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Metalloporphyrin-catalyzed aerobic oxidation of 2-methoxy-4-methylphenol as a route to vanillin

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ABSTRACT

We report the use of simple metalloporphyrins (T(*p*-Cl)PPMnCl, T(*p*-Cl)PPCo, T(*p*-Cl)PPFeCl, T(*p*-Cl)PPCu or $[T(p\text{-Cl})PPFe]_2O$) as a catalyst for the direct oxidation of 2-methoxy-4-methylphenol to vanillin with molecular oxygen under mild conditions. The research results showed that the type of metalloporphyrin used, catalyst loading, temperature, reaction time, the amount of NaOH, solvent, the amount of solvent and the flow rate of oxygen influenced the conversion of 2-methoxy-4-methylphenol and the selectivity of vanillin. Under the optimal conditions, the conversion of 2-methoxy-4-methylphenol was up to 87% and the selectivity of vanillin reached 74%. A possible mechanism was also proposed for the present oxidation.

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is one of the most important flavors and has attracted considerable synthetic interest [1] owing to its importance in various fields; it is extensively used as fragrance in food preparations [1,2], intermediate in the production of antifoaming agents, herbicides or drugs [3,4], ingredient of household products such as air-fresheners and floor polishes, and, because of its antioxidant and antimicrobial properties [5,6], also as food preservative [6–9]. Traditionally, vanillin is mainly obtained by chemical methods from lignin, coniferin, the glucoside of coniferyl alcohol, guaiacol, or eugenol [1,10–12]. However, these methods have drawbacks such as multiple steps, relatively high costs and serious environmental pollution due to the generation of excessive wastes. More recently, the production of vanillin via biotechnological methods has been extensively investigated [1,13–25]. While all of these methods are useful in its own right, each suffers from one or more limitations including long production time, difficult purification, relatively high costs and necessity of selected strains of microorganisms. Besides, there are few reports on the homogeneously or heterogeneously catalytic direct oxidation of 2-methoxy-4-methylphenol by oxygen to vanillin [26–30]. Although great advances have been made, it is still highly desirable to develop efficient and selective catalytic oxidation methods which can be performed under safe and mild conditions.

In our previous studies, metalloporphyrins exhibited high catalytic performance for oxidation of hydrocarbons with molecular oxygen [31–50]. As a continuation of our research involving metalloporphyrins-catalyzed oxidations with dioxygen, we now report a novel catalytic system for the direct oxidation of 2-methoxy-4-methylphenol to vanillin by using molecular oxygen (1 atm) as oxidant and metalloporphyrin as the catalyst under mild conditions. The optimum conditions of the process were obtained through investigating the effects of various reaction parameters such as the type of metalloporphyrin used, catalyst loading, temperature, reaction time, the amount of NaOH, solvent, the amount of solvent and the flow rate of oxygen on the conversion of 2-methoxy-4-methylphenol, and selectivity of vanillin. Furthermore, a possible mechanism for the observed catalytic oxidation reaction was also proposed.

2. Experimental

2.1. General reagents and equipments

All solvents and reagents were obtained commercially and used without further purification unless indicated otherwise. Simple metalloporphyrins (T(*p*-Cl)PPMnCl, T(*p*-Cl)PPCo, T(*p*-Cl)PPFeCl, T(*p*-Cl)PPCu or $[T(p\text{-Cl})PPFe]_2O$) were synthesized according to the literature methods [51,52]. MS spectra were recorded on a Shimadzu OP-2010 GC-MS and an Agilent 1100 LC-MS. UV–Vis spectra

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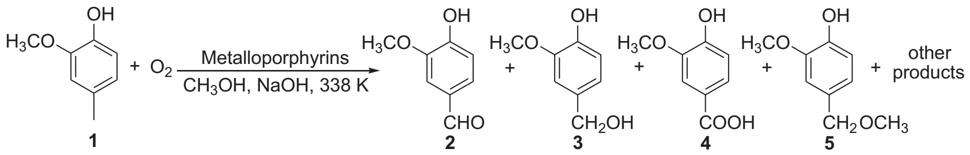


Scheme 1. Aerobic oxidation of 2-methoxy-4-methylphenol catalyzed by metalloporphyrins.

were obtained on a ShimadzuUV-2450 spectrometer. LC analysis was performed on an Agilent 1100.

