ELSEVIER

Chemical Engineering Journal 134 (2007) 276–281

Chemical Engineering Journal

www.elsevier.com/locate/cej

Complete oxidation of low concentration ethanol in aqueous solution with H_2O_2 on nanosized Mn_3O_4/SBA-15 catalyst

Yi-Fan Han*, Fengxi Chen, Ziyi Zhong, Kanaparthi Ramesh,
Luwei Chen, Dou Jian, Wong Wan Ling

Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island, Singapore 627833, Singapore

Abstract

In the present study, a new heterogeneous Fenton-like system consisting of nano-composite Mn_3O_4/SBA-15 catalyst and H_2O_2 has been investigated for the complete oxidation of ethanol (100 ppm) in aqueous solution. Experimental data show that the relative reaction rate for ethanol oxidation can be strongly influenced by several factors, such as reaction temperature, pH value, ratio of catalyst/solution and the concentration of ethanol. A plausible reaction mechanism has been proposed to explain the reaction behavior. The rate for the complete oxidation is supposed to be dependent on the concentration of intermediates (radicals: $^\bullet OH$, O_2^-, and $^\bullet HO_2$) that are derived from the decomposition of H_2O_2. In any case, the complete oxidation of ethanol can be improved only under the conditions that (i) the intermediates are stabilized, such as stronger acid solution and high temperatures, or (ii) scavenging those radicals due to the catalyst is reduced, such as less amount of catalyst and high concentration of reactant. Nevertheless, the reactivity of the presented catalyst is still slightly inferior to the conventional homogenous Fenton catalyst, Fe^{2+}–H_2O_2. A possible reason is that the concentration of intermediates in the latter is might be relatively high.

Keywords: Hydrogen peroxide; Fenton catalyst; Complete oxidation of ethanol; Mn_3O_4/SBA-15; Catalytic oxidation

1. Introduction

Remediation of wastewater containing organic constitutes is of great importance, because organic substances, i.e., benzene, phenol and alcohols etc. may lead to serious intimidation to human and animal life. Organic effluents from pharmaceutical, chemical and petrochemical industry usually contaminate water system by dissolving into groundwater. Up to date, several processes have been developed for treating wastewater that contains toxic organic compounds, such as wet oxidation with or without solid catalysts [1–4], biological oxidation, supercritical oxidation and adsorption [5,6], etc. Among them, catalytic oxidation is a promising alternative, since it avoids the problem of the adsorbent regeneration in the adsorption process, decreases significantly the temperature and pressure in non-catalytic oxidation techniques [7]. Generally, the disposal of wastewater containing low concentration organic pollutants (<100 ppm) can be more costly through all aforementioned processes. Comparatively, catalytic oxidation should be the best option for this purpose with considering its low cost and high efficiency.

Currently, a Fenton reagent that consists of homogenous iron ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) is an effective oxidant and widely applied for treating industrial effluents, especially, which usually contain about 10^{-2} to 10^{-3} M organic compounds [8]. However, several problems associated with homogenous Fenton system are still unsolved, e.g., disposing the iron-containing waste sludge, limiting the pH value (2.0–5.0) of the aqueous solution, and irreversible loss of reactivity of the reagent. To overcome these drawbacks raised from the Fenton system, since 1995, a heterogeneous Fenton reagent using metal ions exchanged zeolites, i.e., Fe/ZSM-5 catalysts, have been developed and proved to be an interesting alterative system for treating wastewater, and it has showed a comparable performance with the homogenous Fenton system [9]. Nevertheless, exploring other heterogeneous catalytic system is still desirable for this purpose.

Mn-containing oxide catalysts have been found to be remarkable active for the catalytic wet oxidation of organic effluents (CWO) [10–14], which is performed at high air pressures (1–22 MPa) and at high temperatures (150–370 °C) [15]. On the other hand, manganese oxide, e.g., MnO_2 [16], is well known

---

* Corresponding author.
E-mail address: han_yi_fan@ices.a-star.edu.sg (Y.-F. Han).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.03.060

to be active for the decomposition of H_2O_2 in aqueous solution to produce hydroxyl radical ($^\bullet OH$), which is the most robust oxidant so far. The organic constitutes can be deeply oxidized by those radicals rapidly [17]. The only by-product is H_2O from decomposing H_2O_2. Therefore, H_2O_2 is a suitable chemical for treating the wastewater containing organic compounds. Due to the recent progress on the synthesis of H_2O_2 directly from H_2 and O_2 [18,19], H_2O_2 is believed to be produced through more economical process in the future. So, the heterogeneous Fenton system can be more economically acceptable.

