

Highly efficient transformation of ethylbenzene into acetophenone catalyzed by NHPI/Co(II) using molecular oxygen in hexafluoropropan-2-ol

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ABSTRACT

Acetophenone is an important industrial intermediate and generally produced by the Friedel-Crafts acylation reaction, suffering from a low reactivity and serious equipment corrosion. Direct oxidation of ethylbenzene to acetophenone by molecular oxygen will be benign and cost-effective. The catalytic performance of NHPI/Co(II) herein was investigated by selective oxidation of ethylbenzene to acetophenone in different solvents at room temperature. The solvent hexafluoropropan-2-ol (HFIP) was found to markedly enhance the transformation efficiency from ethylbenzene to acetophenone in comparison with acetic acid, pyridine and ethanol, and the ethylbenzene conversion and the selectivity to acetophenone was high up to 87.9 % and 61.2 %, respectively. A higher concentration of phthalimide-N-oxyl (PINO) radicals was observed by an in situ electron paramagnetic resonance spectrometer (EPR) in HFIP with respect to other solvents, suggesting that HFIP may facilitate the generation of the N-oxyl radical and thus promote the selective oxidation of ethylbenzene to acetophenone. Furthermore, the benzylic carbon radical (PhCHCH₃) from ethylbenzene was trapped by tetramethylpiperidine N-oxyl radical (TEMPO) and observed by a high resolution mass spectrometer. The findings of both PINO and PhCHCH₃ under reaction conditions indicated that the selective oxidation of ethylbenzene to acetophenone catalyzed by NHPI/Co(II) should proceed via a radical mode. The selective oxidation of ethylbenzene to acetophenone using molecular oxygen by NHPI/Co(II) in HFIP exhibited an important industrial application prospect.

Introduction

The activation and selective oxidation of CH— bonds are of great importance in industrial transformation of inexpensive hydrocarbons into oxygenated compounds with a higher value. The selective oxidation of ethylbenzene to acetophenone is a typical reaction for selective oxidation reaction of benzyl CH— bonds [1,2]. As an important chemical intermediate, acetophenone is widely used in industrial production fields, such as perfumes [3], soaps [4], resins [5] and drugs [6]. Industrially, acetophenone is synthesized by Friedel-Crafts acylation reaction of benzene. However, the process suffers from a low reactivity, serious equipment corrosion and a high cost of wastewater treatment [7]. Therefore, a cost-efficient and benign technology for selective oxidation of ethylbenzene to acetophenone will be crucial.

Different strategies were developed to convert ethylbenzene into acetophenone via vapor phase or liquid phase oxidation in the past years. There are no solvents needed in vapor phase oxidation, in which

the air was used as the oxidant directly. And the reactions via vapor oxidation can be carried out using a fixed-bed flowing reactor without fear of the separating and recovering of catalysts. However, the high temperature reaction in vapor phase oxidation often leads to the production a lot of products, such as styrene, benzaldehyde, benzoic acid, CO and CO₂ [8,9,10]. Compared to the vapor phase oxidation, the liquid phase oxidation of ethylbenzene to acetophenone can be performed in milder reaction conditions, and exhibited a higher ethylbenzene conversion and a lower selectivity to overoxidized products like CO₂, showing a promising industrial application prospect [11,12]. Heterogeneously catalytic transformation of ethylbenzene into acetophenone facilitates the separation of the catalyst, but the conversion of ethylbenzene and the selectivity to acetophenone are generally low [13,14]. The homogeneous catalysts can be molecularly dispersed in solvent, permitting a good contact with ethylbenzene molecules and thus exhibiting higher reactivity and selectivity [15].

Molecular oxygen is an environmentally friendly and cheap oxidant,

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and widely used in catalytic reactions in the oxidation of amines, alcohols and alkane [16,17,18]. However, it is necessary to activate the triplet state of molecular oxygen and/or ground CH— bond to realize the oxygen functionalization of hydrocarbon due to the spin – flip restriction between them [11]. Ishii's group [19] developed a NHPI/Co(II) catalytic system to oxidize toluene and other substrates into value-added products in liquid phase under mild conditions for the first time, indicating the aerobic oxidation of CH— bonds under mild conditions was possible by NHPI/Co(II) catalysts.

