Applied Catalysis A: General 439–440 (2012) 1–7

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

A study on the liquid-phase oxidation of toluene in ionic liquids

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ARTICLE INFO

Article history:
Received 18 January 2012
Received in revised form 16 June 2012
Accepted 18 June 2012
Available online 4 July 2012

Keywords:
Ionic liquids
Liquid-phase oxidation
Solubility
Toluene
Benzaldehyde
Benzyl alcohol
Benzoic acid

ABSTRACT

The effect and mechanism of the hydrophilic ionic liquids (ILs) with cobalt naphthenate as catalyst on the liquid-phase oxidation of toluene were studied systematically. Five ILs with different hydrophilicities were employed as reaction media. The results showed that toluene conversion increased with increasing hydrophilicity of ILs. The toluene conversion and the corresponding selectivity of benzaldehyde reached 19.6% and 19.5%, respectively, in 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4). The solubilities of toluene, benzaldehyde, benzyl alcohol and benzoic acid in [Emim]BF_4 were further measured at temperatures from 299.2 K to 343.2 K. The correlations between solubility and temperature were developed based on the critical point of phase separation or ideal solution model. The low solubility of toluene in [Emim]BF_4 indicated a heterogeneous oxidation mechanism for toluene. The improvement of toluene conversion and product selectivity in [Emim]BF_4 was attributed to the interactions between reaction and extraction separation. The sensitivity study demonstrated that the increase in oxygen pressure was beneficial to the reaction. A much lower reaction temperature of 130 °C was achieved in [Emim]BF_4 instead of a typical 160–170 °C for current commercial plants. The high conversion, low reaction temperature and high product selectivity for the liquid-phase oxidation of toluene in [Emim]BF_4 makes it a green and efficient hydrocarbon oxidation process.

1. Introduction

Ionic liquids (ILs) are known as alternative "green" solvents owing to their unique physical properties, such as good thermal stability, low volatility, low flash point, and tunable polarity. Therefore, there has been an increasing interest in the last decades to study ILs as reaction media, reagents or catalysts [1].

The oxidation of toluene is an important hydrocarbon oxidation process. The products, including benzoic acid, benzyl alcohol and benzaldehyde, are important intermediates in the organic synthesis industry. This reaction is usually allowed to proceed in acetic acid solvent with cobalt carboxylate as catalyst. During the reaction, a significant mass loss of solvent is inevitable by the formation of CO and CO_2 [2]. The corrosion and over-oxidation are also major industrial challenges. In particular, over-oxidation is difficult to control in the hydrocarbon oxidation process.

The application of ILs for oxidation reactions has attracted considerable attention in recent years. In 2000, Howarth [3] reported the oxidation of aromatic aldehydes in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim]PF_6), and Song [4] utilized [Bmim]PF_6 to recycle Jacobsen's chiral (salen) Mn catalyst in asymmetric epoxidations. So far, ILs have been considered as environmentally benign media for oxidation reactions in many chemical processes [5], such as epoxidation of alkenes [6,7], oxidation of alcohols [8,9], catalytic oxidation of alkanes [10] and aromatics [11,12]. Seddon (2002) studied the oxidation of toluene in 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bdmim]BF_4) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4), respectively [13]. The results demonstrated that the liquid-phase oxidation of toluene catalyzed by a transition metal was feasible in the ILs, although the conversion of toluene was rather low under the unoptimized conditions. However, to the best of our knowledge, only few studies have been documented for the oxidation of toluene in ILs [14–16]. It is therefore of great significance to systematically study the oxidation of toluene in ILs for an alternative efficient and green process of hydrocarbon oxidation.

Since there is a significant difference between the polarity of toluene and benzoic acid, the polarity of the reaction medium plays a crucial role in the liquid-phase oxidation of toluene. In order to investigate the effects of the IL's hydrophilicity on the liquid-phase oxidation of toluene, five types of ILs with different hydrophilicities were used as reaction media with cobalt naphthenate as catalyst and oxygen as oxidant. The solubilities of toluene, benzaldehyde, benzyl alcohol, and benzoic acid in 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF_4) were measured to determine mechanism of the improved conversion of toluene and product selectivity in [Emim]BF_4.

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http://dx.doi.org/10.1016/j.apcata.2012.06.026