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Highly selective oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide by biphasic catalysis

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ABSTRACT

An environmentally benign oxidation of benzyl alcohol to benzaldehyde with hydrogen peroxide as oxidant and metal dodecanesulfonate salts as catalysts was conducted under solvent-free condition by biphasic catalysis. Ferric tridodecanesulfonate showed excellent catalytic activity exhibiting complete conversion of benzyl alcohol with 194.4 $\text{mol/mol}_{\text{cat}}$ turnover number (TON) and nearly 100% selectivity to benzaldehyde at ambient pressure and 90 °C. This catalyst can be recovered and reused for three times without a significant loss in its activity and selectivity.

1. Introduction

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic synthesis. Benzaldehyde (BzH), a typical product of alcohol oxidation, is very important chemical used as starting material for the preparation of intermediates in perfumery, pharmaceutical, dyestuff and agrochemical industries. The conventional routes for synthesis of BzH include hydrolysis of benzal chloride and the liquid phase oxidation of toluene [1]. In the former process, traces of chlorine inevitably exist in the product BzH, and in the latter, the selectivity to BzH is very poor. In order to meet practical requirements of chlorine-free BzH for perfumery and pharmaceutical industries, vapor phase oxidation of benzyl alcohol (BzOH) has been extensively investigated in the past [2,3]. The limitation of this process is loss of carbon due to total oxidation of a part of BzOH into carbon dioxide at high temperature. Therefore, the liquid phase oxidation of BzOH into BzH at lower reaction temperature is more convenient.

H_2O_2 is widely used in liquid oxidation of organic compounds due to its clean and environmentally friendly nature. Consequently, many efforts have been made on the liquid phase oxidation of BzOH into BzH using H_2O_2 as oxidant and heteropoly acids as homogeneous catalysts [4–10]. Although these catalysts exhibit good catalytic activity in liquid phase oxidation, but the separation of catalyst from the homogeneous system is difficult. Recently, the catalytic oxidation of BzOH into BzH using $[C_7H_7N(CH_3)_3]_3PMo_4O_{16}$ as reaction-controlled phase-transfer catalyst and H_2O_2 as oxidant has been reported [11]. Wang et al [12] demonstrated the oxidation of cyclohexanol, BzOH and other alcohols with aqueous hydrogen peroxide using mono-substituted Keggin–polyoxometalate complexes as effective catalyst in biphasic system. The liquid phase oxidation of BzOH and other alcohols catalyzed by "sandwich" type transition metal substituted polyoxometalates has also been investigated [13]. In addition, methyltrioxorhenium can also catalyze the oxidation of alcohol into aldehydes or ketones in good yield using H_2O_2 as oxidant [14,15]. These catalysts showed good catalytic activity with recycling ability. However, there are also some drawbacks such as low conversion, selectivity for BzH and bulk organic volatile solvents used. There is, therefore, still a need to develop a new catalytic system and/or an easy-clean technology more suitable for the liquid phase synthesis of BzH.

We have developed aqueous hydrogen peroxide-benzyl alcohol biphasic catalytic oxidation of BzOH into BzH using ferric tridodecanesulfonate as catalyst and the results are presented in this paper.

2. Experimental

2.1. Preparation of the catalyst

Dodecanesulfonate salts of metals were prepared using the reported method [16]. 1.96 g (7.2 mmol) of sodium dodecanesul-

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Table 1
Catalytic activity of various dodecanesulfonate salts.[a]

Entry	Catalysts (0.25 mmol)	Conversion (%)	TON (mol/mol$_{cat}$)
1	Fe(DS)$_3$	100	194.4
2	Cu(DS)$_2$	47.3	92.0
3	Ni(DS)$_2$	7.8	15.2
4	Sn(DS)$_2$	4.0	7.8

[a] Reaction conditions: ratio of H_2O_2 to alcohol (0.22/0.0486) 4.5/1, catalyst 0.2 g, reaction temperature 90 °C, reaction time: 6 h, and stirring speed 250 rpm.

fonate salt was added to 70 mL of distilled water and mixed in a three-necked flask fitted with a reflux condenser and magnetic stirrer. The reaction mixture was stirred and heated at 70 °C on a preheated water bath to form homogeneous solution. A solution of 0.388 g (2.4 mmol) of $FeCl_3$ in 1 mL distilled water was charged into the above solution and stirred at the same temperature for 4 h. At the end of the reaction it was cooled to room temperature resulting orange precipitate which was collected by filtration under reduced pressure, washed and dried at 100 °C. Copper, nickel and tin dodecanesulfonate salts were also prepared following the same procedure.

