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Improved Catalytic Transfer Hydrogenation of levulinate esters with alcohols over ZrO_2 catalyst

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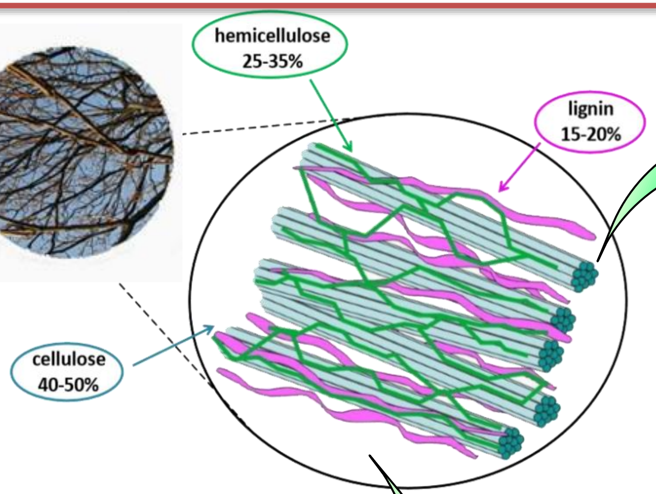
From alkyl levulinates to GVL

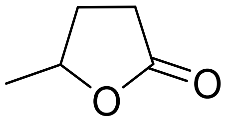
Lignocellulosic biomass



Top 12 value added bio-building block chemicals[1]:

Succinic, Fumaric, and Malic acid
2,5-Furan dicarboxylic acid (FDCA)
3-Hydroxypropionic acid (3-HPA)
Glucaric acid
Glycerol
Aspartic acid
Itaconic acid
3-Hydroxybutyrolactone
Sorbitol
Xylitol/arabinitol
Glutamic acid
Levulinic acid (LA)

Green solvent and fuel additive

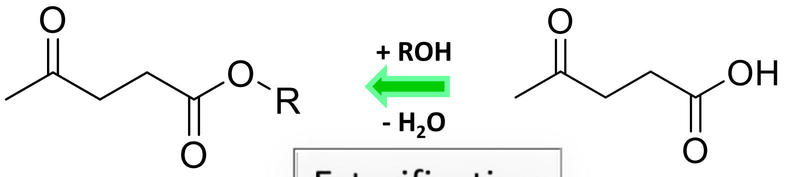


GVL
γ-valerolactone

Cellulose alcoholysis [3]

+ ROH

Cyclisation and reduction



Esterification

No acid functionality, lower boiling point, more stable at high temperature!
Ok for continuous-flow gas-phase reactions.

Alkyl levulinates

LA

LA global market: ca. 4000 tons/y.
Expected annual growth rate: 5%
(increasing demand from both the pharmaceutical and agriculture sectors).[2]

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1) Unites States Department of Energy: T. Werpy, G. Petersen. Top Value Added Chemicals from Biomass: Volume I. United States: N. p., 2004.
2) Grand View Research, Levulinic Acid Market Analysis And Segment Forecasts To 2020, 2015, 1-75.
3) Y-B. Huang, T. Yang, Y.-T. Lin, Y.-Z. Zhu, L.-C. Li and H. Pan. Green Chem., 2018, 20, 1323

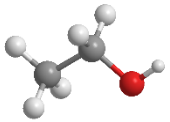
Our approach: Gas-Phase Catalytic Transfer Hydrogenation

CTH: use of light alcohols as reducing agents, no hydrogen pressure nor expensive noble metal catalysts

Catalyst:
synthesized tetragonal zirconia

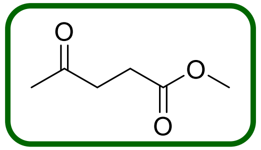
t-ZrO_2

SSA: 120 m^2/g



H-Donor: Ethanol

Methyl levulinate (ML)



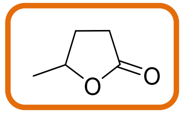
Gas-Phase Catalytic Transfer Hydrogenation

Gas-flow fixed-bed reactor, wide range of operating T (200-450°C) at atmospheric pressure

Innovative approach for the target reaction, not reported in literature so far

Catalyst regeneration

GVL



Comparison of these results with the ones obtainable in batch system and liquid phase:

