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Additional Information

V- and Nb-containing tungsten bronzes catalysts for the aerobic transformation of ethanol and glycerol. Bulk and supported materials

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Abstract

This work report the applicability of reflux to the synthesis of supported tungsten bronzes (i.e. W-V-O and W-Nb-O), using mesoporous KIT-6 as inert support. For comparison, the corresponding bulk materials prepared by reflux or by hydrothermal synthesis have been also prepared. The catalysts were characterized by several techniques (X-ray diffraction, N_2 adsorption, temperature programmed desorption (NH_3), and Raman and FTIR spectroscopies) and tested in the selective aerobic transformation of ethanol and glycerol. These results demonstrate the formation of V- and Nb-containing tungsten oxide bronzes in all of the heat-treated samples (bulk and supported materials), as well as the effective incorporation of metals (V or Nb) in the framework of tungsten bronzes. During the aerobic transformation of ethanol, diethyl ether and ethylene (in Nb-containing catalysts) and acetaldehyde, diethyl ether and ethylene (in V-containing catalysts) were the main reaction products, with very small formation of carbon oxides. During the aerobic transformation of glycerol, acrolein was mainly formed over Nb-containing catalysts, whereas acrylic acid, acrolein and CO_x were mainly observed over V-containing catalysts. The differences between bulk and supported catalysts have been explained according to changes in their physico-chemical properties: V-containing catalysts presenting both acid and redox sites; and Nb-containing catalysts presenting acid sites. In this way, supported materials seems to be effective in both redox and acid reactions due to the small modifications of the acid characteristics of catalysts.

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1. Introduction

Catalytic science goes hand in hand with industrial and environmental needs and challenges. In fact, catalysis plays a key role in all the chemical industry [1, 2], and in the recent decades great attention has been paid to issues concerning the production of olefins. In this context, light olefins constitute one of the most important raw materials for the petrochemical industry, especially ethylene and propylene [3, 4]. They are widely used as building blocks in polymer industry (e.g. polyethylene and polypropylene production), but also as precursors of commodity chemicals, such as ethylene oxide, propylene oxide, 1,2-dicholoroethane, acrolein, acetic acid, acrylic acid, or ethylbenzene among others [5]. However, ethylene and propene are mainly obtained via steam cracking and/or fluid catalytic cracking (FCC), which are high-energy demanding processes [6, 7]. Since both propylene and ethylene markets are steadily expanding and growing each year, several strategies have been proposed to cope with the increasing demand, such as maximizing the selectivity to light olefins in the current processes [8]. Besides alternative processes for the production of olefins, such as DH and ODH of light alkanes [4, 7], another possibility could consist in producing either the olefins or their corresponding derived platform molecules from cleaner bio-based renewable feedstocks. In this sense bio-alcohols like ethanol (obtained through fermentation processes) or glycerol (a by-product in the transesterification of fatty acids in biodiesel production) represent interesting molecules from the sustainable chemistry point of view [9, 10]. Depending on the catalytic system, ethanol can be transformed into ethylene and/or diethyl ether via acid catalysis [11, 12], or into partial oxidation products such as acetaldehyde or acetic acid, via redox catalysis [13, 14]. On the other hand, glycerol can efficiently be transformed into basic chemical products, such as acrolein (using acid catalysts) [15, 16, 17, 18], or into acrylic acid (using

multifunctional acid-redox materials) [19-23]. Over the last years a great deal of interest has been focused on the catalytic properties of partially reduced non-stoichiometric W-based oxides, also known as tungsten bronzes. They constitute very interesting materials when the aim is attaining different chemical functionalities for specific applications, since they can accommodate a great amount of elements in different oxidation states within their framework [20, 24-28]. Indeed, these phases with catalytic interest, which are commonly obtained by hydrothermal synthesis, have already been proposed as active and selective materials in the aerobic transformation of glycerol to acrolein and acrylic acid [19-21, 24-28]. Despite they show an interesting reactivity, they usually display relatively low surface areas, and studies concerning alternative synthesis methods or supported materials are scarce.

Herein we report the novel synthesis of Nb- and V-containing tungsten bronzes by a reflux method. This method has permitted also to successfully support the Nb- and V-containing tungsten oxides bronzes on a mesoporous KIT-6 silica. In addition, their catalytic properties in the aerobic transformation of ethanol and glycerol are presented and compared with the ones obtained with conventional hexagonal tungsten bronzes prepared hydrothermally. Finally, the effect of the support on the acid properties and their catalytic performance is inferred.

