



Epoxidation of propylene with H_2O_2 catalyzed by supported TS-1 catalyst in a fixed-bed reactor: Experiments and kinetics

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HIGHLIGHTS

- Reaction kinetics of the propylene epoxidation in fixed-bed reactors is studied.
- The systematic experimental study and modeling of this reaction are reported.
- Eley–Rideal adsorbed with H_2O_2 model precisely describes the reaction mechanism.

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ABSTRACT

The epoxidation of propylene with H_2O_2 catalyzed by a supported TS-1 catalyst in a fixed-bed reactor has been studied. The effects of methanol concentration (40–70 wt.%), hydrogen peroxide concentration (5–20 wt.%), propylene pressure (0.2–0.6 MPa) and temperature (35–50 °C) on the reaction are investigated. The experimental results show that the reaction rate increases with the increase in methanol concentrations, hydrogen peroxide concentrations, propylene pressure and temperature; the activation energy of the reaction is 46.8 kJ mol⁻¹ and the reaction orders with respect to hydrogen peroxide and propylene are 0.32 and 0.68, respectively. The reaction was modeled with Eley–Rideal (E–R) and Langmuir–Hinshelwood (L–H) models, and the results show that the kinetic model of Eley–Rideal with H_2O_2 being adsorbed can give the best fit among the models compared for the epoxidation of propylene with H_2O_2 .

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1. Introduction

Propylene oxide (PO), an important chemical intermediate used in the synthesis of polyether polyols, propylene glycols, and propylene glycol ethers [1–3], has become increasingly important in the chemical industry since 1950s. PO is one of the largest propylene derivatives in production, ranking second behind polypropylene [4–7]. At present, the industrial production of PO mainly comes from two different oxidation processes: the chlorohydrin process and the hydroperoxidation process [1,7,8]. However, both of the two processes suffer from several disadvantages. The chlorohydrin process is not environmentally friendly due to the utilization of environmentally hazardous chlorine and the production of chlorinated organic byproducts. The economy of hydroperoxidation process depends on the marketability of co-products.

Compared with the PO production processes mentioned above, the process of epoxidizing propylene with hydrogen peroxide to

propylene oxide (HPPO) catalyzed by TS-1 is advantageous in the aspects of co-products and environmental friendliness. In recent years, the HPPO processes developed by Dow/BASF and Evonik/Uhde are the most mature and have been commercialized in Belgium, Korea, and Thailand [7,9–12]. The reactions in the epoxidation of propylene by hydrogen peroxide over TS-1 are shown in Schemes 1 and 2.

Many studies have reported the effects of experimental conditions [13–15] and the kinetics on the epoxidation of propylene with hydrogen peroxide over TS-1 catalysts in batch reactors [8,16]. However, the reaction mechanism is still controversial. Shin and Chadwick [8] proposed a kinetic model following the Langmuir–Hinshelwood mechanism with C_3H_6 and H_2O_2 both adsorbed on the active sites. Liang et al. [16] developed a kinetic model derived from the Eley–Rideal mechanism with H_2O_2 being adsorbed on the active sites and free C_3H_6 .

A few groups have also studied the HPPO process in fixed-bed reactors [17–19]. Liu et al. [20] reported that the catalytic life of the modified TS-1 catalysts in the propylene epoxidation in a fixed-bed reactor was more than 1000 h with H_2O_2 conversion

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