In this study, nanocrystalline Mn_3O_4 highly dispersed inside the mesoporous silica, SBA-15, has been prepared. The catalyst as prepared has been examined for the wet oxidation of ethanol in aqueous solution. Ethanol has been selected as a model organic compound, because (i) it is one of the simplest organic compounds and easily analyzed, (ii) it has high solubility in water, and (iii) the structure of ethanol is quite stable and only changed through catalytic reaction. Ethanol is also the main component in the effluents from beer/wine factory. We aim to investigate the kinetics of complete oxidation of low concentration ethanol (100 ppm) in a Fenton-like system consisting of Mn_3O_4/SBA-15–H_2O_2. Efforts are made to reveal the reactivity affected by factors such as temperature, pH value, ratio of catalyst (g)/volume (l) and concentration of ethanol in aqueous solution. In addition, plausible mechanisms for ethanol oxidation and H_2O_2 decomposition have also been proposed in order to explain the kinetic results.

2. Experimental

2.1. Preparation and characterization of Mn_3O_4/SBA-15 catalyst

2.1.1. Preparation

The synthesis of SBA-15 is similar to the previously reported method [20] by using Pluronic P123 (BASF) surfactant as template and tetraethyl orthosilicate (TEOS, 98%) as silica source. First, the manganese(II) acetylacetonate ($[CH_3COCH=C(O)CH_3]_2Mn$, Aldrich) by a ratio of 2.5 mmol/g (SBA-15) were dissolved in acetone (C.P.) at room temperature, corresponding to ca. 13 wt% of Mn_3O_4 with respect to SBA-15. The SBA-15 powder was then put into the solution after manganese(II) acetylacetonate had been completely dissolved. The precursor was obtained by vigorously stirring the solution till the solvent was evaporated completely. Finally, the obtained material was calcined in an oven at 500 °C for 5 h with a ramping rate of 1 °C/min. The organic compound was transferred directly into Mn_3O_4 through calcination.

2.1.2. X-ray diffraction (XRD)

X-ray diffraction data were obtained with a Bruker D8 diffractometer using Cu Kα radiation ($\lambda = 1.540589$ Å). The diffraction pattern was taken in the Bragg angle (2θ) range from 30° to 60° at room temperature. The XRD patterns were obtained by scanning overnight with a step size: 0.02 °/step, 8 s/step, 14 h for scanning 30°. Several peaks at the high angles of XRD, as shown by Fig. 1, indicate the formation of a well-crystallized hausmannite Mn_3O_4 (JCPDS 80-0382). The details of preparation and characterization of this nano-composite can be referred to one of our recent publications [21]. It has been evidenced that most of the MnO_x nanocrystals were formed inside the pores; and the average size of nanocrystals is estimated to be ca. 15 nm.

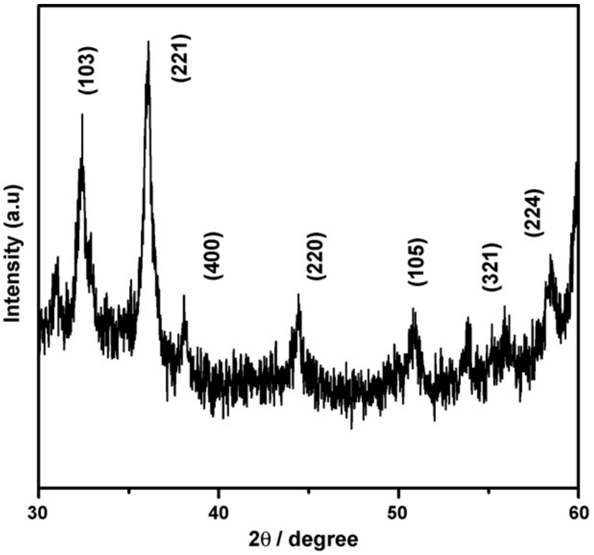

Fig. 1. XRD pattern for the Mn_3O_4/SBA-15 nano-composite catalyst.

2.2. Activity measurement and analysis

2.2.1. Catalytic tests

The experiment for the wet peroxide oxidation of ethanol was carried out in a glass batch reactor connected to a condenser with continuous stirring (400 rmp). Typically, 20 ml of ethanol aqueous solution (100 ppm of ethanol if without any emphasizing) was first added to the reactor together with 5 mg of catalyst, corresponding to ca. 1 (g_{Mn})/30 (l) ratio of catalyst/solution. Then, 1 ml of 30% H_2O_2 solution was dropped into reactor at interval ~0 min (0.5 ml), 32 min (0.25 ml), and 62 (0.25 ml) min. The total molar ratio of H_2O_2/ethanol is about 400/1. Hydrochloric acid (HCl, 0.01 M) was used to acidify the solution if necessary. The pH value for the deionized water is ca. 7.0 (Oakton pH meter) and decreased to 6.7 after adding ethanol. NH_4OH (0.1 M) solution was used to adjust pH to 9.0 when investigating the effect of pH. All reactions were operated under the conditions described on the above if without special noting. For comparison, the reaction was also carried out with a typical homogenous Fenton reagent according to a patent disclosure [17], $FeSO_4$ (5 ppm)/H_2O_2 under the same conditions.