2. Experimental

2.1 Synthesis of the catalysts

The mesoporous support KIT-6 was synthesized using Pluronic P123, n-butanol and TEOS according to the method described elsewhere [29].

W-Nb-O catalyst was prepared from an acidified aqueous solution of ammonium metatungstate hydrate ($\geq$85 wt% WO_3, Sigma-Aldrich) and niobium oxalate

monooxalate adduct (ABCR) (W/Nb/H_2O molar ratio = 1/0.3/64), which was kept under reflux for 48 h at 150 ºC (**Nb-W-r**). For the preparation of supported W-Nb-O catalyst (**NbW/KIT6**), mesoporous KIT-6 was added to the above solution after the reflux treatment, and kept under stirring for 2h at ambient temperature. Finally, solutions were removed using a rotary evaporator and the solids (both bulk and supported materials) were dried at 100 ºC overnight and heat-treated at 400 ºC under N_2 flow for 2 h.

W-V-O catalyst was obtained from an acidified aqueous solution of ammonium metatungstate hydrate and vanadium oxide sulfate (97%, Sigma Aldrich), which was kept under reflux at 150 ºC for 48 h (W/V/H_2O molar ratio = 1/0.3/64). Then the solid was filtered off and washed with deionized water (**V-W-r**). To obtain the supported W-V-O catalyst (**VW/KIT6**), as-synthesized **V-W-r** was suspended in 50 mL of deionized water. Then mesoporous KIT-6 was added to the suspension and kept under stirring for 2h at ambient temperature. Both solutions were rotary evaporated and the solids were dried at 100 ºC overnight. Finally, both bulk and supported catalysts were heat-treated at 500 ºC under N_2 flow for 2 h.

For comparison, hydrothermally synthesized W-Nb-O and W-V-O catalysts (i.e. **WNb-H** and **WV-H** respectively) were prepared following the method reported elsewhere [19, 24]. The samples were finally heat-treated at 550ºC under N_2 for 2 h.

2.2 Catalysts Characterization

BET-surface areas were achieved, from N_2 adsorption isotherms, in a Micromeritics ASAP 2000. Samples were degassed in-situ under vacuum at 400 ºC prior to adsorption.

Powder X-Ray diffraction (XRD) profiles were collected in a PANalyticalX´Pert PRO diffractometer with an X´Celerator detector in Bragg-Brentano geometry, using CuKα radiation.

Scanning electron microscopy (SEM) images were collected using a field emission ZEISS Ultra-55 electron microscope. Micrographs were obtained at an accelerating voltage of 12 kV.

Raman spectra were collected using a 514 nm exciting wavelength in an inVia Renishaw spectrometer equipped with an Olympus microscope and a Renishaw HPNIR laser. Power on the sample was about 15 mW.

Infrared spectra in the 400-4000 cm^{-1} region were acquired at room temperature with a Nicolet 205xB spectrophotometer at a spectral resolution of 1 cm^{-1} and 128 accumulations per scan. Samples were previously milled and mixed with spectroscopic grade KBr and pressed into pellets.

Temperature-programmed desorption of ammonia (NH_3-TPD) experiments were performed in a Micromeritics TPD/2900 instrument, where 100 mg of catalyst were pretreated at 350 ºC for 1 h in a He stream. Chemisorption of ammonia was carried out by pulses at 100ºC until equilibrium was reached. Then samples were fluxed with a He stream for 15 min, prior to increasing temperature up to 600ºC in a He stream of 100 mL min^{-1} at a heating rate of 10 ºC min^{-1}. Ammonia desorption was monitored by mass spectrometry, following the characteristic NH_3 mass of 15 a.m.u., and by a thermal conductivity detector (TCD).

2.3 Catalytic tests

Gas phase aerobic transformation of glycerol was carried out at atmospheric pressure in a fixed-bed reactor at a contact time, W/F, of 81 g_{cat}h $(mol_{glycerol})^{-1}$, in the range of 280-

350 °C, using a reaction mixture glycerol/water/oxygen/helium with a molar ratio of 2/40/4/54. The effluent stream was bubbled through a condenser device at 0-3 ºC, while the remaining gaseous stream containing mainly carbon oxides and oxygen was analyzed by an online gas chromatograph equipped with: (i) molecular sieve 5Å (3m length); and (ii) Porapak Q (3 m). The condensed aqueous solution containing all the reaction products and the unconverted glycerol were analyzed by gas chromatography using a Varian 3900 chromatograph equipped with a 100% dimethylpolysiloxane capillary column (100 m x 0.25 mm x 0.5).