Catalytic Transfer Hydrogenation (CTH) — Liquid Phase (autoclaves)

- High autogenic pressure — Higher risk
- Secondary alcohols — Isopropanol

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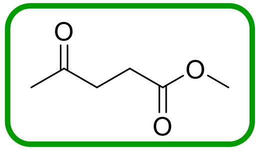
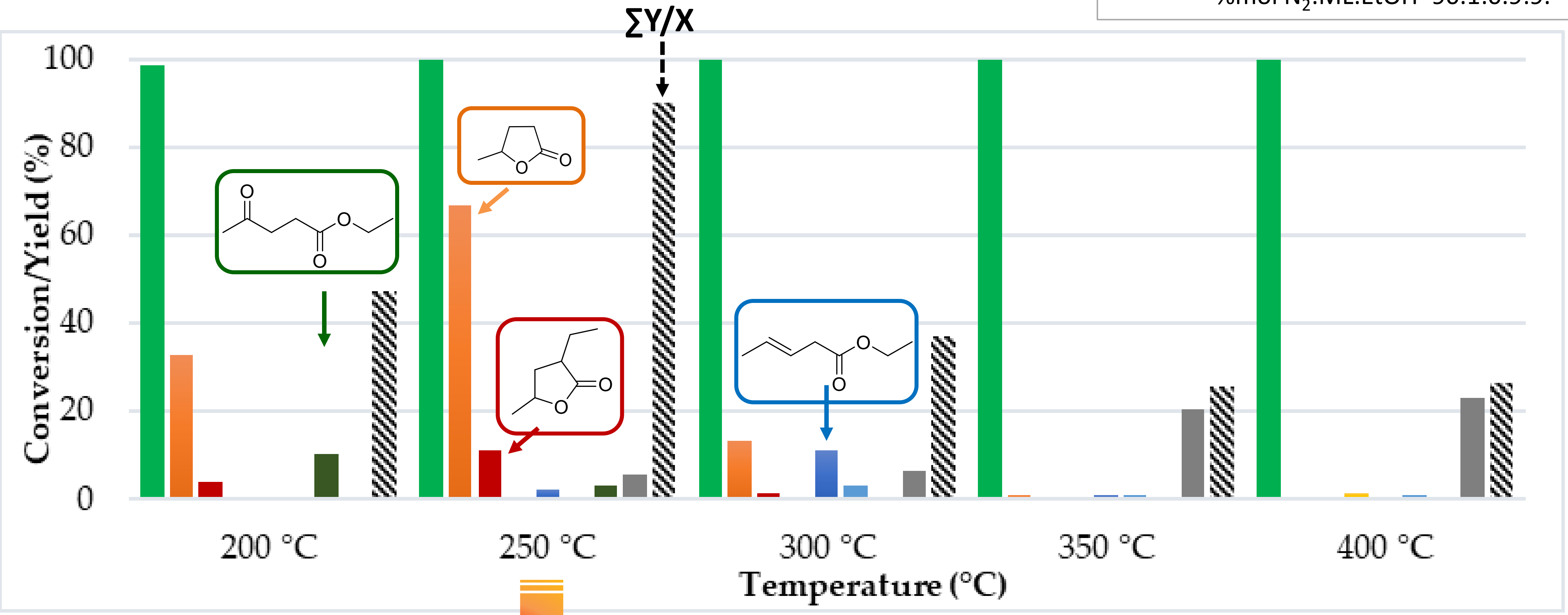
Gas-Phase Catalytic Transfer Hydrogenation: effect of temperature



ML conversion is complete in all the investigated temperature range

Reaction conditions:
ML:EtOH=1:10 (molar ratio), T: variable, catalyst: t-ZrO_2, τ = 1 s, %mol N_2:ML:EtOH=90.1:0.9:9.