2.2.2. Product analysis

The conversion of ethanol during reaction was detected using gas chromatography (GC: Agilent Technologies, 6890N), installed a HP-5 capillary column connecting to a thermal conductive detector (TCD). There is no other species but ethanol determined in the reaction system, as evidenced by GC–MS. Ethanol is supposed to be completely oxidized into CO_2 and H_2O. The variation of H_2O_2 concentration during reaction was analyzed colorimetrically using a UV–vis spectrometer (Epp2000, StellarNet Inc.) after complexation with a $TiOSO_4/H_2SO_4$ reagent [18]. Note that there is almost no measurable leaching Mn ion during reaction using ICP (Vista-Mpx, Varian).

3. Results

3.1. Blank tests

Under the typical reaction conditions, that is, 20 ml of 100 ppm ethanol aqueous solution (pH 6.7) mixed with 1 ml of 30% H_2O_2, at 70 °C, no conversion of ethanol in the systems of the absence of catalyst and presence of bare SBA-15 (5 mg) is observed after running for 120 min. Under the same conditions in a H_2O_2-free solution, ethanol wasn't transformed even with Mn_3O_4/SBA-15 catalyst (5 mg) in the reactor. It indicates that a trace amount of oxygen dissolved in water doesn't have any contribution to ethanol oxidation under reaction conditions. We further examined the concentration of ethanol versus time at different temperature in absence of catalyst and H_2O_2. Loss of ca. 5% ethanol was observed only at 90 °C after running for 120 min. Hence, to avoid the loss of ethanol through evaporation at high temperatures, which may lead to a higher conversion of ethanol than the real value, the kinetic measurements in this study were performed at or below 70 °C.

3.2. Kinetic study

3.2.1. Effect of amount of catalyst

The effect of amount of catalyst on ethanol oxidation is presented in Fig. 2. Different amounts of catalyst were taken for the same concentration of ethanol (100 ppm) aqueous solution under the standard conditions. It can be observed that the conversion of ethanol increases monotonically within 120 min, reaching 15, 20, and 12% for 2, 5, and 10 mg catalysts, respectively. On the other hand, Fig. 2 shows that the initial reaction rates (30 min) decrease from 0.7 to 0.1 mmol/g_{Mn} min with raising the amount of catalyst from 2 to 10 mg. This indicates that more catalyst in the system may reduce the catalytic activity, and a proper ratio of catalyst (g)/solution (l) is required for the reaction. In order to investigate the effects from other factors, 5 mg (catalyst)/20 ml (solution), corresponding to 1 (g_{Mn})/30 (l) ratio of catalyst/solution, has been selected for the followed experiments.

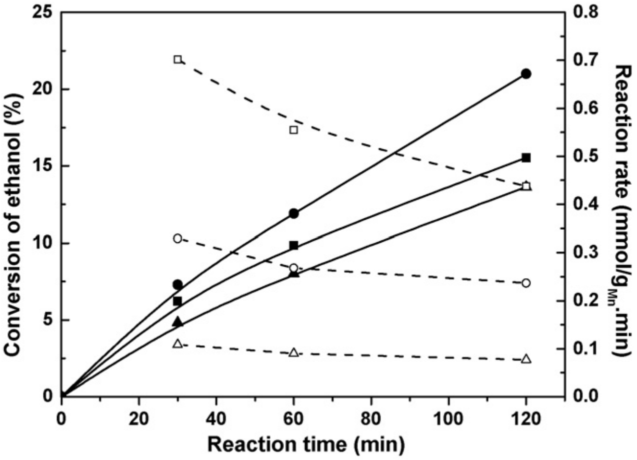

Fig. 2. The ethanol oxidation as a function of time with different amount of catalyst. Conversion of ethanol vs. time (solid line) on 2 mg (■), 5 mg (●) and 10 mg (▲) Mn_3O_4/SBA-15 catalyst, the relative reaction rate vs. time (dashed line) on 2 mg (□), 5 mg (○) and 10 mg (△) Mn_3O_4/SBA-15 catalyst. Rest conditions: 20 ml of ethanol (100 ppm), 1 ml of 30% H_2O_2, 70 °C and pH of 6.7.

