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Kinetics of the nopol synthesis by the Prins reaction over tin impregnated MCM-41 catalyst

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HIGHLIGHTS

- Kinetic model for nopol synthesis based on the Langmuir–Hinshelwood formalism is obtained.
- The main product, nopol, inhibits the activity of the Sn-MCM-41.
- The rate law is robust respect to equilibrium adsorption constants.
- The effect of temperature on kinetic of nopol synthesis is mainly on the surface reaction constant.

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ABSTRACT

The kinetics of the nopol synthesis by Prins condensation of β-pinene and paraformaldehyde over Sn-MCM-41 synthesized by impregnation was evaluated using the initial reaction rate method. The reaction rate equation obtained from a kinetic model based on the Langmuir–Hinshelwood formalism with the surface reaction of adsorbed reactants on catalytic sites of the same nature as the limiting step, gave a good prediction of the experimental data. The effect of temperature on the kinetics of nopol synthesis over Sn-MCM-41 obtained by impregnation was studied between 75 and 100 °C. The robustness analysis of the kinetic model showed that the surface reaction constant, k'_{sr}, should be about 0.185 mol g^{-1} h^{-1} at 90 °C, while the ratio between the adsorption equilibrium constant of β-pinene, K_A, and formaldehyde species, K_B, is approximately 1.2:1 (K_A:K_B). The obtained apparent activation energy and pre-exponential factor are 78 kJ/mol and 2.3×10^{10} mol g^{-1} h^{-1}, respectively, but compensation effect analysis using both experimental and simulated data gave strong evidence of the dependency in temperature of the apparent Arrhenius parameters.

1. Introduction

Nopol is an optically active, unsaturated and bicyclic monoterpenic alcohol obtained from natural β-pinene and it is useful as a raw material for synthesis of fragrances and household products [1]. Nopol is produced from the Prins condensation of β-pinene and paraformaldehyde under anhydrous conditions at temperatures above 180 °C or using $ZnCl_2$ as homogeneous catalyst [2]. Recently, high nopol yields were reported over tin supported MCM-41 [3–7] and SBA-15 [8,9] materials. Sn-MCM-41 synthesized by impregnation of $SnCl_2{\cdot}2H_2O$ in an ethyl acetate dissolution under incipient wetness conditions, exhibits higher activity that Sn-MCM-41 materials obtained by CVD of $SnCl_4$, with the additional advantage that its regeneration is possible by exhaustive washing with acetone instead of thermal treatment under air atmosphere [10]. These promising results encouraged our research group to carry out kinetic studies as they are useful for reactor design purposes and for better understanding of the phenomena related to nopol production. No detailed kinetic studies have been reported for the production of nopol or another α, β-unsaturated alcohol obtained neither by the Prins reaction over heterogeneous catalytic conditions nor under homogeneous acid catalyzed reactions. In the absence of catalyst, Watanabe [11] reported reaction rate of first order respect to each reactant for nopol synthesis at temperatures between 170 and 190 °C. The reaction rate law reported over Sn-SBA-15 was of pseudo-first order [8]. Using Sn-MCM-41 prepared by impregnation [12], with a pseudo-homogeneous rate law determined by the excess method [13], zero and second order respect to β-pinene and formaldehyde, respectively, were obtained. As the rate laws reported for those heterogeneous catalytic systems were not based on a mechanism that included the characteristic adsorption phenomena step of the heterogeneous catalytic phenomena, in this contribution a reaction mechanism based on the Langmuir–Hinshelwood formalism is proposed for nopol synthesis over Sn-MCM-41 material obtained by impregnation. Initial reaction

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