

Supplementary Materials: Aqueous Dehydration, Hydrogenation, and Hydrodeoxygenation Reactions of Bio-Based Mucic Acid over Ni, NiMo, Pt, Rh, and Ru on Neutral or Acidic Catalyst Supports

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Results Obtained by GC-MS Analysis.

Compounds were extracted from the reaction mixture in the diethyl ether phase and derivatized in order to make more volatile counterparts, being able to detect by GCMS.

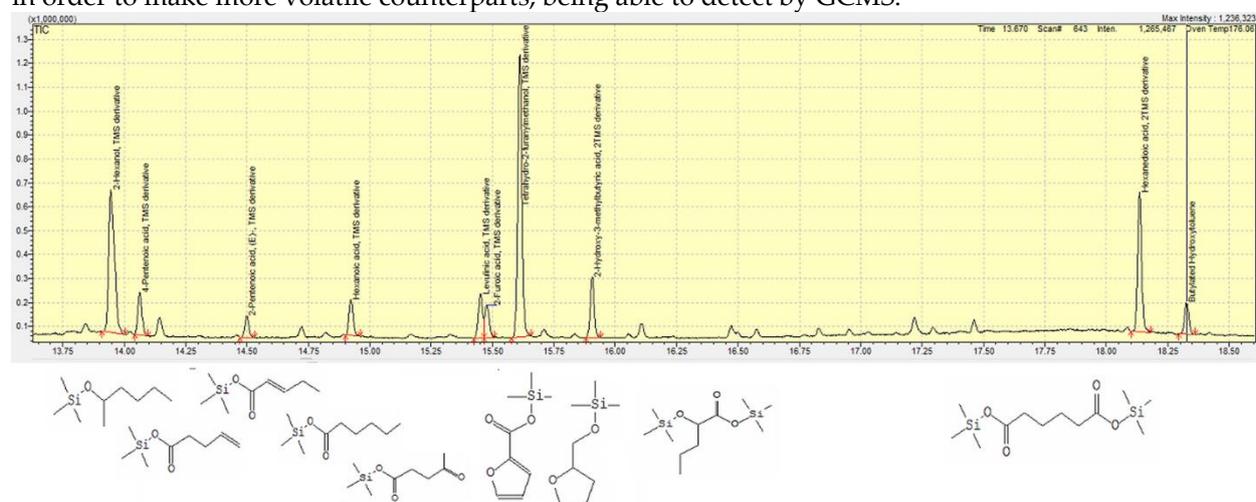


Figure S1. Derivatized compounds, obtained by GC-MS analysis.

Results Obtained by LC-MS Analysis.

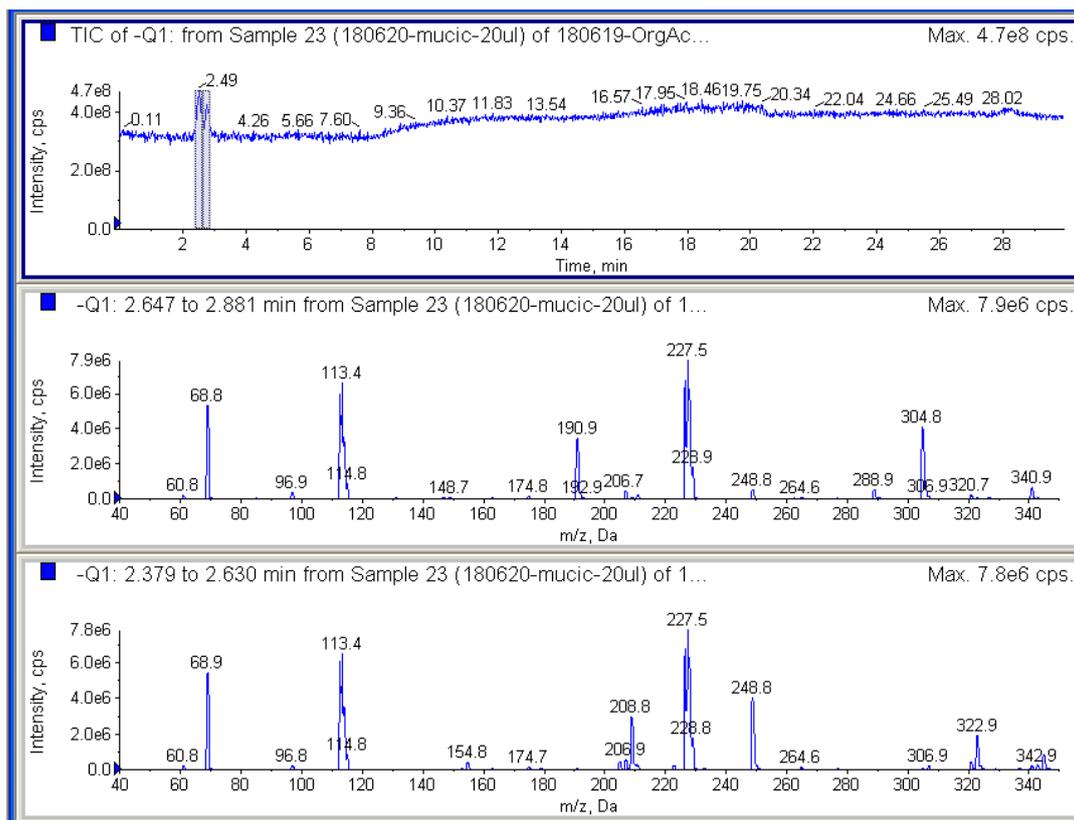


Figure S2. Chromatogram of mucic acid standard and MS spectrum of the detected peaks.

MS spectrum of second formed peak (RT = 2.7 min) confirmed formation of mucic acid lactone. As it was already reported in the literature [1–4], under aqueous conditions mucic acid readily forms lactone. Molar mass of lactone is 192 g/mol. Results showed the main difference in the mass fragment of 190.9 and 208.8 m/z, stands for mucic acid lactone ($M = 192$ g/mol) and mucic acid ($M = 210$ g/mol), respectively.

