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Additional Information

**Promoted hexagonal tungsten bronzes as selective catalysts in the aerobic transformation of alcohols: glycerol and methanol**

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## **Abstract**

M-containing tungsten oxide bronzes (M= Ti, Nb or V) in Hexagonal Tungsten Bronzes (HTB) structure have been investigated as catalysts for the aerobic transformation of glycerol and methanol. The catalysts were prepared hydrothermally and characterized by several physico chemical techniques, i.e. N<sub>2</sub>-adsorption, XRD, Raman spectroscopy and temperature programmed desorption of ammonia. Interesting variations in the thermal stability of the HTB-framework were observed according to the element introduced into the oxide structure. In addition, the incorporation of Ti and Nb modified the acid features of the hexagonal tungsten oxides, whereas V introduced new redox sites. The catalytic results for the aerobic transformation of glycerol and methanol in terms of conversion and nature of reaction products are discussed on the basis of the physico-chemical characteristics of catalysts.

**Key words:** metal oxides, bronze, tungsten, vanadium, titanium, niobium, aerobic transformation, methanol, glycerol

## 1. Introduction

Promoted mixed metal oxides bronzes have attracted the attention in the last years since they are effective catalysts in acid and oxidation reaction [1-4]. As suggested recently, redox and acid–base properties of metal oxides can be strongly changed by tailoring composition and catalyst preparation procedure which determines not only crystal sizes but also the local structure and the electronic/catalytic properties [3].

Metal oxide bronzes present a variety of physical and chemical properties. They can be ternary compounds of the type  $A_xM_yO_z$  in which M is a transition metal (Mo, W, V, Nb, Ta, Ti, ..) and A is an alkali, alkaline earth or  $NH_4^+$  ion [5, 6], and seem to be of interest as catalysts and photocatalysts [7-20].

In the case of molybdenum oxide-based bronzes, the isomorphous incorporation of other elements such as V, W or Nb, modifies the physical-chemical and catalytic properties, and in some cases the thermal stability [7-13]. This is the case of Mo-based materials presenting tetragonal  $Mo_5O_{14}$  [7,8], tetragonal tungsten bronze (TTB) [9] or the MoV-based orthorhombic structure, the so-called M1 phase [1, 4, 13]. In all of these cases, the partial substitution of Mo by other transition metals such as V, W or Nb, strongly improves their catalytic behavior in the partial oxidation of acrolein to acrylic acid [7,8], olefins to aldehydes and acids [9], (amm)oxidation of propane to acrylonitrile and acrylic acid [1, 4, 10-12], or in the oxidative dehydrogenation of ethane to ethylene [13].

Tungsten-based bronzes have been proposed as effective materials [5] but they have been less studied in catalysis. Thus, tungsten bronzes crystals have been proposed as supports [20], catalysts [15-19] and photocatalysts [14a]. One interesting application is the use of multicomponent tungsten-based bronzes as selective catalysts in the one-pot oxidative

transformation of glycerol to acrylic acid [15-18], in which both redox and acid sites are required for selective catalysts [16, 18].

On the other hand, the catalytic aerobic methanol transformation can be used for determining both redox and acid sites in metal oxides [21, 22]. Accordingly, it could be used for determining in situ both characteristics, during the reaction, in M-containing tungsten oxides bronzes in order to comparatively determine changes in catalytic properties.

In this paper we present the synthesis and characterization of promoted tungsten oxide with hexagonal tungsten bronze (HTB) structures, using Nb, Ti and V as promoters. In addition, their catalytic performance in the aerobic selective transformation of both glycerol and methanol will be shown in order to evaluate both redox and acid sites. In the first case, the oxidation reaction is involved in the consecutive reaction occurring on the intermediately formed acrolein, whereas in the second case, it is possible to study both acid and redox characteristics because both reactions type occur directly on methanol. Thus, additional information can be achieved when using both catalytic reactions.

