Electronic Supplementary Information

W-Nb-O oxides with tunable acid properties as efficient catalysts for the transformation of biomass-derived oxygenates in aqueous systems

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Content

Experimental part

Catalytic tests for condensation reaction

Based on the aqueous model mixture composition, a theoretical maximum total organic yield can be calculated, assuming that: a) 100% conversion for all reactants is achieved, b) acetic acid can be equally converted to ethyl acetate and acetone) and c) final products are C_9 compounds (no intermediate or heavier products are present in the final mixture). In this ideal scenario, the calculated composition of the final mixture is: 51.3 wt% of water, 19.1 wt% of ethyl acetate, and 29.6 wt% of C9 products. Therefore, results of catalytic experiments expressed in terms of Total organic yield (TOY) and yield to the main reaction products are calculated by considering that ≈30 wt% is the maximum value attainable. In this way, Total organic products yield (TOY) measured during reaction = 20.0 wt%; Maximum total organic products yield attainable (theoretical) = 30.0 wt%; Calculated total organic products yield (referred to the maximum) = 66.7%.

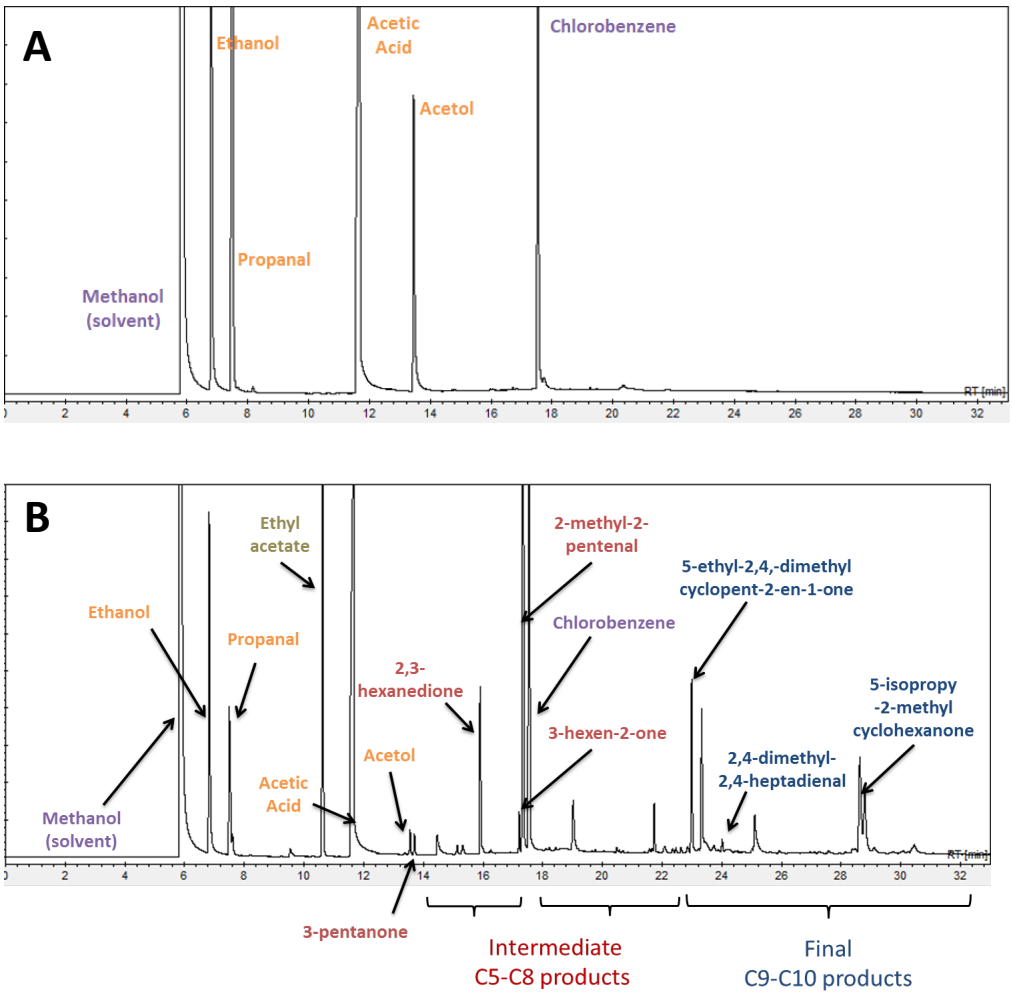

Figure S1. Examples of chromatograms analyzed at 0 h (A) and 5 h (B) of reaction.

