

Influence of phase composition of bulk tungsten-vanadium oxides on the aerobic transformation of methanol and glycerol

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Abstract: A series of W-V-O catalysts which present different m-WO3 and h-WO3 phase contents were hydrothermally synthesized employing different tungsten, vanadium and ammonium precursors. Characterization of these materials was carried out by several physicochemical techniques such as powder X-Ray diffraction, N2adsorption, SEM, XEDS, TG, Raman, FT-IR spectroscopy, TPD-NH₃, H₂-TPR and XPS. Finally, acid-redox properties were analyzed using methanol aerobic transformation as a characterization reaction. A correlation between phase composition as well as acid- and redoxproperties was observed, which were correlated to the catalytic performance of the titled materials in the one-pot glycerol oxydehydration reaction. The hexagonal tungsten bronze, h-WO₃, phase shows a concentration of acid sites significantly higher than that of the monoclinic m-WO3, making acid properties of W-V-O oxides directly related to the presence of h-WO3 crystals. The presence of a higher concentration of acid sites in V-containing h-WO₃ crystals is a key factor to achieve high selectivity to both acrolein and acrylic acid during the one-pot glycerol oxydehydration. Also, V-sites in h-WO₃ present higher selectivity in the consecutive reaction (acrolein partial oxidation to acrylic acid), while V-sites in m-WO₃ phase fundamentally lead to the formation of carbon oxides.

Introduction

Tungsten oxides have received special attention in the last decades since they present potential uses in a wide variety of fields such as electrochromic displays, gas sensing, superconductivity or catalysis.^[1-4] Particularly, they have emerged in the last years as interesting materials for several catalytic applications. Indeed, they are well-known multifunctional materials for fuel cells, being employed as electrocatalysts and supports.^[5-8] Oxygen deficient tungsten oxides-based materials, known as tungsten bronzes, are known as catalysts for the electrochemical oxidation of C_2 - C_3 alcohols ^[9-11] and hydrogen in acid media.^[12] Tungsten oxide bronzes have also been used in electrocatalysts for oxygen reduction, ^[13] photocatalysts ^[14] and as efficient catalysts in the hydrogenation

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of linear and cyclic alkenes, nitroarenes or unsaturated organosulfur compounds.^[15] Moreover, they have been widely studied as acid catalysts for different processes,^[16, 17] but also as acid-redox multifunctional materials, due to their ability to accommodate different kinds of metals and non-metals within the structure. Recently, mixed metal oxides with tetragonal tungsten bronze (TTB) structure have shown high activity and selectivity for the gas phase partial oxidation of olefins,^[18] whereas materials presenting hexagonal tungsten bronze (h-WO₃) structures have been proposed as active and selective catalysts in the aerobic transformation of alcohols, such as the one-pot oxydehydration of glycerol to acrylic acid.^[19, 20] In this way, a parallelism between the selectivity to acrylic acid from glycerol and the catalytic behavior of the corresponding catalysts during the aerobic transformation of methanol was proposed.^[21]

From the synthetic point of view, the control of key parameters of the synthesis, such as pH, organic additives or the precursors used on the formulation, made it possible to obtain different phase compositions, particles sizes and crystal shapes. It was demonstrated that all these features can have an important influence in their functionality, specifically in their catalytic performance.^[22-25]

Herein, we report on the preparation and characterization of a series of W-V-O mixed oxides and their catalytic behavior in both the aerobic transformation of methanol and the oxydehydration of glycerol. Depending on the W-, V- or ammonium-precursors, different morphologies, thermal stabilities and ratios of monoclinic (m-WO₃) to hexagonal (h-WO₃) phases were obtained. The analysis of the selectivity profiles in the aerobic transformation of methanol sheds light on the acid-redox properties of the materials, which appear to be correlated with the m-WO₃/h-WO₃ phase ratio. In order to corroborate these findings, catalysts were finally tested in the glycerol oxydehydration reaction, where both acid and redox sites are necessary to achieve a relatively high yield to acrylic acid. It was found that the presence of h-WO₃ is pivotal to tune the acid and redox properties for the selective transformation of glycerol to acrylic acid.

