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# WO<sub>3</sub> Supported on Zr Doped Mesoporous SBA-15 Silica for Glycerol Dehydration to Acrolein

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#### **Graphical Abstract**



#### Highlights

- WO<sub>3</sub> supported over Zr-SBA-15 catalysts are active in dehydration of glycerol, being always acrolein the main product which is considered as a versatile intermediate for the chemical industry.
- $WO_3$  enhances the total acidity and the Brönsted acid sites ratio of support, consequently improving the activity and stability of catalysts in glycerol dehydration to acrolein.
- Glycerol conversion and acrolein yield are maintained after 8 h for W catalysts, attaining the highest values for a WO<sub>3</sub> loading of 20 wt% which may be related to WO<sub>3</sub>-ZrO<sub>2</sub> phases on catalyst surface.
- Although the H<sub>3</sub>PO<sub>4</sub> treatment enhances acrolein yield for short reaction times, high amounts of acid damage the textural and acidic properties of W catalysts, decreasing the available acid sites.

#### Abstract

Glycerol dehydration to acrolein is one of the most promising routes to valorize the surplus of such by-product of the biodiesel industry. In this context, a family of solid acid catalysts based on tungsten oxide supported over zirconium doped mesoporous SBA-15 silica has been synthesized and the influence of phosphoric acid treatment on the catalytic behaviour has been also evaluated. These catalysts have been characterized by using the following techniques: XRD, N<sub>2</sub> adsorption-desorption at -196 °C, NH<sub>3</sub>-TPD, pyridine adsorption coupled to FT-IR spectroscopy, X-ray photoelectron spectroscopy, Raman and diffuse reflectance UV-visible spectroscopies, and they have been tested in the gas-phase dehydration of glycerol. Under the operating conditions assayed, all catalysts were active and acrolein was always the main product. The catalytic performance of support was enhanced when WO<sub>3</sub> oxide was supported and after treatment with H<sub>3</sub>PO<sub>4</sub>. The best catalytic results were achieved for 20W catalyst which showed values of glycerol conversion and acrolein yield equal to 97% and 41% respectively after 2 h on stream at 325 °C and this activity was even maintained after 8 h. Moreover, the treatment with phosphoric acid improved the acrolein yield at 2 h on stream, but the deactivation of these catalysts was more pronounced probably because of the deterioration of textural properties and total acidity.

**Keywords:** tungsten oxide; phosphoric acid; acid catalysts; glycerol; acrolein; zirconium doped mesoporous silica

#### 1. Introduction

Due to the increasing cost and depletion of fossil fuel reserves, renewable fuels have been spread worldwide in last years, being biodiesel a remarkable example of biofuels. Biodiesel is a mixture of alkyl esters produced by transesterification of vegetable oils and animal fats with short-chain alcohol, obtaining glycerol as by-product [1, 2]. Hence, a large surplus of glycerol has been generated by the biodiesel industry, being essential its valorization to ameliorate the sustainability and economical viability of the biodiesel industry [3, 4]. Glycerol is one of the most versatile and valuable chemical in industry, since more than 1500 direct applications are already known, especially in cosmetics, pharmaceuticals and food industries [5, 6]. Moreover, glycerol is a molecule with a large potential since it offers many opportunities to produce addedvalue chemicals through different reactions, such as hydrogenolysis, partial oxidation, etherification, halogenation, esterification or dehydration [5, 7].

One of the most promising routes of glycerol valorization consists of its catalytic dehydration to acrolein, an important and versatile intermediate for the chemical industry [8]. Most of produced acrolein is employed for the synthesis of acrylic acid which is a chemical with high demand, whose annual global growth rate is of 4%. Likewise, acrolein is widely utilized in the synthesis of 3-methylthiopropionaldehyde, a precursor of D,L-methionine which is an essential amino acid required in meat production to accelerate animal growth [8], as well as in the production of glutaraldehyde, 1,2,6-hexanetriol, quinoline, pentaerythritol, cycloaliphatic epoxy resins, oil-well derivatives and water treatment [9]. In addition, it can be directly used as

an effective aquatic biocide to control the growth of undesired microbial material and aquatic weeds.

Acrolein is currently produced from partial oxidation of propylene catalyzed by complex multicomponent  $BiMoO_x$  catalysts [10]. Its production from dehydration of glycerol is considered of great interest by researchers due to glycerol is a relatively inexpensive raw material which is available from biodiesel industry. Although it is known that acrolein can be obtained from thermal decomposition of glycerol, it is convenient to employ an acid catalyst in order to improve the catalytic performance. Thus, different acid catalysts have been tested for dehydration of glycerol to acrolein, such as zeolites [11-14], heteropolyacids [15-17], sulfated zirconia [18, 19] or metal oxide [20, 21]. Tungsten oxide can be found among the different active phases proposed for this reaction. Thus, Kraleva et al. synthesized a W-SBA-15 catalyst (Si/W molar ratio of 20) and achieved high activities even at low temperatures, obtaining a value of glycerol conversion about 88% at 275 °C. Its catalytic performance was also enhanced after 1,2-tungstophosphoric acid impregnation [16]. Chai et al. have tested WO<sub>x</sub> supported on Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and SiO<sub>2</sub> and they showed that the WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and  $WO_3/ZrO_2$  catalysts were more effective than  $WO_3/SiO_2$  to catalyze the glycerol dehydration in terms of acrolein selectivity, being the most effective catalyst 30 wt% WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> sample since the acrolein yield of 61% was maintained after 10 h [22]. Similarly, other researchers have studied WO<sub>3</sub> supported on ZrO<sub>2</sub> [23-25] and the effect of doping with Si atoms a  $WO_3/ZrO_2$  catalyst and they achieved high values of glycerol conversion and acrolein selectivity [25, 26]. Moreover, mixed oxides of tungsten and niobium have been supported over different materials, demonstrating to be active catalysts for this reaction [27-29]. Comparing niobium oxide with tungsten oxide,

Massa *et al.* observed that the catalytic activity of supported tungsten oxide was slightly better, with an initial yield to acrolein around 78% against 75% for niobium oxide, at complete conversion of glycerol after 3 hours of reaction [29]. In addition, they did not found a synergistic effect using mixed W/Nb oxides.

