

## **Supplementary Material**

# **Insights into the nature of the active sites of Pt-WO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts for the glycerol hydrogenolysis into 1,3-propanediol**

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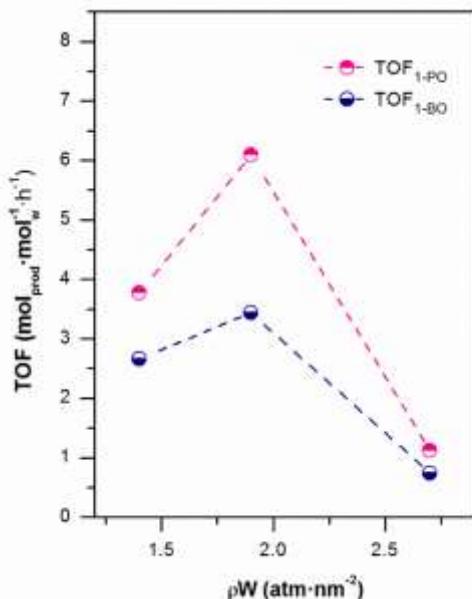
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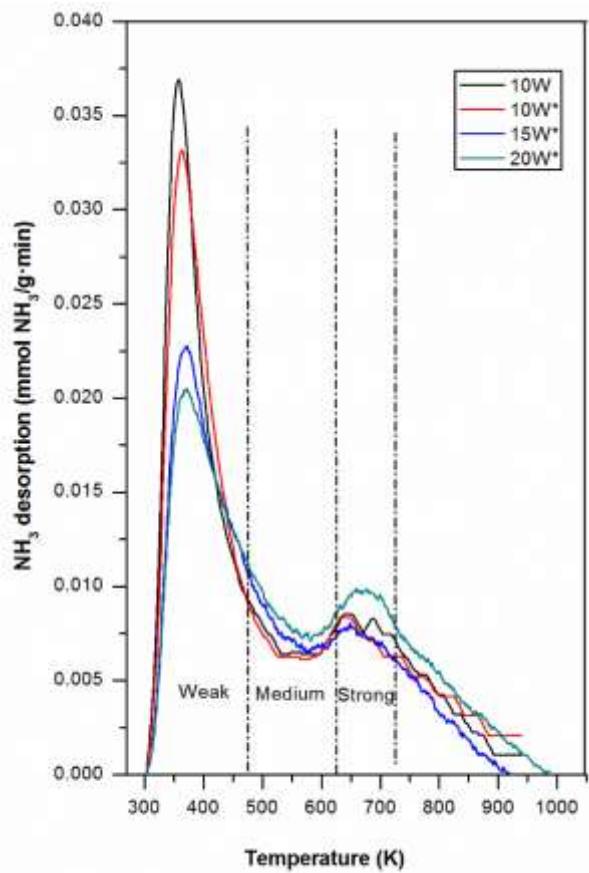
## 1 Figures



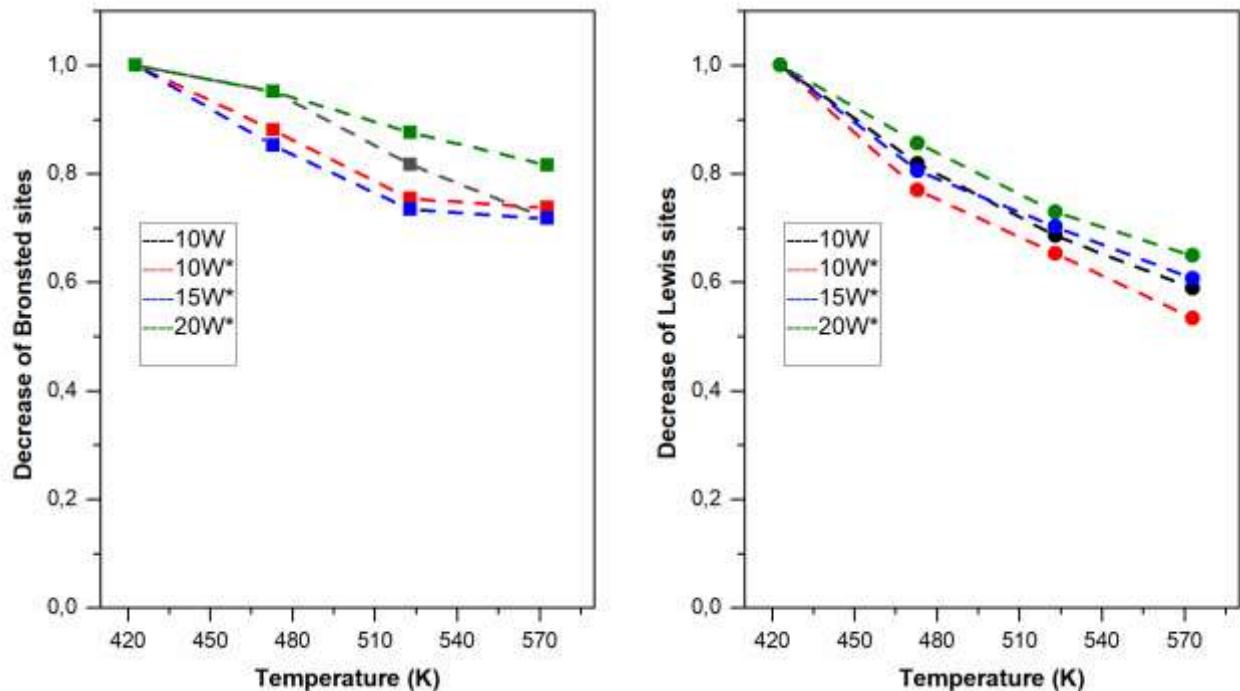
**Figure S1.** Visual identification of bulk WO<sub>3</sub> crystallites (of yellow color) on the 15W/γ-Al<sub>2</sub>O<sub>3</sub> material (right). The 10W/γ-Al<sub>2</sub>O<sub>3</sub> material (left) is shown for comparison.



