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. Isopropanol was found to be the best H-donor under batch conditions, with ethyl levulinate providing 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 a 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 also been tested using a true bio-ethanol, derived from agricultural waste. These results represent the very first examples of the CTH of alkyl levulinates 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 need to promote sustainable industrial development has led to the search for alternatives and renewable raw materials and feedstocks for production. One of the most promising alternatives to petrochemistry are biorefineries based on lignocellulosic biomass valorization. Lignocellulose is composed of three main components 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 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), and 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 a 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 of catalyst separation and recovery [8]. Therefore, the use of heterogeneous catalysts has been investigated over the last 10 years. The use of catalysts containing noble metal nanoparticles supported on high surface area materials, which have permitted reaching complete conversion and high selectivity of GVL (98–99%) has been reported [9]. However, noble-metal catalysts are expensive and harsh conditions (high hydrogen pressure and reaction temperature) are still required to achieve satisfying yields and selectivity toward the target products [9–11]. In addition, most of the published studies still depend on H_2 as the 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 towards the 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 us achieving 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 produced 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]. Additionally, 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].

Presently, 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 the H-donor. Furthermore, levulinate esters are characterized by lower boiling points compared to LA and can be directly obtained by the acid-catalyzed alcoholysis of cellulose-derived carbohydrates. In this way, the need for an additional esterification step of LA is avoided, and finally, the sustainability of their direct utilization as raw materials is increased significantly [24].

For all these reasons, we decided to investigate the CTH of the levulinate ester using a synthesized high specific surface area tetragonal zirconia catalyst in a gas-phase continuous-flow, fixed-bed reactor. In particular, we thoroughly and systematically investigated the effects of different

parameters (contact time, reaction temperature, the type of alcohol used as the H-donor and the effect of the leaving group of the levulinate ester), as well as the study of the reaction and catalyst's deactivation mechanism [25]. The results obtained in the gas-phase were also carefully compared to the ones obtained in the liquid-phase and batch conditions [26]. Herein, the most interesting results are summarized and highlighted.

2. Materials and Methods

Reagents and standards were analytical grade, all supplied by Sigma-Aldrich (Merk, Kenilworth, NJ, USA) and used as received. A real mixture of bio-ethanol (derived from molasses and cereal fermentation) was provided by Caviro, a leading Italian wine producer group. The 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 test procedures please refer to refs. [25,26].

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 the H-donor was investigated in the gas-phase over ZrO_2 (Figure 1). Interestingly, in our reaction conditions (see Figure 1 caption), ML conversion was complete 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 follows a volcano plot with a maximum of 90% at 250 °C. For all these reasons, 250 °C was selected as the best reaction conditions for the following tests.
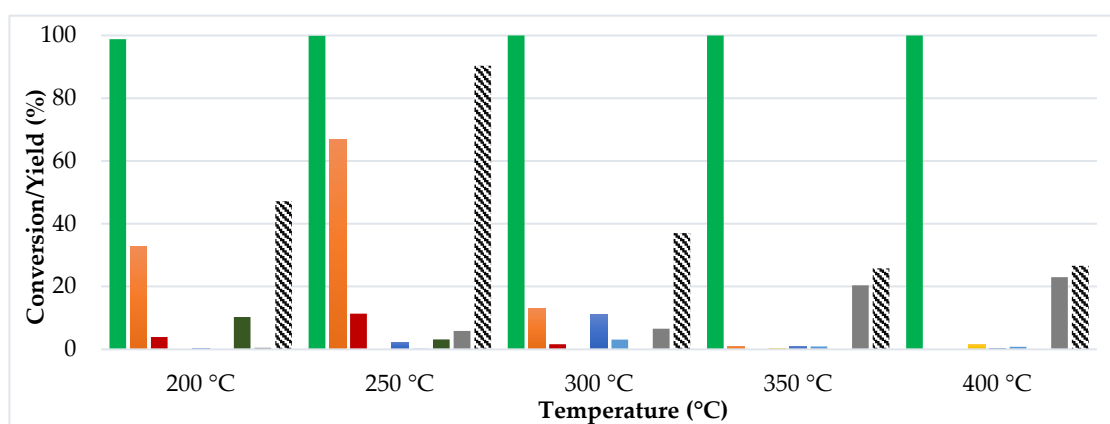