On the other hand, it is well known that the acidity of the active phase is a key parameter which affects the catalytic performance, being relevant the type of acid sites since several authors have proved that Brönsted acid sites provide higher values of acrolein selectivity than Lewis acid sites [30-32]. In this sense, phosphoric acid has been widely used in literature to increase the total acidity of catalysts by providing new Brönsted acid sites [33-35]. This fact has been corroborated by Struzhko et al., who recently treated a mesoporous WO<sub>x</sub>·ZrO<sub>2</sub> solid with phosphoric acid and evaluated its catalytic behavior in dehydration of glycerol, finding an increasing in the acrolein selectivity, although this also depended on the  $WO_x$  loading [36]. Likewise, Rao *et al.* tested tungsten oxide supported on porous zirconium phosphate reaching a high selectivity to acrolein (about 82%) at total glycerol conversion, at 300 °C [37]. They also demonstrated that the catalytic behavior mainly depended on both the fraction of acid sites of moderate strength and those of Brönsted type. Finally, Suprun et al. studied a family of transition metal supported on aluminophosphates (APO), being the highest acrolein selectivity (52-58%) reached with a W-APO catalyst [38]. Likewise, they evaluated the influence of different transition metal oxide on phosphated alumina on the gas-phase dehydration of glycerol in such a way that the highest acrolein selectivity was detected over W contained catalysts [39].

In addition, it should be pointed out that the deactivation of catalysts is an usual drawback in the glycerol dehydration reaction [7, 8]. In some catalytic systems studied, the porous network of the catalysts itself was one of the main source of deactivation since small pores could complicate the diffusion of the products and favored the formation of coke, which finally blocked the access to the active phase [7, 40]. Therefore, there is a great deal of interest to employ supports with high-surface area in order to enhance the dispersion of the active phase and improve the diffusion of reactants and products through the porous network.

The aim of this work was to synthesize solid acid catalysts based on tungsten oxide, as active phase, supported on zirconium doped mesoporous silica with a SBA-15 structure. These catalysts were tested in the gas phase dehydration of glycerol to acrolein, and the effect of the treatment with phosphoric acid was also evaluated. The influence on the catalytic performance of experimental parameters, such as reaction temperature and  $WO_x$  loading, has been studied.

#### 2. Experimental

#### 2.1. Synthesis of catalysts

A zirconium doped mesoporous SBA-15 silica with a Si/Zr molar ratio of 5 was synthesized following the method previously reported by Cecilia *et al.* [34], employing Pluronic P123 (Sigma-Aldrich, average Mn~5800), as structure directing agent, and tetraethyl orthosilicate (Sigma-Aldrich, 98%) and zirconium n-propoxide (Sigma-Aldrich, 70% in n-propanol) as sources of silicon and zirconium, respectively. The final molar composition of the synthesis gel was P123/SiO<sub>2</sub>/ZrO<sub>2</sub>/HCl/H<sub>2</sub>O= 1/55/11/350/11100. The resulting suspension was stirred at 40 °C for 72 h and the solid

product was recovered by filtration, washed with deonized water and dried at 60 °C, and finally calcined in air at 550 °C for 6 h, with a heating rate of 1 °C·min<sup>-1</sup>. This material was denoted as SiZr.

Tungsten oxide was supported on the SiZr support by incipient wetness impregnation, by using ammonium metatungstate hydrate (Sigma-Aldrich,  $\geq 66.5\%$  W) aqueous solutions to achieve WO<sub>3</sub> loadings ranging between 10 and 40 wt%. Then, these materials were dried at 60 °C, and calcined at 400 °C for 4 hours (heating rate of 2 °C·min<sup>-1</sup>) in order to form the WO<sub>3</sub> phase. The catalysts were labeled as *x*W, where *x* stands for wt% of WO<sub>3</sub>.

The 20W catalyst, before calcination, was treated with different amounts of  $H_3PO_4$ , obtaining 20WPy catalysts, where y symbolizes the W/P molar ratio. Next, they were dried at 60°C and calcined at 400 °C for 4 hours (20WPy).

#### 2.2. Characterization of catalysts

Powder diffraction patterns were collected on an PANalytical automated diffractometer, EMPYREAN model, using Cu-K $\alpha_1$ ,2 (1.5406 Å) radiation and a last generation PIXcel detector. The database employed were ICSD, PDF 2-2004 and COD of High Score Plus programme of PANalytical.

The textural parameters were determined from the nitrogen adsorption– desorption isotherms at -196 °C, obtained by using an automatic ASAP 2020 model of gas adsorption analyser from Micromeritics. Prior to N<sub>2</sub> adsorption, the samples were outgassed at 200 °C and 10<sup>-4</sup> mbar for 10 h. Surface areas were determined by using the Brunauer–Emmet–Teller (BET) equation and a nitrogen molecule cross section of 16.2

 $Å^2$ . The Density Functional Theory method (DFT) was employed to determine the pore size distribution.

X-ray photoelectron spectra were obtained with a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg K $\alpha$  radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra were recorded in the constant pass energy mode at 29.35 eV, using a 720  $\mu$ m diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). 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.

Raman spectra were recorded on a FT-Raman spectrometer, using a Nd:YAG laser as the excitation source at 1064 nm and the laser power was set to 150 mW and a standard spectral resolution of 4 cm<sup>-1</sup>. Raman spectroscopy was performed on powder samples without any previous treatment. UV–visible spectroscopy studies were carried out in the diffuse reflectance mode with a Shimadzu MPC3100 spectrophotometer and BaSO<sub>4</sub> as reference.

The temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was carried out to evaluate the total surface acidity of the catalysts. The catalysts (80 mg) were evacuated with helium at 550 °C and then ammonia was adsorbed at 100 °C. Finally, the NH<sub>3</sub>-TPD was performed by raising the temperature from 100 to 550 °C, under a helium flow of 40 mL min<sup>-1</sup>, with a heating rate of 10 °C min<sup>-1</sup> and maintained at 550 °C for 15

min. The evolved ammonia was analyzed by using a TCD detector of a gas chromatograph (Shimadzu GC-14A).

