Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Upgrading of oxygenated compounds present in aqueous biomass-derived feedstocks over NbOx-based catalysts

A. Fernández-Arroyo,[a] D. Delgado,[a] M. E. Domine*[a] and J. M. López-Nieto*[a]

Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas, Avenida de los Naranjos s/n, 46022 Valencia, España

Supporting Information

S1. Experimental Procedure

S1.1. Materials

Acetic acid (99.8%), propanal (97%), acetol (90%) and chlorobenzene (99%) were purchased from Sigma-Aldrich and used as received. Ethanol (reagent grade 99.9%), methanol (reagent grade 99.9%) supplied by Scharlau and water (Milli-Q quality, Millipore) were used as solvents. For catalysts synthesis the following reactants were used: niobium chloride ($NbCl_5$, Aldrich), niobium oxalate monooxalate adduct ($C_{10}H_5NbO_{20}$, ABCR), ammonium hydroxide (NH_4OH, Aldrich 28wt% in water), zirconium (IV) oxynitrate hydrate ($ZrO(NO_3)_2.H_2O$, Aldrich) and cerium(III) nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$, Aldrich).

S1.2. Catalysts preparation

S1.2.1. Niobium oxide via hydrothermal synthesis

Niobium oxide was prepared through hydrothermal synthesis. 30.6 g of niobium oxalate were dissolved in 63.2 g of distilled water and kept 10 minutes under stirring at 80ºC. Afterwards, this mixture was kept during 2 days in an autoclave-type reactor at 75ºC, and the solid obtained was treated at 100ºC for 16h. Finally, the material was heat-treated in air or N_2 at 300-550ºC for 2h, with a heating rate of 2ºC/min.

S1.2.2. Niobium oxide via precipitation

Niobium oxide was synthesized through a precipitation method using $NbCl_5$ as niobium precursor. 10.5 g of $NbCl_5$ were dissolved in 100 ml of distilled water and kept under stirring while a 28wt% NH_4OH aqueous solution was slowly added until pH=9. Finally, the resulting slurry was kept at room temperature for 1h before the solids were separated by filtration, washed with distilled water, dried at 100ºC overnight and heat-treated at 450-550ºC under air or N_2 for 2h, with a heating rate of 2ºC/min.

S1.2.3. Commercial Nb_2O_5

Nb_2O_5 was purchased from Sigma Aldrich and heat-treated at 450-550ºC under air or N_2 atmosphere during 2h, with a heating rate of 2ºC/min prior to its use in catalytic experiments.

S1.2.4. $Ce_{0.5}Zr_{0.5}O_2$ via co-precipitation

This material was prepared to exemplify Ce-Zr-O mixed oxides, commonly used in literature in this type of reactions [16]. The catalyst was prepared through co-precipitation synthesis, following the methodology described in ref [28]. Aqueous solutions of $Ce(NO_3)_3.6H_2O$ and $ZrO(NO_3)_2.H_2O$ were used in equimolar concentration to obtain the desired Ce-Zr ratio. Once the solutions were mixed, a 28wt% NH_4OH aqueous solution was slowly added until pH=10. Afterwards, the solution was kept under stirring at room temperature for 65h, and the solids were separated by filtration, and washed with distilled water. Finally, the catalyst was dried at 100ºC overnight and heat-treated in air at 450ºC for 2h, with a heating rate of 2ºC/min. This sample is named as CeZrO.

S1.3. Catalysts characterization

Crystalline structure was determined by X-Ray Diffraction (XRD) in a PANalytical Cubix diffractometer (CuKα radiation, graphite monochromator). Transmission Electron Microscopy (TEM) images were carried out in a JEOL JEM-2100F field emission gun microscope, which operates at an accelerating voltage of 200 kV. Surface areas of catalysts were calculated by the BET method by carrying out nitrogen adsorption experiments in a Micrometrics ASAP 2420 apparatus. Acidity measurements were carried out by experiments of infrared spectroscopy (FT-IR) using pyridine as adsorbent in a Nicolet710 FTIR spectrometer using self-supported wafers ($\approx$10 mg/cm^2) diluted with silica. Samples were pretreated in vacuum at 200 ºC for 24, prior to pyridine chemisorption. Then pyridine was desorbed at different temperatures (150ºC, 250ºC and 350ºC). Thermogravimetric analyses (TG) were carried out in a Mettler Toledo TGA/SDTA 851 apparatus, using a heating rate of 10ºC/min in an air stream until 800ºC was reached. Elemental analysis (EA) was carried out in a Fisons EA1108CHN-S apparatus. Finally, Ce-Zr-O mixed oxide composition was determined by X-Ray fluorescence (XRF).

S1.4. Catalytic experiments

Catalytic experiments were performed in a 12 mL autoclave-type reactor with PEEK (polyether-ethyl-ketone) interior, equipped with a magnetic bar, pressure control and a valve for either liquid or gas sample extraction. Reactors were situated over a steel jacket individual support equipped with a temperature close loop control system.

The initial feed consisted of an aqueous model mixture containing oxygenated compounds representing aqueous waste streams obtained by phase separation after biomass fast pyrolysis processes in a biorefinery. In all cases the following aqueous model mixture composition has been used: water (30 wt%), acetic acid (30 wt%), propanal (25 wt%), acetol (5 wt%) and ethanol (10 wt%).