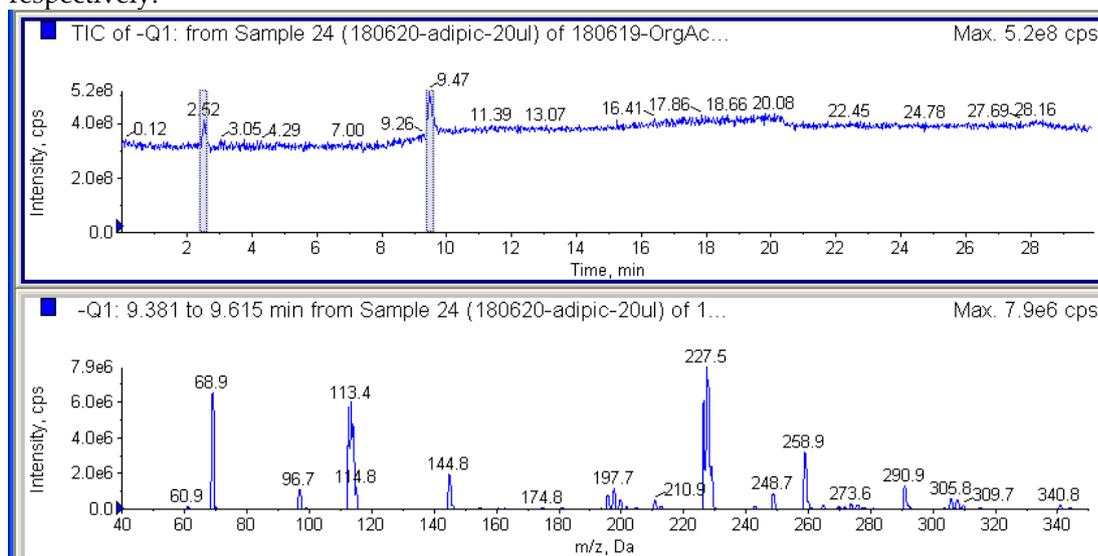


Figure S3. Adipic acid chromatogram and MS spectrum.

The representative peak of adipic acid appears at the retention time of 9.47 min in the chromatogram. The MS spectrum confirms it by mass fragment (m/z) of 144.8, which stands for adipic acid molar mass of 146 g/mol.

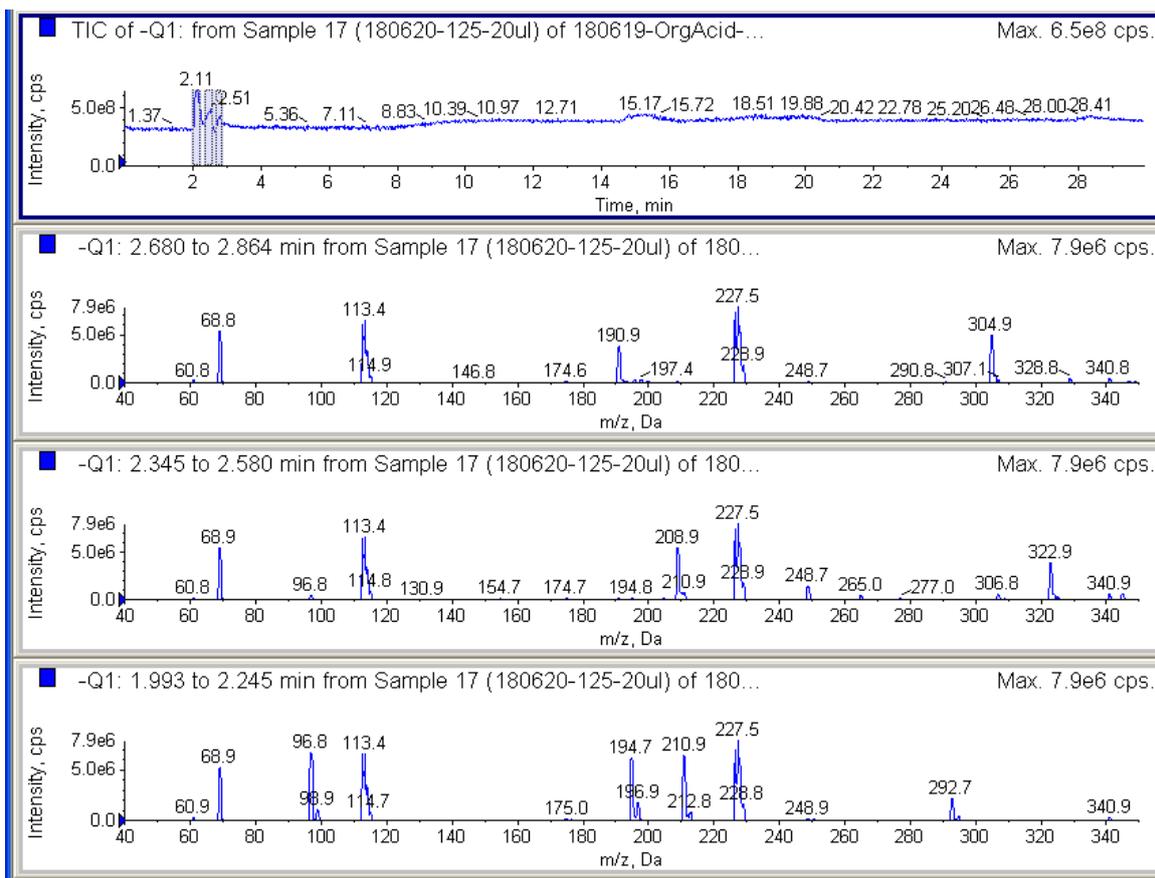


Figure S4. Chromatogram and MS spectrum of liquid sample.

The formation of galctonic acid was detected, confirmed by LC-MS analysis. The peak of galactonic acid appears before the peak of aldaric acid. Its retention time was 2.0 min. Mass fragment of 194.7 stands for galactonic acid with molar mas of 196 g/mol.