2.2. Typical procedure for oxidation of 2-methoxy-4-methylphenol using molecular oxygen catalyzed by metalloporphyrins

To a 100 mL three-neck round bottom flask equipped with a magnetic stirring bar, condenser, and an oxygen gas inlet was added 2-methoxy-4-methylphenol (4.14 g, 30 mmol), catalyst (7.2 mg), sodium hydroxide (6 g, 0.15 mol) and methanol (20 mL). Oxygen (0.1 MPa) was continuously introduced into the flask at flow rate of 0.1 L min^{-1} while the temperature was kept at 338 K (the boiling point of methanol). After the reaction was completed, the mixture was cooled to room temperature and the products were quantitatively analyzed by HPLC

2.3. Products analysis

The oxidation products were identified by GC–MS, LC–MS, by HPLC co-injection of commercially available authentic samples, and quantitated by Agilent 1100 HPLC equipped with a UV (280 nm) detector and a Zorbax SB-C8 (4.6 mm × 250 mm) column. Eluent consisting of 35% CH_3OH and 65% phosphoric acid buffer (pH = 2.5) with a flow rate of 0.6 mL min^{-1} was used. Vanillin, vanillyl alcohol, vanillic acid and 4-hydroxy-3-methoxybenzyl methyl ether were determined by the internal standard method using benzoic acid as the internal standard.

3. Results and discussion

2-methoxy-4-methylphenol (**1**) was efficiently oxidized by dioxygen under mild conditions in the presence of metalloporphyrins (shown in Scheme 1). Based on LC, GC–MS and LC–MS analysis, the major product was vanillin (**2**). In most cases, the by-products were vanillyl alcohol (**3**), vanillic acid (**4**), 4-hydroxy-3-methoxybenzyl methyl ether (**5**) and tarry material.

3.1. Effect of different metalloporphyrins

The performance of different metalloporphyrins (T(*p*-Cl)PPMnCl, T(*p*-Cl)PPCo, T(*p*-Cl)PPFeCl, T(*p*-Cl)PPCu or [T(*p*-Cl)PPFe]$_2$O) for 2-methoxy-4-methylphenol oxidation was studied under the same reaction conditions. The results are shown in Fig. 1. It could be seen that **1** was just oxidized with 16% conversion in the absence of metalloporphyrin catalyst. On the other hand, it was found that various metalloporphyrins presented different catalytic activities in this reaction system. T(*p*-Cl)PPFeCl showed much higher conversion than T(*p*-Cl)PPMnCl. Other metalloporphyrins (T(*p*-Cl)PPCo, T(*p*-Cl)PPCu or [T(*p*-Cl)PPFe]$_2$O) exhibited rather low activity under the same conditions. However, T(*p*-Cl)PPMnCl was superior to other metalloporphyrins for selectivity and yield of **2**. The catalytic reactivity differences between catalyst systems might be related to the redox electric potential and the stability of different valences of the metal atoms [53]. Similar results were also reported by Ye et al. [53] that the catalytic activity of different metal ions in the liquid phase oxidation was not only related to the bond energy between metal and oxygen, but also related to the redox potential of metal ions. This is also consistent with our previous report [54] that the catalytic activity of metalloporphyrin is related to the electronic arrangement of central metal: the catalytic activity of metalloporphyrins with high spin arrangement is much higher than that of metalloporphyrins with low spin arrangement and with antiferromagnetic coupling. As shown in Fig. 1, T(*p*-Cl)PPMnCl will be selected as the best catalyst for optimization of the experimental conditions.