Typically, 3.0 g of aqueous model mixture and 0.15 g of catalyst were introduced in the autoclave-type reactor. The reactor was sealed, pressurized at 13 bar N_2 and heated at 200ºC under continuous stirring. Small liquid aliquots (50-100 µL) were taken at different time intervals, filtered off and diluted in 0.5 g of methanol containing 2wt% chlorobenzene as standard. The liquid samples were analyzed by a Bruker 430 GC equipped with both a FID detector and a capillary column (TRB-624, 60m length).

Reactants and intermediate products are quantified from response factors which are calculated by the use of an internal standard, while long-chain products are classified in intervals (C5-C8 and C9-C10) and group contribution technique is used to predict their response factors. Product identification was done by GC-MS (Agilent 6890 N GC System coupled with an Agilent 5973 N mass detector and equipped with a HP-5 MS, 30 m length capillary column). Besides first-step condensation products as acetone, 3-pentanone and 2-methyl-2-pentenal, groups from 5 to 10 carbon atoms molecules are distinguished and classified in C5-C8 and C9-C10 to simplify its quantification.

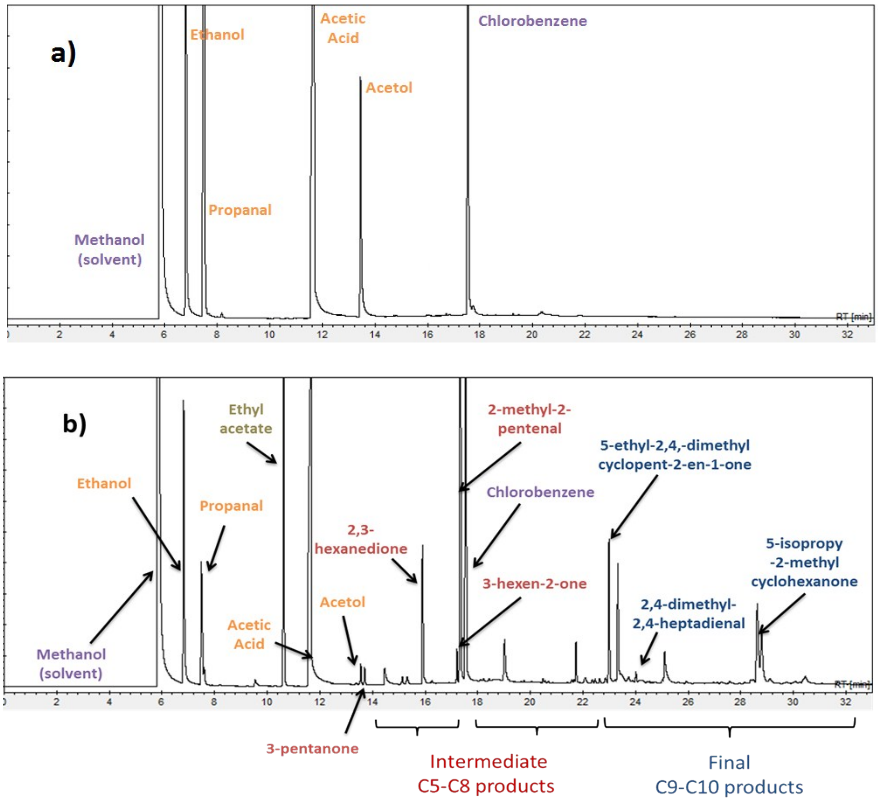
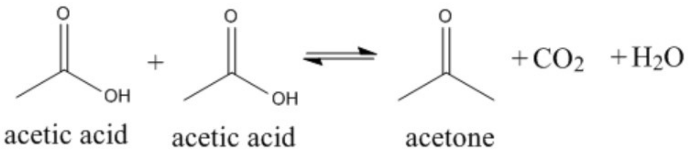


Figure S1. *Chromatograms analyzed by a GC equipped with both a FID detector and a capillary column (TRB-624, 60m length). a) Sample at 0h and b) Sample at 5h.*

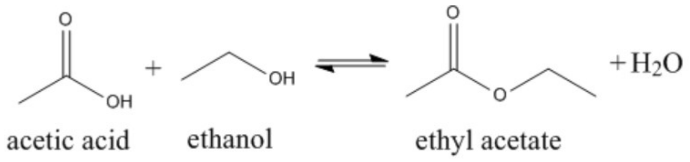
S.1.4.1. Proposed reaction network

Based on this information, a reaction network can be established including the main reaction pathways and products observed along the experiments, which are detailed below:

- 2 molecules of **acetic acid** can react via ketonization to produce one molecule of acetone and CO_2 and H_2O as only subproducts. Acetic acid can also react with **ethanol** via esterification to produce ethyl acetate.