Conversions of Mucic Acid over all Tested Metal Catalysts

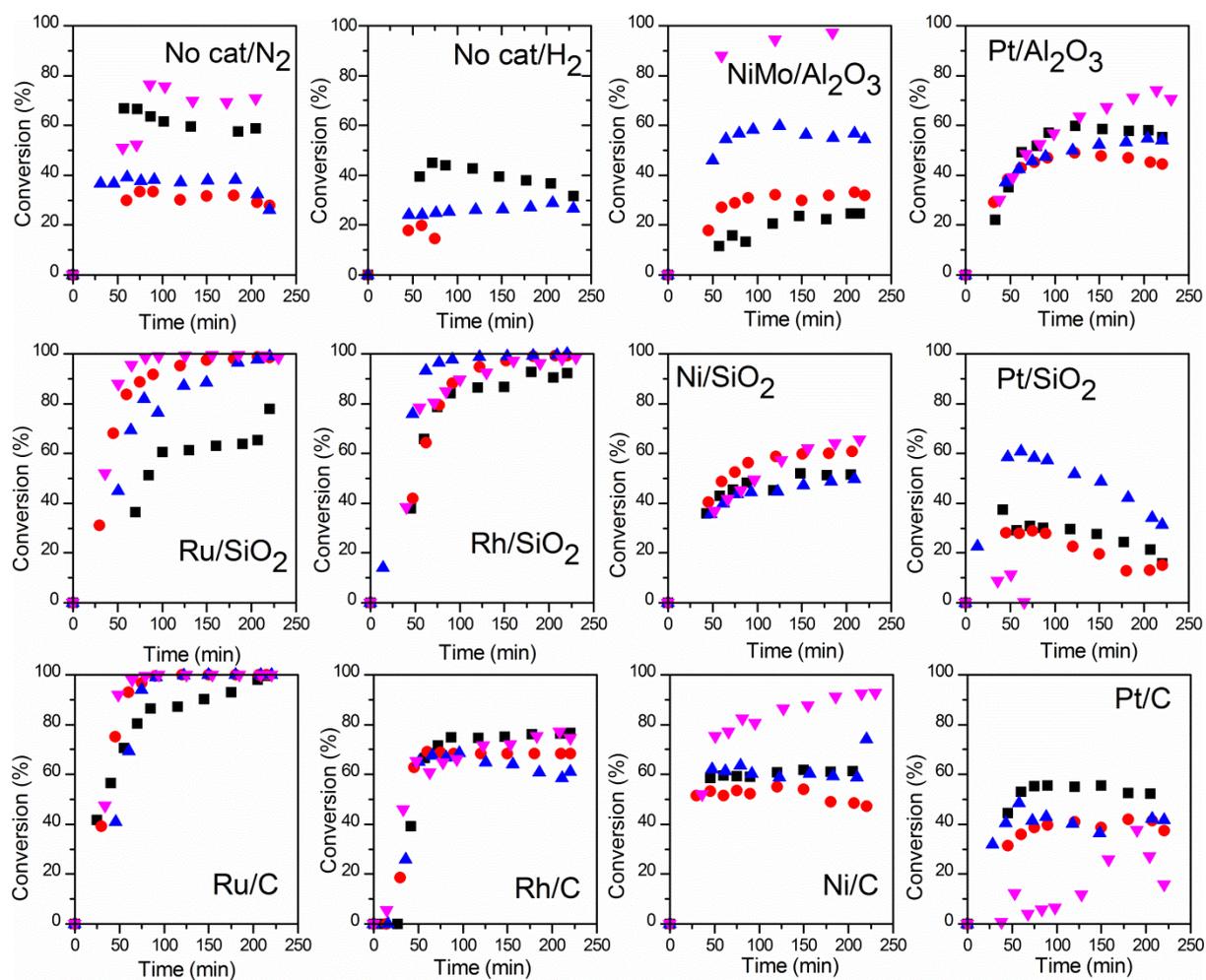


Figure S5. Conversions of mucic acid over noble and transition metals in the temperature range 125 – 175 °C (■ $T = 125$ °C, ● $T = 135$ °C, ▲ $T = 150$ °C, ▼ $T = 175$ °C).

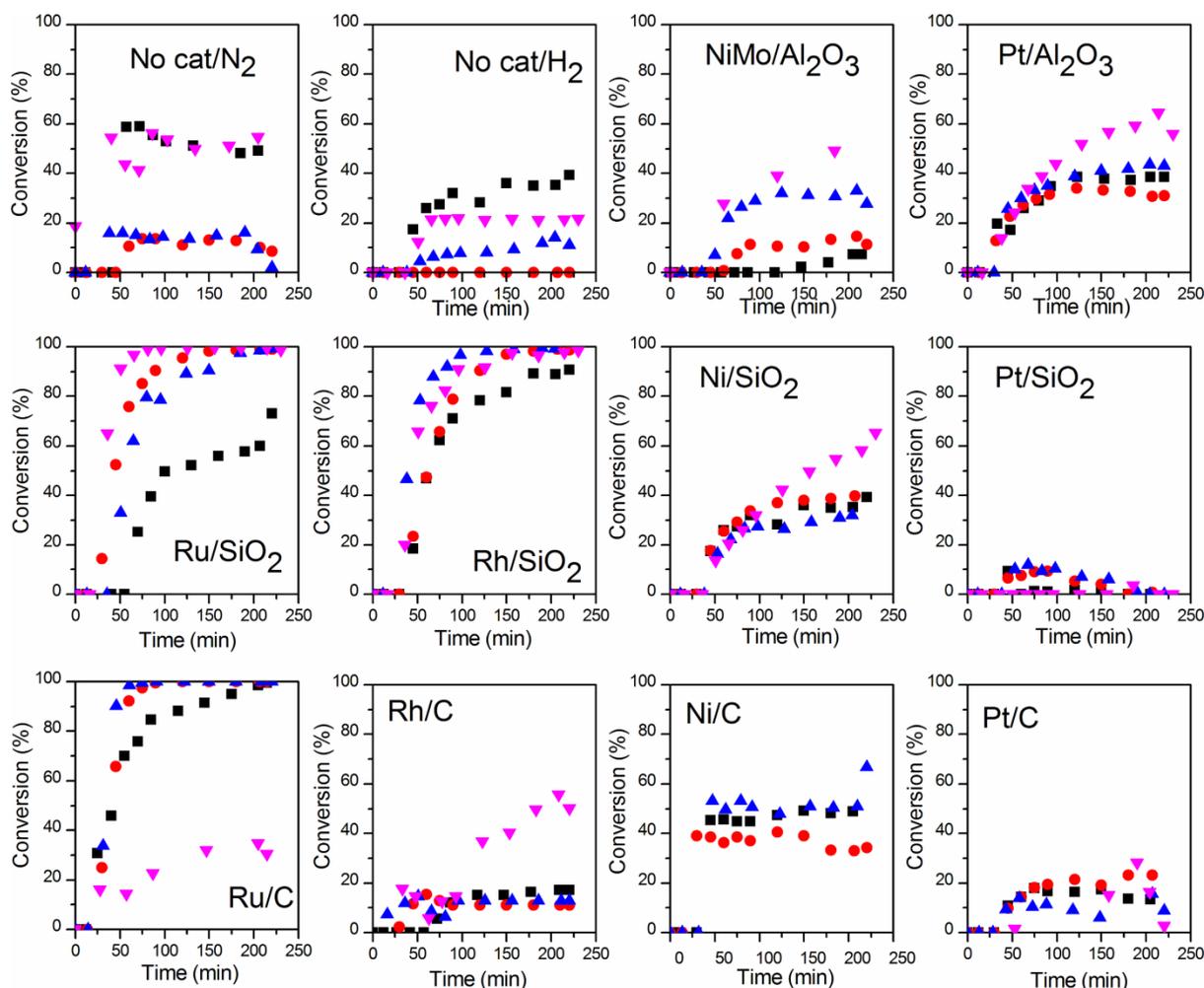


Figure S6. Summarized conversions of mucic acid and its lactone over noble and transition metals in the temperature range 125 – 175 °C (■ $T = 125$ °C, ● $T = 135$ °C, ▲ $T = 150$ °C, ▼ $T = 175$ °C).

