

# Transfer hydrogenation of methyl levulinate with methanol to gamma valerolactone over Cu-ZrO<sub>2</sub>: A sustainable approach to liquid fuels

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## ABSTRACT

Cu-ZrO<sub>2</sub> is demonstrated to be a highly effective catalyst for the transfer hydrogenation of methyl levulinate to  $\gamma$ -valerolactone, using methanol as the hydrogen donor. The emergence of several new strategies for synthesising green methanol, underlines its potential as a sustainable hydrogen source for such transformations. Transfer hydrogenation of methyl levulinate over Cu-ZrO<sub>2</sub> was determined to proceed through a two-step 'hydrogen borrowing' process. The first step involves methanol dehydrogenation (rate limiting) and the second, levulinate reduction. This proof-of-concept study demonstrates that methanol can be used effectively as a hydrogen source for such transformations when a suitable catalyst is employed.

## 1. Introduction

Public opinion towards sustainability is changing; we are all more conscious of the impact our lifestyles exert on the environment. This will undoubtedly influence government legislation over the coming years, as a global drive towards carbon neutrality is sought. Despite recent advancements in vehicle electrification, a recent International Energy Outlook (IEA) report projected that demand for liquid fuels will continue to rise until (at least) 2050 [1]. It is therefore critical, that sustainable routes to liquid fuels continue to be explored.

$\gamma$ -Valerolactone (GVL) is an exceptionally promising bio-derived platform chemical, which can be used either as a fuel additive [2] or be valorised into other chemicals and fuels [3]. Strategies for the synthesis of GVL from lignocellulosic biomass are well documented. Levulinic acid (LA) can be produced through the hydrolysis of both hemicellulose [4,5] (via xylose) and cellulose [6] (via 5-hydroxymethyl furfural). LA can then be hydrogenated catalytically, allowing for high yields of GVL to be obtained. There are numerous examples of different

catalysts which can do this selectively with H<sub>2</sub> [7].

However, when the overall process is considered, the route to GVL from biomass is not as desirable as it may initially appear. Often, acidic reagents are employed to catalyse the hydrolysis of sugars to LA, although heterogeneous catalytic approaches have also been presented [8,9]. The use of stoichiometric reagents for such transformations is detrimental to process sustainability and can lead to further complications downstream, such as humin formation. These undesirable by-products can significantly reduce the yield of LA and promote catalyst deactivation (if employed) [9]. Conducting this hydrolysis reaction in the presence of an alcohol can suppress humin formation; alcohols interact with the active moieties in the hydrolysis intermediates to produce esters [10,11], thus, 'protecting' them against acid catalysed condensation. Running these reactions in methanol is particularly effective and can dramatically improve the yield of the corresponding levulinate (methyl levulinate (ML)) [12]. This provides a clear motivation for developing methods of producing GVL from levulinate esters and considering methanol as a possible hydrogen source that is already

**Abbreviations:** IEO, International Energy Outlook; GVL, Gamma Valerolactone; LA, Levulinic Acid; ML, Methyl Levulinate; ICDD, International Centre for Diffraction Data; AIPP, Aluminium Isopropoxide; MPV, Meerwein Ponderf Verley; EL, Ethyl Levulinate.

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available in the process.

Recent advances in the synthesis of 'green' methanol [13–17], provide a further motive to consider the use of ML as the substrate for this process and methanol as the hydrogen source. The reduction of ML and its subsequent cyclisation would also lead to the formation of equimolar quantities of the desired product, GVL, and methanol. Thus, if done selectively, the methanol consumed for the reduction of ML would be replenished, further improving process sustainability.

