

# Hydrodeoxygenation of levulinic acid over Pd/ZrO<sub>2</sub> catalysts



Esteban G. Gioria<sup>1</sup>, Gyula Novodárszki<sup>2</sup>, Laura Gutierrez<sup>1</sup>, Ágnes Szegedi<sup>2</sup>, József Valyon<sup>2</sup>,  
Dhanapati Deka<sup>3</sup>, Magdolna R. Mihályi\*<sup>2</sup>

<sup>1</sup>Research on Catalysis and Petrochemistry, INCAPE—(FIQ, UNL-CONICET), Santa Fe, Argentina,

<sup>2</sup>Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Budapest, Hungary

<sup>3</sup>Biomass Conversion Laboratory, Tezpur University, Tezpur, Assam, India

\*mihalyi.magdolna@ttk.hu



## Introduction

- Levulinic acid (LA) can be produced from sugars, which can be obtained, for instance, from lignocellulosic waste and by-products, in acid-catalyzed process even at an industrial scale [1].
- The most important product of LA hydrodeoxygenation (HDO) is  $\gamma$ -valerolactone (GVL), that can be blended with gasoline, and is intermediate to get liquid alkenes, polymers, and fine chemicals.
- Both homogeneous and heterogeneous noble metal (mainly Ru) and non-noble metal (Cu, Ni) catalysts are applied for the HDO of LA [2].
- Pd, supported on carbon, silica or niobia were also investigated as catalysts. Only few papers have been published about utilizing Pd/ZrO<sub>2</sub> catalyst.
- Palladium chloride is a widely used precursor for the preparation of oxide-supported Pd catalysts. Thermal decomposition of the Pd precursor, impregnated on the support, results in a catalyst, retaining chloride that can either accelerates or suppress reactions.

### Study of the chloride effect

- Development of novel preparation method to produce chloride-free zirconia-supported Pd catalyst (Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)) for efficient HDO of LA to GVL.
- For comparison a catalyst was prepared by calcining H<sub>2</sub>PdCl<sub>4</sub>-impregnated zirconia (Pd/ZrO<sub>2</sub>(Cl)).

## Catalysts preparation and characterization

### Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)

