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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Abstract

W-Nb-O oxide bronzes, prepared hydrothermally, have been characterized and studied as catalysts for both the gas phase dehydration of glycerol and the liquid phase selective condensation of light oxygenates derived from primary treatments of biomass (a mixture containing acetic acid, ethanol, propanal, hydroxyacetone and water). By controlling the nominal composition of the catalysts it is possible to tune up their textural and acid properties (concentration and nature of acid sites) to selectively produce acrolein from glycerol or C₅-C₁₀ hydrocarbons (with low O contents) and in high yields) from light oxygenates. Interestingly, these catalysts are stable when working in gas phase reaction and they are re-usable, with high resistance to leaching, when working in aqueous media.

INTRODUCTION

Second generation biomass feedstocks constitute one of the main sustainable and renewable alternatives to fossil sources for the production of commodity chemicals and fuels.¹⁻⁵ Regarding the new bio-economy concept, the valorization of some types of waste streams is a key point in the development of bio-refineries. This is the case of glycerol (formed during the biodiesel production)⁶⁻⁹ or the aqueous fraction containing low-value short-chain oxygenates (residues generated from lignocellulosic biomass fast pyrolysis)¹⁰⁻¹⁴. For some specific reactions, solid acids seem to be the most interesting catalysts for the selective transformation of both residues.

Glycerol can be selectively transformed into acrolein, an important intermediate in the chemical industry.⁶⁻⁹ This reaction can be carried out over solid acid catalysts by a dehydration mechanism,^{6-9,15-20} in which Brønsted acid sites seem to be more active and selective than Lewis acid sites.¹⁷⁻²⁰ Several types of materials have been proposed as catalysts for this reaction in the last decade,⁴⁻⁷ including W-containing materials (both bulk and supported ones).¹⁷⁻²⁰ In this sense, tungsten-based metal oxide bronzes, especially the hexagonal tungsten bronze (*h*-WO₃), show interesting catalytic performance for this reaction; although the addition of promoters can modify the reaction products obtained: i) pure *h*-WO₃ and Nb-modified *h*-WO₃ to selectively form acrolein;^{7,21-24} and ii) vanadium and/or molybdenum modified *h*-WO₃ to form acrylic acid in one-pot.^{7,25-28} Moreover, and although dehydration can be carried out in inert atmosphere, it has been reported that, in many cases, the presence of oxygen in the feed has a beneficial effect to avoid catalyst decay.^{18,19}

On the other hand, aqueous fraction containing low-value short-chain oxygenates (aldehydes, ketones, alcohols, among others), derived from the fast pyrolysis of lignocellulosic biomass, could be upgraded by C-C bond formation reactions like

ketonization or aldol condensation, increasing their carbon chain length and reducing oxygen content.²⁹⁻³¹ In this way, catalysts based on CeZrO oxide have been widely studied for the ketonization of small aldehydes in the presence of water or acetic acid,³² whereas ZrO₂ or TiO₂ have been considered for the aldol condensation using acetic acid or propanal as probe molecules.³³ Interestingly, both acids and bases are able to catalyze C-C bond formation reactions, leading to similar product distributions through different reaction mechanisms. In all these cases, the catalytic performance is explained in terms of structural features and specific acid-base properties of the materials. Recently, it has been proposed that niobium oxide based catalysts show interesting catalytic performance in C-C bond formation reactions.^{34, 35}

Bronze-type materials include a vast group of closely related structural phases with the ability of accommodating wide variation range of chemical composition.^{22-26, 36-42} These facts open up the possibility to modulate their specific functionalities. In addition, alternative synthetic routes for obtaining these phases, (like hydrothermal, reflux or evaporation methods) have been proposed, what has made it possible to produce materials with surface areas suitable for catalytic applications.^{22-24, 36-44}

Herein we report the synthesis of a series of W-Nb mixed oxides obtained by the hydrothermal method, which present bronze-type structures and tailored acid and textural properties. Materials have been tested as catalysts in both the gas phase aerobic transformation of glycerol to acrolein and in the transformation of light oxygenated compounds present in an aqueous model mixture, resembling that of a waste effluent at a bio-refinery. The effect of Nb-content in both their physicochemical properties and catalytic performance is discussed in detail, especially in terms of its effect on the crystal structure, textural and acid properties, and on the catalytic behavior.

EXPERIMENTAL

Synthesis of materials

W-Nb-O mixed oxides were synthesized from acidified aqueous solutions ($\text{pH} = 1$) containing stoichiometric amounts ($\text{H}_2\text{O}/(\text{W}+\text{Nb})$ molar ratio: 53/1) of the corresponding metal salts: ammonium metatungstate hydrate (≥ 85 wt% WO_3 basis, Sigma–Aldrich) and niobium oxalate monooxalate adduct (ABCR). These solutions were introduced into Teflon-lined stainless steel autoclaves, purged with N_2 and finally treated at 175°C during 48 h. Resulting solids were filtered off, washed with distilled water and dried at 100°C for 16 h. Finally, they were heat-treated at 550°C under N_2 flow ($15\text{ ml min}^{-1}\text{ g}_{\text{cat}}^{-1}$) during 2 h. The catalysts are named as WNb-x, being x the corresponding Nb/(W+Nb) atomic ratio in solids (measured by XEDS). Table 1 shows the main physico-chemical characteristics of catalysts.

Table 1

Undoped tungsten oxide sample (named as WNb-0) was just heat-treated at 450°C to avoid the transformation into *m*- WO_3 (see below).²⁸ Pure niobium oxide was synthesized from an aqueous solution ($\text{H}_2\text{O}/\text{Nb}$ molar ratio: 53/1) following the process described above (final heat-treatment temperature of 550°C).³⁴

Catalyst Characterization

Powder X-Ray diffraction (XRD) patterns were obtained in a PANalytical X'Pert PRO diffractometer using $\text{CuK}\alpha$ radiation and an X'Celerator detector in a Bragg-Brentano geometry.

