2,4,6-Trimethylphenol oxidation with ferrous chloride catalyst: Effect of acetoxime addition

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Abstract

The promoting effect of acetoxime ($(CH_3)_2C=NOH$) addition on the catalytic performances of $FeCl_2$ catalyst for catalyzing the selective oxidation of 2,4,6-trimethylphenol (2,4,6-TMP) to 3,5-dimethyl-4-hydroxybenzaldehyde (DMHB) was studied with a high-pressure batch reactor in the temperature range of 50–90 °C. A marked increase of the reaction rate upon the addition of acetoxime was observed. The extent of activity improvement increased with the reaction temperature and reached a six-fold increase of the reaction rate at 90 °C. The maximum DMHB yield obtained with the $FeCl_2$-acetoxime catalyst was 80%, which was higher than that (75%) obtained with $FeCl_2$ alone. The rate of 2,4,6-TMP disappearance was found to exhibit zero-order dependence of the TMP concentration up to 76% conversion. A reaction mechanism, similar to that proposed previously for the oxidation of substituted toluene by cobalt(III) acetate in acetic acid solution, was employed successfully to explain the experimental results obtained. The activity improvement with the addition of acetoxime was ascribed to its better electron-donating ability, which enhanced the dissociation rate of the intermediate complex.
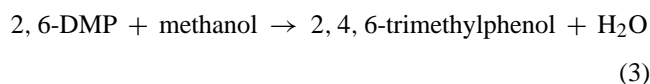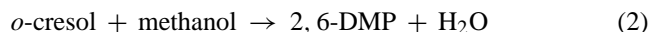© 2005 Elsevier B.V. All rights reserved.

Keywords: 2,4,6-Trimethyphenol oxidation catalyst; 3,5-Dimethyl-4-hydroxybenzaldehyde; $FeCl_2$; Acetoxime; Electron transfer; Oxidation catalyst; Trimethylphenol

1. Introduction

2,6-Dimethylphenol (2,6-DMP) is used as the starting material for the manufacture of an important engineering polymer—poly(2,6-dimethyl-1,4-phenylene oxide), abbreviated as PPO [1–5]. The blends of PPO/polystyrene, PPO/polyamide and PPO/PBT have considerable commercial significance, are widely used in automotive, business machines and computer, house or office appliances, electronic or electrical equipments [1].

The industrial method employed for the synthesis of 2,6-DMP is based on the reaction between phenol and methanol in the presence of a metal oxide catalyst [6]. The following multiple reactions occur during the synthesis of 2,6-DMP:

$$phenol + methanol \rightarrow o\text{-cresol} + H_2O \qquad (1)$$

$$o\text{-cresol} + methanol \rightarrow 2,6\text{-DMP} + H_2O \qquad (2)$$

$$2,6\text{-DMP} + methanol \rightarrow 2,4,6\text{-trimethylphenol} + H_2O \qquad (3)$$

Reaction (3) is a side reaction, which produces an undesired by-product 2,4,6-trimethylphenol (2,4,6-TMP). It is desirable to convert 2,4,6-TMP into 2,6-DMP to improve the process economic benefit because 2,4,6-TMP has little practical use. A known method for converting 2,4,6-TMP back to 2,6-DMP includes the following two steps: (1) selective oxidation of 2,4,6-trimethylphenol to 3,5-dimethyl-4-hydroxybenzaldehyde (DMHB) in the presence of a copper-based catalyst and (2) deformylation of the resulting DMHB to 2,6-dimethylphenol in the presence of a palladium catalyst [7].

In previous papers, Cu(II)-oxime and Cu(II)-amine catalysts have been employed for catalyzing the oxidation of 2,4,6-TMP to 3,5,-dimethyl-4-hydroxybenzaldehyde and

