

Supporting Information

1. Nitrogen adsorption isotherms

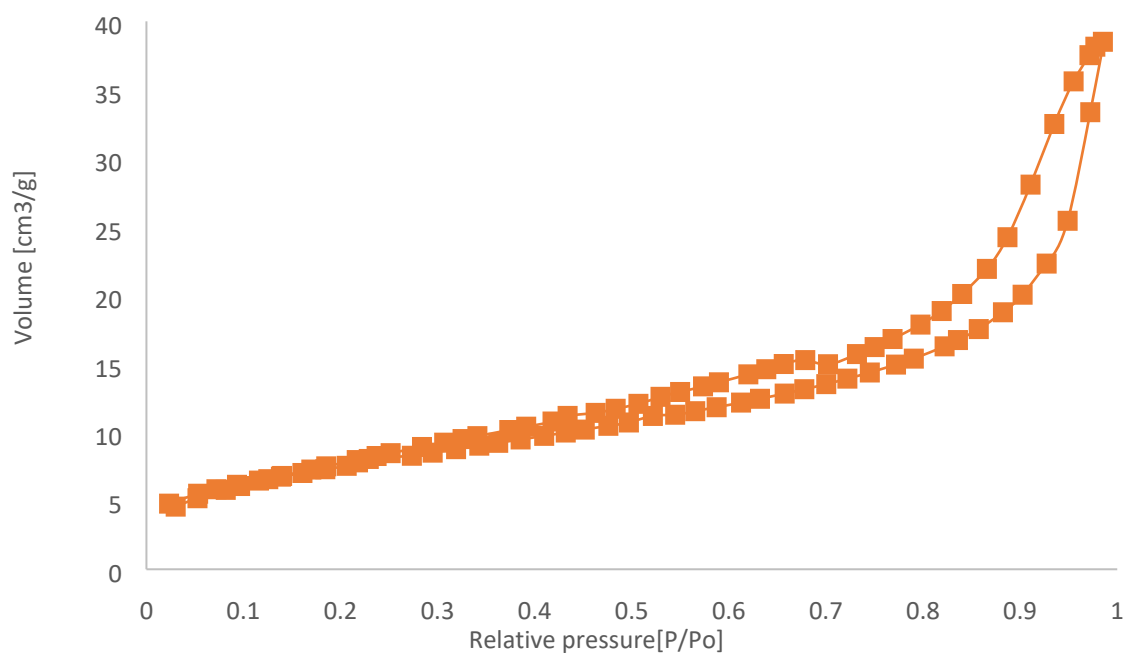


Figure S1. Nitrogen adsorption isotherm at -196.15 °C for sample Nb+N-ie.