Figure 1. Catalytic transfer hydrogenation (CTH) of methyl levulinate (ML) with ethanol as H-donor over ZrO_2. Reaction conditions: ML:EtOH = 1:10 (molar ratio), τ = 1 s, %mol N_2:ML:EtOH = 90.1:0.9:9. ML conversion (■), γ-valerolactone (GVL) (■), ethyl GVL (■), angelica lactones (ALs, ■), ethyl pentenoate (■), 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-donors in the CTH of ML in both the gas-phase (continuous-flow reactor), and liquid-phase (batch, autoclave reactor) conditions. From analysis of the obtained results (Figure 2) a few important points can be highlighted:

- The gas-phase continuous flow conditions produced a superior activity (higher ML conversion) and greater yield of GVL compared to the liquid-phase, regardless the alcohol used as the H-donor;
- Very poor results were obtained using methanol as the H-donor for the target reaction in terms of the desired yield of products. Further investigations using ethyl levulinate (EL) as the chosen

substrate have proved the preferential tendency of methanol to promote both trans-esterification and alcoholysis of the intermediate (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 led to very similar results with complete conversion of ML (at least for six hours of reaction) and a very good GVL yield (from 60 to 80%);

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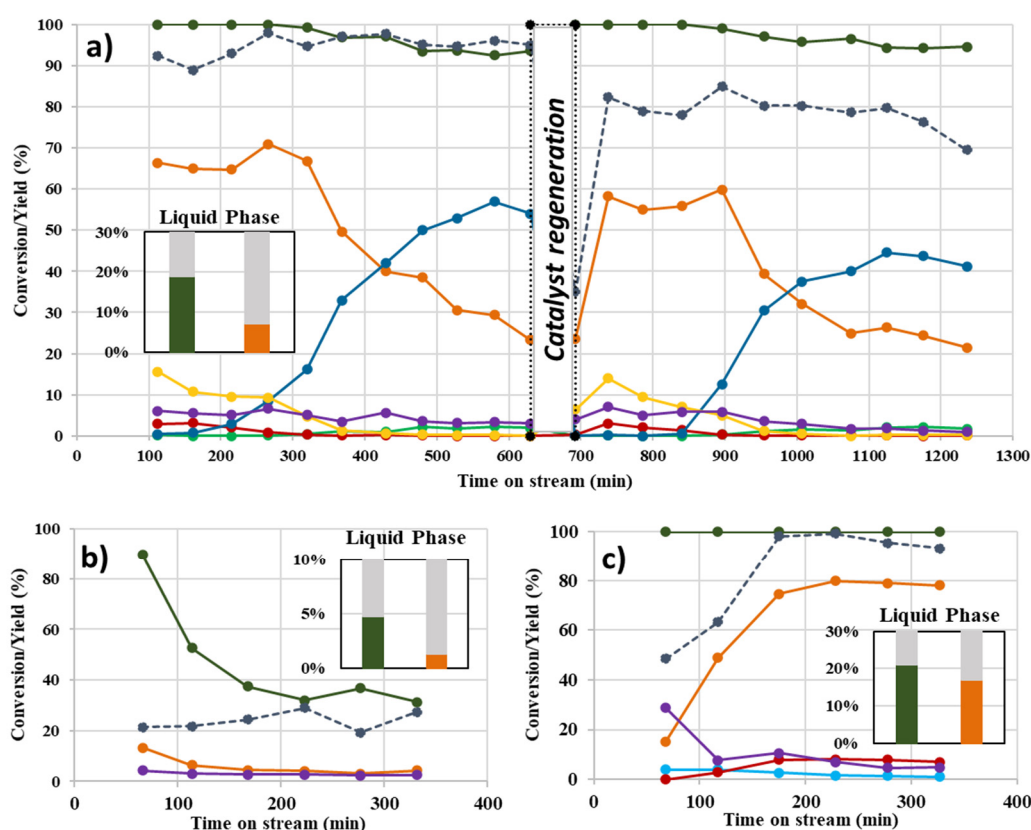