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2,6-dimethyl-*p*-benzoquinone (DMBQ) [8–10]. Following are the reactions for the oxidation of 2,4,6-TMP in alcohol solution to form DMHB and DMBQ [9]:

$$(4)$$

$$(5)$$
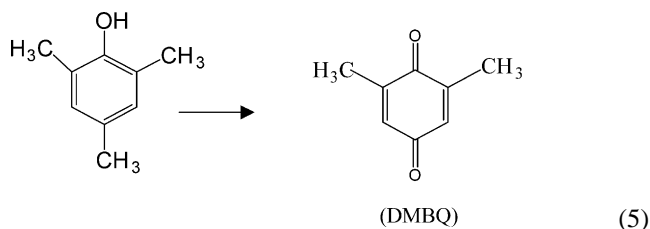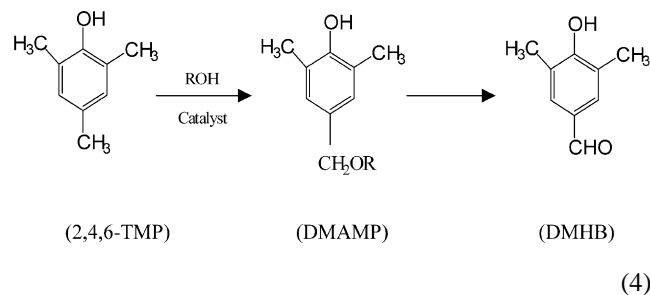
In Eq. (4), 2,6-dimethyl-4-(alkoxymethyl)phenol (DMAMP) is an intermediate in the oxidation of 2,4,6-TMP in alcohol solution (ROH), which further reacts to form DMHB. Therefore, there are three major products in the oxidation of 2,4,6-TMP: DMHB, DMBQ and DMAMP. The relative amounts of these three products depend on the catalyst formulation, and also the reaction conditions, such as 2,4,6-TMP conversion, solvent and reaction temperature.

Recently, we found that $FeCl_2$ catalyst was capable of catalyzing the oxidation of 2,4,6-TMP to DMHB effectively [11]. These iron-based catalysts have an ecological advantage over the copper-based catalysts because iron ion is more environmentally friendly than the copper ion, which can cause serious water pollution. However, the activity of $FeCl_2$ catalyst alone is not satisfactory because it required relatively long reaction time (10 h) to achieve high 2,4,6-TMP conversion.

This paper reports the use of $FeCl_2$-acetoxime complex as the catalyst for catalyzing the oxidation of 2,4,6-TMP to DMHB. We found that the addition of acetoxime significantly improved the activity of $FeCl_2$ catalyst.

2. Experimental

A 300-ml high-pressure autoclave reactor made of titanium (supplied by Parr Instruments Co.) equipped with an impeller and a temperature control unit was employed for carrying out the catalytic oxidation. The autoclave was heated by a thermoregulated oven and a thermocouple was used to monitor the reaction temperature (the temperature was set at 50, 70, or 90 °C). In a typical run, 60 mmol of 2,4,6-TMP (98% purity, Lancaster Synthesis Co., Morecame, UK), 3 mmol of $FeCl_2 \cdot 4H_2O$ (99% purity, Showa Chemicals, Tokyo, Japan), 3 mmol of acetoxime (98% purity, Acros

Organics, Belgium) and 60 ml of methanol (HPLC grade, TEDIA, Fairfield, OH, USA) were placed in the reactor. After reaching the desired temperature, the reactor was pressurized with oxygen to 10 atm. The reaction was continued for 100 min at the reaction temperature of 70 or 90 °C, and was continued for 10 h at the reaction temperature of 50 °C. At the end of the reaction, the reactor content was filtered and EDTA aqueous solution was added to remove iron ions. The composition of product solution was determined by a gas chromatograph equipped with a 15-m long RTX-1 column and a flame ionization detector. The 2,4,6-TMP conversion was defined as the moles of 2,4,6-TMP reacted per mol of 2,4,6-TMP fed to the reactor. The yield of a particular product (DMHB, DMBQ and 2,6-dimethyl-4-(methoxymethyl)phenol, abbreviated as DMMMP) was defined as the moles of the product per mol of 2,4,6-TMP fed to the reactor. The selectivity of a particular product was defined as the yield of the product divided by the 2,4,6-TMP conversion.

3. Results and discussion

The oxidation of 2,4,6-trimethylphenol was carried out at three reaction temperatures: 50, 70 and 90 °C. Fig. 1 presents the dimensionless concentrations in the product solution as a function of reaction time at the reaction temperature of 90 °C. The figure shows that DMHB is the dominant product from 2,4,6-TMP. It can be seen from the figure that the maximum DMHB yield was 80%, which was attained at the reaction time of 100 min with a 96% TMP conversion. This maximum yield (80%) is higher than that (75%) obtain with $FeCl_2$ catalyst alone [11], which was also obtained at 90 °C, but with a much longer reaction time (10 h) and a slightly lower TMP conversion (93%).