## **2. Experimental**

### ***2.1 Synthesis of catalysts***

The materials were prepared hydrothermally at 175°C for 48 h from gels obtained from the aqueous solution of corresponding salts: ammonium metatungstate hydrate ( $\geq 85$  wt%  $\text{WO}_3$  basis, Sigma-Aldrich), vanadium (IV) oxide sulfate hydrate ( $\geq 99.99\%$ , Sigma-Aldrich), niobium oxalate (mono-oxalate adduct, ABCR), and titanium (IV) ethoxide (Sigma-Aldrich) with a W/M molar ratio in gel of 1/(0.1-0.4). Then the solid was washed and dried at

100°C overnight. Lastly, the solid was heat-treated in N<sub>2</sub> between 450-750°C for 2 h. More details on the preparation have already been reported elsewhere [15,16].

## ***2.2 Catalysts characterization***

Surface areas were obtained from N<sub>2</sub> adsorption isotherms using the BET method; a Micromeritics ASAP 2000 instrument was used. Samples were degassed in-situ under vacuum at a 250°C temperature.

Powder X-ray diffraction patterns (XRD) were collected using a PANalytical X'Pert PRO diffractometer with CuK $\alpha$  radiation and an X'Celerator detector in Bragg-Brentano geometry.

Scanning electron microscopy (SEM) micrographs were collected in a JEOL 6300 microscope operating at 20 kV. The quantitative EDX analysis was performed using an Oxford LINK ISIS System with the SEMQUANT program.

Raman spectra were obtained with an “in via” Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 514 nm from a Renishaw HPNIR laser with a power of approximately 15 mW on the sample. The dehydration of catalysts (under 20 mL min<sup>-1</sup> argon flow at 150°C) was carried out by using a home-designed microreactor for in situ Raman spectroscopy measurement.

Experiments of Temperature-programmed desorption of ammonia (TPD) were carried out on a TPD/2900 apparatus from Micromeritics. 0.30 g of sample were pre-treated in a He stream at 450°C for 1 h. Ammonia was chemisorbed by pulses at 100°C until equilibrium was reached. Then, the sample was fluxed with a He stream for 15 min, prior to increasing the temperature up to 500°C in a helium stream of 100 mL min<sup>-1</sup> and using a heating rate of

10°C min<sup>-1</sup>. The NH<sub>3</sub> desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer following the characteristic mass of ammonia at 15 a.m.u.

### ***2.3 Reactivity experiments***

The oxidative transformation of methanol was carried out in a fixed bed reactor at atmospheric pressure in the 250-400°C temperature region. The catalyst weight was either 0.10 g or 0.40 g, and the feed consisted of a methanol/oxygen/nitrogen mixture with a molar ratio of 6/13/81 (total flow of 100 mL min<sup>-1</sup>). The analysis of reactants and products was carried out by-means of gas-chromatography, using two different chromatographic columns: i) Molecular sieve 5A (3 m length) and ii) RT-U-bond (30 m, 0.53 i.d.).

For glycerol oxidehydration, the effluent stream was bubbled through two in-series abatement devices, which were filled with water and held at a temperature of 0-2°C; a third refrigerated condenser was left without any solvent [17]. A semi-capillary wide-bore OV 351 (polyethyleneglycol treated with terephthalic acid) column was used for the separation of condensed compounds [16]. Two wide-bore columns were used for the separation of non-condensable products: a Molecular sieve 5A for oxygen and CO, and a Silica Plot for CO<sub>2</sub> (oven temperature 80°C). Compounds were identified by means of both GC-MS and the injection of pure reference standards for the comparison of retention times in the GC column. The procedure for calculation of conversion, selectivity and time factor have been included as Supplementary information.

## **3. Result and discussion**

### ***3.1 Characterization of mixed-oxide catalysts***

The surface area of the solids synthesized decreased as follows:  $\text{h-WO}_x > \text{WNbO} > \text{WVO} > \text{WTiO}$  (Table 1); the difference in surface area can be attributed to the different element added. The higher surface area of  $\text{h-WO}_x$  can be related to the lower heat-treatment temperature (see sample WV-0 in ref. [19]).