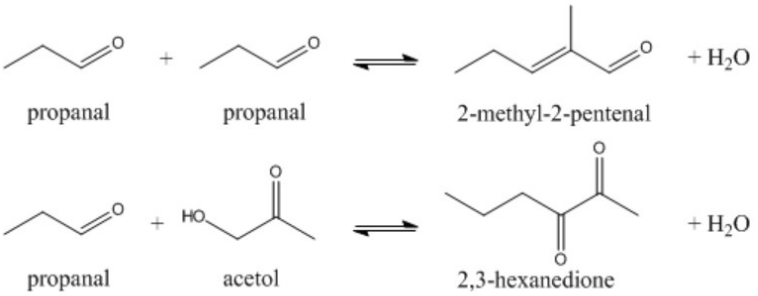


Reaction S1. *Acetic acid ketonization reaction.*



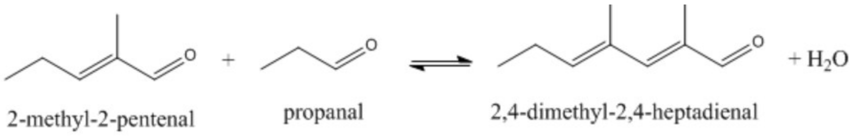
Reaction S2. *Acetic acid and ethanol esterification reaction.*

- **Acetone**, together with **propanal** and **acetol** can react via self- or cross-aldol condensation to produce intermediate products as **2-methyl-2-pentenal**, mesityl oxide, 3-hexen-2-one, or 2,3-hexanedione, which are grouped into **C5-C8 products**. Water is also produced from condensation reactions.



Reaction S3. *Propanal self- and cross-aldol condensation reaction.*

- These intermediate products can keep reacting in a **2nd condensation step** to produce larger **C9-C10 products**. Equimolar amounts of water are likewise generated.



Reaction S4. *2nd condensation step reaction.*

Taking into account all the above-mentioned reaction pathways, the next reaction network for the overall process is proposed (Figure S2):

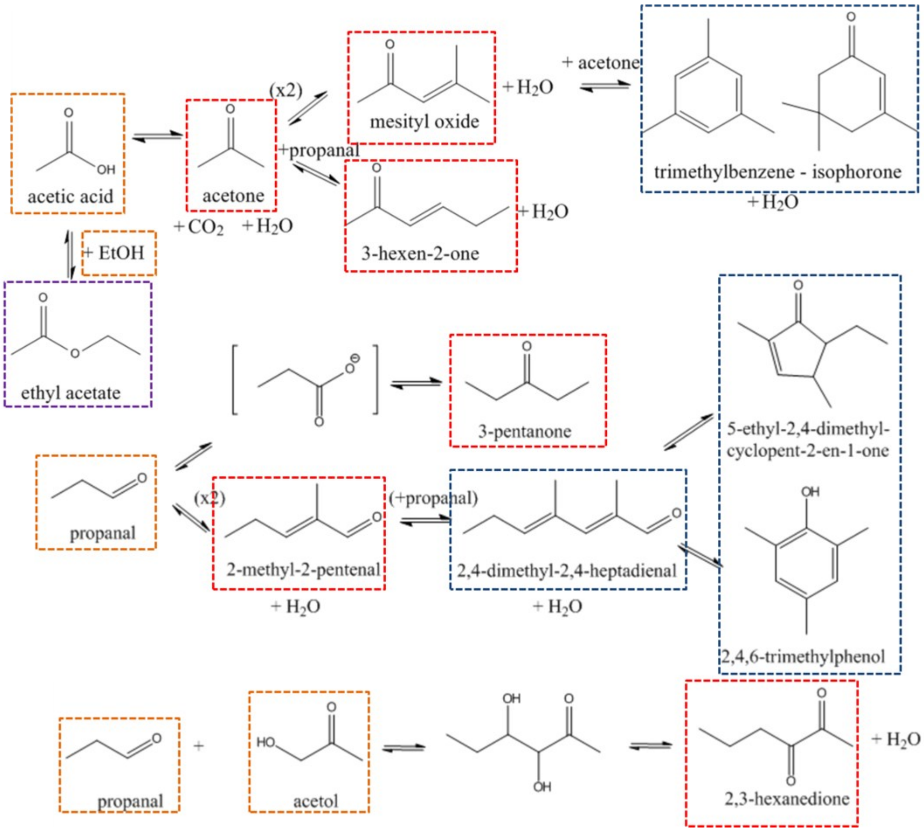


Figure S2. *Reaction network: Reactants (orange), intermediate C5-C8 products (red) and final C9-C10 products (blue) are outlined.*

S.1.4.2. Calculus of total organic product yield and main products yield

Based on the aqueous model mixture composition, a theoretical maximum attainable total organic yield can be calculated, assuming that:

- 100% conversion for all reactants is achieved
- Acetic acid can be equally converted to ethyl acetate and acetone (ketonization product)
- Final products are C9 compounds (no intermediate or heavier products are present in the final mixture).

With all these ideal assumptions, the composition of the final mixture is calculated as: 51.3 wt% of water, 19.1 wt% of ethyl acetate, and **29.6 wt% of C9 products**.

Therefore, results of catalytic experiments (expressed as total organic products yields) are calculated by considering that ≈30% is the maximum value attainable.

Example:

Total organic products yield measured during reaction =	20.0%
Maximum total organic products yield attainable (theoretical) =	30.0%
Calculated total organic products yield (referred to the maximum) =	66.7%

S.1.4.3. Recycling Experiments

Recycling experiments were performed by using (or reusing) the catalysts several times. Once the catalytic experiment was finished, the solid was separated by centrifugation and washed repeatedly with methanol. Finally, after drying it at 100ºC overnight, the solid was analyzed by X-ray diffraction (XRD) and Raman spectroscopy to evaluate catalyst structure, as well as by elemental analysis (EA) and thermogravimetric (TG) measurements to determine the organic compounds deposition in the surface of the catalyst.

