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PTCs promoted biphasic oxidation of ethylbenzene catalyzed by NHPI and CoSPc

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Abstract

An easy workup and environmentally friendly method to convert ethylbenzene into the corresponding oxides, catalyzed by a combined catalytic system consisting of NHPI and CoSPc, was developed in a water involved liquid–liquid heterogeneous system. Experimental results showed that the reaction performed well facilitated by PTCs at multigrams material level, under which the conversion rate of ethylbenzene and the selectivity of acetophenone reached 60.6% and 95.2% after 0.5 h of reaction in oxygen atmosphere. An oxidation process was proposed at the end of this paper.

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Keywords: Ethylbenzene; Aerobic oxidation; NHPI; CoSPc; PTC

Though there are many advantages of utilizing oxygen as the oxidant in organic substrates oxidation, large-scale effective processes of transforming alkane or alkyl with molecular oxygen into the corresponding oxides have been limited due to the inert activity of alkane or alkyl and low oxidation ability of oxygen, so the development of effective and selective catalytic system for the oxidation of alkane or alkyl still faces a big challenge [1]. Recently, more and more attention has been paid to N-hydroxyphthalimide (NHPI) for its catalytic ability in the oxidation of hydrocarbons [2], and which is usually employed combined with some transition metals, such as cobalt, manganese, copper, iron, etc. [3]. The transition metals usually presented in the forms of carboxylic salts, rarely in their more stable complex compounds forms [4]. Herein, we chose a widely used catalyst cobalt sulfonated phthalocyanine (CoSPc) [5] as one part of the catalytic system, and in order to facilitate the separation process of products and catalysts, water was inducted as an environmentally friendly solvent for catalysts, which formed a liquid-liquid biphasic system with ethylbenzene and oxidation products, phase transfer catalysts (PTCs) were employed as the crucial additives aiming to promote the mass transfer between aqueous and organic phases. Until now, there is no report concerning the combination of CoSPc and NHPI for the oxidation of ethylbenzene in a water involved liquid-liquid biphasic system, and which represented a good catalytic activity and selectivity, a 60.6% of conversion rate and a 95.2% of acetophenone selectivity were achieved after 0.5 h of reaction in oxygen atmosphere (Scheme 1). The separating workup process for this approach was simple only by an ordinary separation funnel. Currently, the most developed heterogeneous oxidations of hydrocarbons were concerning liquid-solid and gas-solid biphasic systems [6], they were

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Scheme 1. Heterogeneous oxidation of ethylbenzene.

blamed for their lower catalytic activity or higher energy demand, therefore, a liquid-liquid heterogeneous system may provide a promising way for an easy separating approach.

1. Experimental

In a general process, into a high pressure autoclave, 10 mL of ethylbenzene, 30 mL of H₂O, 10 mol% of NHPI, 0.42 mol% of CoSPc and a certain amount of PTCs were added, then, air in the autoclave was exchanged three times with O₂ to sweep N₂ out. Subsequently, the oxidation was conducted for 0.5 h at 110 °C under stirring and in O₂ atmosphere. The organic layer was separated through a separation funnel, and the products yields were estimated according to the peak areas based on internal standard technique by GC. The predominant product was acetophenone, and 1-phenylethanol was scarce, they were assigned by ¹H NMR and EI-MS after separation on a silica gel column [7]. The conditions of the GC (Agilent 6820 gas chromatograph with a flame ionization detector using a 30 m × 0.32 mm × 0.50 µm capillary column) analyses were as follows: a temperature program from 100 °C (5 min) to 180 °C (10 °C/min), then maintaining 20 min.

2. Results and discussion

Preliminary, optimization of the reaction was performed. Results demonstrated the most optimal conditions were as follow: V(ethylbenzene): $V(\text{H}_2\text{O}) = 1:3$, n(NHPI):n(ethylbenzene) = 1:10, n(CoSPc):n(NHPI) = 1:24, 2.5 mol% (based on ethylbenzene) of TBAB, temperature 110 °C, O₂ pressure 0.75 MPa, stirring rate 350 r/min, reaction time 0.5 h, under which, a moderate conversion rate 60.6% and an excellent acetophenone selectivity 95.2% were achieved, the detailed full paper concerning optimization of the reaction will be released later.

Table 1			
Effect of PTCs	on	ethylbenzene	oxidation

Entry	PTCs	Conversion (%)	Selectivity (%)		
			2	3	Total
1	_ ^a	16.4	82.8	8.8	91.6
2	TBAB ^{b,d}	60.6	95.2	4.5	99.7
3	TBAC ^b	49.7	78.4	5.6	84.0
4	TMAB ^b	12.6	92.2	5.6	97.8
5	CTAB ^c	28.7	87.6	6.0	93.6
6	CTAC ^c	28.7	70.9	4.2	75.1
7	TDMBAC ^b	44.6	89.6	2.9	92.5
8	SDBS ^c	25.4	84.8	8.4	93.2
9	CMC-Na ^d	8.7	0.7	0.1	0.8
10	OP-10 ^c	24.5	75.6	6.2	81.8
11	PEG 6000 ^d	18.3	82.3	5.1	87.4
12	Tween-60 ^c	24.1	83.4	6.5	89.9
13	β -CD ^c	10.4	90.2	7.3	97.5
14	Acetic acid ^e	74.7	74.5	0.1	74.6

^a Without present of PTC.

^b Conc. is 2.5 mol% of ethylbenzene.

