How do random superficial defects influence the electro-oxidation of glycerol on Pt(111) surfaces?

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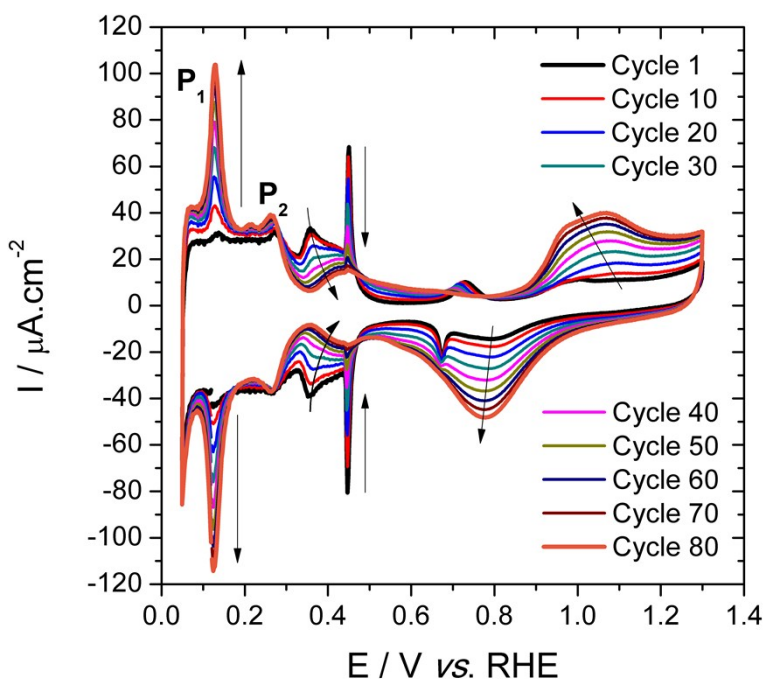
Figure S1. Consecutives cyclic voltammograms performed between 0.05 and 1.30 V. 50 mV s^{-1}; 0.5 mol L^{-1} H$_2$SO$_4$. The arrows show the development of the different features on the (111) surfaces as the number of cycling increases.