Raman spectra were recorded at ambient temperature in an inVia Renishaw spectrometer equipped with an Olympus microscope, a CCD detector and a Renishaw HPNIR laser.

An exciting wavelength of 514 nm was used, with an approximated power of 15 mW on the samples.

In order to obtain the bulk composition of the catalysts energy-dispersive X-ray spectroscopy (XEDS) was performed in a JEOL 6300 scanning electron microscope, with an Oxford LINK ISIS detector connected. Counting time used for each spectrum was 100 s.

Samples for transmission electron microscopy (TEM) were ultrasonically dispersed in *n*-butanol and transferred to carbon coated copper grids. Selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM) were performed on a JEOL JEM300F electron microscope working at 300 kV (point resolution of 0.17 nm). XEDS crystal-by-crystal chemical microanalysis was performed in the same microscope equipped with an ISIS 300 X-ray microanalysis system (Oxford Instruments) with a detector model LINK “Pentafet” (resolution 135 eV).

N₂ adsorption isotherms were collected in a Micromeritics ASAP 2000. Samples were degassed in vacuum at 300 °C. Surface areas were calculated by Brunauer-Emmett-Teller (BET) method. Pore size distributions and pore volumes were obtained by Barrett-Joyner-Halenda (BJH) method.

Infrared spectra of adsorbed pyridine were recorded in a Nicolet 710 spectrometer, where self-supported wafers of 10 mg cm⁻² were degassed in vacuum (10⁻² Pa) at 200 °C during 12 h. Afterwards, pyridine was admitted (6.5x10² Pa) and, after achieving equilibrium, samples were outgassed at 150 °C and cooled down to room temperature. IR spectra were then acquired. The IR spectra recorded before pyridine adsorption were used as a background for pyridine-adsorbed spectra. This background was subtracted from each spectrum by difference, and the absorbance was normalized to weight before

calculations. Concentration of acid sites was calculated from band intensities (signals at ca. 1545 and 1450 cm^{-1} for Brönsted and Lewis sites, respectively) and extinction coefficients, applying a method previously proposed.⁴⁵

Temperature-programmed desorption of ammonia (TPD-NH₃) was carried out in a Micromeritics TPD/2900 device. Samples were pre-treated at 350 °C under He flow during 1h. Then, chemisorption of NH₃ was performed by pulses at 100 °C. After treating the samples with He stream during 15 min (to eliminate physisorbed ammonia), temperature was increased gradually (10 °C min⁻¹) up to 500 °C. Desorbed ammonia was monitored by following NH₃ characteristic mass of 15 a.m.u. (atomic mass unit) by mass spectrometry.

Catalytic tests for glycerol dehydration

The gas phase transformation of glycerol was carried out at atmospheric pressure in a fixed-bed reactor at 295 °C. The feed consisted of a mixture glycerol-water-oxygen-helium with a molar ratio of 2/40/4/54 using a contact time, W/F, of 81 g_{cat} h (mol_{GLY})⁻¹. The effluent stream was bubbled through a condenser device at 0 – 3 °C, while the remaining gaseous products were analyzed by online gas chromatography (HP 6890) equipped with two chromatographic columns: ⁴⁵ i) a molecular sieve 5Å (3.0 m length); and ii) a Porapak Q (3.0 m length) column. The condensed liquids were analyzed by gas chromatography in a Varian 3900 chromatograph equipped with a 100% dimethylpolysiloxane capillary column (100 m× 0.25 mm× 0.5).

Catalytic tests for condensation reaction

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 placed over a steel jacket individual support equipped with a temperature close loop control system.

The initial feed consisted of an aqueous model mixture containing short-chain oxygenated compounds. In all the cases the following composition has been used: water (30 wt%), acetic acid (30 wt%), propanal (25 wt%), acetol (5 wt%) and ethanol (10 wt%). The composition simulates that of a waste stream derived from the aqueous phase separation of a pyrolytic bio-oil. 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 of N₂ and heated at 180-200 °C 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 2 wt% chlorobenzene as standard. The liquid samples were analyzed by a Bruker 430 GC equipped with a FID detector and a capillary column (TRB-624, 60m length).

Reactants and intermediate products were quantified from GC-FID. 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) (Figure S1). A further explanation of the experimental part and calculations is shown in the Supporting Information.

RESULTS AND DISCUSSION

Catalyst Characterization

Powder-XRD patterns of hydrothermal W-Nb-O mixed oxides are depicted in Figure 1A. Pattern *a*, corresponding to WNb-O catalyst, can be assigned to the hexagonal