The gas-phase aerobic transformation of ethanol was carried out in a fixed-bed quartz reactor at atmospheric pressure at temperatures in the range of 180-350 °C, using contact times, W/F, of 6.8-13.6 g_{cat}h $(mol_{ethanol})^{-1}$, using a reactant mixture of ethanol/oxygen/nitrogen with a molar ratio of 6/13/81. The analysis of reactants and products was carried out by gas chromatography, using two different columns: i) Molecular sieve 5Å (3m length) and ii) RT-U bond (30 m, 0.53 i.d.).

3. Results and discussion

3.1. Characterization

Table 1 summarizes the main physicochemical characteristics of the catalysts. In the case of Nb-containing catalysts, the sample prepared by reflux presented a higher surface area than the corresponding material prepared hydrothermally: 82 m^2/g and 38 m^2/g for **Nb-W-r** and **WNb-H**, respectively. This can be due to the different heat-treatment temperature used in the final activation of catalysts. However, for V-containing samples, both hydrothermal and reflux procedures give rise to similar specific surface areas, 25 and 31 m^2/g for **V-W-r** and **WV-H** samples, respectively. Interestingly, when oxides obtained through reflux method are supported on

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mesoporous KIT-6, surface area of resulting materials drastically increases, especially in **VW/KIT6** sample (358 m^2/g), although this behavior corresponds mainly to the characteristics of the support. In this sense a decrease in the pore volumes of supported materials is observed when comparing with the pure support (Fig. S1, A, Table S1, Supporting Information), which is accompanied by the loose of the narrow pore distribution of the original KIT-6 (Fig. S1, B, Supporting Information). Despite this, supported catalysts still present some remaining mesoporosity, what explains their relatively high surface area with respect to unsupported materials (Table S1, Supporting Information).

XRD patterns of unsupported and supported catalysts are shown in Figure 1. It is noteworthy to mention that, despite a crystalline mesoporous KIT-6 support was used [29], the ordered mesoporous structure collapses after the preparation of the supported catalysts (Fig.S1, C, Supporting Information). All Nb-containing materials present diffraction signals corresponding to a hexagonal tungsten bronze-type structure (HTB) (JCPDS: 85-2460), regardless of the synthesis method used (Fig.1, a-c). This structure is characterized by the presence of MO$_6$ octahedra that share their vertices along the three crystallographic directions, displaying hexagonal and trigonal channels along c-axis [30]. It has been reported that the presence of ammonium ions inside the channels of bronze-based structures can give rise to Brönsted acid sites when they are released after thermal treatments [31].

On the other hand, V-containing materials present different crystalline phases depending on the synthesis method (Fig.1, d-f). Hydrothermally synthesized **WV-H** catalyst shows Bragg signals corresponding to HTB structure (Fig.1A, f). However, **V-W-r** and **VW/KIT6** (obtained by reflux) show only two clear diffraction peaks, corresponding to 001 and 002 planes in the HTB phase (c = 3.9 Å), although broad

bands centered at ca. 27, 35, 50 and 56 ° are also observed (Fig.1A, patterns d and e) [19]. These features can be related to an amorphization (or low crystallization) process occurring along the a-b plane of the crystal structure. This amorphization could be a consequence of the synthesis procedure, since the continuous stirring of the solution during the reflux treatment could inhibit the crystal growth in those directions.

In order to corroborate these findings, samples where studied by scanning electron microscopy (SEM) (Fig.2). In the case of Nb-containing samples, all the catalysts display the same platelet-like particles aggregates (Fig.2, a-c), although reflux synthesized materials, both unsupported and supported catalysts, show a particle size lower than that of **WNb-H** sample. Also, spheres of KIT-6 are clearly observed in supported **VW/KIT6** sample, which show a homogeneous distribution of the active phase on the mesoporous silica surface (Fig. 2, b). On the other hand, V-containing materials show important differences in their morphologies depending on the synthesis procedure (Fig.2, d-f). W-V-O mixed oxide prepared by hydrothermal synthesis (**WV-H** sample), presents rod-shape crystals (Fig.2, f). However, cauliflower-shaped particles were observed in samples prepared by reflux (Fig.2, d), which were also homogenously distributed on the surface in the supported **VW/KIT6** sample (Fig.2, e). Therefore, these results suggest that reflux method could hinder the growth of 1D crystals, resulting in a lower crystallization degree, thus giving rise to a pseudo-crystalline structure, as observed by X-ray diffraction, especially in vanadium-containing materials.