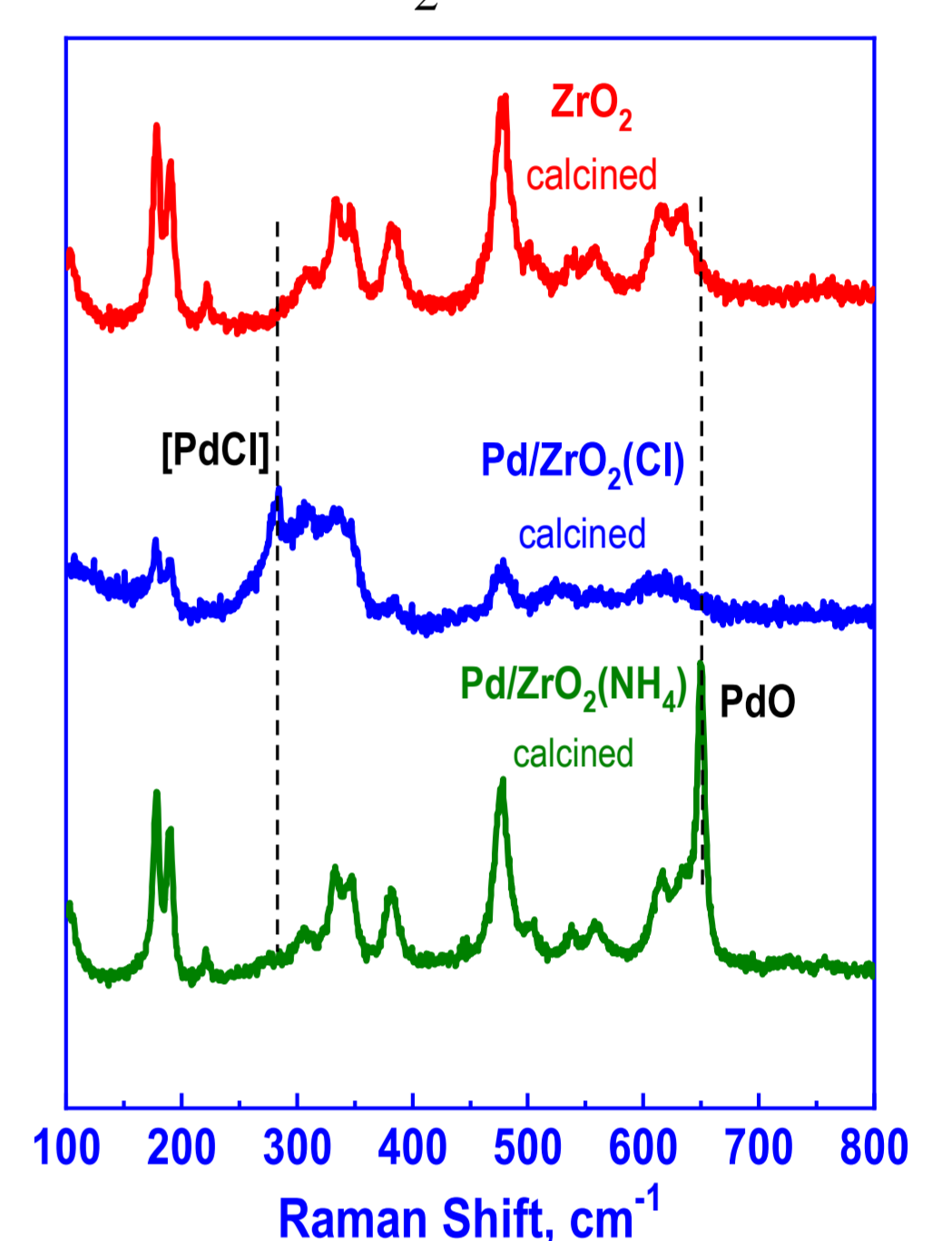
Physical mixture of commercial zirconia (MEI Inc.) and PdCl<sub>2</sub> was simply immersed and stirred in aqueous solution of ammonia. The thus formed Pd-tetraammine complex was reduced with hydrazine, depositing metallic Pd nanoparticles on the zirconia surface. By washing out the formed NH<sub>4</sub>Cl, the catalyst became totally chloride free.

### Pd/ZrO<sub>2</sub>(Cl)

Wet impregnation with aqueous solution of the metallic precursor H<sub>2</sub>PdCl<sub>4</sub> (Vega and Camji 99.9%) on the ZrO<sub>2</sub> support.

Both catalysts were dried at 80 °C for 24 h, calcined air flow at 400 °C for 4 h. Before catalytic run the catalysts were *in-situ* reduced at 350 °C for 1 h in H<sub>2</sub>.

Sample	SSA m <sup>2</sup> /g	Pd content wt. %	CO mmol/g	Pd dispersion %
ZrO <sub>2</sub> calc.	86	-	-	-
Pd/ZrO <sub>2</sub> (NH <sub>4</sub> )	80	5.0	5.6	2.4
Pd/ZrO <sub>2</sub> (Cl)	68	5.1	18.4	7.8