Results and Discussion

Characterization of W-V-O metal oxides

The main physical and chemical features of W-V-O materials are summarized in Table 1. V/(W+V) ratios after synthesis are in the range between 0.12-0.18 for all the studied materials. This means that almost half of the vanadium added into the synthesis gel (W/V ratio in the synthesis of 1/0.3) does not incorporate into the oxides framework after hydrothermal treatment, regardless

Table 1 Characteristics of W-V-O mixed oxides catalysts

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	Sample	Precursors ^[a]			V/(W+V) atomic ratio		h-WO ₃ phase content (%) ^[d]		Sbet	Weight loss at 350 °C ^[e]	TPD-NH ₃ ^[f]		
		W	V	NH4+-salt	Bulk ^[b]	Surface ^[c]	As-prepared	Heat-treated	(m ² g ⁻¹)	(%)	(µmol/g)		
	AMT-1	AMT	VS	-	0.17	0.05	100	100	20.5	5.42	n.d.		
	AMT-2	AMT	VOAC	-	0.17	0.16	n.d. ^[g]	n.d. ^[g]	16.1	5.37	127		
	TA-1	ТА	VS	NH ₃ (aq)/NH ₄ Cl	0.16	0.07	100	100	32.8	5.65	241		
	TA-2	ТА	VS	NH ₄ SO ₄	0.12	n.d.	42	31	13.5	2.58	n.d.		
	TA-3	ТА	VS	NH ₄ Cl	0.12	0.08	46	26	7.2	1.77	50		
	TA-4	ТА	VS	NH ₄ CH ₃ CO ₂	0.17	0.15	41	0	7.9	2.91	86		
	TA-5	ТА	VOAC	NH ₄ CH ₃ CO ₂	0.18	0.19	60	54	26.6	4.82	88	i.	

[a] **AMT**= (NH₄)₆H₂W₁₂O₄₀; **TA**= H₂WO₄; **VS**= VOSO₄; **VOAC**= VO(acac)₂. [b] V/(W+V) ratio obtained by X-Ray energy-dispersive spectroscopy (XEDS). [c] Calculated by X-Ray Photoelectron Spectroscopy (XPS). [d] Calculated from equation: h-WO₃ (%)= 100 x I₁₀₀(h-WO₃)/[I₀₂₂(m-WO₃) + I₁₀₀(h-WO₃)]. [e] Obtained by thermogravimetric analysis. [f] Temperature-programed desorption of ammonia. [g] A pseudocrystalline phase is only observed.

the type of precursor used for the preparation.

Figure 1 shows XRD patterns of both as-prepared (Figure 1A) and heat-treated materials (Figure 1B). Focusing on as-prepared catalysts, two pure bronze phases where obtained when ammonium metatungstate or an ammonia/ammonium chloride mixture were used as ammonium source (Figure 1A, patterns a to c). Characteristic diffraction patterns of these phases correspond to those of an hexagonal tungsten bronze type structure (h-WO₃) (JCPDS: 33-1387) (Figure 1A, patterns a and c),^[19, 26] and a pseudo-crystalline phase related to the ReO₃phase, with long-range order just along c-axis (Figure 1A, pattern b).^[20] On the other hand, when using tungstic acid and other ammonium salts such as ammonium sulfate or ammonium acetate as precursors, mixtures of h-WO3 and perovskite related ReO₃-type monoclinic WO₃ phase (*m*-WO₃) were obtained (JCPDS: 43-1035) (Figure 1A, patterns d-g). An unknown crystalline phase was also formed when using ammonium acetate, tungstic acid and vanadyl acetylacetonate on the synthesis (Figure 1A, pattern g), which decomposes after heattreatment (Figure 1B, pattern g). In this regard, the presence of meta-tungstate in the synthesis gel, or even the possible in-situ formation of isopolytungstates during the hydrothermal treatment could have an important influence in the formation of pure bronze-type compounds.^[18, 27, 28] XRD patterns of heat-treated materials are presented in Figure 1B. It can be seen that asprepared pure h-WO₃ phases remain stable after the thermal treatment (Figure 1B, patterns a and c). However, in the remaining cases bronze-type phases partially decompose into m-WO₃ (Figure 1B, patterns b, d-e). Relative proportions of h-WO3 phase in the samples were estimated from the intensities of (100) and (022) Bragg peaks of h-WO₃ and m-WO₃ phases, respectively (Table 1). As-prepared materials present h-WO3 phase percentages in the range 41-100 %, while after heattreatment percentages in the range 0-100 % were obtained, due to bronze phase partial or total decomposition (Table 1).