2.2. Oxidation of alcohol

5 mL (48.6 mmol) of benzyl alcohol and 0.2 g (0.25 mmol) of ferric Dodecanesulfonate was added into a 50 mL three-necked flask fitted with a reflux condenser and magnetic stirrer. The reactor containing this mixture was heated to 90 °C in an oil bath with electric heater, and then 22.5 mL of 30% H_2O_2 (0.22 mol) was slowly dropped in. The resulting system was stirred with magnetic stirrer at 90 °C for 6 h. At the end of the reaction, the resulting products and unreacted substrate BzOH were extracted by benzene three times. The extracted liquid mixture was analyzed by GC and GC–MS.

3. Results and discussion

3.1. Catalytic activities of dodecanesulfonate salts

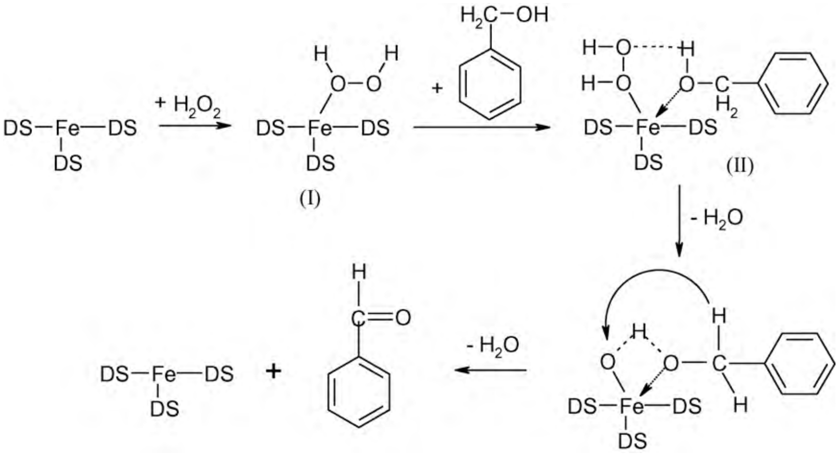
The catalytic activities of dodecanesulfonate salts $M(DS)_x$ [M = Fe^{3+}, Cu^{2+}, Ni^{2+} and Sn^{2+}, DS = dodecanesulfonate, x = 3 or 2] for the oxidation of BzOH were tested under solvent-free condition, and the results are summarized in Table 1. Among the dodecanesulfonate salts screened, Fe(DS)$_3$ showed a surprising high activity exhibiting nearly 100% conversion of BzOH and TON of 194.4 mol/mol$_{cat}$ (entry 1). Cu(DS)$_2$ showed lower activity with 47.3% conversion and TON of 92.0 mol/mol$_{cat}$ (entry 2). While Ni(DS)$_2$ and Sn(DS)$_2$ were found almost inactive for the oxidation of BzOH (entries 3 and 4). However, it was worthy to note that the $M(DS)_x/H_2O_2$ system was found to be nearly 100% selectivity as no other products were detected in the reaction mixture by GC–MS.

As described in documents [17,18], Lewis acid sites were believed as the active sites in catalytic oxidation of BzOH with H_2O_2 in water. The involved reaction mechanism is proposed in Scheme 1. Firstly, Fe Lewis acid site interacts with H_2O_2 to form Fe peroxo complex (I) and the complex further reacts with BzOH to give an intermediate (II) which gives BzH and regenerated active sites by two steps of dehydration. Consequently, the differences in catalytic activity between Fe(DS)$_3$, Cu(DS)$_2$, Ni(DS)$_2$ and Sn(DS)$_2$ shown in Table 1 should be attributed to their different Lewis acidity [19]. Because of water insolubility of BzOH and surface activity of the dodecanesulfonate salts, the aqueous-alcohol biphasic catalysis for oxidation of BzOH was successively established. In this case, H_2O_2 from aqueous phase and BzOH from alcohol phase may interact with the catalyst on the interphase to generate the product BzH. BzH so produced rapidly diffused into bulk of the organic phase as it is more soluble in organic phase than in water. In this way, the biphasic operation minimizes the over-oxidation of BzH into benzylic acid by reducing the contact opportunity between BzH in bulk organic phase and the catalyst on the interphase or H_2O_2 that is soluble in the aqueous phase. It resulted in highly selective oxidation of BzOH to BzH.

