Continuous Flow Production of γ-Valerolactone from methyl-levulinate promoted by MOF-derived Al_2O_3-ZrO_2/C catalysts

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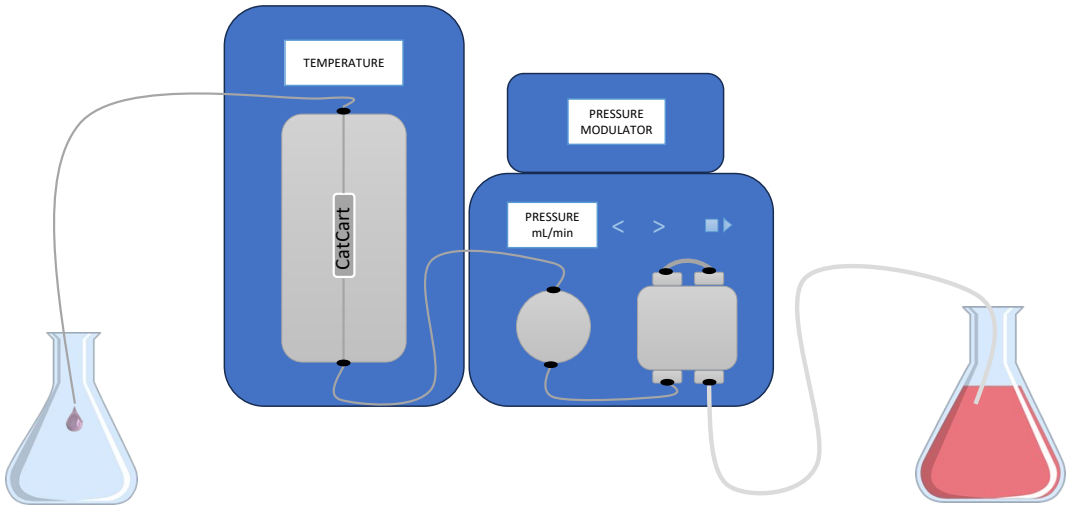
SUPPLEMENTARY INFORMATION

Supporting information contains 7 pages including 1 Scheme, 1 Table and 4 Figures.



Scheme S1. A representative sketch of the Thalesnano Phoenix flow reactor.

Table S1. Representative heterogeneous catalysts used for converting alkyl levulinates to GVL in batch reactors with the results obtained using the Al2O3-ZrO2/C (1:1) catalyst in this study.

Catalyst	Conditions	Conversion (%)	Selectivity (%)	Ref.
UiO-66(Zr)	0.1 g of catalysts, 1 mmol of ML in 5 mL of 2-butanol, 140 °C, Ar, 0.5 MPa, t = 9 h (batch reaction)	70	51	1
UiO-66(Zr)	0.22 g of catalysts, 4 mmol of EEd in 400 mmol of isopropanol, 130 °C, t = 3 h (batch reaction)	43.3	18.5	2
$UiO\text{-}66_{S60}$	100 mg of catalyst, 1 mmolv of ML, 5 mL of 2-BuOH, Ar 0.5 MPa, 140 ºC t= 9 h	98	82	3
UiO-66 (Zr)	150 ºC, 4h, 2-butanol, Ethyl levulinate	63	25	4
$Al_7\text{-}Zr_3\text{-}300$	0.072 g of catalysts, 1 mmol of EEd in 5 mL of isopropanol, 220 °C, t = 4 h (batch reaction)	95.5	87.1	5
ZrO_2	0.30 g of ZrO_2 catalyst, 40 mL solution of β-angelica lactone 10 wt %, t= 8 h, N_2 pressure 10 bar, stirring 500 rpm (batch reaction)	72	77	[6]
Ni-Co	1 g of catalyst, 2-propanol, t= 6h (batch reaction)	98	75	[7]
$Al_2O_3\text{-}ZrO_2/C$ (1:1)	Flow 0.5 mL/min, 220 ºC, 0.5 g cat	100	85	This work