Moreover, catalysts presenting higher percentages of bronze phase also present higher surface areas (Table 1).



Figure 1. XRD patterns of as-prepared (A) and heat-treated (B) W-V-O oxides: a) AMT-1; b) AMT-2; c) TA-1; d) TA-2; e) TA-3; f) TA-4; g) TA-5. Red: *h*-WO₃; Blue: *m*-WO₃.

Figure 2 shows SEM micrographs of as-prepared materials. Pure h-WO₃ and pseudocrystalline phases present mainly 1D morphologies, such as rod and needle-shaped structures (Figure 2, a-c).

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Figure 2. SEM micrographs of as-prepared oxides: a) AMT-1; b) AMT-2; c) TA-1; d) TA-2; e) TA-3; f) TA-4; g) TA-5.



Figure 3. SEM and TEM micrographs of heat-treated materials. a) TA-4; b) AMT-1; c) TA

On the other hand, samples consisting of h-WO₃/m-WO₃ mixtures present both block-shaped and rod/ needle-shaped structures (Figure 2, d-g). This fact could have an important influence in the stability of the tungsten bronze phases since block-shaped morphologies exposing higher proportion of (001) faces could facilitate the elimination of NH₄⁺ cations through the

channels, favoring phase transitions to *m*-WO₃ type structures.^[29, 30] Moreover, it can be noted that after heat treatment block-type particles undergo decomposition into platelet-shaped ones, which has been identified with *m*-WO₃ type structure (Figure 3a). However, 1D morphologies retain their shape after heat-treatment (Figure 3b). According to XRD patterns, and other results reported previously in literature, these morphologies can be attributed to tungsten bronze-type structures.^[31-33] Therefore, heat-treated catalyst, which present a mixture of both tungstenbronze and *m*-WO₃ phases, show both 1D structures and platelet-shaped particles (Figure 3c). Nevertheless, we cannot exclude the influence of the effective substitution of V for W within *h*-WO₃ framework, which has also been reported to increase the thermal stability of the hexagonal tungsten bronze structure.^[21]

Raman spectra of heat-treated samples are depicted in Figure 4. They show typical Raman profiles for tungsten based oxides at ca. 709, 808 and 969 cm⁻¹, that can be assigned to W-O-V, W-O-W and M=O (M: W, V) bond vibrations respectively.^[34-36] It is noteworthy to mention that no bands over 1000 cm⁻¹ are found on the spectra, which means that no V₂O₅ was formed after calcination.^[37] Pure monoclinic *m*-WO₃ phase material presents Raman bands centered at 709, 808 and 983 cm⁻¹ (Figure 4, spectrum f), while a slight shift to lower frequencies occurs on the pure hexagonal bronze phase, *h*-WO₃, with corresponding Raman signals at 683, 800 and 969 cm⁻¹ respectively (Figure 4, spectrum a). Furthermore, the presence of both *h*-WO₃ and m-WO₃ phases gives rise to a Raman spectrum showing characteristic bands from both of them (Figure 4, spectra d-e and g).

