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Toward an Efficient, Continuous-flow, Production of GVL through a Catalytic Transfer Hydrogenation Processes with Ethanol in the Gas Phase

T. Tabanelli[1], L. Conte[1], R. Bacchiocchi[1], E. Paone[2], N. Dimitratos[1], F. Mauriello[2], F. Cavani[1]
[1]Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Bologna, Italy
[2]Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Reggio Calabria, Italy

Abstract

Levulinic acid (LA) and its esters (LE) are important, polyfunctional molecules that can be obtained from lignocellulosic biomass. Nowadays, the most common strategy for their valorization is the chemical reduction (i.e. hydrogenation) 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 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, secondary alcohols (i.e. 2-propanol) as H-donor and ZrO_2 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. Recently, we reported on the possibility to enhance the CTH of alkyl levulinates with ethanol (and bio-ethanol) in a continuous-flow, fixed bed, gas-phase reactor using a high-surface-area tetragonal ZrO_2. In this way, by working at 250°C and atmospheric pressure with a contact time of just one second over the catalyst, methyl levulinate (ML) was completely converted promoting the formation of GVL with yield up to 70%.[3,4]
Unfortunately, ZrO_2 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 addition, 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 improved catalytic systems based on zirconia, including mixed metal oxides (e.g. Ti-doped zirconia) with the aim of promoting both the catalytic activity and the stability of the material. Interestingly, in this way we were able to obtain a much more stable and efficient continuous flow production of GVL and/or C5 esters (ethyl pentenoates and pentanoates) in the gas-phase using ethanol as H-donor.

References

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