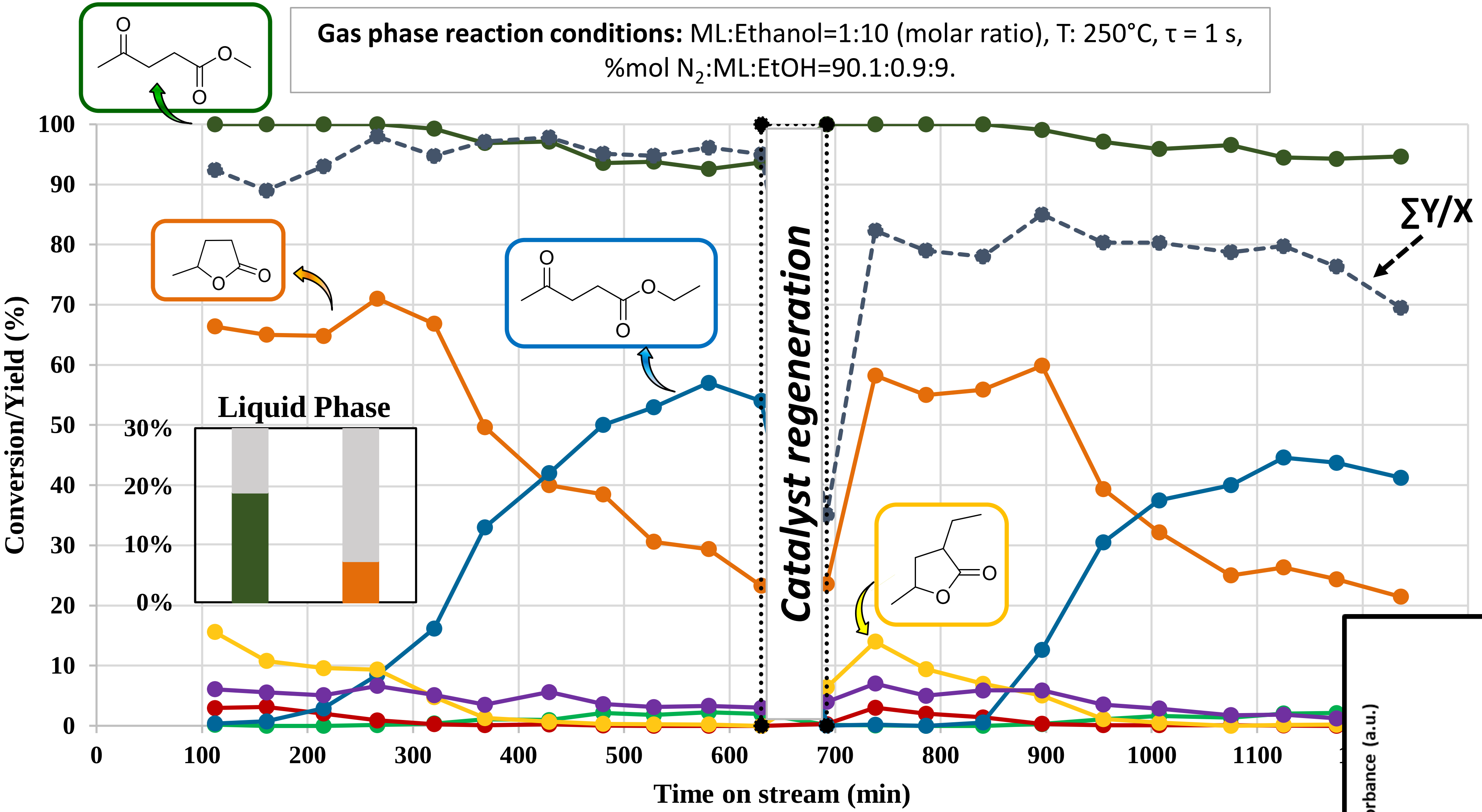


Optimized reaction temperature

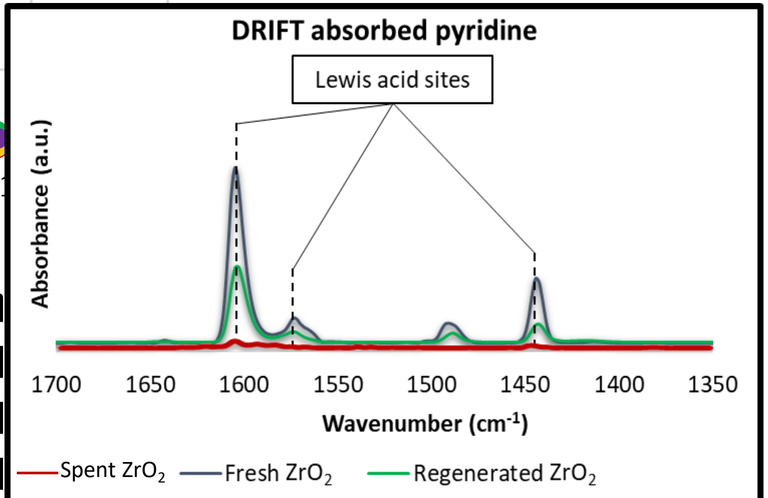
Vásquez, P. B., Tabanelli, T., Monti, E., Albonetti, S., Bonincontro, D., Dimitratos, N. and Cavani F. ACS Sustain. Chem. Eng. 2019, 7, 8317-8330