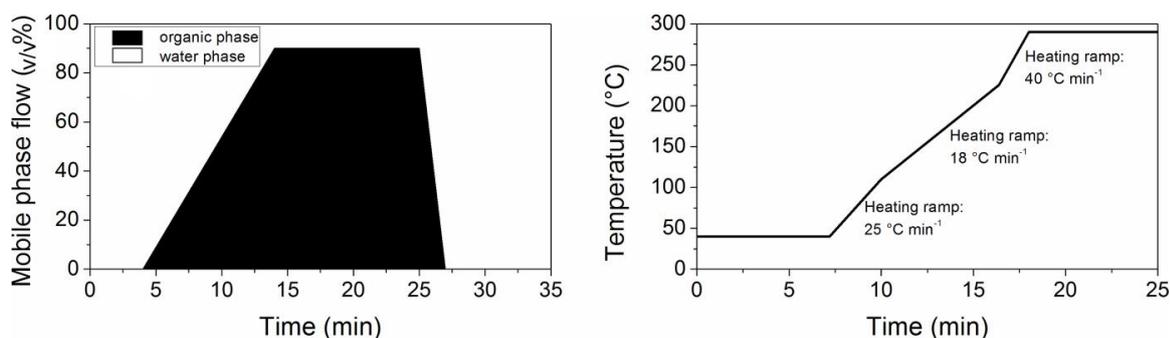


Figure S7. (a) HPLC mobile phase flow a combination of water phase (2.5 mM H_2SO_4) and organic phase (100 % acetonitrile) and (b) GC temperature program with different heating ramps.

Experiments using supports without any deposited metals

Carbon Support

Results over carbon support at 150 °C and initial H_2 pressure of 5 MPa showed the same behaviour for carbon support as for the blank experiment, where no catalyst was used. Mucic acid was converted only into lactone and galacturonic acid, galactonic acid was detected in minor concentration and only after several hours of reaction time. Results (showing empty chromatogram, except of products of homogeneous reactions) are in accordance to the experiment without catalyst, so solely non-catalytic

reactions proceeded and the contribution of carbon support and eventual acidic oxygen-containing functional groups on carbon is negligible.

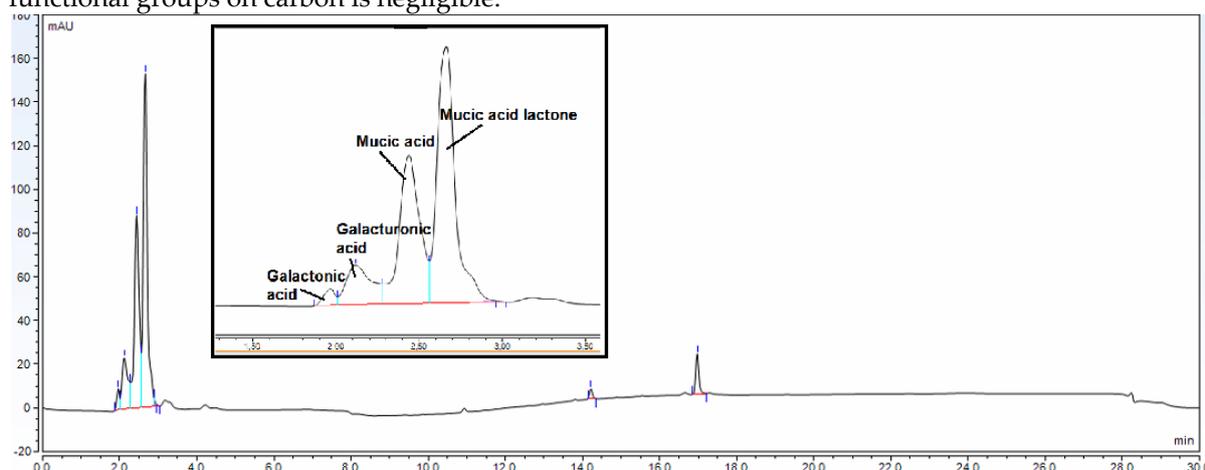


Figure S8. HPLC chromatogram of the final product over neutral C support.

Alumina Support

Experiment over alumina showed slightly different results compared to the carbon support. Mucic acid is firstly converted into mucic acid lactone, same as over C-support or blank experiment. In addition a compound positioned between mucic acid and its lactone in the chromatogram (Figure S9), identified as mucic acid 3,6-lactone was detected. As mentioned in the literature, acidic conditions can lead to the formation of different lactones [1,2], and since alumina is a well-known acidic support, we can conclude that lactonisation is catalysed at low pH in aqueous media and also by the solid acids. On the other hand, mucic acid 3,6-lactone did not form under neutral conditions over C support. Contrary to the C support, galacturonic acid and galactonic acid were not formed over acidic support in noticeable concentrations. Few other products were formed (in smaller concentrations (Σ all compounds < 10 mol%)), with the presence of carboxylic functional groups, hydroxyl functional groups and double bond(s).