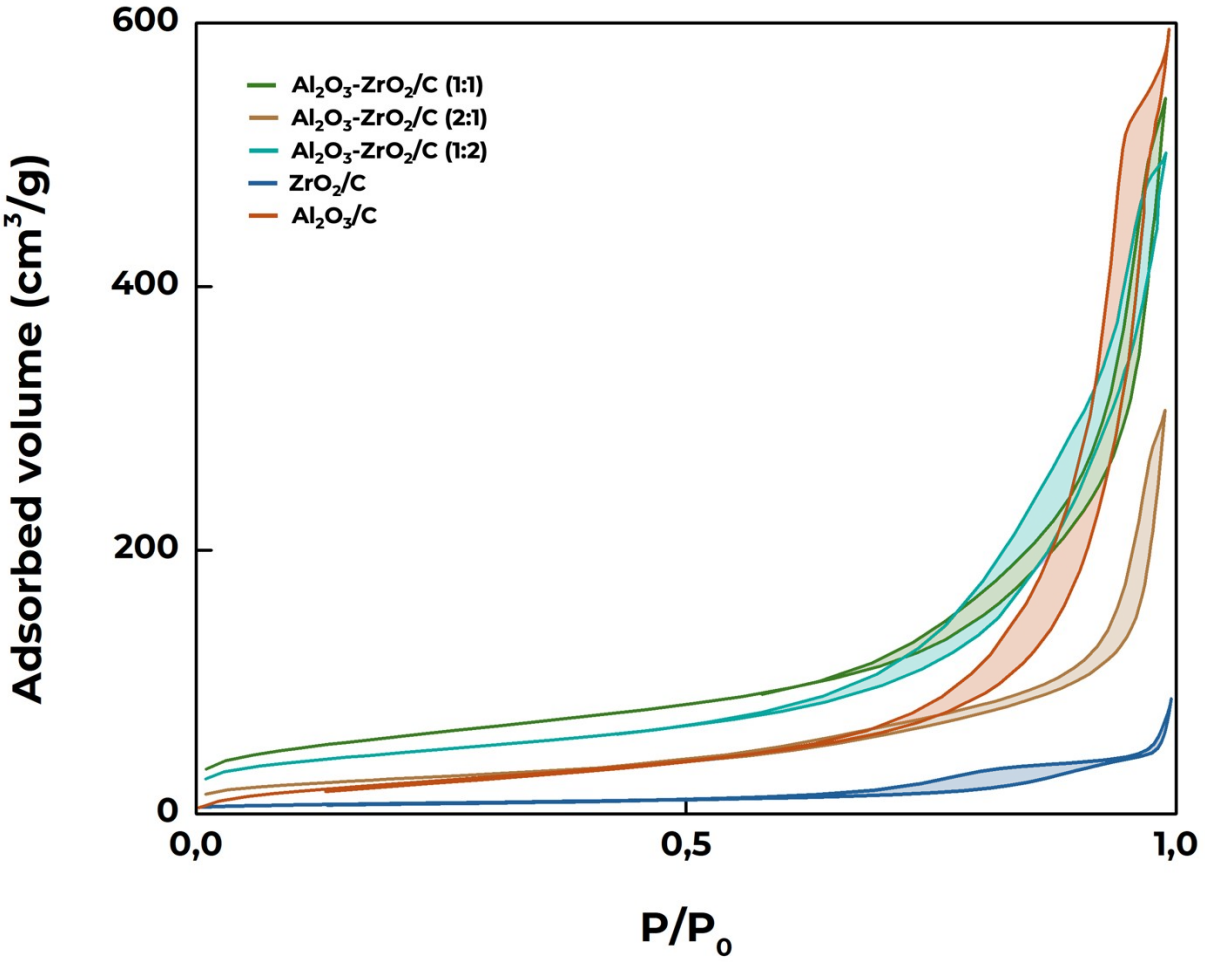


Figure S1. N_2 physisorption isotherms of calcined MOF-derived Al_2O_3-ZrO_2/C catalysts.

