

Research Article

Improvement the Activity and Selectivity of Fenton System in the Oxidation of Alcohols

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The reactivity and selectivity of Fenton system ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) were improved with N-hydroxyphthalimide (NHPI) as cocatalyst. The oxidation process of benzyl alcohol to benzaldehyde has been studied. The reaction catalyzed by this new $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{NHPI}$ system can be well performed under room temperature without adding any organic solvent. Besides, this catalyst system is effective for the oxidation of different alcohols.

1. Introduction

The Fenton reagent is a simple catalyst system which is composed of Fe^{2+} and H_2O_2 . In the reaction process with Fenton's reagent, the hydroxyl radicals are generated rapidly at the presence of ferrous ion. This catalyst system is proved to be successful for the treatment of organic pollutants in industrial wastewater [1–12]. There are numerous reports concerning pretreatment option to improve the biodegradability of complex wastes and recalcitrant from industry wastewater and landfill leachate [2–4]. The original pollutants are often transformed to CO_2 and H_2O due to the strong oxidizing property of the Fenton system [4–7]. In recent studies, Fenton system is coupled with other methods, such as membrane filtration and coagulation, to degrade organic compounds to a larger extent [8, 9]. Besides, the Fenton reagent is also effective in light alcohols and alkane's oxyfunctionalization [10, 13], but the application for selective oxidation is rare [11, 12].

The Fenton system has wonderful water solubility and there are abundant ferrous irons on the earth. Thus, it is possible to develop a mild and inexpensive water phase oxidation process using this system. Despite its numerous advantages, one limitation of traditional Fenton's reagent must be taken into account: its high oxygen reactivity, which often leads to deep oxidation [5, 6, 14–16]. To apply the Fenton system in chemical synthesis, the most crucial problem is how to

control its reactivity and enhance its selectivity. The efficiency of Fenton's reagent is affected by various factors, such as pH, the counterion of Fe^{2+} , solvent, iron chelation, UV, and microwaves, which control the oxidation reactivity and regeneration ability of Fe^{2+} from Fe^{3+} [4, 17–20]. In addition, it has been found that the additives play a vital role to change the reactivity of Fenton system [13, 21–23]. For example, the reaction with KH_2PO_4 as additive provided high conversion and good selectivity in the oxidation of benzyl alcohol [13].

The objective of this study is to control the reactivity of Fenton system and enhance its selectivity. Based on a detailed investigation on a series of additives, we have found that the reactivity of Fenton system can be well controlled and the benzyl alcohol oxidation can be performed with good selectivity at room temperature in water.

2. Experimental

All the chemicals were obtained with purities higher than 99%. A typical experiment was carried out in a water bath. The alcohol (20 mmol), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (0.5 mmol), and NHPI (0.5 mmol) were added to a glass reactor. 44 mmol H_2O_2 (30 wt% in water, 4.5 mL) was added with a syringe pump by 0.2 mL/min speed in 30 min. The reaction mixture was vigorously stirred (about 750 rpm). Reaction mixtures were analyzed using GC and GC-MS.

TABLE 1: Effect of additives for the oxidation of benzyl alcohol to benzaldehyde at 70°C^a.

Entry	Catalyst	Amount ^b (mol%)	Conv. (%)	Sel. ^c (%)
1	FeSO ₄ /NaBF ₄	2.5%/1%	66.6	94.5 (89 : 11)
2		2.5%/10%	71.0	94.3 (88 : 12)
3		2.5%/1%	74.7	96.0 (87 : 13)
4	FeSO ₄ /NaH ₂ PO ₄	2.5%/5%	2.0	96.5 (87 : 13)
5		2.5%/10%	1.6	93.3 (93 : 7)
6		2.5%/1%	64.1	95.9 (90 : 10)
7	FeSO ₄ /KH ₂ PO ₄	2.5%/2.5%	4.4	95.1 (92 : 8)
8		2.5%/5%	1.9	89.2 (88 : 12)
9	FeSO ₄ /KHP ^d	2.5%/1%	51.3	94.7 (82 : 18)
10		2.5%/2.5%	32.8	86.7 (92 : 8)

^a20 mmol of benzyl alcohol (2.16 g), 2.2 equiv. of H₂O₂ (44 mmol, 4.5 mL, 30 wt% in water), reaction time: 0.5 h. H₂O₂ was added with a syringe pump by 0.2 mL/min speed. ^bAmount of catalyst. ^cTotal selectivity to benzaldehyde and benzoic acid. Value in parentheses means the ratio of benzaldehyde/benzoic acid. ^dKHP: potassium hydrogen phthalate.

TABLE 2: Effect of additives for the oxidation of benzyl alcohol to benzaldehyde at 25°C^a.