Vibrational spectroscopy studies have been carried out to elucidate the nature of the metal-oxygen bonds in the heat-treated materials (Fig.3). Figure 3A shows Raman spectra of supported and unsupported catalysts. Nb-containing materials display two main Raman bands at 705 and 790 cm^{-1}, which can be respectively ascribed to O-M-O (M= Nb, W) and O-W-O stretching vibrations in the MO$_6$ octahedral framework of the

hexagonal tungsten bronze (Fig.3A, spectra a to c). Also a low intensity broad band centered at ca. 956 cm^{-1} is observed, which can be attributed to M=O stretching vibrations (M: W, Nb) [30, 32]. With respect to V-containing catalysts (Fig.3A, spectra d to f), Raman bands at 695 and 801 cm^{-1} corresponding to W-O-M (M: W, V) and W-O-W bond vibrations are observed, that are slightly shifted to higher frequencies comparing with Nb materials. In addition, the relative intensity of the signal at 900 cm^{-1} increases notably, which can be attributed to the presence of V=O stretching type vibrations [24]. Interestingly, this Raman band at 982 cm^{-1} in W-V-O catalysts displays a higher relative intensity in **V-W-r** and **VW/KIT6** samples (Fig.3A, spectra d and e), which are also amorphous in the a-b plane of the crystal structure (Fig.1A, patterns d and e), suggesting the presence of a higher amount of V=O species in these catalysts. Indeed, this is also observed in the corresponding FTIR spectra (Fig.3B), in which **V-W-r** and **VW/KIT6** materials present an additional band around 910 cm^{-1}, which can be ascribed to these V=O stretching vibrations (Fig.3B, spectra d and e). In addition, all the spectra show typical signals of tungsten bronze-type materials at 814, 747, 653 and 554 cm^{-1}[24, 25] (Fig.3B, spectra a-f), with extra signals at 1182, 1079, 970, 802 and 459 cm^{-1} in the supported materials, related to the Si-O bond vibrations of the siliceous support [34].

Acid features of the catalysts have been studied by means of TPD-NH$_3$ (Table 1) (Fig.4). The mesoporous KIT-6 support was previously evaluated and exhibited no appreciable acid features, and therefore has been considered as an inert support (Table 1; Fig.S2). In the case of Nb-containing materials, **Nb-W-r** and **NbW/KIT6** catalysts show a number of acid sites per gram of catalyst higher than that of **WNb-H** sample. However, taking into account their surface area, the density of surface acid sites decreases as follows: **WNb-H** = **Nb-W-r** > **NbW/KIT-6** (Table 1). As expected,

supported catalyst displays the lowest density of acid sites, however significant differences in the strength of the acid centers are observed (Fig.4, patterns a-c). In this sense, the catalysts present three main contributions to the TPD-NH$_3$ profile at low (ca. 215 ºC), medium (ca. 300 ºC) and high (ca. 440 ºC) temperatures, which can be ascribed to acid sites with low, medium and high acid strength respectively. According to these results, it can be concluded that **Nb-W-r** (Fig.4, a) shows a contribution of acid sites with medium/high acid strengths higher than those observed for **WNb-H** (Fig.4, pattern c). Interestingly, when comparing unsupported and supported materials, it can be observed that when **Nb-W-r** is supported on KIT-6 (**NbW/KIT6** sample), the relative intensity of these two desorption signals decreases, increasing the low strength acid sites ratio in the catalyst (Fig.4, b). This trend is also observed in V-containing catalysts (Fig.4, d-f), in which **VW/KIT6** displays the highest contribution in the low temperature region (ca. 190 ºC) (Fig.4, e), even higher than that observed in **WV-H** obtained through hydrothermal procedure (Fig.4, f). Indeed, **V-W-r** shows the highest concentration and density of acid sites, which decrease when it is supported on KIT-6 (i.e. **VW/KIT6** sample), likely due to the loss of these medium-high acid strength species (Table 1). Again, the lowest density of acid sites is observed for the supported catalyst, which is 10 and 20 times lower than that obtained in **WV-H** and **V-W-r** materials respectively (Table 1). Accordingly, these findings show that materials synthesized by reflux method show higher number of medium and high strength acid sites than those obtained hydrothermally (i.e. **WNb-H** and **WV-H**). The proportion of this medium-high strength acid centers can be reduced supporting the bronze phases on mesoporous KIT-6, also giving rise to a lower density of acid sites on the surface. However, as observed also in the case of catalysts prepared hydrothermally, both

unsupported and supported oxide bronzes present lower number of high strength acid sites than that observed for pure tungsten oxide bronze (h-WO$_3$) [24, 25].

