The Transfer Hydrogenation of Methyl Levulinate to γ-Valerolactone over Cu-ZrO$_2$

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Abstract: The transfer hydrogenation of methyl levulinate (ML) to γ-valerolactone (GVL) using methanol over Cu-ZrO$_2$ is investigated. Extensive experimental tests and catalytic characterization was conducted in order to determine the catalytic surface mechanism occurring and provide key information regarding the active site of the heterogeneous catalyst.

Keywords: Transfer Hydrogenation, Biomass, Green Chemistry, Noble Metal Free

Introduction

Transfer hydrogenation (TH) strategies for chemical synthesis have the potential to reduce chemical waste and significantly increase atomic efficiency. Methyl levulinate (ML) is considered to be a key platform chemical for the production of fine chemicals and bio-fuels[1]. This work investigates the application of a Cu-ZrO$_2$ catalyst for the production of γ-valerolactone (GVL) from ML by TH. Typically, secondary alcohols such as isopropanol are used as hydrogen donors for these types of transformations[2, 3]. In this study, we use methanol (MeOH) as both the solvent and hydrogen donor. Thus, MeOH consumed in the TH step should theoretically be replenished in the ester hydrolysis as demonstrated in the schematic (**Figure 1**).

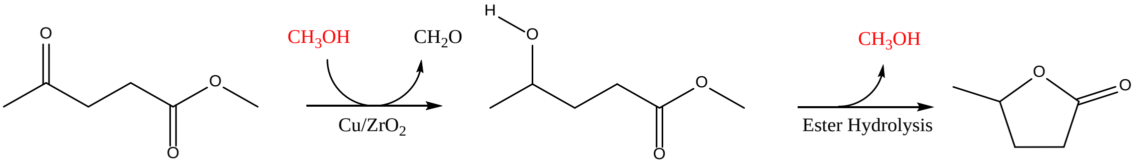

Figure 1: Transfer hydrogenation of ML to GVL. MeOH consumed in the first step is replenished in the ester hydrolysis. All reactions were conducted in a 50 mL Parr autoclave reactor at temperatures ranging 150 – 220 ºC and at 5 bar N$_2$.

Experimental

Cu-ZrO$_2$ catalysts used in this study were prepared by an oxalate sol-gel method. For this, $Cu(NO_3)_2.2.5H_2O$ and $ZrO(NO_3)_2.6H_2O$ were dissolved separately in 100 mL of ethanol (2 x 100 mL flasks – total ethanol volume of 200 mL). Once dissolved, the solutions were combined in a beaker and oxalic acid (moles equal to 120 % of Cu+Zr moles) was added to the solution immediately. The subsequent sol-gel was aged for two hours, filtered and dried in an oven (110 ºC, 16 h). The oxalate precursor was heat treated (400-550 ºC, 2 h, 10 ºC / min, flowing air) and reduced (300-350 ºC, 2 h, 10 ºC / min, flowing 5 % H$_2$/Ar). Reactions concerning the transfer hydrogenation of ML were carried out in a stainless steel Parr autoclave under a range of different reaction conditions (5 bar N$_2$, 160 ºC – 220 ºC, 5 wt.% ML/MeOH, 0.5 – 6 h). Due the participation of MeOH in the reaction an internal standard (mesitylene, 0.5 g) was added to each reaction. Liquid and gas phase samples were analysed by GC-FID and GC-TCD where appropriate. Extensive catalyst characterization was conducted in order to investigate the physical properties of the catalysts. For this, catalysts were investigated using XRD, TGA-DTA, TPR, BET, CuSA titration, SEM and TEM.

Results and discussion

$Cu-ZrO_2$ was found to work exceptionally well as a catalyst for this reaction. The $Cu-ZrO_2$ catalyst significantly outperformed a number of other TH catalysts such as Sn-Beta zeolite and amorphous zirconia as displayed in **Table 1**. In addition, tests were conducted with many different hydrogen sources (isopropanol, ethanol and propanol to name a few) which highlighted the thermodynamic challenges associated with using MeOH as the source of hydrogen. Despite the difficulties associated with using MeOH as the hydrogen source, upon optimization of the reaction conditions exceptionally high yields of GVL were easily obtainable (> 90 %) in the presence of the $Cu-ZrO_2$ catalyst. Interestingly, large quantities of C_1 and C_2 products were observed in both the gas and liquid phase post reaction. Mechanistic studies confirmed that the $Cu-ZrO_2$ was also facilitating the dehydrogenation of MeOH which we would expect to produce large quantities of formaldhyde. However, no formaldehyde was observed in the post reaction effluent. Further experimental work revealed that the absence of formaldehyde was a result of it immediately participating in Tishchenko type and H_2O promoted disproportionation reactions which lead to the formation of large quantities of methyl formate.

Table 1. The TH of ML to GVL over a series of different catalysts. **Reaction conditions:** 220 ºC, 5 bar N_2, 3 h , 200 mg catalyst, 5 % Solution of ML in MeOH.

	$Cu-ZrO_2$	**a-ZrO_2**	**Sn-β Zeolite**
Conversion (%)	97.7	26.1	44.2
GVL Yield (%)	89.9	7.7	17.4
Carbon Mass Balance (%)	92.2	81.5	73.1

Although the observation of these side reactions are interesting from an academic perspective, the large quantities of C_1 and C_2 products produced were essentially undesirable by-products. For this reason, the catalyst preparation method and reaction conditions were altered in order to reduce the quantity of MeOH consumed through these side reactions whilst maintaining the high catalytic performance. Reducing the reaction temperature was found to significantly reduce the dehydrogenation of MeOH while also maintain the high selectivity to GVL. A series of $Cu-ZrO_2$ catalysts containing varying quantities of Cu were subsequently synthesised, tested and extensively characterised in order to determine the role of Cu in the system. The CuSA measurements and microcopy in particular revealed that the activity stems from small Cu particles which grow out of the Cu-Zr-O lattice during the heat treatments. Such growth is only possible when the lattice is close to saturation with Cu.

Conclusion

A Cu/ZrO_2 catalyst was found to be exceptionally active for the TH of ML to GVL. The catalyst preparation conditions were found to significantly influence the physiochemical properties of the material and so, the properties which govern high performance for the TH of ML were identified. Hydrogenation reactions are commonly used in the chemical industry but the application of heterogeneous catalysts in such reactions is often limited due to the economic implications associated with the application of precious metal catalysts and high pressures of H_2. Transfer hydrogenation strategies offer an alternative, atom efficient approach to hydrogenation. The novelty of this Cu/ZrO_2 catalyst is that it is cheap and incredibly straightforward to prepare, yet it is exceptionally active for the transfer hydrogenation of ML to GVL. A fantastic opportunity has emerged for further investigation and application of this material in other similar catalytic systems.

References

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