On the other hand, the chemical composition of these materials (determined by EDS microanalysis), revealed a homogeneous distribution of the elements in all cases, with similar incorporation of metal in the case of  $\text{WNbO}$  and  $\text{WTiO}$ , with a  $(\text{M}/(\text{W}+\text{M}))$  atomic ratio in heat-treated samples of ca. 0.20, but lower in the case of  $\text{WVO}$ . The higher ratio of metal (M) in  $\text{WNbO}$  and  $\text{WTiO}$  catalysts than in the synthesis gel indicates that the Nb and Ti compete with tungsten in the HTB formation; the excess of tungsten, not introduced in the oxide framework, is filtered off after the hydrothermal synthesis, finally determining the higher ratio of the M metal in the catalyst.

Figure 1 shows the powder X-ray diffraction patterns of samples before (Fig. 1A) and after heat-treatments (Fig. 1 B and C). In the as-synthesized samples (Fig. 1A), the diffraction patterns could be assigned to the basic hexagonal tungsten bronze (HTB) structure (JCPDS: 85-2460) in all catalysts studied. Moreover, depending on the precursor used in the synthesis procedure, smaller changes in the intensity of some of the diffraction lines can be observed, which can be related to changes in their morphologies [23]. On the other hand, an additional diffraction peak at  $2\theta = 25.4^\circ$ , as minority, is observed for  $\text{WTiO}$  sample (Fig.1A, pattern b), which is characteristic of  $\text{TiO}_2$  anatase (JCPDS: 89-4921).

Figure 1B shows the XRD patterns of samples heat-treated at 450-600°C in  $\text{N}_2$ . All samples present the hexagonal tungsten bronze (HTB) crystal structure (JCPDS 85-2460). In the case of pure  $\text{h-WO}_x$  sample, it was treated at 450°C because the thermal stability is limited and it turns into  $\text{m-WO}_3$  (Fig. 1C, pattern a) at higher temperatures [24]. However, the



thermal stability increases when an element is incorporated in the hexagonal structure. Thus, the Ti-promoted sample presents a HTB structure at 500°C (Fig. 1B, pattern b), whereas the thermal stability increases until 600°C when vanadium or niobium are incorporated (Fig. 1B, patterns c and d). Similar behavior was observed in the case of tetragonal  $\text{Mo}_5\text{O}_{14}$  bronze [25]; these authors found that a few elements (V, Nb, Ti) were able to substitute Mo into the  $\text{Mo}_5\text{O}_{14}$  structure, and the structure was stabilized by a few hundred degrees above that of binary oxide in most cases.

Figure 1C shows the powder X-ray diffraction patterns of samples treated at high temperature. In the case of pure h- $\text{WO}_x$  (Fig. 1C, pattern a) the different diffraction pattern observed could be assigned to the monoclinic  $\text{WO}_3$  structure (JCPDS: 43-1035) with W-atoms fully oxidized ( $\text{W}^{6+}$ ). However, in the case of promoted samples the hexagonal phase turned into the tetragonal phase (JCPDS: 89-4482), which could be related to the presence of V, Nb or Ti in framework positions (Fig. 1C, patterns b to d).

Figure 2A shows the Raman spectra of catalysts treated with  $\text{N}_2$  at low temperatures. The main Raman vibration mode of pure h- $\text{WO}_x$  sample shows band at 796, 710, 325, 264 and 185  $\text{cm}^{-1}$  (Fig. 2A, spectrum a), which can be assigned to  $\text{WO}_x$  with HTB structure [24]. It is interesting to note the greater width of Raman vibrations in promoted-HTBs than in pure h- $\text{WO}_x$ , which is good evidence that the introduced metal forms new bonds with the oxygen atoms of the hexagonal framework. The bands at 796 and 710  $\text{cm}^{-1}$  characteristic of hexagonal bronzes were always present but shifted towards lower wavenumbers when another metal was introduced in the structure. In the case of V-containing catalysts, a new broad band at 970  $\text{cm}^{-1}$  was observed (Fig. 2A, spectrum d). This may be related to the greater number of W-O bonds generated by a structural defect due to vanadium incorporation and/or V-O bonds associated to polymeric V-O-W chains [16]. On the other

hand, a shoulder at  $636\text{ cm}^{-1}$  in the **WTiO** sample is observed (Fig. 2A, spectrum b). This can be attributed to the presence of  $\text{TiO}_2$  anatase [26].