3.2. Catalytic tests

3.2.1. Aerobic gas-phase transformation of ethanol

Figures 5 and 6 shows the catalytic results achieved during the aerobic transformation of ethanol over Nb- and V-containing catalysts, respectively. In the case of Nb-containing catalysts (Fig. 5), diethyl ether (Fig. 5B) and ethylene (Fig. 5C) were the main reaction products; with the appearance of acetaldehyde or carbon oxides as minorities (the sum of acetaldehyde and CO$_x$ was lower than 6%). Very small differences in both ethanol conversion and selectivity to the main reaction products have been observed in the three catalysts (i.e. **Nb-W-r**, **WNb-H** and **NbW/KIT6**) confirming that metal oxides bronzes, both unsupported and supported ones, can be prepared also by reflux of the corresponding aqueous solutions. However, since the amount of metal oxide bronze per weight of catalysts in **NbW/KIT6** sample was about 80% with respect to bulk samples, we can conclude a higher efficiency for ethanol transformation in the case of supported materials. Probably, the lower crystal sizes of metal oxide bronzes favor the higher catalytic activity for this material. In addition, the effective incorporation of Nb atoms in the framework of bronzes in the three catalysts, as concluded from the characterization results, explain the similar behavior observed in ethanol transformation.

In addition, it has been observed that the diethyl ether/ethylene ratio changes with the ethanol conversion (Fig. S3-supporting information), suggesting that ethylene is formed on our Nb-containing catalysts by both parallel and consecutive reactions. In fact, it is well known that the dehydrated products of ethanol are ethylene (via intramolecular

reaction) and diethyl ether (via intermolecular dehydration reaction); the intramolecular reaction favored at reaction temperature higher than that used for the intermolecular dehydration reaction [11, 12, 35-37].

We can also notice that very small differences in the diethyl ether/ethylene ratio are observed among the Nb-containing catalysts, when comparing the selectivity to main reaction products at an ethanol conversion of 30 or 80% (see Fig. S1, supporting information). This suggests that, independently of the catalyst preparation method, the strength of acid sites is similar in all cases. However, we would like to inform that the diethyl ether/ethylene ratio for Nb-containing catalysts is higher than that observed for pure tungsten oxide bronze (h-WO_3) (Fig. S3, supporting information). Thus, for ethanol conversion of 80%, selectivity to ethylene of 62, 50 and 48% have been achieved on **WNb-H**, **Nb-W-r**, **NbW/KIT6** catalysts, respectively (Fig. S3, supporting information), whereas, a selectivity to ethylene of ca. 82% was observed on pure h-WO_3 at the same conversion of ethanol (Fig. S4, supporting information). Accordingly, the catalytic results presented here confirm that the density of strong of acid sites in Nb-containing catalysts seems to be lower to that achieved on pure h-WO_3, which agrees to previous results over this type of catalysts [19, 24].

On the other hand, the catalytic results during the ethanol aerobic transformation over V-containing catalysts indicate the presence of both redox (in the formation of acetaldehyde) and acid sites (in formation of ethylene and diethyl ether) in all catalysts (Fig. 6). We must inform that in addition to the main reaction products (i.e. acetaldehyde, ethylene and diethyl ether) other reaction products such as acetic acid and ethyl acetate (specially over V-W-r catalyst) were observed as minorities. However, in the reaction conditions studied here, the formation of carbon oxides (CO and CO_2) was lower than 3%.

Figure 6 shows the variation of ethanol conversion with reaction temperature for V-containing catalysts (Fig. 6 A) and the selectivity to acetaldehyde (Fig. 6 B), ethylene (Fig. 6 C) and diethyl ether (Fig. 6 D) with the reaction temperature. At low conversion, acetaldehyde and diethyl ether were mainly formed (with small presence of ethylene). However, at high ethanol conversion ethylene was mainly formed (with small presence of diethyl ether). This behavior is similar to that observed for Nb-containing catalysts in which diethyl ether/ethylene ratio decreases when increasing the ethanol conversion (Fig. 5 and Fig. S3).

