Journal of Industrial and Engineering Chemistry 20 (2014) 3061–3067

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Continuous gas–liquid aerobic oxidation of toluene catalyzed by [T(p-Cl)PPFe]$_2$O in a series of three stirred tank reactors

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ARTICLE INFO

Article history:
Received 20 June 2013
Received in revised form 21 October 2013
Accepted 10 November 2013
Available online 16 November 2013

Keywords:
Porphyrin
Oxidation
Toluene
Benzaldehyde
Catalysis

ABSTRACT

The liquid-phase catalytic aerobic oxidation of toluene by [T(p-Cl)PPFe]$_2$O was studied in a series of three stirred tank reactors. The effects of operation mode (including semi-batch and continuous operation), reaction temperature, catalyst concentration, average residence time, and air flow rate on the oxidation process were examined. The experimental results showed that continuous oxidation had no advantage over the total yield and selectivity of benzaldehyde and benzyl alcohol in comparison with semi-batch oxidation. And the reaction temperature was the most significant factor influencing on continuous oxidation of toluene. It is also found that adopting sequentially decreased temperature in the three series reactors could improve the yield and selectivity of benzaldehyde and benzyl alcohol in this process. Under which at the higher conversion of toluene, the total yield to benzaldehyde and benzyl alcohol increased 17.05% or 43.62% respectively in comparison with adopting sequentially increased or same temperature in the three series reactors.

1. Introduction

The oxidation of toluene is one of the extremely important reaction in chemical industry. The major products, benzaldehyde (BALD), benzyl alcohol (BALC), and benzoic acid (BA), are widely used in pharmaceutical, dyestuff, food, resin, and textile fiber industries [1,2]. It is attractive to obtain BALD and BALC by the direct oxidation of toluene, they are intermediates susceptible to further oxidation. The low selectivity or use of large amounts of solvents and bromides is a big problem [1–6]. Alternatively, BALD and BALC are mostly obtained by a two-step method commercially. In the first step, the methyl group connected to benzene ring was halogenated by chlorine, and in the second step, the halogenated toluene was basic hydrolyzed to BALD and BALC by NaOH [7]. It is a complex process discharging massive pollutant such as HX gas and heavy metal salts, which results in a serious environmental pollution. An environmentally friendly oxidation process of toluene with air to BALD and BALC with high selectivity is highly desirable.

Metalloporphyrins have been proved to be a kind of excellent catalyst for the selective aerobic oxidation of hydrocarbons [8], such as alkanes [9,10], cycloalkanes[11,12], olefins[13] etc. Among them, the oxidation of cyclohexane to cyclohexanone and cyclohexanol catalyzed by metalloporphyrins has been applied industrially in SINOPEC Corp. [14,15]. Recently, the aerobic selective oxidation of toluene to BALC and BALD catalyzed by metalloporphyrins in a semi-batch reactor was reported, in which the gas as one of the reactants was continuously fed, while the liquid was batch fed [16–21]. Effects of reaction conditions as well as the structures and concentrations of catalysts on the oxidation process were studied. The results showed a good selectivity of BALC and BALD, which infers a potentially green and environmentally friendly industrial approach to produce BALC and BALD. The effects of reactor operation mode, i.e., semi-batch, continuous, on the oxidation process have not been considered in previous work. However, Steeman et al. [22] and Spielman [23] studied the reactor operation mode on the aerobic oxidation of hydrocarbons and found it would influence the selectivity and yield of the oxidation intermediates. Although the catalyst systems adopted by Steeman et al. [22] and Spielman [23] were different, the reactor operation mode might affect the selectivity and yield of intermediates BALC and BALD in the biomimetic oxidation of toluene. Unfortunately, if the oxidation technique was industrially applied, the most probably reactor mode might be continuous. So, it is necessary

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Abbreviations: BALC, benzaldehyde; BALD, benzyl alcohol; BA, benzoic acid; CH3OH, methanol; GC, gas chromatography; GC–MS, gas chromatography–mass spectrometry; HPLC, high pressure liquid chromatography; H3PO4, phosphoric acid; HX, Hydrogen halide; i.d., inner diameter; IR, infrared; LC–MS, liquid chromatography–mass spectrometry; NaOH, sodium hydroxide; NMR, nuclear magnetic resonance; min, minute; UV, ultraviolet.

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http://dx.doi.org/10.1016/j.jiec.2013.11.044

Nomenclature

A	temperature, K
B	catalyst concentration, ppm
C	average residence time, min
D	airflow rate, ml min^{-1}
K	the average response of each factor level in Table 3
R	the margin between the maximum and minimum of K in Table 3
R	reactor in Fig. 2
V	vessel in Fig. 2