S2. Characterization Results

S2.1. X-Ray diffraction measurements

X-Ray diffraction patterns of C-, PR- and HT-series, heat-treated in air and N_2, are shown in Fig. S3, where significant differences in the crystallinity of the different niobium oxides can be observed. For comparative purposes, the XRD patterns of the Ce-Zr-O mixed oxide synthesized in this work is also given in Fig. S4.

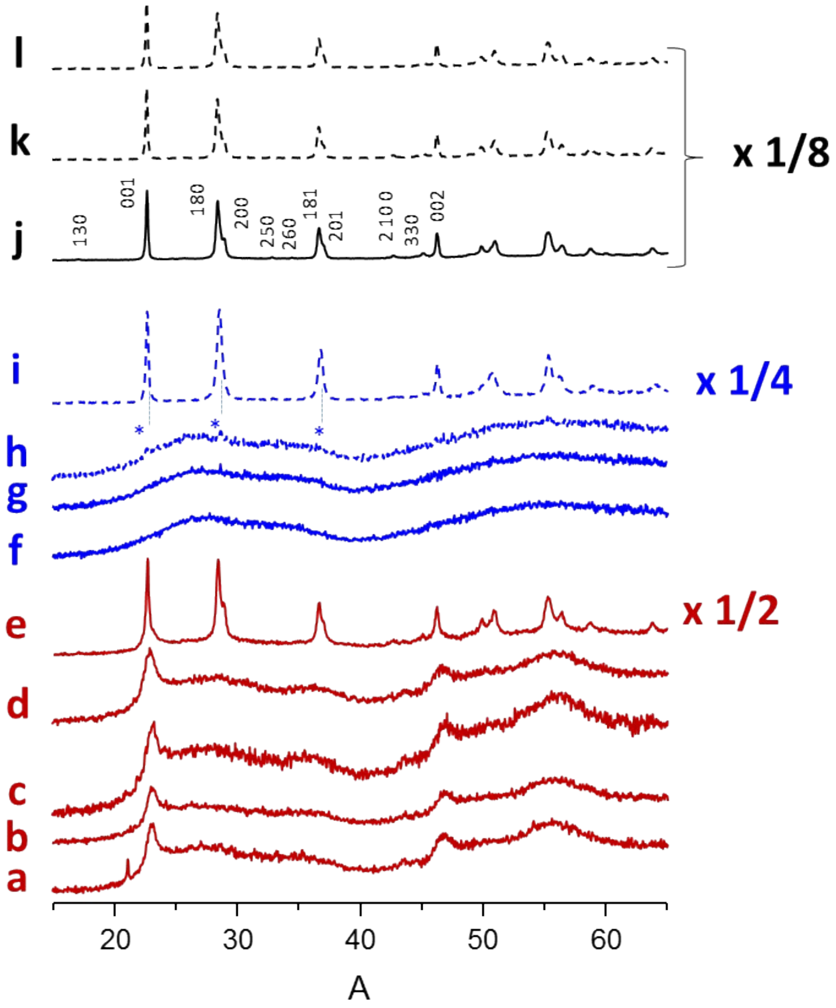


Figure S3. *XRD profiles of NbOx-based catalysts: a) HT-300N; b) HT-400N; c) HT-450N; d) HT-550N; e) HT-550A; f) PR-400N; g) PR-450N; h) PR-450A; i) PR-550A; j) C-450N; k) C-450A; and l) C-550A. Dashed lines: Samples heat-treated in air.*

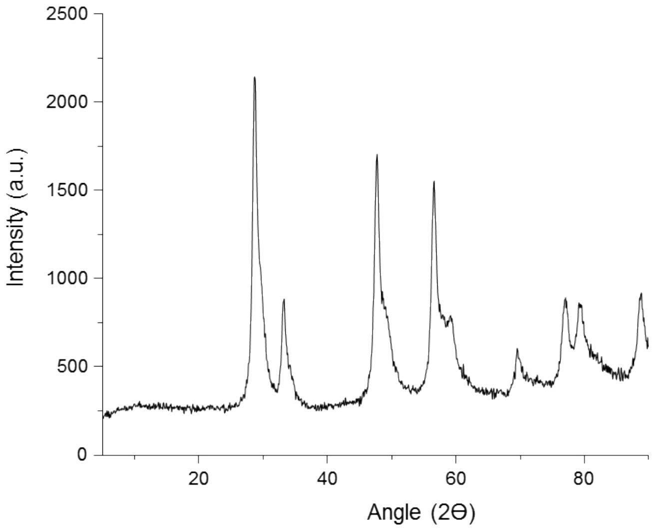
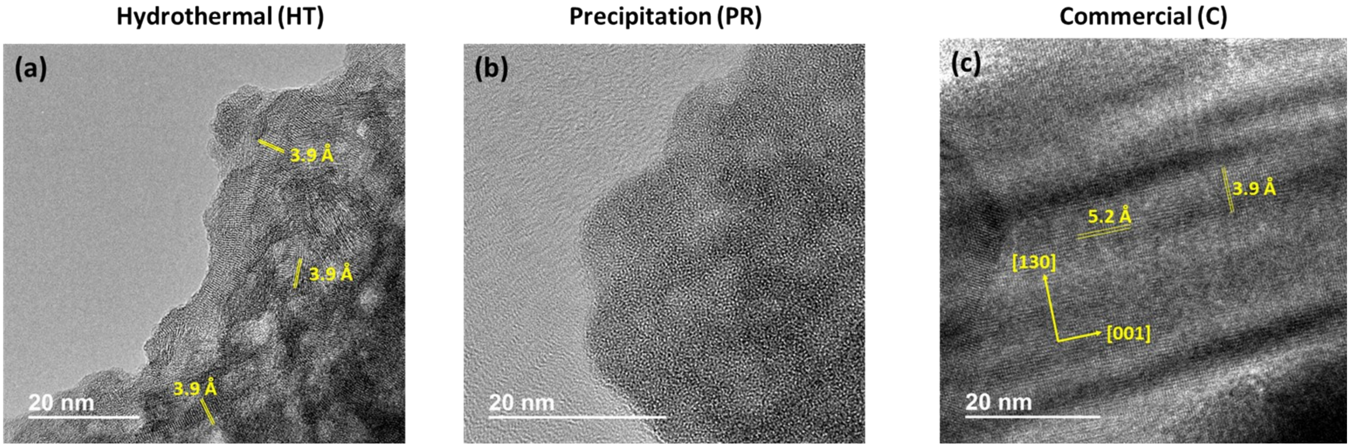