Many studies have investigated the transfer hydrogenation of alkyl levulinates [18,19], although the majority of examples employ the use of secondary alcohols as hydrogen donors. By comparison, research where methanol has been used as the hydrogen donor in such reactions is extremely limited (Table S1). In most of these examples, poor GVL productivities were observed when methanol was used as the hydrogen donor. This is, however, unsurprising as the primary focus of most of these studies involved the use of secondary alcohols as donors and methanol was simply examined, along with other alcohols, for screening purposes. However, one recent study by Luo and co-workers demonstrated that, over a Ni-Fe/SBA-15 catalyst, excellent GVL productivities could be acquired when LA was used as the substrate [20]. The preliminary catalyst testing conducted in this study, clearly highlight that this approach could be advantageous over conventional hydrogenation methods.

We therefore set out to explore this further but, for the reasons discussed above, considered that ML would be a more suitable substrate from a sustainability perspective. Given that we have significant experience in the synthesis and characterisation of Cu-ZrO<sub>2</sub> catalysts, particularly for the hydrogenation of LA to GVL [21–23], we considered this to be an appropriate material on which to base our investigation. This proof-of-concept study confirms that transfer hydrogenation of ML with methanol, over a Cu-ZrO<sub>2</sub> catalyst, was not only feasible but efficient. Through consideration of the by-products formed, and the estimated apparent activation energy, it was hypothesised that methanol dehydrogenation was rate limiting. This understanding illustrates how further increments in activity can be made, moving forward.

## 2. Results and discussion

To begin the investigation, a Cu-ZrO<sub>2</sub> (50/50 mol<sub>Cu</sub>/mol<sub>Zr</sub>) catalyst was synthesised using an oxalate sol-gel method, where desired quantities of Cu(II) nitrate hydrate and Zr(IV) oxynitrate are combined in ethanol and instantaneously precipitated with a stoichiometric excess of oxalic acid. More details of the catalyst preparation are provided in the experimental section of the electronic supplementary information. The Cu–Zr oxalate precursor was subsequently calcined and thermally reduced to produce the final catalyst. We have previously demonstrated that this method can be used to produce highly active catalysts for the hydrogenation of LA to GVL with hydrogen [21–23] and thus, considered this material to be a good starting point for our transfer hydrogenation studies.

X-ray diffraction patterns recorded at each stage of the preparation; after precursor synthesis, calcination, and reduction, are presented in Fig. S1. The diffraction patterns clearly illustrate the phase transformation the material undergoes over the course of its preparation. After reduction, only Cu metal diffraction is observed, diffraction peaks at  $2\theta = 43^\circ$ ,  $51^\circ$  and  $74^\circ$  are characteristic of Cu(111), Cu(200) and Cu(220) planes, respectively (ICDD ref. 01–070-3038). This indicates that most of the Cu species present in the final (reduced) catalyst are in the form of Cu metal. Brunauer-Emmett-Teller surface area analysis confirmed that this catalyst possessed a total surface area of  $71 \text{ m}^2 \text{ g}^{-1}$ , which is comparable to the surface area we reported in our previous study ( $64 \text{ m}^2 \text{ g}^{-1}$ ) [22], thus, confirming that catalyst used in the present study is comparable. The Cu surface area was also evaluated by titration of the catalyst with N<sub>2</sub>O; the Cu metal surface area was confirmed to be  $7.9 \text{ m}^2 \text{ g}^{-1}$ . Further probing of this material by scanning transmission electron microscopy and energy dispersive X-ray analysis revealed that

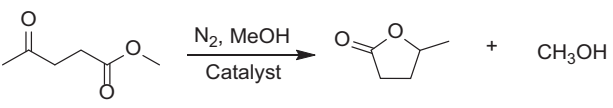
Cu, Zr and O were all well dispersed throughout the material (Fig. S2).

After synthesis of this material, its ability to catalyse the transfer hydrogenation of ML with methanol was examined (Table 1). The reactions were conducted in a stainless-steel autoclave, under 5 bar of N<sub>2</sub>. After loading the reagents, the reaction solution was vigorously purged with N<sub>2</sub> (under stirring) to remove any residual O<sub>2</sub> from the reaction mixture. The autoclave was subsequently heated to the desired reaction temperature for the stated reaction time, after which, it was immediately cooled in an ice/water bath. The gaseous and liquid components were analysed through quantification by gas chromatography.