FTIR spectra of adsorbed pyridine were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR8300). Self supported wafers of the samples with a weight/surface radio of about 15 mg cm<sup>-2</sup> were placed in a vacuum cell greaseless stopcocks and CaF<sub>2</sub> windows. The samples were evacuated at 300 °C and  $10^{-2}$  Pa overnight, exposed to pyridine vapours at room temperature (vapour pressure of 200 mbar) for 10 min and then outgassed at 100 °C, 200 °C and 300 °C.

Carbon content of spent catalysts was measured with a LECO CHNS 932 analyzer. Thermogravimetric analyses (TGA) were carried out in a TGA/DSC 1 (Mettler–Toledo), measuring the weight variation under an air flow of 50 ml·min<sup>-1</sup> in the temperature range of 30-900 °C with a heating rate of 10 °C·min<sup>-1</sup>.

#### 2.3. Catalytic tests

The dehydration of glycerol was carried out, at atmospheric pressure, in a fixedbed continuous-flow stainless steel reactor (9.1 mm in diameter, and 230 mm in length), operated in the down-flow mode. The reaction temperature was measured with an interior placed thermocouple in direct contact with the catalyst bed. For the activity tests, 0.5 g of catalyst (particle size 0.85-1.00 mm), diluted with SiC to 3 cm<sup>3</sup> volume, were used. Catalysts were pre-treated in situ at atmospheric pressure under a N<sub>2</sub> flow of 15 mL min<sup>-1</sup>, at 325 °C for 30 min. The glycerol solution (10 wt% in water) was supplied by means of a Gilson 307SC piston pump (model 10SC) at 0.1 mL min<sup>-1</sup> feed rate in a N<sub>2</sub> flow (15 mL min<sup>-1</sup>). The evolution of the catalytic performance was studied by collecting liquid samples between 2 hours and 8 hours in a vial cooled in an ice trap.

These vials were sealed and analyzed by means of gas chromatograph (Shimadzu GC-14B), equipped with a flame ionization detector and a capillary column (TRB-14 Teknokroma).

The glycerol conversion (mol%), the selectivity of the identified products and the yields have been calculated as follows:

$$C(\%) = \frac{n_{Gly,in} - n_{Gly,out}}{n_{Gly,in}} \times 100$$

$$S_i(\%) = \frac{n_i}{n_{Gly,in} - n_{Gly,out}} \times \frac{z_i}{z_{Gly.}} \times 100$$

$$y_i(\%) = \frac{C \times S_i}{100}$$

where  $n_{in}$  and  $n_{out}$  represent the mol of glycerol at the inlet and outlet of the reactor.  $n_i$  is the molar concentration of the product *i* at the outlet of the reactor and  $z_i$  and  $z_{Gly}$  are the number of carbon atoms of the product *i* and glycerol, respectively. The carbon balance (mol%) was calculated by summing up the unreacted glycerol and the total quantities of detected and calibrated products. The selectivity of non-detected products was evaluated by difference between 100 and all quantified detected products.

#### 3. Results and discussion

#### 3.1. Characterization of catalysts

Powder X-ray diffraction has been used to identify crystalline phases present in these catalysts. Thus, XRD patterns at low-angle of *x*W catalysts (Figure 1A) show an intense peak at ca.  $2\theta = 1.2^{\circ}$  corresponding to the (1 0 0) reflection, confirming the

mesoporous structure, even after incorporation of the highest amount of tungsten oxide (40 wt.%). However, this diffraction peak is attenuated when catalysts are treated with phosphoric acid (20WPy), disappearing for 20WP0.2 catalyst, pointing out the collapse of the mesostructure of the SiZr support. This fact has been previously observed by Wu et al. [41], who found a less ordered structure after treatment of a mesoporous SBA-15 silica with phosphoric acid, although, in the present work, it is more marked in the case of the 20WPy catalysts, which can be attributed to the presence of tungsten oxide. With regard to the XRD patterns in the high-angle region (Figure 1B), the characteristic reflections of monoclinic and triclinic WO<sub>3</sub> phases are detected for all catalysts (Powder Diffraction Line reference codes 98-065-3651 and 98-008-0055, respectively) [42, 43], being mainly observed in 31-37° region (Supplementary Information, Fig. 1S). These diffraction peaks, as expected, are much more intense for WO<sub>3</sub> loadings higher than 10 wt%. However, their intensity is considerably decreased after phosphoric acid treatment, which could be probably due to the formation of amorphous W and P phases. In no case, tetragonal ZrO<sub>2</sub> phase has been found for these catalysts, so that zirconium apparently stays incorporated into the siliceous framework.

The mesoporous character of the *x*W catalysts has been confirmed from the corresponding nitrogen adsorption–desorption isotherms at -196 °C, since all catalysts display Type IV isotherms according to the IUPAC classification. Moreover, the shape of the isotherms is preserved after incorporation of different amounts of tungsten oxide (10-40 wt%) over the SiZr support, and even after treatment with phosphoric acid (Supplementary Information, Figure 2S). The determination of textural parameters reveals that the incorporation of increasing loadings of WO<sub>x</sub> species on the support leads to a decrease of specific surface area and pore volume in comparison with those of

the SiZr support (Table 1). This could be explained by the presence of WO<sub>3</sub> nanoparticles, detected by XRD, partially blocking the pores, thus modifying the pore size distribution of the SiZr support (Figure 2A). Thus, the SiZr support shows a wide range of pore sizes, from micropores to mesopores; however, when the WO<sub>3</sub> particles are generated, both the micropores and the pores with sizes comprised between 2 and 4 nm decreased, with the concomitant increase of the pores within the range of 4 to 6 nm. These two effects lead to an increase of the average pore diameters with respect to the support (Table 1). Likewise, the treatment with H<sub>3</sub>PO<sub>4</sub> provokes a serious damage in the mesostructure of these materials, decreasing markedly the surface area and pore volume, even up to 15 m<sup>2</sup>·g<sup>-1</sup> for 20WP0.2, and raising the average pore diameter, so that the treatment with phosphoric acid is detrimental for the textural properties, as Cecilia *et al.* [34] previously showed, corroborating the blockage of smaller pores (Table 1 and Figure 2B).