3.2. Effect of catalyst loading

T(*p*-Cl)PPMnCl presented the highest selectivity and yield of **2**, so we investigated the effect of the amount of T(*p*-Cl)PPMnCl on the oxidation of **1**. From Fig. 2, it was observed that the conversion of **1** and the selectivity of **2** increased with the increase of the amount of T(*p*-Cl)PPMnCl until its amount reached 7.2 mg. The conversion of **1** was almost unchanged when the amount of T(*p*-Cl)PPMnCl was increased from 7.2 mg to 10 mg, while the selectivity of **2** decreased. Surprisingly, further increase of the catalyst amount led to lower **1** conversion (72% when 15 mg of T(*p*-Cl)PPMnCl was used, 53% when 20 mg of T(*p*-Cl)PPMnCl was used). This observation is consistent with our earlier results that the oxidation reaction can be inhibited at high concentration of metalloporphyrin [34,41,43]. In addition to the desired product 1, by-products such as vanillyl alcohol (**3**), vanillic acid (**4**) and 4-hydroxy-3-methoxybenzyl methyl ether (**5**) were observed. It was found that the selectivity of **3**, **4** and **5** almost remained unchanged with the increase of the amount of T(*p*-Cl)PPMnCl. Besides the above products, a black tarry product was formed in the reaction process. Similar phenomena also observed by Chaudhari in the liquid phase catalytic oxidation of *p*-cresol [55]. The tarry product was obviously observed in the absence of

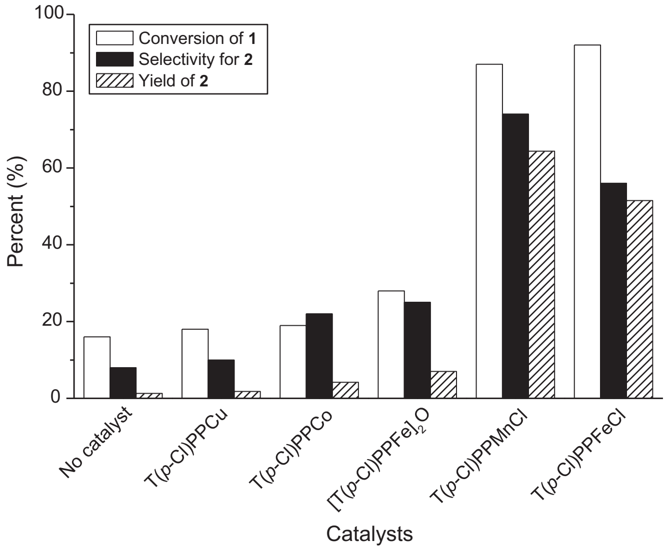


Fig. 1. Catalyst performance over different catalysts. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, catalyst = 7.5 mg, solvent (methanol) = 20 mL, sodium hydroxide = 6.0 g, temperature = 338 K, time = 3.5 h, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

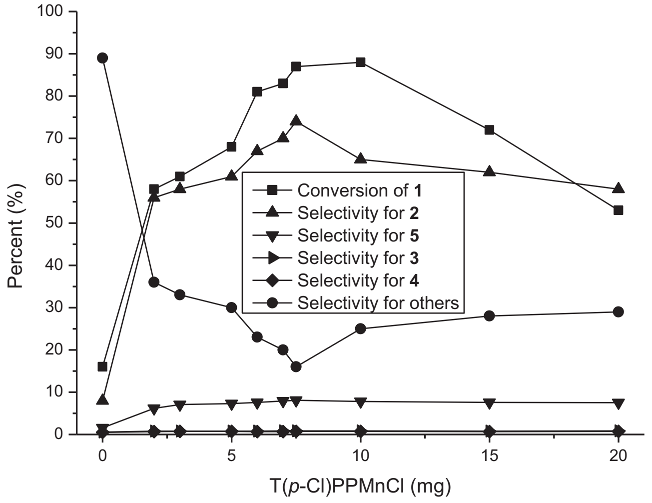


Fig. 2. Effect of catalyst loading on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, solvent (methanol) = 20 mL, sodium hydroxide = 6.0 g, temperature = 338 K, time = 3.5 h, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

catalyst. Some studies on the analysis of the tarry product are currently under investigation.

