

Improved Catalytic Transfer Hydrogenation of Levulinate Esters with Alcohols over ZrO₂ Catalyst

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Abstract

Levulinic acid (LA) and its esters (LE) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Because of LA peculiar structure and reactivity, the United States Department of Energy has classified it as one of the top 12 bio-building block chemicals. Nowadays, the most common strategy for its valorization is the chemical reduction in order to obtain valuable compounds such as fuel additives, solvents and intermediates. In particular, γ -valerolactone (GVL) has been proposed both as an innovative "green" solvent (due to its low toxicity, high stability and high boiling point) and as bio-based liquid fuel. GVL may be obtained from LA by catalytic transfer hydrogenation (CTH) through the Meerwein-Ponndorf-Verley (MPV) mechanism. This approach uses organic molecules (e.g. alcohols) as reducing agents for substrates which contain a carbonyl group. The most promising studies published for the CTH of LA and its esters have been performed in liquid phase using batch reactors and ZrO₂ as heterogeneous catalyst. However, high autogenic pressures are needed in order to work in the liquid phase at high temperature with light alcohols. Moreover, the CTH of alkyl levulinates using methanol or ethanol as solvents/H-donor were found to be inefficient in GVL production. Better results can be obtained by using isopropanol in good agreement with the greater tendency of secondary alcohols to release hydrogen. For all these reasons, we decided to synthesize different high-surface-area ZrO₂ (both tetragonal "t" and monoclinic "m") and test their catalytic activity for the gas-phase continuous-flow production of GVL through CTH of LE. In this way, by working at 250°C with a contact time of one second over t-ZrO₂, both ethyl- and methyl- levulinate can be completely converted promoting the formation of GVL with good to excellent yield of 80% and 68% when 2-PrOH and ethanol are used as reducing agents respectively. For the sake of comparison, under batch conditions the CTH of alkyl levulinates using 2-PrOH leads to a comparable GVL yield only after 24h at 250°C. Unfortunately, the ZrO₂ catalyst undergoes to a progressive deactivation during the time-on-stream. This deactivation was correlated to the deposition of heavy carbonaceous compounds over the Lewis acid sites. However, a complete regeneration of the catalyst can be promoted in-situ, in the same reactor, by feeding air at 400°C. As a matter of fact, the similar behavior showed by ethanol may open interesting scenario in the possibility to use bio-ethanol as reducing agent for these kind of reactions. These results represent the very first examples of the CTH of LE under continuous gas-flow conditions ever reported in literature. Furthermore, the effect of the zirconia phases (monoclinic and tetragonal respectively) on the catalytic activity has been further investigated and now the efforts are directed toward the synthesis of zirconia mixed metal oxides (e.g. Ti-doped zirconia) with the aim of further improve both the catalyst activity and stability for the gas-phase continuous flow production of GVL.