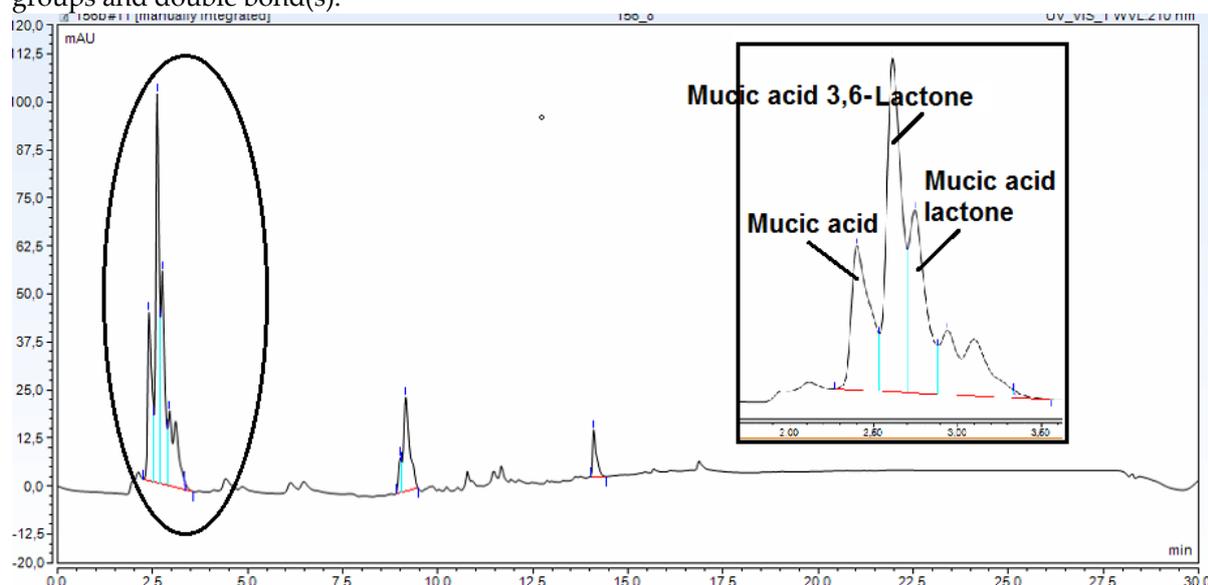


Figure S9. HPLC chromatogram of the final product over acidic alumina support.

Silica Support

Experiments over silica yielded the same products as observed with the use of alumina and carbon combined. Mucic acid was converted into two different lactones (same as over alumina); further hydrogenation into galactonic acid was also noticed. Small amounts of furoic acid and compound with o single double bond were detected in a cumulative concentration below 10 mol%. Concentration profiles obtained over each support are presented in Figure S10. Results are added to the SD.

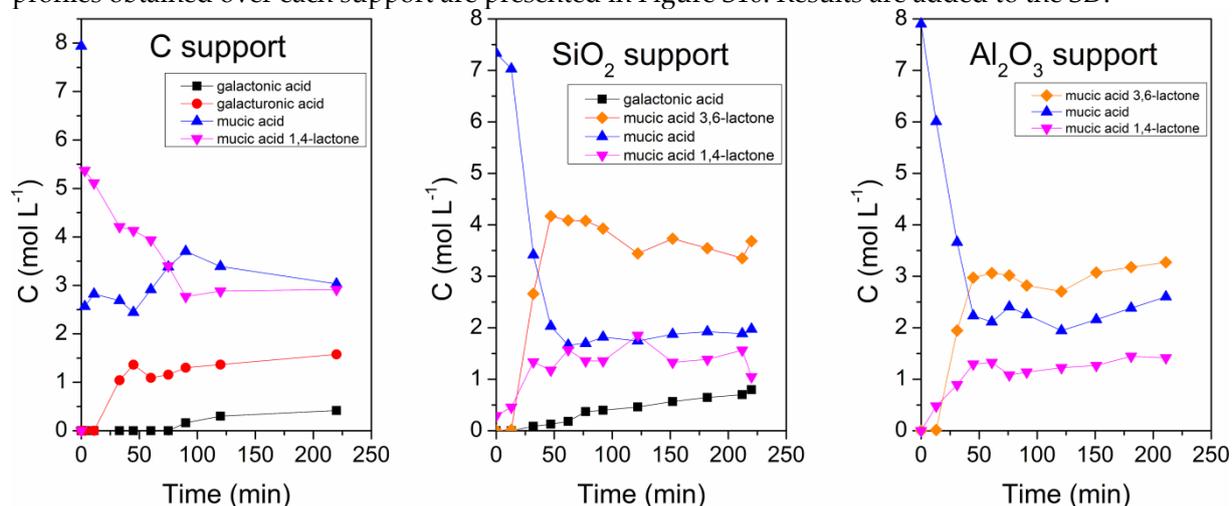


Figure S10. Concentrations of mucic acid, lactones, galacturonic and galactonic acid over different supports.

Catalyst characterization results

Table 1. NiMo/Al₂O₃ catalyst characterization results after the sulphidation [5].

Catalyst	Metal content (wt%)	Active Phase	AS-Active sites ($\mu\text{mol m}^{-2}$)	BET-Surface Area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ^a ($\text{cm}^3 \text{g}^{-1}$)	Pore size ^b (nm)
NiMo/Al ₂ O ₃	3/15 ^c	NiMoS _x	0.33 ^d	170	0.471	8.9

^a Total pore volume at relative pressure of 0.97. ^b Average pore diameter determined from the N₂ desorption branch by using BJH method. ^c As mass content of NiO and MoO₃ respectively for fresh catalyst ^d Determined according NiMoO₄ surface concentration.

Dispersion of metals on different supports was obtained by TEM, while the amount of metal and acidic active sites was provided by CO and NH₃-TPD, respectively. TEM image showed well dispersed metal clusters below 5 nm on the Ru/Al₂O₃ catalyst, similar results were found for other metals on carbon support. Obtained results are presented in Figures below.

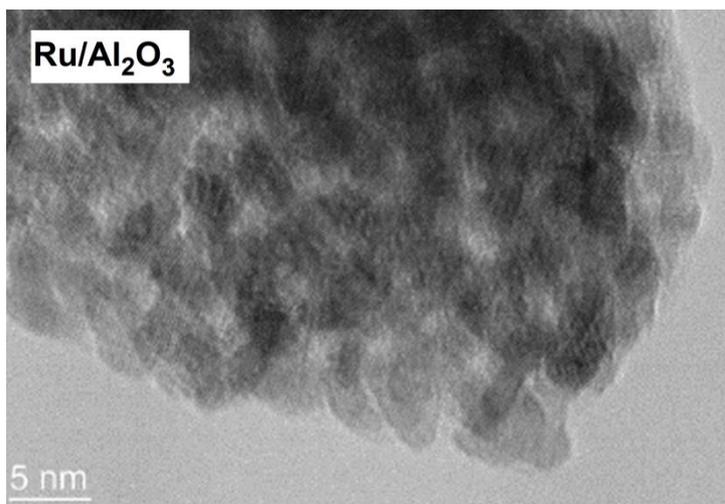


Figure S11. TEM image of Ru/Al₂O₃.

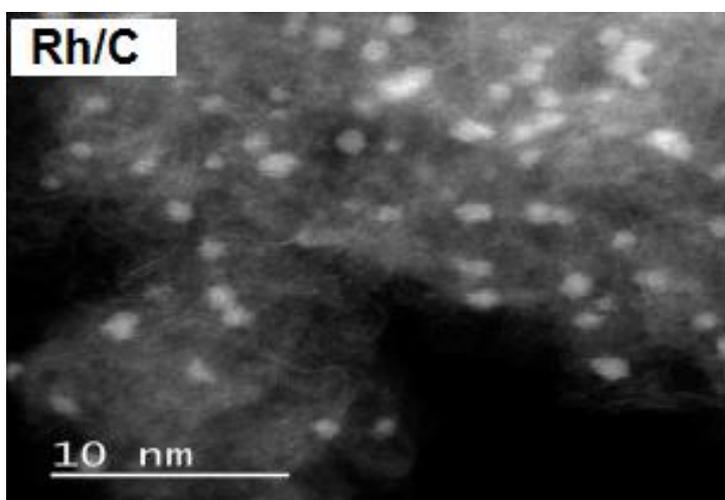


Figure S12. TEM image of Rh/C.