Gas-Phase Catalytic Transfer Hydrogenation: ethanol

Gas phase reaction conditions: ML:Ethanol=1:10 (molar ratio), T: 250°C, τ = 1 s, %mol N_2:ML:EtOH=90.1:0.9:9.



Liquid phase reaction conditions (histograms): 40 mL solution of ML (10 wt %) in ethanol, T: 250 °C, 0.30g of ZrO_2 catalyst, reaction time 8 h, N2 pressure 10 bar, stirring 500 rpm



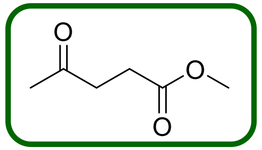
Deactivation is due to heavy carbonaceous species deposited over Lewis acid sites.

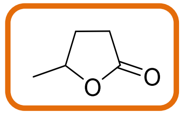
In-situ **regeneration of the catalyst** (feeding air at 400°C for 2 hours) permitted an almost complete recovery of the initial catalytic behavior.

Gas-Phase Catalytic Transfer Hydrogenation: other alcohols

Gas phase reaction conditions: ML:alcohol=1:10 (molar ratio), T: 250°C, τ = 1 s, %mol N_2:ML:alcohol=90.1:0.9:9.

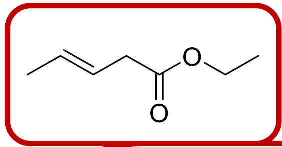
Liquid phase reaction conditions (histograms):
40 mL solution of ML (10 wt %) in ethanol, T: 250 °C, 0.30g of ZrO_2 catalyst, reaction time 8 h, N2 pressure 10 bar, stirring 500 rpm

