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Additional Information

**Tungsten-titanium mixed oxide bronzes: Synthesis, characterization and catalytic
behavior in methanol transformation**

by

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ABSTRACT

Tungsten oxide bronze-based materials show extremely adaptive structural and compositional features that make them suitable for functional properties modulation. Herein we report the preparation of a series of Ti-containing tungsten oxide catalysts presenting a hexagonal tungsten bronze-type structure. The insertion of Ti^{4+} within the structure (likely in the octahedral framework of the hexagonal tungsten bronze) leads to an increase in the number of strong acid sites, and the disappearance of W^{5+} surface species found in the undoped tungsten oxide. With the aim of studying the acid-redox properties of the titled catalysts, the catalytic transformation of methanol has been carried out in the presence and the absence of O_2 in the feed. Both catalytic activity and the acid-redox properties of these catalysts are highly dependent on catalyst composition and reaction conditions applied (i.e. in the presence or in the absence O_2 in the feed). Aerobic experiments show the depletion of the redox functionality (i.e. no formaldehyde detected in the products) when Ti^{4+} is incorporated in the framework (i.e. 100 % selectivity to dimethyl ether). On the other hand, all the catalysts show the loss of the redox function and a decrease in the catalytic activity when anaerobic conditions are used. In the absence of oxygen, the catalysts are still active in the dehydration of methanol to dimethyl ether, i.e. they maintain their acid functionality even when oxygen is not present in the feed. The results are discussed in terms of the available surface active sites present in each case.

Keywords: methanol, dimethyl ether, formaldehyde, tungsten, titanium, oxide, bronze

1. INTRODUCTION

First reported by Wohler in the first half of 19th century, the term “tungsten bronze” was referred to the colored and brilliant crystals that were obtained by heat-treating sodium tungstate in hydrogen [1]. More recently, the term bronze was extended to describe oxides presenting a general formula A_xMO_n , where A is usually an electropositive metal (generally alkaline and alkaline-earth metals) [2-4], and M is a transition metal showing variable oxidation states (Mo, Ti, V, W, Ta, Re, etc.) [4]. The insertion of those electropositive A^{n+} cations leads to the formation of a vast number of stoichiometric and non-stoichiometric mixed-valence phases [5]. Over the years, different types of cations were incorporated in A positions, like rare earths [6], transition metals [7, 8], and even ammonium ions [9]. In addition, the partial substitution in M positions is also possible, leading to mixed metal oxides [4, 10]. Moreover, bronze-type oxides can be considered as intercalation compounds, in which those A^{n+} species are inserted within a MO_n matrix [11, 12]. This structural types show excellent adaptive features, in terms of composition, structure and diversity of oxidation states of their constituent elements. This versatility can be exemplified by Nb-doped tetragonal tungsten bronze system [13], or the partially reduced tungsten oxides family, also known as Magneli phases [5, 14].

The control of both composition and crystal structure opened up the possibility to functional properties modulation. Thereby, metal oxide bronze materials have aroused great interest in a wide variety of research fields, like gas sensors [15], superconductors [16], magnetic [17] or optical materials [18]. Nevertheless, catalytic applications were substantially limited, due to high-temperature solid state methods applied for their preparation, which led to low active surface areas. It was not until the development of synthesis procedures based on soft chemistry that catalytic applications started to emerge [19].

The case of MoVTe(Sb)NbO catalysts, also known as M1 phase (displaying a $\text{Cs}_{0.5}\text{Nb}_{2.5}\text{W}_{2.5}\text{O}_{14}$ -type structure), active and selective in the partial oxidation/ammoxidation of propane [20-23] and in the ODH of ethane [24, 25], represents the paradigmatic case of a bronze-type material obtained by soft methods with outstanding catalytic properties [20-25]. Their excellent catalytic behavior derives from their extremely adaptive compositional features, which make them able to incorporate specific functionalities into the host structure. Also Mo-based metal oxides bronzes with tetragonal tungsten bronze (TTB) structure show interesting catalytic properties. For instance, they have been applied in the partial oxidation of propene [26] or the catalytic abatement of trichloroethylene [27].

Among all tungsten-containing oxide bronze systems with well-defined structures, tetragonal (TTBs) [26, 27] and hexagonal tungsten bronzes (HTBs) [28-33], have been the most studied systems for catalytic applications. In the case of HTB-based materials (formed by an array of corner-sharing octahedra, presenting hexagonal 6-member channels along c crystallographic direction), they have found more diversified catalytic applications, like glycerol dehydration and oxidehydration [28-30], ethanol and methanol dehydration and oxidation [31-32], benzyl alcohol/toluene alkylation [33], or as electrocatalysts [34]. Until now, the incorporation of Nb, Mo, V, or Ti in the octahedral framework have been demonstrated [28-31, 33, 35].

Murayama *et al.* reported that W-Ti-based oxides show tailored surface acid features, depending on heat-treatment procedures applied to as-prepared materials [33]. However, the authors were more focused on the characteristics of the pseudocrystalline layered-phase of W-Ti mixed oxides, leaving aside the HTB-type phase obtained under specific synthesis conditions. In our case we have focused the attention on these Ti-doped hexagonal tungsten bronze materials.

In this work we report the synthesis and characterization of a series of Ti-containing HTBs with varying titanium concentrations, which have been tested in the aerobic and anaerobic transformation of methanol (i.e. in the presence or in the absence of O₂ in the feed). The effect of Ti incorporation on the morphological, structural and physicochemical properties of the materials has been studied. The comparison between the catalytic results obtained in the transformation of methanol in the presence and in the absence of oxygen has allowed us to shed some light on their multifunctional acid-redox features, and also on the influence of the presence O₂ on the activation of methanol over these hexagonal tungsten bronze-based systems.

2. EXPERIMENTAL

2.1. Synthesis of catalysts

W-Ti-O mixed oxides, with hexagonal tungsten bronze (HTB) structure, were prepared according to standard hydrothermal procedures [28]. An aqueous solution of (NH₄)₆H₂W₁₂O₄₀·H₂O and titanium (IV) ethoxide was acidified with HCl. The gels were loaded in Teflon-lined stainless-steel autoclaves and heated at 175°C for 48h. The solid obtained was filtered off, washed and dried at 100°C for 16 h. Finally, the solid was heat-treated at 500°C during 2 h in a N₂-stream.