N-hydroxyphthalimide (NHPI) was employed to catalyze the activation and functionalization of CH— bonds in many reaction systems. Wang et al. [20] achieved a selective aerobic oxidation of cyclohexane to ϵ -caprolactone under mild conditions in the presence of NHPI and aldehyde. Carboxylic functionalized β -carboline were successfully synthesized by aerobic oxidation in the presence of NHPI and transition metal salts using molecular oxygen at room temperature [21]. Li et al. [22] successfully achieved the chlorination of benzylic CH— bond of toluene by NHPI and 2,3-dichloro-5,6-dicyano-benzoquinone (DDQ).

NHPI is also used in liquid phase oxidation of ethylbenzene to acetophenone [11,12,23,24]. Miao et al. [11] successfully achieved highly selective oxidation of ethylbenzene to acetophenone (yield 70 %) in the presence of $\text{Fe}(\text{NO}_3)_3$ and NHPI. However, the reaction was completed in a longer period of time, probably due to the relatively low reactivity of the catalyst. Zhang et al. [12] realized controllable activation of CH— bond in the presence of $\alpha\text{-Fe}_2\text{O}_3$ and NHPI, the conversion of ethylbenzene and the selectivity to acetophenone in 4 h were 55 % and 96 %, respectively. In addition, di-dodecyl-dimethyl ammonium bromide (DDDAB) [23] and ion liquids [24] were found significant promoting role on solvent-free oxidation of ethylbenzene to acetophenone catalyzed by NHPI/Co(II). All of the above researches implied that NHPI is active for oxidation of ethylbenzene to acetophenone in liquid phase, but the efficiency of producing acetophenone currently is relatively low. Therefore, an enhanced efficiency of oxidation of ethylbenzene to acetophenone in liquid phase is raised here to meet increasing needs of industrial application.

1,1,1,3,3,3-Hexafluoropropan-2-ol (HFIP) is a non-nucleophilic polar solvent with weak acidity, high dielectric constants and ionization power [25]. In addition, HFIP is a strong hydrogen-bond donor that pairs with hydrogen-bond acceptor groups, thereby can interfere with the catalytic reactions cycle, promote the kinetics of polar reactions and significantly increase the substrate conversion and selectivity to the desired product [26,27,28]. Pappo et al. [29] developed a simple and efficient method for selective oxidation of toluene to benzaldehyde using HFIP as the solvent. Based on Ishii and his co-author's picture [19], Pappo's group increased significantly the yield of benzaldehyde (> 90 %).

In the present work, we employed HFIP as solvent in liquid phase oxidation of ethylbenzene in the presence of NHPI and Co(II) in molecular oxygen at room temperature. The concentrations of PINO radicals in different solvents were investigated by electron paramagnetic resonance spectrometer (EPR). Further, the benzylic carbon radical was trapped by tetramethylpiperidine N-oxyl (TEMPO) radicals and detected by high resolution mass spectrometry (HRMS). Accordingly, the possible mechanism of ethylbenzene oxidation was proposed.

Experimental section

Chemicals

Ethylbenzene, acetic acid, absolute ethanol, cobalt acetate tetrahydrate and N-hydroxyphthalimide were purchased from China Pharmaceutical Group Chemical Reagents Co., Ltd. 1,1,1,3,3,3-Hexafluoropropan-2-ol was purchased from Aladdin-Reagent. All reagents were not purified before use.

