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The efficient catalytic oxidation of 2,3,6-trimethylphenol with air over composite catalyst to synthesize Vitamin E intermediate

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Abstract

2,3,5-Trimethylbenzoquinone (TMBQ)is a kind of crucial intermediate in the synthesis of Vitamin E, whose demand is increasing rapidly. The traditional synthesis method of TMBQ needs H_2O_2 or pure O_2 as the oxidant, which is expensive and needs much attention in the production, transportation and storage process. In order to overcome the issues, the green oxidant, air, has been developed in this work to prepare TMBQ for the first time. TMBQ was synthesized from 2,3,6-trimethylphenol (TMP) with the oxidant of air in the solvent of isoamylol catalyzed by composite catalyst of inorganic salts at one atmosphere pressure. The critical reaction parameters, including the ingredient of composite catalyst, reaction time, reaction temperature, stirring speed and the addition of ionic liquids were investigated in order to achieve the optimal reaction condition. TMBQ was obtained with the conversion of 100% and selectivity of 96.7% at 90 °C for 7–8 h at one atmosphere pressure, over the composite catalyst, the aqueous solution of $CuCl_2$, $FeCl_3$ and $MgCl_2$, with the help of ion liquid, 1-sulfobutyl-3-methylimidazole hydrochloride ([Bmim]Cl). Moreover, the catalyst could be recycled more than four times. Air is very cheap, abundant, eco-friendly and safe in production, transportation and storage process. The synthesis of TMBQ from TMP with air as oxidant at one atmosphere pressure has obvious advantages, which will bring new inspiration for the industrial production of TMBQ.

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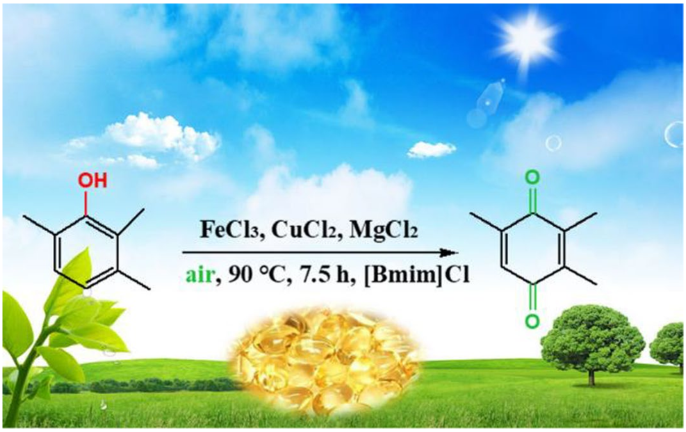
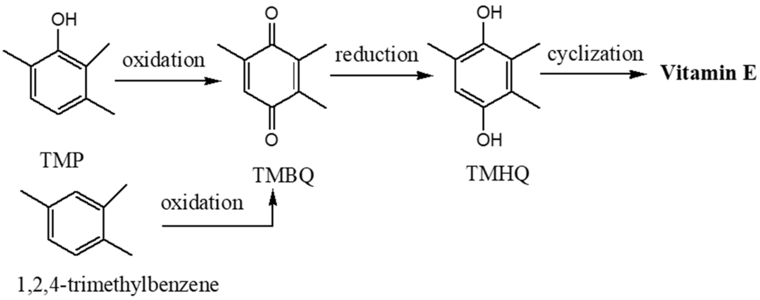
Graphic abstract



Keywords 2,3,6-Trimethylphenol · 2,3,5-trimethylbenzoquinone · Air oxidation · Catalysis · Ionic liquid

Introduction

Vitamin E, also known as α-tocopherol, is a kind of fat soluble vitamin, which widely exists in green plants and slightly in animals [1]. The deficiency of Vitamin E could cause muscle atrophy and other diseases [2]. Vitamin E is widely used as nutrients, antioxidants and additives of drugs and feed, and its demand is increasing rapidly in recent decades [3]. As the natural Vitamin E is very limited, the demand for synthetic Vitamin E is rapidly increasing. 2,3,5-Trimethylbenzoquinone (TMBQ) is an essential intermediate for the synthesis of Vitamin E [4–7]. The industrial production of Vitamin E needs several steps with corresponding key intermediates (Scheme 1). Thereinto, TMBQ is the inevitable intermediate which has two mainly reported industrial production routes. On one hand, metacetone and 1-amino



Scheme 1 The synthesis route of Vitamin E

vinylmethyl ketone reacts to produce 2, 3, 6-trimethylphenol (TMP), which was then oxidized to get TMBQ [8]. On the other hand, 1,2,4-trimethylbenzene could be synthesized into TMBQ [7]. Even though 1,2,4-trimethylbenzene is cheap but the synthesis route of TMBQ from it is long and always gives a low yield [7]. Afterward, TMBQ is reduced to obtain 2,3,5-trimethylhydroquinone (TMHQ), which then condenses with isophytol and esterify to obtain Vitamin E [6].

