

Catalyst loading effect on nopyl acetate synthesis over Amberlyst-15

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Introduction

Organic esters are of great importance, since they are intermediates in the synthesis of drugs, plasticizers, perfumes, flavor chemicals, fine chemicals, pharmaceuticals, cosmetics, solvents and chiral auxiliaries [1]. Nopyl acetate is an artificial fragrance compound with a fruity odor of fresh wood which is not present in nature. It is used in the preparation of soaps, detergents, creams, lotions and perfumes. It is prepared by the carbonyl-ene reaction of β -pinene (1) and paraformaldehyde (2) with subsequent acetylation of the intermediary nopol (3) with acetic anhydride (Figure 1) [2]. Esterification reactions are extremely slow and require the addition of a catalyst to obtain significant ester yields. Commonly used homogenous catalysts are mineral acids such as sulfuric and hydrochloric acid, as well as sulfonic acids [3]. Despite a high catalytic activity, they exhibit some disadvantages such as their corrosive nature, the existence of undesired secondary reactions and a difficult reaction mixture separation. These problems can be overcome by the use of heterogeneous catalysts [3]. Amberlyst-15 ionic exchange resin has shown to be an effective catalyst for esterification reactions [4]. This work aims to study the catalyst loading effect on the esterification of nopol to establish the most suitable conditions for obtaining high nopyl acetate selectivities.

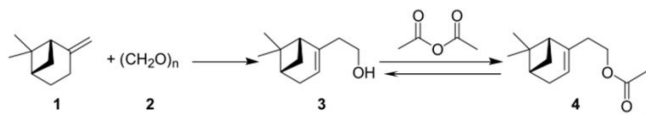


Figure 1. Nopyl acetate (4) synthesis from β -pinene (1) [2].

Materials and Methods

The esterification reaction was performed in a 25 mL three-neck round-bottom flask, coupled to a condenser. The amount of catalyst was varied between 75 and 175 mg, using 20 mL (5 mmol) of nopol/toluene solution (0.25 M) and acetic acid (99.5%) at a 2:1 acid alcohol ratio. The reaction mixture was heated at 80 °C and stirred magnetically at 750 rpm. 0.25 mL samples were taken at 0.5, 1, 1.5, 2, 8 and 24 h. Reaction samples were centrifuged and analyzed by GC equipped with a DB-1 capillary column. He (1 mL/min) was used as carrier gas at a 25:1 split ratio. The oven was kept at 70 °C during 3 min, and then increased to 180 °C at 10 °C/min for 1 min. Nopyl acetate, acetic acid and nopol quantification was performed by multipoint calibration using dodecane as internal standard.

Nopol conversion and nopyl acetate selectivity were determined using equations (1) and (2), respectively.

$$\text{Conversion (\%)} = \frac{(C_i - C_f)_{\text{nopol}}}{(C_i)_{\text{nopol}}} * 100\% \quad (1) \quad \text{Selectivity (\%)} = \frac{(C_f)_{\text{nopyl acetate}}}{(C_i - C_f)_{\text{nopol}}} * 100\% \quad (2)$$

Results and Discussion

Reaction time influences the catalytic activity of the esterification reaction. In Figure 2, nopol conversion (33.3%) and nopyl acetate selectivity (3.8%) increase to 65.8% and 8.2% respectively from 30 to 480 min, using a 6.1 mg/mL catalyst loading. With 3.6 mg/mL, low product selectivity (1%) is obtained at 1440 min, suggesting that the reaction reaches its end at 480 min with remaining catalyst loadings. Slow reaction takes place at low values, 3.6 and 4.9 mg/mL, thus requiring more time to reach an alcohol conversion over 50%.

The most significant nopol conversion (66.4%) and ester selectivity (8.2%) resulted with 6.1 mg/mL of catalyst (Figure 2); at 90 min. Catalyst loading notoriously affects alcohol conversion and ester production due to an availability increase of H^+ ions provided by the resin. Nevertheless, an amount of active catalyst sites higher than those required by the reactant molecules leads to a selectivity lowering, as seen with 7.3 and 8.5 mg/mL of material.

Significance

Best nopyl acetate selectivity (8.2%) is produced at higher reaction times (90-120 min) at 6.1 mg/mL of catalyst, as a result of a suitable amount of catalyst used, contributing with H^+ ions in the reaction, that influence the displacement of the equilibrium towards the product. Evidence of this relies on lower product selectivity with loadings below or exceeding 6.1 mg/mL.

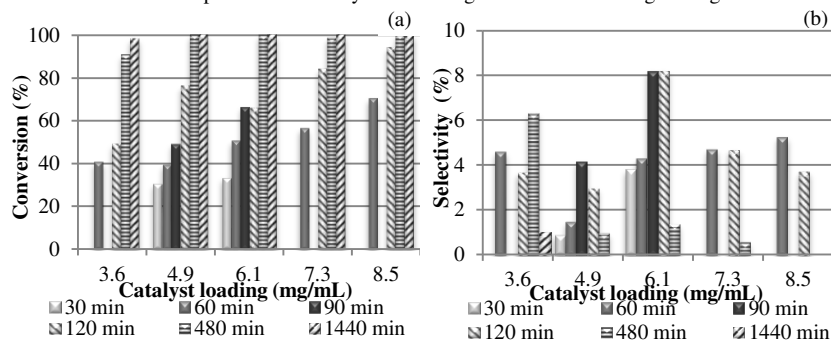


Figure 2. Conversion of nopol (a) and nopyl acetate selectivity (b). Reaction conditions: 80 °C, 750 rpm, nopol/ toluene solution 0.25 M (20 mL), acetic acid (99.5%), Amberlyst-15.

Acknowledgments

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