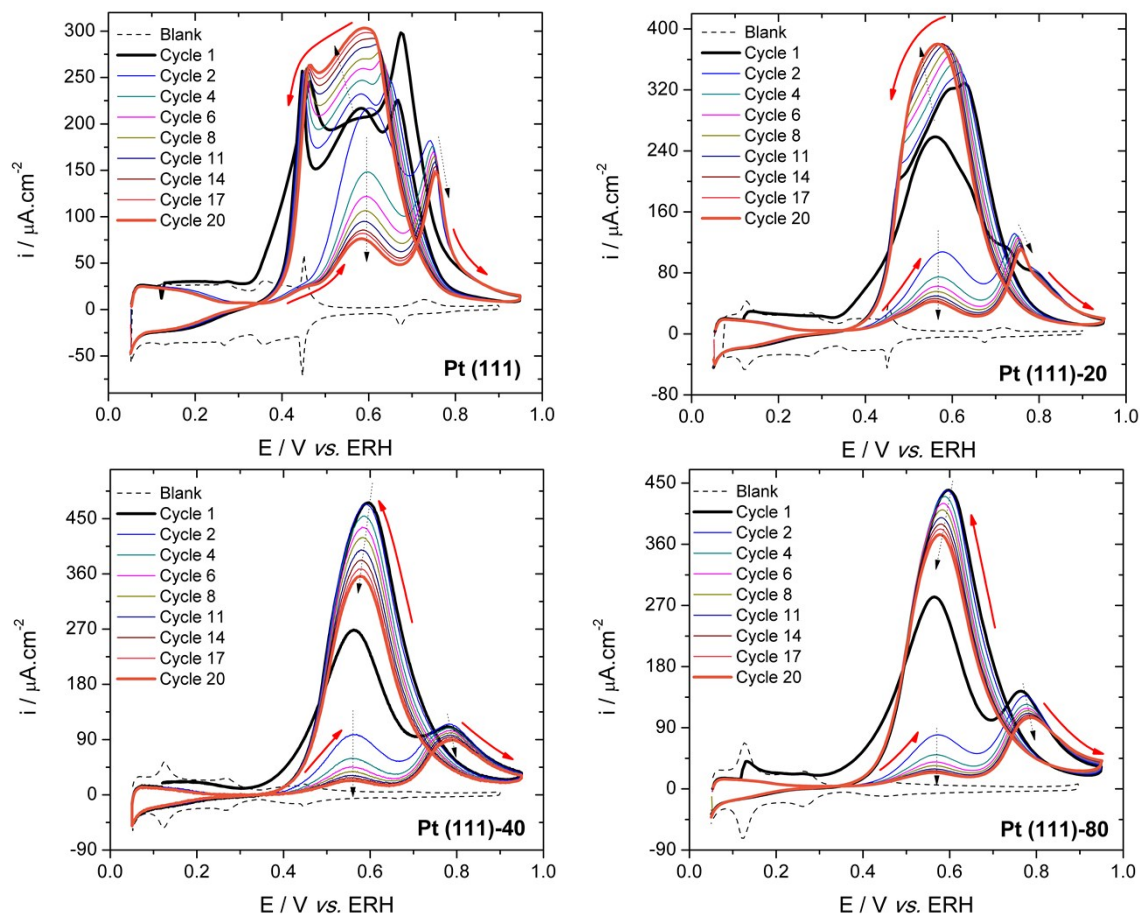
Figure S2. Cyclic voltammograms obtained in 0.2 M GlOH and 0.5 M H_2SO_4 on Pt(111), Pt(111)-20, Pt(111)-40 and Pt(111)-80 (C). v = 0.05 Vs^{-1}. The dashed black arrows indicate the changes in the CVg features along cycling and the thick red arrows indicate the direction of the scanning.
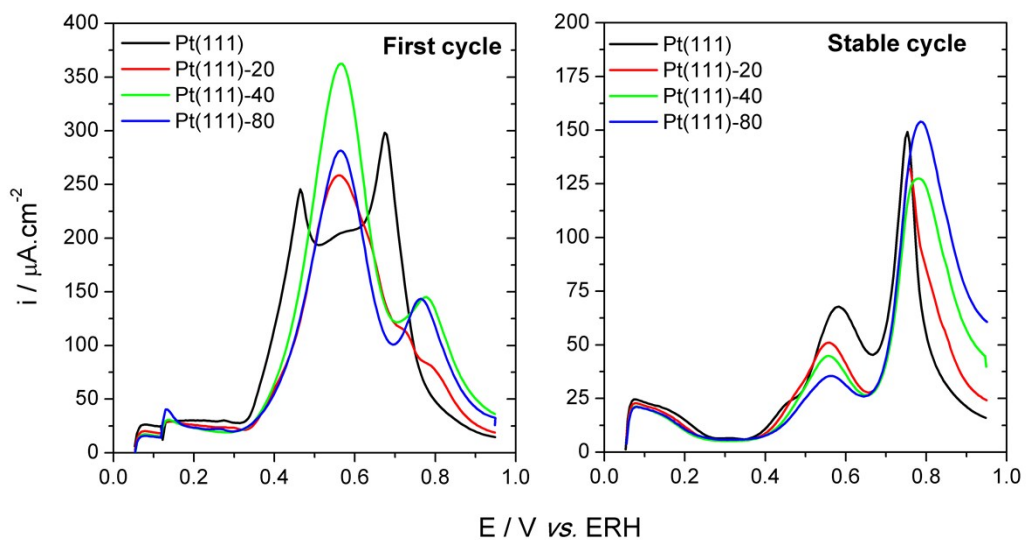