Concentrations of metal sites and acidic sites were determined for the most active catalysts; their values are presented in the following Table. Results were commented in relation to the results in the main text of the manuscript.

Table S2. Concentration of metal sites and acidic sites.

Catalyst	$N_{AS(CO)^2}$ (mol g ⁻¹)
Pt/ γ -Al ₂ O ₃	$8.6 \cdot 10^{-5}$
Ru/SiO ₂	$2.5 \cdot 10^{-5}$
Ru/C	$3.8 \cdot 10^{-5}$
Ni/C	$5.3 \cdot 10^{-5}$
Pt/C	$2.5 \cdot 10^{-4}$
Rh/C	$1.1 \cdot 10^{-4}$

NH₃-TPD results

NH₃-TPD results showed negligible peaks of adsorbed NH₃ at low temperature on C and SiO₂ supports, which indicate low density of acidic sites on the surface. However, compared to the both neutral supports, results with alumina showed significant response at the temperature below 100 °C

proving the presence of acidic sites. NH_3 adsorbed on the acidic sites and desorbed at low temperature (below $100\text{ }^\circ\text{C}$).

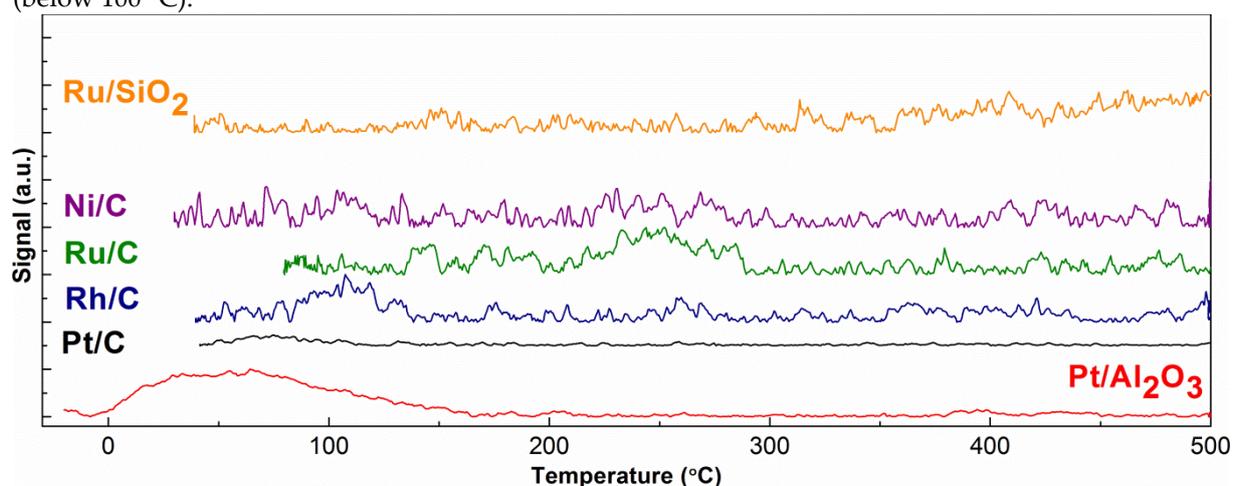


Figure S13. NH_3 -TPD of catalysts on different supports.

Experiment performed with a recycled catalyst

In order to find out if catalyst deactivate under reaction conditions (especially under aqueous environment) we performed experiment with recycled catalyst. The most delicate catalysts are on alumina support, which is known as not appropriate support for reactions under aqueous conditions. HDO of mucic acid over $\text{NiMo}/\gamma\text{-Al}_2\text{O}_3$ was performed at the temperature $175\text{ }^\circ\text{C}$. After complete reaction time, reaction mixture was cooled; solid catalyst was separated from reaction mixture, washed with solvent (water), dried and used again in new experiment at the same reaction conditions. There was 28 % of catalyst loss during autoclave cleaning and catalyst filtering/washing/drying; therefore we kept the same ratio between catalyst and reactant (mucic acid) in the second experiment.

Results showed very similar results for both experiments. In the experiment with fresh catalyst conversion of mucic acid was 89 %, while in the second run with recycled catalyst and the same ratio between mucic acid and catalyst conversion reached 90 %, with very small difference in the products distribution. Slightly higher yield of 2-furoic acid was detected in the experiment with reused catalyst (Figure S15). Results proved suitability of the tested catalyst for at least few HDO cycles. The only issue is mass loss during the whole procedure (experimental set up, cleaning of the autoclave, filtering and washing the catalyst and its drying). Chromatograms of both experiments are presented below (Figure S14). The highest detected peak was 2-furoic acid, in the concentrations of 4.0 and 5.7 mol% over fresh and recycled catalyst, respectively. The UV signal for compounds with double bonds is much higher compared to the compounds without double bonds.