For the formation in redox sites, acetaldehyde is mainly formed at low ethanol conversion, but it is partially transformed into acetic acid and ethyl acetate at high conversion of ethanol (especially in the case of **V-W-r** sample). This fact suggests that the higher acid strength of V-W-r catalyst could promote the esterification of acetaldehyde and/or acetic acid to ethyl acetate at higher temperatures. Also the formation of acetic acid at high conversion can follow different routes in which ethanol, acetaldehyde and/or ethyl acetate can be oxidized on surface redox sites. Thus, small modifications in both the nature and the density of redox/acid sites can be proposed in the case of V-containing catalyst.

3.2.2. Aerobic gas-phase transformation of glycerol

Both Nb- and V-containing catalysts were tested also in the gas-phase dehydration and oxidehydration of glycerol respectively (Figs. 7 and Fig. 8). It is well-known that selecting the appropriate catalytic system it is possible to selectively transform glycerol into acrolein (using a monofunctional acid catalyst, such as W-Nb bronzes) or into acrylic acid (using bifunctional acid-redox catalyst, like W-V bronzes) [24]. Recently,

our group has reported an in-depth study into the mechanism of the one-pot oxidehydration of glycerol by V-based catalysts that points out the role of the acid and redox functions in the consecutive reaction steps [38]. Specifically, it shows the importance of tuning up the acid features of the catalysts (mainly strength and density of acid sites) to prevent secondary oligomerization and over-oxidation reactions, that produce mainly carbon oxides and heavy compounds (oligomers and ketals) [19, 38]. In this sense, materials with optimum acid features are required, i.e., they must present acid sites with sufficient strength and density to perform the dehydration step into acrolein, but not too strong or too close together to block the desorption of intermediates and products (i.e. acrylic acid and/or acrolein), which would favor undesired consecutive reactions.

Figure 7 shows the catalytic performance of Nb-containing catalysts in the gas-phase dehydration of glycerol. Indeed Nb-substituted tungsten bronzes constitute one of the most selective acid catalyst for the gas-phase dehydration of glycerol into acrolein reported in the literature [20, 39]. Thus, all the prepared materials show yields to acrolein over 70 % at ca. 300 ℃ (at conversions of glycerol in the range 99.5-100 %) (Fig. 7, a, c and e), which decreases when increasing reaction temperature, mainly due to the increasing amounts of carbon oxides formed (Fig. 7, b, d and f). **Nb-W-r** catalyst displays the highest yield to carbon oxides and heavy compounds, which is traduced in a lower selectivity to acrolein (71 %) (Fig. 7, a and b). However, for **NbW/KIT6** catalyst, the selectivity to both by-products slightly decreases (Fig. 7 d) and consequently, a concomitant increment in the yield to acrolein is observed (78 %) (Fig. 7c). The highest yield to acrolein was achieved with hydrothermally synthesized **WNb-H** sample (83 %) (Fig. 7 e), which also presents low amounts of heavy compounds, but specially a lower yield to carbon oxides (Fig.7f). These catalytic results can be

explained in terms of the specific acid properties of the materials. As previously stated, the acid strength of **Nb-W-r** decreases when it is supported on mesoporous KIT-6. This fact could explain the slightly higher acrolein production over **NbW/KIT6**, principally due to the lower number of side-reactions, as a consequence of an enhanced desorption of the product. Therefore, **WNb-H**, which presents the lowest acid strength, shows the highest yield to acrolein.