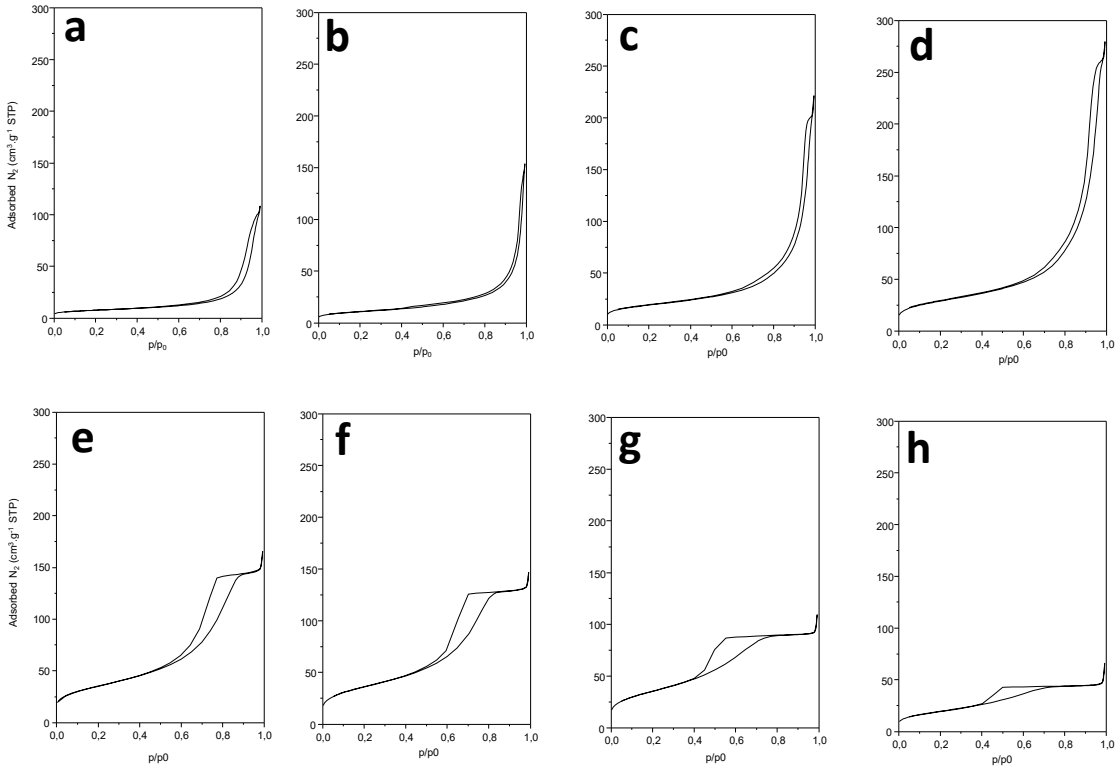

Figure S2. N_2-adsorption-desorption isotherms of W-Nb-O catalysts: a) WNb-0; b) WNb-0.29; c) WNb-0.40; d) WNb-0.53; e) WNb-0.62; f) WNb-0.80; g) WNb-0.95; h) WNb-1.