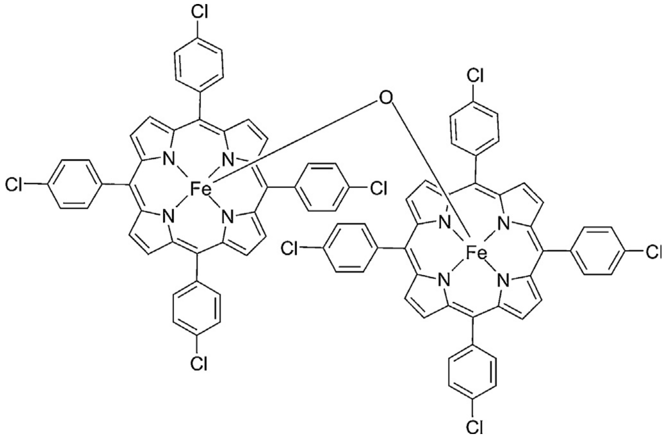

Fig. 1. The molecular structure of catalyst $[T(p\text{-}Cl)PPFe]_2O$.

to quantitatively study the effects of reactor operation mode, especially for the semi-batch and continuous operation, on the oxidation process.

In this work, an apparatus equipped with three autoclaves in series was used to examine the effect of continuous operation on the aerobic oxidation of toluene to BALC and BALD catalyzed by metalloporphyrins. In these experiments, the reactants were continuously fed and the products were also continuously removed. By using orthogonal experimental technique, the effects of temperature, catalyst concentration, air flow rate, and average residence time on the oxidation process were investigated. The experimental results were compared with those obtained from semi-batch reactor. Finally, a possible explanation for why the continuous and the semi-batch operation mode affected the oxidation process differently was proposed.

2. Experimental

2.1. Chemicals

The molecular structure of $[T(p\text{-}Cl)PPFe]_2O$ used as catalyst in this study is shown in Fig. 1. It was synthesized and purified according to reported procedures [24,25] and its structure were determined by ^{1}HNMR spectrum, IR spectra, UV–vis spectra and elemental analysis. All other chemicals used in the experiments were obtained from Changsha Chemical Reagent Co. and had the purity higher than 0.990 (mass fraction).

2.2. Apparatus and procedures

The apparatus employed to carry out continuous oxidation of toluene appears in Fig. 2. It consists of three autoclaves in series. Each autoclave has an effective volume of about 100 ml and is equipped with a gas-dispersion element and a blade stirrer. The oxidation system pressure was maintained at 1.0 MPa by a back-pressure valve. Three Pt 100 thermal resistance thermometers were used to measure the temperature of three autoclaves. The reaction mixture in the every autoclave was heated at 10 K min^{-1} to the experimental temperature. The temperature of each was controlled within ±0.5 K of the desired temperature by a PID controlling system shown in Fig. 2. When the temperature was higher than the desired point, cooling oil would be pumped through the spiral cooling coil each to cool the content of the autoclaves. When the temperature was lower than the desired point, the autoclave walls would be electrically heated. In each experiments, firstly, toluene and $[T(p\text{-}Cl)PPFe]_2O$ were placed into the vessel V_1 pressurized with high-purity nitrogen at 0.3 Mpa; secondly, the toluene and the catalyst from V_1 were pumped to the autoclave R1, and then flew from R1 to R2 and R2 to R3. When the desired temperature was reached, air was sparged into each reactor and the reactions began. The vapor passed through a series of condensers shown in Fig. 2, where the evaporated components were cooled in a tank. The condensed liquid component would be laminated. The major component in the upper layer was toluene, and water in the lower layer. The uncondensed gases passed through a back-pressure regulator into the exhaust. The upper layer was back into each reactor and the lower layer was discharged regularly. Three digital gas detectors were used to measure the oxygen concentration in the vent online. The liquid products in the reactors were sampled at certain intervals and the concentrations of each components were analyzed. When the oxygen concentration in the vent changed un-notably, and relative deviations in the components concentrations for four to five neighbored sampling were less than 3%, the continuous reactions stopped.

The experimental apparatus and procedure used to carry out the semi-batch oxidation experiments were described previously [18]. Semi-batch experiments were performed in a 500 ml steel autoclave with a blade stirrer. Oxidation of toluene was carried out using the following typical procedure: 350 ml of toluene and quantitative $[T(p\text{-}Cl)PPFe]_2O$ were placed into the reactor pressurized with high-purity nitrogen at 0.6 MPa. When the desired temperature was reached, nitrogen was released and air was injected continuously at the same time. A digital gas detector was

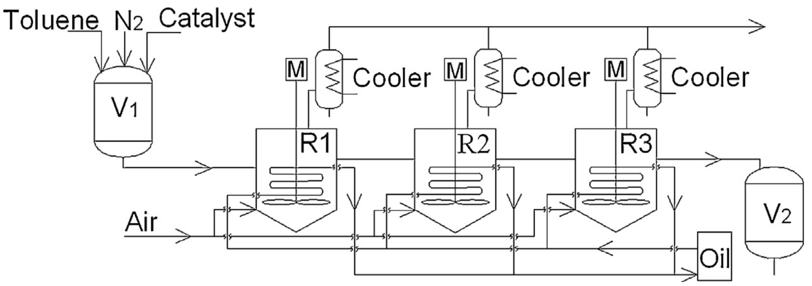

Fig. 2. Flow diagram of continuous stirring tank reactor for the oxidation of toluene.