The **Raman** spectra of *x*W catalysts show major bands at 805, 715, 326 and 270 cm<sup>-1</sup> which can be ascribed to crystalline WO<sub>3</sub> nanoparticles, whose intensity rises with the WO<sub>3</sub> loading (Figure 3) [44, 45]. Thus, the bands at 805 and 715 cm<sup>-1</sup> are associated to bridging W – O – W stretching frequencies, whereas that the band at 270 cm<sup>-1</sup> is ascribed to the corresponding bending mode [46]. The weak band at 326 cm<sup>-1</sup> corresponds to the bending vibration mode of O – W – O bonds of surface WO<sub>x</sub> species [45]. Moreover, a broad and low intense band is discernible about 975 cm<sup>-1</sup> which is related to W=O vibration in hydrated polyoxotungstate clusters interacting with the support [46, 47]. The presence of WO<sub>x</sub> species have been associated with strong Brönsted acid sites [48]. Moreover, the characteristic bands of segregated ZrO<sub>2</sub> nanoparticles for xW catalysts are not observed, therefore the existance of ZrO<sub>2</sub>

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particles could be discarded as the XRD results previously shown. On the other hand, after the acid treatment, the 20WPy catalysts do not display any noticeable band.

**XPS** technique has been employed to get insights about the chemical state of tungsten in these catalysts (Table 2 and Supplementary Information, Fig. 3S). The binding energy (BE) values for Si 2p (103.3-103.5 eV) and Zr  $3d_{5/2}$  (183.2-183.6 eV) are typical of zirconium doped siliceous framework, as previously reported [34, 49, 50]. In the O 1s region, an asymmetric band was observed implying the existence of different oxygen environments which can be deconvoluted into two components: the most intense at 532.7-532.9 eV is associated to oxygen in silica [51, 52], and that a lower BE, 530.4-531.0 eV, corresponds to Si-O-Zr bonds (at 530.7 eV) [49]. For WO<sub>3</sub> loading higher than 10 wt%, the intensity of this latter band is increased and slightly shifted to lower BE values (Table 2), which may be due to the contribution of O 1s from WO<sub>3</sub> (530.4 eV) [53]. On the other hand, the BE of W 4f core level is within the range 35.3-36.3 eV, which is ascribed to  $W^{6+}$  regardless the tungsten loading [53, 54]. The typical line splitting for the W 4f core level due to the spin – orbit coupling is even difficult to discern, showing the W 4f photoelectronic peak a FWHM value of  $c.a. \sim$ 4.12 eV. That means that tungsten could be distributed over many non-equivalent sites, i.e. tungsten interacting with both zirconium and silicon sites, even the presence of  $W^{5+}$ cannot be rule out since  $4f_{7/2}$  and  $4f_{5/2}$  doublet falls in the same spectral region.

Likewise, it can be observed (Table 2) that the W/(Si+Zr) molar ratio determined by XPS increases, as expected, with the  $WO_3$  loading up to 30 wt%. However, this atomic ratio is lower than the corresponding bulk values (Table 2). Therefore, XPS analysis suggests that tungsten oxide could be mainly located inside the porous structure

of the support. This fact was previously observed from the analysis of textural parameters which showed a sharp decline of surface area of catalysts as the metallic loading was increased. Another important conclusion arising from the XPS data is that Si/Zr atomic ratio is increased as the tungsten oxide rises but reaching a plateau for loadings higher than 20 wt%. This behavior seems to indicate that the tungsten oxide is interacting primarily with zirconium domains and, as the metallic loading is increased, these tungsten oxide particles grow in size and spread around such initial seeds of tungsten species. These results are supported by both the XRD results, where the formation of WO<sub>3</sub> particles was detected even at lower tungsten loading, and Raman analysis, which showed the presence of both structures in the *x*W catalysts.

**UV–vis diffuse reflectance absorption spectra** of catalysts have been carried out in order to obtain information about the chemical nature and coordination states of W (Figure 4). The UV-vis spectrum of the SiZr support does not resemble to the bulk zirconia, due to the lack of the characteristic sharp absorption at 210 nm [52]. Nevertheless, it shows a band with a maximum at 293 nm and a broad band extending up to roughly 375 nm. This latter spectral feature has been associated to oligomeric zirconium species [55], whereas the band at 293 nm corresponds to isolated  $Zr^{4+}$  with low coordination [55, 56].

From the UV-vis spectra of the *x*W catalysts, the existence of isolated  $[WO_4]^{2-}$  species could be discarded, since its associated band at 230 nm is absent [57]. Instead, xW catalysts show a broad band extending from 300 up to 450 nm, with a maximum at about 300 nm, which is red-shifted by increasing the tungsten loading, and a shoulder at ~ 375 nm, indicating that different tungstate species are formed. This broad band is

consequence of the overlapping of bands arising from the low-condensed oligomeric tungsten oxide species (300 nm) and  $WO_3$  crystallites (shoulder at 375 nm) [57-60]. These results corroborate the data extracted from Raman and XRD analyses, which showed both the presence of polytungsted species and  $WO_3$  crystallites.

A key parameter in the glycerol dehydration is the catalyst acidity, and therefore the total acidity of xW and 20WPy catalysts has been evaluated by means of NH<sub>3</sub>-TPD (Table 1). Although the SiZr support shows a notable acidity mainly associated to  $Zr^{4+}$ ions with low coordination, this value is considerably enhanced after supporting WO<sub>3</sub> species. Nevertheless, the total acidity decreases for  $WO_3$  loadings higher than 10 wt%, being more pronounced for the 40W catalyst, whose acidity is even lower than that of the SiZr support. Likewise, from the broad NH<sub>3</sub>-TPD profiles (Figure 5) it can be inferred the existence of acid sites with a wide range of strength since it is generally accepted that the acid strength depends on the NH<sub>3</sub> desorption temperature, considering weak (100-200 °C), medium (200-400 °C) and strong acid sites (>400 °C) [49, 61]. Thus, the presence of tungsten oxide leads to an increase of the amount of ammonia desorbed at high temperature, consequently pointing out the generation of stronger acid sites. On the other hand, the H<sub>3</sub>PO<sub>4</sub> treatment increases the acidity of 20W catalyst up to 797  $\mu$ moles NH<sub>3</sub>·g<sub>cat</sub><sup>-1</sup> for a W/P molar ratio equal to 1, decreasing for W/P= 0.6 and 0.2 (741 and 139  $\mu$ moles NH<sub>3</sub>·g<sub>cat</sub><sup>-1</sup>, respectively). This drastic reduction may be due to the serious damage suffered by the mesostructure of 20WP0.2 catalyst after this treatment.

