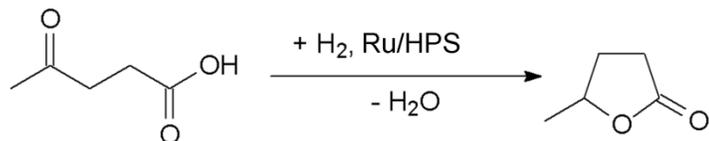# MONO- (Ru) AND BIMETALLIC (Ru-Co) POLYMERIC CATALYSTS FOR LEVULINIC ACID HYDROGENATION

Valentina G. Matveeva, Maxim E. Grigorev, Stepan P. Mikhailov, Linda Zh. Nikoshvili, Esther M. Sulman

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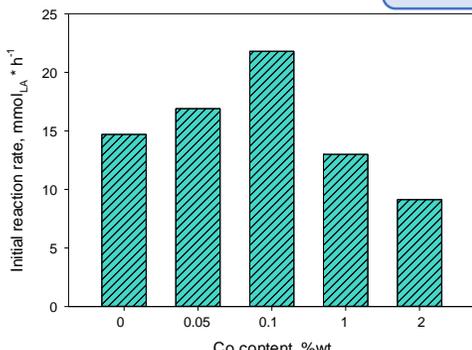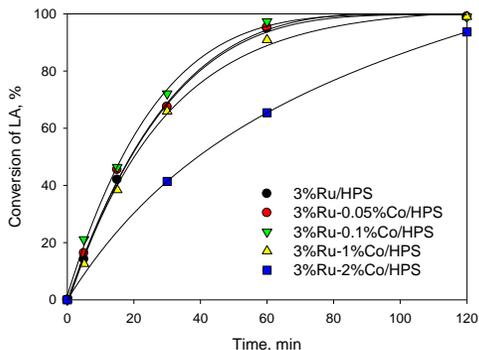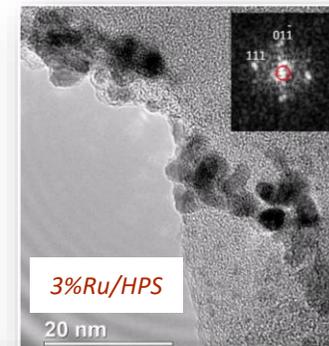
levulinic acid (LA) → gamma-valerolactone (GVL)

+ H$_2$, Ru/HPS
− H$_2$O

Synthesized HPS-based catalysts:
- 3%-Ru/HPS
- 3%Ru-0.05%Co/HPS
- 3%Ru-0.1%Co/HPS
- 3%Ru-1%Co/HPS
- 3%Ru-2%Co/HPS

1500 rpm, 100ºC, 2 MPa of H$_2$, LA-to-catalyst ratio 50 g/g

Selectivity was ~100% in all the experiments

Hypercrosslinked polystyrene (HPS) as catalytic support

HPS of MN100 type (bearing tertiary amino-groups) produced by Purolite Ltd. (UK) was used

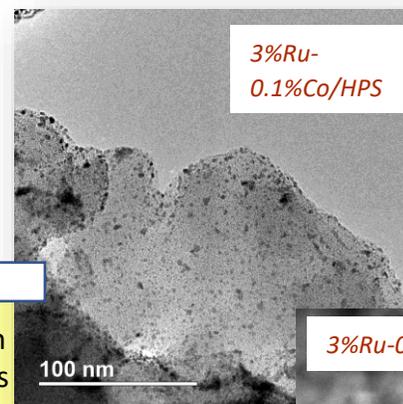*All the samples were activated in H$_2$ flow (300ºC, duration 2 h)*

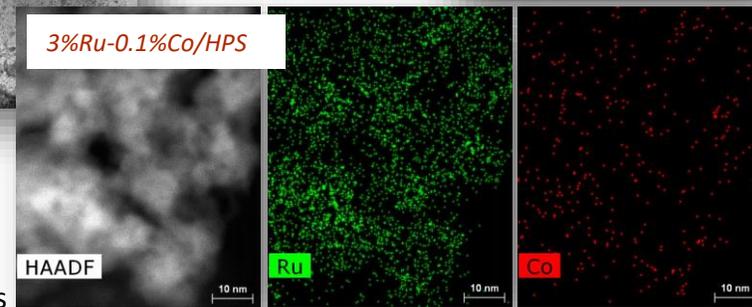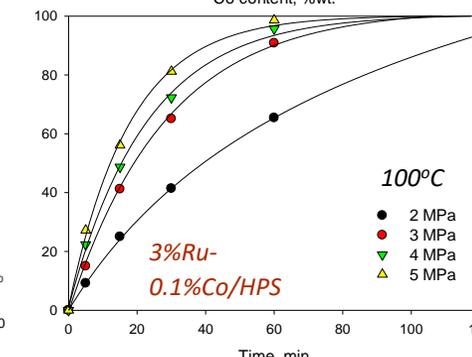After preliminarily activation, small RuO$_2$ nanoparticles (3-4 nm) were found, which formed grapelike aggregates

3%Ru-0.1%Co/HPS

3%Ru/HPS

20 nm

100 nm

No products of chemical interaction of Co- and Ru-containing species were found

3%Ru-0.1%Co/HPS

HAADF   Ru   Co

Introduction of Co in the catalyst composition results in redistribution of nanoparticles of catalytically active phase (RuO$_2$) inside the polymeric matrix of HPS.
This effect was responsible for approximately 1.5-fold increase of initial reaction rate in the case of 3%Ru-0.1%Co/HPS in comparison with monometallic analogue (3%Ru/HPS)

Conversion of LA, % vs Time, min
- 3%Ru/HPS
- 3%Ru-0.05%Co/HPS
- 3%Ru-0.1%Co/HPS
- 3%Ru-1%Co/HPS
- 3%Ru-2%Co/HPS

Initial reaction rate, mmol$_{LA}$ * h^{-1} vs Co content, %wt.

3%Ru-0.1%Co/HPS

2 MPa
- 90ºC
- 100ºC
- 110ºC
- 120ºC

E$_{a,app}$ = 17 kJ/mol
ln(R) vs 1000/T, 1/K

3%Ru-0.1%Co/HPS

100ºC
- 2 MPa
- 3 MPa
- 4 MPa
- 5 MPa

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