The developed synthesis methods of TMBQ include the oxidation of TMP and trimethylbenzene, but the latter has not been employed in the industry [5–7]. The preparation of TMBQ from TMP is widely popular in industry, and the direct oxidation of TMP is the focus recently [9]. According to the reports, oxygen or peroxides are mostly used as oxidants in the solvents like alcohols, toluene, ether, acetonitrile or other organic solvents. The catalyst systems include copper based and cobalt based catalysts, alkali metal and alkaline earth metal halides, transition metal halides, heteropoly acid catalytic systems or ionic liquids [6]. Among the catalysts in oxidation reactions, copper based catalysts are cheap and easy to get, which have shown good catalytic efficiency to obtain high reaction yield [10]. In the technical process of TMP, $CuCl_2$ and LiCl were employed as catalyst with the oxidant of O_2 to achieve the yield of 96% with the pressure of oxygen from 0.03 to 0.1 MPa [6, 11, 12]. Yerramreddy et al. reported the preparation of TMBQ from TMP in the presence of the H_2O_2 oxidant and catalyst of spinel $CuCo_2O_4$ [7]. They obtained an 80% yield of TMBQ. Li et al. [5] reported the oxidation of TMP to TMBQ with the Fenton's reagent (H_2O_2 and $FeSO_4$) under mild conditions. Selvaraj et al. [13–15] also reported the selective synthesis of TMBQ and derivate from TMP and corresponding phenol with H_2O_2 as the oxidant with high selectivity and conversion. However, H_2O_2 is corrosive and is dangerous in terms of transportation and storage. The explosive properties of high concentration H_2O_2, especially when combined with metal salts, may cause serious safety problems [16]. Oxygen is dangerous and also has the problem of transportation and storage. Besides, the consumption of O_2 and H_2O_2 in the industrial production costs much more, especially compared with air. Therefore, it is imperative to develop more natural and safe oxidants. Among the reported oxidation reactions to synthesize TMBQ, all are heterogeneous catalytic reactions as far as we know. Even though the reactants and catalyst are potential to contact and react more adequately in homogeneous catalytic reactions, yet it brings difficulty in the separation and reuse of catalyst.

Ionic liquids have high heat capacity, low vapor pressure, stable properties and good solubility for many inorganic salts and organic compounds [17]. In recent years, ionic liquids have been widely used in the fields of electrochemistry, organic synthesis, catalysis and separation [17]. Sun et al. used $CuCl_2$ as catalyst and 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) as cocatalyst to catalyze the oxidation of TMP to TMBQ under oxygen, which showed that ionic liquid was a very good cocatalyst for the oxidation of TMP, due to the synergistic effect between [Bmim]Cl and $CuCl_2$ [18, 19]. Recently, more and more cases about wet air oxidation have been reported, which has inspired us in the preparation of TMBQ [20]. Air is cheap, clean, stable, convenient, abundant and easy to get as a rich natural resource. If air can be used as oxidant for direct oxidation reaction especially at mild pressure, it will avoid many problems, bring convenience, reduce costs and simplify the process.

Therefore, we developed the direct air oxidation method at one atmosphere pressure to oxidize TMP to TMBQ for the first time. With the catalysis of inorganic salt and ionic liquid, we explored the influence of reaction parameters, and obtained an efficient production process of TMBQ from TMP directly oxidized by air. TMBQ was obtained with a selectivity of 96.7% at 100% conversion of TMP at 90 °C for 7–8 h at one atmosphere pressure with the usage of composite catalyst, in the presence of [Bmim]Cl. At the same time, the oxidation mechanism was proposed.