tungsten bronze-type structure $h\text{-WO}_3$ (HTB, ICDD: 00-33-1387), in which WO_6 octahedra share their vertices along the three crystallographic directions, displaying trigonal and hexagonal channels along c -axis (Figure 1B).²¹ Isomorphic substitution of W by Nb causes the progressive loss of crystallinity and important changes in the corresponding diffraction patterns occur for these materials (Figure 1A, patterns b - h). For Nb/(W+Nb) ratios lower than 0.5, catalysts preserve the HTB crystal structure, although the intensity of diffraction maxima becomes notably lower (Figure 1A, patterns b and c). The crystallinity loss results in a rapid decrease in the intensity of the diffraction maxima. For Nb/(W+Nb) ratios higher than 0.5, broad and ill-defined diffraction maxima at 2θ values of ca. 27° , 35° , 50° and 55° are present but, the XRD patterns are dominated by two diffraction maxima at $2\theta \sim 22$ and 46° (Figure 1A, d - h). These two diffraction maxima are assigned to the (001) and (002) reflections of the HTB structure and the observed transformation can be explained from the progressive loss of the long range order in the ab plane of the structure, that gives rise to the formation of the hexagonal and trigonal tunnels, while keeping inter-octahedral connectivity. In fact, they can correspond to the (001) and (002) d spacing of any structure derived from a corner sharing octahedral framework with a basic unit cell parameter of about $3.8\text{\AA}$ and thus, accounting for the octahedral interconnectivity. The tungsten/niobium ratio plays a crucial role in the stabilization of $h\text{-WO}_3$ and the introduction of Nb finally gives rise to a pseudo-crystalline mixed oxide phase already observed in other Mo, Nb and W-based mixed oxides.^{25, 46, 47} The magnitude of the c -axis, considered as the sharing corner-connection between octahedra was calculated from the (001) diffraction maximum (Figures 1B and 1C). It can be noticed that c parameter increases linearly with Nb content up to Nb/(W+Nb) ratio of 0.53, which is consistent with the relative ionic size of both elements ($r^{\text{VI}}\text{Nb}^{5+} = 0.64\text{ \AA}$, $r^{\text{VI}}\text{W}^{6+} = 0.60$

Å).⁴⁸ For higher Nb-content, c -axis remains almost constant and it is important to mention that the interval of composition for which no variation of c is observed, corresponds to catalysts that are pseudo-crystalline.

Figure 1. A) XRD patterns 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. Miller indices have been assigned according to the hexagonal WO₃ phase (h -WO₃, ICDD: 00-33-1387). B) Projected structural model of the h -WO₃ structure along the [001] and [210] directions. C) Variation of c -axis as a function of Nb content.

Figure 2 shows the Raman spectra of W-Nb-O catalysts. Pure tungsten oxide bronze (sample WNb-0) presents the characteristic bands of h -WO₃: those centered at 780, 691 and 648 cm⁻¹, being assigned to O-W-O stretching vibration; and bands at 331, 291 and 261 cm⁻¹, attributed to O-W-O deformation mode (Figure 2 a).^{41,49}

Figure 2. Raman spectra 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.

The partial substitution of Nb for W gives rise to a new broad signal at 900-1000 cm^{-1} , which is related to M=O type stretching vibrations (M = W, Nb) (Figure 2, *b-h*),⁵⁰⁻⁵¹ whereas the intensity of the band at 780 cm^{-1} progressively decreases. Likewise, a new band at 750 cm^{-1} is observed (Figure 2 *b*), which progressively shifts to 709 cm^{-1} as Nb content in the catalyst increases (Figure 2, *b-h*). The band at 709 cm^{-1} has been ascribed to symmetric stretching mode of slightly distorted NbO₆ octahedra in bulk niobium

oxides and its shift is consistent with the progressive Nb-enrichment along the composition range studied.⁵² Additionally, bands at lower frequencies (below 400 cm⁻¹), related to deformation vibrational modes in the oxide, become broader, probably due to the increasing disorder in the connectivity of polyhedra. Moreover, the signal at 258 cm⁻¹ also shifts to 234 cm⁻¹ as Nb content increases, which can be attributed to Nb-O-Nb deformation modes.⁵³

Due to the unclear identity of the crystal phases present, samples were further investigated by electron diffraction and high-resolution electron microscopy. For the lowest Nb content (WNb-0.29), sample is constituted by crystals of the HTB type phase (average size about 50 nm), as shown by the electron diffraction ring pattern in Figure 3a.

The corresponding high-resolution micrograph on Figure 3b shows a group of crystals representative of this sample, where characteristic *d*-spacing distances corresponding to the HTB type phase can be measured. From the crystal by crystal XEDS microanalysis performed, the atomic composition varies in the range W_{0.82}Nb_{0.18}O_{3-x} – W_{0.70}Nb_{0.30}O_{3-x} for the crystals of this catalyst (bulk composition W_{0.71}Nb_{0.29}O_{3-x}, see Table 1). Further increasing the Nb content implies a progressive loss of the order degree in the *ab* plane of the HTB structure, as well as a reduction of the average crystal size. Figure 3c shows the electron diffraction ring pattern of the WNb-0.53 sample, where the disappearance of the (100) reflection is observed. The average crystallite size is ≈10 nm and chemical heterogeneity is detected, the atomic composition varying in the range W_{0.65}Nb_{0.35}O_{3-x} – W_{0.50}Nb_{0.50}O_{3-x} from crystal to crystal.

Figure 3d corresponds to the high-resolution electron micrograph of a group of crystals of the same sample where *d*-spacing of about 4 Å are measured. There exists a certain

amount of bigger crystals (size >50 nm) which present low niobium content (<15%), high crystallinity and their periodicities can be assigned to the HTB type phase. At this point, it is important to mention that in WNb-0.53 and WNb-0.62 samples small crystallites (≈ 5 nm) are frequently observed in which fragments of the $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase can be clearly recognized (Figures 3e and 3f). This crystal phase is isostructural with the well-known M1-phase, widely studied for the ethane ODH⁴⁰ and the partial oxidation of propane.⁵⁴

Figure 3. (a) Electron diffraction ring pattern for the WNb-0.29 sample; (b) High resolution image showing a group of representative crystals of WNb-0.29; (c) Electron diffraction ring pattern for the WNb-0.53 sample; (d) High resolution micrograph showing several crystallites of this catalyst; (e) High resolution image showing one crystallite (pointed by the red arrow) in which fragments of the $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase can be recognized; (f) Projected structure model of $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase along the [001] direction; (g) Electron diffraction ring pattern corresponding to the WNb-0.80 sample; (h) High resolution image showing several crystallites of WNb-0.80. Miller index in all diffraction patterns have been assigned on the basis of the HTB-type phase (ICDD: 00-33-1387).