The as-prepared materials have been also studied by Differential Thermogravimetric (DTG) analysis. DTG profiles show two main weight losses in the temperature ranges already reported for other tungsten oxide-based materials (Fig. S1,

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supporting information): i) below 200 °C; and ii) in the range 250-450 °C, which have been assigned to the elimination of physisorbed water and ammonium cations from the channels respectively.^[38, 39] These weight losses are notably higher in samples with high proportion of *h*-WO₃ or pseudocrystalline phase (Table 1), which also present a weight gain around 500 °C, fact that could be associated to the oxidation of V⁴⁺ and/or W⁵⁺ centers to V⁵⁺ and W⁶⁺, respectively (Figure S1, patterns ac). In this way, an additional weight loss is also observed at 400 °C in sample **TA-5**, that could be related to the previously mentioned unknown phase found by XRD (Fig. S1, pattern g).



Figure 4. Raman spectra of heat-treated W-V-O catalysts: a) AMT-1; b) AMT-2; c) TA-1; d) TA-2; e) TA-3; f) TA-4; g) TA-5.

FTIR spectra of as-prepared and heat-treated materials were collected in order to study the activation process of the catalysts (Figure 5). As-prepared materials present three main bands in the range 3700-3000 cm⁻¹ (Figure 5A). The signal centered at 3430 cm⁻¹ has been attributed to O-H groups stretching vibrations, while remaining signals appearing at 3215 and 3144 cm⁻¹ are associated to N-H stretching vibrations of the corresponding ammonium cations located inside the channels.^[38, 40, 41] However, heat-treated samples show no bands in the NH₄⁺ region due to the elimination of these ions from the structure (Figure 5B). The substitution of H⁺ for ammonium ions within the channels has been reported to be the origin of the acid centers in tungsten bronze-type structure-based catalysts.^[42]



Figure 5. FTIR spectra of as-prepared (A) and heat-treated (B) catalysts: a) AMT-1; b) AMT-2; c) TA-1; d) TA-2; e) TA-3; f) TA-4; g) TA-5.

Acid features of heat-treated materials were studied by means of temperature programmed desorption of ammonia (Figure 6). It can be noted that the highest concentration of acid sites is obtained for high contents of bronze-type phases, either h-WO₃ or pseudocrystalline phase (Table 1).



Figure 6. TPD-NH_3 profiles of selected W-V-O materials: a) TA-4; b) TA-3; c) TA-5: d) AMT-2; e) TA-1.

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Thus, these results suggest that the presence of relatively wider channels could favor the formation of Brönsted acid sites, by elimination of NH_4^+ ions during the activation at high temperature as reported elsewhere,^[42] meanwhile *m*-WO₃ structure would present a lower concentration of surface acid sites.

Despite this, the influence of other variables, such as surface area or surface vanadium concentration cannot be ruled out. Thus, XPS experiments show very different vanadium surface contents (much lower than that of bulk composition in some cases) depending on the synthesis procedure (Table 1). The V $2p_{3/2}$ core level spectra of all the studied W-V-O mixed oxide catalysis shows a single peak at 517.1-517.6 eV assigned to the presence of V⁵⁺, except in the case of sample AMT-1 were two contributions at 517.1 eV (86%) and 515.7 eV (14%) assigned to V⁵⁺ and V⁴⁺ are observed, respectively (Figure S2). The W 4*f* core level spectra for the studied catalysts are very similar, with a W 4*f*_{7/2} peak centered at 35.9-36.3 eV, assigned to W⁶⁺ (Figure S3).^[43]

Interestingly, H₂-TPR profiles of phase-pure W-V-O materials, i.e. presenting monophasic *h*-WO₃-type (**AMT-1** sample) and *m*-WO₃-type (**TA-4** sample) structures, display two main reduction peaks (Figure S4). The peak appearing at a lower temperature (528 and 597 °C for *h*-WO₃ and *m*-WO₃-type phase, respectively) can be attributed to the reduction of V⁵⁺ species, whereas H₂-uptakes at higher temperatures (635 and 662 °C for *h*-WO₃ and *m*-WO₃-type phases respectively) can be ascribed to the reduction of W⁶⁺ cations. ^[19] In this sense, the reducibility V⁵⁺ and W⁶⁺ species within the hexagonal tungsten bronze framework is higher with respect to those in the *m*-WO₃-type phase. This fact can have important implications when we deal with oxidation reactions, as it will be discussed later.

