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Highly efficient selective oxidation of alcohols to carbonyl compounds catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride in the presence of molecular oxygen

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Abstract—Efficient selective oxidation of alcohols to carbonyl compounds by molecular oxygen with isobutyraldehyde as oxygen acceptor in the presence of metalloporphyrins has been reported. Ruthenium (III) *meso*-tetraphenylporphyrin chloride (Ru(TPP)Cl) showed excellent activity and selectivity for oxidation of various alcohols under mild conditions. Moreover, different factors influencing alcohols oxidation, for example, catalyst, solvent, temperature, and oxidant, have been investigated. In large-scale oxidation of benzyl alcohol, the isolated yield of benzaldehyde of 89% was observed.

Oxidation of alcohols to the corresponding carbonyl compounds is a very important step for organic synthesis.[1] From an environmental and cost-effective viewpoint, catalytic oxidation processes with molecular oxygen or air are extremely valuable and particularly attractive.[2] Accordingly, variety of transition metal based catalysts (mainly cobalt,[3] vanadium,[4] ruthenium,[5] palladium,[6] and copper[7]) have been intensively investigated for aerobic oxidation of alcohols so far.

As model catalysts of cytochrome P-450, metalloporphyrins could be used as the intermediate of oxygen carrier to biological systems, and have been widely used as catalysts for various oxidation reactions, for example, hydroxylation of hydrocarbon and epoxidation of olefins under mild conditions.[8] Although metalloporphyrins have been used to catalyze the oxidation of alcohols with PhIO,[9] Cl_2PyNO,[10] *t*-BuOOH,[11] $KHSO_5$,[12] Bu_4NHSO_5 (tetrabutylammonium peroxymonosulfate),[13] and *m*-CPBA (*m*-chloroperbenzoic acid)[14] as oxidants, few studies on metalloporphyrins-catalyzed oxidation of alcohols by molecular oxygen were reported.[15] For example, Woo and co-authors ever reported the aerobic homogeneous oxidation of benzyl alcohol with oxotitanium porphyrin (TTP)Ti=O, which gave benzaldehyde in modest yields (48%) after 94 h in refluxing chlorobenzene.[5a] Kato ever reported heterogeneous aerobic oxidation of benzyl alcohol by using microporous dinuclear ruthenium (II, III) carboxylate tetrafluoroborate containing porphyrin, $[Ru_2^{II,III}(H_2TCPP)]BF_4$($H_2TCPP$ = 4,4,4,4-(21H, 23H-porphine-5,10,15,20-tetrayl)tetrakis benzoic acid), as catalyst, in which high selectivity of benzaldehyde (95%) was obtained after 24 h and the TON (turnover number) of catalyst was 21.[15b]

In our previous studies, metalloporphyins exhibited high catalytic performance for oxidation of alkanes, olefins, and sulfides with molecular oxygen.[16] We also developed procedures for highly selective oxidation of alcohols to carbonyl compounds with β-cyclodextrin,[17] a ruthenium cation combined with microcrystals of cobalt hydroxide and cerium oxide[18] and nanoparticle spinel as catalysts.[19] As part of our ongoing interests in metalloporphyrins-catalyzed oxidations with dioxygen, the aerobic oxidation of alcohols to carbonyl compounds catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride (Ru(TPP)Cl) in the presence of isobutyraldehyde has been developed (Scheme 1).[20] The catalytic system has been proved to be efficient for oxidation of alcohols with high yields for carbonyl compounds under mild conditions.

The catalytic activity and selectivity of different metalloporphyrins for alcohol oxidation by molecular oxygen were investigated with benzyl alcohol as model com-

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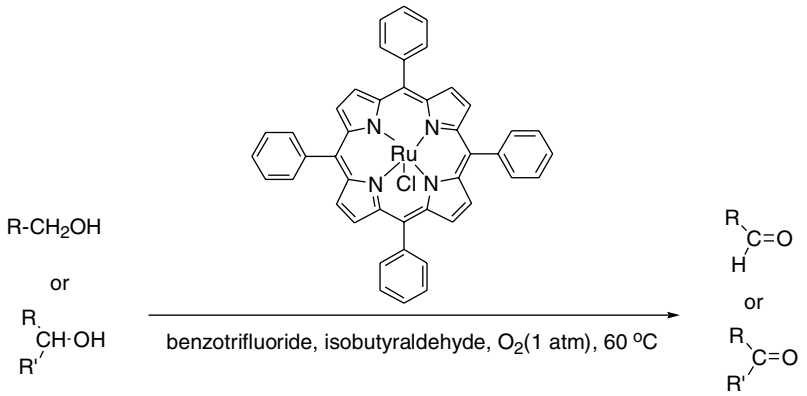

Scheme 1. Aerobic oxidation of alcohols catalyzed by ruthenium (III) *meso*-tetraphenylporphyrin chloride.

pound.[21] The engaged catalysts for the oxidation reactions were simple structural metalloporphyrins that have the same ligand, *meso*-tetraphenylporphyrin (TPP), but different metals including Ru(TPP)Cl, Co(TPP)Cl, Mn(TPP)Cl, and Fe(TPP)Cl. The results are summarized in Table 1.