On the other hand, **pyridine adsorption coupled to FTIR spectroscopy** has been employed to evaluate the nature (Brönsted and/or Lewis) of acid sites, since the selectivity to acrolein is correlated to the presence of Brönsted acid sites [30-32]. The

concentration of both types of acid sites has been estimated from the integrated absorption at 1550 and 1450 cm<sup>-1</sup>, using the extinction coefficients  $E_B=0.73$  cm·µmol<sup>-1</sup> and  $E_L=1.11 \text{ cm}\cdot\mu\text{mol}^{-1}$  for Brönsted and Lewis sites, respectively [62]. The concentration of Brönsted and Lewis acid sites measured by FTIR spectra after pyridine adsorption are presented in Table 1S (Supplementary Information). The SiZr support evidences both types of acid sites [63], and a maximum concentration is reached for the 10W catalyst, whereas for higher WO<sub>3</sub> loadings, a decline is observed. For the xW catalysts, the Lewis acid sites have been ascribed to W=O terminal groups [29], whereas the Brönsted acid sites are associated to W - (OH) - W or W - OH bonds [29, 44]. In the case of Zr-WO<sub>x</sub>/SiO<sub>2</sub> catalysts, Kim *et al.* ascribed the presence of strong Brönsted acid sites to the formation of Zr-WO<sub>x</sub> nanoclusters, whereas the generation of tungstates of smaller sizes from such species led to a gradual decrease of Brönsted acidity [64]. Moreover, it has been reported that the formation of Brönsted acid sites depends on the coverage of support surface, and the highest concentration of Brönsted acid sites is attained for a monolayer of tungsten oxide [29, 44]. This fact has been explained by the increasing number of boundaries existing between the domains of tungsten oxide, because such W - (OH) - W or W - OH groups are more abundant in this region. On the other hand, Kitano et al. have demonstrated that monoclinic WO<sub>3</sub>, detected in tungsten supported on alumina, did not show Brönsted acidity [44]. The acid character of WO<sub>3</sub> nanoparticles was also studied by Cortés-Jácome et al., who found the formation of WO<sub>3</sub> nanocrystallites after annealing WO<sub>3</sub>/ZrO<sub>2</sub> at 800 °C, which causes a concomitant decrease in the acid site density, being more reduced the amount of Brönsted acid sites than Lewis ones [65]. Furthermore, Massa et al. observed the formation of Lewis acid sites above the monolayer, due to the presence of

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coordinatively unsaturated oxo sites [29]. These findings allow us explaining the gradual change observed in the type and number of acid sites, firstly, by taking into account the tungsten loading and the support surface, and assuming that all WO<sub>3</sub> was present as WO<sub>6</sub> octahedra covering an area of 0.22  $\text{nm}^2$  [44, 66], so none catalyst reaches a WO<sub>3</sub> monolayer (Table 2S). Secondly, Raman and UV-visible spectroscopies have shown the existence of polytungstates on the support surface, and XPS analysis has suggested that tungsten species are mainly interacting with zirconium domains. Therefore, it seems reasonable to propose that the 10W catalyst exhibits the highest amount of polytungstate species due to its highest amount of both types of acid sites (Figure 6). As the tungsten loading is increased, these polytungstate species transform into larger crystalline WO<sub>3</sub> particles, and thereby decreasing the amount of Lewis and Brönsted acid sites.

However, it can be observed that the B/B+L ratio increases with the tungsten oxide content up to 30 wt%, showing the same trend that the intrinsic acidity (Table 1). Interestingly, the Brönsted acid sites exhibit a higher strength than Lewis sites. This fact could be related to the interaction between  $Zr - WO_x$  as Yong Kim *et al.* previously proposed [64].

Likewise, new Brönsted acid sites are generated after phosphoric acid treatment in such a way that Lewis acid sites are not detected for a W/P molar ratio of 1 (Table 1 and 1S). However, the B/B+L ratio decreases when a higher amount of phosphoric acid is incorporated compared to 20WP1, though being still higher than the corresponding ratio of the 20W catalyst.

#### 3.2. Catalytic Results

The WO<sub>3</sub>-based catalysts have been tested in the gas-phase dehydration of glycerol at 325 °C, during 8 h of time-on-stream (TOS). The only identified products under the experimental conditions used in the present work were acrolein, acetaldehyde and hydroxyacetone.

Firstly, the influence of the WO<sub>3</sub> loading has been evaluated on the catalytic performance (Table 3 and Figure 4S, in Supplementary Information). The catalytic results point out that both SiZr support and xW catalysts are very active, although the presence of WO<sub>3</sub> ameliorates the selectivity to acrolein (Table 3). The 40W catalyst shows the lowest stability among the xW catalysts, as well as lower acrolein selectivity after 8 h of TOS (Time On Stream). The deactivation of 40W catalyst might be related to its low concentration of acid sites, which are readily poisoned by carbonaceous deposits, in spite of the fact that the carbon content of this spent catalyst is the lowest among the tested catalysts (Table 3). The NH<sub>3</sub>-TPD plots (Figure 5) of the xW catalysts showed a similar distribution of acid sites, being the most abundant those considered as weak acid sites [67] (Fig. 5S). This similar low proportion of strong acid sites could explain the analogous percentage of carbon found in spent catalysts. Furthermore, several authors have highlighted the key role played in catalyst deactivation by both the presence of strong acid sites [26, 37, 67, 68] and the porous network [69-73]. Therefore, the deactivation of xW catalysts would be influenced not only by the distribution of acid sites but also by the mesoporosity of catalysts, which facilitates the diffusion of reactants and products in the pore network.