For comparison, a Ti-free *h*-WO₃ sample was also prepared by treating an aqueous solution of (NH₄)₆H₂W₁₂O₄₀·H₂O and oxalic acid under the same hydrothermal conditions. After filtering and drying, the solid was heat-treated at 450°C during 2 h in a N₂-stream.

2.2. Catalyst characterization

Surface areas were obtained from N₂ adsorption isotherms using the BET method. Micromeritics ASAP 2000 instrument was used. The samples were degassed in situ under vacuum at 400 °C prior to N₂ adsorption.

Powder X-Ray diffraction (XRD) patterns were collected in a PANalytical X'Pert PRO diffractometer equipped with an X'Celerator detector in a Bragg-Brentano geometry using K_{α1} radiation of copper.

Infrared spectra were recorded at room temperature in the 300-4000 cm⁻¹ region with a Nicolet 205xB spectrophotometer equipped with a Data station, at a spectral resolution of 1 cm⁻¹ and accumulations of 128 scans.

Raman spectra were obtained with an inVia Renishaw spectrometer, equipped with an Olympus microscope. The exciting wavelength was 514 nm, generated with a Renishaw HPNIR laser with a power of approximately 15 mW on the sample. Dehydration of catalysts (under 20 ml min⁻¹ argon flow at 150°C) was carried out using a home-designed microreactor for in situ Raman spectroscopy measurements.

Temperature-programmed desorption of ammonia (TPD-NH₃) experiments 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 increase the temperature up to 500 °C in a helium stream of 100 ml min⁻¹, using a heating rate of 10 °C min⁻¹. The NH₃ desorption was monitored with a thermal conductivity detector (TCD) and a mass-spectrometer, following the characteristic mass of ammonia at 15 a.m.u.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a SPECS spectrometer equipped with a Phoibos 150 MCD-9 detector using a monochromatic Al K α (1486.6 eV) X-ray source. Spectra were recorded using an analyzer pass energy of 50 eV, an X-ray power of 100W, and an operating pressure of 10⁻⁹ mbar. Spectra treatment was performed using CASA software. Binding energies (BE) were referenced to C1s at 284.5 eV.

Morphological and structural characterization of the samples was performed by Transmission Electron Microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) by using a FEI Field Emission Gun (FEG) TECNAI G2 F20 S-TWIN microscope operated at 200 kV. Energy Dispersive X-ray Spectroscopy (EDS) in TEM nanoprobe mode was used to obtain the chemical composition of the samples. The samples were sonicated in ethanol for few minutes, and a drop of the resulting suspension was deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

Methanol adsorption FTIR experiments (in the presence or in the absence of oxygen) were performed in transmission mode in a Nicolet 8700 FTIR spectrometer. Initially, heat-treated catalysts were activated during 2h at 300 °C. In the case of MeOH adsorption in the presence of oxygen, the sample was cooled down to room temperature and treated in vacuum for 1h (10⁻⁴ mbar). Then a mixture MeOH/O₂ (20/40 mbar) was admitted into the infrared cell, and temperature was increased up to 80, 160 and 240 °C. A spectra was recorded at each temperature (after 45 min of stabilization). For MeOH adsorption in the absence of oxygen, the vacuum treatment was carried out at 300 °C for 1h (10⁻⁴ mbar). After cooling to room temperature 20 mbar of MeOH were admitted, and temperature was increased to 80, 160 and 240. Spectra were recorded at each temperature after 45 min of stabilization.

2.3. Catalytic tests

Aerobic transformation of methanol was carried out in a fixed bed reactor at atmospheric pressure in the 200-400°C temperature range. The catalyst weight was 0.10 g (0.25-0.40 mm diameter), and the feed consisted in a methanol/oxygen/nitrogen mixture with a molar ratio of 6/13/81 (total flow of 100 mL min⁻¹). For the anaerobic transformation of methanol, oxygen in the feed was replaced by N₂ (MeOH/N₂ molar ratio of 6/94). The analysis of reactants and products was carried out by gas chromatography using a thermal conductivity detector (TCD) and with two different chromatographic columns: i) Molecular sieve 5 Å (3 m length) and ii) RT-U-bond (30m, 0.53 i.d.); [31].

3. RESULTS

3.1. Characterization of catalysts

A series of Ti-containing tungsten bronzes have been prepared by hydrothermal synthesis with increasing titanium loadings, i.e. Ti/(W+Ti) from 0 to 0.38. The main physicochemical characteristics of heat-treated samples are displayed in **Table 1**.

Figure 1 shows the XRD patterns of both as-prepared and heat-treated W-Ti-O catalysts (**Fig. 1A** and **Fig. 1B** respectively). For comparison, a Ti-free sample has been also included. In all cases Bragg peaks corresponding to a hexagonal tungsten bronze structure (*h*-WO₃) are observed ($2\theta = 14.41^\circ, 23.00^\circ, 24.25^\circ, 27.22^\circ, 28.23^\circ, 33.95^\circ, 36.92^\circ, 43.13^\circ, 44.90^\circ, 49.66^\circ, 55.90^\circ$ and 58.27°) (JCPDS: 33-1387) [28, 32], which is present as the major phase in both as-prepared and heat-treated materials (**Fig. 1**). Apparently, no other crystalline phases are found at low Ti contents (**Fig. 1**, patterns b and c). However, at higher Ti-loadings (**Fig. 1**, patterns d to f), a low intensity peak appears at ca. $2\theta = 25.3^\circ$.

This line can be assigned to the (111) Bragg reflection of anatase-type TiO₂ (JCPDS: JCPDS: 078-2486), which is present as a minor impurity.