3.2.2. Effect of temperature

As shown in Fig. 3, the initial reaction rate increases from 0.08 to 0.33 mmol/g_{Mn} min with varying temperature from 25 to 70 °C. After running for 120 min in the same temperature, the total conversion of ethanol increases from 12.5 to 20%. Further increasing the temperature was not performed in case the loss of ethanol by evaporation. Interestingly, it was observed that the relative reaction rate increased with time within initial 60 min at 25 and 40 °C, but the tendency turns up above 60 °C.

3.2.3. Effect of pH

In the pH range from 2.0 to 9.0, as illustrated in Fig. 4, the reaction rate drops down from 0.75 to 0.1 mmol/g_{Mn} min with the rise of pH. It suggests that acid environment, or to say, proton concentration ($[H^+]$) in the solution is essential for this reaction. With considering our target for this study, purifying water, pH approaching to 7.0 in the reaction system is preferred. Because acidifying the solution with organic/inorganic acids may cause a second time pollution and a surplus cost. Actually, the change of the pH from 5.5 to 6.7 has not any impact on the conversion of ethanol (Fig. 4).

3.2.4. Effect of ethanol concentration

The investigation of the effect of ethanol concentration on the reaction rate was carried out in the ethanol range from 50 to 500 ppm. Fig. 5 shows that the relative reaction rate increases

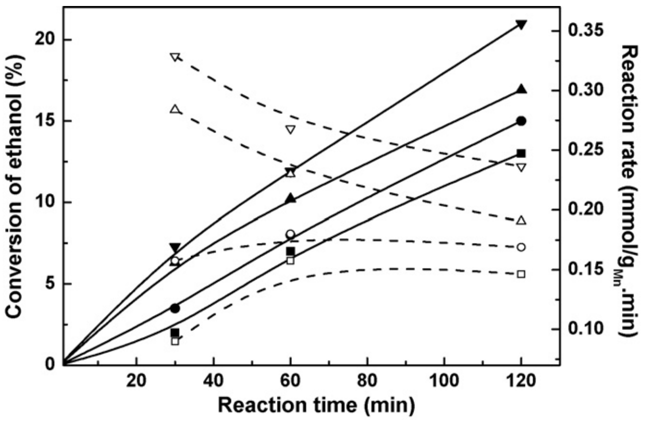

Fig. 3. The ethanol oxidation as a function of temperature. Conversion of ethanol vs. time (solid line) at 25 °C (■), 40 °C (●), 60 °C (▲) and 70 °C (▼), the relative reaction rate vs. time (dashed line) at 25 °C (□), 40 °C (○), 60 °C (△) and 70 °C (▽). Rest conditions: 20 ml of ethanol (100 ppm), 1 ml of 30% H_2O_2, pH of 6.7 and 5 mg of catalyst.

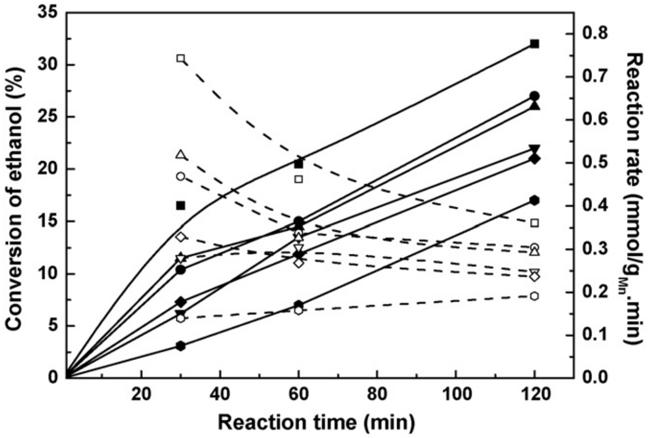

Fig. 4. The ethanol oxidation as a function of pH value. Conversion of ethanol vs. time (solid line) at pH value of 2.0 (■), 3.5 (●), 4.5 (▲), 5.5 (▼), 6.7 (♦) and 9.0 (⬢), the relative reaction rate vs. time (dashed line) at pH value of 2.0 (□), 3.5 (○), 4.5 (△), 5.5 (▽), 6.7 (◇) and 9.0 (⬡). Rest conditions: 20 ml of ethanol (100 ppm), 1 ml of 30% H_2O_2, 70 °C and 5 mg of catalyst.

from 0.07 to 2.37 mmol/g$_{Mn}$ min after running for 120 min with increasing the concentration of ethanol from 50 to 500 ppm. Note that the pH value decreased slightly from 6.7 to 6.5 when increasing the ethanol concentration from 100 to 500 ppm.