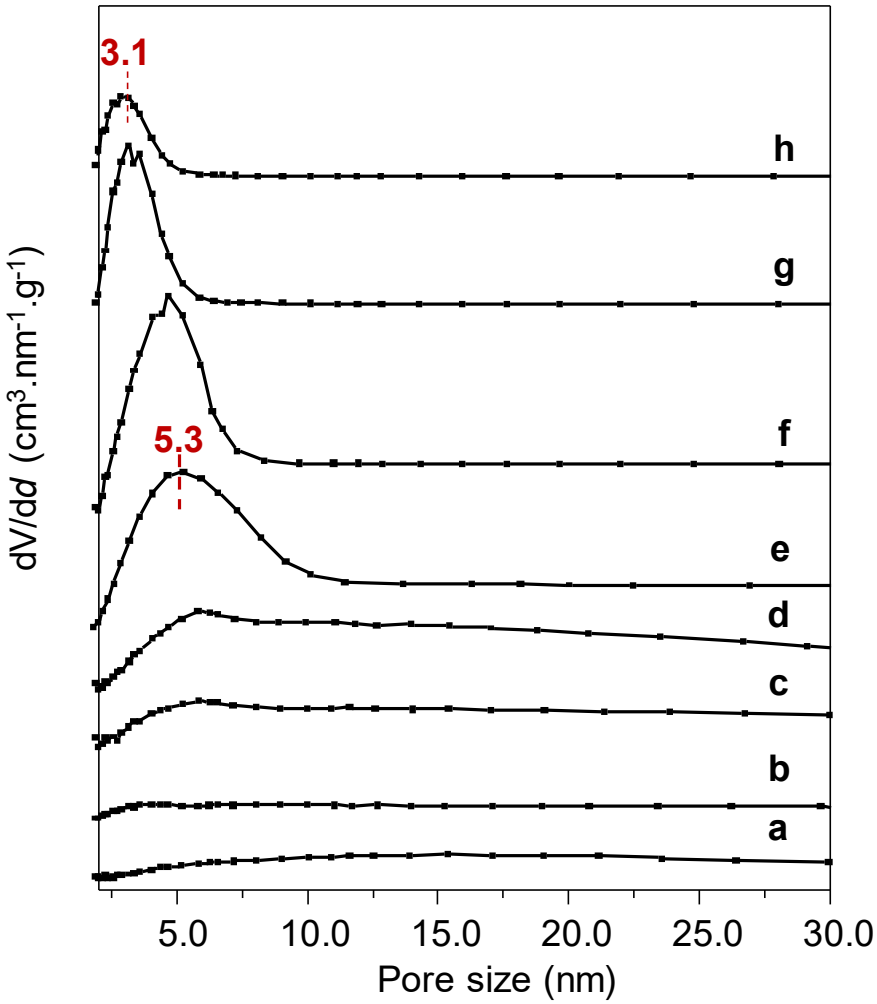

Figure S3. BJH pore size distribution of W-Nb-O catalysts: a) WNb-0; b) WNb-0.29; c) WNb-0.40; d) WNb-0.53; e) WNb-0.62; f) WNb-0.80; g) WNb-0.95; h) WNb-1.

Table S1. Catalytic properties of W-Nb-O oxides in the aerobic transformation of glycerol.

Catalyst	Glycerol conversion (%)	Yield (%)			
		Acrolein	CO_x	Heavy compounds [a]	Others [b]
WNb-0	100.0	82.2	8.9	4.4	4.1
WNb-0.29	99.9	83.5	7.8	6.1	2.8
WNb-0.53	99.7	67.6	11.2	15.8	5.5
WNb-0.80	99.7	62.6	11.0	22.4	4.0
WNb-1	100.0	45.3	15.7	35.8	3.2

[a.] Considered as compounds that are not eluted into the gas chromatograph. [b.] Small amounts of acetaldehyde, acetic acid and acrylic acid. Reaction conditions: 295 ºC, glycerol/oxygen ratio of 2/4.

Table S2. Catalytic results of W-Nb-O mixed oxides catalysts in the valorization of the aqueous model mixture at 200 ºC.[a]

Sample	Total organic yield (%)	Conversion (%)				Yield (%)				Carbon balance (%)
		Acetol	Propanal	Ethanol	Acetic acid	C_5-C_8	C_9-C_{10}	2M2P [b]	ethyl acetate	
WNb-0	52.9	100	86.6	49.8	0.0	12.4	11.2	29.3	22.3	90.9
WNb-0.29	56.6	100	85.1	50.8	8.2	13.4	10.7	32.5	19.0	87.2
WNb-0.40	59.3	100	94.1	47.1	8.0	13.9	16.0	29.4	23.6	87.8
WNb-0.53	64.2	100	93.8	56.7	8.0	13.5	18.0	32.7	19.4	90.8
WNb-0.62	64.5	100	90.0	51.3	9.8	11.2	17.7	35.6	19.2	94.0
WNb-0.80	63.9	100	91.0	52.8	10.1	9.5	19.0	35.4	20.5	94.5
WNb-0.95	63.5	100	94.6	52.1	4.3	10.4	19.0	34.1	19.4	94.0
WNb-1	65.2	100	92.0	51.9	6.5	10.5	19.2	35.5	20.2	95.0

[a] Reaction conditions: aqueous model mixture (3.0 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar (under N_2) and 200˚C under continuous stirring during 7 h.
[b] 2M2P = 2-methyl-2-pentenal.