Figure S3. Forward scanning of the Cyclic Voltammograms obtained at 50 mV s^{-1} in 0.2 mol L^{-1} GlOH and 0.5 mol L^{-1} H_2SO_4.
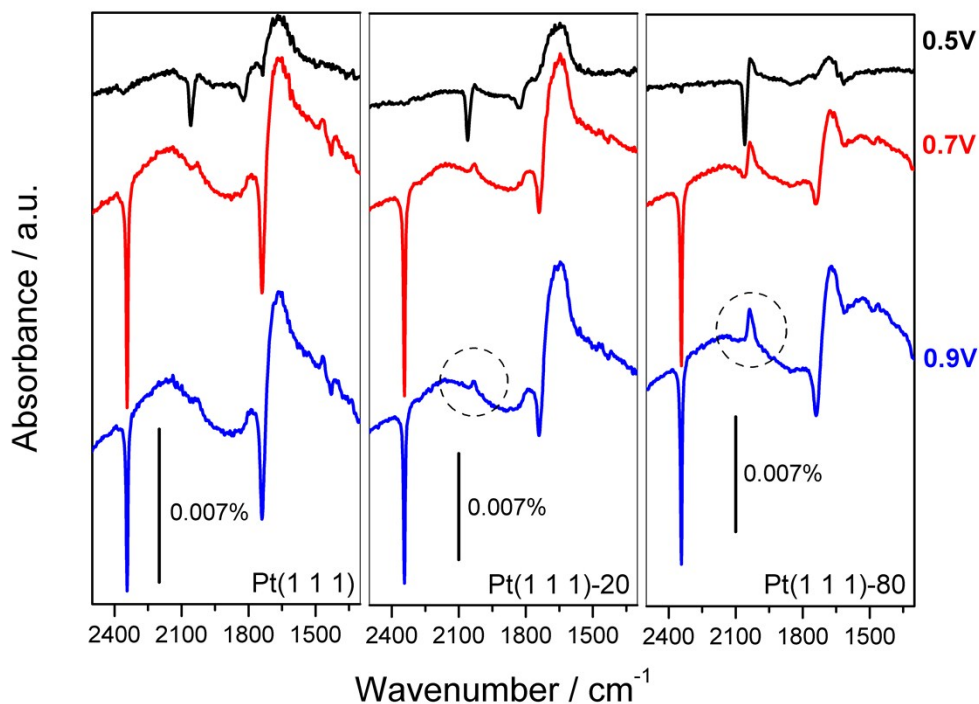
Figure S4. Comparison between the FTIR results obtained with the surfaces studied here. The dashed circles show the negative on-top CO band generated by the oxidation of the CO measured at the beginning of the experiment, i.e., the band was already present in the reference scan taken at 0.10 V.
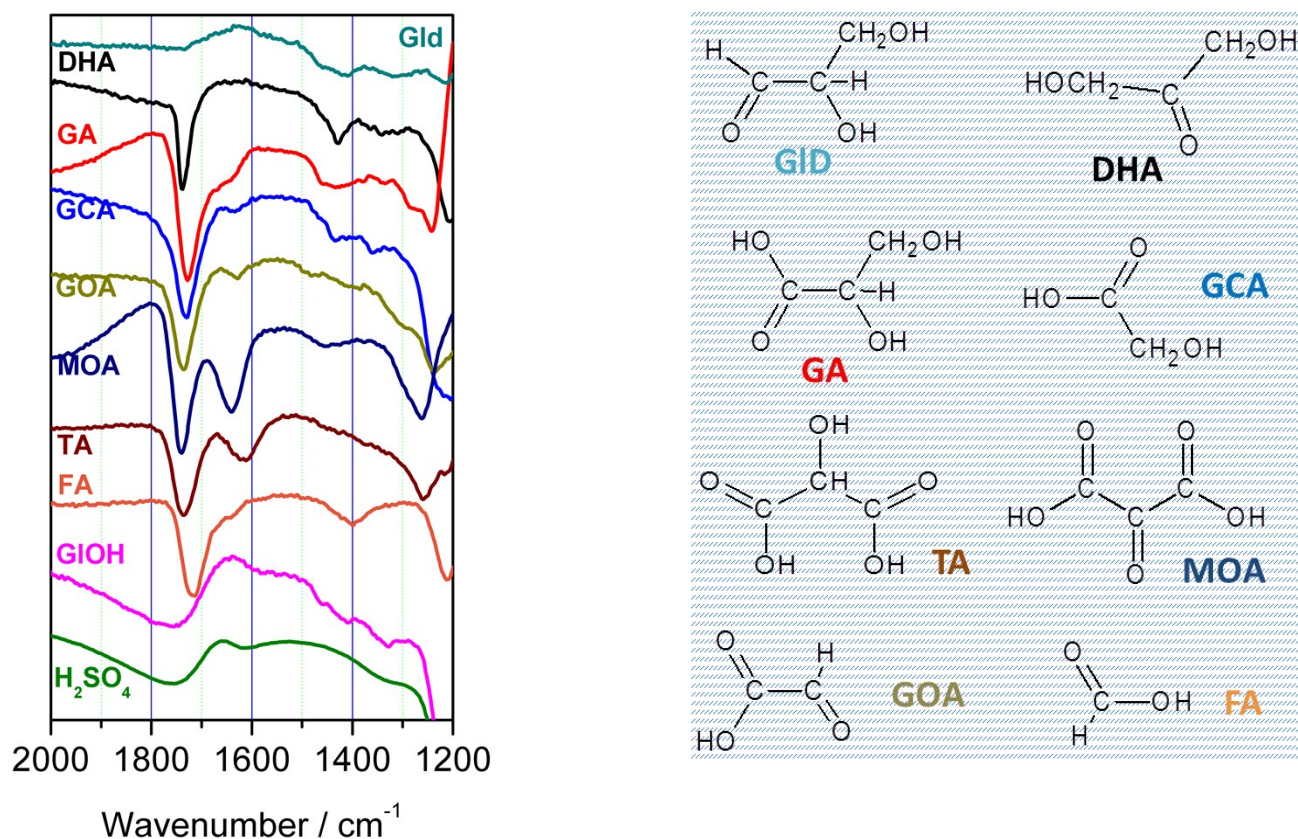