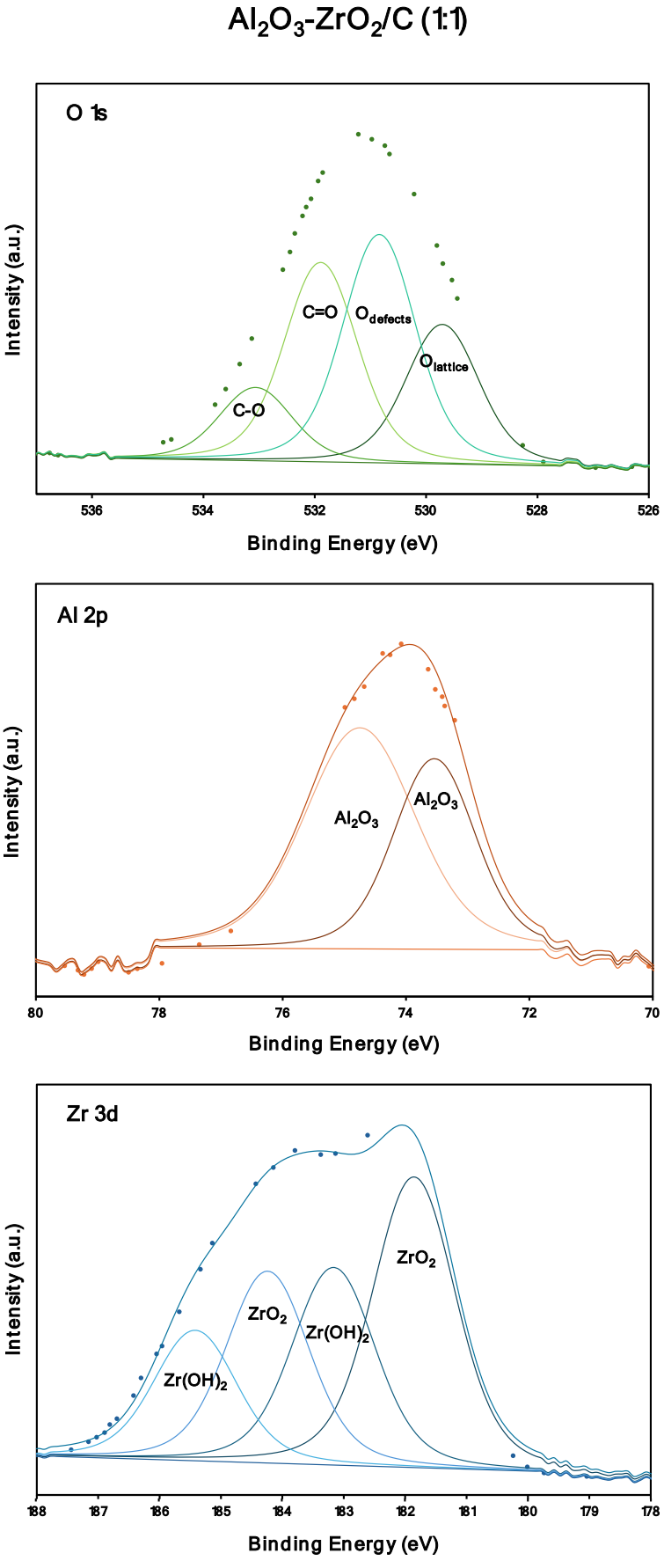


Figure S2. XPS spectra of Al_2O_3-ZrO_2/C (1:1).