3.3. *Effect of temperature*

The effect of temperature on both conversion of **1** and selectivity of **2** was studied in the temperature range of 328–343 K, and the results are presented in Fig. 3. It was shown that the selectivity of **3**, **4** and **5** almost kept unchanged and the conversion was increased from 70% to 89% with the reaction temperature increasing. The selectivity for **2** increased from 66 to 74% with the increase of temperature from 328 K to 338 K. After that, selectivity to **2** decreased drastically due to excessive formation of tar. When the temperature was 338 K, an 87% conversion and 74% selectivity of **2** were obtained in the presence of T(*p*-Cl)PPMnCl. So the temperature of 338 K has been demonstrated to be satisfactory.

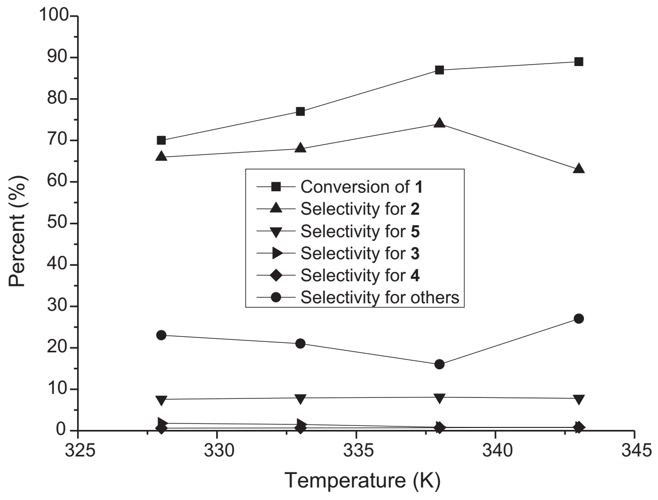


Fig. 3. Effect of temperature on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, solvent (methanol) = 20 mL, sodium hydroxide = 6.0 g, time = 3.5 h, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

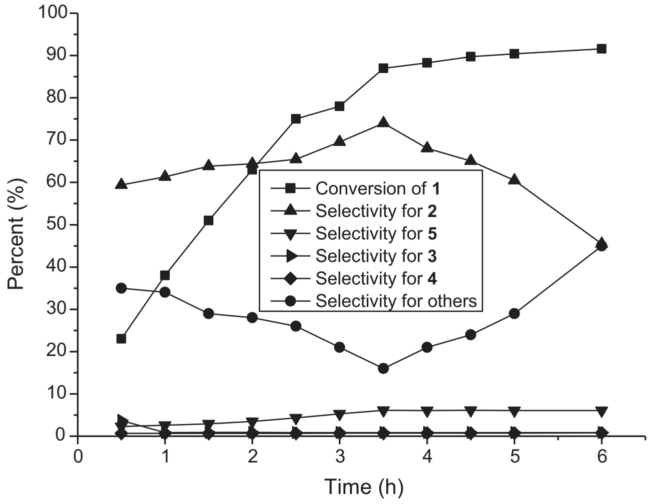


Fig. 4. Effect of the reaction time on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, solvent (methanol) = 20 mL, sodium hydroxide = 6.0 g, temperature = 338 K, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