Temperature programmed desorption of ammonia (TPD- $\text{NH}_3$ ) experiments are shown in Figure 2B. All samples present two desorption peaks at ca.  $200\text{ }^\circ\text{C}$  and at ca.  $350\text{-}450\text{ }^\circ\text{C}$ , indicating the presence of both medium and strong acid sites, which is in agreement with the fact that hexagonal tungsten bronzes are acid materials [27]. Pure h-WO sample shows a higher fraction of acid sites with higher strength. Ti-containing samples present a similar profile, but the desorption temperature of strong acid site increase. When Nb or V were added the number of strong acid sites decreased and that of medium acid sites increased.

On the other hand, it can be seen that h- $\text{WO}_x$  and **WNbO** catalysts had a higher amount of acid sites when considering the number of acid sites per unit weight (i.e.  $121\text{-}135\text{ }\mu\text{mol}_{\text{NH}_3}\text{ g}^{-1}$ ). However, they showed a relatively lower number of acid sites if the latter is referred to the catalyst surface area (ca.  $4.3\text{-}4.4\text{ }\mu\text{mol}_{\text{NH}_3}\text{ m}^{-2}$ ) with respect to **WTiO** catalysts (ca.  $5.3\text{ }\mu\text{mol}_{\text{NH}_3}\text{ m}^{-2}$ ).

### ***3.2 Methanol and Glycerol conversion under aerobic conditions***

The pure hexagonal tungsten oxide, indicated as h- $\text{WO}_x$ , was tested with methanol in oxidative conditions as a function of the time factor (TF) (Fig. 3). At the lower TF values methanol was converted to dimethyl ether -DME- and only traces of  $\text{CO}_x$ , whereas formaldehyde -FA- was not detected. This stresses the strong acid properties of h- $\text{WO}_x$ , particularly of the Brønsted type [2,3,21,22]. Indeed, strong acid sites hamper the desorption of the adsorbed methoxy intermediate, favoring the molecular encounter with a second molecule of ethanol to form DME, as reported previously [2].

At higher TF the methanol conversion kept increasing almost linearly, whereas the FA selectivity increased significantly up to 12%. Taking into consideration the absence of redox elements in this catalyst, the formation of FA can be attributed to consecutive reactions that led to decomposition of either DME and/or the adsorbed methoxy species [21, 28]. Another possible explanation might be that the mixed valence state of tungsten in HTBs ( $W^{5+}$  and  $W^{6+}$ ) allowed the occurrence of a redox cycle; however, the electronic and nuclear configuration of W make this option less likely. Moreover, as it was proved by the thermal treatment at high temperatures and related XRD analyses -vide supra-, when the valence state of tungsten changed, the h- $WO_x$  sample collapsed into a monoclinic phase (m- $WO_3$ ); since the oxide structure was preserved after the catalytic tests, as confirmed by XRD analysis (supplementary information, Fig S-2), the chance of a redox state for tungsten can be discarded.

Another oxide that was used by numerous authors (either supported or as a bulk catalyst) to perform the glycerol dehydration is monoclinic  $WO_3$  (m- $WO_3$ ) [29]. The  $NH_3$ -TPD profiles reported as supplementary information (Figure S-1) highlight well the lower acid features of the monoclinic sample, both as density and strength of acid sites; to further explore the differences of the h- $WO_x$  and m- $WO_3$  samples, reactivity test of methanol aerobic transformation were carried out as a function of temperature (Fig. 4). Methanol conversion and FA selectivities were always higher for the HTB tungsten oxide. These trends can be attributed to its higher acid properties, since the stronger adsorption of the methoxy species can favor at high reaction temperature the C-H bond breaking required for the formation of FA from methanol. However, the presence of  $W^{5+}$  species in pure sample could also favor FA formation at high temperature. Thus, a role might be played also by the mixed valence state of tungsten in the hexagonal sample; indeed, radical species  $W^{5+}-O\cdot$  could form by a