The Nb:W ratio close to 1 seems to favor the formation of the structural framework of the mentioned crystal phase in these catalysts. The coexistence of all these different crystal phases is compatible with the X-ray diffraction patterns of the corresponding samples, and the presence of $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase can be inferred from the faint and broad diffraction maxima at 2θ values of ca. 8° (see Figure 1A, patterns *d* and *e*). In samples with high Nb-contents, i.e. from WNb-0.80 to WNb-1, the formation of the $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase is not observed. Figure 3g shows the electron diffraction ring pattern of the sample WNb-0.80 where only rings corresponding to (001) and (002) reflections are visible, other maxima being in the form of diffuse halos. Figure 3h corresponds to the high-resolution electron micrograph of a group of crystals of this catalyst and the average crystal size is slightly smaller (5-10 nm). Samples from WNb-0.62 to WNb-1 are chemically homogeneous from crystal to crystal with compositions close to the nominal one, as revealed by crystal by crystal XEDS microanalysis. In this interval, samples also present uniform crystal size and crystallites appear constituting nanocrystalline agglomerates.

Textural properties of W-Nb-O mixed oxides were studied by means of N_2 adsorption. N_2 -adsorption isotherms show a transition from type II (for samples with $\text{Nb}/(\text{Nb}+\text{W})$ lower than 0.50) to type IV (for samples with high Nb contents), which are typical of mesoporous materials (Figure S2). Indeed, these changes are accompanied by a concomitant variation in average pore sizes, pore size distributions and pore volumes (Table 1). In this sense, materials with $\text{Nb}/(\text{Nb}+\text{W})$ lower than 0.50 present a broad size distribution whereas for higher Nb concentrations narrower distributions are observed, with pore sizes in the range 5.3-3.5 nm (Figure S3). Likewise, average pore size of the catalysts decreases from 17.2 nm for sample WNb-0 to 3.5 nm for sample WNb-1, when increasing the Nb content (Table 1). Interestingly, a drastic drop in the average

pore size (from 14.6 to 5.9 nm) is observed when Nb content exceeds ca. 50% as further introduction of niobium also gives rise to a strong increase in the percentage of mesopores (Table 1). There is a connection between this fact and the microstructural modifications observed in this composition range, the mesoporous structure (i.e. the narrow mesopore size distributions) being related to the packed agglomeration of uniform nanoparticles.

Acid properties of the catalysts were elucidated by means of FTIR of adsorbed pyridine and temperature-programmed desorption of ammonia (TPD-NH₃) (Table 1) (Figures 4 and 5, and Figure S4). It is noteworthy that both techniques lead to the same trends with regard to the variation of the amount of acid sites per gram of catalyst and per catalyst surface area, at increasing Nb contents (Figure 4 and Figure S4). However, absolute values of adsorbed pyridine were much lower than the amount of adsorbed NH₃, likely due to steric hindrance caused by the bigger size of pyridine molecule (Figure 4 and Figure S4). Considering the concentration of acid sites in terms of the total number of acid sites per gram of catalyst, the acidity of W-Nb-O oxides increases with Nb content, reaching a maximum for Nb/(W+Nb) atomic ratios of ca. 0.8 (Figure 4a). On the contrary, the surface density of acid sites (i.e. the number of acid sites per surface area) decreases when increasing Nb content, due to the higher surface areas observed (Figure 4b). Additionally, the Brönsted/Lewis acid sites ratio (BAS/LAS) decreases when increasing the Nb-content (Figure 4c). We must inform that the lower BAS/LAS ratio observed for undoped tungsten oxide (i.e. WNb-0 sample) can be ascribed to the presence of ammonium ions in the hexagonal channels of the crystal structure, due to the lower heat-treatment temperature used for this material. The elimination of NH₄⁺ cations after calcination has been reported to be the cause of the generation of Brönsted type acidity in bronze-type catalysts.⁵⁵

Figure 4. Acid features of W-Nb-O mixed oxides catalysts obtained by FTIR of adsorbed pyridine: a) Concentration of acid sites sites (in $\mu\text{mol}_{\text{py}} \text{g}^{-1}$); b) Surface density of acid sites (in $\mu\text{mol}_{\text{py}} \text{m}^{-2}$); and c) BAS/LAS ratio (BAS: Brönsted Acid Sites; LAS: Lewis Acid Sites).

Figure 5 displays TPD- NH_3 profiles of synthesized catalysts. All the catalysts show two main contributions to the desorption profile, at ca. 200 and 300 °C, which can be attributed to desorption of ammonia from acid sites with low and medium-high acid strength, respectively (Figure 5). The incorporation of Nb^{5+} atoms within the bronze framework leads to an increase of the relative intensity of the signal appearing at low

temperature (ca. 200 °C), i.e. favoring an increase in proportion of low strength surface acid sites.

Figure 5. TPD-NH₃ profiles 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.

Catalytic tests for aerobic glycerol dehydration

W-Nb-O mixed metal oxides have been tested in the aerobic transformation of glycerol.

The catalytic results are comparatively shown in Figure 6 and Table S1. Total

conversion of glycerol is observed all along the series, regardless the Nb-content. In all the cases, the main reaction product was acrolein, which is obtained via a double dehydration mechanism:⁶⁻⁹ i) the removal of the internal OH⁻ group, and ii) tautomerization-dehydration of the terminal OH⁻ group of glycerol. Although acrolein is observed in all the cases, the selectivity to the different products is highly dependent on the Nb-content in the materials.