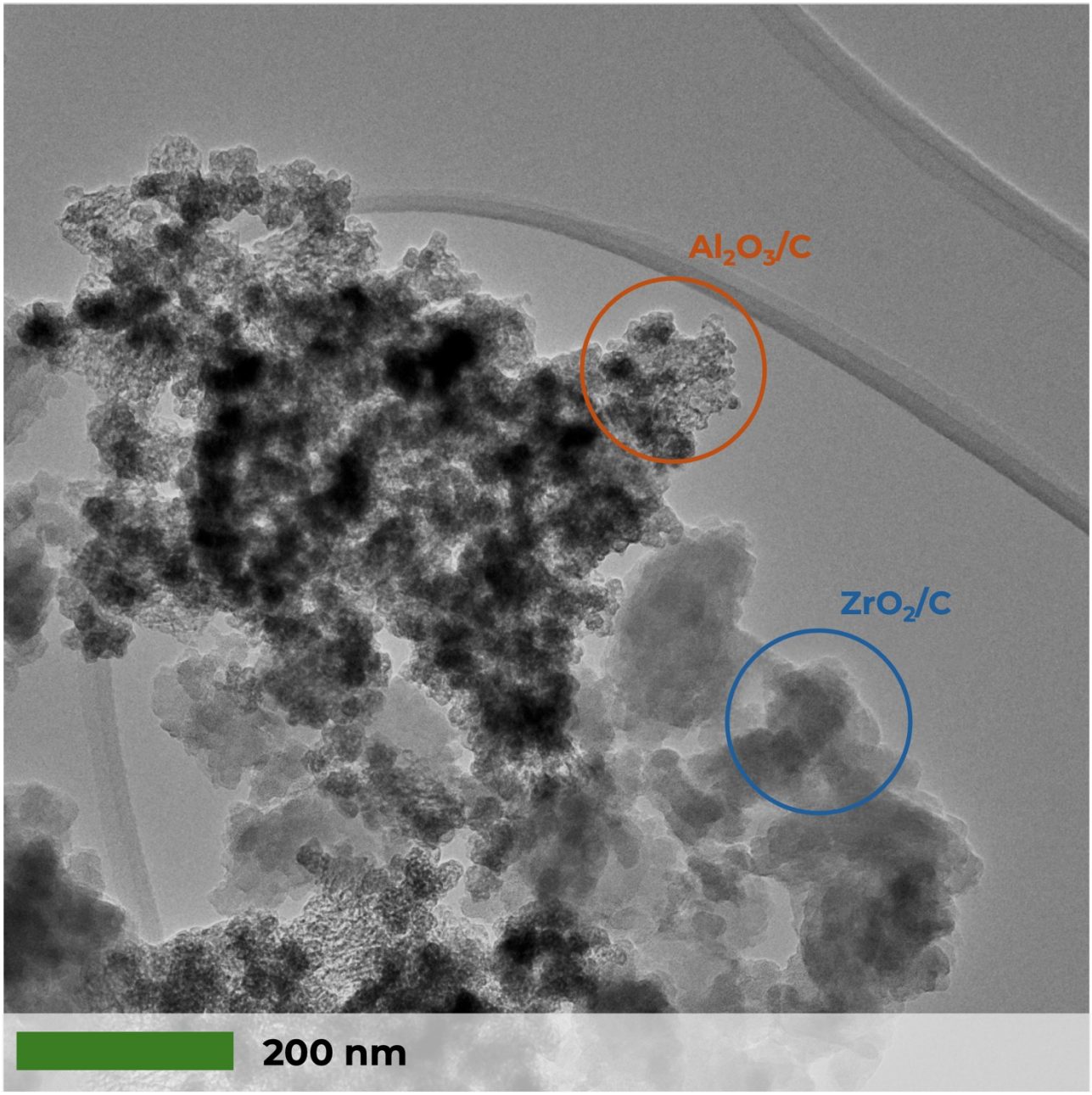


Figure S3. TEM images of Al_2O_3-ZrO_2/C (1:1) catalyst.