It is noteworthy to mention that heat-treatment temperature differs for Ti-free and Ti-containing materials. Undoped WTi-0 catalyst was heat-treated at 450 °C, since higher temperatures would promote the phase transition to the monoclinic structure of tungsten trioxide (*m*-WO₃) [28]. This takes place due to the complete release of NH₄⁺ cations from the hexagonal channels, with the subsequent oxidation of W⁵⁺ sites to W⁶⁺. In the case of Ti-containing materials heat-treatment temperatures of 500 °C were applied, with no decomposition of the as-synthesized hexagonal bronze into the monoclinic polymorph (**Fig. 1B**). This behavior during the heat-treatment suggests an effective substitution of Ti⁴⁺ for W^{5+/6+} in the framework [31].

The atomic composition of W-Ti-O samples was determined by EDX analysis of large areas of the materials (**Table 1**). It can be observed that at low Ti-loadings (i.e. WTi-1 and WTi-2) the measured atomic concentration fits well with the theoretical values added in the synthesis (**Table 1**). However, when higher amounts are loaded (i.e. WTi-3, WTi-4 and WTi-5 samples), titanium content resulted to be much lower than the theoretical one (**Table 1**). This fact suggests a limit in the incorporation of Ti⁴⁺ as promoter by this hydrothermal procedure. As far as oxide bronze based materials are concerned, a theoretical composition of A_xMO₃ for the hexagonal tungsten bronze (A= NH₄⁺, B= W^{5+/6+}), in which a maximum A⁺ cation content in the hexagonal channel of x= 0.33 has been reported by several authors [36-38]. The presence of those A species (in our case NH₄⁺ in the as-synthesized material) within the hexagonal channels of the structure is associated with the existence of reduced metal species in the oxide (either W⁵⁺ or Ti⁴⁺), which are necessary to maintain the electron neutrality in the solid. Thereby, the maximum amount of titanium that can be incorporated in tungsten positions will be

closely associated with the maximum concentration of ammonium ions that the structure is able to admit within the hexagonal channels. The elimination of those ammonium ions within hexagonal tunnels by heat treatments gives rise to the formation of Brønsted acid sites [39].

FTIR and Raman spectroscopy analyses of representative as-prepared and heat-treated W-Ti-O catalysts have also been conducted. Thus, IR (Fig. S1 and S2) and Raman (Fig. S3) spectra of Ti-free and Ti-containing samples display the characteristic signals of the hexagonal tungsten bronze structure (Raman bands at 796 and 692 cm^{-1}) [10], whereas bands related to the presence of the monoclinic *m*- WO_3 phase (Raman bands at 805 and 714 cm^{-1}) [10] were always absent. A more detailed explanation of these results is shown in the Supporting Information. Up to this point the characterization performed shows that: i) W-Ti-O samples present predominantly the hexagonal tungsten bronze phase; and, ii) high Ti-loadings promote the formation of TiO_2 -anatase as a minor phase.

In order to get further insights into the morphological and compositional characteristics of the catalysts, an in depth study by means of high-resolution electron microscopy (HRTEM) has been carried out on selected samples (WTi-0, WTi-2, WTi-4 and WTi-5). **Figure 2** shows representative HRTEM images of the W-Ti-O materials. As it can be seen, the samples mainly consist of rod-shaped nanoparticles, with varying dimensions depending on catalyst composition. Titanium-free sample (WTi-0) shows rod lengths over 500 nm, and diameters in the range 30-70 nm (**Fig. 2A**). In the case of samples WTi-2, WTi-4 and WTi-5, rod lengths lay between 100-200 nm and rod diameters increase to 70-120 nm (**Fig. 2B to 2D**). In addition, the presence of small nanoparticles (with an average diameter of 4-5 nm) can be appreciated in samples presenting high Ti-contents (i.e. samples WTi-4 and WTi-5) (**Fig. 2C** and **Fig. 2D**, respectively). Due to their crystalline nature, interplanar distances were measured on individual particles (3.56, 2.32

and 1.71 Å), which can undoubtedly be assigned to (101), (112), and (105) Bragg lines of TiO₂-anatase type phase (space group I4₁/amd; JCPDS: 078-2486) (**Fig. S4**). The concentration of these particles increases with Ti-content in the catalysts, being hardly detected in WTi-2 sample (**Fig. 2B**).

Figure 2E displays an EDX map of a single rod in WTi-4 sample. The homogeneous distribution of W and Ti all along the particle suggests the effective incorporation of Ti within the hexagonal tungsten bronze framework. This fact was further confirmed by selected area electron diffraction (SAED) analysis.

Figure S5 displays the SAED patterns of a group of nano-rods in WTi-0 and Ti-containing catalysts. At least seven well-defined diffraction rings, characteristics of a polycrystalline sample are observed in all cases. Concentric rings in the zero order Laue zone (ZOLZ) are produced by randomly dispersed particles that provide a continuous angular distribution of (*hkl*) spots at a distance $1/d_{hkl}$ from (0 0 0) spot. Ring radius $r(hkl)$, and interplanar lattice spacing, $d(hkl)$, are related by the expression: $r(hkl) \times d(hkl) = L\lambda$; where $L\lambda$, is the camera constant of the transmission electron microscope ($L\lambda=1$). The ring radius can be directly measured in SAED pattern and, subsequently lattice spacing $d(hkl)$ can be calculated. Thus, for WTi-0 catalyst (**Fig. S5**, picture A), determined interplanar distances are 6.369, 3.883, 3.704, 3.289, 2.674, 2.475, 2.146, 1.942, and 1.688, which can be indexed to (100), (001), (110), (101), (111), (201), (300), (002) and (202) of the hexagonal *h*-WO₃ phase (JCPDS: 33-1387). It is important to note that all Ti-containing samples show the same distribution of SAED fringes (**Fig. S5**, pictures B and C), and that not obvious lattice rings corresponding to other crystal phases were observed, indicating that obtained rods present a hexagonal tungsten bronze structure all along the series. Moreover, EDX analysis on the nano-rods show Ti-contents in the range 5-15 at.%.

Hence, lattice parameters of the hexagonal cell (i.e. a and c parameters) for each sample can be calculated from the abovementioned interplanar distances and their corresponding Miller indexes, using the following expression derived from Bragg equation for a hexagonal symmetry (**Table 1**):

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}$$

According to the obtained values (**Table 1**), a lattice distortion takes place for Ti-containing catalysts, by which: i) a -parameter increases and; ii) c -parameter decreases. This confirms the effective incorporation of titanium in framework positions.

