

Improved Catalytic Transfer Hydrogenation of levulinate esters with alcohols over ZrO₂ catalyst †

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Abstract: Levulinic acid (LA) and its esters (alkyl levulinates) are polyfunctional molecules that can be obtained from lignocellulosic biomass. Herein, the catalytic conversion of methyl and ethyl levulinates into γ -valerolactone (GVL) via catalytic transfer hydrogenation (CTH) by using methanol, ethanol, and 2-propanol as the H-donor/solvent, was investigated under both batch and gas-flow conditions. In particular, high-surface-area, tetragonal zirconia has proven to be a suitable catalyst for this reaction. 2-propanol was found to be the best H-donor under batch conditions, with ethyl levulinate giving the highest yield in GVL. However, long reaction times and high autogenic pressures are needed in order to work in the liquid phase at high temperature with light alcohols. The reactions occurring under continuous gas-flow conditions, at atmospheric pressure and relatively low contact time (1 s), were found to be much more efficient, also showing excellent GVL yields when EtOH was used as the reducing agent (GVL yield of around 70% under optimized conditions). The reaction has been tested also using a true bio-ethanol, derived from agricultural waste. These results represent the very first examples of the CTH of LE under continuous gas-flow conditions reported in the literature.

Keywords: zirconia; catalytic transfer hydrogenation (CTH), alkyl levulinates, ethanol, propanol, continuous-flow processes.

1. Introduction

The increased needs to promote a sustainable industrial development has led to the search of alternatives and renewable raw materials and feedstocks for our productions. One of the most promising alternatives to petrochemistry are biorefineries based on lignocellulosic biomass valorization. Lignocellulose is composed of three main component and bio-polymers, namely lignin, hemicellulose, and cellulose from which a wide plethora of valuable bio-platform molecules can be obtained [1,2]. Among them, levulinic acid (LA) can be obtained from cellulose through a multi-step sequence of reactions in which hydrolysis of the bio-polymer is followed by dehydration and hydration reactions to yield the target product and formic acid [3]. With both a ketonic and carboxylic function group, LA is a molecule of great interest and with a great versatility. In particular, LA has been studied and used for the synthesis of various value-added chemicals (namely tetrahydrofuran, γ -valerolactone (GVL), angelica lactones (AL), 1,4-pentanediol (1,4-PDO), among others) [4]. For all of these reasons, its production has increased from 450,000 kg/year (in the 1990s), to around 3800

tons/year in 2020 [3]. It is therefore not surprising that the United States Department of energy has classified LA as one of the top twelve most promising bio-based building block chemicals [5].

Nowadays, the most applied strategy in LA valorization is through reduction by means of catalytic hydrogenation with molecular hydrogen (H_2) in gas and liquid phase. Some studies show the catalytic transformation of LA and its esters using homogeneous catalysts [6,7]. However, this approach is not attractive given the complexity for catalyst separation and recovery [8]. Therefore, the use of heterogeneous catalysts has been investigated the last 10 years. It has been reported the use of catalysts containing noble metal nanoparticles supported on high surface area materials, which have allowed to reach complete conversions and high selectivity to GVL (98-99%) [9]. However, noble-metal catalysts are expensive and harsh conditions (high hydrogen pressure and reaction temperature) are still required to achieve satisfying yield and selectivity toward the target products [9-11]. In addition, most of the published studies still depend on H_2 as reducing agent. This renders the process less sustainable since, through an energetically intensive procedure (e.g. methane steam reforming), fossil fuels are still the main feedstock for hydrogen production [12-13]. A suitable and sustainable alternative, is represented by the catalytic transfer hydrogenation (CTH) using the Meerwein-Ponndorf-Verley (MPV) mechanism. This approach uses organic molecules, such as alcohols, that behave as hydrogen donors toward a carbonyl group in the presence of a catalyst containing both acid and base Lewis sites [7,9,14]. Secondary alcohols, such as isopropanol, are more suitable for the chemical process, since the proposed reaction mechanism has shown a greater stability of the secondary carbocation formed as an intermediate during the reaction [15].

Typically, noble-metal catalysts have been used for the CTH of LA. In particular, the use of supported Ru with isopropanol as the preferred H-donor has led to achieve yields above 80% for GVL working on the liquid phase and using alkyl levulinates as the main substrates [16,17]. In addition, Raney Ni has led to yields of up to 99% for GVL while working with mild conditions (room temperature-80 °C), however with the use of an excess of isopropanol [17].