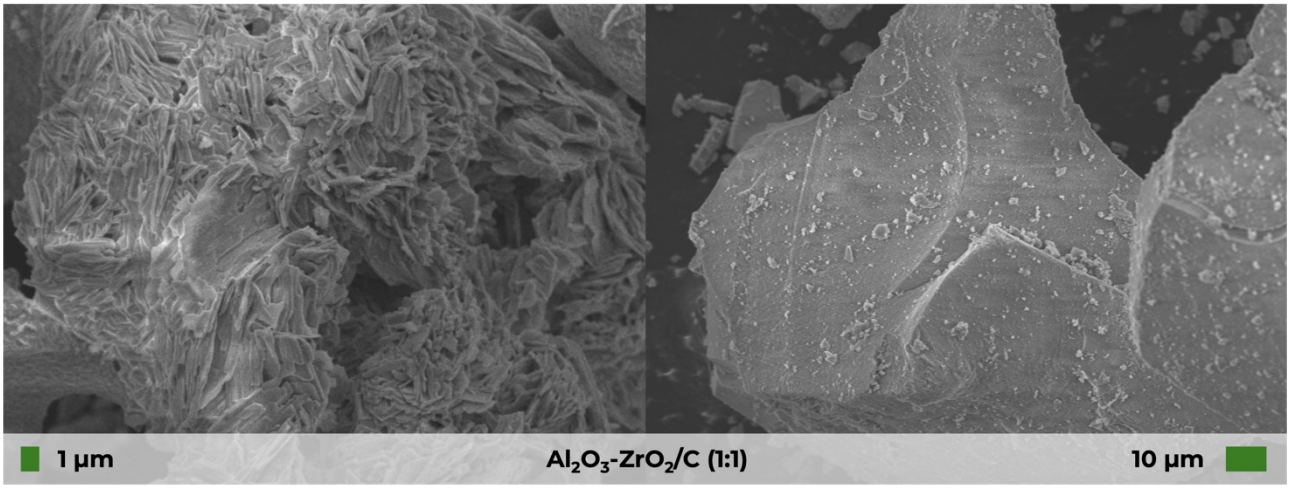


Figure S4. SEM images of Al_2O_3-ZrO_2/C (1:1) catalyst.

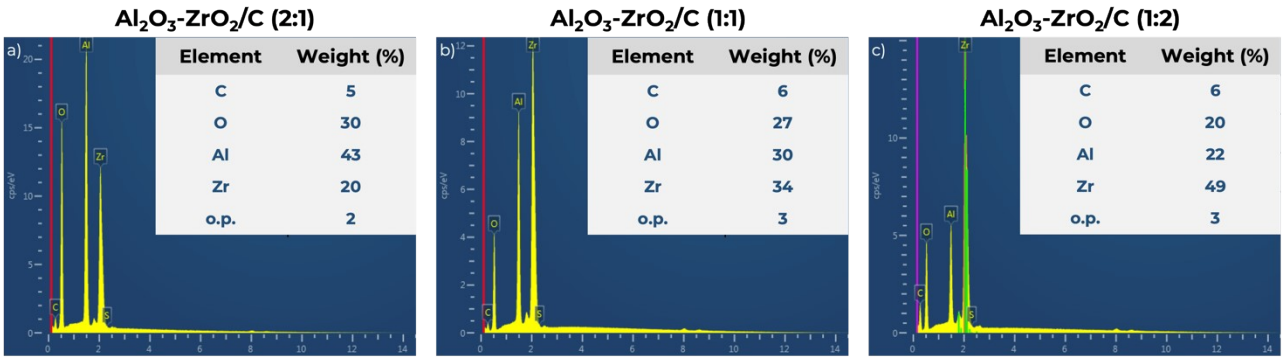


Figure S5. EDS images of a) Al_2O_3-ZrO_2/C (2:1) b) Al_2O_3-ZrO_2/C (1:1) c) Al_2O_3-ZrO_2/C (1:2) catalyst.