Figure S4. *XRD patterns of Ce-Zr-O mixed oxide, heat-treated at 450 ºC in air (CeZrO).*

S2.2. TEM measurements

Transmission Electron Microscopy (TEM) images were carried out in a JEOL JEM-2100F field emission gun microscope, which operates at an accelerating voltage of 200 kV.


Hydrothermal (HT)

Precipitation (PR)

Commercial (C)

Figure S5. *TEM images of pseudo-crystalline HT-450N (a), amorphous PR-450N (b) and crystalline C-450N (c) niobium oxide catalysts.*

S2.3. Surface area and acidity (Bronsted vs Lewis) measurements

The type, both the amount and the nature of acid sites present in niobium oxide catalysts, prepared by hydrothermal synthesis (HT-series), and heat-treated in the 300 to 550 ºC temperature range were studied and compared with those present in C- and PR-series by means of FT-IR spectroscopic measurements through pyridine adsorption and desorption at different temperatures. The calculated values for pyridine adsorption-desorption in the solids are given in Table S1**.** Additionally, as can be seen in Figure S6, the IR band assigned to the Lewis acid sites is well defined for all the hydrothermally prepared samples (HT-series), being this IR band much higher by lowering the heat-treatment temperature in these HT-Nb-based materials.

***Table S1a**. Physico-chemical and textural properties of catalysts used in this work.*

Samples	Calcination Conditions	Surface Area[a] (m^2/g)	Acidity Measurements			
			LAS [b]	BAS [b]	BAS/LAS	Total Acidity[c]
HT-series	300ºC (N_2)	163	135.3	41.5	0.31	1.08
	400ºC (N_2)	152	54.7	57.4	1.05	0.74
	450ºC (N_2)	108	65.4	33.5	0.51	0.92
	550ºC (N_2)	70	20.6	16.1	0.78	0.52
PR-series	450ºC (air)	13	6.9	2.7	0.39	0.74
	550ºC (air)	13	10.3	4.9	0.48	1.17
	450ºC (N_2)	13	4.5	3.0	0.68	0.58
C-series	450ºC (air)	36	10.6	5.0	0.47	0.44
	550ºC (air)	9	10.0	7.4	0.74	1.94
CeZrO	450ºC (air)	112	87.6	17.4	0.20	0.94

[a] Calculated values from N_2 adsorption isotherms (BET method). [b] Values calculated by pyridine adsorption FT-IR measurements, in (µmol/g). [c] Total acidity (BAS + LAS) or density of acid sites, in µmol/m^2.

***Table S1b**. Textural properties of catalysts used in this work.*

Samples	Calcination Conditions	Surface Area[a] (m^2/g)	Pore Volume (cm^3/g)[a]	Mesopore Volume (cm^3/g)[b]
HT-series	300ºC (N_2)	163	0.131	0.059
	400ºC (N_2)	152	0.107	0.068
	450ºC (N_2)	108	0.104	0.074
	550ºC (N_2)	70	0.075	0.061
PR-series	450ºC (air)	13	n.d.[c]	0.007
	450ºC (N_2)	13	n.d.[c]	0.009
C-series	450ºC (air)	36	0.033	0.022
	550ºC (air)	9	0.031	0.021
CeZrO	450ºC (air)	112	0.093	n.d.[c]

[a] Calculated values from N_2 adsorption isotherms (BET method). [b] Calculated by BJH method. [c] n.d. = Non determined.