Since CTH through the MVP mechanism is achieved while in the presence of a catalyst containing Lewis acid/base pairs, several studies have focused on the use of ZrO_2 for the CTH of LA and its esters [18]. Indeed, ZrO_2 has been found to be a suitable catalyst for the target reaction due to its amphoteric character. This allows the simultaneous activation of both the carbonyl group of LA and the alcohol on the active sites of the support [18,19]. Also for this reason, modified- ZrO_2 (e.g. Zr-Al mixed oxides), were tested for the liquid-phase (batch configuration) CTH of ethyl levulinate (EL) using different alcohols as H-donors: methanol, ethanol, 1- and 2-propanols, and cyclohexanol. As expected, isopropanol gave the highest selectivity for GVL (83-84%) at 95% of EL conversion [20].

Even though isopropanol seems to be a great H-donor, it is known that secondary alcohols are likely to form their corresponding ketones which may favor unwanted side reactions (e.g. aldolic condensations). Therefore, simpler molecules such as methanol and ethanol have become attractive alternatives [7,15,21]. However, mechanistic studies have shown that primary alcohols are less available to undergo hydride shift [22]. Nevertheless, ethanol represents an interesting alternative given its high abundance, non-toxicity, sustainability, environmentally benign nature and finally it can be obtained through fermentation of biomasses [17, 23].

At the moment, most of the published studies for the CTH of LA and its esters using ZrO_2 based catalyst have been performed in the liquid phase using batch reactors and isopropanol as H-donor. Furthermore, levulinate esters are characterized by a lower boiling points compared to LA and can be directly obtained by the acid-catalyzed alcoholysis of cellulose-derived carbohydrates. In this way the needs of an additional esterification step of LA is avoided, and finally the sustainability of their direct utilization as raw material is increased significantly [24].

For all these reasons, we decided to investigate the CTH of levulinate ester using a synthesized high specific surface area tetragonal zirconia catalyst in a gas-phase continuous-flow, fixed-bed reactor. In particular, we investigated systematically/thoroughly the effects of different parameters (contact time, reaction temperature, the type of alcohol used as H-donor and the effect of the leaving group of the levulinate ester) as well as the study of reaction and catalyst's deactivation mechanism [25]. The results obtained in the gas-phase were also carefully compared to the ones obtainable in

liquid phase and batch conditions [26]. Herein the most interesting results are summarized and highlighted.

2. Materials and Method

Reagents and standards were analytical grade, all supplied by Sigma-Aldrich (Merk) and used as received. A real mixture of bio-ethanol (derived from molasses and cereal fermentation) was provided by Caviro, a leading wine Italian producer group. Bio-ethanol volumetric composition was: ethanol 95%, acetic acid 1.3%, ethyl acetate 1.2%, methanol 1.8%, aldehydes and acetals 0.7%.

For all the details related to catalyst preparation and characterization refer to ref. [25].

For all the details related to both the continuous-flow gas-phase reactor and the liquid phase autoclave reactor and catalytic tests procedures please refer to ref. [25] and [26].

3. Results and discussion

Firstly, the effect of the reaction temperature on the feasibility of the methyl levulinate (ML) reduction to GVL using ethanol as H-donor has been investigated in the gas-phase over ZrO_2 (Figure 1). Interestingly, in our reaction conditions (see Figure 1 caption), ML conversion was complete also at the lowest temperature, while GVL was formed only between 200 and 300°C with a maximum yield of 65% at 250°C. In addition, the carbon balance of the reaction follow a volcano plot with a maximum of 90% at 250°C. For all these reasons, 250°C was selected as best reaction conditions for the following tests.

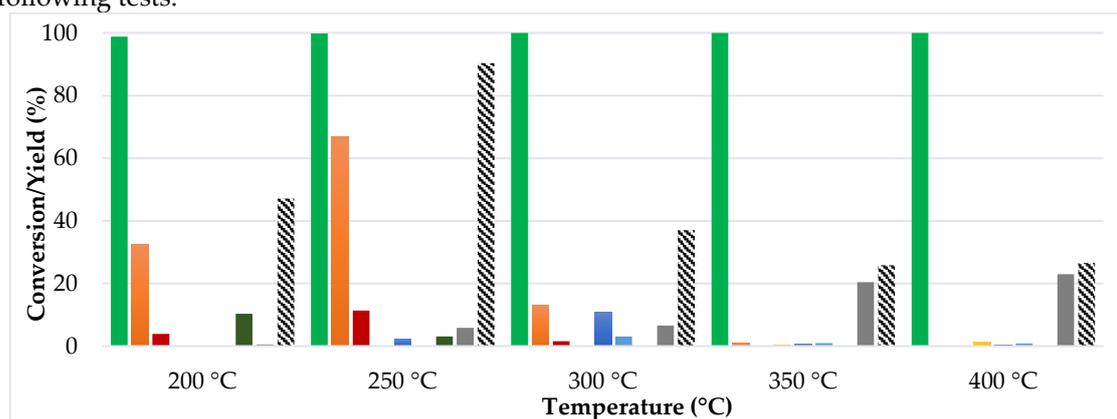


Figure 1. CTH of ML with ethanol as H-donor over ZrO_2 . Reaction conditions: ML:EtOH=1:10 (molar ratio), $\tau = 1$ s, %mol N_2 :ML:EtOH=90.1:0.9:9. ML conversion (■), GVL (■), ethyl GVL (■), angelica lactones (ALs, ■), ethyl pentenoate (■), ethyl pentanoate (■), ethyl levulinate (EL, ■), other (■), carbon balance (black, striped).