3.4. *Effect of reaction time*

The influence of reaction time on catalytic performance was investigated and the results are shown in Fig. 4. It was found that the selectivity of **3**, **4** and **5** almost kept unchanged and the conversion gradually increased during the oxidation of **1** from 0.5 h to 6 h. The selectivity of **2** increased with the reaction time and reached the maximum at about 3.5 h. The reaction speed sharply increased during 0.5–2.5 h, which matched with the chain propagation process in the radical oxidation. Moreover, if the oxidation was continuingly preceded to 6 h or longer reaction time, the selectivity of **2** drastically decreased due to formation of side products, viz., vanillic acid (**4**) and tarry product, in higher amount. The increase in reaction time facilitated deep oxidation of **2** to vanillic acid (**4**) and tarry product [55], leading to a decrease in selectivity of **2**. So 3.5 h is considered as a preferable reaction time. From Fig. 4, it was also observed that the selectivity of **2** linearly correlated with the reaction time during 0.5–2.5 h, thus displaying a zero-order reaction characteristic in the reaction kinetics. This also agrees with the kinetic relationship in the reaction catalyzed by an enzyme [56]. After 2.5 h, this linear relationship deviated gradually. This phenomenon is consistent with our earlier reports [57–59].

3.5. *Effect of the amount of NaOH*

It has been reported in the literature [60–62] that sodium hydroxide was crucial for oxidation at the benzylic position of phenols for two reasons: firstly, it reacts with the hydroxyl of **1** and prevents oxidation on the benzene ring; secondly, it is generally believed that acid media lead to hypo oxidation and base media are beneficial for selective oxidation. The reaction did not proceed at all without sodium hydroxide. Hence, it was important to study the effect of the amount of NaOH on catalytic performance. In Fig. 5, the conversion of **1** increased from 61 to 87% with increase in NaOH to **1** mole ratio from 3 to 5, and it sharply decreased with further increase in mole ratio to 6. One possible reason could be that the mass transfer resistance of the overall reaction system increased when a higher amount of NaOH was employed. To support this, on one hand, the solubility of NaOH in methanol was measured through acid–base titration using phenolphthalein as indicator; NaOH solubility at 1 atmosphere in 1 mL solvent at 338 K is 0.32 g. This showed that the viscosity of the overall reaction

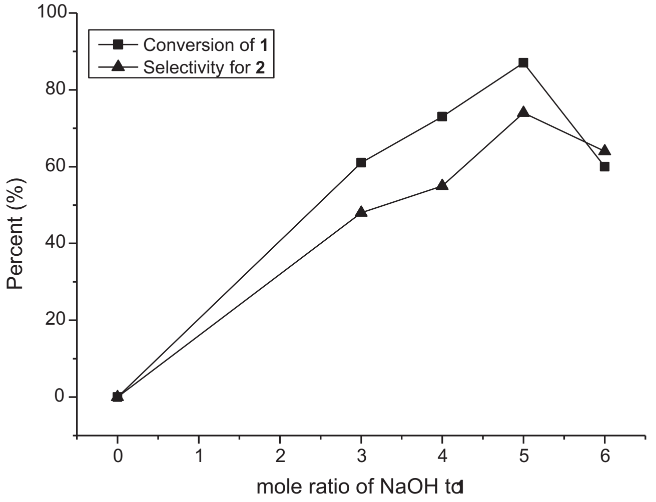


Fig. 5. Effect of mole ratio of NaOH to **1** on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, solvent (methanol) = 20 mL, time = 3.5 h, temperature = 338 K, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

system increased with the increase of the amount of NaOH, which in turn affected mass transfer of the overall reaction, resulting in a decrease in conversion of **1** and selectivity of **2** at the molar ratio 6:1. On the other hand, the influence of the stirring speed on the activity and the selectivity was investigated. The conversion and the selectivity increased with stirring speed (75% conversion and 67% selectivity of **2** were realized when the stirring speed reached 600 r.p.m., 82% conversion and 70% selectivity of **2** were realized when the stirring speed reached 700 r.p.m., 87% conversion and 74% selectivity of **2** were realized when the stirring speed reached 800 r.p.m.). This indicated that mass transfer resistance was important in the reaction system. Further experiments for ascertaining the importance of mass transfer resistance is in progress for kinetic studies. Moreover, a maximum selectivity for **2** was obtained at the molar ratio 5:1. With further increases of the NaOH to **1** ratio, the selectivity decreased.