3.2. Effect of reaction conditions

Effect of amount of catalyst upon the oxidation of benzyl alcohol was studied by varying its amount from 0.05 g to 0.40 g, as shown in Fig. 1. The results indicated that the conversion of BzOH increased with increasing the amount of catalyst, which should be due to increase in Lewis acidic sites. Maximal conversion (ca.100%) was obtained when using 0.2 g of catalyst. The excess amount of the catalyst caused decrease of selectivity to BzH, which was likely attributed to further oxidation of BzH into benzoic acid catalyzed by the excess amount of Lewis acidity sites.

The conversion of BzOH and the selectivity to BzH using Fe(DS)$_3$ as catalyst at different reaction time are shown in Fig. 2, which indicated that the initial conversion of BzOH increased with the reaction processing and reached the maximal conversion of 100% after reaction for 6 h, and then remained stable. The selectivity to BzH remained ca. 100% in the range of reaction time from 1 h to 6 h. A slightly decrease of the selectivity observed at 7 h implied that the prolonged reaction time may also cause further oxidation of BzH into benzoic acid.



Scheme 1. Reaction mechanism (DS = $C_{12}H_{25}SO_3^-$).

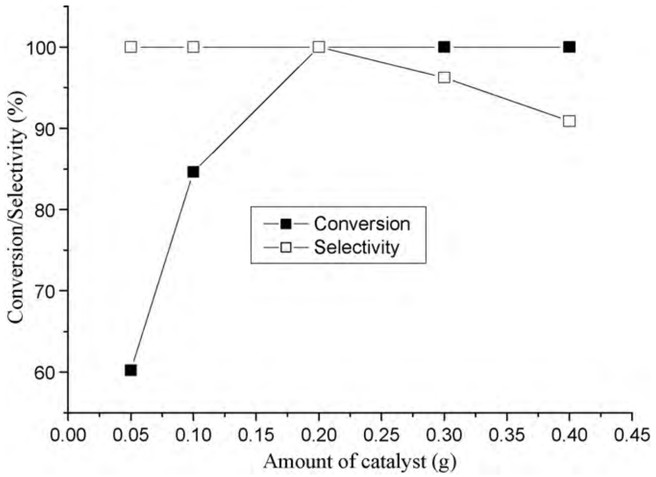


Fig. 1. Dependence of the conversion of BzOH and selectivity to BzH on amount of the catalyst. Reaction conditions: reaction temperature 90 °C, time 6 h, and molar ratio of H_2O_2 to alcohol 4.5:1.

It has been reported that reaction temperature has strong influence on the process of BzOH oxidation [20]. Effect of the temperature on the process of oxidation of BzOH was studied in the temperature range of 20–110 °C and the results are presented in Fig. 3. The results suggested that the conversion of BzOH increased with increasing the reaction temperature. The nearly 100% conversion of BzOH and TON of 194.4 mol/mol$_{cat}$ was achieved at 90 °C. The selectivity for BzH was almost unchanged, preserving ca. 100% in the whole range of the reaction temperatures. This finding exhibits that temperature rising can accelerate the reaction and has almost no impact on the selectivity for BzH in the temperature range from 20 °C to 110 °C. So the selective oxidation reaction is dominant when the reaction is conducted at higher temperature, resulting in a high conversion of BzOH and a high selectivity for BzH.

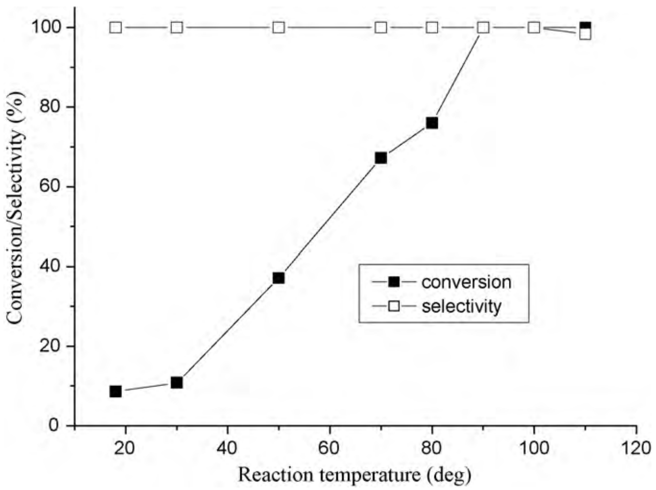


Fig. 3. The conversion of BzOH and selectivity to BzH at various reaction temperatures. Reaction conditions: reaction time 6 h, molar ratio of H_2O_2 to alcohol 4.5:1, and catalyst 0.2 g.