The turnover frequency (TOF) at time zero was calculated in order to minimize the effect of catalytic deactivation on the intrinsic catalytic activity. This extrapolation

was made by supposing a first order deactivation kinetic [70, 72],  $X(t) = X(0) \exp(-k_d)$ t), where X(t) and X(0) accounts for consumption of glycerol at time t and t = 0, respectively, and k<sub>d</sub> represents the deactivation constant. Thus, the TOF was calculated by dividing the rate of glycerol consumption per the total acidity measured by NH<sub>3</sub>-TPD (Table 2S). It could be expected that catalysts with the most suitable acid properties should exhibit the highest TOF values. However, the highest TOF value was attained for the 40W catalyst, nearly more than twice the rest of catalysts, in spite of its lower total acidity. Nevertheless, it should be considered that the intrinsic surface acidity is similar for the xW catalysts (Table 1), and therefore, the location of acid sites might play an important role. This fact can be drawn in Figure 7, where both TOF(0) and total acidity are represented as a function of external surface of catalysts. As expected, the total acidity runs in parallel to the external surface, but the TOF(0) follows the inverse trend, that is, it decreases as the external surface increases. This would point out that the acid sites of the 40W catalyst could be located preferentially in the outer surface, ready to activate the glycerol molecules, whereas the rest of catalysts could have part of the acid sites inside the pores, not being easily accessible to reactant molecules. The evolution of mmol of glycerol converted per unit time and square meter of external surface (mmol Glycerol  $\cdot$  h<sup>-1</sup> m<sup>-2</sup>) as a function of W atoms per square nanometer gives rise to a straight line, corroborating the aforementioned assumption (Fig. 6S). This availability of acid sites would be also related to the velocity of catalyst deactivation, since this is faster for the 40W catalyst, which shows the highest value of k<sub>d</sub> (Table 2S). Choi et al. found that TOF values were higher for aluminosilicates with a low surface acid density, since in that case, if the acid sites were sufficiently far apart,

they could be more easily accessible for glycerol molecules and therefore the interaction between neighbor glycerol molecules would be avoided [70].

Regarding the acrolein selectivity, it has been pointed out that Brönsted acid sites are more adequate than Lewis ones in order to obtain the highest acrolein yield [29, 69, 70, 74, 75], whereas both Lewis acid and basic sites are involved in the formation of hydroxyacetone [68, 76, 77]. Acetaldehyde selectivity stems from different routes including the decomposition of hydroxyacetone over acidic sites [11, 26], the homogenous decomposition of 3-hydroxypropanal desorbed from an acid site [69] or at expense of acrolein at high temperature [22]. Table 3 gathers the products distribution after 2 and 8 h of TOS. The acrolein yield is increased with the tungsten loading, but both hydroxyacetone and acetaldehyde yields do not follow the same trend, since they remain constant regardless of TOS. Thus, the 20W catalyst shows the highest acrolein yield, reaching a value of 41 mol% after 2 h, and maintaining a 38 mol% after 8 h of TOS. Thus, Chai et al. found that tungsten oxide dispersed on ZrO<sub>2</sub> are active for dehydration of glycerol to acrolein, being maximum the acrolein selectivity when the WO<sub>3</sub> loading was in range of 15–30%, similar to the data obtained for xW catalysts [22]. As it has been previously mentioned, glycerol is converted into acrolein on Brönsted acid sites, and therefore, it is expected that the selectivity towards acrolein enhances with the B/B+L ratio. Figure 6 shows that both B/B+L ratio Brönsted ratio and acrolein yield follow a similar trend, and the maximum acrolein yield would be achieved for a catalyst with a WO<sub>3</sub> loading within the range 20–30 wt%. Although these catalysts predominantly possess Lewis acid sites, the main product detected is acrolein instead of hydroxyacetone. This fact was already observed in the case of a zirconium doped MCM-41 silica, and it was justified by the generation of new Brönsted acid sites

due to the presence of water (the solvent of the glycerol) which was able to hydrolyze some Si – O – Zr bonds forming new Brönsted acid sites [49]. In the case of tungsten based catalysts, it has been proved that alcohols, hydrogen or other reductants can generate  $W^{(6-\delta)}$  from  $W^{6+}$  [48]. This partial reduction implies an excess of negative charge which can be neutralized by protonation of oxygen atoms, thus generating Brönsted acid sites. In this dehydration process, glycerol, acrolein, acetaldehyde and other hydrocarbons could cause such partial reduction, generating new species of reduced tungsten which would have a Brönsted character and contributing to the formation of acrolein [75].

The comparison of different catalytic systems is not straightforward, mainly due to the different experimental conditions used (reaction temperature and time, concentration of glycerol solution, WHSV or GHSV, carrier gas, inert or oxygen, among others). For instance, although Lauriol-Garbey *et al.* previously found high values of glycerol conversion and acrolein yield (100% and 76%, respectively) in presence of WO<sub>3</sub>/ZrO<sub>2</sub> catalysts doped with SiO<sub>2</sub> after 30 h at 300 °C [26], they employed a higher catalyst loading, in such a way that glycerol fed per time unit and mass of catalyst, 0.33 µmol glycerol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup>, was much lower than 3.91 µmol glycerol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> used in this work. Therefore, the mesoporous structure of SiZr support improves the catalytic performance of tungsten oxide, generating 1.60 µmol acrolein·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> from 3.79 µmol converted glycerol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> at 325 °C after 2 h of TOS in presence of the 20W catalyst. Several authors have also studied different WO<sub>3</sub>/ZrO<sub>2</sub> based catalysts for dehydration of glycerol, usually reaching high values of glycerol conversion and acrolein yield, but using different feeding of glycerol per time and mass of catalyst, as for example Ginjupalli *et al.* (1.51 µmol converted glycerol·g<sub>cat</sub><sup>-1</sup>·s<sup>-1</sup> and

1.13 µmol produced acrolein $\cdot g_{cat}^{-1} \cdot s^{-1}$  [23], Massa *et al.* (2.85 µmol converted glycerol $\cdot g_{cat}^{-1} \cdot s^{-1}$  and 2.24 µmol produced acrolein $\cdot g_{cat}^{-1} \cdot s^{-1}$ ) [29] and Chai *et al.* (3.79 µmol converted glycerol $\cdot g_{cat}^{-1} \cdot s^{-1}$  and 2.67 µmol produced acrolein $\cdot g_{cat}^{-1} \cdot s^{-1}$ ) [22]. Consequently, the 20W catalyst can be considered as an interesting catalyst due to its stability and productivity to convert glycerol to acrolein, since the amount of acrolein produced per time unit and mass of catalyst is an important parameter to its possible use.