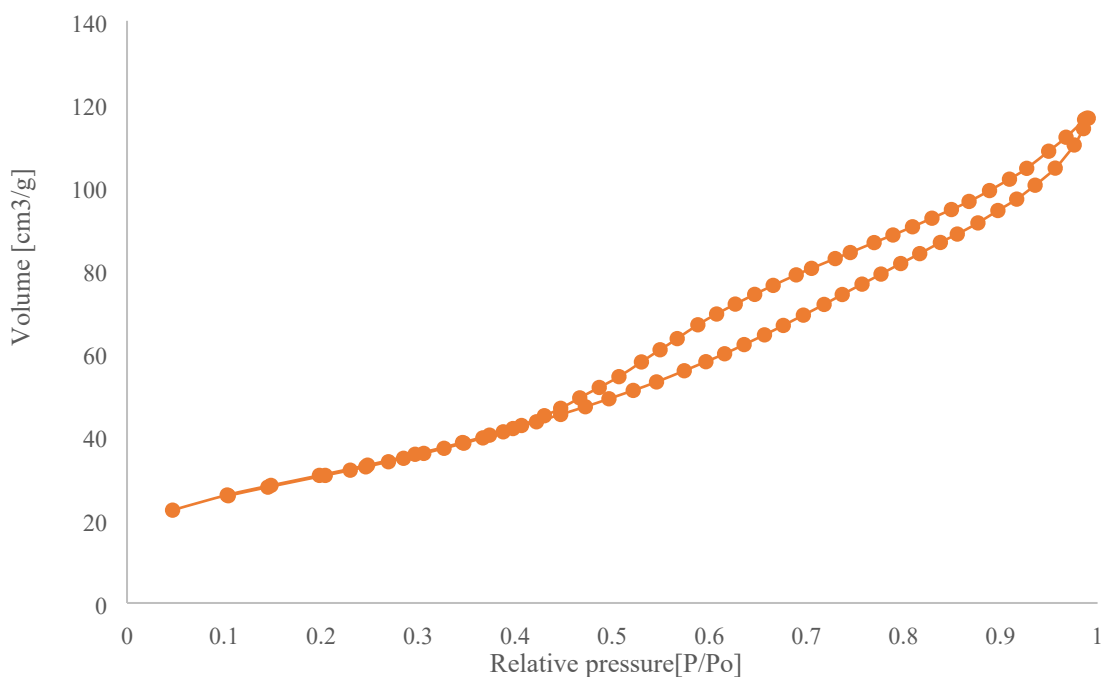


Figure S2. Nitrogen adsorption isotherm at -196.15 °C for sample Zr+N-ie.

2. Conversion of levulinic acid in the esterification with ethanol catalyzed by zirconia

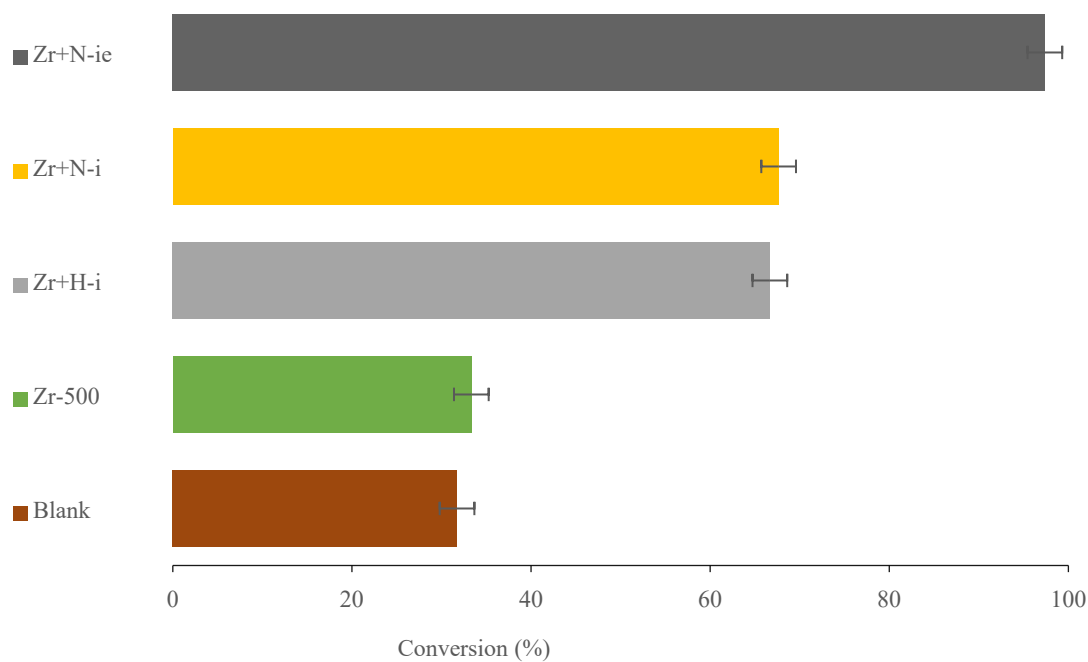


Figure S3. Conversion of LAc in the esterification with ethanol for the zirconia catalysts studied. Reaction conditions: 700 rpm, alcohol/acid molar ratio 12:1, 5 wt% catalyst relative to levulinic acid mass, for 2 hours at 140 °C.