For a better understanding of the electronic structure of these materials, XPS experiments have also been undertaken with the aim of identifying the presence of near surface oxidation states. **Figure 3** shows the XPS W $4f$ core level spectra of Ti-free (WTi-0) and Ti-containing catalysts (WTi-1 and WTi-4). Two signals, that can be assigned to W^{6+} (B.E. W $4f_{7/2}$ = 35.7-35.4 eV) and W^{5+} (B.E. W $4f_{7/2}$ = 33.7 eV) species in an octahedral coordination, are observed in Ti-free sample (**Fig. 3A**, spectrum a) [10]. When Ti^{4+} is incorporated, the band corresponding to W^{5+} is no longer found in the spectra (**Fig. 3A**, spectra b and c). In contrast, Ti $2p_{3/2}$ XPS core level spectra of WTi-1 and WTi-4 catalyst display one signal at a B.E. = 459.0 eV, associated to the only presence of Ti^{4+} species (**Fig. 3B**) [40]. These results suggest that the location of titanium, as Ti^{4+} , in the hexagonal tungsten bronze structure is likely that of W^{5+} in the Ti-free catalyst. Titanium surface content in the catalysts was calculated from the corresponding XPS spectra (**Table 1**). They show similar Ti-concentration than that obtained by EDX, suggesting a good dispersion of the promoter in the samples.

Specific surface areas of the catalysts were determined from N_2 -adsorption isotherms using the BET method (**Table 1**). The highest surface area along the series was found for

undoped WTi-0 catalyst. This can be explained in terms of the lower heat-treatment temperature applied for this sample (450 °C), which would favor a lower sintering degree (i.e. smaller crystal size and higher surface areas). As it was commented above, higher temperatures would also promote the phase transition towards the monoclinic phase of tungsten trioxide (*m*-WO₃). Considering Ti-containing samples, which were heat-treated at 500 °C, the specific surface area increases with titanium content in the materials.

The acid features of the whole series of catalysts have been studied by means of NH₃-adsorption and subsequent temperature-programmed desorption (TPD-NH₃). TPD-NH₃ profiles are shown in **Figure 4**, whereas the amount of the ammonia adsorbed per both mass and unit area of catalyst is displayed in **Table 1**. Again, the highest concentration of acid sites per gram of catalysts was observed for Ti-free WTi-0 sample, likely due to its highest surface area derived from the lower heat-treatment temperature applied. Considering Ti-containing samples, the concentration of acid centers per gram of material increases constantly with Ti content (**Table 1**). Interestingly, similar surface density of acid sites is observed for Ti-free sample and catalysts presenting low titanium loadings (WTi-1 and WTi-2 samples) (**Table 1**). However, at higher loadings (WTi-3, WTi-4 and WTi-5) the amount of acid sites per unit area decreases (**Table 1**).

In addition, TPD-NH₃ profiles show differences depending on the catalyst composition (**Fig. 4**). Three main regions can be differentiated at ca. 200, 300 and 410°C, which can be assigned to ammonia desorbed from acid sites presenting weak, medium and strong acid strength, respectively. In this way, Ti-free catalyst displays ammonia desorption only in the weak and medium strength acid sites zone (**Fig. 4**). After the incorporation of titanium, the signal assigned to the NH₃ desorption from middle-strength acid sites (ca. 300°C) progressively shifts to higher temperatures at increasing Ti-contents, (until ca.

410°C). Accordingly, the inclusion of titanium promotes the formation of stronger surface acid sites, which in fact were absent in WTi-0 catalyst.

3.2. Aerobic transformation of methanol on W-Ti-O catalysts

In a first approximation, the whole series of W-Ti-O catalysts were tested in the aerobic transformation of methanol, i.e. in the presence of O₂ in the reaction mixture. The variation of methanol conversion with reaction temperature for W-Ti-O catalysts is shown in **Figure 5**, whereas their summarized catalytic results are displayed in **Table 2**. In general, the catalytic activity increases with titanium content in the catalysts (**Table 2**) (**Fig. 6A**). However, Ti-free WTi-0 sample does not present the lowest catalytic activity, likely due to the lower heat-treatment temperature applied (as it was commented above) (**Table 2**). In fact, the catalytic activity increases linearly with the surface area of the catalysts (Fig. S6). Therefore, specific activity (i.e. the catalytic activity per unit area) does not vary substantially along the series, regardless of the concentration of titanium in the catalyst (**Fig. 6B**).

Figure 7 displays the variation of the selectivity to the main reaction products as a function of methanol conversion for W-Ti-O catalysts. All the materials show dimethyl ether (DME) as the main reaction product in the aerobic transformation of methanol. Nevertheless, some differences in the selectivity profiles can be noted, which mainly depend on the presence or absence of titanium in the catalysts.

The selectivity to DME decreases at increasing methanol conversions for undoped WTi-0 sample. Concomitantly, the selectivity to formaldehyde (FA) increases, up to 20 % at high methanol conversion (ca. 80 %). On the other hand, the selectivity to FA never exceeds 5 % in the case of Ti-containing samples. Hence, the selectivity to DME remains almost constant in Ti-doped catalysts (ca. 95-100 %).

According to this, it seems that undoped WTi-0 tends to decompose DME into FA by partial oxidation, while Ti-containing samples maintain a high selectivity to DME even at high conversion of methanol. Spent catalysts were also examined by X-ray diffraction (Fig. S7). XRD patterns show that all the catalysts retain their crystal structure after the catalytic tests. Then, it is very likely that the presence of W^{5+} could be affecting the catalytic behavior of this material, since the existence of a W^{+6}/W^{5+} pairs on the surface could lead to some redox activity [41]. Accordingly, these redox sites could lead to formaldehyde production either via oxidative dehydrogenation of methanol, or partial oxidation of DME. It must be mentioned that in the presence of oxygen in the feed these catalysts are highly stable since both conversion and selectivity do not vary with the time on line. A 6-hour experiment was undertaken on WTi-3 catalyst under fixed reaction conditions and no change was observed along the experiment (Fig. S8).