Figure S5. ATR spectra obtained with Glyceraldehyde (Gld), Dihydroxyacetone (DHA), Glyceric Acid (GA). Glycolic Acid (GCA), Glyoxylic Acid (GOA), Mesoxalic Acid (MOA), Tartronic Acid (TA), Formic Acid (FA), Glycerol (GlOH) and Sulfuric Acid. The solutions were 0.1 M of each product and 0.5 M of H_2SO_4, however spectra were multiplied for different constant values to show all the results in the same graph. The equipment and spectra's parameters were the same used for the spectroelectrochemical experiments showed in the Manuscript file.

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Table S1. Structural parameters of GlOH and Water in gas-phase and on the defected Pt surface. d_{C-C}, d_{C-O}, d_{O-H}, and d_{C-H} (in Å) stands for C-C, C-O, O-H and C-H mean bond lengths, respectively, the angles CCC (HOH in the case of water (in °)) and the torsion angles CCCO, OCCO (in °).

Structure	d_{C-C}	d_{C-O}	d_{O-H} d_{C-H}	CCC (HOH)	CCCO	OCCO
GlOH gas-phase	1.53	1.42-1.44	0.97-0.98 1.10-1.11	113	61.2-73.3	62-49
1GlOH/Pt	1.51-1.53	1.42-1.46	0.98 1.10-1.13	115	178.5-163.8	59-70
2GlOH/Pt	1.52-1.53	1.42-1.46	0.97-0.99	113-115	146 ; 172 71 ; 164	88 ; 65 42 ; 170
1Water gas phase			0.97	104		
1Water/Pt			0.97-0.98	106		
12Water/Pt			0.98-1.02	102-111		
2GlOH+12Water+6CO/Pt	1.51;1.53 1.52;1.54	1.43-1.45	0.98-1.00 1.10-1.11	109;112 104-108	166;168 161;169	48,74 40;71

Table *S*2. Structural parameters of GlOH and Water on the defected Pt surface. The following parameters are shown: i) bond lengths between O and Pt, d_{O-Pt} (in Å), ii) angle between the edge O atoms and surface vertical, β (in °), and iii) O-H bonds, d_{O-H} (in Å), calculated without and with vdW.

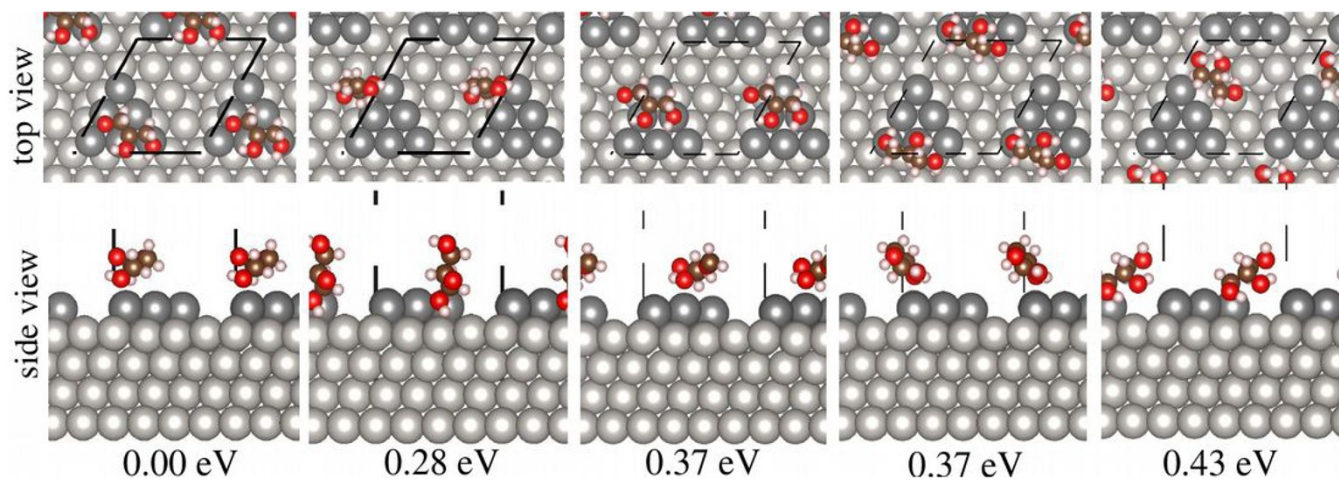| Structure	d_{O-Pt} (Å)	d_{O-Pt}^{vdW} (Å)	β (°)	β^{vdW} (°)	d_{O-H-O} (Å)
1GlOH/Pt	2.30	2.34	71	71.05	
2GlOH/Pt	2.29-2.28	2.32-2.31	72-52		1.82/1.81
1Water/Pt	2.33	2.34	8-17	16.7	
12Water/Pt	2.28-2.33 (5) 3.30-4.01 (7)	2.29-2.33 (5) 3.34-4.01 (7)			1.68-2.24

