Journal of Molecular Catalysis A: Chemical 402 (2015) 79–82

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Efficient metal-free oxidation of ethylbenzene with molecular oxygen utilizing the synergistic combination of NHPI analogues

Qiming Zhao[a], Kexian Chen[b], Wensong Zhang[a], Jia Yao[a], Haoran Li[a,b,*]

[a] *Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou 310027, PR China*

[b] *State Key Laboratory of Chemical Engineering, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China*

ARTICLE INFO

Article history:
Received 25 November 2014
Received in revised form 17 March 2015
Accepted 21 March 2015
Available online 24 March 2015

Keywords:
Oxidation
Organocatalyst
Molecular oxygen
Ethylbenzene
Metal-free
N-hydroxyphthalimide

ABSTRACT

A metal- and initiator-free catalytic system comprising *N*-hydroxyquinolinimide (NHQI) and 4-carboxyl-*N*-hydroxyphthalimide (Car-NHPI) was developed for the oxidation of ethylbenzene using molecular oxygen as the terminal oxidant. The catalytic activity of Car-NHPI/NHQI catalytic system was higher than that of Car-NHPI or NHQI alone. The high catalytic performance of Car-NHPI/NHQI catalytic system could be attributed to the dual interactions of radical exchange and acid-base neutralization, which resulted in the increment of the conversion of ethylbenzene up to 70% and the selectivity of acetophenone up to 66% at 120 °C under 1 atm O_2 for 15 h.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Selective oxidation of hydrocarbons by molecular oxygen to useful intermediates plays important roles in the academic and industrial chemistry [1,2]. *N*-hydroxyphthalimide (NHPI), a powerful organocatalyst, has attracted increasing attention in the last decades due to its established high efficiencies in oxidation studies [3–10]. Since Ishii and coworkers developed NHPI/metallic salts systems to promote the oxidation of various organic compounds with molecular oxygen [11–14], considerable efforts have been made to develop many catalytic systems containing NHPI or its derivatives towards the oxidation of various substrates [15–22]. Initiators, especially metal-based ones, are necessary to achieve the good catalytic performance of NHPI-based catalytic systems. Because, they can efficiently convert NHPI to reactive phthalimide *N*-oxyl radical (PINO) [23–25], which is able to abstract hydrogen atoms from hydrocarbons, subsequently promoting the oxidation [26–30]. However, these metal compounds are potentially detrimental to environment or costly. Therefore, the development of metal- and initiator-free NHPI-based catalytic systems is an urgent need from the perspective of green chemistry, which still remains a scientific challenge [31–33].

Our group have prepared an acetylacetone-metal catalyst modified by pyridinium salt group and have found that it was efficient in the NHPI-catalyzed oxidation of cholesteryl acetate [34]. Our results showed that the pyridinium salt group played a crucial role for the observed high performance in this catalytic system. Recently, oximes, structurally similar to NHPI, has been found to facilitate the oxidation of hydrocarbons catalyzed by NHPI and its derivatives [35–37]. Mechanistic study revealed that the corresponding *N*-oxyl radicals of oximes were produced easily due to its lower >NO—H bond dissociation enthalpy (BDE) than that of NHPI. These *N*-oxyl radicals could smoothly transform NHPI to PINO through the hydrogen-atom transfer reaction, which opened up the catalytic oxidation of diversified substrates. Meanwhile, the hydrogen-atom transfer reaction between PINO and substituted NHPI was also confirmed and investigated in the kinetic studies [38]. These works encourage us to suppose that the combination of two *N*-hydroxyimides with different >NO—H BDEs, possibly structurally modified with ionic compounds, have decent synergistic effects to promote the oxidation of hydrocarbons without any initiators [33].

In this paper, we report a new metal- and initiator-free organocatalytic system consisting of *N*-hydroxyquinolinimide (NHQI) and 4-carboxy-*N*-hydroxyphthalimide (Car-NHPI) and study its catalytic performance in the oxidation of ethylbenzene

---

[*] Corresponding author at: Department of Chemistry, ZJU-NHU United R&D Center, Zhejiang University, Hangzhou, 310027, PR China. Fax: +86 517 87951895.
E-mail address: lihr@zju.edu.cn (H. Li).

http://dx.doi.org/10.1016/j.molcata.2015.03.017
1381-1169/© 2015 Elsevier B.V. All rights reserved.

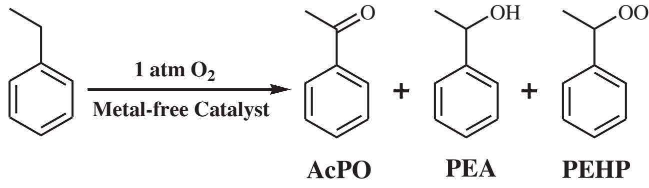

Fig. 1. The oxidation of ethylbenzene.

by molecular oxygen (Fig. 1). As we expected, the combination of NHQI and Car-NHPI has better performance than them being used alone. The synergistic effects between them are proved to be the radical exchange and acid-base neutralization. The obtained results afford a new methodology for the design of efficient metal- and initiator-free catalytic systems.