Catalytic results in the aerobic transformation of methanol

Methanol transformation has been widely used as a test reaction, either for determining acid and/or redox features, or for the elucidation of surface structure-reactivity relationships of bulk metal oxide catalysts.^[44-46] Indeed, the selective transformation of methanol in aerobic conditions has been reported to be an efficient method to estimate acid/redox multifunctional properties in tungsten bronze-based catalysts.^[21, 47] When a molecule of methanol reacts with Brönsted acid sites, it essentially leads to the formation of dimethyl ether (DME). On the other hand, when the reaction takes place on redox sites (e.g., V^{4+/5+} sites) it leads to the formation of partial oxidation products (mainly formaldehyde, but also other oxygenates products such as methyl formate or dimethoxymethane, as minorities) and carbon oxides (CO_x).^[46]

Figure 7 shows the variation of the selectivity to partial oxidation products (i.e. mainly formaldehyde, and small amount of methyl formate and dimethoxymethane, grouped as "POPs") and dimethyl ether (DME) with methanol conversion during the aerobic transformation of methanol over W-V-O catalysts. According to these results, there are important differences depending on both the physico-chemical and structural characteristics of catalysts.

Acid/redox features of W-V-O oxides were evaluated taking into account the selectivity profiles obtained for each material at low methanol conversion (c.a. 10%) (Figure 8). Hence, selectivity to DME progressively increases with the amount of h-WO₃ phase in the catalysts (Figure 8), while the opposite trend is observed in the selectivity to partial oxidation products, i.e. POPs (Figure 8). On the one hand, as m-WO₃ concentration increases in the catalysts, the acid function is progressively lost, for the benefit of the redox one, achieving the highest selectivity to POPs in the absence of h-WO₃ phase.



Figure 7. Selectivity to dimethyl ether (DME) and selectivity to partial oxidation products (POPs) of W-V-O catalysts: AMT-1 (\triangleleft); AMT-2 (**x**); TA-1 (\triangleright); TA-2 (\blacklozenge); TA-3 (O); TA-4 (\blacksquare); TA-5 (\bigtriangledown). Experimental conditions in text.



Figure 8. Variation of the selectivity to DME (\Box, Δ) and to partial oxidation products, POPs $(\bullet, \blacktriangle)$ vs. the amount of *h*-WO₃ phase in catalysts during the aerobic transformation of methanol on W-V-O oxides at a methanol conversion of 10 %. The amount of *h*-WO₃ phase as in Table 1. The percentage of bronze phase of AMT-2 catalyst (Δ, \blacktriangle) has been estimated by considering the selectivity to DME and POPs during the catalytic experiment.

On the other hand, the presence of h-WO₃ phase leads to multifunctional acid/redox catalysts, in which its acid character increases with the concentration of hexagonal tungsten bronze phase, achieving a maximum DME selectivity of c.a. 50 %. Thus, a clear relationship exists between the amount of h-WO₃ phase in W-V-O catalysts and the acid/redox properties of the samples, as shown in Figure 8. Accordingly, the selectivity to POP's and DME observed over sample AMT-2 (with a pseudocrystalline phase) should correspond to a material presenting ca. 88 % of h-WO₃ phase. In fact, XRD pattern shows a slight decomposition of this phase into m-WO₃ after the heat-treatment (Figure 1B, pattern b).

