ISGC 2022

N°226 / OC
TOPIC(s) : Biomass conversion / Industrial chemistry

Improved Catalytic Transfer Hydrogenation of alkyl levulinates with ethanol over ZrO2 based catalysts

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PURPOSE OF THE 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, gamma-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.[1] 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. Most of the studies published for the CTH of LA and its esters have been performed in liquid phase using batch reactors and ZrO2 as heterogeneous catalyst.[2] However, very long reaction time and 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 in the traditional liquid phase conditions. 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 and alcohols at atmospheric pressure. In this way, by working at 250°C with a contact time of just one second over t-ZrO2, methyl levulinate (ML) can be completely converted promoting the formation of GVL with good to excellent yield of 68% and 80% when ethanol or 2-PrOH are used as reducing agents respectively. [3] These results represent the very first examples of the CTH of LE under continuous gas-flow conditions ever reported in literature and the interesting reactivity showed by ethanol may open new perspectives in using actual bio-ethanol mixtures as reducing agent for the upgrading of bio-based platform chemicals. Unfortunately, ZrO2 undergoes to a progressive deactivation during the

time-on-stream, due to the deposition of heavy carbonaceous compounds over the Lewis acid sites leading to unwanted alcoholysis and transesterification reactions (i.e. formation of ethyl levulinate, EL). In particular, we proved that the deactivation rate is strongly affected by the zirconia crystalline phase, being the monoclinic one promptly promoting parasite oligomerization reactions of the intermediate angelica lactones. Nonetheless, an effective regeneration of the catalyst can be promoted in-situ, in the same reactor, by feeding air at 400°C.

Finally, new efforts have been done toward the synthesis of zirconia mixed metal oxides (e.g. Ti-doped zirconia) with the aim of promoting both the catalytic activity and the stability of the material allowing a more sustainable continuous flow production of GVL in the gas-phase using ethanol as H-donor.

FIGURES

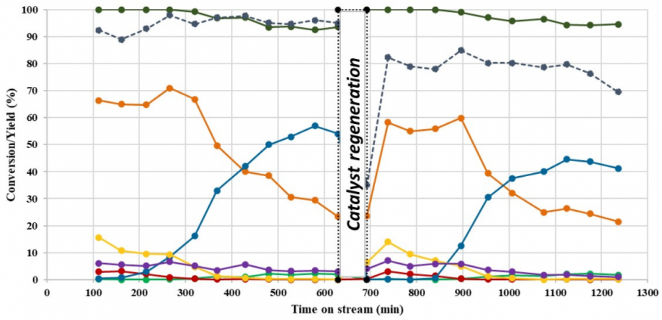

FIGURE 1

Figure 1: Gas-phase CTH of ML and ethanol.

250°C, contact time = 1 s, %mol N_2:ML:EtOH=90.1:0.9:9. ML conversion (dark green), yields of GVL (orange), EL (blue), ethyl-GVL (yellow), ethyl-pentenoates (red), angelica lactone (light green), others (purple). ML molar balance (dashed line)

FIGURE 2

KEYWORDS

Levulinic esters | gamma valerolactone | Hydrogen transfer | continuous-flow reactions

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