Fig. 2 shows the variation of DMHB yield as a function of TMP conversion for the $FeCl_2$-acetoxime catalyst at three different reaction temperatures (50, 70 and 90 °C). It can be seen that the yield of DMHB increases monotonically with
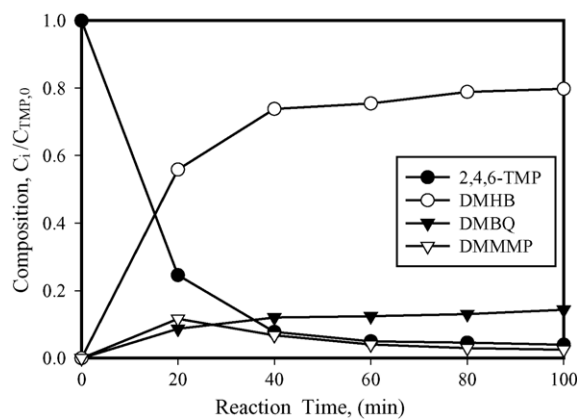

Fig. 1. Product concentration as a function of reaction time for $FeCl_2$-acetoxime catalyst. *Reaction conditions*: catalyst, 3 mmol; 2,4,6-TMP, 60 mmol; methanol, 60 ml; *P*, 10 atm; *T*, 90 °C.
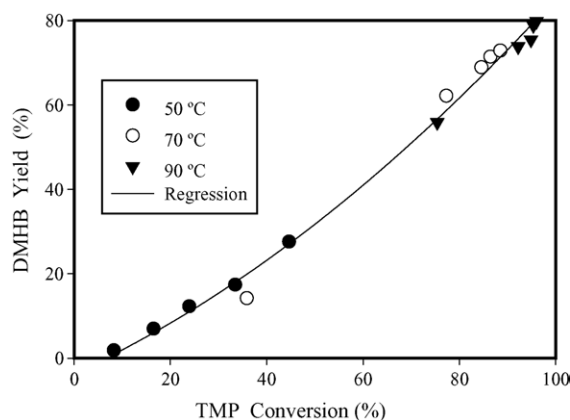
Fig. 2. Variation of DMHB yield as a function of 2,4,6-TMP conversion for FeCl$_2$-acetoxime catalyst at three reaction temperatures (50, 70 and 90 °C).

Fig. 4. Variation of DMMMP yield as a function of 2,4,6-TMP conversion for FeCl$_2$-acetoxime catalyst at three reaction temperatures (50, 70 and 90 °C).

TMP conversion and reaches a maximum value of 80% at the maximum conversion of 96%. This is different from the performance of FeCl$_2$ catalyst alone; in this case, DMHB yield decreased rapidly after TMP conversion exceeded 93%. All data points in Fig. 2 can be represented by a single curve, which suggest that the DMHB yield can be treated as a function of TMP conversion only.

Fig. 3 shows the effect of reaction temperature on the yield of the by-product DMBQ. At the same 2,4,6-TMP conversion, the yield of DMBQ obtained at the reaction temperature of 90 °C was much greater than that obtained at the reaction temperature of 70 °C. For example, at the conversion of 76%, the yields of DMBQ obtained at 70 and at 90 °C were 0.5 and 8.7%, respectively. The results indicate that the DMBQ yield was very sensitive to the reaction temperature and the side reaction for DMBQ formation became relatively important at high temperature. Therefore, the oxidation of 2,4,6-TMP should not be carried out at a high reaction temperature in order to avoid the production of the undesired product DMBQ and to improve the yield of the desired product DMHB. Fig. 3 also indicates that the DMBQ yield increased much rapidly in the range of high TMP conversion (i.e., in the range of low
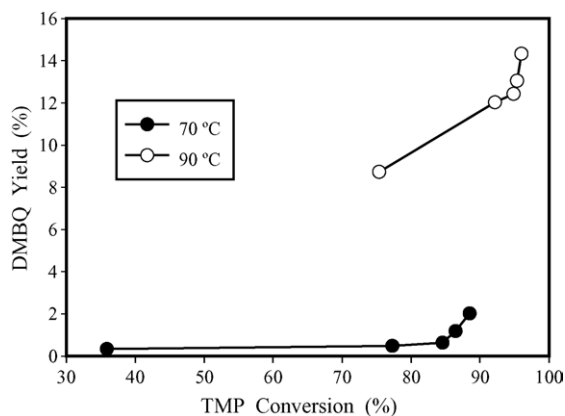
TMP concentration), which suggests that most of the DMBQ should be formed from the desired product DMHB, not by the direct oxidation of 2,4,6-TMP.