Figure 8 shows the catalytic results for V-containing catalysts in the one-pot oxidehydration of glycerol. In this case the reaction takes place in two main stages: i) glycerol dehydration into acrolein in acid sites and ii) oxidation of acrolein into acrylic acid via redox sites (V^{+4}/V^{+5}). It is worth insisting that specific acid features will play an important role in both reaction steps, as adsorption-desorption of intermediates and products during the catalytic cycle is governed fundamentally by the strength and distribution of the acid sites on the surface. Interestingly, the highest yields to acrylic acid for **V-W-r** and **VW/KIT6** are attained at higher temperatures (327 ºC) (Fig. 8, a and c) comparing to **WV-H** (300 ºC) (Fig. 8 e)**.** In fact **WV-H** appears to be the most active catalyst, showing the maximum total yield to acrolein and acrylic acid ($Y_{(AC+AA)}$ = 44%, T = 300 ºC). Also, an increment of reaction temperature favors the formation of increasing amounts of carbon oxides in all the cases, showing 5-20 % yield to heavy compounds in all the range examined (Fig. 8, b, d and f). Regarding the highest yields to acrylic acid, **VW/KIT6** has resulted to be the most selective catalyst (S_{AA}= 31%), showing a selectivity even higher than **WV-H** (S_{AA}= 26 %), and much better than **V-W-r** (S_{AA}= 19 %). Again, acid strength seems to play a key role in the catalytic performance, as the highest selectivity is achieved with the catalyst presenting the lowest acid strength and density of acid sites. In fact, **V-W-r** enhances it selectivity to acrylic acid in 12 points when it is supported on KIT-6 (**VW/KIT6**) (Fig. 8, a and c),

probably as a result of the loss of high and medium strength acid sites (Fig. 4, patterns d and e). Despite this, the influence of specific vanadium species in the pseudocrystalline phase on selectivity to acrylic acid cannot be ruled out. In fact, according to Raman and FTIR results, the number of $V^{5+}=O$ species in catalysts prepared by reflux (both unsupported and supported) is higher than that observed on sample prepared hydrothermally. These could facilitate more efficiently the formation of acrylic acid than the pure HTB phase [19,38].

4. Conclusions

In conclusion, we have reported, for the first time, the synthesis of bulk Nb- and V containing metal oxide tungsten bronzes by using a reflux procedure. This method has resulted also effective for the preparation of the corresponding supported catalysts, using mesoporous KIT-6 as support. The characterization results confirm the effective incorporation of Nb- and V-atoms in the framework of HTB crystals, with the presence of acid sites (Nb-containing catalysts) and both redox/acid sites in V-containing catalysts.

The catalytic tests for both ethanol and glycerol aerobic transformation for bulk catalysts prepared by reflux indicate a catalytic behavior similar than those observed for the corresponding materials prepared hydrothermally. The same conclusion can be also proposed for the main results achieved over V- and Nb-containing tungsten bronzes supported on KIT6. In addition, a higher selectivity to acrylic acid from glycerol is observed on supported W-V-O catalyst (named as VW/KIT6).

It has been previously proposed the one-pot aerobic transformation of glycerol to acrylic acid requires [19, 38]: i) Brönsted acid sites with medium acid strength for the selective

transformation of glycerol to acrolein; ii) octahedral VO_6 sites, in the framework of tungsten bronze, for the selective in oxidation of acrolein to acrylic acid; iii) the elimination of strong acid sites, which could be involved in the consecutive reactions of both acrolein and acrylic acid.

According to our results, we can conclude that in the case of supported catalysts, the small crystal size of V-containing tungsten bronze could favor a higher interaction with support, decreasing both the number of the strong acid sites and the degradation of acrolein and acrylic acid during the selective transformation glycerol.

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Caption to figures

Fig.1. XRD patterns of Nb-containing (a-c) and V-containing (d-f) catalysts: a) **Nb-W-r**; b) **NbW/KIT6**; c) **WNb-H**, d) **WV-r**; e) **VW/KIT**6; and f) **WV-H**.

Fig.2. SEM images of Nb-containing (a-c) and V-containing (d-f) catalysts: a) **Nb-W-r**; b) **NbW/KIT6**; c) **WNb-H**, d) **WV-r**; e) **VW/KIT**6; and f) **WV-H**.

Fig.3. Raman (A) and FTIR (B) spectra of the catalysts: a) **Nb-W-r**; b) **NbW/KIT6**; c) **WNb-H**, d) **WV-r**; e) **VW/KIT**6; and f) **WV-H**. For comparison, the FTIR spectrum of pure **KIT-6** (g) has been also included.

Fig.4. NH_3-TPD profiles (m/z = 15) of Nb-containing (a-c) and V-containing (e-f) catalysts: a) **Nb-W-r**; b) **NbW/KIT6**; c) **WNb-H**, d) **WV-r**; e)**VW/KIT**6; and f) **WV-H**.

Fig. 5. Variation of ethanol conversion with reaction temperature (A) and variation of selectivity to diethyl ether (B) and ethylene (C) with ethanol conversion achieved during the ethanol aerobic transformation over Nb-containing catalysts: **Nb-W-r (♦)**; **NbW/KIT6 (▲)**; **WNb-H (◨)**.