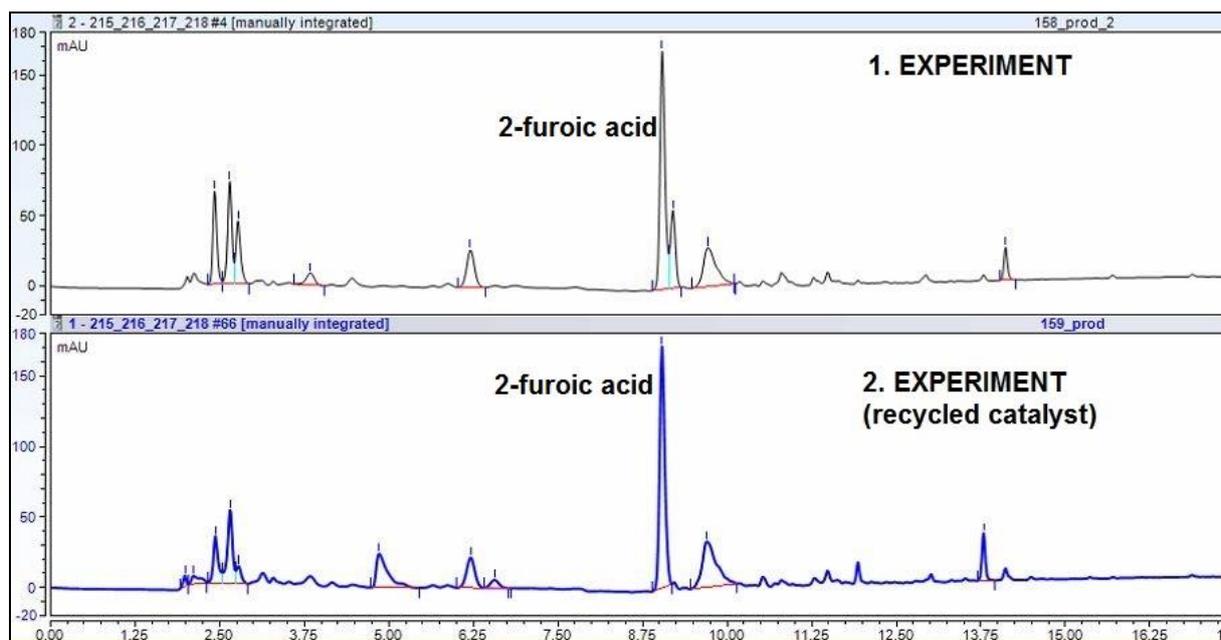


Figure S14. Chromatograms of products, obtained in the experiment with fresh and recycled NiMo/ γ -Al₂O₃ catalyst.

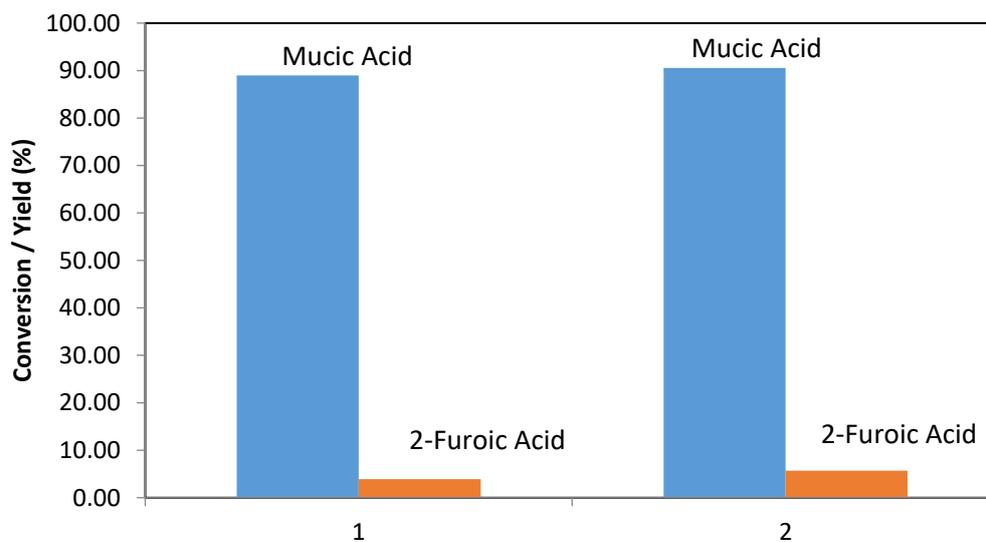


Figure S15. Conversion of mucic acid and yield of 2-furoic acid (the highest detected peak on HPLC) over fresh (1) and recycled catalyst (2).

Table S3. Selectivity data for each compound detected in the esterified phase over carbon supported metal catalysts, analyzed by GCMS.

Name	Rh/C				Pt/C				Ni/C				Ru/C			
	125 °C	135 °C	150 °C	175 °C												
1-Hydroxy-2-propanone	1.0	0.9	1.1	1.7	3.0	3.0	n.d.	5.1	1.5	2.0	n.d.	n.d.	n.d.	2.7	n.d.	n.d.
2-Oxo-propanoic acid	0.7	0.4	0.4	0.0	0.0	0.3	n.d.	0.0	0.0	0.0	n.d.	n.d.	n.d.	0.0	n.d.	n.d.
2-Hydroxyl-propanoic acid	0.1	0.0	0.0	0.0	2.5	0.7	n.d.	0.8	6.9	3.9	n.d.	n.d.	n.d.	0.6	n.d.	n.d.
Ethanedioic acid	1.9	1.0	1.5	3.1	9.9	5.6	n.d.	11.4	1.4	9.7	n.d.	n.d.	n.d.	9.4	n.d.	n.d.
2-Hydroxy-butanoic acid	0.4	1.1	1.0	10.8	7.6	1.8	n.d.	7.2	1.3	10.4	n.d.	n.d.	n.d.	6.2	n.d.	n.d.
2-Acetylfuran	3.6	6.8	5.9	6.0	7.8	5.7	n.d.	7.7	3.5	4.1	n.d.	n.d.	n.d.	6.7	n.d.	n.d.
2-Hydroxy-pentanoic acid	3.3	4.5	4.4	6.5	4.1	3.6	n.d.	6.9	0.9	0.5	n.d.	n.d.	n.d.	2.9	n.d.	n.d.
γ -Valerolactone	8.3	8.3	9.8	11.6	10.9	13.8	n.d.	5.1	13.6	4.2	n.d.	n.d.	n.d.	7.0	n.d.	n.d.
2-furoic acid	8.0	12.2	11.4	8.7	8.4	8.5	n.d.	4.8	5.3	6.6	n.d.	n.d.	n.d.	1.6	n.d.	n.d.
Tetrahydrofurfuryl alcohol	21.7	29.4	30.5	31.0	25.8	31.7	n.d.	16.3	15.2	8.9	n.d.	n.d.	n.d.	10.4	n.d.	n.d.
5-Oxo-2-tetrahydrofurancarboxylic acid	6.6	8.0	7.4	6.6	11.2	8.9	n.d.	8.1	9.5	10.1	n.d.	n.d.	n.d.	6.0	n.d.	n.d.
Butyl butyrate	2.0	1.8	2.3	5.0	1.0	2.7	n.d.	3.6	0.0	0.0	n.d.	n.d.	n.d.	2.0	n.d.	n.d.
Dodecanoic acid	1.4	0.5	0.5	0.0	0.0	0.6	n.d.	1.9	3.1	3.9	n.d.	n.d.	n.d.	1.9	n.d.	n.d.
Hexadecane	0.6	0.4	0.4	0.9	3.3	1.2	n.d.	0.7	4.4	4.7	n.d.	n.d.	n.d.	2.5	n.d.	n.d.
Tetrahydro-2H-pyran-4-ol	38.6	21.8	17.7	3.9	0.8	8.8	n.d.	2.4	2.8	1.4	n.d.	n.d.	n.d.	0.7	n.d.	n.d.
Hexadecanoic acid	1.4	2.2	5.4	3.2	2.2	2.2	n.d.	12.8	20.2	17.9	n.d.	n.d.	n.d.	23.5	n.d.	n.d.
Octadecanoic acid	0.4	0.9	0.5	1.1	1.4	1.0	n.d.	5.1	10.3	11.5	n.d.	n.d.	n.d.	15.9	n.d.	n.d.