Fig. 4 shows the variation of the yield of the intermediate, 2,6-dimethyl-4-(methoxymethyl)phenol, as a function of the TMP conversion for the FeCl$_2$-acetoxime catalyst. The yield of DMMMP passed through a maximum (at around 18%) at the TMP conversion of about 50%. At the higher TMP conversion, there was a decline in the DMMMP yield, which should be due to the conversion of DMMMP to DMHB. The maximum DMMMP yield obtained for FeCl$_2$ catalyst alone was around 30% at the TMP conversion of about 55% [11]. That is, the addition of acetoxime decreased the amount of DMMMP yield obtained. The reaction mechanism that will be proposed later (Eqs. (8)–(13)) suggests that DMHB can also be formed without going through the intermediate DMMMP (i.e., Eq. (13)). The results shown in Fig. 4 suggest that more DMHB was formed via Eq. (13) when FeCl$_2$-acetone oxime was used as the catalyst for 2,4,6-TMP oxidation.

Fig. 5 compares the reaction time needed to achieve a specific 2,4,6-TMP conversion for (a) FeCl$_2$ catalyst with acetoxime and (b) FeCl$_2$ catalyst alone when the reaction temperature was 70 °C. Similar comparisons for the reaction temperature of 90 °C are presented in Fig. 6. At 70 °C, the reaction time required to achieve 88% conversion was 1.6 and 8 h for FeCl$_2$-acetoxime and for FeCl$_2$ alone, respectively. At 90 °C, the reaction time required to achieve 93% conversion was 0.77 and 10 h for FeCl$_2$-acetoxime and for FeCl$_2$ alone, respectively. Therefore, the time required to achieve a specific 2,4,6-TMP conversion was shortened dramatically with the addition of acetoxime.

Fig. 7 compares the reaction rate of 2,4,6-TMP oxidation obtained at the reaction temperature of 50 °C for (a) FeCl$_2$ catalyst with acetoxime and (b) FeCl$_2$ catalyst alone. The reaction rate with the FeCl$_2$-acetoxime system (curve a) was maintained at an approximately constant value, while the reaction rate with FeCl$_2$ catalyst alone (curve b) decreased

Fig. 3. Variation of DMBQ yield as a function of 2,4,6-TMP conversion for FeCl$_2$-acetoxime catalyst at two reaction temperatures (70 and 90 °C).
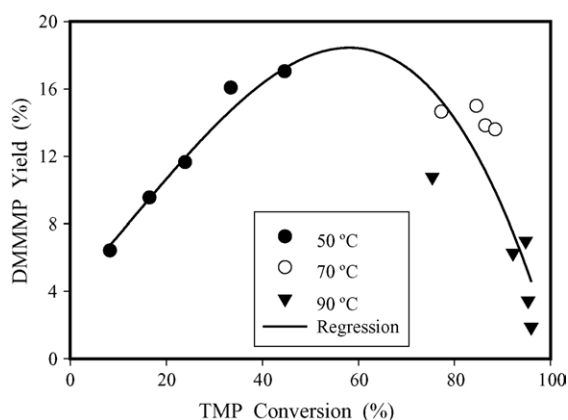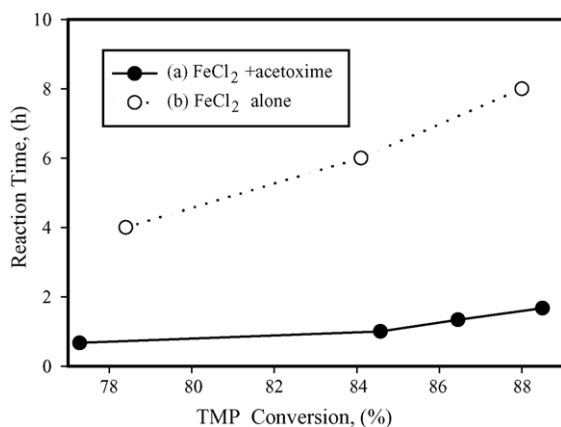
Fig. 5. Comparisons of the reaction time needed to achieve a specific 2,4,6-TMP conversion for (a) FeCl$_2$ catalyst with acetoxime and (b) FeCl$_2$ catalyst alone when the reaction temperature was 70 °C.