Figure S6. The lowest energy structure and higher energy isomers for 1 Glycerol on Pt6/Pt15/Pt(111) surface. The numbers below the figures correspond to the relative total energy.
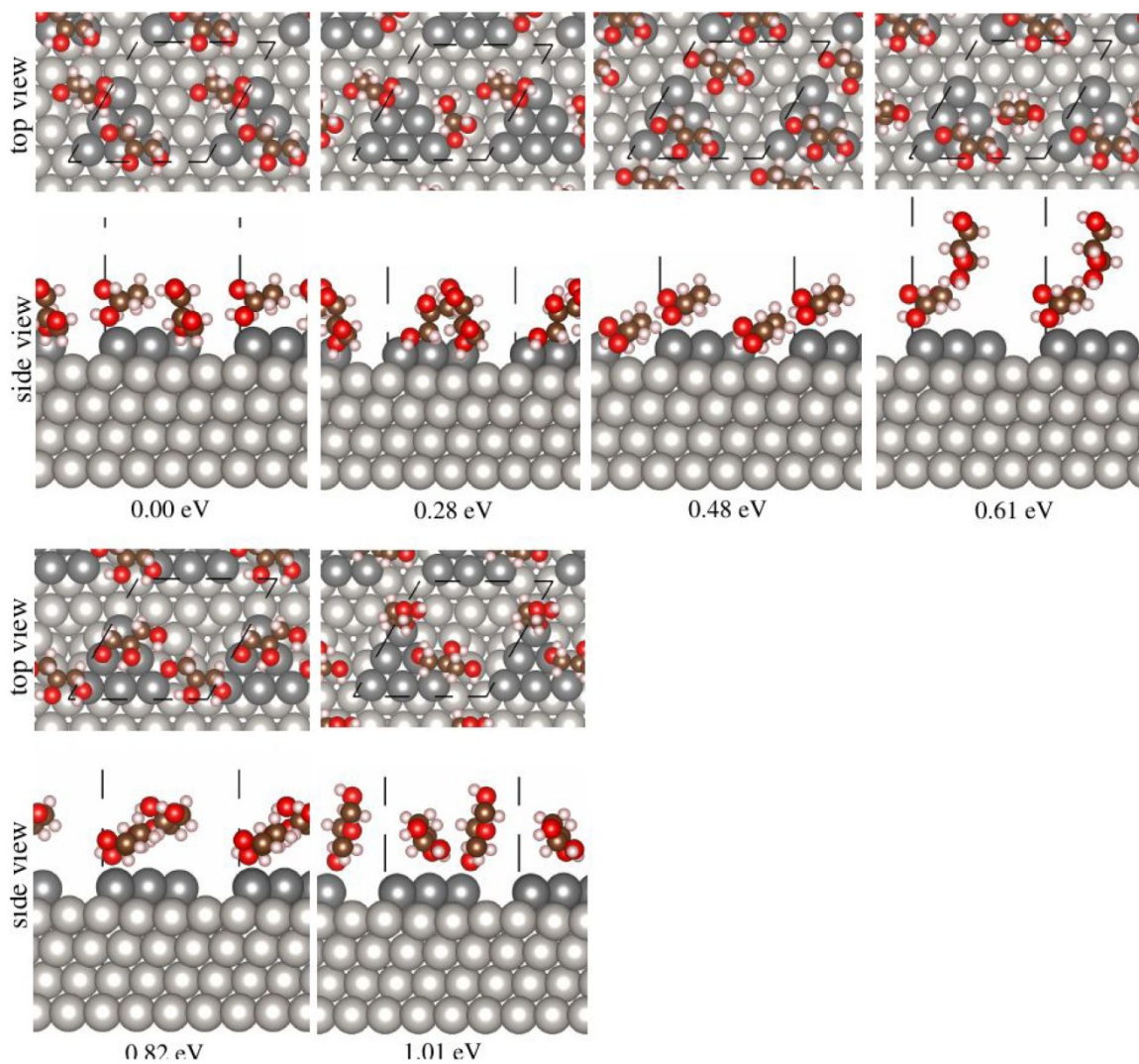