The Cu-ZrO<sub>2</sub> catalyst exhibited an exceptionally high selectivity towards GVL; a GVL yield of 76.7% was observed after just 20 min of reaction at 220 °C (Entry 2), which increased to 87.5% after a further 40 min of reaction (Entry 3). An analogous Ni-ZrO<sub>2</sub> (50/50 mol<sub>Ni</sub>/mol<sub>Zr</sub>) catalyst was also synthesised and tested, as these catalysts are also effective for LA hydrogenation [24]. For transfer hydrogenation however, this catalyst was determined to be less productive (Entry 4) with only a 12.0% GVL yield (at a ML conversion of 57.1%) after 180 min of reaction. The ZrO<sub>2</sub> support alone, prepared in the same way as the Cu-ZrO<sub>2</sub> and Ni-ZrO<sub>2</sub> catalysts, was also assessed (Entry 1). This also exhibited a poor GVL productivity and selectivity (7.7% GVL yield at 26.1% ML conversion), evidencing that the introduction of other metals, Ni or more effectively Cu, into the ZrO<sub>2</sub> formulation has a significant impact on the catalytic performance. Subsequent experiments employed the use of more conventional transfer hydrogenation catalysts, Sn- $\beta$  zeolite and aluminium isopropoxide (AIPP), which are known to be highly effective catalysts for Meerwein-Ponndorf-Verley (MPV) reduction with secondary alcohol hydrogen donors [25,26]. However with methanol, and under these conditions, these catalysts performed comparatively poorly (Entries 5 and 6).

Given that the Cu catalyst exhibited such promise, its reactivity over time was investigated (Fig. 1). The GVL yield reached a maximum after 60 min of reaction, before slowly beginning to drop off; after a further 60 min, the GVL yield dropped to 84.6%. It is known that GVL can undergo further hydrogenation to other products including 1,4-pentanediol and subsequently, 2-methyltetrahydrofuran [27]. However, given that the rate of these subsequent hydrogenation reactions are evidently significantly slower than the rate of GVL formation, it demonstrates great promise for the proposed application. At each stage of the reaction, the gaseous and liquid products formed were also quantified (Fig. 1B). Significant quantities of H<sub>2</sub> were produced, along with smaller quantities of methyl formate and CO. Only trace amounts of CO<sub>2</sub> were observed. To ensure, that these products were formed from the reaction of methanol, and not the ML (or its products), an additional set of experiments were conducted in the presence of the catalyst but in the absence of the substrate (Fig. 1C). The product distributions, in the

**Table 1**  
Catalyst transfer hydrogenation of ML with methanol.

				
Catalysts	Time (min)	Temperature (°C)	Conversion (%)	GVL Yield (%)
ZrO <sub>2</sub>	120	220	26	8
50% Cu-ZrO <sub>2</sub>	20	220	85	77
50% Cu-ZrO <sub>2</sub>	60	220	99	88
50% Ni-ZrO <sub>2</sub>	180	220	57	12
Sn- $\beta$ Zeolite	180	220	44	17
AIPP	180	85	0	0

Reaction Conditions: ML (0.5 g); Mesitylene (0.5 g); MeOH (9.5 g); Catalyst (0.2 g); Temperature (Stated); N<sub>2</sub> Pressure (5 bar). KEY: AIPP (aluminium isopropoxide).