In this way, we performed a comprehensive investigation of the effect of the alcohols used as H-donor in the CTH of ML in both gas-phase, (continuous-flow reactor), and liquid phase (batch, autoclave reactor) conditions. From an overview of the obtained results (Figure 2) few important points can be highlighted:

- the superior activity (higher ML conversion) and yield to GVL obtained in the gas-phase continuous flow conditions compared to the liquid phase, regardless the alcohol used as H-donor;
- the very poor results obtained using methanol as H-donor for the target reaction in terms of desired yield of products. Further investigations by using ethyl levulinate (EL) as the chosen substrate have proved the preferential tendency of methanol to promote both trans-esterification and alcoholysis of the intermediates (angelica lactones) reactions;
- isopropanol has been confirmed as the best H-donor for the liquid phase conditions while, in the continuous-flow system in the gas-phase conditions, ethanol and isopropanol have led to very similar results with complete conversion of ML (at least for six hours of reaction) and very good GVL yield (from 60 to 80%);

- performing the catalytic tests using EL as substrate (instead of ML), using the same reaction conditions as shown in Figure 2, a slight improvement of the obtained results in terms of catalytic activity and GVL yield have been observed. This phenomenon may be attributed, to a limited extent, to an increased efficiency of EtOH as the leaving group in the intramolecular cyclization of EL to angelica lactones [26].

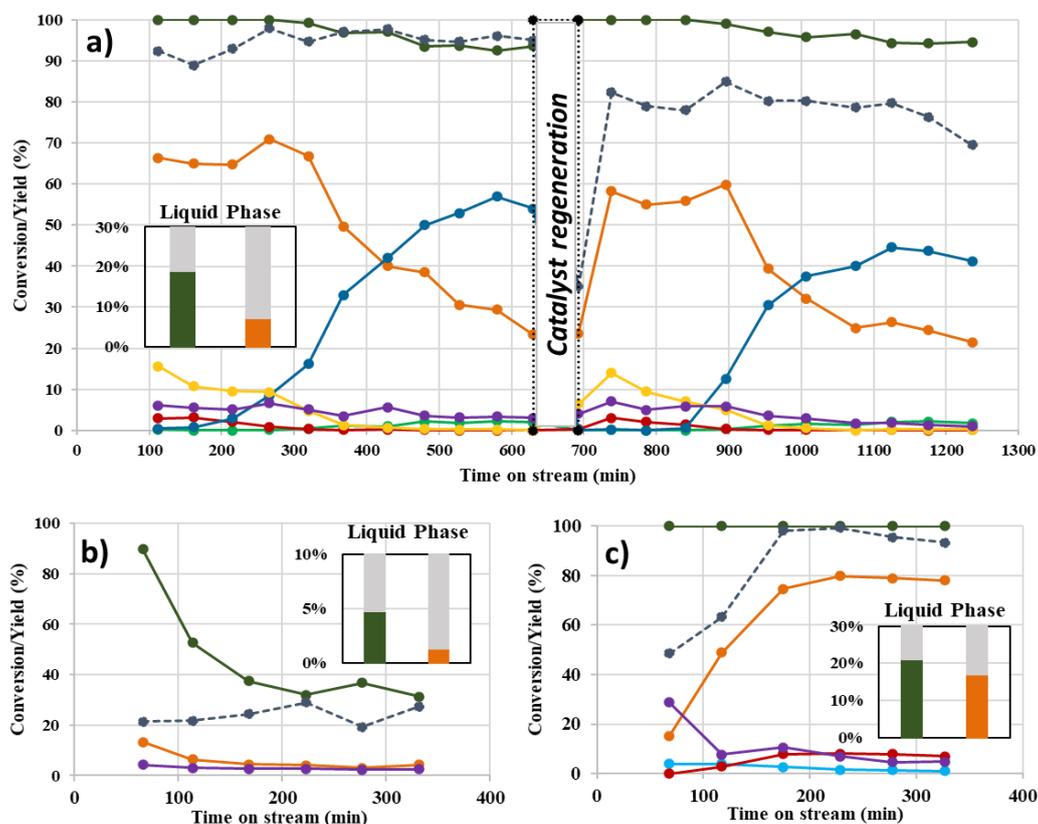


Figure 2. CTH of ML with different H-donor over ZrO₂: a) Ethanol; b) Methanol; c) isopropanol. Reaction conditions for the gas phase (scatter charts): ML:Alcohol=1:10 (molar ratio), $\tau = 1$ s, %mol N₂:ML:Alcohol=90.1:0.9:9. Reaction conditions for the liquid phase (histograms): 40 mL solution of ML or EL (10 wt %), T: 250 °C, 0.30g of ZrO₂ catalyst, reaction time 8 h, N₂ pressure 10 bar, stirring 500 rpm. ML conversion (dark green), GVL (orange), ethyl GVL (yellow), angelica lactones (light green), ethyl pentenoate (red), ethyl levulinate (EL, blue), other (purple), carbon balance (dashed line).