3.3. Anaerobic transformation of methanol on W-Ti-O catalysts

Since the presence or absence of oxygen in the feed can have a great influence in the catalytic performance when dealing with gas-phase partial oxidation reactions [42], we have conducted anaerobic catalytic tests on W-Ti-O catalysts (Fig. 8 and Fig. 9). The experiments were initially carried out in the presence of oxygen at a fixed reaction temperature (i.e. 311°C) during the first 1.5 h of reaction. After 1.5 h, oxygen is replaced by N_2 in the feed, and the evolution of both methanol conversion (Fig. 8) and selectivity profiles (Fig. 9) is followed.

Figure 8 shows the variation of methanol conversion as a function of time on stream (with and without oxygen in the reaction mixture) for W-Ti-O catalysts. In all cases catalysts display conversions in the range 65-75 % when O_2 is present in the feed. When oxygen is eliminated, methanol conversion decreases gradually down to 25-45 %

depending on the catalysts composition. Interestingly, the incorporation of Ti decreases the deactivation degree of the catalysts. It can be observed that for high Ti contents (i.e. WTi-4) the conversion achieved after 8 h on stream is higher than in the case of undoped WTi-0 catalyst. In addition, after 6.5 hours in the absence of oxygen (i.e. 8 h on stream), methanol conversion seems to be stabilized for both catalysts, at ca. 45 and 35 % for WTi-4 and WTi-0, respectively; with no further deactivation occurring.

Important differences in the selectivity profiles are also observed depending on the presence or absence of oxygen in the feed, especially in the case of Ti-free catalysts (**Fig. 9**). As it was commented previously, WTi-0 shows the formation of formaldehyde in the aerobic transformation of methanol. After the elimination of oxygen from the feed, the selectivity to formaldehyde starts decreasing, not being detected after 3 h on stream (**Fig. 9A**). After this, the only product detected is DME, with 100 % selectivity. On the contrary, the selectivity profile of Ti-containing catalysts does not vary significantly, regardless of the presence or absence of O₂ in the reaction mixture (**Fig. 9B**). The small amounts of formaldehyde found for sample WTi-2 in aerobic conditions (ca. 2%) are no longer observed when oxygen is replaced by N₂ in the feed (**Fig. 9B**). Accordingly, Ti-containing catalysts are 100 % selective to DME in both situations, i.e. with or without the presence of oxygen in the reaction mixture.

It is worth noting that, even though Ti-containing catalyst do not show any redox activity under these reaction conditions, methanol conversion and selectivity profiles could be highly dependent on both contact time and reaction temperatures used in the experiments.

Figure 10 displays a series of experiments carried out in the presence and absence of oxygen at different contact times and reaction temperatures with WTi-2 catalyst. In this sense, catalytic tests were carried out maintaining a fixed initial methanol conversion in

the presence of O₂ (ca. 60-70 %), by varying the reaction conditions in each case (i.e. the lower the contact time, the higher the reaction temperature). After 1.5 h on stream in aerobic conditions, oxygen is substituted by N₂, and the conversion and selectivity to the main products is monitored as previously.

Figure 10A shows the variation of methanol conversion with time on stream for WTi-2 at different temperatures. The tests show that in the presence of oxygen, initial methanol conversion is maintained at least during 1.5 h on stream. After the substitution of oxygen by N₂, catalysts undergo different deactivation trends. It can be seen that the higher the reaction temperature, the faster the deactivation of the catalyst. Moreover, the remaining activity, i.e. the stabilized methanol conversion at long times on stream (ca. 8 h) also decreases at higher reaction temperatures (**Fig. 10A**).

Also important changes are observed in selectivity profiles depending on the reaction conditions. **Figure 10B** displays the variation of the selectivity to dimethyl ether and formaldehyde with time on stream under varying W/F and temperatures, for WTi-2 catalyst. When the reaction is conducted in aerobic conditions, the formation of formaldehyde increases with reaction temperature. Then, increasing the reaction temperature favors partial oxidation reactions. However, when anaerobic conditions are applied, the selectivity to formaldehyde drops down to zero, leading to 100 % selectivity to dimethyl ether in all cases.

These results suggest that oxidation activity is very low in these catalytic systems, and could be related to the presence of W⁵⁺ species. In addition, the selectivity to formaldehyde (which can be formed either by the oxidative dehydrogenation of methanol, or the partial oxidation of DME) drops down in the absence of oxygen in the feed, although temperature plays an important role in the appearance of oxidation reaction (when working in aerobic conditions). As far as catalytic oxidations are concerned, they

are favored at higher reaction temperatures. Although Ti-containing catalysts display a lower oxidation activity than undoped hexagonal tungsten bronze catalyst (WTi-0), they are also able to transform methanol into formaldehyde in aerobic conditions when higher reaction temperatures are applied.

On the other hand, when anaerobic conditions are used, a progressive decrease in methanol conversion is observed in all cases. However, zero-conversion is not achieved in any case, reaching constant values after 6-7 h on stream. In this respect, methanol conversion at long times on stream lies in the range 5-30 % when O₂ is not present in the feed, depending on composition and reaction conditions. In this latter case, catalysts lead to DME as the only reaction product (i.e. 100 % selectivity). This means that, although redox activity is lost in the absence of O₂, there are still active surface sites for DME formation. According to anaerobic experiments, the number of these sites should be lower when O₂ is not present in the reaction mixture.

In order to gain further insights into methanol activation in aerobic and anaerobic conditions, methanol sorption FTIR experiments were carried out on sample WTi-4. **Figure 11** displays FTIR spectra of adsorbed methanol in the 1500-900 cm⁻¹ region before and after methanol adsorption in the presence (**Fig. 11A**) and in the absence of oxygen (**Fig. 11B**) in the cell (i.e. MeOH/O₂ molar ratio of 1/0 and 1/2, respectively). After methanol adsorption, samples were heated up to 80, 160, and 240 °C; and spectra were recorded at each temperature.