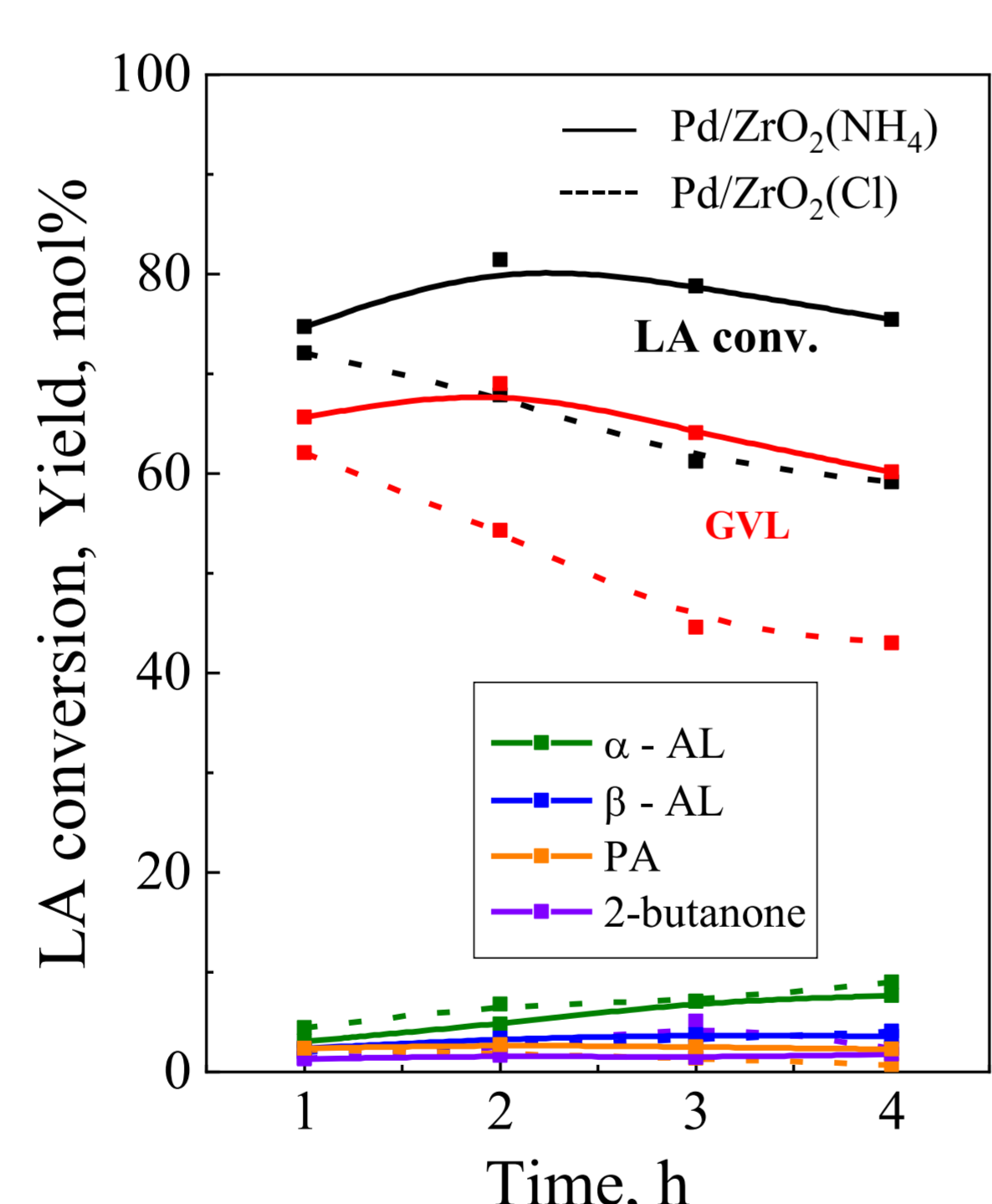
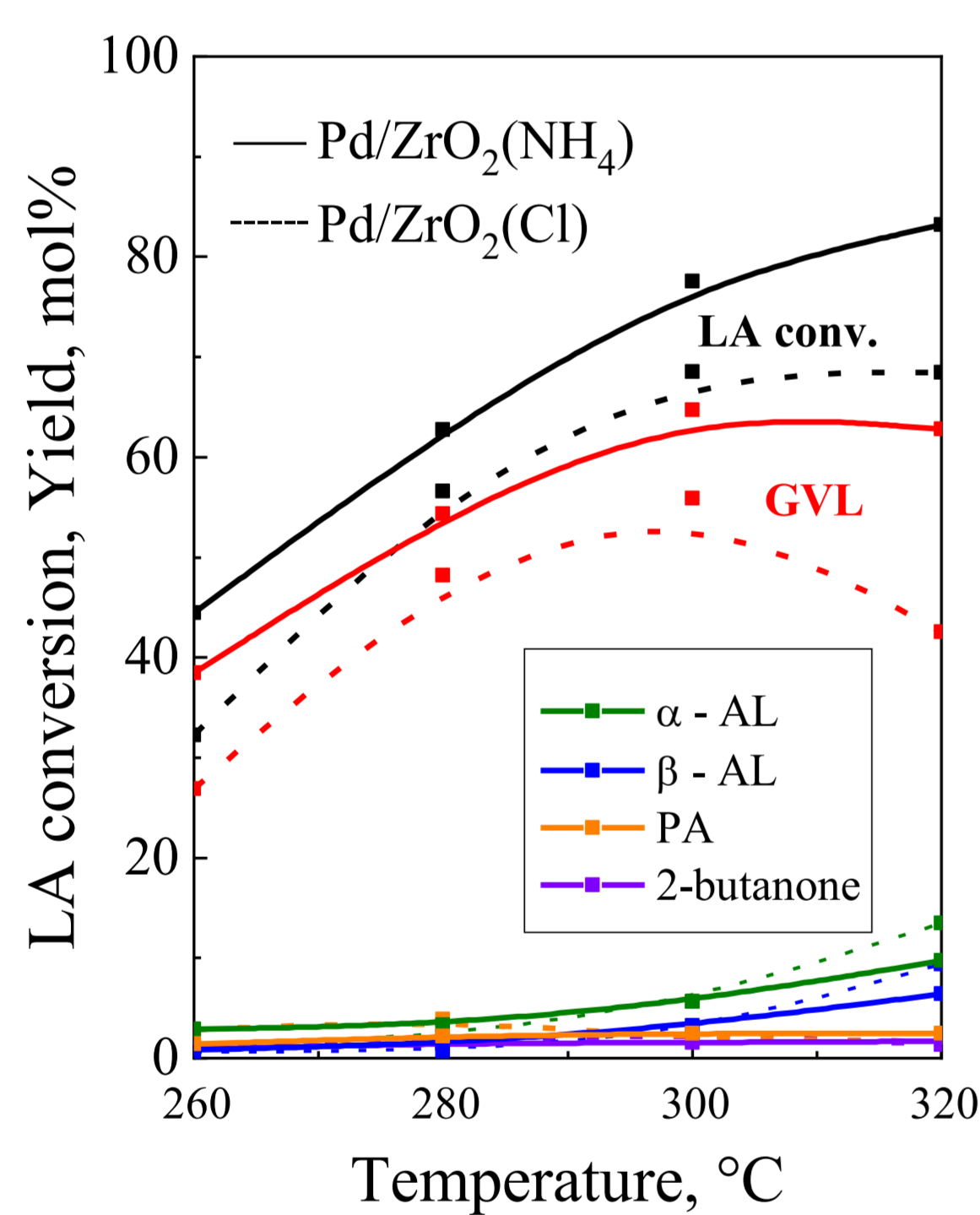
RAMAN: Pd/ZrO<sub>2</sub>(Cl) contains chloride, bound to the zirconia support and/or to the metal;  
Pd/ZrO<sub>2</sub>(NH<sub>4</sub>) has no chloride-containing species