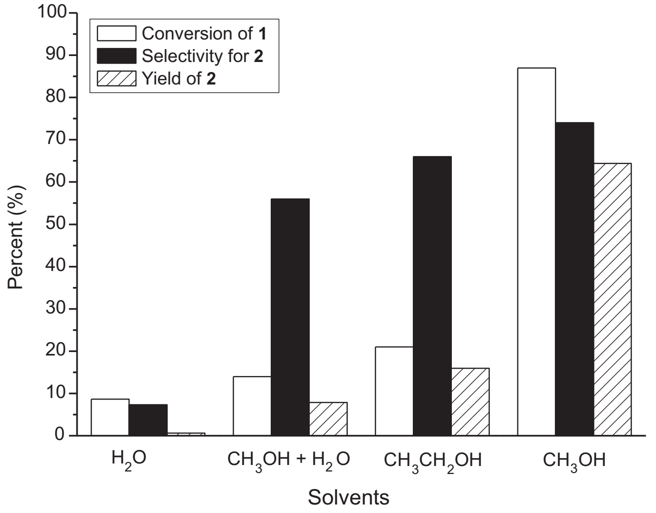


Fig. 6. Oxidation of benzyl alcohol in different solvents. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, solvent = 20 mL, sodium hydroxide = 6.0 g, time = 3.5 h, temperature = 338 K, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

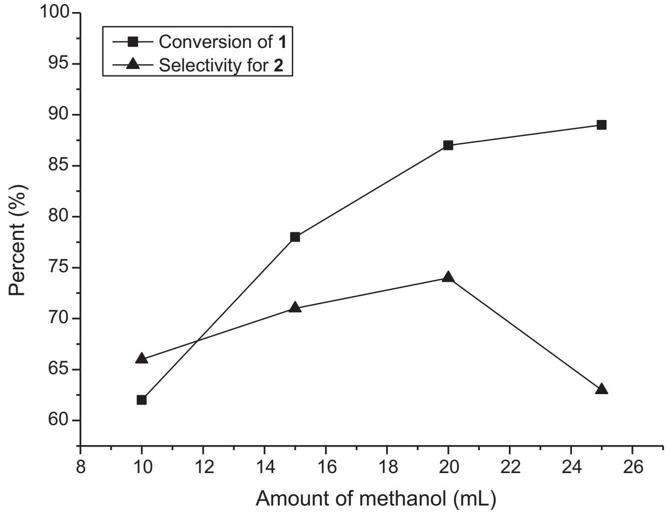


Fig. 7. Effect of the amount of methanol on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, sodium hydroxide = 6.0 g, time = 3.5 h, temperature = 338 K, O_2 pressure = 0.1 MPa, O_2 flow rate = 0.1 L min^{-1}.

3.6. Effect of solvent

To evaluate the suitability of a solvent for **1** oxidation, three common solvents (water, ethanol, and methanol) were screened. As can be seen from Fig. 6, the conversion of **1** was markedly affected, while the selectivity of **2** was dramatically altered for water and ethanol as oxidation solvents. A trace product was observed in water except for tar. When methanol and water were mixed in the volume ratio of 1:1 and employed as solvent, 14% conversion of **1** and 56% selectivity of **2** were obtained. Among the solvents examined, methanol was the best solvent in the catalytic oxidation of **1**. One of the reasons for the high conversion of **1** and the high selectivity of **2** in methanol should come from the higher solubility of oxygen in methanol than that in water and ethanol; oxygen solubilities at 1 atmosphere in 1 mL solvent at 293 K are 0.256, 0.220 and 0.031 mL for methanol, ethanol and water, respectively [63]. Moreover, water, as one of the oxidation products, offers resistance to the forward reaction kinetically [64,65].