3.2.5. Comparing to a typical homogenous Fenton reagent

Under the same reaction conditions, the oxidation of ethanol was performed using a conventional homogenous reagent, Fe^{2+} (5 ppm)/H_2O_2 (1 ml) at pH of 5.0, it has been reported to be an optimum condition for this system [17]. As shown in Fig. 6, the reaction in both catalytic systems exhibits a similar behavior, that is, the conversion of ethanol increases with extending the reaction time. Varying temperature from 25 to 70 °C seems not to impact the conversion of ethanol when using the homogenous Fenton reagent. Furthermore, the conversion of ethanol (defining at 120 min) in the system of Mn_3O_4/SBA-15–H_2O_2 is about 60% of that obtained from the conventional Fenton reagent.

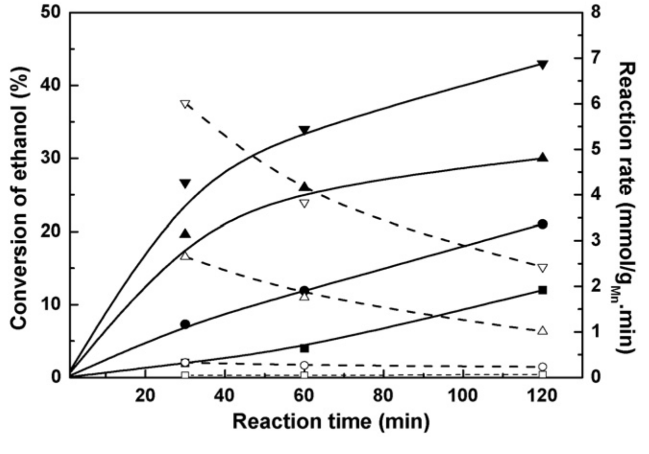

Fig. 5. The ethanol oxidation as a function of ethanol concentration. Conversion of ethanol vs. time (solid line) for ethanol concentration (ppm) of 50 (■), 100 (●), 300 (▲), 500 (▼), the relative reaction rate vs. time (dashed line) for ethanol concentration (ppm) of 50 (□), 100 (○), 300 (△), 500 (▽). Conditions: 20 ml of ethanol, pH of 6.7, 1 ml of 30% H_2O_2, 70 °C and 5 mg of catalyst.

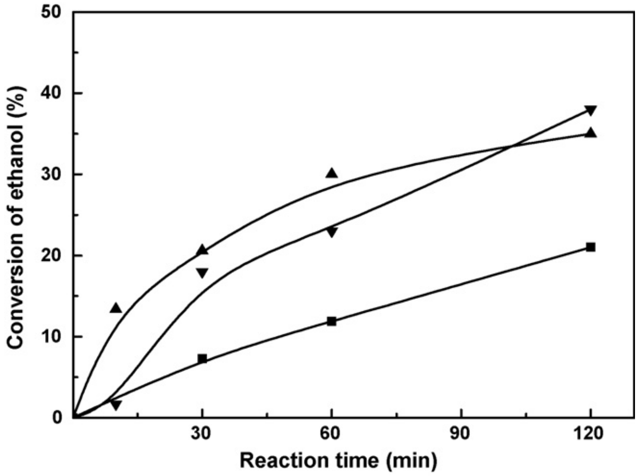

Fig. 6. Comparison of ethanol oxidation in systems of typical homogenous Fenton catalyst (5 ppm of Fe^{2+}, 20 ml of ethanol (100 ppm), 1 ml of 30% H_2O_2, pH of 5.0 acidified with HCl) at room temperature (▲) and 70 °C (▼), and Mn_3O_4/SBA-15 catalyst (■) under conditions of 20 ml of ethanol (100 ppm), pH of 6.7, 1 ml of 30% H_2O_2, 70 °C and 5 mg of catalyst.

3.2.6. Decomposition of H_2O_2

In the aqueous solution, metal ions such as Fe^{2+} and Mn^{2+} have long been evidenced in the decomposition of H_2O_2 to produce the hydroxyl radical ($^{\bullet}OH$), which is oxidant for the complete oxidation of ethanol [9,17]. Therefore, ethanol oxidation is supposed to be affected by H_2O_2 decomposition. The investigation of H_2O_2 decomposition has been performed under the reaction conditions (ethanol-free) with different catalysts. As we introduced in Section 2, H_2O_2 was introduced into the reaction system by three intervals, initially 0.5 ml followed by twice 0.25 ml at 32 and 62 min, the pH of 6.7 is set for all experiments except pH of 5.0 for Fe^{2+}. As shown in Fig. 7, using Mn_3O_4/SBA-15, we observed that H_2O_2 (ca. 90%) rapidly