The influence of reaction temperature on the catalytic behavior has been also studied for the 20W catalyst (Figure 8). It is observed that glycerol conversion increases with the reaction temperature from 300 to 350 °C, although similar values of acrolein yield are attained after 2 h of TOS. Nonetheless, acrolein yield is slightly enhanced at higher reaction times when the reaction temperature is increased from 300 up to 325 °C, but it does not follow this trend when the temperature is further risen up to 350 °C, being even more important its deactivation after 8 h of TOS. Thus, a higher amount of non-identified products is obtained when reaction temperature is 350 °C. On the other hand, acetaldehyde yield increases with the reaction temperature from 11% at 300°C up to 16% at 350 °C, after 2 h of TOS, similarly to that reported by other authors [49, 78]. With respect to hydroxyacetone yield, insignificant differences are observed in the range of 300-350 °C.

On the other hand, it has been previously demonstrated that treatment with phosphoric acid improves the acidity of some metal oxides and the amount of Brönsted acid sites, which are more selective to acrolein [34-36]. Thus, the 20W catalyst has been treated with different amounts of  $H_3PO_4$  and tested in dehydration of glycerol at 325 °C (Figure 9). It can be observed that deactivation is more severe for catalysts treated with

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phosphoric acid, mainly for the 20WP0.2 catalyst, which may be due to its lowest total acidity. In regard to acrolein yield, an increase is detected with H<sub>3</sub>PO<sub>4</sub> content for short reaction times, in such a way that a value of 51% is attained for 20WP0.2 catalyst after 2 h of TOS, in spite of a lower glycerol conversion. This increase is probably related to the Brönsted acid sites concentration of these materials, since the B/B+L molar ratio respect to total number of acid sites is higher after treatment with phosphoric acid (Table 1), and it has been previously demonstrated that this type of acid sites are more selective to acrolein [30, 31]. However, this more pronounced deactivation, in comparison with the 20W catalyst, limits the potential of the treatment with phosphoric acid of WO<sub>3</sub> based catalysts, under these experimental conditions, in spite of the slight increase of acrolein yield after 2 h of TOS, because of the 20W catalyst stays stable after H<sub>3</sub>PO<sub>4</sub> treatment, as previously detected by Cecilia *et al.* for vanadium oxide based catalysts treated with phosphoric acid [34]. On the other hand, the hydroxyacetone yield remains virtually unchanged after this treatment (Table 3).

In order to justify the stability of the 20W catalyst in the dehydration of glycerol at 325 °C after 8 h of TOS, the spent catalyst (R20W) has been characterized by XPS and XRD (Table 2). The binding energy and atomic ratio values are similar to those of the fresh 20W catalyst, although the triclinic WO<sub>3</sub> phase is not already detected in the diffractogram of the spent catalyst (Fig. 10A and 10C), being only observed the monoclinic WO<sub>3</sub> phase, mainly in the region of 31-37° (Figure 10C). Therefore, it can be affirmed that the reaction conditions affect to the crystalline phases of the catalyst, but those changes do not influence on the catalytic performance since deactivation was not observed for the 20W catalyst. With regard to the spent 20WPO.2 catalyst, although

the values of BE are also maintained after reaction (Table 2), significant differences for atomic concentrations are detected by XPS. Thus, this spent catalyst displays a considerable amount of carbon (59%), which would explain its severe deactivation and the decrease of the Si/Zr molar ratio by the presence of carbonaceous deposits on the catalyst surface. However, an increase of the W/Si+Zr and W/P molar ratios is observed after catalytic test, so it is likely that a sintering of W and P phases takes place during reaction. This fact has been corroborated by XRD (Fig. 10B), since new diffraction lines belonging to W and W-P phases are observed ( $W_{17}O_{47}$ , PDF code 01-079-0171;  $H_{34}O_{38}W_7$ , PDF code 98-020-0767 and  $O_{20}PW_6$ , PDF code 98-005-4054) which were not present in the fresh 20WP0.2 catalyst, indicating that they are amorphous or well dispersed on the catalyst surface before reaction, but they crystalize after 8 h of TOS at 325 °C. Thus, the presence of these crystalline phases could explain the fast deactivation that this catalyst suffers during dehydration of glycerol.

Likewise, the thermal stability of carbonaceous deposits in both catalysts, 20W and 20WP0.2, has been studied by TGA (Figure 7S). Although a first weight loss is found at low temperature probably due to adsorbed water, the main contribution is located between 300-650 °C, indicating the presence of different types of carbonaceous deposits on the catalysts surface. In the case of the 20W catalyst, the range of temperatures is narrower and it is centered about 500 °C, which may be due to the existence of unsaturated hydrocarbon or polyaromatic molecules more resistant to combustion [49]. However, the 20WP0.2 catalyst also displays a shoulder between 300-400 °C which could be ascribed to carbon deposits easily oxidized like aliphatic molecules [30]. Taking into account these results, the regeneration of spent catalysts

could be accomplished by thermal treatment at 550 °C under oxygen, thus allowing the removing of the carbonaceous deposits.

#### 4. Conclusions

A family of tungsten oxide and tungsten oxide-phosphorous supported on a zirconium doped mesoporous SBA-15 silica has demonstrated to be active catalysts for glycerol dehydration. The incorporation of WO<sub>3</sub> to the SiZr support increases the total acidity and the Brönsted acid sites proportion, improving the stability in glycerol dehydration. Thus, the 20W catalyst displays the highest glycerol conversion and acrolein yield values (97% and 41% after 2 h, and 90% and 38% after 8 h of TOS, respectively, at 325 °C) which may be related to the existence of WO<sub>3</sub>-ZrO<sub>2</sub> phases on catalyst surface, as deduced from XPS data. Although the H<sub>3</sub>PO<sub>4</sub> treatment increases the total acidity and the B/B+L molar ratio, when small amounts of acid are utilized, enhancing acrolein yield at the beginning of reaction, the deactivation of 20WPy catalysts is much more pronounced due to the important reduction of specific surface area and total acidity, decreasing the number of available acid sites, mainly for 20WP0.2 catalyst.

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#### **Figure Captions**

**Figure 1**. XRD patterns of xW and 20WPy catalysts at low-angle (A) and high-angle (B) regions.

Figure 2. Pore size distribution of xW (A) and 20WPy (B) catalysts.