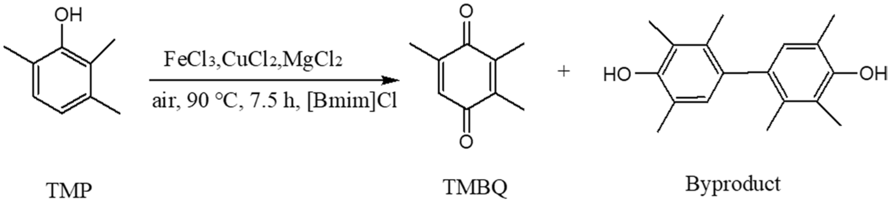
Experimental

Materials

TMP is from Nantong Baisheng Company. Isoamylol, $CuCl_2·2H_2O$, $MgCl_2·6H_2O$, $CoCl_2·6H_2O$ and $FeCl_3·6H_2O$ were from Sinopharm Chemical Reagents Co. Ltd. 1-Butyl-3-methylimidazolium hydrochloride ([Bmim]Cl), 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$), 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($[Bmim]CF_3SO_3$), 1-butyl-3-methylimidazolium disulfate $[Bmim]HSO_4$, 1-butyl-3-methylimidazolium dihydrogen phosphate ($[Bmim]H_2PO_4$) were from Shanghai Chengjie Chemical Co., Ltd.

Synthesis of TMBQ

The synthesis route of TMBQ is shown in Scheme 2. With the proper catalyst, TMBQ is obtained with a small part of byproduct, 2,2',3,3',5,5'-hexamethyl-4,4'–diphenol. In a typical procedure, the aqueous solution of catalyst Y (630 g) and isoamylol were charged into a vessel. TMP (80 g) was dissolved into isoamylol (300 mL) and charged in the dropping funnel. The temperature was increased to the reaction temperature. The air was blown into the reaction solution with an air pump with the flow rate of 1L/min to control the pressure at one atmosphere pressure. The reaction system was stirred at certain stirring speed. The TMP solution in the dropping funnel was dropped into the reaction system. The reaction was monitored with gas chromatography (GC). At the end of the reaction, the mixture was divided with a separating funnel. 40 g of water was added into the upper organic layer and washed five times separately. The water obtained for the first washing was recycled



Scheme 2 The synthesis route of TMBQ

with the catalyst for further reaction. The organic layer was analyzed with GC. The lower aqueous layer will be collected and supplemented with catalyst for reuse.

Results and discussion

Catalytic oxidation of TMP

$CuCl_2$, Fe(III) aquacomplex and Fenton reagent have been reported as effective catalysts for the oxidation of TMP and other oxidation reactions due to the catalytic oxidation activity of the ion salt [5, 6, 21, 22]. Herein, the mixture of $CuCl_2$ and $FeCl_3$ (marked as Y for short) was used as catalyst. In the initial catalytic oxidation reaction, TMP was oxidized with the catalyst of Y in the solvent isoamylol. The ratio of Y to TMP was investigated and found that when 90 g of TMP dissolved in 270 mL of isoamylol with the addition of 630 g of Y solution, the highest yield of TMBQ was achieved, 92.5% after 16 h of reaction. According to the related reports, there was a kind of byproduct, 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol, and intermediate product, 4-chloro-2,3,6-trimethylphenol (TMPCl), respectively [9]. The generation of 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol and the incomplete transformation of TMPCl contributes to the 7.5%. Compared with typical reaction oxidized by O_2 or H_2O_2, the concentration of oxidant, O_2, involved in the reaction is greatly reduced in the direct air oxidation way. What's more, the pressure of air was expected at one atmosphere pressure to achieve mild condition. Therefore, it is necessary to improve the intensity of catalytic oxidation. The optimal catalyst has been investigated based on the original catalyst Y. As to the choice of solvent, the usage of alcohol solvent always leads to a high yield according to the reports [6]. The boiling point should be high enough for this reaction. Therefore, isoamylol, hexyl alcohol and n-heptanol have been considered for the reaction. In the biphasic liquid reaction system, the high mutual solubility is benefit to the adequate contact of catalyst and reactants. The order of solubility in water is: isoamylol (28 g/L) > exyl alcohol (6 g/L) > n-heptanol (2.8 g/L). Therefore, isoamylol is chosen as the solvent. To achieve the best catalytic performance, several influence factors has been explored including cocatalyst, temperature, and stirring speed.

The exploration of catalyst

The reported reactions to prepare TMBQ are heterogeneous catalytic reactions. Inorganic metal salts, like the salts or mesostructured compounds containing Co, Cu and other metals, have been used as catalysts in the oxidation of TMP to TMBQ [7, 16–18, 23]. The related studies have shown that LiCl has a positive effect on the reaction [24]. However, the needed ratio of Li to TMP is large and Li is too expensive for the industrial usage. Therefore, chloride of alkaline earth metal Mg is considered. Therefore, in order to improve the catalytic performance, $MgCl_2$ and $CoCl_2$ were added into the original catalyst Y to form a new catalyst. Meanwhile, the optimum ratio of $CuCl_2$ and $FeCl_3$ was explored and they were added to Y, respectively, to investigate the catalytic oxidation performance.

