



CAMURE-11 11th International Symposium on Catalysis in Multiphase Reactors

ISMR-10 10th International Symposium on Multifunctional Reactors

MILANO, ITALY - 21-24 March, 2021

Catalytic Transfer Hydrogenation of Levulinate Esters with Alcohols: Comparison of Batch vs Continuous Gas-Flow Conditions

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1. Introduction

Levulinic acid (LA) and its esters (e.g. methyl and ethyl levulinates, ML and EL respectively) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Because of LA particular structure and reactivity, the United States Department of energy has classified it as one of the top 12 building block chemicals [1]. Nowadays, the most common strategy for its valorisation is the chemical reduction in order to obtain valuable compounds such as fuel additives, solvents and other added-value chemicals. In particular, γ -valerolactone (GVL) has been proposed both as an innovative "green" solvent (due to its low toxicity, stability and high boiling point) and as bio-based liquid fuel and additive with properties similar to ethanol but with a lower vapor pressure, which improved the combustion at similar octane numbers and a higher energy density. The most common approach for the GVL production is the LA hydrogenation with molecular hydrogen (H_2). This is typically performed in batch systems, with high H_2 pressures and with noble metal catalysts, making it expensive and less applicable due to the extreme conditions [2]. The need for an alternative approach has led to the study of catalytic transfer hydrogenation (CTH) through the Meerwein-Ponndorf-Verley (MPV) mechanism. This approach uses organic molecules (e.g. alcohols) that are capable of acting as a hydride transfer agent (H-donor), in order to reduce a molecule containing a carbonyl group.

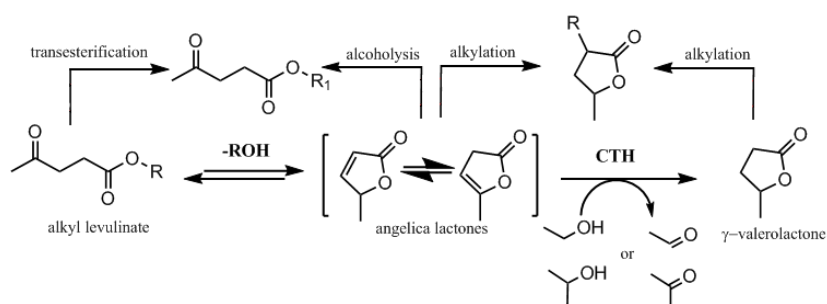
2. Methods

In this study a high SSA ZrO_2 (120 m^2/g) was synthesized and tested in CTH of alkyl levulinates (methyl and ethyl levulinates, ML and EL respectively) with alcohols (methanol, MeOH; ethanol, EtOH, and isopropanol, 2-PrOH) in batch liquid-phase and gas-phase continuous-flow reactors. In the latter case, products and unreacted reagents in the outlet stream were condensed in a cold trap containing 25 mL of acetonitrile. Both the reaction mixtures derived from the gas and liquid phase reactions were analysed by means of Thermo Focus GC equipped with a capillary column Agilent HP-5 and a flame ionization detector (FID). A complete characterisation of both the fresh and the exhaust catalysts has been performed by both ex-situ and in-situ techniques (NH_3 and CO_2 -TPD, DRIFTS, TGA, XRD, Raman).

3. Results and discussion

The performances of the synthesized ZrO_2 catalyst in the CTH of ML or EL using MeOH or EtOH as solvents/H-donor molecules under batch conditions were found to be inefficient in GVL production. As expected, 2-PrOH is by far the most effective in the production of GVL, in agreement with the well-known greater tendency of secondary alcohols to release hydrogen [3]. The reaction occurring in the presence of 2-

PrOH as the solvent/H-donor achieves GVL selectivity higher than 80% at 250°C. Interestingly, at the same temperature, the results obtained by feeding ML under continuous gas-flow conditions over ZrO₂ showed a complete ML conversion for more than 300 min of time-on-stream, promoting the formation of GVL with an excellent yield (80%), when 2-PrOH are used as reducing agents. Surprisingly, also EtOH shows similar behaviour allowing to achieve GVL yield of around 60-70%. A completely different behaviour was observed using MeOH, which selectively promote the alcoholysis and/or transesterification reactions (with both ML or EL), with a very low average GVL yield (4 and 15% respectively). The enhanced GVL yield obtained feeding EL may be attributed to an increased efficiency of EtOH as the leaving group in the intramolecular cyclization to angelica lactones. The results obtained by feeding EL and EtOH were found to be similar to that of ML. In a similar way, the CTH of EL with 2-PrOH led to a complete and stable conversion of the substrate. In this case, however, both the GVL yield and the carbon balance of the reaction are considerably lower compared to the same test performed starting from ML, probably due to the formation of lighter compounds. Moreover, long-term stability tests were carried out over 10 hours and a progressive deactivation of the catalysts was observed. This behaviour was ascribed to both the deposition of heavy carbonaceous compounds over the catalytic surface and to a progressive shift from Lewis to Brønsted acid sites. Finally, the in-situ regeneration of the catalyst, performed by calcination at 400°C in an air flow, allowed an almost total recovery of the initial catalytic performance. The CTH ability of alcoholic solvents is the main driving force for the transformation of alkyl levulinates into GVL, which changes in the order 2-PrOH > EtOH ≫ MeOH. Furthermore, it is also necessary to consider the fact that, in the transesterification, the reactivity takes place in the order MeOH > EtOH > 2-PrOH. Therefore, the catalytic results obtained under batch and gas-flow conditions support the reaction mechanism shown in **Scheme 1**.



Scheme 1. Simplified reaction pathway for the CTH of alkyl levulinates with alcohols toward GVL and the main by-products.

4. Conclusions

The performance of ZrO₂ catalyst in the CHT of ML and EL with different alcohols was investigated under both batch and continuous gas-flow conditions. The bifunctional properties of ZrO₂ surface sites, characterised by the presence of both Lewis acid and basic sites, was proved to lead to a synergistic effect on the concurrent activation of both the alcohol (H-donor) and the carbonyl of the substrate [4]. In the liquid phase (batch), the product selectivity was found to be dependent on the choice of the H-donor. When 2-PrOH was used, a very high selectivity (>80%) to GVL was observed, whereas the reactions carried out in EtOH and MeOH were found to be much less efficient. On the other hand, for the first time in literature, we reported the CTH of ML (or EL) under continuous gas-flow conditions [5]. This approach allows us to obtain complete levulinates conversions and very high GVL yield (>70%) with both 2-PrOH and EtOH (or bio-EtOH) as H-donor.

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