Figure 3. Raman spectra of *x*W catalysts.

Figure 4. Diffuse reflectance UV–vis absorption spectra of *x*W and 20WPy catalysts.

**Figure 5.** NH<sub>3</sub>-TPD profiles of *x*W and 20WPy catalysts.

**Figure 6.** Evolution of Lewis and Brönsted acid site concentration measured after evacuation at 100 °C, the B/B+L ratio and acrolein yield as a function of the surface atomic concentration of tungsten atoms per nm<sup>2</sup>.

**Figure 7.** Influence of external surface on total acidity and turnover frequency at time zero.

**Figure 8.** Influence of reaction temperature on glycerol conversion and acrolein yield over 20W catalyst (0.5 g diluted with SiC to 3 cm<sup>3</sup> volume; 0.1 mL min<sup>-1</sup> of 10 wt.% glycerol in water and N<sub>2</sub> flow=15 mL min<sup>-1</sup>).

**Figure 9.** Glycerol conversion and acrolein yield over 20WPy catalysts as a function of the reaction time (0.5 g diluted with SiC to 3 cm<sup>3</sup> volume; 0.1 mL min<sup>-1</sup> of 10 wt.% glycerol in water; N<sub>2</sub> flow=15 mL min<sup>-1</sup> and 325 °C).

**Figure 10**. XRD patterns at high-angle region of 20W (A) and 20WP0.2 (B) fresh and used catalysts. Zoom of XRD patterns for 20W and R20W between  $2\theta$ =31-37° (C).



**(B)** 



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7



Figure 8



Figure 9





Figure 10

#### ACCEPTED NUSCRIPT MA

#### Tables

Sample	S <sub>BET</sub>	$V_P$	Pore size	<sup>a</sup> urralaa NILLaa -1	B/B+L <sup>b</sup>	
	$(m^2 \cdot g^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	(nm)	µmoles NH <sub>3</sub> ·g <sub>cat</sub>		
SiZr	812	0.61	3.3	474 (0.6)	0.28	
10W	395	0.38	4.0	766 (1.9)	0.25	
20W	267	0.29	4.2	601 (2.3)	0.32	
30W	173	0.22	3.9	521 (3.0)	0.39	
40W	148	0.19	3.9	392 (2.7)	0.34	
20WP1	227	0.25	4.5	797 (3.5)	1	
20WP0.6	94	0.14	5.5	741 (7.9)	0.63	
20WP0.2	15	0.07	15.7	139 (9.3)	0.49	

**Table 1.** Textural and acidic properties of xW and 20WPy catalysts.

<sup>a</sup>Intrinsic acidity expressed as µmoles NH<sub>3</sub>·m<sup>-2</sup> (in brackets) <sup>b</sup>Ratio of concentration of Brönsted respect total acid sites from the adsorption of pyridine evacuated at 100°C.

**Table 2.** XPS parameters of fresh catalysts.

Sample	Binding Energy (eV)		Atomic ratio					
	O 1 <i>s</i>	W 4f <sub>7/2</sub>	Si/Zr <sub>XPS</sub>	W/(Si+Zr) <sub>XPS</sub>	W/(Si+Zr) <sub>bulk</sub>	W/P <sub>XPS</sub>	W/P <sub>bulk</sub>	
SiZr	530.7 (2.2%) 532.8 (97.7%)	_	36.05	_	_	_	_	
10W	530.4 (2.7%)	35.9	38.72	0.016	0.034			
20W	530.7 (8.0%)	36.0	42.91	0.040	0.076			
	532.9 (92.0%) 530.5 (7.4%)	35.8	41.29	0.057	0.131			
	532.7 (92.6%) 530.6 (7.5%)							
40W	532.7 (92.5%)	35.6	42.96	0.060	0.203	_	_	
20WP1	530.8 (9.4%) 532.8 (90.6%)	36.2	23.48	0.031	0.076	0.249	1	
20WP0.6	531.0 (11.2%)	36.3	22.09	0.031	0.076	0.171	0.6	

	532.8 (88.8%)						
20WP0.2	530.9 (12.7%)	36.2	19.43	0.036	0.076	0.116	0.2
	532.7 (87.3%)		17.45	0.050	0.070	0.110	
R20W	531.0 (7.9%)	36.2	42.80	0.038	0.076		_
	532.9 (92.1%)		42.00	0.050	0.070		
R20WP0.2	531.0 (15.4%)	36.2	10.05	0.267	0.076	0.210	0.2
	532.9 (84.6%)		10.05	0.207	0.070	0.210	

Sample	T <sup>a</sup>	Cglycerol (%)	Y <sub>acrolein</sub> (%)	Y <sub>acetaldehyde</sub> (%)	Y <sub>hydroxyacetone</sub> (%)	Y <sub>others</sub> (%)	C <sub>balance</sub> (%)	%C <sub>CHN</sub>
SiZr	325	91 (72)	22 (17)	20 (15)	4 (5)	45 (36)	55 (64)	10.2
10W	325	94 (80)	23 (24)	9 (8)	7 (10)	56 (38)	44 (62)	10.0
20W	325	97 (90)	41 (38)	11 (8)	5 (6)	39 (38)	61 (62)	9.2
30W	325	94 (76)	41 (30)	5 (4)	7 (9)	41 (33)	59 (67)	9.6
<b>40W</b>	325	95 (52)	35 (24)	7 (4)	7 (5)	46 (19)	54 (81)	6.8
20WP1	325	96 (68)	45 (26)	1 (1)	7 (7)	43 (34)	57 (66)	7.7
20WP0.6	325	99 (55)	42 (17)	1 (0.3)	7 (4)	49 (33)	51 (67)	4.8
20WP0.2	325	78 (26)	51 (10)	0.6 (0.1)	5 (2)	20 (13)	80 (87)	3.7

Table 3. Glycerol conversion and product yields over *x*W and 20WPy catalysts.

Data measured after 2 h and 8 h (in brackets)

**Experimental conditions**: weight of catalyst = 0.5 g diluted with SiC to 3 cm<sup>3</sup> volume. Feed composition: 10 wt% glycerol in water; liquid flow=  $0.1 \text{mL} \cdot \text{min}^{-1}$ ; N<sub>2</sub> flow =15 mL·min<sup>-1</sup>