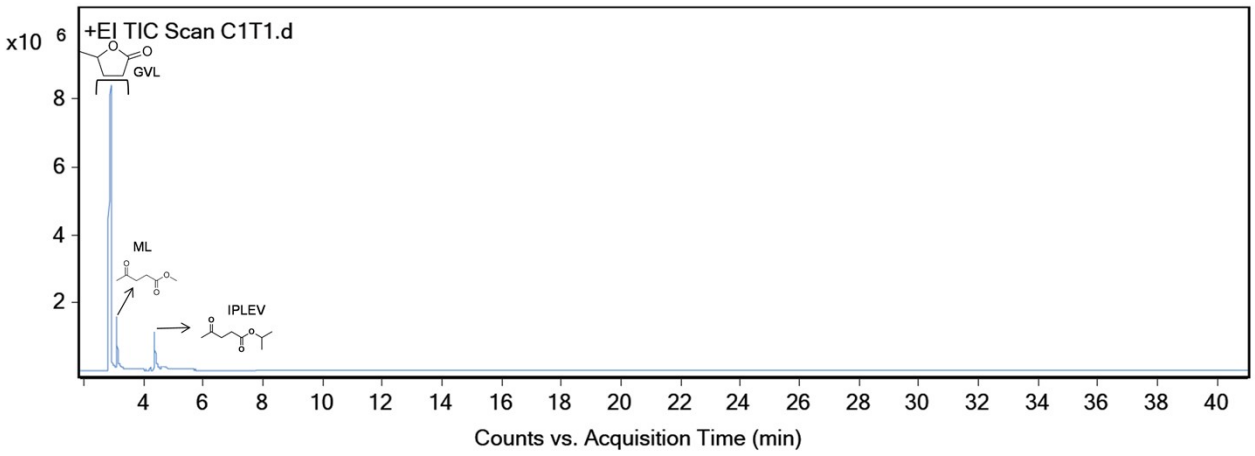


Figure S6. Chromatogram spectrum from GC-MS of reaction at 30 min from Al_2O_3-ZrO_2/C (1:1). Reaction conditions: 200 ºC, 0.5 mL/min, 30 bar pressure, 0.2 mol/L of ML in 2-propanol.

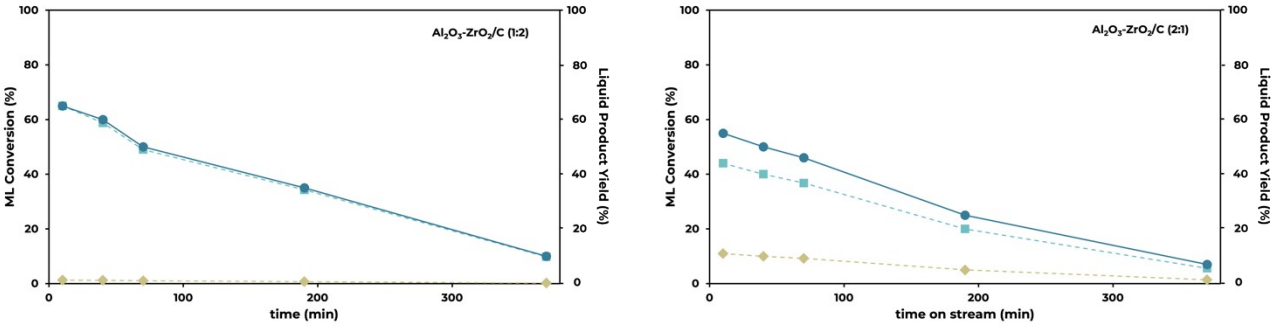


Figure S7. CTH of methyl levulinate into γ-valerolactone promoted by Al_2O_3-ZrO_2/C (1:2) and Al_2O_3-ZrO_2/C (2:1) catalysts against time (reaction conditions: 0.5 mL/min flow rate; ML 0.2 M in 2-propanol; 0.500 g of catalyst; 30 bar of pressure; reaction temperature: 200 °C).

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