3. Chromatographic analysis of reactants and products

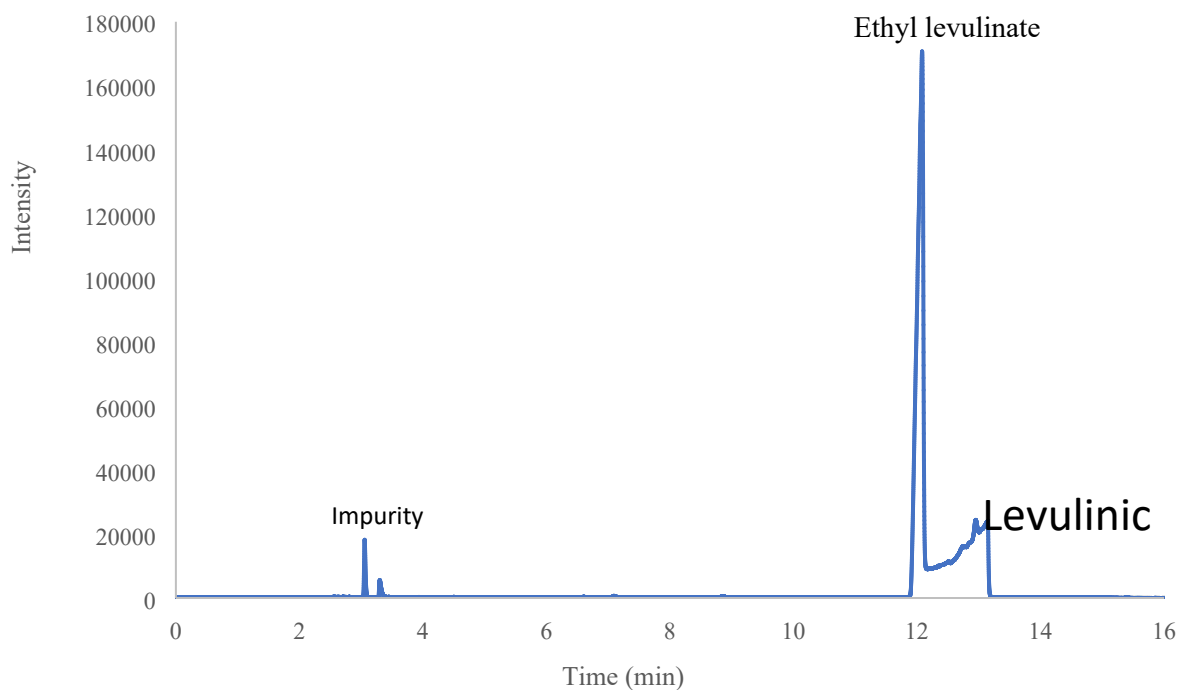


Figure S4. Chromatogram of the reaction product at 140 °C catalyzed with Nb+N-ie.

