

Effect of catalyst deactivation on limonene epoxidation over PW-Amberlite

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Introduction

It has been shown that PW-Amberlite is a highly active and selective catalyst for limonene epoxidation with aqueous hydrogen peroxide in a triphasic system [1]. Although several kinetic models have been proposed [2], catalyst deactivation has not been considered. However, preliminary studies have shown that the main cause of catalyst deactivation is the presence of limonene epoxide; however, activity is recovered by catalyst washing with acetone [1]. Different analyses are being conducted in our group in order to determine important parameters related with catalyst deactivation. In this contribution, a kinetic expression that describes catalyst deactivation is proposed and validated with experimental data free of mass transfer limitations.

Materials and Methods

PW-Amberlite was prepared as previously described [1]. Typically, limonene (0.5 g), acetonitrile (3.2 g), aqueous hydrogen peroxide 30 wt-% (0.83 g) and PW-Amberlite catalyst (0.1 g) with an average particle diameter lower than 0.425 μm were magnetically stirred (1000 rpm) in 8 mL glass flasks immersed in a thermally controlled oil bath (33 ± 0.5 °C). Sampling was done between 0-24 h and reaction products were analyzed by gas chromatography (Varian Star 3400) equipped with a FID and a capillary column (DB-1, 50 m). Plots of limonene concentration as a function of reaction time were compared with those obtained using several kinetic models. Rate constants and reaction orders were estimated by minimization of the square difference of experimental and predicted data with the optimization toolbox "slqnonlin" of Matlab 6.0.

Results and discussion

The empirical reaction rate equation of limonene epoxidation, eq. 1 previously deduced from experimental data [2], is used in the design equation of a batch reactor, eq.2.

$$-r_L = k[C_{10}H_{16}]^a[H_2O_2]^b \quad (1) \quad \frac{dX}{dt} = k[C_{10}H_{16}]^a[H_2O_2]^b \frac{W}{N_{A_0}} \quad (2)$$

Where $k = 0.019$, $a = 1.53$ and $b = -1.06$ [2]; W is the mass of catalyst and N_{A_0} the initial moles of limonene. In terms of fractional conversion X , eq. 3 is obtained.

$$\frac{dX}{dt} = k[C_{10}H_{16}]^{a+b}(1-X)^a(2.003-X)^b \frac{W}{N_{A_0}} \quad (3)$$

Figure 1 shows that at short reaction times, the equation adequately describes experimental data but at long reaction times conversions obtained from eq. 3 are higher than experimental

values [1, 2]. The effect of catalyst deactivation on reaction rate can be modeled including a time-dependent term [3] as shown in eq. 4.

$$\frac{dX}{dt} = k[C_{10}H_{16}]^{a+b}(1-X)^a(2.003-X)^b \frac{W}{N_{A_0}} e^{-k_d t} \quad (4)$$

As observed in figure 1, the best prediction of experimental data is obtained with the introduction of an empirical term, a^* , which takes into account the asymptotic activity or residual catalyst activity [3], eq. 5.

$$\frac{dX}{dt} = k[C_{10}H_{16}]^{a+b}(1-X)^a(2.003-X)^b \frac{W}{N_{A_0}} (a^* + (1-a^*)e^{-k_d t}) \quad (5)$$

Where the activity term, $a(t) = (a^* + (1-a^*)e^{-k_d t})$, obtained by non-linear regression was $a(t) = 0.2857 + 0.7143e^{-15.863t}$.

According to the deactivation model, the maximum catalytic activity lost is around 71.4 %.

Significance

Limonene epoxidation over PW-Amberlite under triphasic conditions was modeled with a rate expression that adequately represents experimental data.

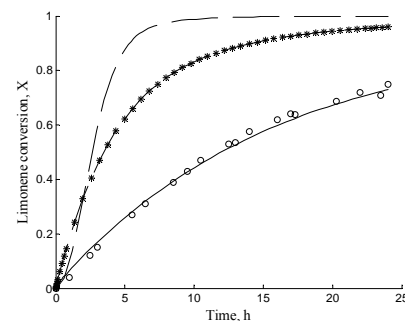


Figure 1. Conversion profiles of limonene epoxidation over PW-Amberlite under triphasic conditions. Experimental data (o), eq. 3 (---); eq. 4 (*) and eq. 5 (—). Reaction conditions: limonene 0.5 g, acetonitrile 3.2 g, aqueous hydrogen peroxide 30 wt-%, 0.83 g, catalyst 0.1 g, 33 °C.

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