In addition to acrolein, heavy compounds (products that are not eluted into the gas chromatograph due to their high molecular weight) and carbon oxides, together with small amounts of acetaldehyde, acetic acid and acrylic acid (grouped as “others” in Table S1) are obtained. Thus, the selectivity to acrolein decreases when the Nb-content in the catalysts increases (Figure 6). In a parallel way, a concomitant increase in the yield to carbon oxides and heavy by-products is observed (Figure 6).

Figure 6. Variation of the yield to the main reaction products, acrolein, CO_x and heavy-compounds, as a function of Nb content in catalyst. Reaction conditions: glycerol/H₂O/O₂/He molar ratio of 2/40/4/54, T = 295 °C, Contact time, W/F, of 81 g_{cat} h (mol_{gly})⁻¹.

Additionally, we have studied the effect of reaction temperature on the selectivity to acrolein, heavy compounds and carbon oxides during the gas phase aerobic transformation of glycerol (Figure S5). The same selectivity trends are observed when reaction temperature is increased, i.e. the formation of heavy compounds is favored at higher Nb concentrations. Interestingly, the variation of the selectivity to heavy products with reaction temperature depends also on Nb content in the catalysts. Materials with low Nb/(W+Nb) ratios (i.e. WNb-0 and WNb-0.29) show a drop in the yield to heavy compounds at higher temperatures. On the other hand, samples with high Nb/(W+Nb) ratios show an increase in the formation of heavy compounds when temperature increases.

Thereby, acid characteristics seem to control the selectivity profiles in the aerobic transformation of glycerol, being the increase in the yield to heavy compounds and carbon oxides related with the increment in the Lewis acid nature of the surface. Although both the decrease of acid strength and surface density of acid sites with Nb-content should favor the acrolein desorption, it seems that the higher concentration of Lewis sites (Figure 5) has a drastic effect in the selectivity profiles. In particular, Lewis sites (mainly Nb⁵⁺ species) can coordinate acrolein,¹⁶ hindering its desorption, and promoting the formation of heavy compounds and carbon oxides. Therefore, the most selective catalysts in this case are those with low Nb/(W+Nb) ratios, presenting a high proportion of Brönsted acid sites. In this way, it has been proposed that the presence of Brönsted acid sites favors the dehydration of secondary alcohol group from glycerol forming 1,3-propanediol, which after tautomerization forms 3-hydroxypropionaldehyde and finally gives acrolein.¹⁶ However, the presence of Lewis acid sites, favors the dehydration of a primary alcohol group to form hydroxyacetone.¹⁶

Catalytic activity for condensation reactions

As shown in the previous sections, the control of Nb-content in W-Nb-O oxides allows us to obtain catalysts presenting well-defined textural properties, nature, concentration and density of acid sites. In this sense, tuning Nb content gives rise to materials with tailored physicochemical properties for a specific application. In the case of light oxygenated compounds valorization, it has been reported that Lewis acid/base pairs can assist the formation of the intermediates in ketonization and aldol condensation reactions. Meanwhile, Brønsted acid/base sites are necessary in the case of esterification reactions.^{56,57} Thus, catalysts were tested in the transformation of short-chain oxygenates present in an aqueous model mixture, which resembles that of a waste effluent at bio-refineries. The tests were performed in Teflon-lined stainless steel autoclaves under moderate temperature (180 and 200 °C) and pressure ($P_{N_2} = 13$ bar). Results have been discussed in terms of conversion of the different oxygenated compounds and selectivity to the main condensation and/or ketonization products (i.e. 2-methyl-2-pentenal, C₅-C₈ and C₉-C₁₀ fractions) and to ethyl acetate as the main by-product (Figure S6).

C₅-C₁₀ molecules mainly come from condensation reactions among the different organic compounds present in the model aqueous mixture. In this sense, most of these compounds are derived from consecutive self-condensation reactions of propanal, as it is one of the compounds with a higher concentration in the aqueous mixture (30 wt%). Additionally, cross-condensation reactions also occur among propanal and acetol leading to a different C₆ compound (2,3-hexanedione) compared to the main intermediate compound (2-methyl-2-propanal) derived from propanal self-condensation. Small amounts of acetone (derived from acetic acid ketonization) are also observed,

which can also react via aldol condensation with propanal and acetol. These compounds can continue reacting via condensation reactions to produce different C₉ compounds. Due to the complexity of this system, other reactions including cyclation, and decarbonylation, among others can also take place leading to different C₅-C₁₀ molecules. The main reaction products can be observed in Figure S6.

Figure 7a shows the variation of the conversion of each reactant in the aqueous model mixture as a function of Nb/(Nb+W) atomic ratio in catalysts, achieved at 180 °C and a time on stream of 7h (Table 2). Conversion of acetol (100%), ethanol (37-47%) and acetic acid (13-19%) remain nearly constant regardless Nb content in the catalyst. However, propanal conversion increases with Nb content, reaching the highest value for Nb/(W+Nb) around 0.53 (84-90%), pure tungsten oxide (WNb-0 sample) displaying the lowest conversion (61.2%) (Figure 7a, Table 2). In this way, a concomitant increment in the selectivity to 2-methyl-2-pentenal (2M2P, via self-aldol condensation of propanal, Figure S6) can be observed when increasing Nb content in the catalysts (Figure 7b). Selectivity to C₉-C₁₀ products shows the same trend, since they are mainly formed via aldol condensation of C₅-C₈ fractions with smaller molecules (Figure S6).

Figure 7. Variation of the conversion of each reactant in the aqueous model mixture (i.e. acetol, propanal, ethanol and acetic acid) (a) and variation of selectivity to the main products (i.e. 2-methyl-2-pentenal, ethyl acetate, and C₅-C₈ and C₉-C₁₀ compounds) (b) as a function of Nb content in catalyst. Reaction conditions: Aqueous model mixture (3.0 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar N₂ and 180°C under continuous stirring; time on stream of 7 h.

