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Selective methoxylation of limonene over ion-exchanged and acid-activated clays

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ABSTRACT

In this study, we report the use of clay-based catalysts in the methoxylation of limonene, for the selective synthesis of α-terpinyl methyl ether. Na-SAz-1, Ca-SWy-2 and Sap-Ca source clays and a montmorillonite (SD) from Porto Santo, Madeira Archipelago, Portugal were modified by (i) ion-exchange with Al, Fe, Ni and Na and (ii) acid activation, to produce catalysts with markedly different acidic and textural properties. The lack of activity of Ni^{2+}-SAz-1 (with Lewis acidity maximized), provided evidence that the process occurs preferentially on Brönsted acid sites. 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 located in the clay gallery and this coincided with the maximum catalytic activity. The influence of various reaction conditions, to maximize limonene conversion and selectivity, was studied over Al-SAz-1. When the reaction was performed for 20 h at 40° C, the conversion reached 71% with 91% selectivity to the mono-ether. Mild acid activation (1 M HCl, 30 min, reflux) of the raw SAz-1 clay leads to a material with a good catalytic behaviour (slightly inferior to Al-SAz-1), while any increase in the severity of the acid-treatment (6 M HCl, 30 min, reflux), caused a marked decrease in catalytic activity.

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