Catalytic results in the oxydehydration of glycerol

Tungsten and molybdenum/vanadium-based bronze phases have been reported to be one of the best catalytic systems for the production of acrolein (AC) and acrylic acid (AA) from alvcerol.^[19-21, 47-51] In this regard, the acid-redox character of the catalysts is pivotal. Acrolein is obtained by the direct dehydration of glycerol on acid sites of moderated strength, while acrylic acid is generated in a consecutive step by partial oxidation of acrolein on redox sites. In fact, the presence of $V^{4+/5+}$ and $Mo^{5+/6+}$ species within the crystal structure gives rise to the redox function in these materials (likely structural O2- sites via Mars-van Krevelen mechanism, as typically observed for redox oxides).^[51] Therefore, the presence of a bifunctional acid-redox catalyst, in which both functions work at the same temperatures is necessary in order to obtain acrylic acid in a one-pot reaction system. Figure 9 shows the effect of h-WO₃ phase-content (in %) on the selectivity to both acrolein and acrylic acid (AA+AC) and CO_x, and the acrylic acid/acrolein ratio. As it can be seen, the presence of V-containing h-WO₃ crystals promotes the formation of both acrolein and acrylic acid. In the opposite trend, lower amounts of h-WO₃ phase in the catalyst give rise to the main formation of carbon oxides (rather than acrylic acid) and heavycompounds.^[19] This is in line with H₂-TPR results, in which Vcontaining h-WO₃ crystals present V⁵⁺ sites with higher reducibility than those in V-containing m-WO₃ crystals (Figure S4), favoring the oxidation via structural O²⁻ species, which would give rise to the partial oxidation of acrolein to acrylic acid. On the other hand, the lower reducibility of V5+ sites in W-V-O catalysts presenting m-WO3 would favor the oxidation via adsorbed oxygen species (i.e. $O^{\text{-}}$ or $O_2^{\text{-}})$ which would lead to total oxidation of acrolein to carbon oxides.[51] Moreover, the AA/AC ratio increases with h-WO3 content in the catalysts. These observations not only mean that vanadium sites in m-WO3 containing catalysts are not selective in the partial oxidation of acrolein to acrylic acid, but also that their low acid characteristics (as it can be inferred from TPD-NH3 and methanol aerobic transformation results) give rise to low selectivity to acrolein in the first reaction step, favoring the formation heavy by-products. [19]





Figure 9. Variation of the selectivity to acrylic acid + acrolein (\bullet) selectivity to CO_x (\Box) and the acrylic acid / acrolein ratio (\uparrow) as a function of the amount of *h*-WO₃ phase in catalysts during the glycerol oxidehydration over W-V-O materials. Reaction conditions: T= 320 °C; Contact time, W/F, of 81 g_{CAT} h (mol_{GLY})⁻¹. The amount of *h*-WO₃ phase as in Table 1.

In this way, adjusting the reaction conditions (mainly temperature, feed composition and contact time) when dealing with multifunctional catalysts and multi-step reactions is a key factor in order to achieve maximum yields to products. Thus, using 100 % *h*-WO₃-type W-V-O mixed oxide (**AMT-1** sample) at optimum reaction conditions it is possible to attain yields to acrolein and acrylic acid of 23.6 and 32.5 %, respectively (T= 266°C, and a rate of formation of acrylic acid per unit mass of catalyst, STY, of 0.36 g_{AA} h⁻¹ g_{cat}⁻¹) (Table S1).