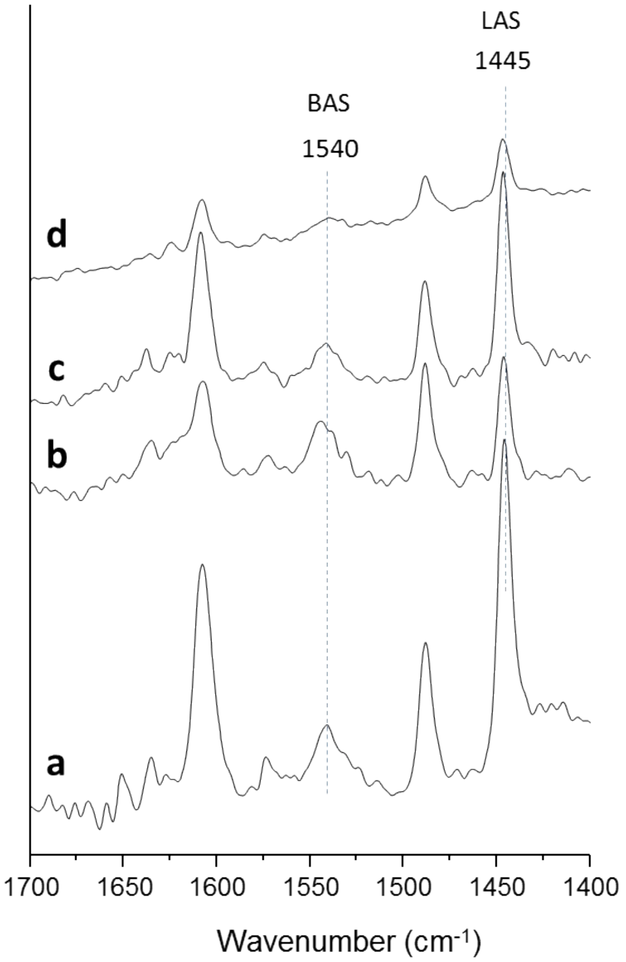


Figure S6. *Pyridine IR adsorption spectra for samples prepared through hydrothermal method calcined under* N_2 *atmosphere: a) HT-300N b) HT-400N c) HT-450N d) HT-550N.*

BAS: Brönsted acid sites
LAS: Lewis acid sites

S3. Catalytic Results

S3.1 Catalytic activity in the transformation of oxygenated compounds present in aqueous model mixtures of different Nb-based catalysts.

In the following tables and Figures contained in this section, data obtained from different catalytic experiments using HT-, PR- and C-series catalysts here prepared are summarized.

Table S2. *Catalytic activity in the conversion of oxygenated compounds in aqueous model mixture of HT-, PR- and C-series catalysts heat-treated under different conditions.*[a]

Catalyst	Total Organic Yield (%)	Conversion (%)				Products Yield (%)				Carbon balance (%)
		Acetol	Propanal	Ethanol	Acetic Acid	C5-C8	C9-C10+	2M2P[a]	Ethyl acetate	
HT-300N	59.0	100.0	91.7	53.3	7.8	10.3	16.0	32.7	19.3	90
HT-400N	69.7	100.0	94.0	45.5	9.9	12.3	18.0	39.4	22.3	98
HT-450N	69.3	100.0	92.6	44.1	16.5	11.0	17.3	41.0	25.0	97
HT-550N	65.3	100.0	92.0	51.9	6.5	10.7	19.3	35.3	20.3	96
HT-550A	64.0	100.0	88.8	52.4	1.0	10.7	19.0	34.3	20.0	96
PR-450N	52.0	100.0	74.5	44.5	14.3	11.3	14.3	26.4	23.3	97
PR-450A	50.3	100.0	74.4	53.5	14.2	8.0	16.7	25.6	21.0	87
PR-550A	48.3	100.0	61.8	47.7	23.4	7.7	15.6	25.0	24.0	85
C-450N	61.0	100.0	80.0	47.9	6.2	8.3	21.7	31.0	21.7	97
C-450A	52.3	100.0	76.4	53.5	8.6	7.3	18.0	27.0	20.7	91
C-550A	49.0	100.0	70.6	50.7	15.4	6.0	16.3	26.7	22.3	86
CeZrO	68.7	100.0	93.8	47.8	17.4	6.7	25.3	36.7	20.3	93

[a] *Reaction Conditions: aqueous model mixture (3.00 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar* N_2 *and 200ºC under continuous stirring; time on stream = 7 h;* [b] *2M2P = 2-methyl-2-pentenal.* [c] *Atmosphere: Air (A) or Nitrogen (N).*