The catalytic performance of catalyst Y with inorganic salts was studied. It can be seen from Table 1 that when 4 g of $MgCl_2 \cdot 6H_2O$ is added, the reaction time is shortened by 5 h, and the selectivity increased from 92.5 to 95.5%, indicating that the addition of $MgCl_2$ can significantly promote the reaction. As the amount of $MgCl_2 \cdot 6H_2O$ increased to 12 g, the reaction selectivity get higher, but too much $MgCl_2$ will bring difficulty in the later separation of water and oil. Therefore, adding 4 g of $MgCl_2 \cdot 6H_2O$ is appropriate. With the addition of $CuCl_2$, the reaction time was significantly prolonged, but the selectivity only improved slightly. The original catalyst Y contained enough $CuCl_2$, which has got the optimal ratio with TMP. When $FeCl_3$ and $CoCl_2$ were added, the selectivity of the catalytic reaction was slightly improved to 94–95%. Mg^{2+}, Cu^{2+} Fe^{3+} and Co^{2+} metal ions can promote the activation of TMP to phenoxy radical, and the presence of Cl^- is also conducive to the conversion of intermediate products to target products, leading to the increase in conversion rate. However, the induction of $CuCl_2$, $FeCl_3$ and $CoCl_2$ will darken the color of the mixture, which makes it hard to judge the interface between water and oil in the later separating process. On the contrary, $MgCl_2$ aqueous solution is colorless, conducive to judge the interface. Therefore, 4 g $MgCl_2 \cdot 6H_2O$ is selected to combine with Y as the new catalyst in the catalytic oxidation reaction.

Table 1 The catalytic performance with different addition of inorganic salt as catalyst

Entry[a]	Amount (g)	Reaction time (h)	Selectivity of TMBQ (%)[f]
Control	0	13.5	92.5
1[b]	2	8	88.9
2[b]	4	8.5	95.5
3[b]	8	10.5	93.5
4[b]	12	12	96.7
5[c]	2	19	92.3
6[c]	4	19	85.7
7[c]	8	21	84.0
8[c]	16	20	93.3
9[d]	2	8.5	94.4
10[d]	4	10	94.1
11[e]	2	8.5	95.0
12[e]	4	12	94.6

[a] Temperature of 90 °C and stirring speed of 700 r/min

[b] $MgCl_2 \cdot 6H_2O$

[c] $CuCl_2 \cdot 2H_2O$

[d] $FeCl_3 \cdot 6H_2O$

[e] $CoCl_2 \cdot 6H_2O$

[f] Conversion of 100%

Effect of ionic liquid

Ionic liquid $[Bmim]BF_4$ has been employed as an effective solvent and cocatalyst in the oxidation of TMP to TMBQ [9, 25]. In other oxidation reactions, ionic liquid has also been proved effective. Besides, ionic liquid could work together with Cu^{2+}-based catalyst [26]. Herein, several ionic liquids, including [Bmim]Cl and $[Bmim]BF_4$ have been investigated in the direct air oxidation of TMP. It is shown in Table 2 that the reaction time is effectively shortened from 13.5 h to 7–10 h, and the selectivity of TMBQ reaches 96.3% after adding 0.2–1.0 g of [Bmim]Cl. When 0.5 and 0.8 g of $[Bmim]BF_4$ were added, the reaction time was shortened to 7 and 8 h, with the selectivity of 95.2 and 95.8%, respectively. However, if the amount of [Bmim]Cl or $[Bmim]BF_4$ is too much or little, the improvement of reaction effect is limited or even worse than the original reaction condition, indicating that there is an optimal amount of ionic liquid. Ionic liquids could promote the reaction for two reasons: (1) $[Bmim]Cl/[Bmim]BF_4$ acts as the cocatalyst. There is the synergistic effect between [Bmim]Cl /$[Bmim]BF_4$ and the $CuCl_2/FeCl_3$, which is conducive to the formation of reaction intermediates, thus effectively promoting the reaction; (2) the addition of imidazolyl ionic liquid promoted the miscibility of water phase and

Table 2 The catalytic performance with addition of ionic liquid

Entry[a]	Amount (g)	Reaction time (h)	Selectivity of TMBQ (%)[f]
Control	0	13.5	92.5
1[b]	0.2	9.5	95.6
2[b]	0.5	9	96.3
3[b]	0.8	8	93.4
4[b]	1.0	10	93.4
5[b]	1.2	7	94.7
6[c]	0.2	13	86.1
7[c]	0.5	7	87.9
8[c]	0.8	8	5.2
9[c]	1.0	10	95.8
10[c]	1.2	16	93.2
11[d]	0.2	11	89.1
12[d]	0.5	9	94.1
13[e]	0.2	13.5	93.8
14[e]	0.5	8	93.8

[a] Temperature of 90 °C and stirring speed of 700 r/min

[b] [Bmim]Cl

[c] [Bmim]BF4

[d] [Bmim]HSO4

[e] [Bmim] CF4SO3

[f] Conversion of 100%

oil phase, resulting in the sufficient contact between TMP and catalyst, which accelerated the reaction [9].

