



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

ISMR-10 10th International Symposium on Multifunctional Reactors

MILANO, ITALY - 21-24 March, 2021

Hydrogenation of levulinic acid to γ -valerolactone *via* green microwave-assisted reactions either in continuous flow or solvent-free batch processes

Giorgio Grillo¹, Maela Manzoli¹, Fabio Buccioli¹, Silvia Tabasso^{2*}, Fabrizio Cavani³, Tommaso Tabanelli³, Giancarlo Cravotto¹

1 Department of Drug Science and Technology, University of Turin, Via Giuria 9, 10125, Turin, Italy; *2* Department of Chemistry, University of Turin, Via Giuria 7, 10125, Turin, Italy; Department of Industrial Chemistry "Toso Montanari, University of Bologna Viale del Risorgimento 4, 40136 Bologna, Italy

*Corresponding author E-Mail: silvia.tabasso@unito.it

1. Introduction

Aiming to a more sustainable future, the biorefinery approach could help replacing fossil feedstocks with wastes. In the frame of green chemistry, the goal is the production of new platform chemicals from residual lignocellulosic biomasses. γ -valerolactone (GVL) is one of the most attractive bio-derived compounds, because it is an excellent green solvent, a liquid fuel, and a peculiar additive for his fragrance [1]. GVL is commonly synthesized by hydrogenation of levulinic acid (LA). One pathway entails the reduction to 4-hydroxypentanoic acid and the subsequent lactonization. Recent synthetic protocols involve the use of supported noble metals as catalysts under H₂ pressure in dioxane [2]. Further investigations demonstrated that ruthenium-based solid catalysts show a good activity in the conversion LA-to-GVL, with good performances also using H-donors such as 2-propanol, 2-butanol and formic acid [3]. The industrial demand of sustainability and green process intensification, boosted the use of enabling technologies, particularly microwaves (MW) [4]. The peculiar properties of MW may significantly promote energy-transfer, enhancing the conversion of platform chemicals [5]. A challenging design of sustainable processes with high productivity and automation, aside from the energy consumption, may exploit continuous flow reactors [6]. This technology should be able to handle a multiphase system, involving a solid catalyst crossed by liquid reagent(s), and possibly properly mixed with reactive gases.

The present work reports the screening of different heterogeneous Ru-based catalysts for LA reduction into GVL under MW irradiation. Different metal loadings and supports were considered, such as active carbon (Ru/AC), titania (Ru/TiO₂) and alumina (Ru/Al₂O₃). The experimental work with batch and flow systems aimed to optimize all relevant working parameters both with H₂ or H-donors.

2. Methods

Batch reactions were carried out in a multimodal MW reactor (SynthWAVE - Milestone srl), equipped with pressure resistant close cavity that can be heated up to 300°C and pressurized up to 200 bars (maximum power of 1500W). High-throughput and parallel synthesis are allowed by multi-sample racks (up to 15 tubes).

Continuous flow reactions were conducted using a multimodal MW flow reactor (FlowSYNTH - Milestone srl), with a customized set up for multi-phase reactions. Screw-on sintered glasses ensure the catalyst immobilization inside cartridges of different volumes. A three-way connection fitted with a non-return valve

allows to pump simultaneously solutions and gaseous feeds. Products analyses were performed by GC-MS (Agilent Tech.). Identifications and quantifications were achieved by means of external standards. Catalysts were characterized by Diffuse Reflectance UV-Vis Spectroscopy, powder X-Ray Diffraction and High Resolution Transmission Electron Microscopy, to define the electronic, structural and morphological properties. Catalyst robustness, Ru coalescence or leaching have been determined before and after the reaction.

3. Results and discussion

Batch screenings allowed to study different hydrogen sources and catalysts, even in solvent-free conditions. The optimized protocol was then transposed to a flow system. According to batch tests, the very first screening involved the application

of MeOH, 2-propanol (2-PrOH) and formic acid (FA) as H-donors. The best results were achieved using 2-PrOH on Ru/AC, with complete conversion of LA and more than 80% of selectivity to GVL. MeOH led to the formation of the methyl levulinate as the main product, whilst using FA neither reagent nor products were recovered. These results have been compared with reactions carried out with molecular H₂. Removing H-donors allowed solvent-free conditions, testing harsher protocols (up to 200 °C and 50 bar H₂) that led to the total conversion of LA with complete selectivity to GVL. Further screenings dramatically reduced the reaction time, temperature and pressure, finally designing a fast reduction process prone to flow transposition. Comparison among the catalysts confirmed Ru/AC as the catalyst of choice, followed by Ru/TiO₂ and Ru/Al₂O₃. By data elaboration, we could design a flow process with less than 5 min of residence time, into a MW-assisted reactor. The catalyst-immobilized cartridge enabled the contact of the supported Ru with H₂ and the reagent. Due to very fast conversion kinetics, it was possible

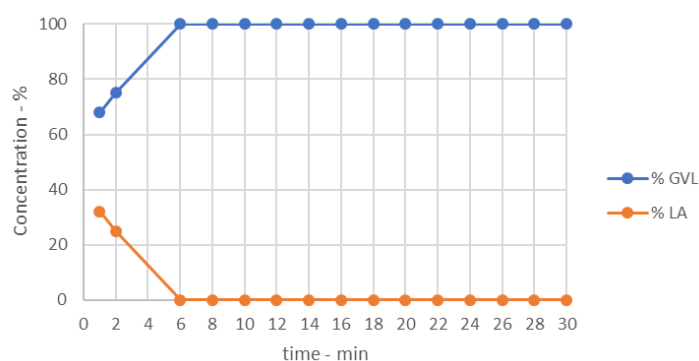


Figure 2. Flow reduction of LA to GVL with Ru/AC and H₂

to achieve complete conversion and selectivity without recirculation. The steady state was reached in approximately 6 min and appeared to be stable during the following 30 min. Limited overall reaction time was selected to test the recyclability of the catalyst in stress conditions (heating/cooling cycles). GVL was still achieved with complete selectivity after 3 cycles.

4. Conclusions

Screenings performed for the Ru-catalysed hydrogenation of LA to GVL showed interesting results for H₂ application. Among the different hydrogen sources, molecular hydrogen led to milder reaction conditions in comparison with the literature. Furthermore, between the tested Ru-based catalysts, different supports were evaluated, evidencing the better performances of AC. The synergistic effects of Ru/AC and MW irradiation paved the way to the scaling up using a flow reactor.

References

- [1] J.J. Bozell, G.R. Petersen, *Green Chem.* 12 (2010) 539–554.
- [2] W.R.H Wright, R. Palkovits, *ChemSusChem* 5 (2012) 1657–1667.
- [3] P.J. Deuss, K. Barta, J.G. de Vries, *Catal. Sci. Technol.* 4 (2014) 1174–1196.
- [4] A. De La Hoz, A. Loupy, in: *Microwaves in Organic Synthesis*, 3rd ed., Springer Sci., NY, 2012, pp. 541–562.
- [5] S. Tabasso, D. Carnaroglio, E. Calcio Gaudino, G. Cravotto, *Green Chem.* 17 (2015) 684–693.
- [6] C. Moreno-Marrodan, P. Barbaro, *Green Chem.* 16 (2014) 3434–3438.



Figure 1. FlowSYNTH, Milestone srl