Catalytic reactions and product analysis

Liquid phase oxidation of ethylbenzene was performed in a Schlenk tube. Ethylbenzene (2 mmol), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol), NHPI (0.05 mmol) and solvent (1 mL) were added to the Schlenk tube. Nitrobenzene of 0.5 mmol was added as an internal standard after catalytic tests. The rest of the tube was repeatedly purged by O_2 (99.999 %) before measurements, then the reaction was carried out at 303 K and a flowing atmospheric O_2 of 50 ml/min under a continuous stirring. The resulting reaction mixture was analyzed by an off-line gas chromatograph (SHIMADZU GC-2014) with a SGE AC-10 capillary column and a flame ionization detector.

Characterization

Electron paramagnetic resonance (EPR) tests were performed at room temperature on an EPR spectrometer (A300–10/12) with a field modulation of 100 kHz. The microwave frequency was maintained at 9.848 GHz. The resulting reaction solution of ethylbenzene oxidation was transferred from the Schlenk tube into a capillary quartz tube under the reaction condition, then analyzed immediately.

Ethylbenzene benzylic carbon radical ($\text{PhCH}_2\text{CH}_2\cdot$) was determined by a high resolution mass spectrometer (HRMS) (maXis, Bruker). TEMPO (2 mmol) was added to the reaction mixture after 30 min of reaction. Then, the HRMS experiments are carried out immediately to detect the captured intermediates.

Results and discussion

Table 1 compares the effects of different solvents on the liquid phase oxidation of ethylbenzene. There were no products from ethylbenzene oxidation detected when ethanol was used as the solvent (entry 1), and very low ethylbenzene conversion was observed in pyridine (entry 2). Under the same reaction conditions, an ethylbenzene conversion of 21.2 %, a selectivity to acetophenone of 73.5 %, a selectivity to 1-phenylethanol of 22.7 % and a selectivity to benzaldehyde of 2.4 % were observed when acetic acid (HOAc) was used as the solvent (entry 3). It is worthwhile to note that the conversion of ethylbenzene was significantly increased to 87.8 % when HFIP was used as the solvent, and the selectivities to acetophenone and 1-phenylethanol was 61.2 % and 34.7 %, respectively, and a small amount of benzaldehyde was observed (entry 4). The results indicated that HFIP not only promotes the activation of the CH— bonds of ethylbenzene and the selective formation of acetophenone, but also leads to the cleavage of the CC— bonds of the ethyl groups in ethylbenzene. It was suggested that the distinctive HFIP might anticipate and markedly promote some reaction by stabilizing radical intermediates [30,31]. Compared with the catalytic performance reported by Zhang et al. [12], a lower selectivity to acetophenone was observed, and a part of ethylbenzene was converted into 1-phenylethanol. The decrease in the selectivity to acetophenone might be related to the lower capability of homogeneous NHPI/Co in comparison to NHPI/ Fe_2O_3 for the transformation of 1-phenylethanol to the desired acetophenone.

Table 1
Aerobic autoxidation of ethylbenzene in different solvents^a.

Entry	Solvent	Conv. (%)	Selectivity (%)			
			AP	1-PEO	BA	Others
1	Ethanol	0	–	–	–	–
2	Pyridine	0.1	100.0	0	0	0
3	HOAc	21.2	73.5	22.7	2.4	1.4
4	HFIP	87.8	61.2	34.7	3.2	0.9

^a Reaction conditions: ethylbenzene (2 mmol), NHPI (0.05 mmol), $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.01 mmol), O_2 (1 atm), solvent (1 mL), 30 °C, 4 h. AP: Acetophenone, 1-PEO: 1-Phenylethanol, BA: Benzaldehyde.

The dependence of ethylbenzene reactivity in different solvents on the reaction time is shown in Fig. 1. No products from ethylbenzene oxidation were detected in 4 h when ethanol was used as the solvent. The ethylbenzene conversion increased slightly with reaction time in the case of HOAc as the solvent. It is surprising that a markedly enhanced reactivity was observed when HFIP was used as the solvent, and the ethylbenzene conversion presented a sharp rise in the initial stage of the reaction (0–40 min) and then was retained at 80–90 % after 1 h.