Fig. 6. Variation of ethanol conversion with reaction temperature (A) and variation of selectivity to acetaldehyde (B), to ethylene (C) and to diethyl ether (D) with ethanol conversion achieved during the ethanol aerobic transformation over V-containing catalysts: **V-W-r (●)**;**VW/KIT6 (▼)**;**WV-H (◨)**.

Fig. 7. Yield to acrolein (AC, blue), acrylic acid (AA, red), heavy compounds (HC´s, orange) and carbon oxides (CO_x, black) as a function of the reaction temperature in the dehydration of glycerol using Nb-containing catalysts: a-b) **Nb-W-r**; c-d) **NbW/KIT6**; and e-f) **WNb-H**. Acrylic acid (AA); Acrolein (AC); carbon oxides (CO_x); and Heavy compounds (HC).

Fig. 8. Yield to acrolein (AC, blue), acrylic acid (AA, red), heavy compounds (HC´s, orange) and carbon oxides (CO_x, black) at different reaction temperatures in the oxidehydration of glycerol using V-containing catalysts: a-b) **V-W-r**, c-d) **VW/KIT6,** and e-f) **WV-H**. Acrylic acid (AA); Acrolein (AC); carbon oxides (CO_x); and Heavy compounds (HC).

Table 1. Physicochemical characteristics of bulk and supported Me-W-O metal oxides bronzes (Me= Nb or V).

Catalyst	Synthesis method	Atomic Composition [a]				Surface area [b]	TPD-NH$_3$ [c]		Crystalline phase
		Si	W	Nb	V	(m^2 g^{-1})	μmol_{NH3} g^{-1}	μmol_{NH3} m^{-2}	(XRD)
KIT-6	Hydrothermal	100	---	---	---	971	10	0.01	KIT-6
WNb-H	Hydrothermal	---	0.71	0.29	---	38	139	3.6	h-WO$_3$
Nb-W-r	Reflux	---	0.74	0.26	---	82	308	3.7	h-WO$_3$
NbW/KIT6	Reflux/Supported	0.46	0.39	0.15		179	332	1.8	h-WO$_3$
WV-H	Hydrothermal	---	0.82	---	0.18	31	102	3.29	h-WO$_3$
V-W-r	Reflux	---	0.78	---	0.22	25	151	6.04	Pseudocrystalline
VW/KIT6	Reflux/Supported	0.85	0.12	---	0.03	358	107	0.30	Pseudocrystalline

a) Calculated by Energy-Dispersive X-Ray Spectroscopy (EDS); b) Obtained by BET method using N$_2$-adsorption isotherms; c) TPD-NH$_3$: Temperature programmed desorption of ammonia.

Supporting information

Table S1: Textural properties of the support and prepared catalysts

Sample	Total pore volume (cm^3 g^{-1})	Mesopore Volume (cm^3 g^{-1}) [a]
KIT-6	1.58	1.44
VW/KIT-6	0.41	0.32
NbW/KIT-6	0.31	0.20
V-W-r	0.07	0.02
Nb-W-r	0.15	0.08

a. Calculated by BJH method

Fig. S1. N2-adsorption isotherms (A), pore size distribution calculated by BJH method (B) and small-angle XRD patterns (C) of as-prepared KIT-6 and unsupported and/or supported catalysts.

Fig. S2. TPD-NH$_3$ profiles of KIT-6 support and supported Nb- and V- containing catalysts.

Fig. S3. Variation of the selectivity to the main reaction products (DEE, ethylene and acetaldehyde) at ethanol conversion of 30% (left) and 80% (right) achieved during the ethanol aerobic transformation over Nb-containing catalysts: **WNb-H**; **Nb-W-r**; and **NbW/KIT6**.

Fig. S4. Variation of the selectivity to the main reaction products (DEE, ethylene and acetaldehyde) at ethanol conversion of 30, 50 and 80%, achieved during the ethanol aerobic transformation over **h-WO$_3$**, i.e. hexagonal tungsten bronze.

Fig. S5. Variation of the selectivity to the main reaction products (DEE, ethylene, acetaldehyde, Acetic acid and Ethyl acetate) at ethanol conversion of 30% (left) and 80% (right) achieved during the ethanol aerobic transformation over V-containing catalysts: **WV-H**; **V-W-r**; and **VW/KIT6**.