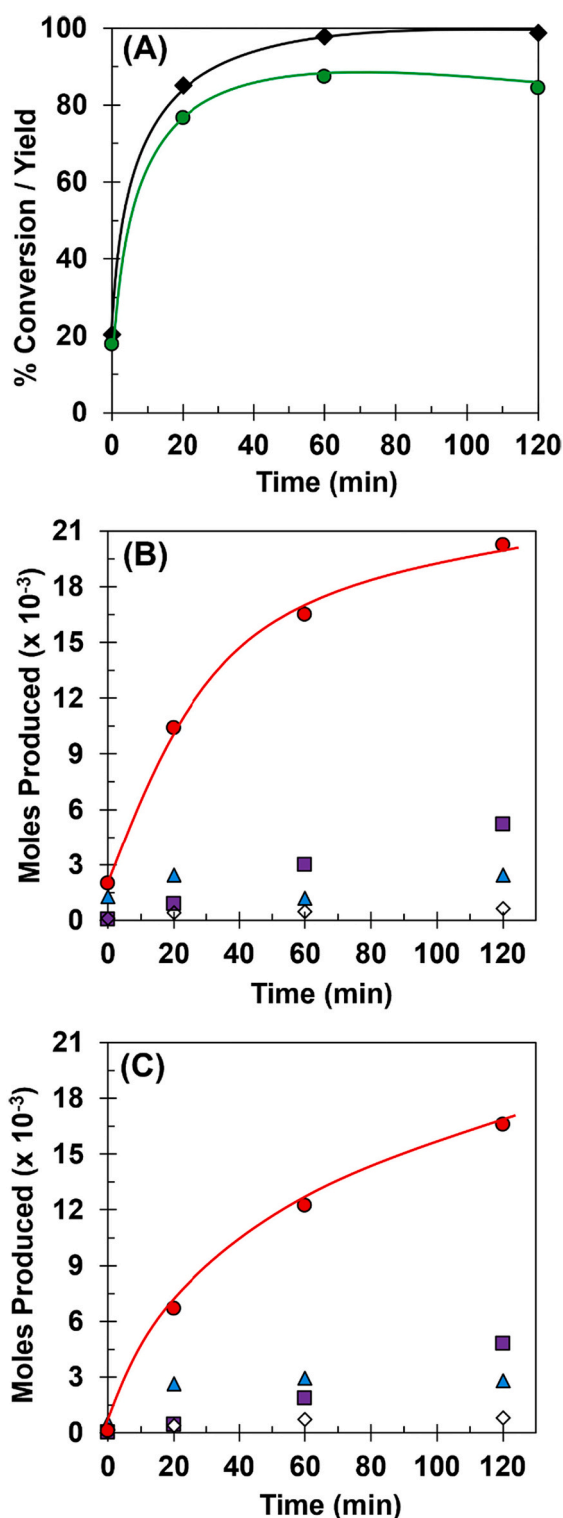


Fig. 1. Substrate consumed, and products formed in the transfer hydrogenation of ML to GVL (a) and (b). (c) corresponds the C<sub>1</sub> and C<sub>2</sub> products formed in the absence of ML. Reaction Conditions: ML (0.5 g – where used); Mesitylene (0.5 g); MeOH (9.5 g); Cu-ZrO<sub>2</sub> (0.2 g); Temperature (220 °C); N<sub>2</sub> Pressure (5 bar). KEY: ML Conversion (black diamonds); GVL yield (green circles); moles of hydrogen (red circles); moles of methyl formate (blue triangles); moles of CO (purple squares); moles of CO<sub>2</sub> (white diamonds). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

presence and absence of substrate, were remarkably similar. The only notable difference was a slight drop in the moles of hydrogen observed in the reactions conducted in the presence of ML. This drop is attributed to the moles of hydrogen consumed in the hydrogenation of the ketone in ML, as highlighted by the derived hydrogen balances of 92.7, 94.6 and 98.0% at 20, 60 and 120 min, respectively (Table S2). It was also noted from these time on-line studies that the reaction appears to be taking place before the reaction temperature is reached; approximately 20% of the ML is already reacted before reaching temperature. This suggests that operation at a lower reaction temperature should be possible.