In the oxidation process of TMP, the acidity of ionic liquid showed an influence on the selectivity of TMBQ. In the oxidation of aromatic hydrocarbons to quinones, Brønsted acids, such as glacial acetic acid and acetic anhydride, were used as catalysts [27]. In order to investigate the effect of acidity on the reaction, different acidic ionic liquids [Bmim]H_2PO_4, [Bmim]HSO_4, [Bmim]CF_3SO_3H were employed. The results showed that the selectivity of the reaction was slightly improved to around 94% (Table 3). As a result of the investigation of ionic liquid, 0.2–1.0 g of [Bmim]Cl or 0.5–0.8 g of [Bmim]BF_4 has been proven as the optimal reaction conditions.

Based on the above research, the comprehensive catalytic performance of Y, $MgCl_2$ and [Bmim]Cl/[Bmim]BF_4 were investigated. It is shown in Table 3 that when 4 g of $MgCl_2 \cdot 6H_2O$ and 0.5 g of [Bmim]Cl are added, the reaction time is 8 h, and the selectivity of TMBQ is as high as 96.7%. When $MgCl_2$ and 0.5 g of [Bmim]BF_4 were added, the selectivity of TMBQ was 94%—95%, which was lower than that of [Bmim]Cl. The reason may be as follows: The addition of $MgCl_2$ and [Bmim]Cl is beneficial to the formation of intermediates and improves the selectivity of the reaction. When $MgCl_2$ and [Bmim]BF_4 were added, the selectivity of TMBQ was lower, due to the large volume of BF_4^-which hindered the formation of intermediates. Consequently, 4 g of $MgCl_2 \cdot 6H_2O$ and 0.5 g of [Bmim]Cl was selected as the optimum conditions for the following research of reaction temperature, stirring speed and recycle of catalysts.

Effect of temperature

There was no noticeable change in the reaction time, which fluctuates between 7 and 8 h, as the reaction temperature varied from 50 to 90 °C, as shown in Fig. 1. The yield of TMBQ increased from 90.3 to 96.7%, undergoing a decrease to 88.6% at 60 °C, with the increase in temperature. The formation of active intermediates is

Table 3 The catalytic performance with addition of $MgCl_2 \cdot 6H_2O$ and [Bmim]Cl/[Bmim]BF_4

Entry[a]	Reaction time (h)	Selectivity of TMBQ (%)	Conversion of TMP (%)
Control	13.5	92.5	100
1[b]	9.5	93.4	100
2[c]	8	96.7	100
3[d]	8.5	94.7	100
4[e]	8	94.3	100

[a] Temperature of 90 °C and stirring speed of 700 r/min

[b] 2 g of $MgCl_2 \cdot 6H_2O$, 0.5 g of [Bmim]Cl

[c] 4 g of $MgCl_2 \cdot 6H_2O$, 0.5 g of [Bmim]Cl

[d] 2 g of $MgCl_2 \cdot 6H_2O$, 0.5 g of [Bmim]BF_4

[e] 4 g of $MgCl_2 \cdot 6H_2O$, 0.5 g of [Bmim]BF_4

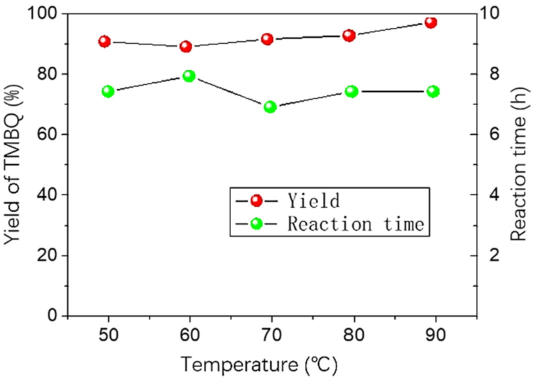


Fig. 1 The influence of reaction temperature on yield and reaction time

hindered, which leads to the low selectivity of TMBQ. Therefore, 90 °C is the optimal temperature for the reaction.