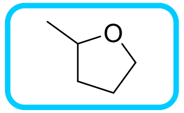


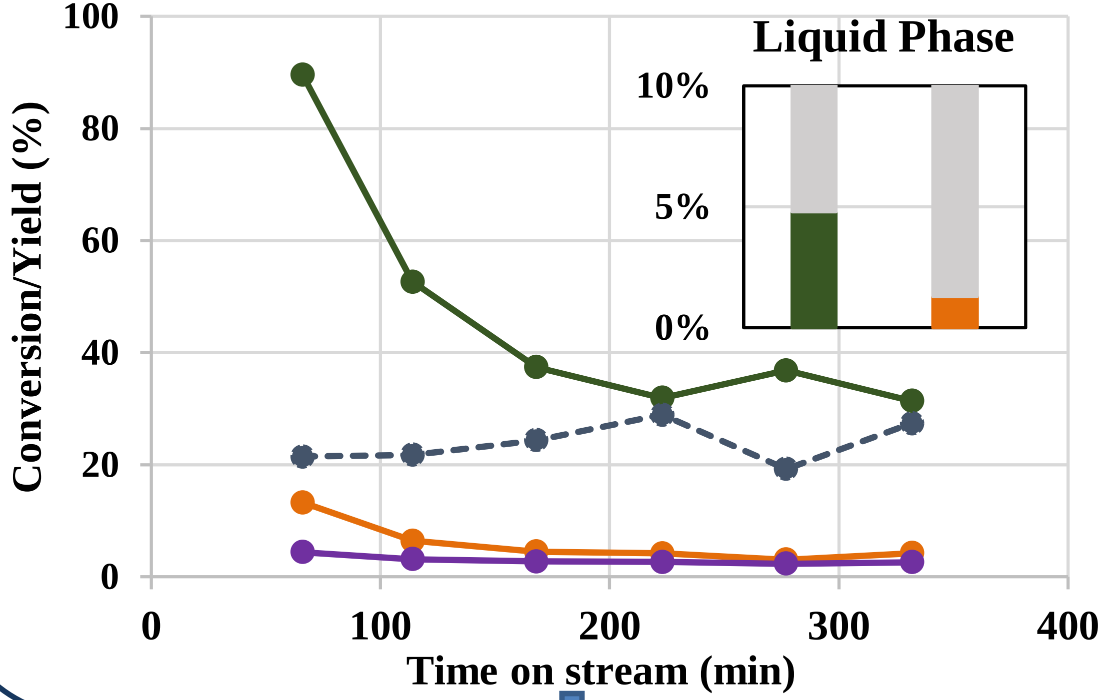


ΣY/X

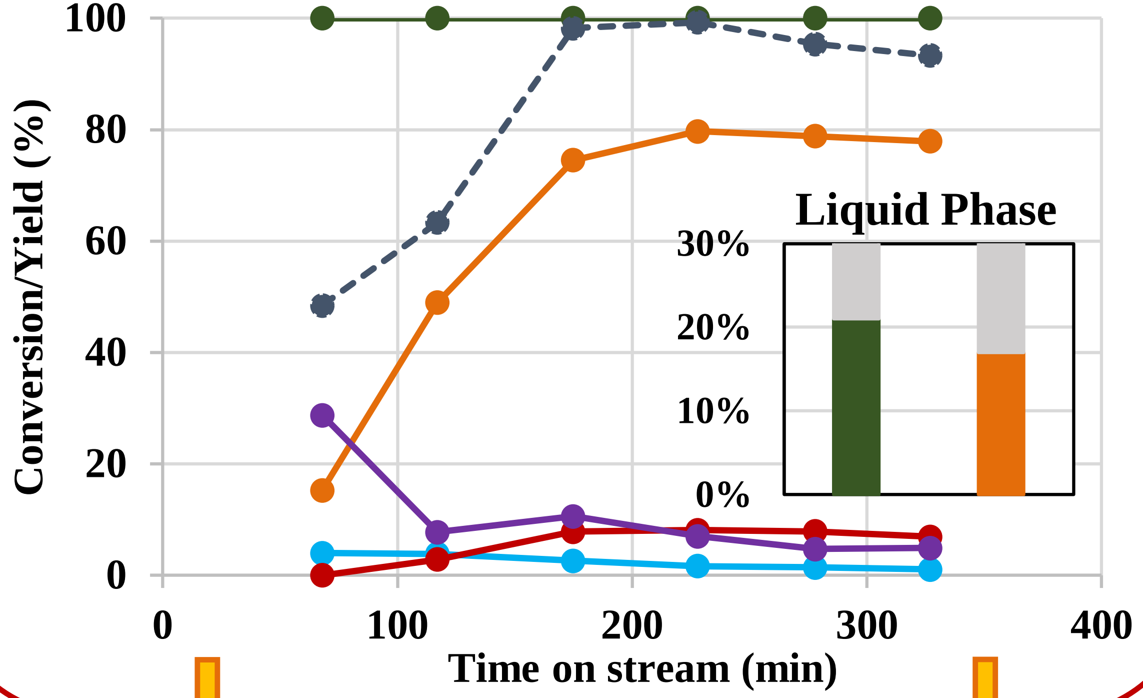
"Others"