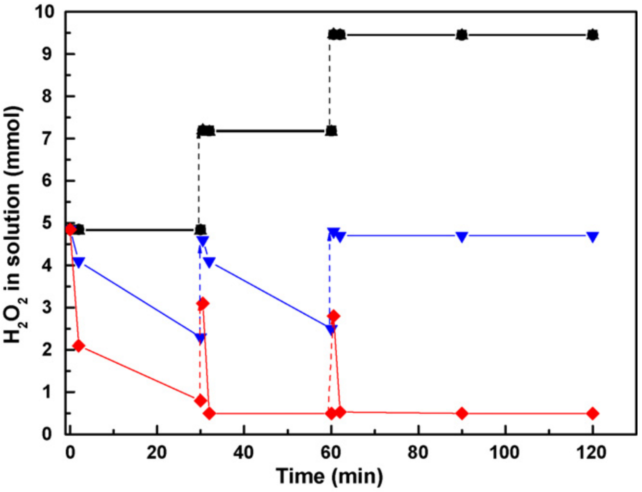

Fig. 7. An investigation of H_2O_2 decomposition under different conditions. One milliliter of 30% H_2O_2 was dropped into the 20 ml deionized water by three intervals, initial 0.5 ml followed by twice 0.25 ml at 32 and 62 min. H_2O_2 concentration vs. time: by calculation (■), without catalyst (●), SBA-15 (▲), 5 ppm of Fe^{2+} (▼) and Mn_3O_4/SBA-15 (♦). Rest conditions: 5 mg of solid catalyst, pH of 7.0 (5.0 for Fe^{2+}), 70 °C.

decomposed, but it doesn't occur for the systems of catalyst-free and bare SBA-15 (5 mg). Those results suggest that catalytic decomposition of H_2O_2 is mainly caused by Mn_3O_4 nanoparticles. Comparatively, the rate of H_2O_2 decomposition is relatively slow for the homogenous Fenton reagent, total conversion of H_2O_2 was ca. 50% after running for 120 min. The similar behavior of H_2O_2 decomposition was also observed for all catalysts during ethanol oxidation. It is interesting to note that the rate for ethanol oxidation is lower for Mn_3O_4/SBA-15 comparing to the conventional Fenton reagent.

4. Discussion

In general, the wet peroxide oxidation of organic constitutes has been suggested to proceed via four steps [15]: activation of H_2O_2 to produce $^\bullet OH$, oxidation of organic compounds with $^\bullet OH$, recombination of $^\bullet OH$ to form O_2 and wet oxidation of organic compounds with O_2. It can be further described by the following equations:

$$H_2O_2 \xrightarrow{\text{catalyst/temperture}} 2^\bullet OH \qquad (1)$$

$$^\bullet OH + \text{organic compounds} \xrightarrow{\text{temperature}} \text{product} \qquad (2)$$

$$2^\bullet OH \xrightarrow{\text{temperature}} 1/2O_2 + H_2O \qquad (3)$$

$$O_2 + \text{organic compounds} \xrightarrow{\text{temperature/pressure}} \text{product} \qquad (4)$$

The reactive intermediates produced from step 1 (Eq. (1)) participate in the oxidation through step 2 (Eq. (2)). Hasan et al. [22] have identified that the rate for H_2O_2 decomposition will increase with the rise of temperature over various MnO_x-based catalyst. In fact, several kinds of radical including $^\bullet OH$, perhydroxyl radicals ($^\bullet HO_2$) and superoxide anions ($O_2{}^-$) may be created during reaction. Previous studies [22–24] suggested that the process for producing radicals could be described by Eqs. (5)–(7) when H_2O_2 was catalytically decomposed by metal ions, such as Fe and Mn:

$$S + H_2O_2 \rightarrow S^+ + OH^- + {}^\bullet OH \qquad (5)$$

$$S^+ + H_2O_2 \rightarrow S + {}^\bullet OH_2 + H^+ \qquad (6)$$

$$^\bullet OH_2 \leftrightarrow H^+ + O_2{}^- \qquad (7)$$

where S and S^+ represent reduced and oxidized metal ions. It has been proposed [22] that the decomposition of H_2O_2 on MnO_x surface is likely performed over Mn^{3+}/Mn^{4+} ionic couples. Note that both the $^\bullet HO_2$ and $O_2{}^-$ are not stable and react further with H_2O_2 to form $^\bullet OH$ through the following equation:

$$^\bullet HO_2 + H_2O_2 \rightarrow {}^\bullet OH + H_2O + O_2 \qquad (8)$$

$$O_2{}^- + H_2O_2 \rightarrow {}^\bullet OH + OH^- + O_2 \qquad (9)$$

Presently, $^\bullet OH$ radical has been suggested to be the main intermediate responsible for oxidation/degradation of organic compounds. Therefore, the rate for ethanol oxidation in the studied system is assumed to be dependent on the concentration of $^\bullet OH$ in the solution.