The detailed product distribution from the aerobic oxidation of ethylbenzene catalyzed by NHPI/Co(II) in HFIP in 4 h is listed in Table 2. In the initial stage of the reaction, acetophenone was the main product (entry 1). In a reaction time of 2 min, 1-phenylethanol (49.2 %) and a small amount of benzaldehyde (6.3 %) were observed (entry 2). In the first 40 min of the reaction time (entry 1–6), the ethylbenzene conversion increased rapidly, indicating a high reactivity. However, the reaction rate presented an apparent decrease after 40 min of reaction, leading to a slow increase of the ethylbenzene conversion (entry 7–11). The selectivity to 1-phenylethanol and benzaldehyde decreased monotonously with the reaction time, the selectivity to acetophenone, however, exhibited a monotonously increasing trend. After 4 h of reaction (entry 11), the conversion of ethylbenzene was up to 87.8 %, and the selectivity of ethylbenzene to acetophenone, 1-phenylethanol and benzaldehyde were 61.2 %, 34.7 %, and 3.2 %, respectively. However, it is worthwhile to note that the selectivity to acetophenone nearly stopped increasing after 1 h. NHPI will be converted into N-oxyl anion instead of N-oxyl radical in the presence of water, which is a strong acceptor of proton [32]. Here, water was produced when ethylbenzene or 1-phenylethanol was converted into acetophenone and its concentration continuously increased, which might lead to the fact that the selectivity to acetophenone stopped increasing.

In order to probe the influence of other factors on oxidation of ethylbenzene to acetophenone, the reaction temperature, the concentration of NHPI and the kind of cobalt salts were chosen as the variations and the resulting catalytic performance of the homogeneous NHPI/Co are shown in Table S1, S2 and S3. It was found that the ethylbenzene conversion increased from 54.0%–81.8% when increasing the reaction temperature varied from 20 °C to 40 °C with other reaction conditions unchanged (Table S1). At the same time, an increase in the selectivity to acetophenone and a decrease in the selectivity to 1-phenylethanol were observed (Table S1), suggesting that the enhanced reaction temperature promoted the conversion of 1-phenylethanol into acetophenone. Furthermore, the higher NHPI concentration was found favorable for the transformation from ethylbenzene to acetophenone, which might be ascribed to the enhancement of the concentration of active PINO radicals (Table S2).

Table S3 shows effect of the kind of cobalt salts on the ethylbenzene

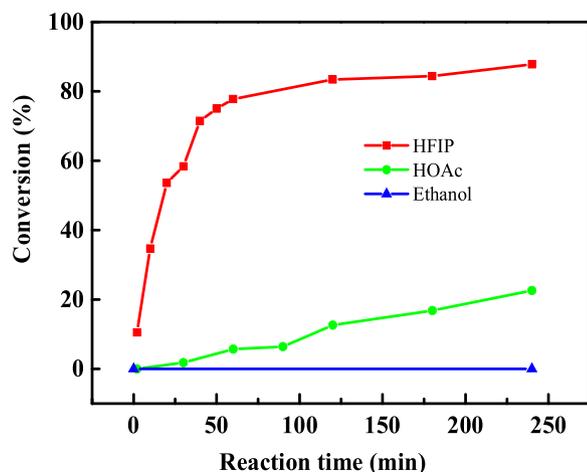


Fig. 1. Effects of different solvents on oxidation of ethylbenzene.

Table 2

The product distribution of the aerobic oxidation of ethylbenzene catalyzed by NHPI/Co(OAc)₂ at room temperature in HFIP in 4 h.