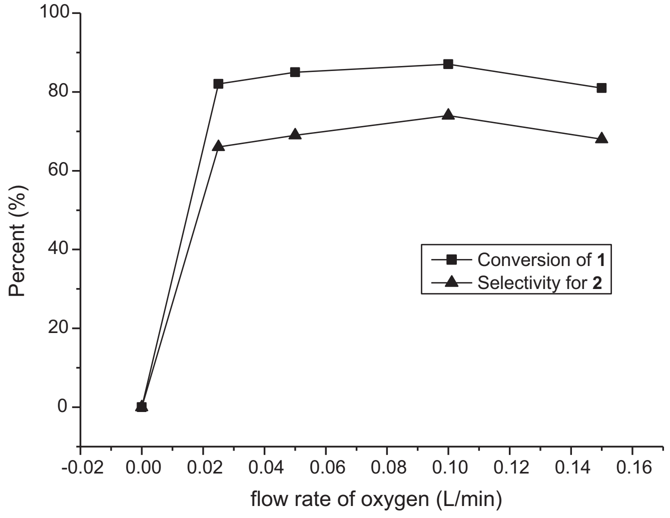
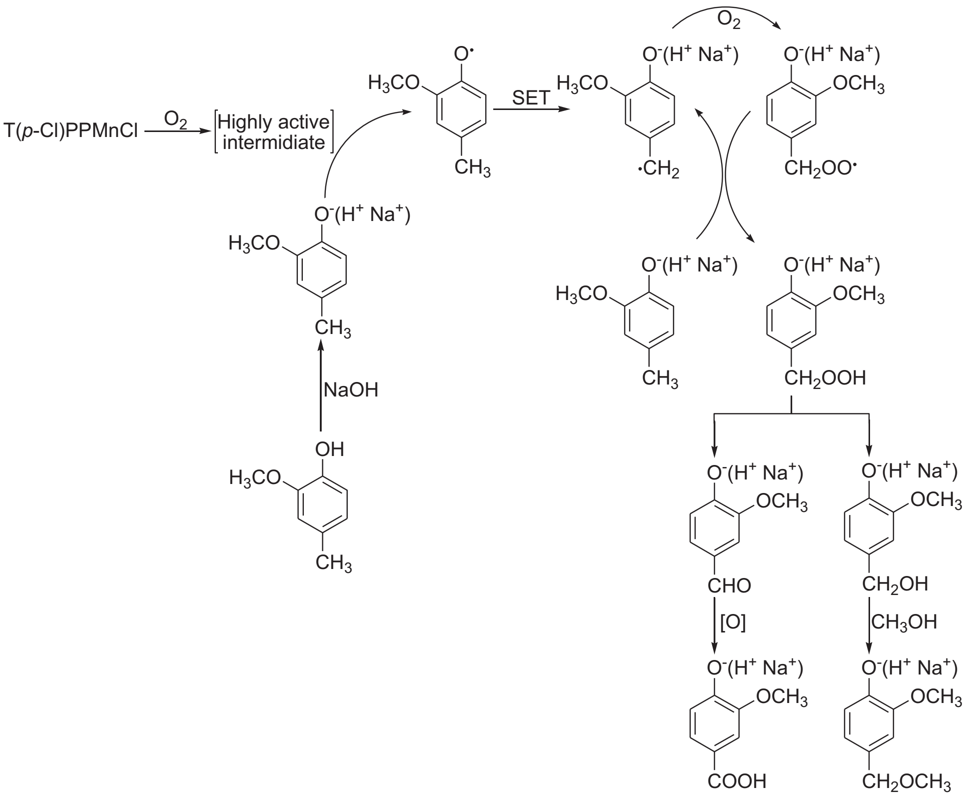


Fig. 8. Effect of the flow rate of oxygen on catalytic performance. Reaction conditions: 2-methoxy-4-methylphenol = 4.14 g, T(*p*-Cl)PPMnCl = 7.5 mg, solvent (methanol) = 20 mL, sodium hydroxide = 6.0 g, time = 3.5 h, temperature = 338 K, O_2 pressure = 0.1 MPa.



Scheme 2. Proposed reaction mechanism.