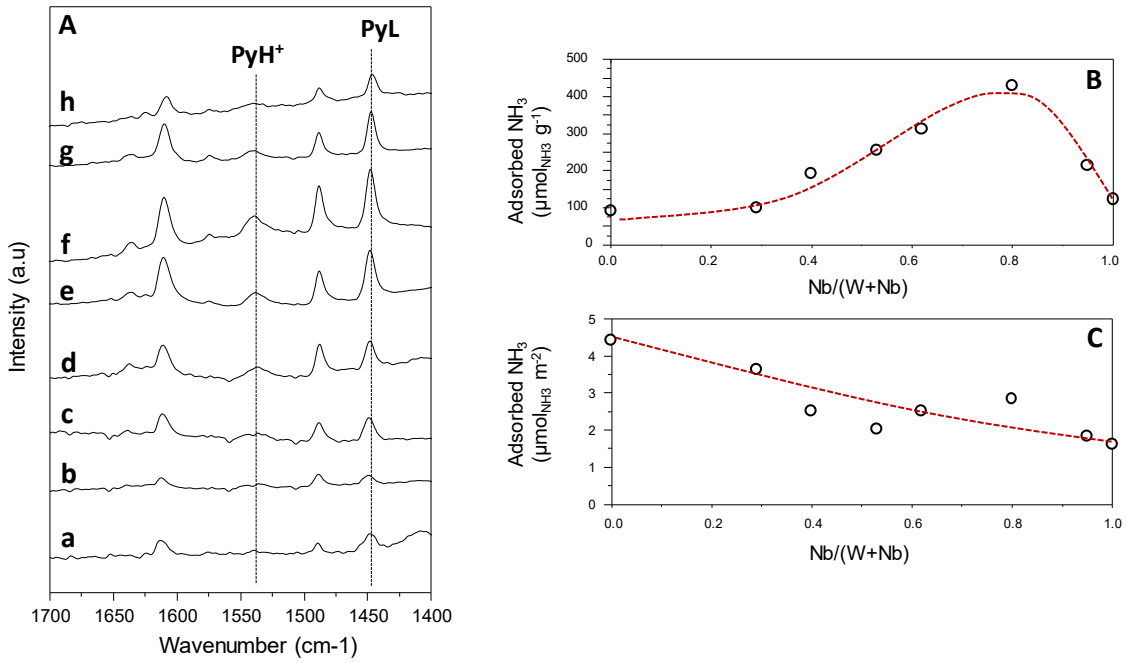

Figure S4. A) FTIR spectra of adsorbed pyridine: a) WNb-0; b) WNb-0.29; c) WNb-0.40; d) WNb-0.53; e) WNb-0.62; f) WNb-0.80; g) WNb-0.95; h) WNb-1. B) Amount of adsorbed ammonia per gram of catalysts as a function of Nb-content. C) Amount of adsorbed ammonia per surface area of catalyst as a function of Nb-content.