Entry	Reaction time (min)	Conv. (%)	Selectivity (%)			
			AP	1-PEO	BA	Others
1	0	0.6	44.9	0	0	55.1
2	2	9.7	39.5	49.2	6.3	5.2
3	10	34.7	47.8	44.8	4.4	3.0
4	20	53.6	50.1	45.6	3.5	0.8
5	30	58.4	54.4	39.9	4.4	1.3
6	40	71.5	49.6	43.6	4.3	2.5
7	50	75.0	54.2	37.4	4.3	4.1
8	60	77.8	58.8	36.6	3.5	1.1
9	120	83.4	60.9	34.7	3.7	0.7
10	180	84.4	60.1	36.0	3.3	0.6
11	240	87.8	61.2	34.7	3.2	0.9

Reaction conditions: ethylbenzene (2 mmol), NHPI (0.05 mmol), Co(OAc)₂·4H₂O (0.01 mmol), O₂ (1 atm), HFIP (1 mL), 30 °C. AP: Acetophenone, 1-PEO: 1-Phenylethanol, BA: Benzaldehyde.

oxidation. It was found that Co(acac)₂ presented a slightly lower activity and similar selectivity to acetophenone or 1-phenylethanol in comparison with Co(OAc)₂·4H₂O. However, vitamin B12 gave a much lower activity for ethylbenzene oxidation. This can be attributed to the higher chemical state of cobalt ions in vitamin B12 in comparison with those in Co(acac)₂ and Co(OAc)₂·4H₂O.

Table S4 (ESI) demonstrates the tendency of the conversion and selectivities of ethylbenzene versus reaction time in HOAc. It was shown that the conversion of ethylbenzene slowly increased with the reaction time compared to that observed in HFIP. After 4 h of reaction, the conversion of ethylbenzene was ca. 21.2 %. In the first 90 min of reaction time, acetophenone was only the product. 1-Phenylethanol and benzaldehyde were gradually observed when the longer reaction time was applied. The selectivity to acetophenone decreased monotonously with the reaction time, while selectivity to 1-phenylethanol showed a contrary trend after 2 h of reaction. Under the applied reaction conditions, the selectivity to benzaldehyde decreased monotonously with the reaction time.

Previous researches suggested that CH— bonds can be activated by PINO radical generated from NHPI to abstract hydrogen and form carbon radical [19,29,33,34,35,37]. Here, electron paramagnetic resonance (EPR) was used to explore the PINO radicals and their concentration. As far as we know, there was no report that confirmed that both PINO and PhCHCH₃ were present in the oxidation of ethylbenzene. When ethanol was used as the solvent, there was no the signal of PINO radical observed (Fig. S1, ESI). Comparatively, the g-factor of this triplet signal was detected in 2.0070 in HFIP and HOAc, indicating the generation of the PINO radical (g = 2.0070) (Fig. 2A) [12,19,36,38]. Based on the facts that there was no products generated from ethylbenzene oxidation in ethanol, it was concluded that PINO radical should be related to the ethylbenzene oxidation. Furthermore, compared the concentration of PINO radical in the HFIP reaction solution to that in acetic acid, it was found that the conversion of ethylbenzene and the concentration of PINO were well in agreement in different solvents.

Fig. 2 (B) further explored the change of PINO radical concentration versus reaction time in HFIP. It was found that the concentration of PINO radical increased before 20 min and then decreased with reaction time. The signal of PINO radical nearly disappeared after 2 h. Compared with the trend of ethylbenzene conversion versus reaction time, it can be concluded that the higher concentration of PINO radicals promoted the ethylbenzene conversion and the reaction rate, and PINO concentration were well positively correlated.

Tetramethylpiperidine N-oxyl radicals (TEMPO) were added to the reaction solution to trap the possible PhCHCH₃ radical, the possible adduct generated by the coupling of PhCHCH₃ radical and TEMPO were detected by high resolution mass spectrometry (HRMS) (Scheme 1)[39].