The amount of H_2O_2 used in this system is another important factor influencing the oxidation of alcohol. The effect of H_2O_2/BzOH molar ratio on the oxidation of BzOH into BzH was investigated and the results are shown in Fig. 4. The conversion increased with increasing the molar ratio of H_2O_2/BzOH. 100% conversion of BzOH and yield of BzH was obtained when the molar ratio of H_2O_2/BzOH reached at 4.5/1, and then with the ratio increasing the conversion and yield was completely unchanged in the range from 4.5/1 to 5.1/1. According to stoichiometry, one mole of H_2O_2 is required for oxidation of one mole of BzOH into BzH. The large excess amount of H_2O_2 is a result of its decomposition in the presence of the catalysts as 58.5–59.9% consumption of H_2O_2 was found when using $Fe(DS)_3$, $Cu(DS)_2$, $Ni(DS)_2$ and $Sn(DS)_2$ as catalysts, respectively. Therefore, oxygen released in the decomposition reaction plays no role in the oxidation of alcohol. No oxidation taking place by performing a reaction under similar conditions but using oxygen as oxidant should also confirm this conclusion.

In addition, stirring speed has a great influence on the oxidation of BzOH by biphasic catalysis. The effect of stirring speed was investigated at stirring speed of 100 and 250 rpm. The results showed that the conversion of BzOH greatly increased with increase in stirring speed. When the speed is 250 rpm the conversion is up to 100%, which is much higher than 58.7% at stirring speed of 100 rpm. This behavior suggested that the conversion of BzOH was strongly dependent on the dispersed extent of alcohol phase in aqueous phase, which promoted the mass transfer between the two phases.

In short, the effect of various reaction conditions on the catalytic oxidation of BzOH was investigated and the optimal operational

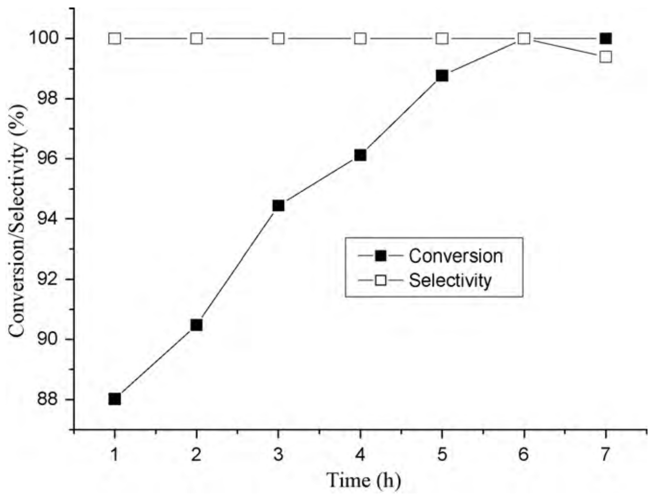


Fig. 2. The conversion of BzOH and selectivity to BzH as a function of reaction time. Reaction conditions: reaction temperature 90 °C, catalyst 0.2 g, and molar ratio of H_2O_2 to alcohol 4.5:1.

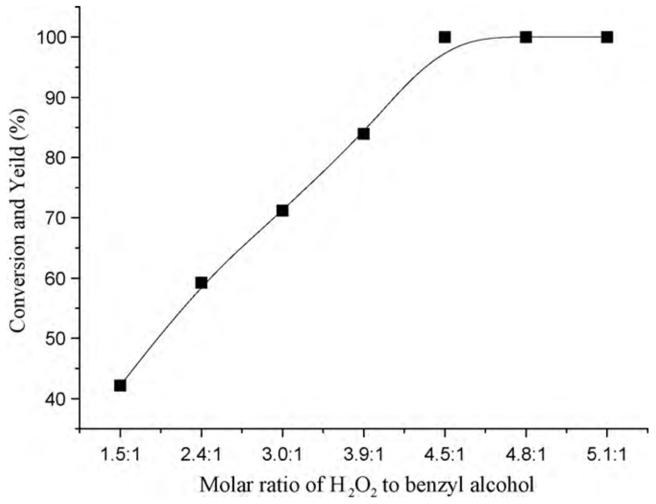


Fig. 4. The conversion of BzOH and selectivity to BzH at various molar ratio of H_2O_2 to BzOH. Reaction conditions: reaction temperature 90 °C, time 6 h, and catalyst 0.2 g.