Influence of stirring speed

The interfacial area between aqueous and organic phase as well as the air and liquid phase is crucial in the heterogeneous catalytic reaction. Therefore, the interfacial area has been tuned through the change of stirring speed. Figure 2 shows that the stirring speed has a nonnegligible effect on the reaction time and yield. With the increase in stirring speed from 500 to 800 r/min, the reaction time was significantly shortened, and the yield of TMBQ was significantly increased, which indicated that the increase in stirring speed would significantly increase the mass transfer rate of the gas–liquid two-phase reaction system. The contact of gas and liquid phase increases with the increase of rotating speed, and the liquid is more easily dispersed into tiny droplets to react. However, the high rotational speed of 800 r/min will bring instability to the whole reaction system. In addition, high stirring speed leads to severe mechanical wear and energy consumption, but the yield of TMBQ almost does not increase. Therefore, 700 r/min is considered as the optimal stirring speed.

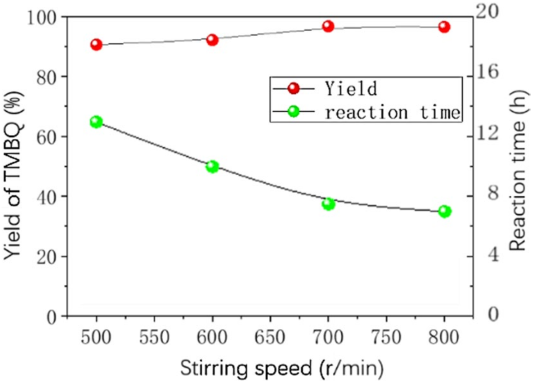


Fig. 2 The influence of stirring speed on yield and reaction time

Research on reaction kinetics

After the above exploration, the optimal reaction condition as follow: reaction temperature of 90 °C, stirring speed of 700 r/min, original catalyst Y was added with 4 g of $MgCl_2 \cdot 6H_2O$ and 0.5 g of [Bmim]Cl and the pressure of reaction is one atmosphere pressure. The conversion of TMP is 100% and the yield of TMBQ is 96.7%, which has been verified with the NMR spectra as seen in Fig. 3. The ^1H spectrum shows that the peaks of byproduct, 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol, are much weaker compared with the peak of TMBQ. The ratio of the sum of the intensity of H in 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol to that of H in TMBQ is roughly 6%, verifying that the percentage of 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol is almost 3% (the ratio of H atoms is 22:10). The peaks of byproduct in the ^{13}C spectrum are too weak to be observed clearly. The kinetic of the reaction is researched under the optimal reaction condition. The relationship of the TMP conversion and TMBQ selectivity vs reaction time is shown in Fig. 4. Only 14% TMBQ is obtained at the reaction time of 1 h. As the reaction time increases, the conversion gets increased to 96.7% at 7.5 h. The selectivity also gets increased. The curves indicate that the intermediate product, is generated at the beginning and converts to the aim product, TMBQ as the reaction goes on.

Recycle of catalyst

In order to reduce the production cost, the catalyst needs reuse. The catalytic activity and stability were checked in the recycle trials four times. The catalyst was separated from the organic phase and reused under the optimum condition. The recycled catalytic performance has been shown in Table 4. The conversion keeps 100% after four cycles and the selectivity keeps around 95%. Besides, the reaction time does not get prolonged. It proves that composite catalyst has a stable catalytic activity after successive cycling.

The possible mechanism of reaction

The catalytic oxidation mechanism of TMP over the composite catalyst of $FeCl_3$, $CuCl_2$ and $MgCl_2$ was described in Scheme 3, consistent with previous reports [8, 13]. Fe^{3+} and Cu^{2+} could oxidize TMP to TMP radical to trigger the following reaction. Fe^{3+} and Cu^{2+} have similar function and therefore, Fe^{3+} was used to present in the scheme. Mg^{2+} shows a synergistic effect. In the first step, TMP was active to TMP radical by Fe^{3+} or Cu^{2+}, which then have three possible reaction routes. In route (1), Fe^{3+} or Cu^{2+} activate O_2 molecules to form the product TMBQ and water. In the second route, two TMP radicals react to one form 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol molecule, the by product. In the third route, TMP radical react with Cl^- to form hydrogen radical and the intermediate product, TMPCl, which react with O_2 in the presence of Fe^{2+} to form the product TMBQ. During the whole process, the ionic liquid does not work as a catalyst because the ionic liquid alone has