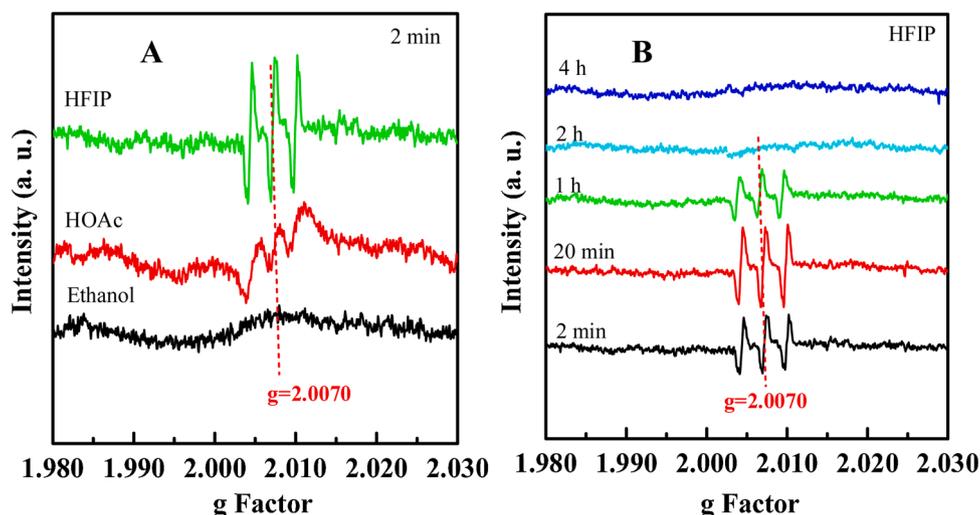
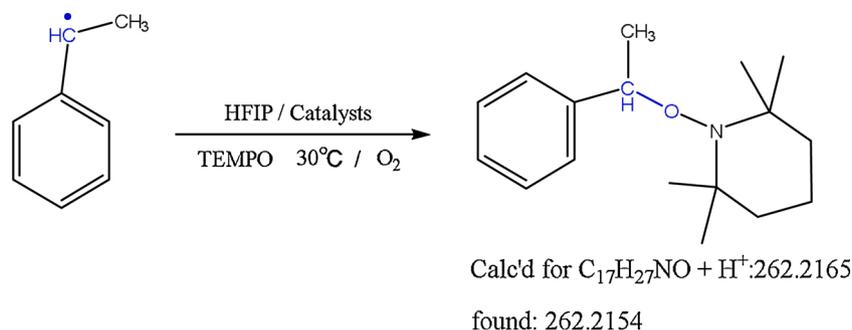


Fig. 2. PINO determine by EPR: (A) in different solvents at 2 min; (B) in HFIP with different reaction time.



Scheme 1. Trapping of the $PhCHCH_3$ radicals by TEMPO.

The HRMS of the reaction solution after adding the trapping agent are shown in Fig. 3. TEMPO was added to the reaction solution after 30 min of reaction, the MS signal at m/z 262.2154 ($C_{17}H_{27}NO + H^+$) was observed. This signal is related to the formation of the adduct of $PhCHCH_3$ with the trapping agent TEMPO, implying that the hydrogen atom of benzylic $CH-$ bonds in ethylbenzene was abstracted and the $CH-$ bonds of ethylbenzene was activated (Fig. 3A). After 4 h of reaction, the signal at m/z 262.2154 was very weak (Fig. 3B). No signal was observed to show the presence of the adduct between $PhCHCH_3$ and TEMPO in the absence of TEMPO (Fig. 3C). Combined the results from catalytic test and EPR analysis, it is suggested that PINO radicals may activate the benzylic $CH-$ bond by abstracting hydrogen from the benzylic carbon to generate carbon radical. At the initial stage of the reaction (30 min) in HFIP, the high concentration of PINO radical led to a high concentration of $PhCHCH_3$ radical. No PINO radical was detected after 4 h of reaction, while the concentration of $PhCHCH_3$ was also very low that was determined by HRMS analysis. The above results indicated that the concentration of PINO radical may be crucial to the activation of benzylic carbon $CH-$ bonds. In addition, the signal at m/z 262.2158 was also detected when HOAc was used as solvent (Fig. S2, ESI), indicating that the $PhCHCH_3$ is the intermediate of ethylbenzene oxidation in both acetic acid and HFIP.