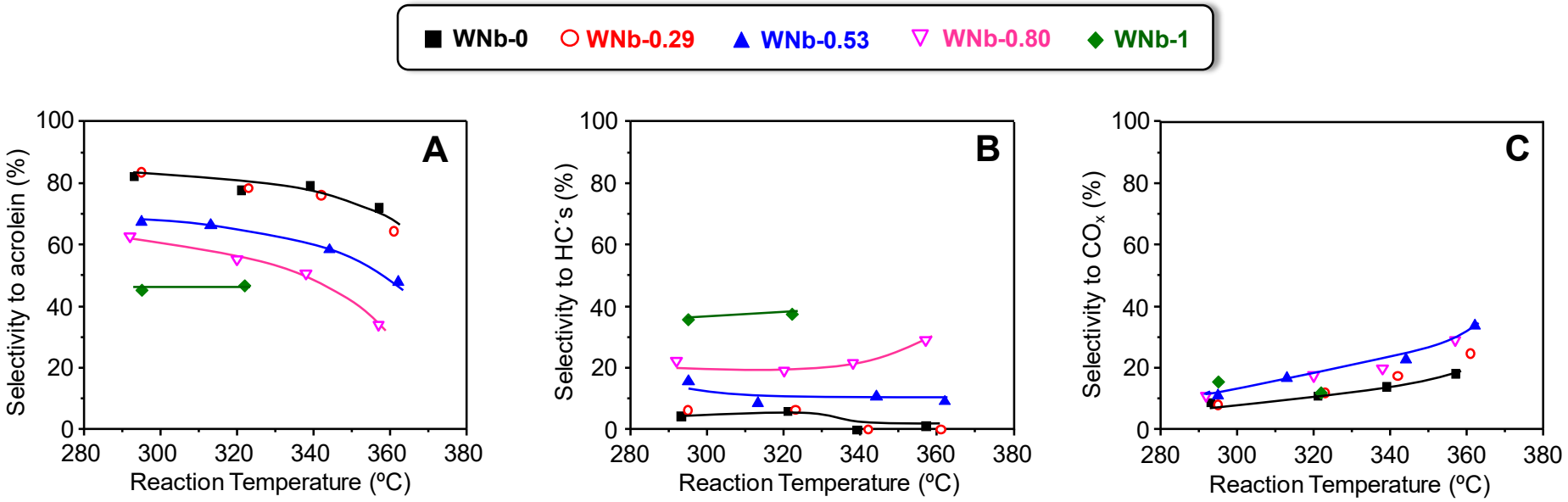

Figure S5. Selectivity to acrolein (A), heavy compounds (HC´s) (B) and carbon oxides (C) as a function of reaction temperature during the aerobic transformation of glycerol. Complete conversion of glycerol is achieved in all cases. Reaction conditions: glycerol/H_2O/O_2/He molar ratio of 2/40/4/54, Contact time, W/F, of 81 g_{cat} h $(mol_{gly})^{-1}$.