Both aerobic (**Fig. 11A**) and anaerobic (**Fig. 11B**) methanol adsorption FTIR spectra display bands in the 1200-900 and 1500-1400 cm⁻¹ ranges, which can be attributed to C-O stretching and CH₃ bending modes of adsorbed methoxy species, respectively [43-45]. Interestingly, spectra recorded in aerobic conditions show higher number of bands in the C-O stretching region (**Fig. 11A**) than those recorded in the absence of O₂ (**Fig. 11B**),

what suggests additional surface sites for MeOH adsorption when oxygen is present in the feed. In fact, the intensity of these IR bands increase at increasing temperatures when methanol is adsorbed in the presence of O₂ (**Fig. 11A**). On the contrary, when O₂ is not present, FTIR bands assigned to MeOH chemisorption display weaker intensities, and show a decreasing trend when temperature is increased (**Fig. 11B**). Interestingly high intensity bands related to the presence of coke or heavy compounds are not observed in any case (1600-1500 cm⁻¹).

According to these observations, methanol activation seems to be highly influenced by the presence or the absence of oxygen. In this respect, methanol adsorption, and consequently its activation, is favored when oxygen is co-fed.

This behavior could tentatively be explained if we take into consideration the specific properties of the tungsten bronze-type materials under oxidative or reducing conditions, especially their non-stoichiometric nature [5]. The generation of oxygen vacancies, and their effect on functional properties of this type of materials is widely reported in literature [46-50]. Specifically, reduction or vacuum treatments at high temperatures favor the creation of anionic vacant sites [51, 52]. In particular, near surface vacancies can have an important effect on the catalytic phenomena. In our case, these O²⁻ surface species could be affecting to: i) methanol activation (i.e. by the reception of the abstracted hydrogen from the -OH group of methanol) and; ii) partial oxidation reactions. Then, the depletion of those surface oxygen species in the catalysts under reducing conditions (i.e. anaerobic reaction conditions) would explain both the decrease in methanol conversion, and the drop in formaldehyde selectivity when the reaction is carried out in the absence of O₂ in the feed.

3.3. General discussion

We have observed that the incorporation of titanium into tungsten oxide framework by hydrothermal synthesis leads to the stabilization of the hexagonal tungsten bronze structure. Thus, in titanium-free material, the hexagonal phase is only retained if the heat-treatment temperature does not exceed 450°C [30]. Higher heat-treatment temperatures favor the phase transition towards the monoclinic polymorph of tungsten trioxide.

On the contrary, the incorporation of titanium leads to the preservation of the HTB structure, even if the precursors are heat-treated at 500°C. A similar increase in the thermal stability promoted by isomorphic substitution has been observed in the case of undoped and Ti-doped molybdenum oxide bronzes [53]. Thus, Mo_5O_{14} is stable up to 400°C, whereas Ti-doped materials were stable up to 700°C.

According to the XRD and TEM data, almost all the Ti is incorporated into the HTB structure at low Ti-loadings (Ti/(W+Ti at.% lower than 16 %). On the other hand, at higher Ti-loadings, part of the titanium added is not incorporated into the hexagonal structure, and also small amounts of TiO_2 -anatase nanoparticles are present in the catalysts.

The catalytic performance observed in the aerobic transformation of methanol is similar regarding the catalytic activity per unit area for all the catalysts tested. Thereby, if surface areas of the catalysts are considered, the specific activity does not present substantial differences along the series. Ti-free catalyst (due to the lower heat-treatment temperature applied) and those catalysts with high Ti-loadings, show higher surface areas and total concentration of surface acid sites. This gives rise to a higher catalytic activity per gram of catalyst, although the catalytic activity per surface area does not vary significantly.

On the contrary, the nature of the reaction products during the aerobic transformation of methanol strongly depends on the presence of titanium, especially when working at high temperature. Ti-free catalyst has dimethyl ether as the main reaction product, but

formaldehyde is also observed at methanol conversions over 40%. At higher methanol conversions (ca. 80%) selectivity to formaldehyde exceeds 20% for WTi-0 catalyst. When titanium is present within HTB framework, dimethyl ether is essentially the only reaction product observed. The formation of formaldehyde is remarkably lower in comparison with Ti-free catalyst, never exceeding 5% selectivity.

Apparently, DME is a primary reaction product, whereas formaldehyde is a secondary product obtained due to DME decomposition. We must note that by using any of the Ti-containing hexagonal tungsten bronzes tested in the present article, dimethyl ether is almost the unique product observed. DME is industrially produced either directly from syngas or indirectly through methanol dehydration. The typical reaction conditions used for methanol dehydration involve oxygen-free atmosphere, reaction temperatures below 220°C, the classical catalysts being alumina and zeolites [54]. Unfortunately, alumina usually presents problems of stability which can be mitigated by the use of certain zeolites [55]. In spite of the fact that further optimization of the catalytic performance towards DME formation has not been attempted, high yields to dimethyl ether (ca. 80%) have been achieved over W-Ti-O hexagonal tungsten bronzes.

Dai et al., [41] studied the catalytic performance of supported WO_3 catalysts for methanol selective transformation. They observed that when using Al_2O_3 , TiO_2 , Nb_2O_5 or ZrO_2 as support, the corresponding supported tungsten catalysts were very selective to DME, whereas when using CeO_2 as support, formaldehyde was the main reaction product. These authors suggested that WO_3/CeO_2 catalyst has only redox properties (favoring the formation of formaldehyde) due to the presence of microcrystalline CeWO_4 phase on the surface.

Therefore, the differences in the catalytic behavior of Ti-free and Ti-containing tungsten oxide bronzes could be ascribed to the presence or absence of W^{5+} in the catalysts. In

fact, and according to XPS results, W^{5+} species are present in *h*- WO_3 , which are relatively active (at high reaction temperatures) in partial oxidation reactions. The presence of this W^{5+} species are not observed in Ti-containing samples (as a consequence of the W^{5+} substitution by Ti^{4+}).