Figure S7. The lowest energy structure and higher energy isomers for 2 Glycerol on Pt6/Pt15/Pt(111), and their relative total energy.
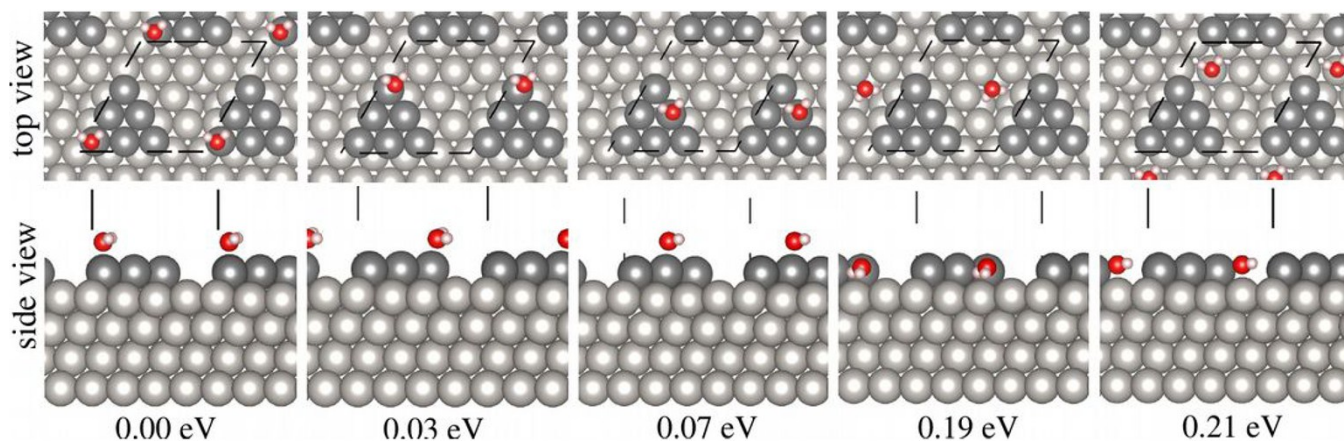
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Figure S8. The lowest energy and higher energy structures for 1 water on Pt6/Pt15/Pt(111). Numbers given below are their relative total energy.
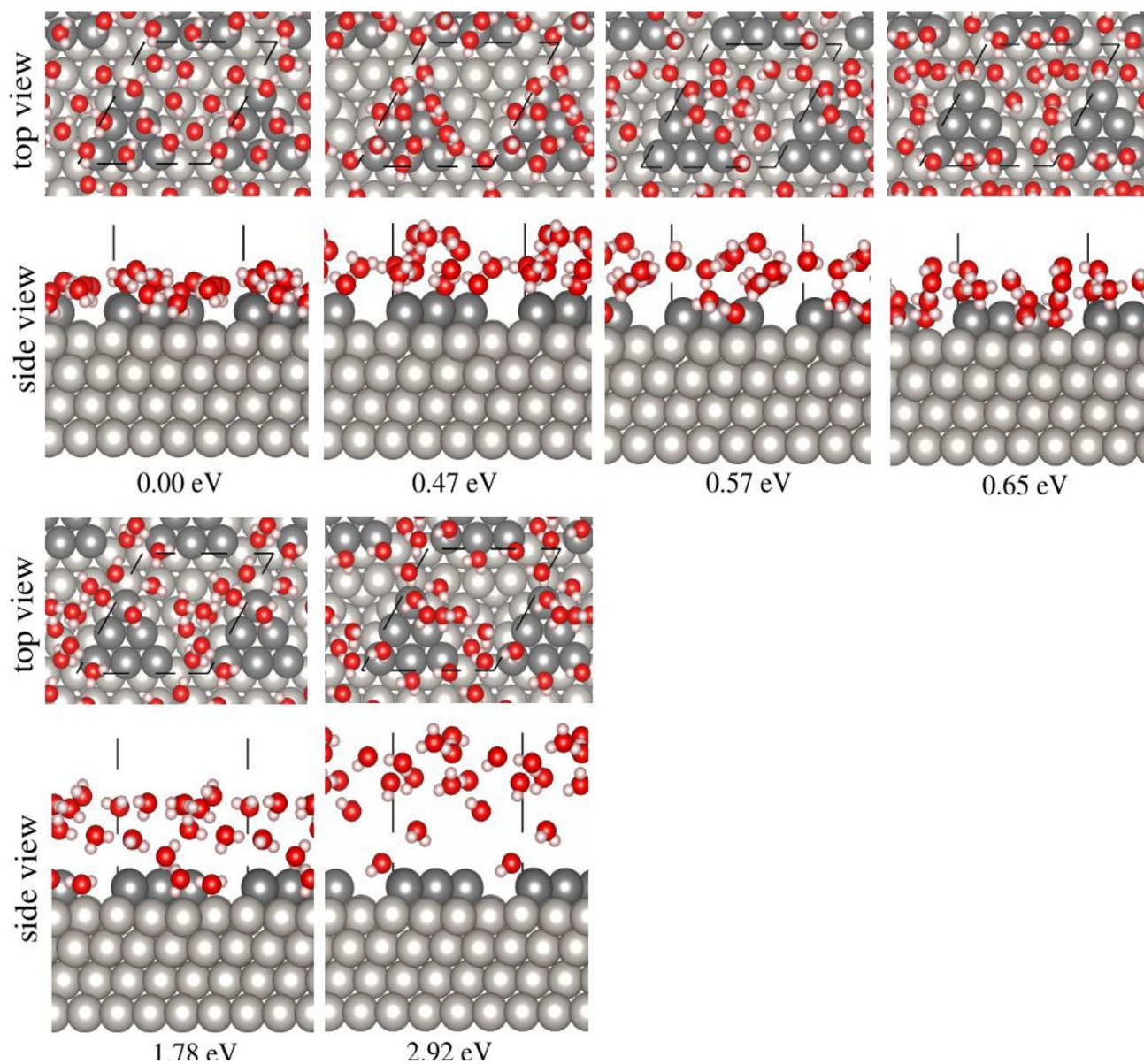