3.7. Effect of the amount of methanol

The influence of the amount of methanol on catalytic performance was investigated and the results are depicted in Fig. 7. In this figure, the conversion of **1** increased with the increase of the amount of methanol. The selectivity of **2** increased from 66 to 74% with increase in methanol from 10 mL to 20 mL, and it dramatically decreased with further increase of the amount of methanol. One plausible explanation was the increase of the oxygen supply due to the use of a larger amount of methanol and lower NaOH concentration at the higher amount of methanol. Moreover, the increase in the amount of methanol resulted in deep oxidation of **2** to tarry.

3.8. Effect of the flow rate of oxygen

To assess the effect of the flow rate of oxygen on **1** oxidation, the catalytic performance was investigated in 0–0.15 L min^{-1} oxygen flow rates. As indicated in Fig. 8, no 1 oxidation was observed in the absence of molecular oxygen. In Fig. 8, it could be clearly seen that the best flow rate of oxygen is about 0.1 L min^{-1}. When the flow rate is below 0.1 L min^{-1}, the conversion of **1** and the selectivity of **2** increased with the increase of the flow rate of oxygen. But when the flow rate is higher than 0.1 L min^{-1}, the conversion of **1** and the selectivity of **2** are decreasing with the increasing of the flow rate of oxygen. This indicated that the aerobic oxidation of **1** was influenced by the diffusion rate of oxygen when the flow rate of oxygen is small than 0.1 L min^{-1}, and that the oxidation reaction was controlled by the kinetic factors [47].

3.9. Mechanism of oxidation of 2-methoxy-4-methylphenol

Several control experiments were carried out to probe the reaction mechanism. The oxidation of **1** in the presence of 0.1 or 1.2 equiv of hydroquinone [66] was examined. The addition of the radical inhibitor can quench substantially the oxidation reaction. This showed that the oxidation probably proceeded in a radical pathway. When the oxidation of vanillyl alcohol was performed with this catalytic system, the reaction was very fast and the conversion was more than 95% under the same conditions, but the selectivity of **2** was less than 50%. According to the results that we obtained here and the above, a direct pathway leading from **1** to **2** seemed likely. In addition, the oxidation did not occur in the absence of molecular oxygen even with NaOH present (see above), further indicating that molecular oxygen is the ultimate oxidant rather than the oxygen contained in the OH^- anion.

In metalloporphyrin/O_2 system, the active species is recognized to be high-valent metal-oxo species [67]. Here we have not identified the short-lived intermediate derived from T(p-Cl)PPMnCl, but the candidates are the manganese-oxo complexes ([$\text{PMn}^{IV}=\text{O}$]). On the basis of these preliminary data and related reports [31,32,68–71], a possible mechanism for the present process is proposed as shown in Scheme 2. Under the reaction conditions, T(*p*-Cl)PPMnCl react with O_2 to give intermediate [$\text{PMn}^{IV}=\text{O}$]. The intermediate [$\text{PMn}^{IV}=\text{O}$] readily abstracts one electron from phenoxyl anion formed by **1** reacting with sodium hydroxide to produce phenoxyl radical, which was further transformed to benzyl radical through a single-electron transfer process. The resulting benzyl radical being trapped by molecular oxygen provides peroxy radical, which is eventually converted into products through hydroperoxide. Nevertheless, a detailed mechanism on the present catalytic oxidation reaction remains to be fully investigated.

4. Conclusion

In summary, we have developed simple metalloporphyrins for catalytic oxidation of 2-methoxy-4-methylphenol with molecular oxygen. The main oxidation product was vanillin. Under mild conditions, this research realized 74% selectivity for vanillin at 87% conversion of 2-methoxy-4-methylphenol. Further experiments are underway to fully elucidate the reaction mechanism. Continued development of metalloporphyrin-based catalytic oxidation of hydrocarbons also remains.

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[1] The definition of conversion and selectivity are as follows: conversion = moles of 2-methoxy-4-methylphenol consumed/moles of 2-methoxy-4-methylphenol used ×100%; selectivity = moles of product/moles of 2-methoxy-4-methylphenol consumed × 100%.