In order to clarify how ethylbenzene is converted into acetophenone and 1-phenylethanol, the possible intermediate ethyl phenyl hydrogen peroxide (EPHP) was analyzed using triphenylphosphine (TPP). The results are shown in Table S5 in ESI. An increase of ca. 6.3 % in the selectivity to 1-phenylethanol (1-PEO) was observed after adding TPP to reaction mixture. At the same time, a roughly same decrease in the selectivity to acetophenone was found. However, 1-PEO is stable under the analytical conditions by gas chromatography. Therefore, it is

believed that ca. 6.3 % of ethyl phenyl hydrogen peroxide (EPHP) was produced under the optimized experimental conditions, which was oxidized to acetophenone under the normal analytical conditions by gas chromatography.

Based on the PINO radical, $PhCHCH_3$ and ethyl phenyl hydrogen peroxide observed under the experimental conditions and the activation mechanism of $CH-$ bonds proposed by other researchers [19,29,33–37], a possible reaction route for liquid phase oxidation of ethylbenzene under our experimental conditions was proposed (Fig. S3, ESI). First, the initiator Co^{2+} reacts with O_2 to form cobalt oxygen complexes. The complexes abstract a hydrogen atom of NHPI to generate PINO radical. Then, PINO radical activates ethylbenzene to form $PhCHCH_3$. $PhCHCH_3$ reacts with O_2 to form $PhCH(OO)CH_3$ and then abstract a hydrogen atom from NHPI to become $PhCH(OOH)CH_3$. The generated hydroperoxide will decompose and produce acetophenone and 1-phenylethanol.

The liquid phase oxidation reaction network of ethylbenzene in different solvents was further investigated using acetophenone and 1-phenylethanol as starting materials under the same reaction conditions, and the results are shown in Table S6 (ESI). No further oxygenated product from acetophenone was detected in both HOAc and HFIP, while 1-phenylethanol can be further oxidized to acetophenone under the same conditions. The conversion of 1-phenylethanol was much higher in HFIP than that in HOAc (91.5 % vs. 64.3 %) with a similar selectivity to acetophenone of ca. 100 %. Based on the above results and the fact that ethyl phenyl hydrogen peroxide (EPHP) was confirmed as the intermediate of the products (Table S5, ESI), the reaction network of the ethylbenzene oxidation in HFIP as solvent was proposed (Fig. 4). Benzaldehyde and ethyl phenyl hydrogen peroxide (EPHP) were directly generated from ethylbenzene. 1-phenylethanol was directly generated