Poor performance in the CTH of ML



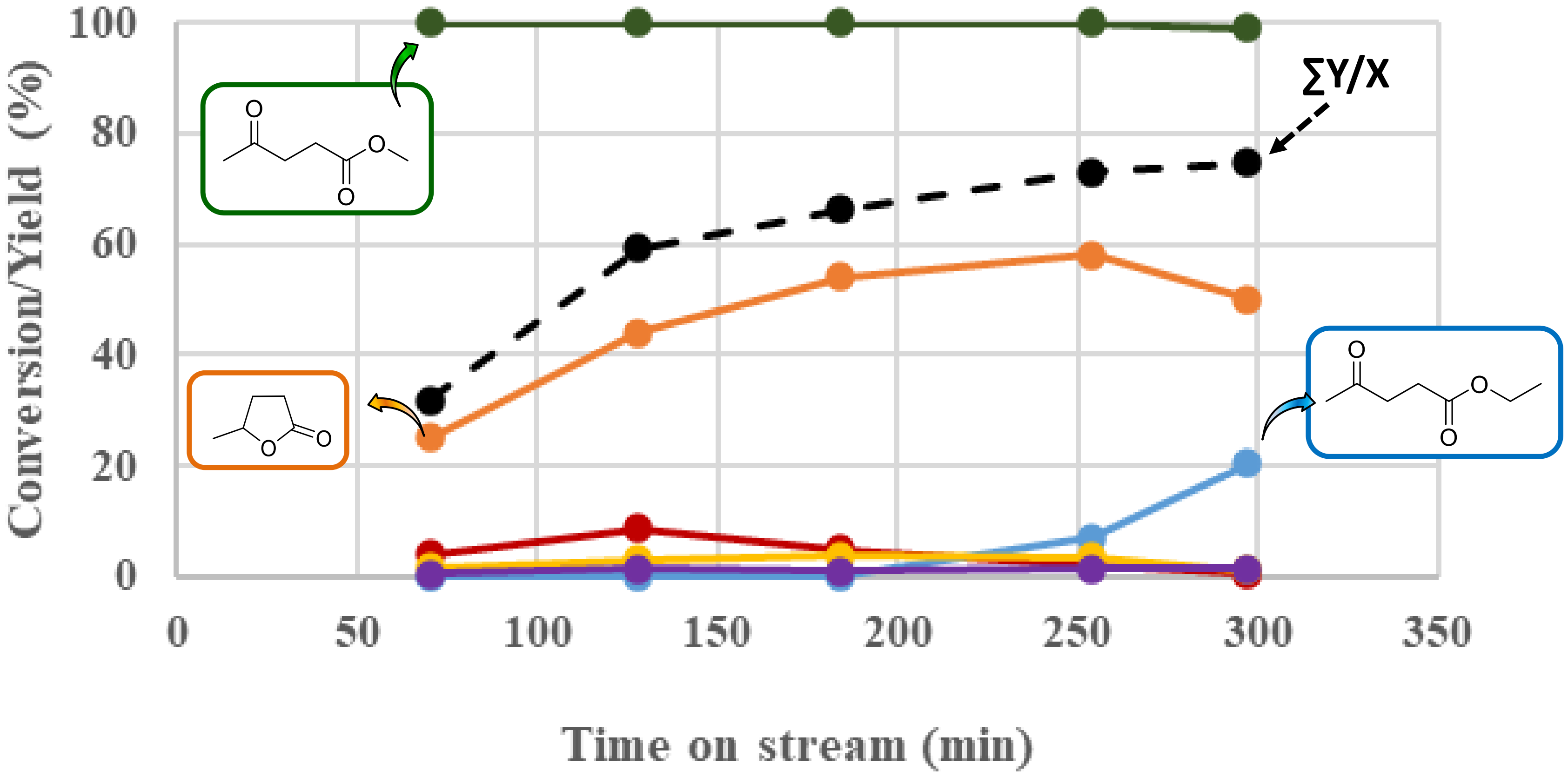
Very good GVL yield and selectivity.
Superior performance in the CTH of ML but similar to the ones obtained with EtOH

Tabanelli, T., Paone, E., Vásquez, P. B., Pietropaolo, R., Cavani, F., and Mauriello F. ACS Sustain. Chem. Eng. 2019, 7, 9937-9947.

Gas-Phase Catalytic Transfer Hydrogenation: bio-ethanol

Reaction conditions: ML:bio-EtOH=1:10 (molar ratio), T: 250°C, τ = 1 s, %mol N_2:ML:EtOH=90.1:0.9:9.

H-transfer of ML with bio-ethanol over ZrO_2



Continuous GVL production with both bio-ethanol and methyl levulinate obtainable from renewable feedstocks

Conclusions

Synthetic zirconia shows a superior catalytic behavior for the CTH of ML to GVL in the continuous flow, fixed-bed, gas-phase system compared to the traditionally employed liquid, batch reactors

Ethanol and bio-ethanol were proved to be suitable H-donors for the target reaction

Catalysts deactivation was proved to be linked with the deposition of heavy carbonaceous compound on the catalyst surface.

Catalysts regeneration can be easily performed *in-situ*, by feeding air at high temperature (e.g. 400°C).