Consequently, the selectivity to C₅-C₈ compounds decreases when increasing Nb content, since second condensation reactions are favored at high Nb-contents. In addition, the selectivity to ethyl acetate also decreases when increasing Nb concentration (Figure 7b), although this effect seems to be more related to an increase in the yield of condensation products rather than an effective decrease in ethyl acetate formation. In fact, ethyl acetate yield remains almost constant in all the series (Table 2).

These observations are in agreement with the specific acid properties of the materials, in which BAS/LAS ratio decreases when increasing Nb content, what would benefit the reactivity via a condensation reaction instead of the esterification reaction (Figure 4c). Moreover, this behavior was also observed when the catalytic activity (in terms of total organic yields and reaction rates) of the WNb-O samples were compared at iso-conversion level (see Table S6). Even in this case, the increasing in total organic yields observed is coincident with the level of Nb incorporation and, more importantly, with the increase in total acid sites and the decrease in the BAS/LAS ratio. The optimal values in total organic yield, reaction rates, and remarkably in the formation of C9-C10+ products are attained for the WNb-0.62 and WNb-0.80 samples.

Table 2

In this context, the catalytic performance of W-Nb-O oxides should be interpreted considering the concentration and the nature of acid sites on the surface of catalysts (Fig. 5). Thus, an increase of the concentration of acid sites in the samples gives rise to an increase in the yield to both the intermediate compounds (2M2P and C₅-C₈ fraction) and final (C₉-C₁₀ fraction) products, as well as in the Total organic yield (Figure 7b). The control of BAS/LAS ratio in the catalysts is also an important issue in order to increase the yield to condensation products. On one hand, a very high BAS/LAS ratio (i.e. catalysts with low Nb-contents) does not favor the condensation reactions, neither to reaction intermediates nor to final products (C₉-C₁₀), leading mainly to esterification and other Brönsted acid catalyzed reactions. On the other hand, higher concentration of Lewis acid sites (i.e. catalysts with high Nb-contents) favors the desired condensation reactions to produce C₅-C₈ and C₉-C₁₀ products, being these conditions attained on catalysts with Nb/(W+Nb) ratios above 0.53 (Table 1). Interestingly catalysts with Nb/(W+Nb) ratios of 0.53 or higher lead to products mixtures showing phase

separation, in which compounds with high carbon number are preferentially present in the upper organic phase (Figure S7). Nevertheless, a very high concentration of Lewis acid sites in the catalysts produces the over condensation of C₉-C₁₀ compounds with indiscriminate growing of the carbon chain to give heavier compounds (i.e. polymers), thus decreasing the amount of the desired C₅ to C₁₀ range products obtained in the final mixture. Accordingly, an adequate BAS/LAS ratio with an optimized amount of Lewis acid sites is required in the catalyst for the desired condensation reaction to occur. The optimum value is achieved at a Nb/(W+Nb) atomic ratio in the 0.62-0.80 range (Figure 7b) (Table 1).

Catalysts were also tested at higher reaction temperature (200 °C) (Table S2), whereas Figure 8 compares the catalytic performance of all the catalysts at 180 and 200 °C. Increasing the reaction temperature improves second condensation reaction steps, as it can be deduced from the decrease in the yield to intermediates (2M2P and C₅-C₈) and the concomitant increase in the yield to C₉-C₁₀ products (Figure 8a and 8b).

However, a slight decrease (from ca. 93% to ca 88%) in the carbon balance is also observed at 200 °C, due to polymerization/over-condensation reactions, that give rise to higher molecular weight compounds, which are not detected by gas chromatography (Table S2).

According to the complexity of the aqueous reaction mixture, additional experiments have been conducted using a simpler feed, containing propanal and ethanol (EtOH), in the presence of H₂O (propanal-EtOH-H₂O weight ratios of 25/45/30) (Figure 9 and Table S3). In this case, the tests were carried out using 50 mg of catalyst during 1h of reaction.

Figure 8. Variation of yields to C₅-C₈ products (a, c) and C₉-C₁₀ products (b, d) with the Nb-content of catalysts during the reaction at 180 °C (a, b) and 200 °C (c, d). Time on stream of 7 h.

Figure 9. Total organic yield during propanal self-aldol condensation on representative W-Nb mixed oxides in the presence of H₂O. Reaction conditions: $m_{\text{CAT}} = 50$ mg; reaction time = 1 h; propanal/EtOH/H₂O wt% ratio of 25/45/30.

As observed above for the complex aqueous mixture, catalysts showing a higher Lewis acidity i.e. sample WNb-0.62, display the best catalytic performance, in terms of propanal conversion and total organic yield (Figure 9). In addition, total organic yield values normalized in function of the surface density of acid sites parameter (see Table 2 and Table S7) are included in Fig. 9. This parameter takes into account both the total quantity of acid sites and their dispersion on the catalytic surface, as it was already evidenced for Nb-based materials in a previous report [35]. The normalization of the catalytic activity by considering this parameter confirms the general trend in total organic yields previously observed, with sample WNb-0.62 as the best catalyst (Fig. 9).

The recyclability of the catalysts was evaluated by performing several consecutive reuses (Figure 10 and Table S4). Studies on the catalyst stability are essential in this case, when dealing with aqueous solutions, especially in acidic media (model aqueous solution containing diverse organic compounds used in this work has a $\text{pH} = 1.5$ due to the high concentration of acetic acid, 30 wt%).

Figure 10. Total organic yield and distribution of the main reaction products achieved after several uses over WNb-0.62 and WNb-1. For comparison, the catalytic results over a Ce-Zr-O catalyst have been included. Reaction conditions: 13 bar N₂ and 200 °C under continuous stirring; time on stream of 7 h.