Conclusions

Several W-V-O catalysts presenting different proportions of h- WO_3 and *m*- WO_3 phases have been synthesized. Selecting the appropriate tungsten, vanadium and ammonium precursors, materials with different morphologies and thermal stability can be obtained. Indeed, block-shaped crystals undergo a higher thermal decomposition of the initial *h*-WO₃ phase into *m*-WO₃, while bronze-type phases, presenting 1D-type morphologies (mainly rod and needle-shaped), show higher stability under the same thermal treatment. Catalytic tests on the aerobic transformation of methanol show that pure *m*-WO₃-type phase presents very low concentration of acid sites, showing mainly redox sites (initial selectivity to POPs of c.a. 98 %). As h-WO₃ phase proportion increases, acid function is progressively generated, as it can be inferred from the selectivity profiles that show increasing amounts of DME, reaching approximately 50 % of initial selectivity to both POPs and DME over catalysts presenting mainly h-WO₃ type phase. Catalytic tests on glycerol oxydehydration reaction indicate that the absence of acid sites in m-WO₃ type phases has a negative effect in the production of acrolein and, accordingly, in the production of acrylic acid. The presence of h-WO3 phase containing both acid and redox sites working in a cooperative way increases the production of acrolein in the first step and acrylic acid in the consecutive

reaction. Moreover, acrylic acid/acrolein ratio increases with the h-WO₃ proportion, which means that V-sites into the bronze structure are selective to the partial oxidation of acrolein to acrylic acid, whereas redox sites in m-WO₃-type phase are less selective in the partial oxidation of glycerol, producing essentially carbon oxides (and also heavy-compounds).

Experimental Section

Synthesis of W-V-O oxides

Preparation of W-V-O materials was carried out under hydrothermal conditions from gels containing different tungsten, vanadium and ammonium precursors, while maintaining a constant W/V ratio of 1/0.3 in the synthesis gel (Table 1). Gels were obtained from aqueous solutions of the corresponding metal- (W- and V-) and ammonium-precursors: ammonium metatungstate hvdrate (≥85 wt% WO₃ basis, Sigma–Aldrich). tungstic acid (99%, Sigma Aldrich), vanadium(IV) oxide sulfate hydrate (≥97%, Sigma–Aldrich), vanadyl acetylacetonate (99.98%, Sigma– Aldrich), ammonium chloride (99.998%, Sigma-Aldrich), ammonium sulfate (99.0 %, Sigma-Aldrich), ammonium acetate (98%, Sigma-Aldrich) or aqueous ammonia (25 %, Panreac). These materials will be named as AMT-series or TA-series, depending on the tungsten precursors, i.e. ammonium metatungstate or tungstic acid, respectively. The synthesis gels were introduced in Teflon-lined stainless steel autoclaves, under N₂ atmosphere (1 bar), and treated at 175 °C for 48h. The resulting solids were then filtered, washed with water, and dried at 100 °C overnight. Finally, heat-treatment was carried out in two steps: i) a heat-treatment at 200 °C for 1 h, in air flow; and ii) a heat-treatment at 600 °C for 2 h under N₂ flow (15 mL min⁻¹ g⁻¹).

Characterization of catalysts

Powder X-Ray diffraction (XRD) patterns were collected in a PANalytical X'Pert PRO diffractometer equipped with and X'Celerator detector in a Bragg-Brentano geometry using K α radiation of copper.

Surface areas were calculated by BET method, from adsorption isotherms recorded on a Micromeritics ASAP 2000. Solids were degassed previously under vacuum at 400 °C.

X-Ray energy-dispersive spectroscopy (XEDS) analyses were performed using an Oxford LINK ISIS system connected to a JEOL 6300 electron microscope with the SEMQUANT program, which introduces ZAF correction. The counting time for each analysis was 100s.

Scanning electron microscopy (SEM) micrographs were carried out in a field emission ZEISS Ultra-55 scanning electron microscope operating at an accelerating voltage of 2 kV.

Raman spectra were collected with an inVia Renishaw spectrometer using an exciting wavelength of 514 nm. The laser used was a Renishaw HPNIR with an approximate power on the samples of about 15 Mw.

Thermogravimetric experiments were carried out in a Mettler-Toledo TGA/SDTA 851 thermobalance. Approximately 10 mg of sample were heated at 600 °C at 10 °C/min heating rate in a 50 mL/min synthetic air flow.

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.