Entry	Catalyst	Amount ^b (mol%)	Time (h)	Conv. (%)	Sel. ^c (%)
1	FeSO ₄ /NaH ₂ PO ₄	2.5%/1%	0.5	3.8	95.9 (91 : 9)
2			2	8.6	95.1 (90 : 10)
3			4	9.5	91.2 (90 : 10)
4	FeSO ₄ /NaH ₂ PO ₄	2.5%/2.5%	0.5	1.1	98.2 (92 : 8)
5			2	1.9	98.2 (93 : 7)
6	FeSO ₄ /NaH ₂ PO ₄	2.5%/10%	0.5	1.1	98.8 (92 : 8)
7			19	1.3	98.9 (91 : 9)
8	FeSO ₄ /KBr	2.5%/10%	0.5	3.4	100 (89 : 11)
9	FeSO ₄ /NaBF ₄	2.5%/10%	0.5	1.7	>99.9 (100 : 0)
10	FeSO ₄ /KH ₂ PO ₄	2.5%/2.5%	0.5	1.2	98.3 (93 : 7)
11	FeSO ₄ /N ₁₁₁ Gly	2.5%/2.5%	0.5	20.6	91.7 (96 : 4)
12	FeSO ₄ /N ₂₁₁ OAc	2.5%/2.5%	0.5	25.7	98.4 (87 : 13)
13	FeSO ₄ /[HMIM][HSO ₄]	2.5%/10%	0.5	1.3	>99.9 (100 : 0)

^a20 mmol of benzyl alcohol, 2.2 equiv. of H₂O₂ (30 wt% in water). H₂O₂ was added with a syringe pump by 0.2 mL/min speed. ^bAmount of catalyst. ^cTotal selectivity to benzaldehyde and benzoic acid. Value in parentheses means the ratio of benzaldehyde/benzoic acid.

Different reaction conditions (temperature, concentration, Fe salt, and speed of adding H₂O₂) have been optimized. Limited by the length, these results were listed in the Supplementary data (Figures S1 and S2 and Tables S1-S2) (see Supplementary Material available online at <http://dx.doi.org/10.1155/2014/823054>).

3. Results and Discussion

3.1. The Influence of Different Additives. It has been revealed that some additives (such as KH₂PO₄ and KHSO₄) to Fenton system can lead to a more effective oxidizing process at 70°C [13]. The role of KH₂PO₄ was to control the pH of the solution which can change the rate to generate hydroxyl radicals. As a result, the selectivity of the reaction was enhanced [13]. Encouraged by this idea, we have tried to further improve the reaction by adding different inorganic buffers in Fenton system. The influence of different additives (NaBF₄, NaH₂PO₄, KH₂PO₄, and KHP) at 70°C was studied (Table 1). Our results with KH₂PO₄ as additive were very close to those of a previous report [13]. It seems that the adding of NaBF₄, NaH₂PO₄, or KHP cannot give better results.

Performing reaction at room temperature is beneficial to save energy and develop safe process. The performance of these inorganic buffers was investigated at 25°C. Unfortunately, the reactivity of these catalyst systems is quite poor at room temperature (Table 2, entries 1–10). Though good selectivity can be obtained, the conversion is quite low. Increasing reaction time or changing the amount of additive could not improve the results at all.

Though ionic liquids have shown attractive role in improving the reactivity of oxidation system [24–27], it seems that this compound cannot cooperate well with Fenton system (Table 2, entries 11–13). The conversion with [HMIM][HSO₄] (hexylmethylimidazole hydrosulfate) as additive is only 1.3% at 25°C. Adding N₁₁₁Gly (tetramethylammonium glycinate) or N₂₁₁OAc (trimethylethylammonium acetate) can accelerate the reaction, but the selectivity is also not so good.

3.2. NHPI/FeSO₄ Oxidation Process. How to improve the selectivity of Fenton system and maintain its reactivity at the same time are a challenge. To solve this problem and find out an excellent additive, the classical free radical mechanism

TABLE 3: Oxidation of benzyl alcohol with different catalyst systems at 25 °C^a.