Figure S9. 12 water molecules on Pt6/Pt15/Pt(111): the lowest energy and higher energy structures with the relative total energy.

Table S3. Structural parameters of CO molecules on the defected Pt surface, such as bond lengths between C and Pt, d_{C-Pt} (in Å), and C and O, d_{C-O} (in Å), calculated without and with vdW.

Structure	d_{C-Pt} (Å)	d_{C-Pt}^{vdW} (Å)	d_{C-O} (Å)	d_{C-O}^{vdW} (Å)
CO gas-phase			1.14	1.14
1CO/Pt	1.84	1.84	1.16	1.16
6CO/Pt	1.85-1.86 (3) 2.00-2.03 (3)	1.85-1.86 (3) 2.00-2.04 (3)	1.15-1.19	1.15-1.19

Table S4. Structural parameters of GlOH and water on the defected Pt surface. This table presents: i) bond lengths between O and Pt, d_{O-Pt} (in Å), ii) angle between the edge O atoms and surface vertical, β (in °), and iii) O-H bonds, d_{O-H} (in Å), calculated without and with vdW.

Structure	d_{O-Pt} (Å)	d_{C-Pt} (Å)	β (°)	d_{C-O} (Å)	d_{O-H-O} (Å)
2GlOH+12Water+6CO/Pt	2.16; 2.20 (2) 5.26-12.51 (10)	1.83-1.99 (6)	95; 71	1.16-1.20	1.58-2.07