In addition, we have observed that both activity and selectivity in methanol transformation are highly influenced by O_2 cofeeding. Then, the catalytic transformation of methanol in the absence of oxygen (i.e anaerobic conditions) leads to: i) the suppression of the redox function and, ii) a partial deactivation of the catalysts. Hence, the whole series of materials show a 100 % of selectivity to DME under anaerobic conditions, and a substantially lower methanol conversion, which decreases from ca. 70 % to values in the 5-45 % range, depending on catalyst composition and reaction conditions. Interestingly, the only suppression of redox activity does not account for such a decrease in the catalytic activity, i.e. the presence or the absence of O_2 in the feed must be affecting also methanol activation process. In fact, methanol chemisorption is disfavored when O_2 is not present in the feed, as deduced from methanol adsorption FTIR experiments. Taking into consideration the non-stoichiometric character of tungsten bronze-based materials and the dynamic nature of their anionic sub-lattice, we could tentatively ascribe the catalytic behavior of W-Ti-O catalysts under anaerobic conditions (i.e. partial deactivation and disappearance of the oxidation activity), to the loss of part of O^{2-} surface lattice sites, which in fact are necessary to: i) receive the hydrogen of $-OH$ groups of methanol to form activated surface methoxy species; and ii) partially oxidize methanol and/or dimethyl ether to formaldehyde.

The interest of the selective transformation of methanol is not only due to the importance of the possible reaction products, as formaldehyde and dimethyl ether, but also because

this transformation can be used as a reaction test to determine the amount and nature of the surface active sites. Thereby, redox sites lead to the oxidative dehydrogenation of methanol or partial oxidation of DME, yielding formaldehyde. On the other hand, acid sites (Lewis and/or Brønsted) lead to methanol dehydration to yield dimethyl ether [32, 56]. This association between the reaction product and the type of active sites is more suitable when working at low methanol conversion. In the present work formaldehyde is hardly obtained at low conversion with any catalyst of the series (Scheme S1).

4. CONCLUSIONS

Titanium has been successfully incorporated into the hexagonal bronze phase of tungsten oxide. At low Ti-loadings, all (or almost all) the titanium is inserted into the HTB framework. For high Ti-loadings, not all the titanium is incorporated into the HTB structure. Then, small anatase TiO₂ particles are also observed in this case. According to EDX results, it seems that there exists a limit in the incorporation of Ti within *h*-WO₃ phase.

The incorporation of Ti leads to an increase in the amount and strength of surface acid sites. Interestingly, this also gives rise to a higher thermal stability of the materials. In fact, Ti-free catalyst retains the hexagonal structure until 450°C, whereas Ti-containing samples endure heat-treatment temperatures over 500°C.

Tungsten is present in two oxidation states (W⁵⁺ and W⁶⁺) in Ti-free catalyst. However, Ti-containing catalysts display only W⁶⁺ surface species. Thus, apparently, when being incorporated into the HTB structure, Ti⁴⁺ replaces W⁵⁺, this way modifying the thermal stability, the physicochemical characteristics and the catalytic properties of the undoped material.

Dimethyl ether is the main reaction product observed in both the aerobic and anaerobic transformation of methanol, thus confirming the acid character of the whole series of catalysts. However, some formaldehyde is formed in the case of WTi-0 sample when the reaction is carried out in the presence of oxygen, fact that is associated with the presence of redox sites. Thus, it seems that redox sites in Ti-free catalyst are related to the presence of W^{5+} species. The existence of an easily interchangeable W^{5+}/W^{6+} pair (continuous reduction and oxidation taking place), would promote the oxidative dehydrogenation of methanol or the decomposition of dimethyl ether to formaldehyde. The effective substitution of Ti for W in the HTB structure leads to the elimination of those W^{5+} species, and consequently redox W^{5+}/W^{6+} pairs are no longer present on the surface. Therefore, the absence of W^{5+}/W^{6+} pairs in Ti-containing catalysts avoids also the formation of formaldehyde when aerobic conditions are applied. Nevertheless, formaldehyde can also be obtained on Ti-containing catalysts, but much higher reaction temperatures are necessary to favor the oxidation reaction path in comparison with undoped hexagonal tungsten bronze. This fact confirms the lower redox activity of Ti-doped catalysts when O_2 is present in the reaction mixture.

On the contrary, the anaerobic transformation of methanol performed on these materials leads to the formation of dimethyl ether as the only reaction product, i.e. the surface redox functionality is lost when oxygen is not present in the feed. In addition, methanol conversion decreases, achieving constant values at long reaction times (5-45 % after ca. 7-8 h).

The comparison of the catalytic behavior in the presence and absence of O_2 , and the specific features observed in FTIR spectra during methanol adsorption show that both methanol activation and redox activity are favored when O_2 is present in the feed. Thereby, considering the dynamic nature of lattice oxygen in tungsten bronze-based

materials, it can be tentatively proposed that the different catalytic behavior observed in the transformation of methanol under anaerobic conditions can be due to: i) a decrease in the number of surface sites for methanol activation (likely due to the generation of near surface O^{2-} vacancies) and; ii) the depletion of O^{2-} redox surface sites for the partial oxidation of methanol and/or dimethyl ether.

5. ACKNOWLEDGMENTS

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Table 1. Physicochemical features of W-Ti-O catalysts.

Catalyst ^a	Ti/(W+Ti)			S _{BET} (m ² g ⁻¹)	TPD-NH ₃ ^d		Crystal phases ^e	Lattice parameters (Å) ^g	
	Gel	Final ^b	Surface ^c		μmol _{NH3} g ⁻¹	μmol _{NH3} m ⁻²		<i>a</i>	<i>c</i>
WTi-0	0	0	0	27	135	5.0	HTB	7.355	3.883
WTi-1	0.09	0.10	0.10	14	68.3	5.1	HTB	n.d.	n.d.
WTi-2	0.17	0.16	n.d.	17	87.5	5.3	HTB	7.426	3.845
WTi-3	0.25	0.17	n.d.	26	77.7	3.0	HTB ^f	n.d.	n.d.
WTi-4	0.29	0.21	0.24	31	94.5	3.1	HTB ^f	7.402	3.831
WTi-5	0.38	0.23	n.d.	38	104	2.7	HTB ^f	7.402	3.840

- a) Ti-free tungsten oxide (WTi-0) was heat treated at 450°C (*h*-WO_x) whereas Ti-containing WTi-O catalysts were heat treated at 500 °C. b) Calculated by EDX. c) Determined by X-ray Photoelectron Spectroscopy; d) by TPD-ammonia; e) Crystalline phases from XRD patterns: Hexagonal Tungsten Bronze (HTB) (JCPDS: 33-1387); f) TiO₂ anatase (JCPDS: 078-2486) as minority; g) Calculated from SAED patterns of groups of nanorods in the catalysts; n.d. not determined

Table 2. Catalytic properties of W-Ti-O catalysts in the aerobic methanol transformation at 300°C ^a.