Table S4. Selectivity data for each compound detected in the esterified phase over silica supported metal catalysts, analyzed by GCMS.

Name	Rh/SiO ₂				Pt/SiO ₂				Ni/ SiO ₂				Ru/ SiO ₂			
	125 °C	135 °C	150 °C	175 °C	125 °C	135 °C	150 °C	175 °C	125 °C	135 °C	150 °C	175 °C	125 °C	135 °C	150 °C	175 °C
1-Hydroxy-2-propanone	4.6	1.5	0.7	3.0	8.1	3.7	n.d.	2.2	2.8	0.7	1.1	0.7	3.6	0.4	n.d.	0.4
2-Oxo-propanoic acid	0.0	0.0	0.0	0.0	0.0	0.0	n.d.	0.0	0.0	0.0	0.0	0.1	0.0	0.0	n.d.	0.0
2-Hydroxyl-propanoic acid	1.4	0.4	0.7	2.5	3.4	0.0	n.d.	0.0	2.7	3.8	5.3	0.7	3.2	0.1	n.d.	0.1
Ethanedioic acid	4.0	7.5	3.5	9.9	11.0	0.0	n.d.	2.1	10.6	0.3	7.0	0.8	3.0	3.0	n.d.	1.4
2-Hydroxy-butanoic acid	1.6	4.5	2.9	7.6	5.4	1.5	n.d.	1.4	8.8	1.3	7.7	1.2	6.5	2.5	n.d.	0.9
2-Acetylfuran	6.6	7.3	6.8	7.8	2.9	3.5	n.d.	4.1	7.1	7.7	6.9	6.6	9.1	6.6	n.d.	6.2
2-Hydroxy-pentanoic acid	3.6	3.9	4.7	4.1	0.0	1.5	n.d.	6.6	2.0	4.8	1.9	5.5	1.8	4.5	n.d.	4.9
γ -Valerolactone	16.3	14.0	8.0	10.9	17.0	8.9	n.d.	12.4	12.7	12.3	18.9	11.8	9.8	11.2	n.d.	10.4
2-furoic acid	10.1	9.0	12.5	8.4	3.4	12.1	n.d.	10.0	6.2	12.0	5.0	10.1	6.4	9.2	n.d.	10.3
Tetrahydrofurfuryl alcohol	25.3	26.9	26.5	25.8	28.1	39.5	n.d.	29.8	13.6	38.6	11.2	33.8	22.7	33.4	n.d.	32.4
5-Oxo-2-tetrahydrofurancarboxylic acid	10.1	9.2	12.0	11.2	9.1	10.6	n.d.	10.2	8.6	9.2	5.2	9.8	16.3	10.7	n.d.	12.6
Butyl butyrate	0.0	0.9	2.9	1.0	0.0	0.0	n.d.	6.2	0.0	0.4	0.0	7.2	3.7	3.1	n.d.	2.6
Dodecanoic acid	0.0	0.4	5.8	0.0	0.0	0.0	n.d.	0.0	1.0	0.4	2.0	0.7	0.0	5.1	n.d.	3.4
Hexadecane	3.3	5.2	1.5	3.3	3.6	0.0	n.d.	2.8	6.1	2.1	1.9	1.9	4.3	2.2	n.d.	1.0
Tetrahydro-2H-pyran-4-ol	3.3	1.9	1.6	0.8	0.0	10.3	n.d.	3.6	3.3	1.4	0.8	4.5	0.7	0.7	n.d.	1.1
Hexadecanoic acid	6.4	5.3	6.7	2.2	5.1	5.8	n.d.	6.1	8.9	2.8	16.0	3.2	6.6	5.2	n.d.	10.7
Octadecanoic acid	3.3	2.0	3.4	1.4	2.9	2.6	n.d.	2.5	5.5	2.1	9.1	1.5	2.4	2.1	n.d.	1.5

Table S5. Selectivity data for each compound detected in the esterified phase over alumina supported metal catalysts, analyzed by GCMS.

Name	Pt/Al ₂ O ₃				NiMo/ Al ₂ O ₃			
	125 °C	135 °C	150 °C	175 °C	125 °C	135 °C	150 °C	175 °C
1-Hydroxy-2-propanone	2.9	2.3	n.d.	2.3	6.3	8.3	0.7	n.d.
2-Oxo-propanoic acid	0.3	0.0	n.d.	0.0	0.0	0.0	0.1	n.d.
2-Hydroxyl-propanoic acid	1.7	0.8	n.d.	0.5	1.2	4.7	0.3	n.d.
Ethanedioic acid	6.7	4.4	n.d.	0.3	12.1	7.6	1.9	n.d.
2-Hydroxy-butanoic acid	5.6	1.8	n.d.	0.0	7.9	7.7	2.8	n.d.
2-Acetylfuran	5.6	7.2	n.d.	0.0	9.0	13.3	9.2	n.d.
2-Hydroxy-pentanoic acid	2.8	4.6	n.d.	3.6	4.8	5.2	5.9	n.d.
γ -Valerolactone	22.4	9.6	n.d.	3.7	13.7	11.5	12.2	n.d.
2-furoic acid	6.2	9.9	n.d.	2.9	9.2	9.0	11.4	n.d.
Tetrahydrofurfuryl alcohol	16.0	32.1	n.d.	31.1	16.9	6.8	30.4	n.d.
5-Oxo-2-tetrahydrofurancarboxylic acid	10.3	10.0	n.d.	9.9	9.2	10.4	9.7	n.d.
Butyl butyrate	2.8	0.4	n.d.	20.9	0.0	2.4	0.9	n.d.
Dodecanoic acid	0.2	0.4	n.d.	6.4	0.0	0.0	0.8	n.d.
Hexadecane	4.3	3.0	n.d.	1.6	2.4	3.3	1.4	n.d.
Tetrahydro-2H-pyran-4-ol	7.9	10.0	n.d.	11.7	1.1	0.8	8.6	n.d.
Hexadecanoic acid	3.0	2.3	n.d.	3.2	4.1	5.7	2.5	n.d.
Octadecanoic acid	1.2	1.2	n.d.	2.0	2.2	3.2	1.3	n.d.

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