After each cycle, catalysts were separated from the reaction mixture by centrifugation, washed with methanol and dried at 100 °C overnight. Nb-containing catalysts show a high stability, presenting similar total organic yield after three consecutive uses (Figure 10) (Table S4), with no leaching of the active components.

It is important to note that these recycling results are better than those obtained previously over Ce_{0.5}Zr_{0.5}O₂ catalyst,⁵⁶ which shows a drastic decrease in the total organic yield after the second use and displayed a loss of ca. 30 wt% of Ce, as it was detected in the liquids after the first use (Table S5).

The catalytic performance of W-Nb mixed oxides have also been compared with other simple oxides, as ZrO_2 , CeO_2 , Al_2O_3 , and TiO_2 (anatase and rutile); typically used in aldol-condensation reactions (Figure S8). Figure S8 shows that W-Nb-O catalysts display higher organic yield compared to simple oxides. Only CeO_2 catalyst reaches similar catalytic behavior. However, this catalyst is completely dissolved in the reaction media, mainly due to the presence of acetic acid ($\text{pH} = 1.5$).

4. CONCLUSIONS

A series of W-Nb-O bronze oxides have been prepared by the hydrothermal method, heat-treated at $550\text{ }^\circ\text{C}$, and tested in two reactions related to the biomass-derived oxygenates transformation processes that require different acid characteristics: i) the aerobic transformation of glycerol to acrolein; and ii) the valorization of light oxygenates present in an aqueous model mixture simulating an aqueous effluent in a bio-refinery. The crystal structure of W-Nb-O materials corresponds to the HTB-type phase for $\text{Nb}/(\text{W}+\text{Nb})$ ratios lower than 0.4. Higher Nb-contents progressively eliminates the presence of HTB phase, and periodicity is only assignable to the connectivity between octahedra. In addition, $\text{Nb}/(\text{W}+\text{Nb})$ ratios close to 0.5 promote the formation of small crystallites showing a $\text{Cs}_{0.5}\text{W}_{2.5}\text{Nb}_{2.5}\text{O}_{14}$ type-phase,⁵³ isostructural to the so-called M1-phase proposed as active and selective catalysts for the ethane ODH^{40} and the partial oxidation of propane.⁵⁴ Textural and acid properties can be tuned by controlling the niobium amount. Materials progressively present both higher surface area and higher concentration of acid sites, but lower surface density of acid sites and lower BAS/LAS ratio. In this way, the mesoporosity increases for samples with $\text{Nb}/(\text{Nb}+\text{W})$ ratios higher than 0.53, which runs in parallel with a narrow pore size distribution and packed agglomeration of uniform nanoparticles.

Hexagonal tungsten bronzes are selective catalysts in the transformation of glycerol to acrolein. Increasing the Nb-content initially favors a higher selectivity to acrolein. The formation of heavy-compounds and carbon oxides, mainly related to higher concentration of Lewis acid sites, is observed at high Nb-contents.

On the contrary, increasing Nb content gives rise to higher yields to first and second condensation products in the valorization of aqueous organic fraction, (close to 70% of Total organic yield). These improved yields can be explained in terms of the specific acid properties of the catalysts. In this sense, the control of both the concentration of acid sites and the BAS/LAS ratio seems to be the key factors for improving the yield to intermediates (2M2P and C₅-C₈) and final (C₉-C₁₀) reaction products. The best catalytic performance has been observed for samples with a Nb/(W+Nb) atomic ratio higher than 0.53, the maximum total organic yield being found for a ratio of ca. 0.62 (which seems to present the optimum BAS/LAS ratio).

The effect of temperature of reaction in the valorization of aqueous organic fraction has also been studied, showing a decrease in the yield to intermediates at higher reaction temperatures, since second condensation reactions are favored. This leads to an increment in the yield to C₉-C₁₀ products. However, since higher temperatures also favor polymerization/over-condensation reactions, reaction conditions must be optimized. More importantly, the catalysts are stable under reaction conditions, maintaining their catalytic performance after several uses.

The W-Nb-O materials have shown higher stability than Ce-Zr oxide (reference catalyst) and show promising results for further research and application in this type of processes. Interestingly, the heavier fraction (C₅ to C₁₀ products) formed during light oxygenates condensation spontaneously forms a new upper-organic phase, which separates from aqueous phase, thus reducing further separation and processing costs.

In summary, W-Nb-O mixed oxides shows an outstanding catalytic performance in the aqueous phase transformation of both glycerol and short chain oxygenated compounds mixtures. More interestingly, W-Nb-O mixed oxide bronzes can be stated as very promising systems according to their tailored acid properties, especially for catalytic applications in which a specific Bronsted/Lewis acid sites ratio is necessary to improve the catalytic performance.

Conflict of interest

There are no conflicts to declare

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Table 1. Physicochemical Features of W-Nb-O Mixed Oxides Catalysts.

Sample	Nb/(W+Nb) atomic ratio in bulk solid ^a	Nb/(W+Nb) in the synthesis gel	S _{BET} (m ² g ⁻¹) ^b	Pore size (nm) ^c	Mesopore volume (cm ³ g ⁻¹) ^c	Concentration of acid sites (μmol _{py} g ⁻¹) ^d	Surface density of acid sites (μmol _{py} m ⁻²) ^d	BAS/LAS ^d
WNb-0	0.00	0.00	28	17.2	0.045	27.4	0.98	0.3
WNb-0.29	0.29	0.25	38	11.1	0.050	29.7	0.78	1.8
WNb-0.40	0.40	0.35	67	13.6	0.095	56.2	0.84	1.1
WNb-0.53	0.53	0.50	102	14.6	0.176	73.2	0.71	1.2
WNb-0.62	0.62	0.59	124	5.9	0.216	89.2	0.70	0.5
WNb-0.80	0.80	0.80	129	5.4	0.192	122.3	0.95	0.7
WNb-0.95	0.95	0.95	129	3.7	0.130	62.2	0.48	0.4
WNb-1	1.00	1.00	70	3.5	0.061	36.4	0.54	0.8

^a As determined by XEDS. ^b Calculated from N₂ adsorption isotherms. ^c Calculated by BJH method. ^d From FTIR of adsorbed pyridine.