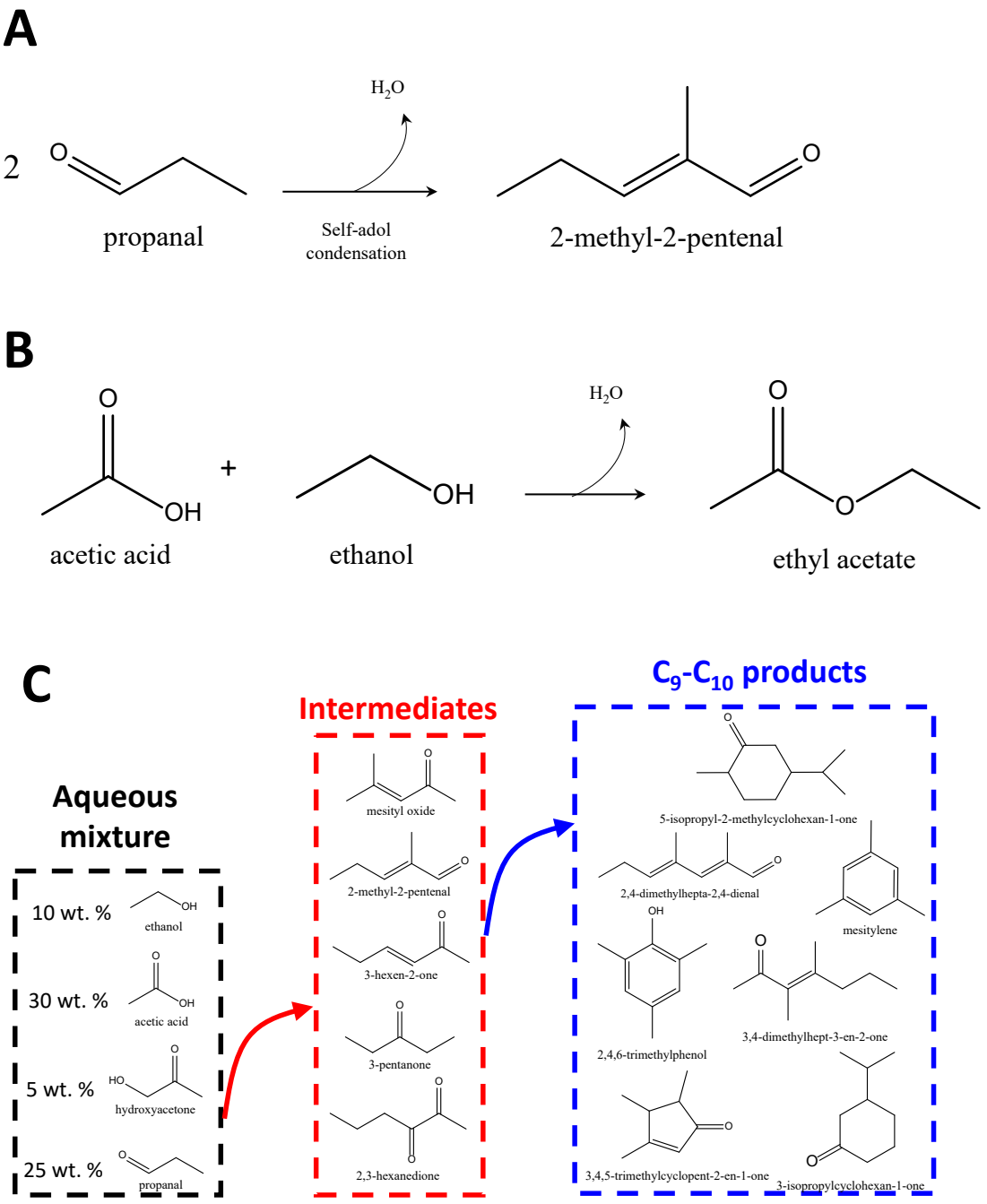

Figure S6. Reaction network: A) Self-aldol condensation of propanal to 2-methyl-2-pentenal; B) Esterification of acetic acid and ethanol to ethyl acetate; C) Summarized reaction network.