2. Experimental

2.1. Materials

The ethylbenzene [99.5%], toluene [99.5%], anthraquinone [98%], benzoic acid [99.5%], acetophenone (AcPO) [99.0%], and 1-phenylethyl alcohol (PEA) [98%] were purchased from Aladdin. Chromatographically pure benzonitrile [99.5%], acetonitrile [99.9%], acetic acid [99.9%], trichloroacetic acid [99.8%] and benzotrifluoride [99.0%] were bought from commercial sources and used without further treatment.

NHQI and Car-NHPI were synthesized *via* the reactions of the corresponding anhydrides with hydroxylamine hydrochloride according to previous studies [39,40]. The products were purified and identified by H-NMR and electrospray ionization mass spectrometry (ESI–MS) before they were used as catalysts.

2.2. Catalytic studies

All reactions were conducted in three-necked flask (50 mL) with a O_2 inlet tube, thermometer and reflux condenser. The 1 atm dioxygen was supplied by standard oxygen bottle. Typically, 1.0616 g (10 mmol) ethylbenzene, 25 ml benzonitrile, the desired amount NHQI and Car-NHPI were added into the flask. The oxygen was bubbled into the system at a constant speed (15 mL min^{-1}), and the system was heated by IKA RCT basic to the desired temperature.

The oxidation reaction were analyzed by gas chromatography (GC) equipped with a DB-17 column (30 m × 0.25 mm × 0.25 μm). All GC experiments were carried out and recorded using a Shimadzu GC-2010. The products were determined by GC with toluene as internal standard substance. The conversion of ethylbenzene and the selectivity of AcPO and PEA were calculated by the internal standard curves. As the amount of 1-phenylethyl hydroperoxide (PEHP) could not be immediately measured as a result of its decomposition to AcPO during GC analysis, it was detected through its quantitative conversion to PEA by mixing with excess Ph_3P at room temperature for 1 h, where the increment of PEA equaled to the quantity of PEHP. The products were confirmed by comparison with standard chemicals via GC–MS analysis.

3. Results and discussion

3.1. The synergistic combination of Car-NHPI and NHQI in the oxidation of ethylbenzene

The catalytic performances of different catalytic systems were examined in the oxidation of ethylbenzene to three main products (AcPO, PEA and PEHP) (Fig. 1) at 120 °C under 1 atm O_2 for 15 h. The results were listed in Table 1.

The autoxidation of ethylbenzene was carried out, and only 4% conversion with 16% selectivity of AcPO was obtained (Table 1, entry 1). The 10 mol% NHPI, 10 mol% NHQI, and 10 mol% Car-NHPI were used in the oxidation of ethylbenzene, and the conversion were 43%, 42%, and 55% and the selectivity of AcPO were 20%, 40%, and 46%, respectively (Table 1, entries 2–4). When anthraquinone (AQ) initiator was added, the conversion of ethylbenzene was improved (Table 1, entries 2–7). Compared with AQ/NHQI catalytic system or AQ/Car-NHPI catalytic system, Car-NHPI/NHQI catalytic system had a better catalytic effect in the oxidation of ethylbenzene using the same catalytic amount (Table 1, entries 6–8). Therefore, there must be some synergistic effects between NHQI and Car-NHPI.

To understand such synergistic effects, it was prerequisite to analyze the process of this catalytic oxidation. During the reaction, the carboxyl group of the Car-NHPI lost a proton due to the alkalinity of NHQI, and turned to an electron-donating acetate group. The resultant Car-NHPI had smaller >NO—H BDE than its precursor, therefore, Car-PINO radical could be easily produced. Simultaneously, the pyridine ring in NHQI was protonated to be the pyridinium salt substituent, which had stronger electron-

Table 1
Oxidation of ethylbenzene catalyzed by the different combinations of NHPI, NHQI, and Car-NHPI.[a]

Entry	NHPI (mol%)	NHQI (mol%)	Car-NHPI (mol%)	Conv. (%)	Select. (%)		
					AcPO	PEA	PHEP
1	0	0	0	4	16	21	60
2	10	0	0	43	20	18	58
3	0	10	0	42	40	13	40
4	0	0	10	55	46	12	36
5[b]	10	0	0	48	32	19	37
6[b]	0	10	0	51	31	12	44
7[b]	0	0	10	66	36	10	41
8	0	5	5	67	64	12	16
9	5	5	0	50	39	13	38
10	5	0	5	65	47	11	30
11[c]	0	10	0	41	49	12	25
12[d]	0	10	0	39	53	11	20
13[e]	0	0	10	56	67	5	8

[a] Reaction conditions: 10 mmol ethylbenzene, 25 ml PhCN, 1 atm O_2, 120 °C, 15 h.
[b] 1.25 mol% of anthraquinone was added.
[c] 10 mol% of benzoic acid was added.
[d] 10 mol% of trichloroacetic acid was used.
[e] 10 mol% of pyridine was used.

Download English Version:

https://daneshyari.com/en/article/65020

Download Persian Version:

https://daneshyari.com/article/65020

Daneshyari.com