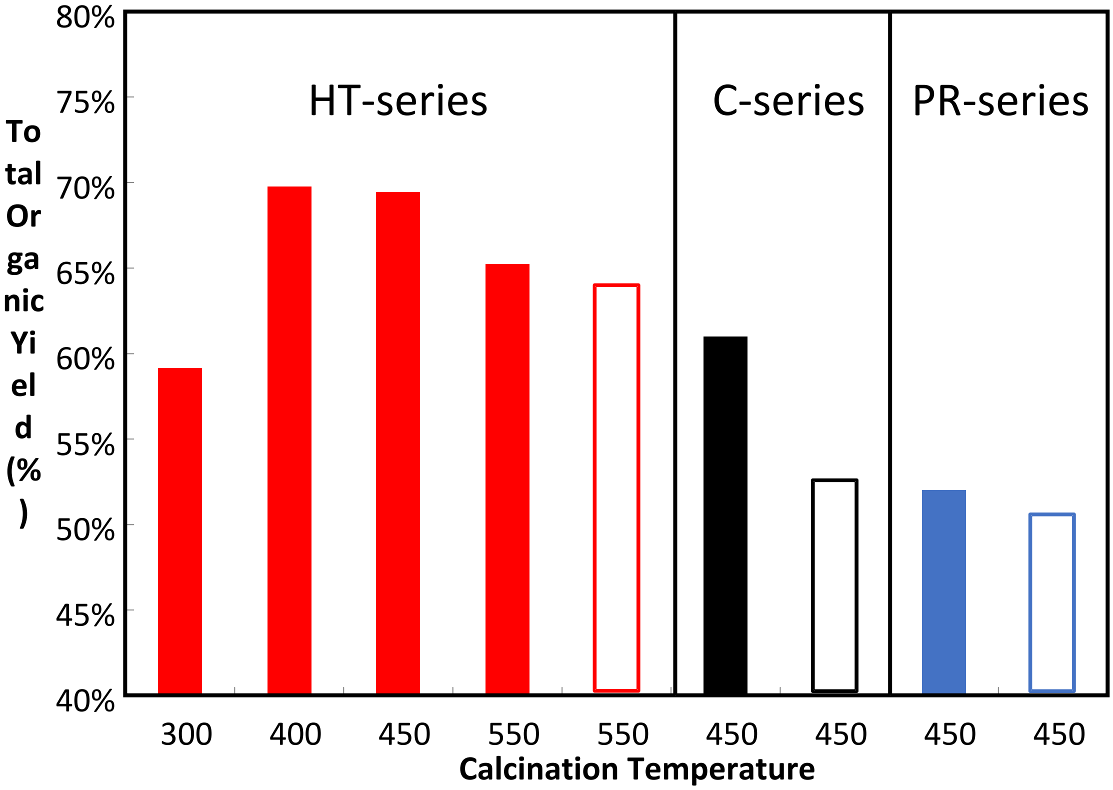


Figure S7. *Catalytic activity (in total organic yield) in the conversion of oxygenated compounds in aqueous model mixture of HT-, PR- and C-series catalysts heat-treated under different conditions:* N_2 *(filled column) or air (empty column).*

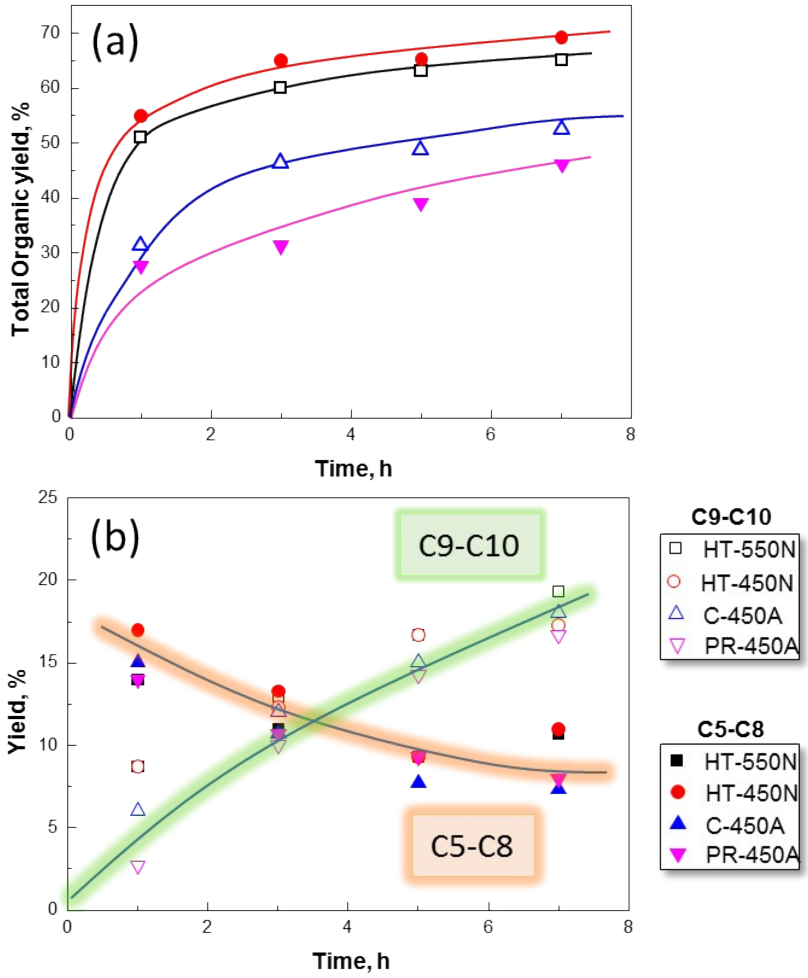


Figure S8. *Catalytic activity in total organic yield (a) and intermediates (C5-C8) and C9-C10 product yields (b) in the conversion of oxygenated compounds in aqueous model mixture of different HT-, PR- and C-series catalysts.*

Table S3*. Initial reaction rate and total organic products yield normalized taking into account density of acid sites calculated for different catalysts used in this work after 1hour of reaction.*

Catalyst	Reaction rate		Total Organic Yield (1h)	Density of acid sites µmol/m^2	Total Organic Yield (1h) / Total acid sites
	µmol/min.g	mmol/min.g			
HT-300N	1881	1,881	58,7	1,08	54,4
HT-400N	1644	1,644	53,0	0,74	71,6
HT-450N	1667	1,667	55,0	0,92	59,8
HT-550N	1577	1,577	51,0	0,52	98,1
C-450N	1051	1,051	31,7	0,54	58,7
C-450A	1051	1,051	31,3	1,94	16,1
C-550A	872	0,872	32,3	0,58	55,7
PR-450A	1029	1,029	27,7	0,74	37,4
PR-550A	912	0,912	24,0	1,17	20,5
CeZrO	1650	1,65	51,7	0,94	55,0

S3.2 Reuses of catalysts on the transformation of oxygenated compounds present in aqueous model mixtures.