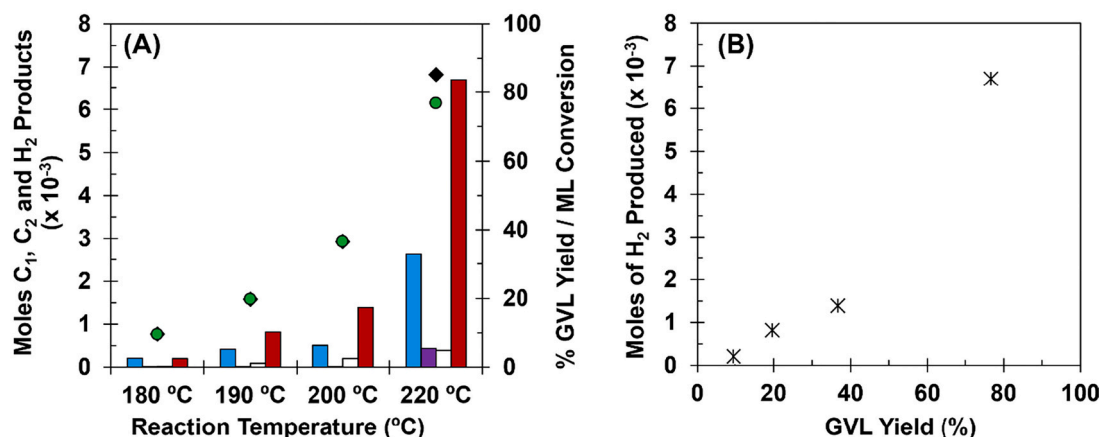
To explore this further, additional transfer hydrogenation experiments were conducted at 180, 190 and 200 °C (Fig. 2). As expected, as the reaction temperature is increased, the ML conversion and GVL yield also increase. However, the selectivity to GVL clearly decreased at the highest temperature (220 °C). This slight drop in selectivity is likely to be attributed to the subsequent hydrogenation of GVL. At the lower reaction temperatures, it is evident that the number of products formed from methanol is also lower. The correlation between ML conversion/GVL yield and hydrogen produced (at different temperatures) is illustrated in Fig. 2B. Evidentially, the rate at which hydrogen is produced from methanol, influences the rate at which ML converts to GVL.

Based on the experimental data provided a mechanism is proposed, which accounts for the reaction of interest (ML to GVL) and the primary C<sub>1</sub> and C<sub>2</sub> products observed (Scheme 1). First, methanol undergoes dehydrogenation to methyl formate. Cu based catalysts are known to be highly effective for this reaction and are used commercially for this process [28–30]. It is then proposed that the methyl formate undergoes decomposition to produce methanol and CO, which can occur catalytically [31] or simply through gas phase decomposition [32]. The formation of methyl formate, from two molecules of methanol, produces two molecules of hydrogen. As the cleavage of the O–H bonds and C–H bonds in methanol are unlikely to occur simultaneously, its logical to hypothesise that the surface bound hydrogen atoms can either reduce an adjacent adsorbed ML molecule or recombine and desorb as molecular H<sub>2</sub>. Given that; (i) conventional MPV reduction proceeds via a direct hydride transfer between adjacently adsorbed surface intermediates, (ii) MPV reduction does not typically result in the formation of H<sub>2</sub>, (iii) catalytic MPV reductions typically rely on the use of secondary alcohols as hydrogen donors and (iv) conventional MPV catalysts (AIPP and Sn-β zeolite) performed poorly with methanol (Table 1) under these conditions, we propose that the transfer hydrogenation reaction over Cu-ZrO<sub>2</sub> proceeds via a hydrogen borrowing surface mechanism.

