

## Innovative Heterogeneous Catalysts for the Reduction of Levulinic Acid Derivatives to $\gamma$ -valerolactone and Consecutive Reduction Products

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### Abstract

Levulinic acid (LA) and its esters (e.g. methyl levulinate, ML) are polyfunctional molecules that can be obtained directly from lignocellulosic biomass by hydrolysis or alcoholysis respectively<sup>1</sup>. Regard to LA valorisation, the most investigated strategy is its hydrogenation toward valuable compounds such as fuel additives, solvents and other added-value chemicals. Most of the published manuscripts on this topic mainly focused on the conversion of LA to  $\gamma$ -valerolactone (GVL) using relatively high pressure of H<sub>2</sub>. However, few studies in literature report on the production of consecutive reduction products, namely 2-methyltetrahydrofuran (2-MTHF), 1,4-pentadiol (1,4-PDO)<sup>2</sup>, valeric acid (VA) and its ester (e.g. methyl valerate, MV)<sup>3</sup>. In this context, the use of noble metal catalysts supported over acid supports (e.g. zeolites) is reported as a suitable strategy in order to promote GVL over reduction to VA or its esters. **Fig.1** shows the results in terms of ML conversion, GVL yield, MV+VA yield and carbon balance (expressed as yield sum/conversion ratio, Y/C) in function of the reaction temperature, using Rh/H-ZSM-5 as catalyst. Increasing the reaction temperature caused an increase of MV+VA yield with a concomitant decrease in GVL yield. This is mainly due to the strong acidity of the support which promote the ring-opening hydrogenolysis of GVL, usually identified in literature as the rate determining step<sup>3</sup>. Furthermore, a different strategy has been investigated by preparing a bimetallic system supported over silica (i.e. 4wt%Rh4wt%Re/SiO<sub>2</sub>). Interestingly, this material shows that is possible to reduce GVL, obtaining 2-MTHF as main product. In conclusion, these preliminary results demonstrate the enhanced catalytic activity of Rh/H-ZSM-5 in promoting the consecutive reduction of GVL to valeric acid and its esters. A completely different behavior was observed using Re-based catalyst, which promotes the selective hydrogenation of carboxylic group<sup>4</sup>. In the near future more efforts will be directed toward the synthesis of Re-based bimetallic catalysts supported on zeolites (e.g. RhRe/H-ZSM-5) with the aim of further improve the catalytic activity and the production of consecutive reduction products, like pentanol.

### References:

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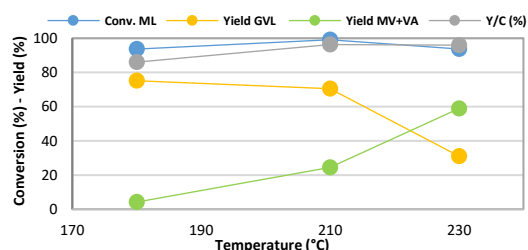


Fig. 1 Reaction conditions: Solvent free, P<sub>H<sub>2</sub></sub> = 40 bar; time = 4 h  
m<sub>cat</sub> = 5wt% of Rh/H-ZSM-5