Fig. 7. Comparisons of the 2,4,6-TMP oxidation rate for (a) FeCl$_2$ catalyst with acetoxime and (b) FeCl$_2$ catalyst alone when the reaction temperature was 50 °C.

rapidly with the reaction time. The decrease in the reaction rate in curve b might be due to the product adsorption. The products (DMHB and H$_2$O) are often preferentially coordinated to the metal center because of their better donor properties than the reactant (2,4,6-TMP). The addition of acetoxime might reduce the effect of product adsorption on the active site, resulting in a nearly constant reaction rate. It is known that better electron-donating ligands (such as acetoxime) can be expected to enhance the rates of dissociative reactions (i.e., product desorption) since they donate more electrons to compensate for the reduction in the total number of ligands [12].

The curve a in Fig. 7 exhibits zero-order behavior because the reaction rate was almost independent of the reactant concentration. In addition, the reaction data at 70 °C also follow zero-order behavior for 2,4,6-TMP conversion up to 76%, as shown in Fig. 8. The results in Fig. 8 and in curve a of Fig. 7 suggest that the reaction rate law for 2,4,6-TMP oxidation might be in the form similar to the Langmuir–Hinshelood

Fig. 8. Test of zero-order kinetic model for 2,4,6-TMP oxidation at 70 °C.

model used in the heterogeneous catalysis:

$$\text{rate} = \frac{kK_A C_A}{1 + K_A C_A} \tag{6}$$

where C_A is the concentration of reactant A (2,4,6-TMP), K_A the equilibrium constant for the adsorption of reactant A on the catalytically active center and k is the reaction rate constant of the rate determining step. When $K_A C_A \gg 1$ (i.e., A is strongly adsorbed or the concentration of A is large), Eq. (6) reduces to

$$\text{rate} = k \tag{7}$$

Eq. (7) is zero-order with respect to the concentration of 2,4,6-TMP, which is consistent with the experimental results. The observed zero-order kinetics suggests that the catalyst is strongly bonding to 2,4,6-TMP (i.e., the value of K_A is large). Rate equations similar to Eq. (6) were proposed before [13–15] for the oxidation of catechols by O$_2$ catalyzed by Mn(II), Co(II) and Fe(II) complexes, based on a mechanism involving an anion radical intermediate.

Figs. 5–7 clearly indicates that the addition of acetoxime significantly improved the activity. Fig. 9 shows the effect of
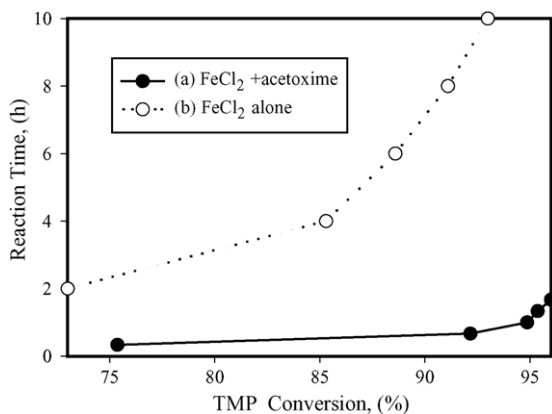