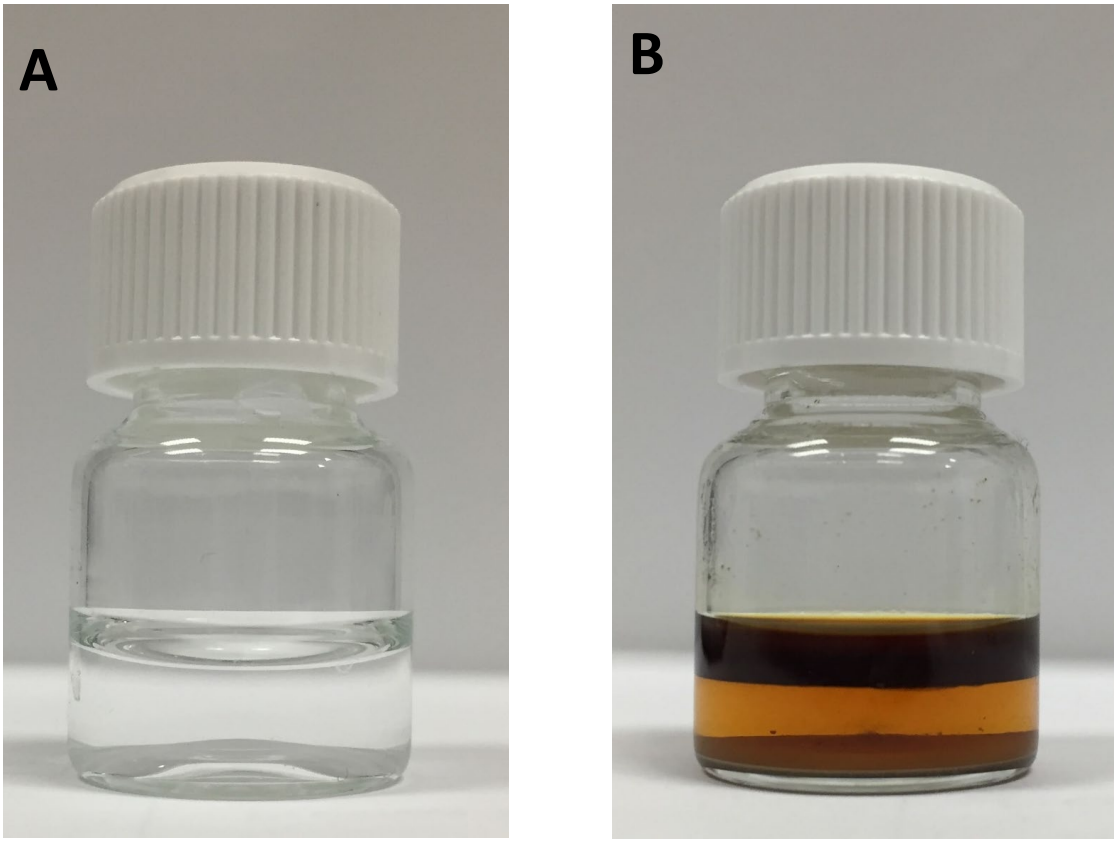

Figure S7. Aqueous model mixture before (A) and after (B) reaction using WNb-0.62 catalyst: Reaction conditions: 7h at 180 ºC (P_{N2}=13 bar).

Table S3: Catalytic results of W-Nb-O oxides during propanal self-aldol condensation at lower contact time.[a]

Catalyst	Propanal Conversion (%)	Total Organic Product Yield (%)
WNb-0	38.7	20.0
WNb-0.29	42.2	26.0
WNb-0.62	59.6	59.0
WNb-1	39.7	29.0

[a] Reaction Conditions: Initial mixture (3.00 g), with a Propanal/Ethanol/H_2O wt% ratio of 25/45/30; weight of catalyst = 0.05 g. In autoclave-type reactor, at 13 bar N_2 and 200 ºC under continuous stirring; time on stream = 1 h.

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

Catalyst	Reuse cycles[b]	Total Organic Yield (%)	Conversion (%)				Products Yield (%)				Carbon balance (%)
			Acetol	Propanal	Ethanol	Acetic Acid	C_5-C_8	C_9-C_{10}	2M2P [c]	Ethyl acetate	
WNb-0.62	0	64.5	100	90.0	51.3	9.8	11.2	17.7	35.6	19.2	94
	1	61.7	100	87.1	51.1	7.6	10.2	18.2	33.3	20.5	95
	2	60.3	100	86.4	51.3	4.9	9.6	17.9	32.8	20.1	93
WNb-1	0	65.2	100	92.0	51.9	6.5	10.5	19.2	35.5	20.2	95
	1	64.3	100	92.8	45.6	5.9	11.0	16.3	37.0	22.7	97
	2	64.3	100	90.9	45.4	6.3	12.0	15.7	36.6	22.3	96

[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] Reuse cycles; R0 = 1st use; R1 = 2nd use; R2 = 3rd use.
[c] 2M2P = 2-methyl-2-pentenal.

Table S5. Metal loss of catalysts after first catalytic use.

Sample	**Metal Loss after first use (wt%)** [a]
$Ce_{0.5}Zr_{0.5}O_2$	30.0
WNb-0.62	Not detected.
WNb-1	Not detected