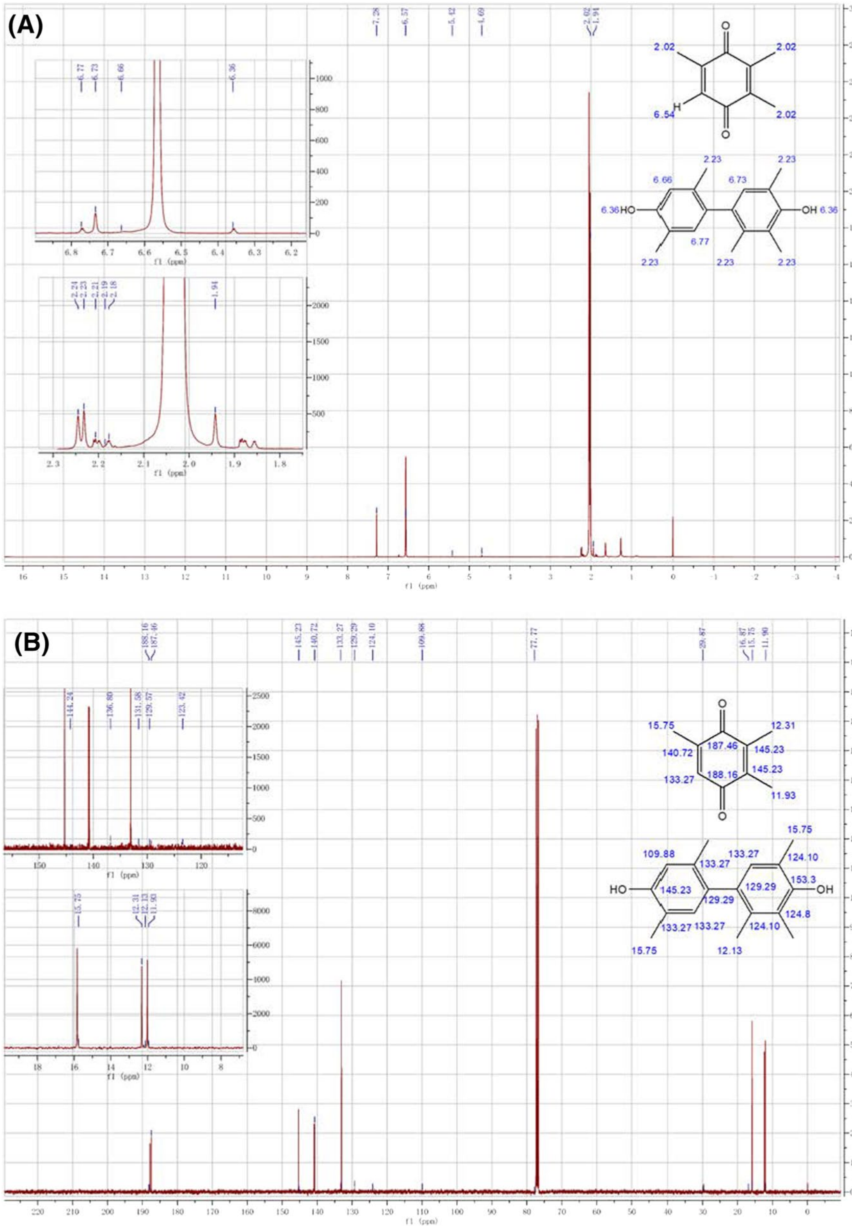


Fig. 3 **A** ^{1}H NMR spectrum of TMBQ with byproduct (400 MHz, $CDCl_3$). TMBQ δ 6.54 (*s*, 1H), 2.02 (*s*, 9H), 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol δ 6.66–6.77 (*t*, 3H), 2.18–2.24 (*m*, 15H). **B** ^{13}C NMR spectrum of TMBQ with byproduct (400 MHz, $CDCl_3$). TMBQ δ_c 188.16–187.46 (*d*, 2C) 133.27 (*s*, 1C), 140.72 (*s*, 2C), 145.23 (*s*, 1C), 15.75 (*s*, 1C) 11.93–12.31 (*m*, 2C) 2,2′,3,3′,5,5′-hexamethyl-4,4′-diphenol δ_c 11.93–12.31 (*m*, 2c), 15.75–16.87(*m*, 3C), 123.42–144.24 (*m*, 11C), 109.88. (*s*, 1C)

