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Modeling the liquid phase autoxidation of cyclohexylbenzene to hydroperoxide

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ABSTRACT

The liquid phase autoxidation of cyclohexylbenzene (CHB) to CHB hydroperoxide (CHBHP) is the key step of green production of phenol. The CHB oxidation kinetics was originally investigated by semibatch experiments under various oxygen partial pressures. Kinetic models to deal with oxygen-rich and oxygen-poor conditions were developed on the basis of free radical chain mechanism. It was found that the activation energy of the rupture of the bond O–O of molecule CHBHP was close to that of cumene hydroperoxide, while the activation energy of hydrogen abstraction from the tert-butyl carbon of CHB was reasonably larger than that of cumene due to the steric effect. The kinetic model involving the oxygen addition to R^{*} (Model II) can be used to deal with various oxygen partial pressure conditions. Based on the developed kinetic model, the simulation of well-mixed reactor operated under continuous conditions was performed, and the results were in good agreement with continuous experiments.

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1. Introduction

The liquid phase oxidation of hydrocarbons into oxygenated chemicals is of vital importance to modern industrial economy due to its efficient conversion from cheap petroleum feed stocks to value-added organic chemicals important in petrochemical and polymer industries (Suresh, 2000). Some notable examples include the oxidation of *p*-xylene (PX) to terephthalic acid (Cao et al., 1994; Shang et al., 2015; Wang et al., 2007), that of cyclohexane to cyclohexanone and cyclohexanol (Suresh et al., 1988a,b,c), that of cumene to hydroperoxide (Andrigo et al., 1992; Bhattacharya, 2008), and so on. The cumene oxidation to hydroperoxide followed by acid decomposition to produce phenol (also called Hock process) is one of the most well known commercial processes. However, currently the Hock process is not economically favorable due to market saturation of the co-product, acetone, and utilization of the valuable resource propylene as starting material.

One promising alternative route to produce phenol is through the liquid phase oxidation of cyclohexylbenzene (CHB), the production process is shown in Scheme 1 (Arends et al., 2002). For this route the only starting hydrocarbon raw material is benzene, which is cheap and easily obtained by economic entities like China whose coal resources are abundant. The exclusive formation of the final product, phenol, makes this route more competitive. In Scheme 1, the selective aerobic oxidation of CHB to CHB hydroperoxide (CHBHP) is the key step, since the oxidation process is slow and produces by-products. Although a few reports can be found for the liquid phase oxidation of CHB (Aoki et al., 2005; Arends et al., 2002; Bond et al., 1999), there is far fewer publications focusing on the oxidation kinetics and modeling, which is fundamental for the design and optimization of industrial reactor and insightful understandings of reaction mechanism.

The liquid phase autoxidation of hydrocarbons proceeds via a free radical chain mechanism (Emanuel et al., 1984). It is called autoxida-

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