[a] determined by ICP measurements of reaction liquids

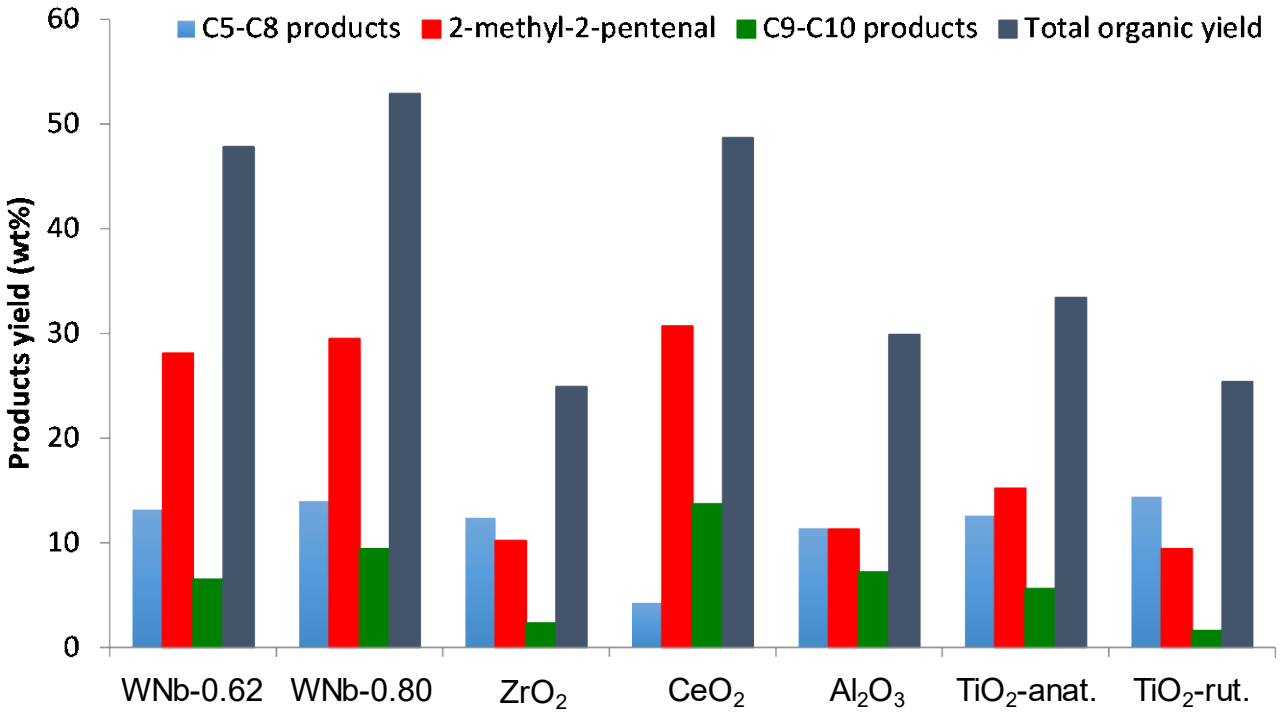

Figure S8: Main products and total organic yields (wt%) for different catalysts in the condensation of an aqueous mixture of oxygenated compounds after 1 h of reaction at 200 ºC.

Table S6. *Catalytic activity in the conversion of oxygenated compounds in aqueous model mixture of WNbO catalysts at 200 ºC.*[a]

Catalyst	Total Organic Yield (%)	Conversion (%)				Products Yield (%)			Reaction Rate (mmol/min·g)[e]
		Acetol	Propanal	Ethanol	Acetic Acid	C5-C8	C9-C10+	2M2P[d]	
WNb-0.00	46.6[b]	100.0	77.2	47.5	5.9	13.9	6.3	26.4	1467
WNb-0.29	46.5[b]	100.0	74.9	48.8	6.5	16.9	5.5	24.1	1589
WNb-0.40	50.6[b]	100.0	82.8	49.1	6.8	15.1	7.8	27.7	1763
WNb-0.53	50.2[c]	100.0	80.4	51.2	4.0	18.5	5.8	25.9	1816
WNb-0.62	**52.3[c]**	100.0	82.1	48.3	4.8	13.0	**10.7**	28.6	**1854**
WNb-0.80	**52.9[c]**	100.0	79.0	39.5	12.6	14.0	**9.4**	29.5	**1882**
WNb-0.95	51.4[c]	100.0	68.8	52.2	11.4	11.3	8.6	31.5	1757
WNb-1.00	51.0[c]	100.0	71.2	42.6	11.4	14.0	8.7	28.3	1577

[a] *<u>Reaction Conditions</u>: aqueous model mixture (3.00 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar N_2 and 200 ºC under continuous stirring;* [b] *time on stream = 3 h;* [c] *time on stream = 1 h;* [d] *2M2P = 2-methyl-2-pentenal;* [e] *Calculated as the mmol of products formed per minute and gram of catalyst at time on stream = 1 h.*

Table S7: *Total organic yield and normalized total organic yield values for different WNb-O samples in the condensation of propanal in aqueous phase.*

Catalysts	Total Organic Yield (%)	Surface density of acid sites (mmol/m^2)	Normalized Total Organic Yield (%)[a]
WNb-0.00	20	0.98	20.4
WNb-0.29	26	0.78	33.3
WNb-0.62	59	0.70	84.3
WNb-1.00	29	0.54	53.4

[a] Total organic yield (%) / Surface density of acid sites (mmol/m^2).