Table 2
The experiment results for the oxidation of other alcohols.[a].

Entry	Alcohols	Yield (%)	Selectivity (%)
1	Propyl alcohol (PA)	84.0	85.6
2	Butanol (BA)	72.2	89.2
3	Amyl alcohol (AA)	72.2	88.9
4	Isobutanol (MBA)	46.6	89.7
5	Isoamyl alcohol (IAA)	37.0	89.5
6	Isopropyl alcohol (IPA)	20.8	86.9

[a] Reaction conditions: ratio of H_2O_2 to alcohol 4.5/1, catalyst 0.2 g, reaction temperature 90 °C, reaction time 6 h, and stirring speed 250 rpm.

Table 3
Reusage of the catalyst.[a].

Times	T (K)	Time (h)	Molar ratio of Bz/BC	Conversion (%)	Yield (%)
1	363	6	4.5:1	100	100
2	363	6	4.5:1	97.9	97.9
3	363	6	4.5:1	93.8	93.8
4	363	6	4.5:1	67.9	67.9

[a] Reaction conditions: ratio of H_2O_2 to alcohol (0.22/0.0486) 4.5/1, catalyst 0.2 (first run), reaction temperature 90 °C, reaction time: 6 h, and stirring speed 250 rpm.

conditions for the catalytic system were obtained: reaction temperature 90 °C, reaction time 6 h, H_2O_2/BzOH molar ratio 4.5/1, amount of the catalyst 0.2 g (0.25 mmol) and stirring speed 250 rpm. The complete conversion of BzOH with TON of 194.4 mol/mol$_{cat}$ and nearly 100% selectivity are achieved, giving ca. 100% yield of BzH under the optimal conditions.

3.3. *Oxidation of other fatty alcohols*

It was well known that the oxidation of BzOH is often used as a model reaction of alcohol oxidation due to its relatively higher reactivity. When other fatty alcohols such as propanol (PA), isopropanol (IPA), butanol (BA), isobutanol, amyl alcohol and isoamyl alcohol were used as alternatives of BzOH, the oxidation reactions were also examined in the presence of Fe(DS)$_3$ as catalyst (Table 2). Obviously lower reactivity for the oxidation of these primary alcohols, such as propanol, butanol and amyl alcohol, to corresponding aldehydes was observed under the same conditions with the yield range from 72.0 to 84.0%. The difference in reactivity between these alcohols and benzyl alcohol is ascribed to their different composition and structure. For the aliphatic secondary alcohols, isobutanol and isoamyl alcohol, the catalyst showed lower activity for their oxidation with the yields of 46.6% and 37.0%, respectively and the lowest active for isopropanol oxidation was found, which are likely due to the steric effect of secondary alcohols.

It is worthy to note that oxidation of butanol, isobutanol, amyl alcohol and isoamyl alcohol approached to biphasic catalysis due to their less solubility in water. However, the systems of propanol and isopropanol oxidation exhibited characteristic of analogously homogeneous catalysis due to easy solubility of them and their reaction products in water. Therefore, these catalytic systems showed relatively lower selectivity to their corresponding products than that of the oxidation of BzOH.

3.4. *Reusability of the catalyst*

In order to further evaluate performance of the catalyst, reuse experiments of the catalyst were carried out. The catalyst was precipitated out in aqueous phase when the extraction of organic phase to separate product from the biphasic system was carried out at the end of the reaction. The obtained precipitate was washed with benzene and water at 80 °C for 2 h, respectively. After dried, the catalyst was reused for the next run under the same conditions. The results as shown in Table 3 indicated that the activity of the catalyst was almost not affected even at the third run with the reused Fe(DS)$_3$. This phenomenon implied that the catalyst can be efficiently recovered and recycled. By this token, the catalyst possesses potential application foreground in industry.

4. Conclusion

Ferric dodecanesulfonate [Fe(DS)$_3$] was prepared and used as catalyst for the biphasic oxidation of Benzyl alcohol (BzOH) into Benzaldehyde (BzH) with hydrogen peroxide as oxidant under solvent-free condition. Fe(DS)$_3$ exhibited outstanding catalytic performance with complete conversion of BzOH or turnover number of 194.4 mol/mol$_{cat}$ and 100% of selectivity to BzH at 90 °C and ambient pressure for 6 h. This high activity and selectivity is likely ascribed to Lewis acidity of the catalyst and the nature of biphasic catalysis. However, the catalyst is cheap, easily recycled and reused that shows its highly potential application foreground in industry.

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