Fig. 6. Comparisons of the reaction time needed to achieve a specific 2,4,6-TMP conversion for (a) FeCl$_2$ catalyst with acetoxime and (b) FeCl$_2$ catalyst alone when the reaction temperature was 90 °C.
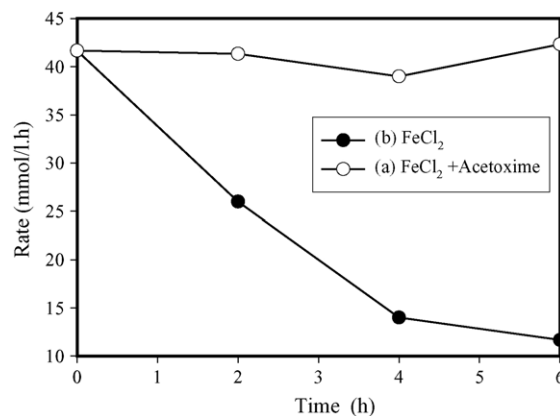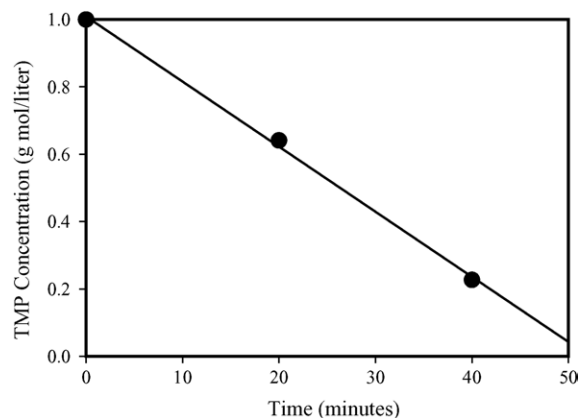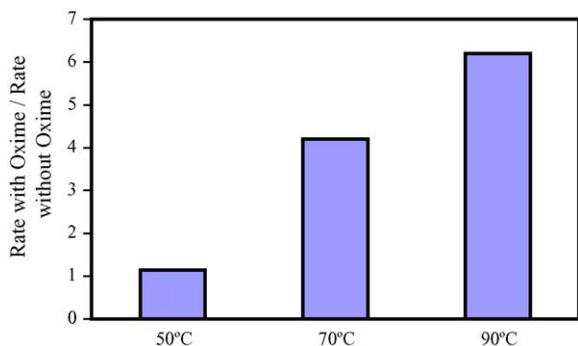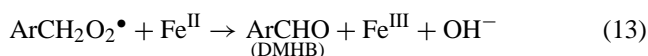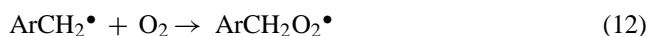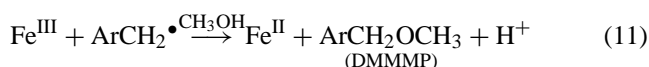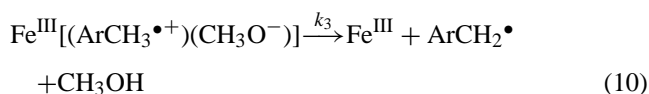
Fig. 9. Effect of reaction temperature on the ratio of (the initial rate obtained with FeCl$_2$ + acetoxime)/(the initial rate obtained with FeCl$_2$ alone).

reaction temperature on the initial rate ratio, which is defined as the initial rate obtained with FeCl$_2$-acetoxime catalyst divided the initial rate obtained with FeCl$_2$ catalyst alone. The figure clearly indicates that the promoting effect of acetoxime addition became more profound with the increase in reaction temperature. At 90 °C, a six-fold increase in the reaction rate was observed.

The proposed mechanism for Fe(III) catalyzed oxidation of 2,4,6-TMP (denoted by ArCH$_3$) to DMHB in methanol solution is expressed as Eqs. (8)–(13), in which a radical cation ArCH$_3^{\bullet+}$ is formed via the direct electrophilic attack of the iron(III) species on the electron-rich substrate (2,4,6-TMP). The mechanism is analogous to that proposed by Hendriks et al. [16] for the oxidation of substituted toluenes by cobalt(III) acetate in acetic acid solution.

$$Fe^{III} + ArCH_3 \underset{k_1(-CH_3OH)}{\overset{k_1(+CH_3OH)}{\rightleftarrows}} [(ArCH_3^{\bullet+})(CH_3O^-)]$$

$$+ Fe^{II} + H^+ \tag{8}$$

$$Fe^{III} + [(ArCH_3^{\bullet+})(CH_3O^-)] \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Fe^{III}[(ArCH_3^{\bullet+})$$

$$(CH_3O^-)] \tag{9}$$

$$Fe^{III}[(ArCH_3^{\bullet+})(CH_3O^-)] \overset{k_3}{\longrightarrow} Fe^{III} + ArCH_2^{\bullet}$$

$$+ CH_3OH \tag{10}$$

$$Fe^{III} + ArCH_2^{\bullet} \overset{CH_3OH}{\longrightarrow} Fe^{II} + \underset{(DMMMP)}{ArCH_2OCH_3} + H^+ \tag{11}$$