Temperature programmed desorption of ammonia (TPD-NH₃) was carried out to evaluate the total acidity of the catalysts. Prior to the adsorption of NH₃, 80 mg of each sample were heated from room temperature to 500°C (heating rate: $10 \, ^{\circ}$ C min⁻¹) and then maintained at 500°C during 10 min under flowing He (35 mL min⁻¹). Subsequently,

samples were cooled to 10 °C and then exposed to flowing pure ammonia for 5 min. With the aim to remove the physisorbed ammonia, samples were cleaned using He flow (35 mL min⁻¹) again. TPD-NH₃ was performed between 100 °C and 500 °C with a heating rate of 10 °C min⁻¹ by using a helium flow and maintained at 500 °C for 15 min. The desorbed ammonia was analyzed by online gas chromatography (Shimadzu GC-14A) provided with a TCD.

X-ray photoelectron spectra were registered using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg-K α radiation (300 W, 15 kV, and 1256.6 eV) with a multi-channel detector. Spectra of powder samples were recorded in the constant pass energy mode at 29.35 eV, using a 720 μ m diameter analysis area. Charge referencing was measured against adventitious carbon (C 1*s* at 284.8 eV). A short acquisition time of 10 min was first used to examine C 1*s*, V 2*p* regions to avoid photoreduction of vanadium(V) species. A PHI ACCESS ESCA-V6.0 F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine the binding energies of the different element core levels more accurately.

Temperature programmed reduction experiments (H₂-TPR) were carried out under a N₂/H₂ flow (10% H₂ at a total flow of 50 mL min⁻¹) with 15 mg of catalyst. The measurements were conducted in the temperature range 100-800 °C at a heating rate of 10 °C min⁻¹.

Reactivity tests

The aerobic transformation of methanol was carried out in a fixed bed reactor in the 180-380 °C temperature range, at atmospheric pressure and a contact time, W/F, of 6.8 g_{CAT} h (mol_{CH3OH})⁻¹. The feed consisted of methanol/oxygen/nitrogen with a molar ratio of 6/13/81. Analysis of reactants and reaction products was performed by means of gas chromatography using two different chromatographic columns: i) Molecular sieve 5 Å (3m length); and ii) RT-U-bond, fused Silica PLOT (30 m, 0.53 i.d.).

The catalytic tests for the gas phase glycerol oxydehydration were also conducted in a fixed-bed reactor at atmospheric pressure, with the following reaction mixture: 2 mol% glycerol, 40 mol% water, 4 mol% oxygen and 54 mol% helium, and a contact time W/F of 81 g_{CAT} h (mol_{GLY})⁻¹. The effluent stream was bubbled through a condenser, which was refrigerated at 0-3 °C. The remaining gaseous stream containing carbon oxides and oxygen was analyzed by an online gas chromatograph equipped with: (i) molecular sieve 5 Å (3 m); and (ii) Porapak Q (3 m). The condensed aqueous solution containing all the reaction products and the unconverted glycerol was 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).

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Keywords: glycerol • acrylic acid • oxydehydration • W–V mixed oxides • hexagonal tungsten bronze

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Influence of phase composition of bulk tungsten-vanadium oxides on the one-pot synthesis of acrylic acid from glycerol

Layout 2:

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By selecting the appropriate W-, V-, and NH_4^+ -precursors it is possible to tune the acid-redox properties in the system W-V-O. These catalytic properties depend on the content of *h*-WO₃-type (acid/redox sites) and/or *m*-WO₃ (redox sites) phases in the catalysts. The presence of V-containing *h*-WO₃ type crystals is pivotal to achieve good yields to acrolein and acrylic acid in the one-pot gas-phase oxydehydration of glycerol.

D. Delgado, A. Chieregato, M. D. Soriano, E. Rodríguez-Aguado, L. Ruiz-Rodríguez, E. Rodríguez-Castellón and J. M. Lopez Nieto*

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