Figure 2. CTH of ML with different H-donors over ZrO_2: (**a**) ethanol; (**b**) methanol; (**c**) isopropanol. Reaction conditions for the gas-phase (scatter charts): ML:Alcohol = 1:10 (molar ratio), τ = 1 s, %mol N_2:ML:Alcohol = 90.1:0.9:9. Reaction conditions for the liquid-phase (histograms): 40 mL solution of ML or EL (10 wt %), T: 250 °C, 0.30 g of ZrO_2 catalyst, reaction time 8 h, N_2 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, led to the blockage and poisoning of the active Lewis acid sites, and therefore, led to a progressive decrease in the conversion and change in chemo-selectivity, promoting the alcoholysis of angelica lactones back to EL. Nevertheless, in situ regeneration of the catalyst was successfully achieved, by performing a heat treatment, by feeding air at 400 °C for 2 h and permitted the almost complete recovery of the initial catalytic behavior, proving that the deactivation of ZrO_2 is reversible and that regeneration could be achieved in a simple and practical manner.

Finally, a real bio-ethanol mixture was used as the 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 in bioethanol (i.e., acetic acid and aldehydes) that could foster the formation of heavy carbonaceous compounds on the catalytic surface, promoting the faster deactivation of the catalyst and in this way decreasing the maximum obtainable GVL yield.
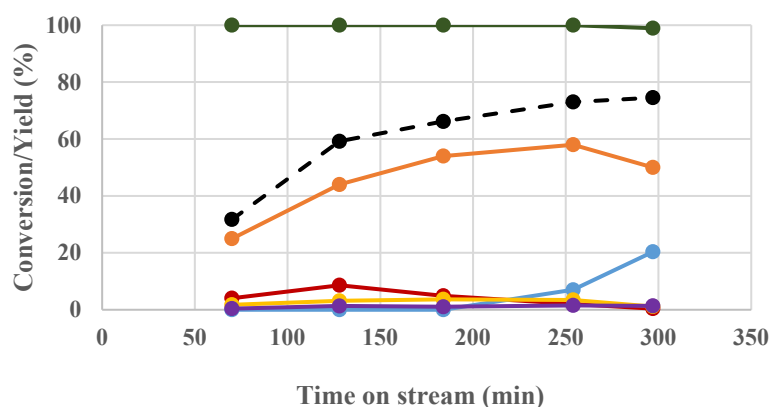

Figure 3. CTH of ML with a real bio-ethanol mixture as H-donor over ZrO_2. Reaction conditions: ML:bio-ethanol = 1:10 (molar ratio), τ = 1 s, %mol N_2:ML:bio-ethanol = 90.1:0.9:9. ML conversion (dark green), GVL (orange), ethyl GVL (yellow), angelica lactones (light green), ethyl pentenoate (red), ethyl levulinate (EL, blue), other (purple), carbon balance (dashed line).

4. Conclusions

The CTH of alkyl levulinates with a range of alcohols compared to a 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 ZrO_2 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 min of the 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 or 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 2 h, restoring its initial catalytic behavior. On the other hand, ZrO_2 was not able to activate methanol as the H-donor, achieving a low conversion of ML and low amounts of GVL. Isopropanol was proven to be an excellent H-donor, allowing the complete conversion of ML and high yield of GVL. Nevertheless, when ethanol (and bio-ethanol) was used as the H-donor, a similar catalytic behavior was observed in this way opening new possibilities towards a sustainable route to GVL production.

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