

Methoxylation of α -pinene over ion-exchanged clays

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Abstract

The use of renewable feedstocks, such as monoterpenoids, to produce fine chemicals *via* heterogeneous catalytic processes is considered a sustainable approach which conforms with the principles of green chemistry [1]. Pinene is a natural bicyclic monoterpene that could be separated, by steam distillation, from gum and sulphate turpentine and which presents two structural isomers (α - and β -). α -pinene is the most widely encountered terpenoid in nature. and finds numerous uses in the food, fragrance and pharmaceutical sectors as well as in the synthesis of chemical intermediates. Thus, α -pinene is considered a versatile building block for the synthesis of high-value added chemicals, mainly through catalytic processes, such as isomerization, epoxidation and pinene oxide isomerization, hydration and dehydroisomerization, esterification, etherification and also in a four-step synthesis of linalool.

In this study, we report the use of clay-based catalysts in the methoxylation of α -pinene, for the selective synthesis of α -terpinyl methyl ether, TME. The main reaction products and intermediates were identified by GC-MS and quantified by GC-FID. The reaction conditions (stirring rate and catalyst load) that afford a kinetic regime were established. SAz-1 (Cheto, Arizona, USA) source clay and a montmorillonite (SD) from Porto Santo, Madeira Archipelago, Portugal, were modified by ion-exchange with Al^{3+} to produce catalysts with markedly different acidities and textural properties. The catalysts based on the high layer-charge SAz-1 montmorillonite proved to be the most active. Ion-exchange with Al^{3+} , followed by thermal activation at 150 °C, afforded the highest number of Brønsted acid sites - a significant proportion of which were located in the clay gallery - and this coincided with the maximum catalytic activity. The influence of various reaction conditions, to maximize α -pinene conversion and selectivity, was studied over AISAz-1. When the reaction was performed for 1h at 60 °C, the conversion reached 65% with 65 % selectivity towards the mono-ether, TME. The kinetic dependencies of this reaction on temperature and reagent concentration, over the selected clays were also investigated. It was established that, in the temperature and reagent concentration regime studied, the reaction was first order with respect to α -pinene. The apparent activation energies over the two catalysts, calculated from Arrhenius plots, were almost identical at 72 kJ mol⁻¹.

Keywords: Ion-exchanged clays, clay acidity, catalysis, pinene, methoxylation, terpinyl methyl ether