SYNTHESIS OF γ -VALEROLACTONE FROM BIOMASS-DERIVED COMPOUNDS BY AQUEOUS-PHASE PROCESSING USING SUPPORTED MONO- AND BIMETALLIC CATALYSTS

<u>Carlos Luna</u>^a,Chen Zhihao^b, Nicole Wilde^b, Majd Al-Naji^b, Roger Gläser^b.

^aDepartment of Organic Chemistry, University of Córdoba, Campus of Rabanales, Ed. Marie Curie,14014, Córdoba, Spain (qo2luduc@uco.es) ^bInstitute of Chemical Technology, Universität Leipzig, Linnéstr. 3, 04103 Leipzig, Germany.

For modern biorefineries, a major challenge is to develop cost-efficient processing methods for the transformation of highly functionalized carbohydrates into value-added chemicals. Towards that goal, several investigations have been devoted to the conversion of biomass-derived model compounds into biofuels bycatalytic aqueous-phase processing (APP)¹.Y-Valerolactone (GVL), useful as renewable solvent or fuel additive, can be subsequently converted into a broad slate of valuable fine chemicals². It can be obtained by heterogeneously catalyzed hydrogenation of levulinic acid (LA) (Fig.1),which is accessible from lignocellulosic biomass through a simple and robust hydrolysis process³. Furthermore, a stable support containing acid sites is of high importance in APP of lignocellulosic biomass-derived feedstocks. Thus, the present work aimed to investigate the potential of mono- and bimetallic Ru, and Ni catalysts supported on sulfated ZrO₂ towards the production of GVL from biomass derived LA by APP.

Monometallic Ru, Ni as well as bimetallic Ru-Ni catalysts supported on sulfated ZrO_2 (ZrO_2 -S) were prepared through incipient wetness impregnation (IWI). The catalytic experiments were carried out at mild conditions (150°C, 5MPa H₂). The catalysts before and after the experiments were thoroughly characterized (temperature-programmed reduction, temperature-programmed desorption, N₂-sorption and elemental analysis). It is found that ZrO_2 -S supported Ru is the only active component for GVL synthesis. Due to the loss of acid sites during the calcination and reduction of the catalysts, the yield of GVL was only 10% after 6 h over the ZrO_2 -S-supported Ru-Ni(0.5/2%) catalyst. However, since no significant change in the textural properties occurred for the ZrO_2 based catalysts and no Ru and Ni leaching is observed during the reaction, these catalysts show great potential for APP in terms of stability and reusability.

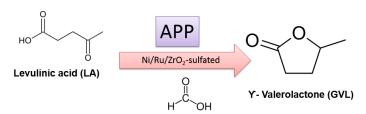


Figure 1: Reaction scheme for the aqueous-phase processing of LA to GVL.

Acknowledgements: The subsidies granted by the Ministerio de Economía y Competitividad (Project ENE 2011-27017), Ministerio de Educacion y Ciencia (CTQ2010-18126 and CTQ2011-28954-C02-02), FEDER funds and Junta de Andalucía PO8-RMN-03515 and TEP-7723, funding for research stays to obtain the award of "International Doctorate" received from CeiA3 trough the eidA3, are gratefully acknowledged.

¹Chheda, J. N.; Huber, G.W.; Dumesic, J. A. Angew. Chem. Int. Ed., **2007**, 46, 7164.

²Luo, W.; Deka, U.; Beale, A. M.; Van Eck, E. R. H.; Bruijnincx, P. C. A.; Weckhuysen, B.M. *J Catal*, **2013**, 301, 175.

³Wright, W. R. H.; Palkovits, R. ChemSusChem, **2012**, 5, 1657.