more facile electron transfer from oxygen to tungsten, as it was reported for molybdenum oxides [30]. These species can react with methanol to form  $\cdot\text{CH}_2\text{OH}$  radicals which are further transformed into FA. Other phenomena related to the different valence state of tungsten but which avoid the radical formation cannot be used to justify these trends. Provided the higher nucleophilicity of oxygen atoms in  $m\text{-WO}_3$ , due to the presence of  $\text{W}^{6+}$  only, one should indeed expect a reverse behavior with a higher formation of FA on  $m\text{-WO}_3$ , since the C-H rupture would be easier. Finally, it is worth mentioning that at lower TF both catalysts showed 100% selectivity to DME, a phenomenon which highlights the acid properties of these materials and the absence of redox features.

As it was previously discussed, HTBs can be functionalized by substituting tungsten atoms in the oxide framework with other transition metals; these systems can be prepared by means of hydrothermal synthesis [15-18]; these materials also showed to be effective catalysts for glycerol (oxi)dehydration. The substituted-HTBs with pure acid properties, i.e.  $h\text{-WO}_x$ , **WNbO** and **WTiO** were also tested in the aerobic methanol transformation. The overall results are reported in Fig. 5. At the lower TF, all catalysts displayed total selectivity towards DME. At TF equal of  $0.24 \text{ g}_{\text{cat}} \text{ mL s}^{-1}$  also FA was observed with  $h\text{-WO}_x$  sample, whereas **WNbO** and **WTiO** showed always an almost complete selectivity to DME with only traces of  $\text{CO}_x$  and a 2% FA selectivity with the latter catalyst. The much higher formation of FA on the unpromoted HTB supports the hypothesis that the mixed valence state of tungsten is the main driving force for easier the C-H breaking in adsorbed methoxy species, likely through a radicalic pathway. Indeed, by means of XPS analysis and CO-adsorption [15, 16, 17], we demonstrated that the substitution of transition metals with lower valence state than tungsten, e.g.  $\text{V}^{5/4+}$  and  $\text{Nb}^{5+}$ , lowered the surface content of  $\text{W}^{5+}$

sites, because since the overall electroneutrality of the hexagonal oxide as well as its structure could be preserved without the need for the reduction of tungsten from 6+ to 5+.

The bi-functional catalysts **WVO** with HTB-structure, previously studied for glycerol oxidehydration [15], were also studied as catalysts for methanol transformation under oxidative conditions. The catalytic results are summarized in Fig. 6. The incorporation of vanadium even at low V/W ratios completely changed the product distribution, since a remarkable selectivity to oxidation products (FA and CO<sub>x</sub>) was registered. Increasing the amount of vanadium led to a change in the selectivity profiles, since FA and CO<sub>x</sub> formation shifted towards lower temperature. Moreover, the catalysts activity also increased up to the catalyst with composition **W<sub>1</sub>V<sub>0.3</sub>O<sub>x</sub>**, but then it remained constant for **W<sub>1</sub>V<sub>0.4</sub>O<sub>x</sub>**. This indicates that the extra-framework vanadium species formed at high V-content did not improve the catalyst activity but increased only the selectivity to partial and total oxidation products, as it was also observed for glycerol oxidehydration to acrylic acid [15-17].

How it has been shown in the DRX, the stability of these materials increase when tungsten is partially substituted. So, they have been characterized after catalytic test to check this stability (supplementary information, Fig S-2). No modification on the diffraction patterns are shown for the materials with Ti, Nb or V in the framework after catalytic tests. Thus, these materials are more stables than h-WO<sub>x</sub>, which is transformed into a monoclinic phase (m-WO<sub>3</sub>) after the catalytic tests.

Sample **WTiO** was also tested for the glycerol dehydration in oxidative conditions (supplementary information, Fig S-3), so as to compare its performance to the previously studied oxides. These results point out that this catalyst shows the highest selectivity to acrolein at lower contact time than h-WO<sub>x</sub> (0.15 s vs. 0.4 s). This behavior is similar to that previously observed over **WNbO** [15,16]. The presence of oxygen is not formally required

during glycerol dehydration, but the presence of oxygen prevents a fast catalyst deactivation allowing the oxidation of carbon deposit during the catalytic test [31].