According to Wolfenden's study [25], we envisaged that the complete oxidation of ethanol may proceed through a route like Eq. (10):

$$C_2H_5OH + {}^\bullet OH \xrightarrow{-H_2O} {}^\bullet C_2H_4O \xrightarrow{^\bullet OH} CO_2 + H_2O \qquad (10)$$

whereby, it is believed that organic radicals containing hydroxy-groups α and β to carbon radicals centre can eliminate water to form oxidizing species. With the degrading of organic intermediates step-by-step as the way described in Eq. (10), the final products should be CO_2 and H_2O. However, no other species but ethanol was detected by GC and GC–MS in the present study possibly due to the rapid of the reaction that leads to unstable intermediate.

Fig. 2 indicates that a proper ratio of catalyst/solution is a necessary factor to attain the high reaction rate. It can be understood that over exposure H_2O_2 to catalyst will increase the rate for H_2O_2 decomposition. On the other hand, more $^\bullet OH$ radical produced may be scavenged by catalyst with increasing the amount of catalyst, and it will be transformed into O_2 and H_2O as expressed in Eq. (3), instead of participating in the oxidation reaction. This may explain well the decrease of reaction rate with the rise of ratio of catalyst/solution in the system, because $[^\bullet OH]$ in the solution is not proportional to the amount of catalyst due to scavenging. The same reason may also explain the decrease of reaction rate with prolonging the time, because the intermediates concentration could be gradually reduced with the time. Actually, the H_2O_2 decomposition (ca. 90%) over the Mn_3O_4/SBA-15 catalyst may be completed within a few minutes according to Fig. 7, irrespective of the amount of catalyst (not shown for the sake of brevity); in contrast, the rate for H_2O_2 decomposition became dawdling for Fe^{2+} catalyst. This may lead to a relative high concentration of radicals in the homogenous Fenton system that shows superior reactivity to the presented system as depicted in Fig. 6. Therefore, reducing scavenging radicals, especially in the heterogeneous Fenton reagent system [21], is believed to be crucial for enhancing the reaction rate.

On the other hand, as illustrated by Eqs. (1)–(4), all steps in the oxidation process are affected by the reaction temperature. Fig. 3 demonstrates that increasing temperature may significantly improve ethanol oxidation in the system of the Mn_3O_4/SBA-15–H_2O_2. It is possibly attributed to the increase of the rates for reactions in Eqs. (2) and (4) at elevated temperatures.

In terms of Eqs. (6) and (7), acidic conditions may detain the H_2O_2 decomposition but improve the formation of $^\bullet OH$ (Eqs. (5), (8) and (9)). In several previous studies [18,19], the proton role in stabilizing of H_2O_2 has been elucidated. As a result, ethanol oxidation could be largely improved in the strong acidic environment. Fig. 4 shows a maximum rate at pH of 2.0 and the lowest at pH of 9.0. However, it is reported that dissolution of MnO_x to form Mn^{2+} can occur in the acid solution, exactly $pH < 5.0$ [26]. That means the surface of MnO_x crystals will be deteriorated in the slight acid solution with prolonging the reaction. It will be not acceptable for application since the metal ions result in new source of pollution. With considering all factors effacing this reaction, the pH ranging from 5.0 to 7.0 is suitable for the current process.

Interestingly, a different behavior for the decomposition of H_2O_2 was observed for Fe^{2+} and Mn_3O_4/SBA-15, see Fig. 7. Obviously, the rate for H_2O_2 decomposition catalyzed by Fe^{2+} is lower than that by Mn_3O_4/SBA-15. Due to the strong scavenging for Mn_3O_4/SBA-15, the concentration of intermediates such as $^\bullet$OH in Fe^{2+}–H_2O_2 system should be relatively high even under the same reaction conditions.

We observed that the reaction rate for ethanol oxidation is proportional to the concentration of ethanol in the range of 50–500 ppm, as shown in Fig. 5. It hints that most of the radicals might not take part in the reaction before scavenged by catalyst, especially at low concentration of ethanol, e.g., 100 ppm. With increasing the ethanol concentration, the possibility for the interaction between ethanol and radicals can be significantly increased. As a result, the rate of scavenging radicals is reduced relatively. Thus, it may explain the faster rate at higher concentration of ethanol in aqueous solution. However, several puzzles for this process still need to be answered, e.g., what is the role of the solid catalyst in the reaction except for producing radicals? Does the oxidation occur on the catalyst surface or solely in the liquid phase as well as in homogenous Fenton process? Obtaining more insights of those questions will help us to establish more accurate kinetic models in the future.

