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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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rates for nopol synthesis were estimated under several reactant concentrations and at temperatures between 75 and 100 °C.

2. Experimental

2.1. Catalyst synthesis

Tin supported MCM-41 material was synthesized by incipient wetness impregnation following previously reported procedures [10]. The support (2 g), synthesized according to the method developed by Grün et al. [14], was mixed with 3 mL of a solution of $SnCl_2 \cdot 2H_2O$ in ethyl acetate (28.7 μmol Sn/mL) under inert atmosphere, then the solvent was allowed to evaporate for 24 h at room temperature; finally, the solid was calcined at 550 °C for 5 h. The material was coded as Sn(0.28)-I, where the number in parentheses corresponds to the tin weight percent loading determined by atomic absorption.

2.2. Catalytic tests

The reactions were performed in 2 mL capped vials covered with inert silicone septa and immersed in an oil bath which temperature was controlled with an IKA fuzzy controller, and the stirring rates of the stir plate were calibrated and measured with an Extech Instrument digital stroboscope. The catalytic tests were carried out at least by duplicate in six batch reactors under identical reaction conditions (Fig. 1 and Table 1), that is, 1 mg of catalyst Sn(0.28)-I, 1 mL of β-pinene in toluene solution at a concentration between 0.063 and 0.5 M, and paraformaldehyde (0.046–2.5 M). Each reactor was removed from the oil bath every 5 min and cooled immediately with pressurized air, then the solid and the liquid phases were separated by centrifugation. The size of the catalyst was classified with standard series mesh of 170, 270, 325 and 400. The particle size distribution was measured with laser diffraction using a Master Sizer 2000 ver. 5.6 (model Hydro 2000S AWA, Malvern Instruments Ltd., UK) on solids dispersed in water under ultrasound. Table 2 shows the properties of the sieved solids. The temperature effect on the nopol production was evaluated between 75 and 100 °C, with increases of 5 °C (Table 3). The reaction products in the liquid phase were identified in a GC–MS Agilent 7890 N equipped with a HP-5 capillary column, FID detector and autosampler. The carrier gas was He (1 mL min^{-1}) and the split ratio 100:1. The oven temperature was kept at 90 °C for 1 min and then it was raised to 160 °C at 10 °C min^{-1} for 7 min. The quantification of nopol and β-pinene was carried out by multi point calibration curves using dodecane as internal standard. The initial reaction rates of β-pinene disappearance and nopol formation were determined from the slopes of the curves of concentration of the corresponding compound against the time evaluated at $t = 0$.

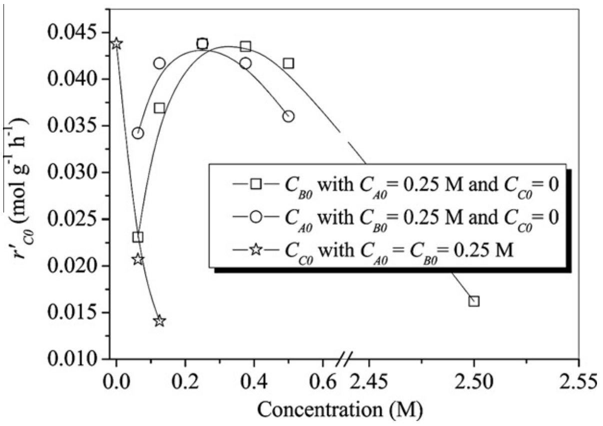

Fig. 1. Effect of the concentrations of reagents on the initial reaction rate of nopol formation, r'_{C0}.

3. Results and discussion

3.1. Mass transfer considerations

The reaction conditions that avoided mass transfer limitations were determined. Particle sizes estimated by the average between standard meshes are in good agreement with those values obtained by the particle size distribution analyzer. Average particle size below 38 μm, could actually correspond to particles of 33.4 μm and lower. To evaluate the effect of external diffusion on the reaction rate, the reaction was carried out at different stirring rates (650–2000 rpm) under standard reaction conditions and with a fixed average particle size of 41.5 μm (Fig. 2). The highest initial reaction rate was obtained above 2000 rpm. The effect of the internal diffusion on the reaction rate was evaluated by changing the average particle size (38–71.5 μm) under the standard reaction conditions and at a stirring rate of 2000 rpm (Fig. 2). These results indicated that the initial reaction rate is almost constant when the average particle size of the catalyst is between 38 and 41.5 μm. Thus, all further experiments were carried using catalyst with an average particle size of 38 μm and at a stirring rate of 2000 rpm.

3.2. Determination of the kinetic rate law

Table 1 shows the effect of the substrate concentrations on the experimental initial reaction rates of β-pinene disappearance and nopol formation. Although, the results suggest that parallel reactions of β-pinene take place from the starting of the reaction, since $-r'_{A0} \geqslant r'_{C0}$, for next analysis only nopol production is taken into account. Side product formation was favored over Sn(0.28)-I with a large excess of β-pinene or paraformaldehyde (runs 1 and 6). We previously reported that byproducts from isomerization of β-pinene, such as camphene and limonene, and from allylic oxidation such as myrtenol, are observed at high conversions (above 60%) over Sn-MCM-41 obtained by chemical vapor deposition (CVD) or by direct hydrothermal synthesis [6]. Over Sn(0.28)-I not only the aforementioned byproducts but also nopyl acetate, pinocarveol and myrtenyl acetate byproducts were observed.

Fig. 1 shows the effect of the concentration of reactants on the initial reaction rate of nopol formation. The decrease of the initial reaction rate in the presence of nopol suggests a strong adsorption of the main reaction product on active catalytic sites. A maximum in the r'_{C0} was observed in the absence of nopol in the initial reaction mixture and under stoichiometric conditions. The type of profile obtained is typical of bimolecular processes where the two reactants are adsorbed in one kind of site [15], which corresponds to mechanism 1 (Table 4). The model M1 had the best fitting of the experimental data (higher R^2, lower RSS and MSE, with randomly distribution of residuals); the predicted initial rate is showed in Fig. 3. Model M1 was obtained from the mechanism 1 according to the Langmuir–Hinshelwood formalism, where the surface reaction was assumed as the rate determining step, as it is the case of the most of heterogeneous catalytic reactions [13,15]. The mechanism 2 and its corresponding model M2 are included for comparison, but it is clear from its statistics that the experimental data fitting is not better than for model M1.

3.3. Sensibility analyses of the kinetic parameters of model M1

The constants determined with the nonlinear regression of model M1 at 90 °C were $k'_{sr} = 0.185 \pm 0.009$ mol g^{-1} h^{-1},