However, in the long-term stability tests performed with ethanol (Figure 2a), the progressive continuous deposition of heavy carbonaceous compounds over the catalytic surface, have led to the blockage and poisoning of the active Lewis acid sites, and therefore have led to a progressive decrease of conversion and change in the chemo-selectivity, promoting the alcoholysis of angelica lactones back to EL. Nevertheless, the *in situ* regeneration of the catalyst was achieved successfully, by performing a heat treatment, by feeding air at 400 °C for 2 h and allowed an almost complete recovery of the initial catalytic behavior, proving that the deactivation of ZrO₂ is reversible and regeneration could be achieved in a simple and practical manner.

Finally, a real bio-ethanol mixture was used as H-donor for ML at the previously optimized conditions. Figure 3 shows that bio-ethanol gave a slightly less satisfactory catalytic performance compared to the one obtained with HPLC-grade ethanol. This is probably due to the presence of impurities on bioethanol (i.e. acetic acid and aldehydes) that could foster the formation of heavy carbonaceous compounds on the catalytic surface, promoting a faster deactivation of the catalyst and in this way decreasing the maximum obtainable GVL yield.

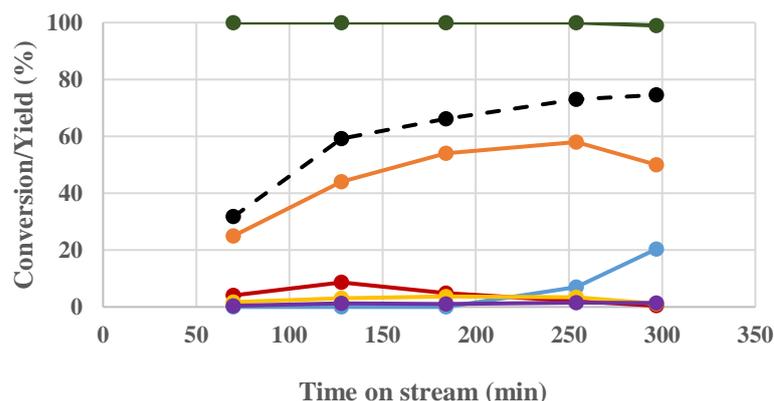


Figure 3. CTH of ML with a real bio-ethanol mixture as H-donor over ZrO₂. Reaction conditions: ML:bio-ethanol=1:10 (molar ratio), $\tau = 1$ s, %mol N₂:ML:bio-ethanol=90.1:0.9:9. ML conversion (dark green), GVL (orange), ethyl GVL (yellow), angelica lactones (light green), ethyl pentenoate (red), ethyl levulinate (EL, blue), other (purple), carbon balance (dashed line).

4. Conclusions

The CTH of alkyl levulinates with a range of alcohols over heterogeneous zirconia catalyst showed a superior catalytic behavior when the reaction is performed in a fixed-bed, continuous flow system in the gas phase. In particular, high surface tetragonal ZrO₂ is a suitable catalyst for the target reaction due to its ability to activate both the substrate and the alcohol over Lewis acid and basic sites. During the first 300 minutes of reaction, under the optimized conditions, a full conversion was achieved, and the reaction was selective towards the formation of GVL. At longer reaction times on stream, the deposition of heavy carbonaceous compounds over the active sites was observed. In this way deactivation of the catalyst and in addition a change in the chemo-selectivity of the reaction was observed (e.g. alcoholysis of angelica lactones to yield EL). The latter effect was observed in all the catalytic tests performed in the gas-phase regardless the type of alkyl levulinate nor the chemical nature of the alcohol used. Moreover, the *in situ* regeneration of the catalyst was achieved when exposing it to a flow of air at 400 °C for 2h, restoring its initial catalytic behavior. On the other hand, ZrO₂ was not able to activate methanol as H-donor, achieving low conversion of ML and low amounts of GVL. Isopropanol was proven to be an excellent H-donor, allowing complete conversion for ML and high yield of GVL. Nevertheless, when ethanol (and bio-ethanol) was used as H-donor, a similar catalytic behavior was observed in this way opening new possibilities toward a sustainable route to GVL production.

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