The highest acrolein selectivity (76%) with WTiO catalysts was observed at higher temperature (310°C) than with both h-WO<sub>x</sub> [15] or **WNbO** [16], both showing their maxima at 290°C and a steep decrease of selectivity while rising the temperature; moreover the glycerol conversion was not complete up to 310°C. However, at higher temperature the catalytic behavior showed an abrupt change in product distribution and the spent catalyst showed a change in color compared to the fresh catalyst, which suggested changes in the catalyst. The spent catalyst, named spent-**WTiO**, underwent a second catalytic test for glycerol dehydration in the same reaction conditions (Fig. 7b) in order to evaluate if the structural change had caused also a variation in catalytic performance. Spent-**WTiO** was not able to convert glycerol completely up to 360°C, acrolein selectivity decreased significantly and heavy compounds formed in remarkable amounts at all temperatures. In this way, Raman spectra of spent-**WTiO** catalyst, before and after reaction in glycerol transformation, have been compared (supplementary information, Fig S-4). According to these results, no structural differences between fresh and spent-**WTiO** catalysts can be concluded (Fig. S-4). However, we can inform on the presence of a small band at ca. 1590 cm<sup>-1</sup> in Raman spectrum of spent-**WTiO** catalyst, which is related to the presence of coke on the catalyst surface.

The great changes observed in the spent catalyst suggest that (i) the hexagonal structure - and its characteristic acidity- is fundamental to efficiently dehydrate glycerol into acrolein, (ii) the substitution of W for Ti allows to obtain acrolein selectivity higher than that of pure h-WO<sub>x</sub> (76% vs. 67%) but at a higher temperature, (iii) Ti-substituted HTBs are stable

under oxidative conditions and temperatures at above 300°C but coke can also be formed decreasing its catalytic performance in several cycles.

#### **4. Conclusions**

Metal promoted tungsten oxides with hexagonal tungsten (HTB) structure have been prepared and characterized. In all cases the metal occupied mainly framework positions. The incorporation of heteroatoms strongly improved thermal stability. Thus, if in the case of h-WO<sub>x</sub>, the HTB structure was transformed into monoclinic m-WO<sub>3</sub> at 450°C, the HTB structure was stable until 500°C in Ti-containing sample and until or 600°C in Nb- and V-promoted samples. However, contrary to the other samples, the WTi oxide decomposed at ca. 300°C in aerobic conditions.

From a catalytic point of view, changes were also observed after the incorporation of the heteroatoms. In the case of Ti- and Nb-containing catalysts, the catalytic behavior was similar to that observed for pure h-WO<sub>x</sub> although the catalyst stability increased, especially for Nb-containing catalyst.

In the case of V-containing catalysts both redox and acid sites were presents as concluded from the catalytic results achieved for the oxidative transformation of either methanol, with formation of formaldehyde and DME at low reaction temperature and formaldehyde at high reaction temperature, or glycerol, showing the formation of acrolein and acrylic acid according to the one-pot mechanism.

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**Table 1.** Characteristics of M-promoted *h*-WO<sub>x</sub> catalysts (M= Nb, V or Ti)

Sample	S <sub>BET</sub> <sup>a</sup> m <sup>2</sup> g <sup>-1</sup>	M/(W+M) ratio		TPD-NH <sub>3</sub>	
		In gel	In catalyst <sup>a</sup>	μmol <sub>NH3</sub> g <sup>-1</sup>	μmol <sub>NH3</sub> m <sup>-2</sup>
<i>h</i> -WO <sub>x</sub>	31	0	0	135	4.4
WNbO	21	0.17	0.20	121	4.3
WVO	19	0.17	0.12	72.3	3.8
WTiO	17	0.17	0.19	87.5	5.3

a) In heat-treated samples, i.e. 450 °C (*h*-WO<sub>x</sub>), 500 (WTiO), or 600 °C (WNbO, WVO).

b) TPD-NH<sub>3</sub> experiments