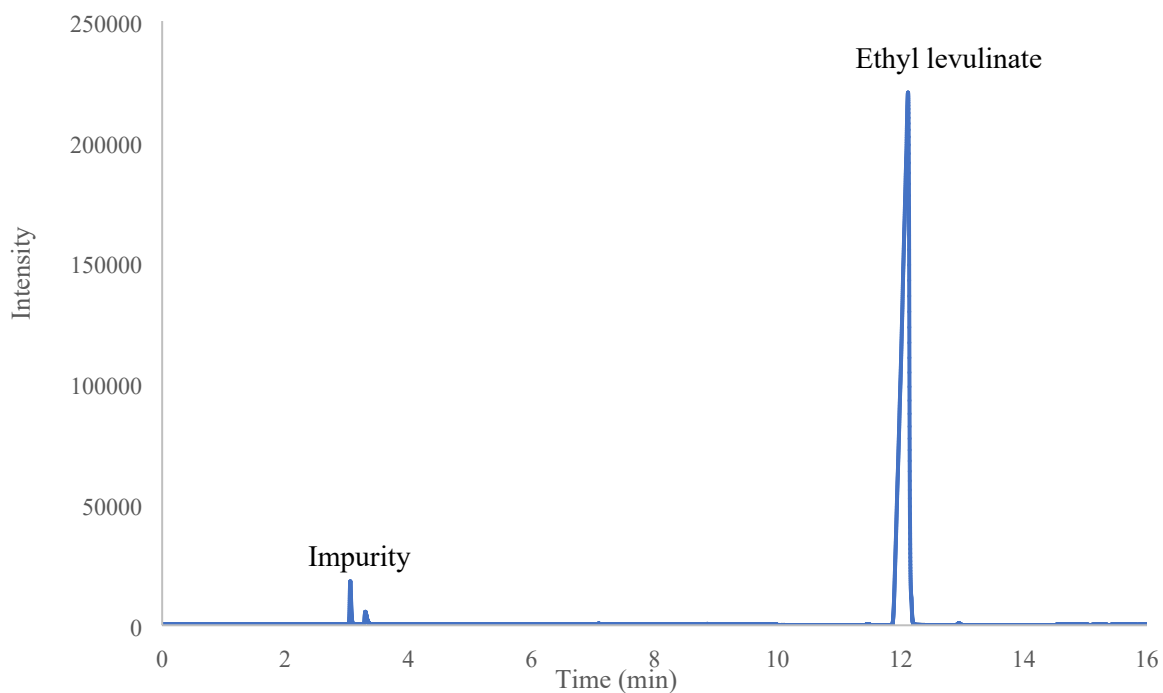


Figure S5. Chromatogram of the reaction product at 140 °C catalyzed with Zr+N-ie.

4. TOF and kinetic fitting

Table S1. TOF for the esterification of LAc with ethanol at 140 °C.

Catalyst	TOF (s ⁻¹)
Nb-500	1.90x10 ⁻³
Nb+H-i	5.85x10 ⁻³
Nb+N-i	1.00x10 ⁻²
Nb+N-ie	1.34x10 ⁻²
Zr-500	1.28x10 ⁻²
Zr+H-i	1.86x10 ⁻²
Zr+N-i	1.96x10 ⁻²
Zr+N-ie	3.69x10 ⁻²

Table S2. Power law kinetic model for the reactions in the absence of catalyst and catalyzed with Zr+N-ie and Nb+N-ie at 70 and 140 °C.

Catalyst	T = 70 °C				T = 140 °C			
	$\eta=0$	$\eta=1$	$\eta=2$	k_{70}	$\eta=0$	$\eta=1$	$\eta=2$	k_{140}
No Cat	0.949	0.992	0.955	3.16E-04	0.963	0.999	0.984	1.02E-03
Nb+N-IE	0.861	0.896	0.992	7.69E-04	0.667	0.868	0.995	2.90E-03
Zr+N-ie	0.924	0.935	0.995	3.95E-03	0.924	0.937	0.995	1.82E-01

Table S3. Benchmarking of sulfated zirconia- and niobia-based catalysts reported in the literature for the esterification of levulinic acid (LAc) with ethanol. The table summarizes sulfate precursor (S source), calcination

Catalyst	S source	Calcination treatment		Reaction operating conditions				Levulinic acid conversion (%)	Reference
		T (°C)	t (h)	Catalyst load (%)*	LAc/EtOH molar ratio	Temperature (°C)	Reaction time (h)		
SO ₄ ²⁻ /Six-ZrO ₂	H ₂ SO ₄	600	3	5	1:10	70	10	65	1
				10				76	
SO ₄ ²⁻ /ZrO ₂		600	3	5	1:10	70	10	21	
				10				26	
SO ₄ ²⁻ /bulkZrO ₂	H ₂ SO ₄	500	3	2.5	1:5	70	8	62	2
								SO ₄ ²⁻ /ZrO ₂ (100)	
SO ₄ ²⁻ /15ZrKI L-2	H ₂ SO ₄	500	3	2.5	1:5	70	5	20	3
						100		70	
Zir-5/1-C@SO ₄ ²⁻	H ₂ SO ₄	500	2	1.25	1:5	80	8	95	4
SO ₄ /Nb ₂ O ₅	H ₂ SO ₄	550	5	2.5	1:5	70	5	14	5
								SO ₄ /ZrO ₂ (NH ₄) ₂ SO ₄	

* Catalyst load, mass percentage with respect to levulinic acid.

References

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- 2 M. Popova, Á. Szegedi, H. Lazarova, M. Dimitrov, Y. Kalvachev, G. Atanasova, A. Ristić, N. Wilde, R. Gläser, *Reac. Kinet. Mech. Cat.*, 2017, **120**, 55-67.
- 3 M. Popova, Á. Szegedi, H. Lazarova, A. Ristić, Y. Kalvachev, G. Atanasova, N. Wilde, N. N. Tušar and R. Gläser, *Micropor. Mesopor. Mater.*, 2016, **235**, 50–58.
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