^c Conc. are their CMCs: CTAB (9.12 × 10⁻⁵ mol/L), CTAC (1.6 × 10⁻² mol/L), SDBS (1.2 × 10⁻³ mol/L), OP-10 (0.4 g/L), Tween-60 (2.528 g/L), β-CD (4 g/L).

^d Utilized at the same weight amount of TBAB 7.6%.

^e Acetic acid as solvent in absence of PTC.

Based on the examination of TBAB, a variety of other PTCs were investigated, results are summarized in Table 1, PTCs are divided into three classes, one class are quaternary ammonium cationic PTCs (entry 2–7), one class are anionic PTCs (entry 8 and 9), and the other one are nonionic PTCs (entry 10–13). The dosages of PTCs were outlined under the table. TBAC, TMAB and TDMBAC were utilized at the same molar amount of TBAB, and CTAB, CTAC, SDBS, OP-10, Tween-60 and β -CD were used at their critical micelle concentrations (CMC), in the cases of CMC-Na and PEG 6000, which do not bear CMC, utilized at the same weight amount of TBAB.

Table 1 indicated that the oxidation performed unsatisfactorily without presence of PTC, only 16.4% of conversion rate was gotten (entry 1), so PTC is a crucial additive, and among the three kinds of PTCs, cationic PTCs significantly favored the biphasic oxidation (entry 2, 3, 5–7), except TMAB (entry 4), which bearing the shortest aliphatic chains in its molecular, therefore, the mass transfer initiated by TMAB was not distinct. Comparing with that of in aqueous phase, the solubility of CoSPc in ethylbenzene is limited, therefore, the mass transfer process owing to the sulfonic substituents on the phthalocyanine ring, which could facilitate the formation of ionic pair [8] with cationic PTCs. Anionic and nonionic PTCs had an inconspicuous effect on the oxidation (entry 8–13) due to their helplessness in the formation of ionic pair with CoSPc, in the cases of CMC-Na and β -CD, were even inferior to that of without PTC. Counterion bromide in PTC (entry 2) did favored the oxidation compared to their counterpart which combined with chloride anion (entry 3), due to the better surface activity for bromide as a counterion of quaternary ammonium than chloride did [9], CTAC performed similarly to the result of CTAB, but with a much higher concentration than that of CTAB.

A comparative reaction was conducted, employing acetic acid as the solvent in absence of PTC and without other conditions changed. Empirical results indicated homogeneous system exhibited a much higher oxidation activity, but with a much lower selectivity of acetophenone, the generation of benzoic acid *via* over oxidation of acetophenone was detected by TLC, this phenomenon attributed to the better dissolubilities of O_2 , NHPI and CoSPc in acetic acid, at the same time, it was also blamed for its higher catalytic activity, which resulted in the lower product selectivity. The inducting of water involved liquid-liquid heterogeneous system separated the substrate and catalysts, and restrained the over oxidation of acetophenone, so the products selectivities were higher then that of in acetic acid.

Ultimately, the possible process of the oxidation was proposed according to the empirical results, it is well known, β -CD bear a lipophilic inner cavity and a hydrophilic outside surface, the cavity diameter of β -CD is between 6.0 and 6.5 Å [10], which favored the ethylbenzene mass transfer from organic to aqueous phase [11], nevertheless, when β -CD was utilized as PTC, the ethylbenzene conversion rate was lower (entry 13) even than that of without present of PTC (entry 1). It indicated that the oxidation did not mainly take place in aqueous phase. In the cases of quaternary ammonium PTCs, they promoted the mass transfer of CoSPc from aqueous phase to organic one, which fulfilled the oxidation. This also supported the organic phase oxidation process. NHPI can be slightly dissolved both in organic and aqueous phases, so the influence initiated by PTCs on NHPI was not significant. In summary, a conclusion can be drawn that PTCs promoted oxidation of ethylbenzene was mainly affected by the mass transfer of CoSPc, which is an aqueous dissolved molecular. A proposed procedure is outlined in Scheme 2. Preliminary, CoSPc yielded hyperoxide



Scheme 2. Proposed reaction procedure.

radical complex with dissolved oxygen in aqueous phase, then generated ionic pair with cationic PTCs, after that, it was transferred into the organic phase, therein, PINO was generated *via* hydrogen abstraction by hyperoxide radical complex, and then, PINO was involved in the oxidation circulation, similar to that of homogeneous oxidation process [2].

3. Conclusions

In summary, an easy workup and environmentally friendly method to convert ethylbenzene into the corresponding oxides, promoted by PTCs, was developed in a water involved liquid–liquid biphasic system, among which, TBAB was the most favorable PTC, due to its appropriate aliphatic chain length and capability of forming ionic pair with CoSPc, contrary to that, anionic and nonionic PTCs exhibited less helpfulness to the oxidation.

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- [7] 2: ¹H NMR (400 MHz, CDCl₃): δ 7.95 (d, 2H, J = 7.6 Hz), 7.55 (t, 1H, J = 7.4 Hz), 7.45 (t, 2H, J = 7.6 Hz), 2.59 (s, 3H); EI-MS (70 eV) *m/z* (%): 120 (M+, 1), 119 (2), 105 (25), 85 (64), 83 (100), 77 (17), 47 (27). 3: ¹H NMR (400 MHz, CDCl₃): δ 7.32–7.22 (m, 5H), 4.81 (q, 1H, J = 6.4 Hz), 2.46 (s, 1H), 1.44 (d, 3H, J = 6.4 Hz); EI-MS (70 eV) *m/z* (%): 122 (M+, 17), 107 (71), 105 (100), 79 (37), 77 (21), 51 (11).
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