$$ArCH_2^{\bullet} + O_2 \rightarrow ArCH_2O_2^{\bullet} \tag{12}$$

$$ArCH_2O_2^{\bullet} + Fe^{II} \rightarrow \underset{(DMHB)}{ArCHO} + Fe^{III} + OH^- \tag{13}$$
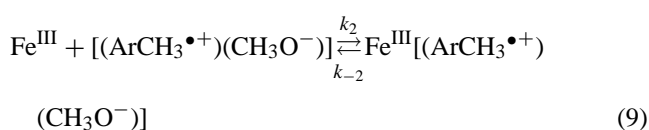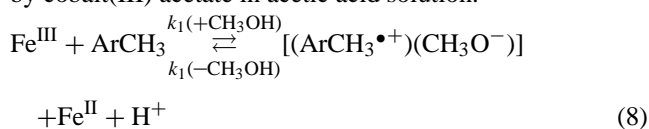
The intermediate, 2,6-dimethyl-4-(methoxymethyl)phenol (denoted by ArCH$_2$OCH$_3$) formed in Eq. (11), can be converted to the desired product (DMHB) non-catalytically [9]. The iron(III) species can be regenerated by the reaction of Fe^{II} with ArCH$_2$O$_2^{\bullet}$ according to Eq. (13), which

leads to the formation of the desired product 3,5-dimethyl-4-hydroxybenzaldehyde (denoted by ArCHO) [11].

The catalyst originally added into the reaction mixture was FeCl$_2$·4H$_2$O. The Fe^{III} in Eq. (8) is formed by the oxidation of Fe^{II}. It is known that iron-peroxo species (Fe^{III}–O–O$^-$) can be obtained by the electron transfer from Fe^{II} ion to oxygen [17]:

$$Fe^{II} + O_2 \rightleftarrows Fe^{III}-O-O^- \tag{14}$$

The (CH$_3$O$^-$) in Eq. (8) might be generated by deprotonation of the coordinated CH$_3$OH molecules [12].

Assuming Eq. (10) is the rate determining step [16], the reaction rate of 2,4,6-TMP oxidation is taken to be proportional to the concentration of Fe^{III}[(ArCH$_3^{\bullet+}$)(CH$_3$O$^-$)] complex (denoted by C_{AX}). Then,

$$rate = k_3 C_{AX} \tag{15}$$

The value of C_{AX} is given in Eq. (16) in term of the equilibrium constants (K_1, K_2) of Eqs. (8) and (9) and the appropriate concentrations.

$$C_{AX} = K_1 K_2 [ArCH_3][Fe^{III}]^2 [Fe^{II}]^{-1} \tag{16}$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$.

The mass balance for iron species is given by Eq. (17).

$$[Fe]_0 = [Fe^{III}] + [Fe^{II}] + C_{AX} \tag{17}$$

where $[Fe]_0$ is the total concentration of iron species in the reaction mixture, which is a constant value.

For the oxidation of substituted toluene by cobalt(III) acetate under the condition of 0.7 atm O$_2$, Hendriks et al. [16] found that the concentration ratio of Co^{III}/Co^{II} was kept constant over a wide range of hydrocarbon conversion (2–95%). Therefore, a constant concentration ratio of Fe^{III}/Fe^{II} should be maintained under the condition of large excess oxygen (10 atm) used in this study. That is,

$$Fe^{II} = (K_4)^{-1} Fe^{III} \tag{18}$$

where K_4 is related to the equilibrium constant of Eq. (14).

Combining Eqs. (16)–(18) gives

$$C_{AX} = \frac{K[ArCH_3][Fe]_0}{1 + K[ArCH_3]} \tag{19}$$

where $K = K_1 K_2 K_4/(1 + K_4^{-1})$. The value of K_4 is large due to the large excess of oxygen. Therefore, $K \approx K_1 K_2 K_4$. Eq. (19) is similar to the Langmuir equation used in heterogeneous catalysis.

Substituting Eq. (19) into Eq. (15) gives

$$rate = \frac{k_3 K[ArCH_3][Fe]_0}{1 + K[ArCH_3]} \tag{20}$$

Under the condition of $K[ArCH_3] \gg 1$, Eq. (20) becomes

$$rate = k_3 [Fe]_0 \tag{21}$$

Eq. (21) is zero-order with respect to the concentration of 2,4,6-TMP, which is consistent with the experimental data observed in the curve a of Figs. 7 and 8. The consistence suggests that the proposed mechanism agrees with the observed kinetics.