**Figure S2.** Correlation between TOF<sub>product-W</sub> and tungsten surface density for 5Pt<sup>PH10</sup>yW\* catalysts. 1-propanol (1-PO) and 1-butanol (1-BO) are the products obtained after the hydrogenolysis of the secondary hydroxyl group, when 1,2-propanediol (1,2-PDO) or 1,2-butanediol (1,2-BDO) are used as substrate.



**Figure S3.** TPD- $\text{NH}_3$  profiles for different tungsten oxide  $\gamma\text{-Al}_2\text{O}_3$  materials.



**Figure S4.** Fraction of Brønsted sites (left) and Lewis sites (right) remaining in the surface of the catalyst as a function of the vacuum treatment temperature.

## 2 Tables

**Table S1.** Ratio between the H<sub>2</sub> consumption in peaks related to the PtO reduction (peaks 1,2 and 3 from Figure 1) and the theoretical H<sub>2</sub> consumption to reduce all the PtO present in the catalyst to Pt<sup>0</sup>.

Catalyst / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	TPR H <sub>2</sub> Consumption	
	H <sub>2</sub> Theoretical Consumption	
5Pt <sup>pH4</sup> 10W		1.30
5Pt <sup>pH6</sup> 10W		1.13
5Pt <sup>pH8</sup> 10W		1.79
5Pt <sup>pH10</sup> 10W		1.32
5Pt <sup>pH10</sup> 10W*		1.05
5Pt <sup>pH10</sup> 10W*		0.97
5Pt <sup>pH10</sup> 10W*		0.95

**Table S2.** Total acidity (measured by TPD-NH<sub>3</sub>), and Brønsted to Lewis ratio (measured by FTIR of adsorbed pyridine after vacuum treatment at different temperatures) of supported tungsten oxide materials.

Material / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	TPD-NH <sub>3</sub> (mmol NH <sub>3</sub> /g)				FTIR Pyridine Brønsted/Lewis (B/L) ratio			
	Total acidity	weak (353-473 K)	medium (473-623 K)	strong (623-723K)	423 (K)	473 (K)	523 (K)	573 (K)
10W	1.046	0.674	0.209	0.162	0.043	0.050	0.051	0.052
10W*	1.007	0.657	0.202	0.148	0.058	0.078	0.102	0.130
15W*	0.874	0.513	0.220	0.141	0.078	0.082	0.081	0.092
20W*	0.922	0.485	0.254	0.184	0.246	0.274	0.294	0.310

**Table S3.** Textural properties and tungsten surface density of different supported tungsten oxide materials.

Material $\text{/}\gamma\text{-Al}_2\text{O}_3$	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{pore}}$ ( $\text{cm}^3/\text{g}$ )	$\rho_W$ ( $\text{at}_W \cdot \text{nm}^{-2}$ )
<b>10W</b>	216	0.63	1.28
<b>10W*</b>	212	0.60	1.39
<b>15W*</b>	214	0.59	1.93
<b>20W*</b>	176	0.50	2.71