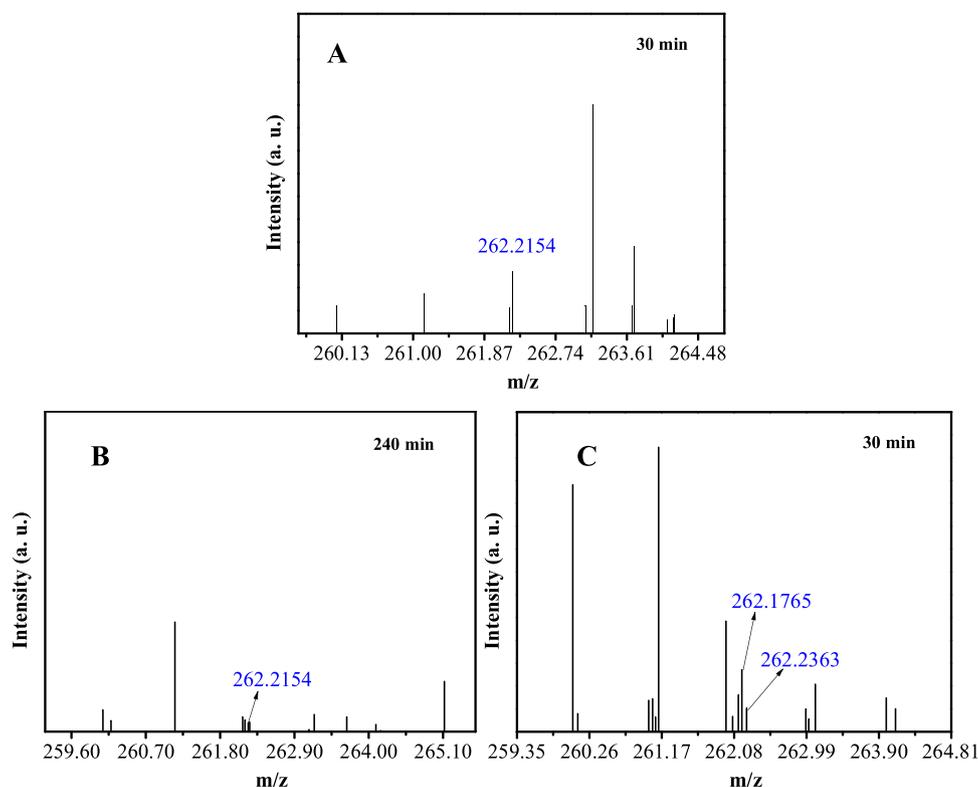


Fig. 3. HRMS of the reaction solution after adding TEMPO at (A) 30 min, (B) 4 h and (C) without TEMPO.

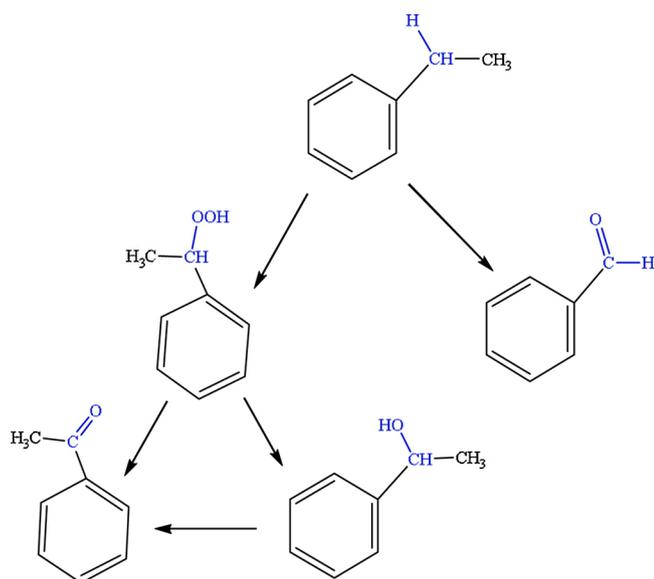


Fig. 4. Possible reaction network of the ethylbenzene oxidation catalyzed by NHPI/Co(II) in HFIP.

from 1-phenylethyl hydrogen peroxide, but acetophenone may be from oxidation of 1-phenylethanol and/or decomposition of ethyl phenyl hydrogen peroxide.

Conclusions

In summary, the solvent HFIP markedly improved the transformation of ethylbenzene into acetophenone in liquid phase using molecular oxygen. Under the experimental conditions, the conversion of ethylbenzene was as high as 87.8 % in 4 h, and the selectivity to

acetophenone was up to 61.2 %. The analysis via EPR indicated that the solvent HFIP is beneficial to the rapid generation of PINO radical. The PINO radical may be the actual catalyst for the reaction, which activates the ethylbenzene benzylic CH— bonds by abstracting hydrogen on the benzylic carbon to produce PhCHCH₃, which was confirmed by HRMS detection. The ethylbenzene oxidation reaction in HFIP was suggested to proceed according to the picture proposed by Ishii.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Sihao Xu: Conceptualization, Methodology, Funding acquisition, Writing - review & editing, Conceptualization, Methodology, Funding acquisition, Writing - review & editing. **Guojun Shi:** Investigation, Writing - original draft. **Ya Feng:** Investigation. **Chong Chen:** Resources, Investigation. **Lijun Ji:** Methodology.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.mcat.2020.111244>.

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