Table S4. *Reuse of catalysts on the transformation of oxygenated compounds present in aqueous model mixtures.*[a]

Catalyst	Use (R)	Total Organic Yield (%)	Conversion (%)				Products Yield (%)				Carbon balance (%)
			Acetol	Propanal	Ethanol	Acetic Acid	C5-C8	C9-C10+	2M2P[b]	Ethyl acetate	
HT-450N	0	69.3	100.0	92.6	44.1	16.5	11.0	17.3	41.0	25.0	97
	1	65.3	100.0	92.4	48.1	5.8	11.0	17.3	37.0	21.0	94
	2	65.3	100.0	90.0	44.7	8.6	11.9	15.7	37.7	22.7	95
HT-550N	0	65.3	100.0	92.0	51.9	6.5	10.7	19.3	35.3	20.3	96
	1	64.3	100.0	92.8	45.6	5.9	11.0	16.3	37.0	22.7	97
	2	64.3	100.0	90.9	45.4	6.3	12.0	15.7	36.6	22.3	96
C-450N	0	61.0	100.0	80.0	47.9	6.2	8.3	21.7	31.0	21.7	97
	1	54.0	100.0	72.6	42.4	5.9	9.3	16.7	28.0	22.3	97
	2	53.3	100.0	72.6	46.4	2.7	9.3	16.0	28.0	22.3	97
PR-450N	0	52.0	100.0	74.5	44.5	14.3	11.3	14.3	26.4	23.3	97
	1	51.3	100.0	70.2	48.8	14.9	12.1	11.5	27.7	27.0	95
	2	47.8	100.0	70.0	49.8	14.8	12.1	9.8	25.9	26.0	94
CeZrO	0	68.7	100.0	93.8	47.8	17.4	6.7	25.3	36.7	20.3	93
	1	66.7	100.0	87.8	49.7	13.4	7.7	25.0	34.0	20.0	98
	2	57.7	100.0	81.2	55.3	3.8	8.0	21.7	28.0	21.0	98

R0 = 1st use; R1 = 2nd use; R2 = 3rd use.

[a] *Reaction Conditions: For each use, aqueous model mixture (3.00 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar N_2 and 200ºC under continuous stirring; time on stream = 7 h.* [b] *2M2P = 2-methyl-2-pentenal.*

Equation S1. *Maintenance of catalytic activity calculation.*

$$Maintenance\ of\ catalytic\ activity_i\ (\%) = \frac{Total\ organic\ yield\ (R_i)}{Total\ organic\ yield\ (R_0)} * 100$$

Table S5. *Maintenance of catalytic activity (in %) of different catalysts in the conversion of oxygenated compounds in aqueous model mixture and organic compounds deposition on catalyst after reuse catalytic experiments.*

Catalyst	RO	R1	R2	TG[a] (R2)	EA[b] (R2)	Metal Lost[c]
CeZrO	100.0%	97.2%	84.0%	13.8%	4.8%	>30.0%
HT-550N	100.0%	98.5%	98.1%	6.9%	1.9%	Non det.[d]
HT-450N	100.0%	93.5%	93.4%	11.9%	3.7%	Non det.[d]
C-450N	100.0%	88.6%	87.4%	0.6%	0.3%	<0.5%

R0 = 1st use; R1 = 2nd use; R2 = 3rd use.

[a] TG: Mass loss (wt.%) measured by thermogravimetric analysis.

[b] EA: Carbon composition (wt.%) measured by elemental analysis.

[c] Amount of metal lost (in wt.%) from the solid catalyst determined by ICP measurements of metal concentration in liquids after first use (R0).

[d] Non det.: Nb was non detected in liquids after first use (R0) by ICP measurements.

It is known that catalysts under aqueous environments can suffer from surface changes or reconstruction processes that can modify their catalytic activity. Raman spectroscopy (Figure S9) was used to study why C-450N experienced activity decay even when low carbon deposition was observed by TG and EA. A change in the intensity of the band at 550-750 cm^{-1} attributable to Nb-O-Nb was observed in the case of C-450N-R1.

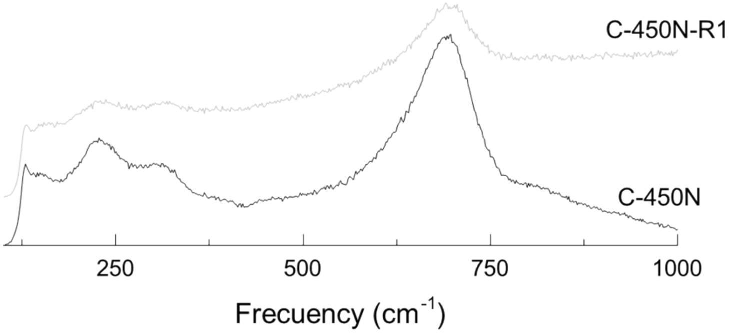


Figure S9. *Raman spectroscopy analysis for C-450N (fresh catalyst) and C-450NR1 (used catalyst).*