] M. H. Alkordi, Y. L. Liu, R. W. Larsen, J. F. Eubank, M. Eddaoudi, Zeolite-*like* Metal−Organic Frameworks as Platforms for Applications: On Metalloporphyrin-Based Catalysts, J. Am. Chem.Soc. 2008, 130, 12639.

[101] C.C. Guo, X. Y. Liu, M. S. Yang, S. J. Zhu, M. D. Gui, Study on the Mechanism of Cyclohexanone Formation in Cyclohexane Hydroxylation Catalyzed by Metalloporphyrins, Chem. J. Chin. Univ. 1991, 12(12), 1617.

[102] P. E. Ellis Jr., J. E.Lyons, Selective Air Oxidation of Light Alkanes Catalyzed by Activated Metalloporphyrins, The search for a Suprabiotic System, Coord. Chem. Rev. 1990, 105(2): 181.

[103] J. E. Lyons, P. E. Ellis Jr., H. K. Mayers, R. W. Wagner, Halogen Substituent Effects on the Catalytic Activity of Iron Porphyrin Complexes for the Decomposition of *tert*-Butyl Hydroperoxide, J. Catal. 1993, 141, 311.

[104] M. W. Grinstaff, M. G. Hill, J. A. Labinger, H. B. Gray, Mechanism of Catalytic Oxygenation of Alkanes by Halogenated Iron Porphyrins, Science, 1994, 264, 1311.

[105] J. A. Labinger, A Simplified Model for Catalyzed Isobutane Autoxidation: Implications for the Mechanism of Catalysis by Halogenated Porphyrin Complexes, Catal. Lett. 1994, 26(1-2): 95.

[106] K. T. Moore, I. T. Horvath, M. J. Therien, High-Pressure NMR Studies of (Porphinato)iron-Catalyzed Isobutane Oxidation Utilizing Dioxygen as the Stoichiometric Oxidant, J. Am. Chem. Soc. 1997, 119(7), 1791.

[107] K. T. Moore, I. T. Horvath, M. J. Therien, Mechanistic Studies of (Porphinato)Iron-Catalyzed Isobutane Oxidation. Comparative Studies of Three Classes of Electron-Deficient Porphyrin Catalysts, Inorg. Chem. 2000, 39(15): 3125.

[108] J. Haber, L. Matachowski, K. Pamin, J. Połtowicz, Manganese Porphyrins as Catalysts for Oxidation of Cyclooctane in Lyons System, J. Mol. Catal. A: Chem. 2000, 162, 105.

[109] J. Haber, L. Matachowski, K. Pamin, J. Połtowicz, The Effect of Peripheral Substituents in Metalloporphyrins on Their Catalytic Activity in Lyons System, J. Mol. Catal. A: Chem. 2003, 198, 215.

[110] M. Takeuchi, M. Kodera, K. Kano, Z. I. Yoshida, Mechanisms for (Porphyrinato)iron(III)-Catalyzed Oxygenation of Styrenes by O2 in Presence of BH−4, J Mol. Catal. A: Chem. 1996, 113, 51.

[111] A. Maldotti, B. G. Varani, A. Molinari, P. Battioni, D. Mansuy, Oxidation of Cyclohexane by Molecular Oxygen Photoassisted by *meso*-Tetraarylporphyrin Iron(III)−Hydroxo Complexes , Inorg. Chem. 1996, 35, 1126.

[112] S. Evans, J. R. Lindsay Smith, The Oxidation of Ethylbenzene and Other Alkylaromatics by Dioxygen Catalysed by Iron(III) tetrakis(pentafluorophenyl) porphyrin and Related Iron Porphyrins, J. Chem. Soc., Perkin Trans. 2, 2000, 11, 1541.

[113] D. Dolphin, T. G. Traylor, L. Y. Xie, Polyhaloporphyrins: Unusual Ligands for Metals and Metal-Catalyzed Oxidations, Acc. Chem. Res. 1997, 30, 251

[114] D. Hendrickson; M. G. Kinnaird, K. S. Suslick, Photochemistry of (5,10,15,20-tetraphenylporphyrinato)iron(III) halide complexes, Fe(TPP)(X), J. Am. Chem. Soc. 1987, 109, 1243

[115] C.C. Guo, X. B. Zhang, L. B. Hou, J. B. Xu, X. D. Hao, G. M. Guo, B. X. Liang, X. B. Chen, Study on the Mechanism of Cyclohexanone Formation in Cyclohexane Hydroxylation Catalyzed by Metalloporphyrins, Chem. J. Chin. Univ. 1991, 12(12), 1617

[116] J.M.,Thomas, R, Raja, G. Sankar and R. G. Bell, Molecular Sieve Catalysts for the Regioselective and Shape- Selective Oxyfunctionalization of Alkanes in Air, Acc. Chem. Res, 2001, 34, 191

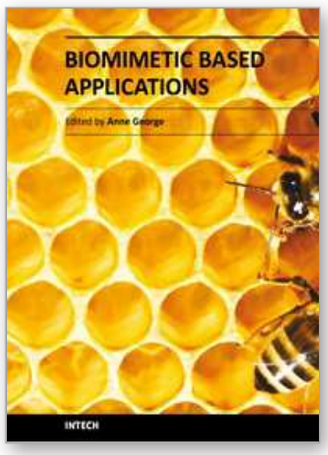
[117] B. Meunier, Metalloporphyrins as Versatile Catalysts for Oxidation Reactions and Oxidative DNA Cleavage, Chem. Rev, 1992, 92, 1411

[118] J. A. Labinger and J. E. Bercaw. Understanding and Exploiting C–H Bond Activation, Nature, 2002, 417, 507

[119] C. C. Guo, X. Q. Liu, Q. Liu, Y. Liu, M. F. Chu and W. Y. Lin, First Industrial-Scale Biomimetic Oxidation of Hydrocarbon with Air over Metalloporphyrins as Cytochrome P-450 Monooxygenase Model and Its Mechanistic Studies, J. Porphyrins Phthalocyanines, 2009, 13, 1250

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The interaction between cells, tissues and biomaterial surfaces are the highlights of the book "Biomimetic Based Applications". In this regard the effect of nanostructures and nanotopographies and their effect on the development of a new generation of biomaterials including advanced multifunctional scaffolds for tissue engineering are discussed. The 2 volumes contain articles that cover a wide spectrum of subject matter such as different aspects of the development of scaffolds and coatings with enhanced performance and bioactivity, including investigations of material surface-cell interactions.

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