The rate equation in Eq. (21) suggested that the rate increase due to acetoxime addition should be due to the increase in k_3 (rate constant of Eq. (10)). The rate constant k_3 of Eq. (10) is related to the kinetic lability (or cage escape ability) of the iron intermediate complex $Fe^{III}[(ArCH_3^{\bullet+})(CH_3O^-)]$, which was constrained by the solvent (methanol) cage [18]. It is known that the better electron-donating ligands (such as acetoxime) can enhance the rates of dissociative reactions (such as Eq. (10)), since they donate more electron density to compensate for the reduction in the total number of ligands. This is called electron-donor effects [12]. They are several possible modes for the coordination of oxime ($RR'C=NOH$) ligand to a metal [19]. The most probable mode for the binding of acetoxime (($(CH_3)_2C=NOH$) ligand to the iron ion is

$$Fe\text{-}N=C\,(CH_3)_2$$
$$|$$
$$OH \qquad ,$$

in which oximato group binds through nitrogen only and the oxygen atom is involved in hydrogen bonds. The coordination of acetoxime to iron thus increased the rate of Eq. (10), which resulted in the increased reaction rate for the oxidation of 2,4,6-TMP, as shown in Figs. 5–7 and 9. It has been demonstrated in the literature that the rate of direct hydrolysis (in the absence of protonic acid) of acetoxime to acetone and NH_2OH was very low [20]. In addition, the methanol used in our experiments was HPLC grade which contained very little (0.05%) water. Therefore, the amount of acetoxime hydrolysis was negligible under our experimental conditions, and the active catalytic promoter should be acetoxime itself.

In alkaline solutions, the phenolic OH group in 2,4,6-TMP is easily dissociated to form phenoxyl radical and proton. Sheldon and de Heij [21] studied the cobalt-based catalytic oxidation of *p*-cresol to *p*-hydroxy benzaldehyde in alkaline (with NaOH addition) methanolic solution, and proposed a reaction pathway involving a phenolate anion (formed due to the basic nature of the reaction medium), a phenoxy radical (oxidation product of phenolate anion) and an anion benzyl radical (formed via the reaction of phenoxy radical). Based on the Sheldon's mechanism, the possible reaction pathway for the Fe(III) catalyzed 2,4,6-TMP oxidation in alkaline methanolic solution can be represented by the following steps:

$$HOArCH_3 \rightleftarrows {}^-OArCH_3 + H^+ \qquad (22)$$

$${}^-OArCH_3 + Fe^{III} \rightleftarrows {}^{\bullet}OArCH_3 + Fe^{II} \qquad (23)$$

$${}^{\bullet}OArCH_3 \rightleftarrows {}^-OArCH_2^{\bullet} \qquad (24)$$

$${}^-OArCH_2^{\bullet} \overset{Fe^{II},O_2}{\rightleftarrows} {}^-OArCH_2OOFe^{III} \qquad (25)$$

$${}^-OArCH_2OOFe^{III} + CH_3OH \rightleftarrows \underset{(DMMMP)}{{}^-OArCH_2OCH_3}$$
$$+ Fe^{III}OOH \qquad (26)$$

$${}^-OArCH_2OOFe^{III} \rightleftarrows \underset{(DMHB)}{{}^-OArCHO} + Fe^{III}OH \qquad (27)$$

In our study, no NaOH was added during the oxidation of 2,4,6-TMP. Therefore, the mechanism involving phenoxy radical (Eqs. (22)–(27)) is hardly likely to occur (compared to the reaction mechanism proposed in Eqs. (8)–(13)) because of the very low acid dissociation constant of 2,4,6-TMP in methanol ($K_a < 10^{-14}$) [22,23].

4. Conclusions

In the present study, the effect of acetoxime addition on the performance of $FeCl_2$ catalyst for the selective oxidation of 2,4,6-trimethylphenol to 3,5-dimethyl-4-hydroxybenzaldehyde was investigated in the temperature range of 50–90 °C with methanol as the solvent. The addition of acetoxime significantly increased the reaction rate (up to six times) and also improved the yield of the desired product—3,5-dimethyl-4-hydroxybenzaldehyde. Zero-order rate equation was found to satisfactorily describe the rate of 2,4,6-trimethylphenol disappearance. By analogy to the oxidation of substituted toluene catalyzed with Co(III) acetate, a reaction mechanism involving a radical cation was proposed for the Fe-acetoxime complex catalyzed 2,4,6-trimethylphenol oxidation system. Based on the mechanism, the activity increase with the acetoxime addition might be due to the increase in the dissociation rate of $Fe^{III}[(ArCH_3^{\bullet+})(CH_3O^-)]$ complex.

Acknowledgement

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