## Catalytic activity and stability in the HDO of LA

Continuous flow, tubular, fixed-bed microreactor

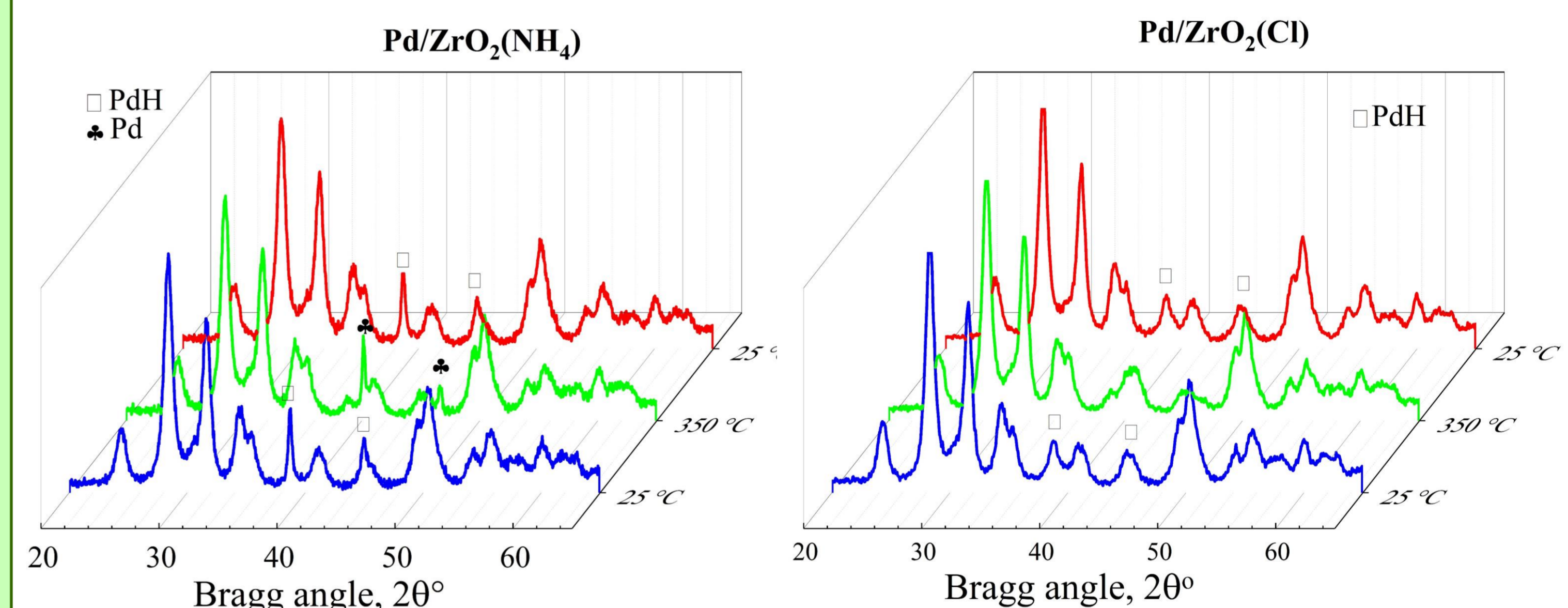
1 bar, 1 g<sub>cat</sub> g<sub>LA</sub><sup>-1</sup> h, H<sub>2</sub>/LA = 12.6

300 °C, 1 bar, 1 g<sub>cat</sub> g<sub>LA</sub><sup>-1</sup> h, H<sub>2</sub>/LA = 12.6



- The LA conversion and GVL yield are higher on the chloride-free catalyst (Pd/ZrO<sub>2</sub>(NH<sub>4</sub>)).
- The Pd/ZrO<sub>2</sub>(NH<sub>4</sub>) is more stable at 300 °C.
- Angelica lactones intermediates ( $\alpha$ -AL,  $\beta$ -AL), pentanoic acid (PA) and 2-butanone by-products were also formed.