From Table 1, the catalytic activity of metalloporphyrins appeared to be dependent on the nature of central ions for benzyl alcohol oxidation. Comparing with cobalt, manganese, and iron porphyrin, ruthenium porphyrin was the most effective catalyst for the alcohol oxidation system since benzyl alcohol could be completely converted to benzaldehyde. Cobalt porphyrin also presented similar high activity toward benzyl alcohol oxidation (entry 2), but poor selectivity for benzaldehyde was obtained after the reaction was carried out for 30 min. Similar results of alcohol oxidation were obtained with other cobalt catalysts, for example, $Co(acac)_3$[22] and cobalt Schiff base.[23] It seems that manganese and iron porphyrins were not effective catalysts for benzyl alcohol oxidation by molecular oxygen (entries 3 and 4). The catalytic activity and selectivity of different metalloporphyrins were probably influenced by stability of different valences of metal atoms and their electric potential.[24]

Aerobic oxidation of benzyl alcohol with Ru(TPP)Cl catalyst using various solvents and the effect of reaction temperature on its conversion were also investigated and the results are summarized in Table 2.

As shown in Table 2, it seemed that solvent played an important role in the oxidation system. The strong electrophilic effect of benzotrifluoride was favorable to the oxidation of benzyl alcohol, which gave 99% yield of benzaldehyde. When toluene and benzene were used instead, only about 60% benzaldehyde could be obtained, together with a little of benzoic acid. Very low yield of benzaldehyde (18%) could be obtained when acetonitrile was used as solvent in the oxidation system (entry 6). The distinct results should be attributed to the solvation effect of each solvent. The three fluorine atoms of the benzotrifluoride resulted in better solvation effect,[25] which could make the O–H bond cleavage much easier.

Table 1. Oxidation of benzyl alcohol by molecular oxygen in the presence of various metalloporphyrin catalysts[a]

Entry	Catalyst	Conv. (%)	Yield (%)[b]
1	Ru(TPP)Cl	>99	>99
2	Co(TPP)Cl	>99	42(58)[b]
3	Mn(TPP)Cl	45	33(12)[b]
4	Fe(TPP)Cl	32	32

[a] Benzyl alcohol (1 mmol), catalyst (1×10^{-3} mmol), isobutyraldehyde (3 mmol), benzotrifluoride (5 mL), O_2 bubbling (1 atm), 60 °C, 0.5 h.
[b] The numbers in parentheses indicate the yields of benzoic acid.

Table 2. The effect of solvent and temperature on the oxidation of benzyl alcohol by molecular oxygen in the presence of Ru(TPP)Cl[a]

Entry	Solvent	T (°C)	Conv. (%)	Yield (%)[b]
1	Benzotrifluoride	60	>99	>99
2	Benzotrifluoride	50	61	61
3	Benzotrifluoride	40	43	43
4	Toluene	60	73	61(12)
5	Benzene	60	74	60(14)
6	Acetonitrile	60	26	18(8)

[a] Benzyl alcohol (1 mmol), Ru(TPP)Cl (1×10^{-3} mmol), isobutyraldehyde (3 mmol), solvent (5 mL), O_2 bubbling (1 atm), 60 °C, 0.5 h.
[b] The numbers in parentheses indicate the yields of benzoic acid.

The effect of temperature on oxidation of benzyl alcohol was also investigated. It was shown that the conversion was increased with raising temperature from 40 to 60 °C. When the temperature was 60 °C, benzyl alcohol could be oxidized to benzaldehyde stoichiometrically by molecular oxygen with 1×10^{-3} mmol Ru(TPP)Cl catalyst. It is notable that the increasing temperature could hardly influence the selectivity of benzaldehyde, that is, no over-oxidation product, for example, benzoic acid could be detected as the temperature was raised.

The effects of oxidant on oxidation of benzyl alcohol were also investigated, and the results are summarized in Table 3. Table 3 shows that dioxygen was more effective than H_2O_2, *t*-BuOOH, and NaOCl for oxidation of benzyl alcohol catalyzed by Ru(TPP)Cl/isobutyraldehyde (entries 1, 4, 7, and 10), indicating that the metalloporphyrins have excellent performance for activating