5. Conclusions

In the present study, we have addressed a new catalytic system fitting for remediation of trivial organic compound in aqueous solution with H_2O_2. A nano-composite catalyst, Mn_3O_4/SBA-15, has exhibited well performance in the oxidation of ethanol. Under a typical reaction condition of pH of 6.7, 70 °C, 1 (g_{Mn})/30 (l) ratio of catalyst/solution, and 400/1 of the molar ratio of H_2O_2/ethanol, the reaction rate could be 0.33 mmol/g_{Mn} min at 30 min and decreased to 0.23 mmol/g_{Mn} min after running for 120 min. Experimental data revealed that the reaction could be strongly affected by several factors. It was observed that the reaction rate for ethanol oxidation could be significantly reduced with increasing the amount of catalyst and the reaction time. On the other hand, the reaction was found to be favored under the conditions of strong acidic environment and elevated temperatures. The reaction rate was also observed to be dependant on the concentration of ethanol. The plausible mechanisms for the ethanol oxidation and H_2O_2 decomposition during reaction have been suggested. Comparing with a typical homogenous Fenton system, Fe^{2+}–H_2O_2, ca. 60% of reactivity was observed for the presented Mn_3O_4/SBA-15–H_2O_2 system.

Acknowledgement

Authors like to acknowledge the funding for this work by ICES, A*STAR, Singapore.

References

[1] Y.I. Matatov-Meytal, M. Sheintuch, Ind. Eng. Chem. Res. 37 (1988) 309.
[2] J. Donglagic, J. Levec, Enviro. Sci. Technol. 32 (1998) 1294.
[3] J. Levec, A. Pintar, Catal. Today 24 (1995) 51.
[4] A. Santos, P. Yustos, A. Qiutanilla, G. Ruiz, F. Garcia-Ochoa, Appl. Catal. B: Environ. 61 (2005) 323.
[5] S. Gopalan, P.E. Savage, AIChE J. 41 (1995) 1864.
[6] T.D. Thornton, P.E. Savage, Ind. Eng. Chem. Res. 31 (1992) 2451.
[7] A. Pintar, Catal. Today 77 (2003) 451.
[8] G. Centi, S. Perathoner, T. Torre, M.T. Verduna, Catal. Today 55 (2000) 61.
[9] E.V. Kuznetsova, E.N. Savinov, L.A. Vostrikova, V.N. Parmon, Appl. Catal. B: Environ. 51 (2004) 165.
[10] D. Duprez, F. Delanoë, J. Barbier Jr., P. Isnard, G. Blanchard, Catal. Today 29 (1996) 317.
[11] J. Qin, Q. Zhang, K.T. Chuang, Appl. Catal. B: Environ. 29 (2001) 115.
[12] H. Chen, A. Sayari, A. Adnot, F. Larachi, Appl. Catal. B: Environ. 32 (2001) 195.
[13] S. Hamoudi, F. Larachi, A. Sayari, J. Catal. 177 (1998) 247.
[14] A.M.T. Silva, I.M. Castelo-Branco, R.M. Quinta-Ferreira, J. Levec, Chem. Eng. Sci. 58 (2003) 963.
[15] B. Karl, G. Karl-Heinz, L. Gerhard, S. Hermann, Y. Farsin, WO 95/30627 (1995).
[16] S.B. Kanungo, K.M. Parida, B.R. Sant, Electrochim. Acta 26 (1981) 1157.
[17] M.J. Stoltz, S.R. Temple, US Patent 6,645,450 (2003).
[18] Y.-F. Han, J.H. Lunsford, Catal. Lett. 99 (2005) 13.
[19] Y.-F. Han, J.H. Lunsford, J. Catal. 230 (2005) 322.
[20] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[21] Y.-F. Han, F. Chen, Z.-Y. Zhong, K. Ramesh, E. Widjaja, L.-W. Chen, Catal. Commun. 7 (2006) 739.
[22] M.A. Hasan, M.I. Zaki, L. Pasupulety, K. Kumari, Appl. Catal. A: Gen. 181 (1999) 171.
[23] C.M. Miller, R.L. Valentine, US Patent 5,817,240 (1998).
[24] N. Kitajima, S.-I. Fukuzumi, Y. Ono, J. Phys. Chem. 82 (1978) 1505.
[25] B.S. Wolfenden, R.L. Wilison, J. Chem. Soc., Pekin Trans. II (1982) 805.
[26] S. Bakardjieva, P. Bezdička, T. Grygar, J. Solid State Electrochem. 4 (2000) 306.