Fig. 4 The reaction kinetics of the synthesis of TMBQ

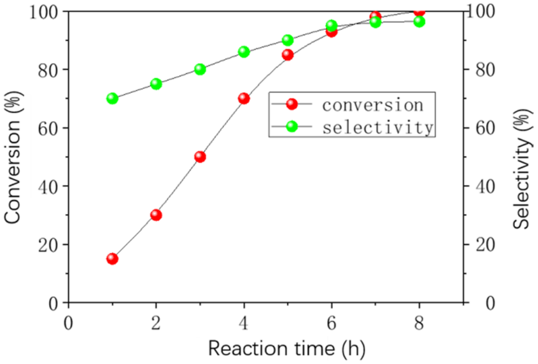


Table 4 The catalytic performance of recycled catalyst

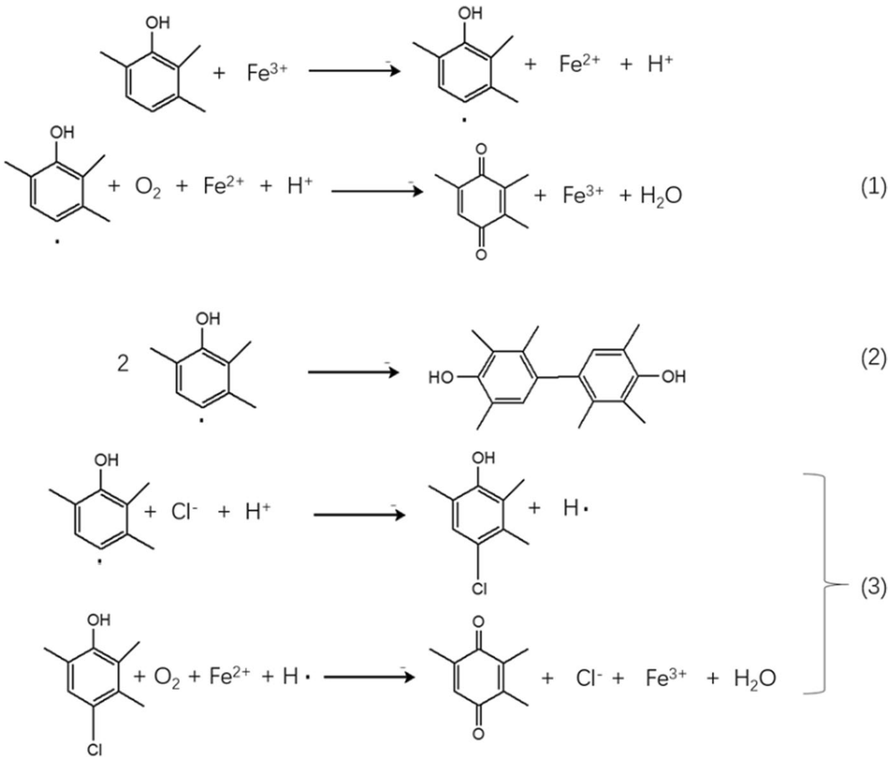
Catalyst[a]	Reaction time (h)	Selectivity of TMBQ (%)	Conversion of TMP (%)
Fresh	7.5	96.7	100
First reuse	7.5	95.7	100
Second reuse	8	95.0	100
Third reuse	8	95.1	100
Fourth reuse	7.5	94.7	100

[a] Temperature of 90 °C; stirring speed 700 r/min; 4 g of $MgCl_2 \cdot 6H_2O$, 0.5 g of [Bmim]Cl

no catalytic performance. In the presence of [Bmim]Cl, the water phase and organic phase gain miscibility, which are initially insoluble, leading to the sufficient contact between inorganic ions, (Fe^{3+}, Cu^{2+}, Mg^{2+} and Cl^-) and organics (TMP, TMP radical·and TMPCl).

Conclusion

The catalytic oxidation of TMP to synthesize TMBQ with the oxidant of air at one atmosphere pressure was developed in this work and this is the first report of this reaction oxidized by air. After a series of investigations, 630 g of original catalyst Y ($CuCl_2$ and $FeCl_3$) aqueous solution was added with 4 g of $MgCl_2 \cdot 6H_2O$ to achieve optimal catalytic performance. 0.5 g of [Bmim]Cl is critical because it works as the cocatalyst and can promote the miscibility of water phase and oil phase. The conversion of TMP is 100% and the yield of TMBQ reaches 96.7% at the temperature of 90 °C and the stirring speed of 700 r/min. The oxidation reaction undergoes a free radical mechanism, among which, Cl^- ion in the catalyst solution works as the bridging role. The catalyst has shown good stability after recycling trials four times with the yield around 95%. The usage of atmospheric air as the oxidant has noteworthy advantages than traditional O_2 or H_2O_2. We believe this effective air oxidation



Scheme 3 The possible catalytic oxidation mechanism of TMP to TMBQ

method developed in the research work will inspire the industrial production of TMBQ and other related products.

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