Entry	Catalyst	Amount ^b (mol%)	Conv. (%)	Sel. ^c (%)
1	FeSO ₄ /NHPI	2.5%/2.5%	36.7	99.1 (94 : 6)
2		2.5%/1.25%	36.0	98.2 (92 : 8)
3		2.5%/5.0%	31.8	95.9 (90 : 10)
4	FeSO ₄ /TEMPO	2.5%/2.5%	20.5	98.9 (96 : 4)
5	FeSO ₄ /4-OH-TEMPO	2.5%/2.5%	13.9	99.6 (99 : 1)
6	Fe ₂ (SO ₄) ₃ /NHPI	2.5%/2.5%	32.1	95.2 (87 : 13)
7	Fe(NO ₃) ₃ /NHPI	2.5%/2.5%	59.9	94.2 (82 : 18)
8	FeCl ₃ /NHPI	2.5%/2.5%	43.3	87.6 (84 : 16)

^a20 mmol of benzyl alcohol, 2.2 equiv. of H₂O₂ (30 wt% in water), reaction time: 0.5 h. H₂O₂ was added with a syringe pump by 0.2 mL/min speed. ^b Amount of catalyst. ^cTotal selectivity to benzaldehyde and benzoic acid. Value in parentheses means the ratio of benzaldehyde/benzoic acid.

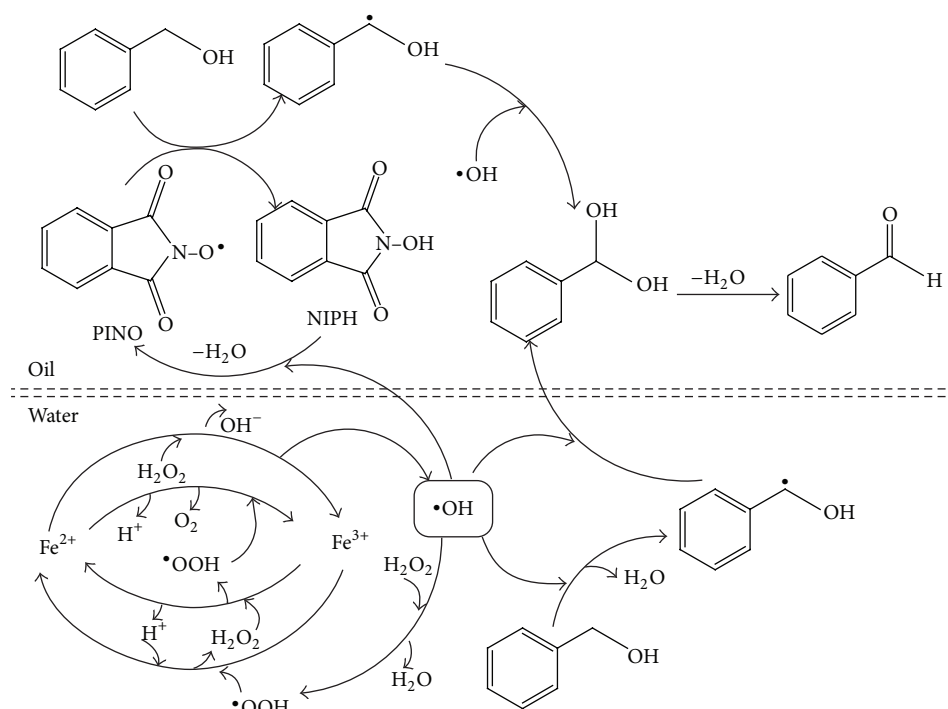
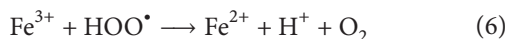
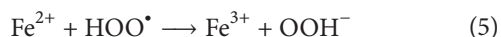
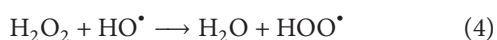
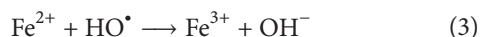
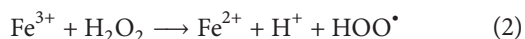
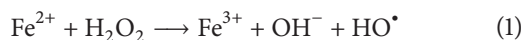


FIGURE 1: Proposed mechanism for the oxidation of benzyl alcohol using NHPI/Fenton system.

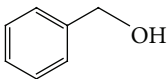
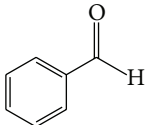
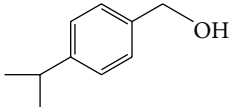
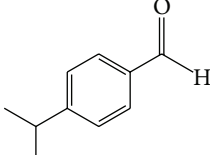
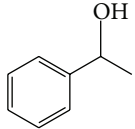
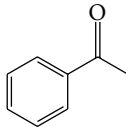
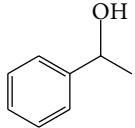
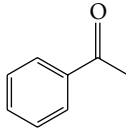
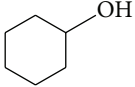
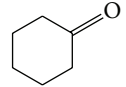
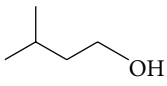
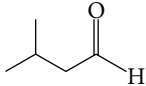
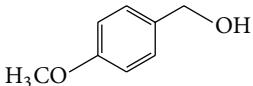
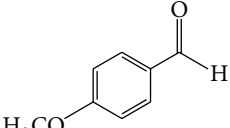
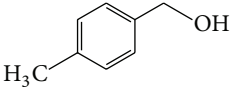
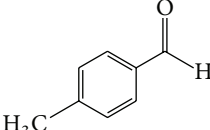
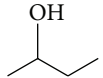
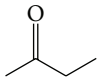
of Fenton system was carefully analyzed. The whole radical reaction process of Fenton system is shown as follows [28–30]:



Hydroxyl radical was generated in water phase by a series of complex reactions; then hydroxyl radical can abstract

a hydrogen atom from alcohols to form alkyl radicals. If large numbers of hydroxyl radicals accumulate without control, this may cause deep and nonselective oxidation [31]. Therefore, we believed that there should be at least two ways to improve reaction selectivity of Fenton system. One is to control the generation rate of hydroxyl radicals, and the other is to reduce the accumulation of nonselective hydroxyl radicals and convert them to radicals with higher selectivity, such as phthalimide N-oxyl (PINO), which has been widely used in oxidation reaction [32–35]. Adding inorganic buffers can change the pH of reaction mixture and control the generation rate of radicals. This is the first way mentioned above and it has been widely investigated [13, 18–23]. Selectivity can be enhanced by this way, but the catalytic activity of this system is quite low at room temperature (Table 2).

TABLE 4: Oxidation of several alcohols^a.

Entry	Substrate	Temp. (°C)	Product	Con. (%)	Sel. (%)
1		25		36.7	93.6
2		25		4.3	>99.9
3		25		12.3	>99.9
4		55		50.5	>99.9
5		55		4.8	>99.9
6		55		13.3	90.0
7		55		49.3	97.5
8		55		41.1	96.0
9		55		54.8	82.5

^aCatalyst: FeSO₄/NHPI, 20 mmol of benzyl alcohol, 2.2 equiv. of H₂O₂ (30 wt% in water), reaction time: 0.5 h. H₂O₂ was added with a syringe pump by 0.2 mL/min speed.

So far, there is no report about the second way. If a method can be developed to achieve the second way, the selectivity should be improved without losing catalytic activity. There are two keys to successfully develop this method: first, the additive should mainly exist in the organic phase, which can avoid possible influence on the Fenton system induced by the additive; second, the additive can react with hydroxyl radicals to generate other radicals with high oxidation selectivity quickly (Figure 1). N-Hydroxyphthalimide (NHPI) is an excellent choice under these two restrictions, and PINO radical can be generated from NHPI, which has been proven to be catalyst with high oxidation selectivity [32–35]. Then, the effect of NHPI as additive was studied. Indeed, the result is satisfying as expected. Both the selectivity and conversion

are obviously improved by adding NHPI (Table 3, entries 1~3). TEMPO (2,2,6,6-tetramethylpiperidinoxy) and 4-OH-TEMPO (4-hydroxy-TEMPO) also gave better conversion and selectivity comparing with those using inorganic buffers. However, the conversion with TEMPO or 4-OH-TEMPO is lower than that with NHPI. The reactivities of different iron salts were evaluated in the oxidation of benzyl alcohol (Table 3). Obviously, FeSO₄·7H₂O cooperating with NHPI gives the highest selectivity in comparison with Fe₂(SO₄)₃, Fe(NO₃)₃·9H₂O, and FeCl₃.

3.3. Oxidation of Several Alcohols. To investigate the universality of NHPI/FeSO₄/H₂O₂ system, oxidations of different alcohols were performed (Table 4). Most of these oxidations

gave good results. Though the result of benzyl alcohol is satisfying at 25°C, the converting rates of 4-isopropyl benzyl alcohol and α -phenylethyl alcohol are a little low at 25°C, which may be caused by the replacement of electron donating groups. The conversion of α -phenylethyl alcohol achieved 50.5% at 55°C with excellent selectivity. It should be noted that ortho substituent and bulky groups may also reduce the reaction rate (Table 4, entries 5 and 6). 4-Methoxybenzyl alcohol and 4-methylbenzyl alcohol were tested at 55°C because of the high melting points, and the results were fairly satisfactory (Table 4, entries 7~8). However, the selectivity of the 2-butanol oxidation is a little poor with this catalyst system.

4. Conclusion

To improve the selectivity of Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) in oxidation reaction, the cooperation between Fenton reagent and a series of additives has been investigated. It was found that the reactivity and selectivity of Fenton system were improved with NHPI as cocatalyst. The oxidation of benzyl alcohol catalyzed by this new $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{NHPI}$ system can be well performed under room temperature without adding any organic solvent. Besides, this catalyst system is effective for the oxidation of different alcohols. We hope the catalyst systems developed here provide a new way for a green, innocuous, and cheap candidate for the oxidation of alcohols and similar compounds.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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