Table 2. Catalytic Results in the Valorization of the Aqueous Model Mixture over W-Nb-O Catalysts at 180 °C. ^a

Sample	Total organic yield (%)	Conversion (%)				Selectivity (%)				Carbon balance (%)
		Acetol	Propanal	Ethanol	Acetic acid	C ₅ -C ₈	C ₉ -C ₁₀	2M2P ^b	Ethyl acetate	
WNb-0	49.2	100	61.2	40.4	17.2	19.5	8.6	38.1	33.8	96.5
WNb-0.29	51.5	100	77.8	38.0	15.2	21.2	8.8	38.7	31.3	94.8
WNb-0.53	62.2	100	84.5	43.4	13.3	18.5	13.3	40.2	28.0	92.1
WNb-0.62	68.4	100	90.1	47.2	17.8	17.6	14.3	42.3	25.8	96.7
WNb-0.80	65.2	100	84.0	36.7	19.9	13.3	15.7	45.2	25.7	97.1
WNb-0.95	64.6	100	89.7	43.3	13.7	11.4	13.9	46.3	28.4	96.4
WNb-1	61.2	100	80.3	40.9	18.1	16.3	14.2	41.8	27.7	95.6

^a Reaction conditions: aqueous model mixture (3.0 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar (under N₂) and 180 °C under continuous stirring during 7 h. ^b 2M2P = 2-methyl-2-pentenal.

Caption to Figures

Fig. 1. A) XRD patterns 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. Miller indices have been assigned according to the hexagonal WO_3 phase ($h\text{-WO}_3$ JCPDS: 00-33-1387). B) Projected structural model of the $h\text{-WO}_3$ structure along the [001] and [210] directions. C) Variation of c -axis as a function of Nb content.

Fig. 2. Raman spectra 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.

Fig. 3. (a) Electron diffraction ring pattern for the WNb-0.29 sample; (b) High resolution image showing a group of representative crystals of WNb-0.29; (c) Electron diffraction ring pattern for the WNb-0.53 sample; (d) High resolution micrograph showing several crystallites of this catalyst; (e) High resolution image showing one crystallite (pointed by the black arrow) in which fragments of the $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase can be recognized; (f) Projected structure model of $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ type phase along the [001] direction; (g) Electron diffraction ring pattern corresponding to the WNb-0.80 sample; (h) High resolution image showing several crystallites of WNb-0.80. Miller index in all diffraction patterns have been assigned on the basis of the HTB-type phase (ICDD: 00-33-1387).

Fig. 4. Acid features of W-Nb-O mixed oxides catalysts obtained by FTIR of adsorbed pyridine: a) Concentration of acid sites sites (in $\mu\text{mol}_{\text{py}} \text{g}^{-1}$); b) Surface density of acid sites (in $\mu\text{mol}_{\text{py}} \text{m}^{-2}$); and c) BAS/LAS ratio (BAS: Brönsted Acid Sites; LAS: Lewis Acid Sites).

Fig. 5. TPD- NH_3 profiles 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.

Fig. 6. Variation of the yield to the main reaction products (acrolein, CO_x and heavy-compounds) as a function of Nb content in catalyst. Reaction conditions: glycerol/ H_2O / O_2 /He molar ratio of 2/40/4/54, $T = 295^\circ\text{C}$, Contact time, W/F , of $81 \text{ g}_{\text{cat}} \text{ h} (\text{mol}_{\text{gly}})^{-1}$.

Fig. 7. Variation of the conversion of each reactant in the aqueous model mixture (i.e. acetol, propanal, ethanol and acetic acid) (a) and variation of selectivity to the main products (i.e. 2-methyl-2-pentenal, ethyl acetate, and C₅-C₈ and C₉-C₁₀ compounds) (b) as a function of Nb content in catalyst. Reaction conditions: Aqueous model mixture (3.0 g) and catalyst (150 mg) in autoclave-type reactor, at 13 bar N₂ and 180 °C under continuous stirring; time on stream of 7 h.

Fig. 8. Variation of yields to C₅-C₈ products (a) and C₉-C₁₀ products (b) with the Nb-content of catalysts during the reaction at 180 °C and 200 °C. Time on stream of 7 h.

Fig.9. Total organic yield during propanal self-aldol condensation on representative W-Nb mixed oxides. Reaction conditions: m_{CAT} = 50 mg; propanal-EtOH-H₂O weight ratio of 25/45/30 and a time of stream of 1h..

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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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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 C₉ 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%.

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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 °C, 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 °C.^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 N₂) 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.

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A **B** **C**

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 °C (P_{N_2} =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/H₂O wt% ratio of 25/45/30; weight of catalyst = 0.05 g. In autoclave-type reactor, at 13 bar N₂ and 200 °C 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 N₂ and 200°C 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 °C.

Table S6. Catalytic activity in the conversion of oxygenated compounds in aqueous model mixture of WNbO catalysts at 200 °C.^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 Reaction Conditions: aqueous model mixture (3.00 g) and catalyst (0.15 g) in autoclave-type reactor, at 13 bar N₂ and 200 °C 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/m²).