Catalyst	Methanol Conversión (%)	Yield to Dimetylether (%)	Catalytic Activity ^b		Selectivity to CO _x (%)
			mmol _{CH₃OH} h ⁻¹ g _{CAT} ⁻¹	mmol _{CH₃OH} h ⁻¹ m ⁻²	
WTi-0	56	49	20.5	0.76	2.8
WTi-1	35	35	12.9	0.92	1.0
WTi-2	49	48	18.1	1.06	1.4
WTi-3	62	62	22.8	0.87	0.4
WTi-4	73	72	26.5	0.85	0.5
WTi-5	81	76	29.8	0.78	1.1

a) Reaction conditions: W/F = 0.073 g_{cat} min mL⁻¹; 0.4 g of catalyst; 6/13/81 %, MeOH/O₂/N₂. Total flow of 100 ml min⁻¹;
Catalytic activity for methanol conversion, in mol_{CH₃OH} h⁻¹ g_{CAT}⁻¹·10² or in mol_{CH₃OH} h⁻¹ m⁻²·10⁴.

Caption to Figures

Figure 1. XRD patterns of as-prepared and heat-treated materials: a) WTi-0; b) WTi-1; c) WTi-2; d) WTi-3; e) WTi-4; f) WTi-5. Symbols: (■) Hexagonal Tungsten Bronze (HTB), (●) TiO₂-anatase.

Figure 2. HRTEM images of W-Ti-O catalysts: A) WTi-0; B) WTi-2, C) WTi-4 and D) WTi-5. An additional HRTEM image with the corresponding EDX map of WTi-4 catalyst is also included (E).

Figure 3. W 4*f* (A) and Ti 2*p*_{3/2} (B) core-level spectra of heat-treated samples: a) WTi-0; b) WTi-1; c) WTi-4.

Figure 4. TPD-NH₃ profiles (*m/z* = 15) of heat-treated samples: a) WTi-0; b) WTi-1; c) WTi-2; d) WTi-4; e) WTi-5.

Figure 5. Variation of methanol conversion with reaction temperature for W-Ti-O catalysts during the aerobic transformation of methanol. Reaction conditions: catalyst weight = 0.4 g; W/F = 0.073 g_{cat} min mL⁻¹; Methanol/O₂/N₂ = 6/13/81 (molar %); Total flow = 100 mL/min. Symbols: WTi-0 (▷); WTi-1 (▲); WTi-2 (*); WTi-3 (●); WTi-4 (■); WTi-5 (◆).

Figure 6. Variation of the catalytic activity per gram (A) and per unit area (B) as a function of Ti content in W-Ti-O catalysts in the aerobic transformation of methanol at a reaction temperature of 300 °C.

Figure 7. Variation of the selectivity to dimethyl ether and formaldehyde as a function of methanol conversion for Ti-free catalyst (continuous line) and Ti-containing catalysts (dotted line) during the aerobic transformation of methanol. Reaction conditions: Methanol/O₂/N₂ = 6/13/81 (molar %); Total flow = 100 mL/min; catalyst weight = 0.4 g; and contact time, W/F, of 0.073 g_{cat} min mL⁻¹. Symbols: WTi-0 (▷); WTi-1 (▲); WTi-2 (*); WTi-3 (●); WTi-4 (■); WTi-5 (◆).

Figure 8. Variation of methanol conversion with time on stream, during the transformation of methanol over W-Ti-O catalysts, in the presence and in the absence of O₂ in the feed: WTi-0 (■, □); WTi-2 (▶, ▷); WTi-3 (◆, ◇); (▲, △) WTi-4. Bold symbols: aerobic conditions (MeOH/O₂/N₂ molar ratio of 6/13/81). Empty symbols: anaerobic conditions (MeOH/N₂ molar ratio of 6/94). Reaction conditions: Contact time W/F = 0.073 g_{CAT} min mL⁻¹, T = 311 °C.

Figure 9. Variation of the selectivity to dimethyl ether, DME (A), and formaldehyde, FA (B), with time on stream during the transformation of methanol over W-Ti-O catalysts, in the presence and in the absence of O₂ in the feed: WTi-0 (■, □); WTi-2 (▶, ▷); WTi-3 (◆, ◇); WTi-4 (▲, △). Bold symbols: aerobic conditions (MeOH/O₂/N₂ molar ratio of 6/13/81). Empty symbols: anaerobic conditions (MeOH/N₂ molar ratio of 6/94). Contact time W/F = 0.073 g_{CAT} min mL⁻¹. Reaction temperature of 311 °C.

Figure 10. Variation of methanol conversion (A) and selectivity to the main reaction products (dimethyl ether, DME, and formaldehyde, FA) (B) for WTi-2 catalysts at different reaction conditions and a reaction temperature of 311 °C. Symbols and reaction conditions: a) at T = 383 °C and W/F = 0.018 g_{CAT} min mL⁻¹ (■, □); at T = 339 °C and W/F = 0.037 g_{CAT} min mL⁻¹, (●, ○); at T = 311 °C and W/F = 0.073 g_{CAT} min mL⁻¹ (▶, ▷). The experiments were carried out in the presence of oxygen (MeOH/O₂/N₂ molar ratio of 6/13/81) and in the absence of oxygen (MeOH/N₂ molar ratio of 6/94).

Figure 11. FTIR spectra of adsorbed methanol in the presence (A) and in the absence of O₂ (B) on WTi-4 catalyst at different temperatures of evacuation: a) 80 °C; b) 160 °C; and c) 240 °C. For comparative purposes, the spectra of the corresponding fresh catalyst recorded at 25 °C is also included in the figure (*).