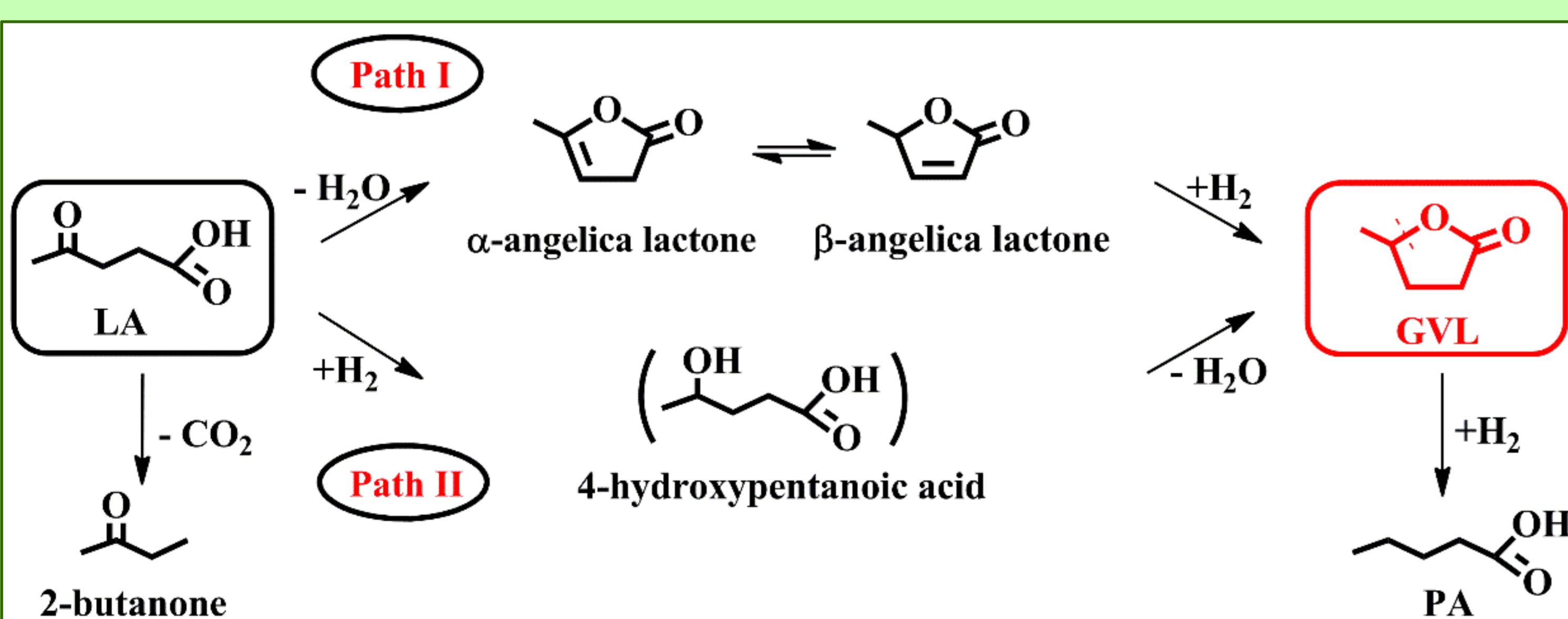
### In-situ XRD in H<sub>2</sub> flow



- In H<sub>2</sub> Pd-hydride (PdH) was formed in both catalysts at room temperature.
- At 350 °C the PdH phase released hydrogen and metallic Pd is detected in Pd/ZrO<sub>2</sub>(NH<sub>4</sub>). Cooling the catalyst to room temperature the PdH phase reappeared.
- No metallic Pd was detected for the reduced Pd/ZrO<sub>2</sub>(Cl) catalyst, i.e., crystallite size was lower than 5 nm. Pd is detectable in the presence of hydrogen only in PdH phase.

## Conclusions

- Chloride-free zirconia-supported Pd catalyst was successfully prepared using Pd-chloride as Pd source.
- At atmospheric pressure, in presence of hydrogen, in the temperature range of 280-320 °C, zirconia-supported Pd catalysts are active in LA hydrodeoxygenation to GVL through angelica lactone (AL) intermediate. LA is first dehydrated to unsaturated lactones and then hydrogenated to GVL.
- A fraction of  $\alpha$ -AL intermediate was isomerized to  $\beta$ -AL. Formation of a low amount of 2-butanone indicated that decarboxylation of levulinic acid also occurred. By-product pentanoic acid (PA) was formed in GVL hydrogenolysis.
- Although the Pd dispersion was higher in Pd/ZrO<sub>2</sub>(Cl) than in Pd/ZrO<sub>2</sub>(NH<sub>4</sub>), the latter catalyst showed better catalytic performance in LA hydrodeoxygenation. Higher LA conversion, higher selectivity to GVL and higher stability were achieved over the chloride-free catalyst than over the chloride-containing one.



## References

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[2] S. Dutta, I.K.M. Yu, D.C.W. Tsang, Y.H. Ng, J.S. Ok, J. Cherwood, J.H. Clark, *Chem. Eng. J.*, **372**, 992 (2019). W.L.H. Wright, R. Palkovits, *Chem. Sus. Chem.* **5**, 1 (2012).

## Acknowledgment

The authors thank the financial support of the National Research, Development and Innovation Office of Hungary (Indo-Hungarian project, 2019-2.1.13-TÉT\_IN-2020-00043).