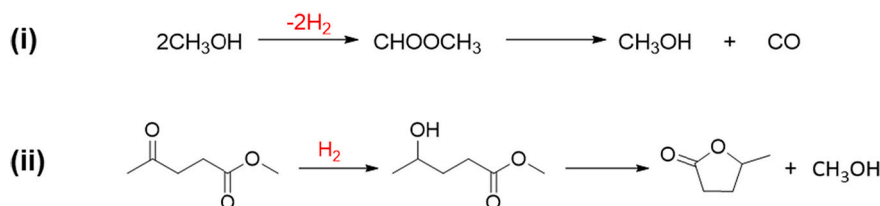
To provide further evidence for this hypothesis, the data from Fig. 2A was used to calculate the apparent activation energy for the process (Fig. S3). The derived activation energy for the transfer hydrogenation of ML over Cu-ZrO<sub>2</sub> was determined to be 118.9 kJ mol<sup>-1</sup>. Pertinently, this value is consistent with the apparent activation energy reported for methanol dehydrogenation over a skeletal Cu catalyst [33] (120 kJ mol<sup>-1</sup>), suggesting that methanol dehydrogenation is likely to be the rate determining step. Therefore, by comparison, the reduction of ML and the subsequent cyclisation can be considered facile. This is further evidenced by the fact that the activation energy for LA hydrogenation to GVL is considerably lower (68 kJ mol<sup>-1</sup>) over similar Cu-ZrO<sub>2</sub> catalysts [22], where H<sub>2</sub> dissociative adsorption was determined to be rate determining.

### 3. Conclusions

ML transfer hydrogenation with methanol was determined to proceed selectively over a Cu-ZrO<sub>2</sub> catalyst. With methanol as the H-donor, this catalyst was found to be significantly more effective than conventional MPV catalysts. Through consideration of the C<sub>1</sub> and C<sub>2</sub> products which form, and the abundance of H<sub>2</sub> which is produced in the reaction, we propose that ML to GVL proceeds via a hydrogen borrowing type surface mechanism. We therefore consider that ML reduction predominantly occurs through its surface interaction with dissociated hydrogen surface



**Fig. 2.** Substrate consumed, and products formed in the transfer hydrogenation of ML to GVL over Cu-ZrO<sub>2</sub> at different reaction temperatures. Reaction Conditions: ML (0.5 g); Mesitylene (0.5 g); MeOH (9.5 g); Catalyst (0.2 g); Temperature (stated); N<sub>2</sub> Pressure (5 bar); 20 min. KEY: ML Conversion (black diamonds); GVL yield (green circles); moles of hydrogen (red bar); moles of methyl formate (blue bar); moles of CO (purple bar); moles of CO<sub>2</sub> (white bar). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Scheme 1.** Routes to the formation of different products observed in the reaction of Cu-ZrO<sub>2</sub>. (I) methanol dehydrogenation to methyl formate and subsequent decomposition to CO and methanol. (II) transfer hydrogenation of ML to GVL.

species, prior to their recombination and desorption. Given that LA hydrogenation over this catalyst is limited by H<sub>2</sub> dissociation and not LA reduction, we hypothesise that methanol dehydrogenation is rate limiting in the transfer hydrogenation reaction over Cu-ZrO<sub>2</sub>. The apparent activation energy determined for GVL formation (118.9 kJ mol<sup>-1</sup>) correlated well with a previous report investigating methanol dehydrogenation over a Cu based heterogeneous catalyst. We therefore consider that further advancements can be made through the design and synthesis of a catalyst which is more efficient at promoting methanol dehydrogenation. Follow up work will be undertaken to specifically tackle this issue; thorough characterisation of Cu-ZrO<sub>2</sub> catalysts will be conducted to understand how the catalysts physicochemical properties can promote methanol dehydrogenation and consequentially, promote ML transfer hydrogenation.

#### Author contributions

All authors contributed to the design of the study. M.D. and B.Z. conducted experiments and data analysis. M.D. and B.Z. conducted catalyst characterisation and processed the corresponding data. M.D. wrote the manuscript and the supporting information. All authors discussed the work and contributed to the planning of the experiments.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2022.106430>.

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