0.00 eV   0.04 eV   0.06 eV   0.11 eV

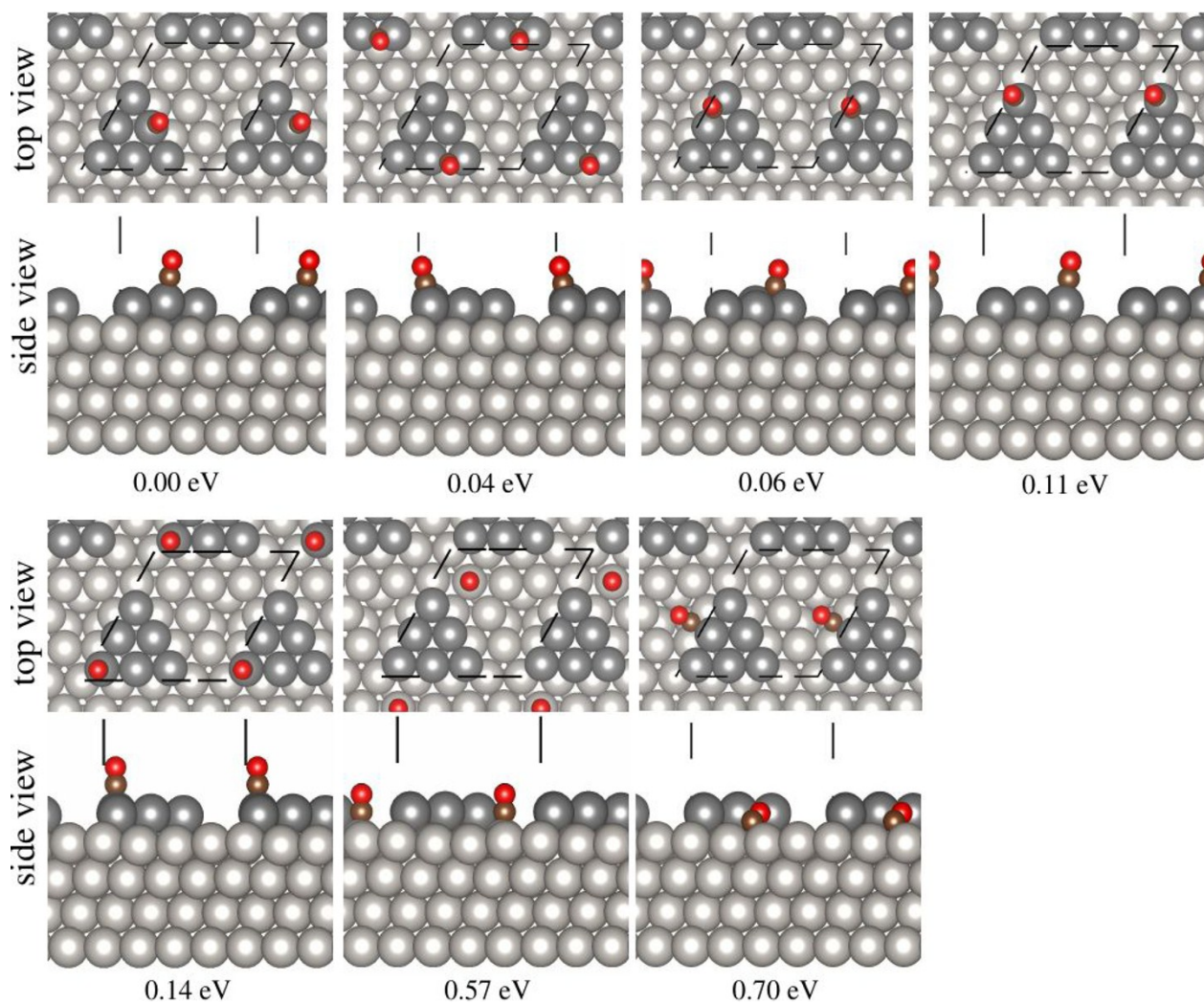0.14 eV   0.57 eV   0.70 eV

Figure S10. 1 CO on Pt6/Pt15/Pt(111): the lowest energy and higher energy structures with the relative total energy.
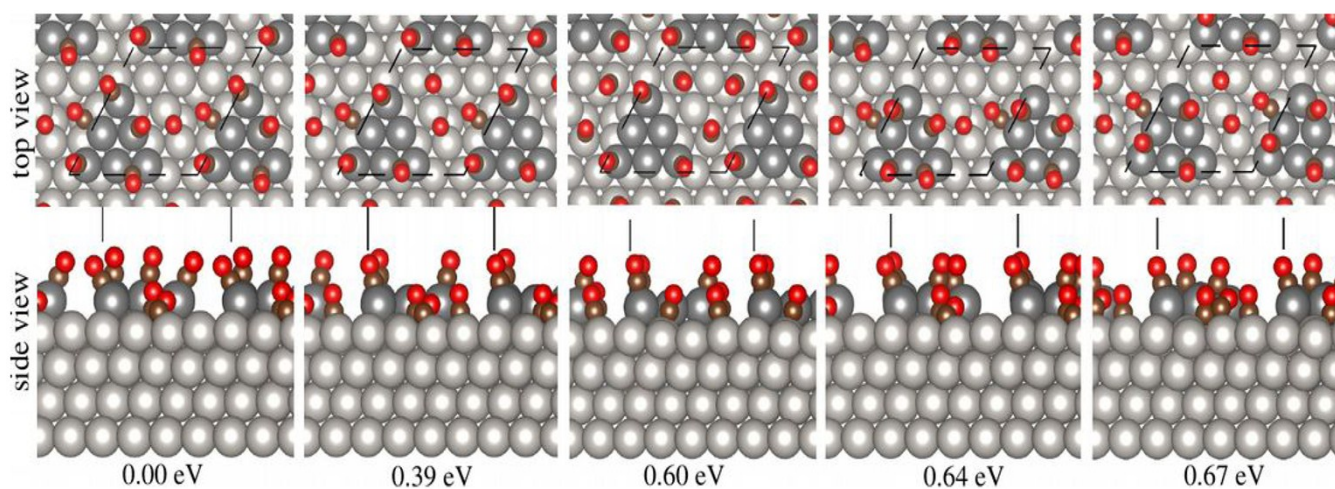
Figure S11. 6 CO on Pt6/Pt15/Pt(111): the lowest energy and higher energy structures with the relative total energy.
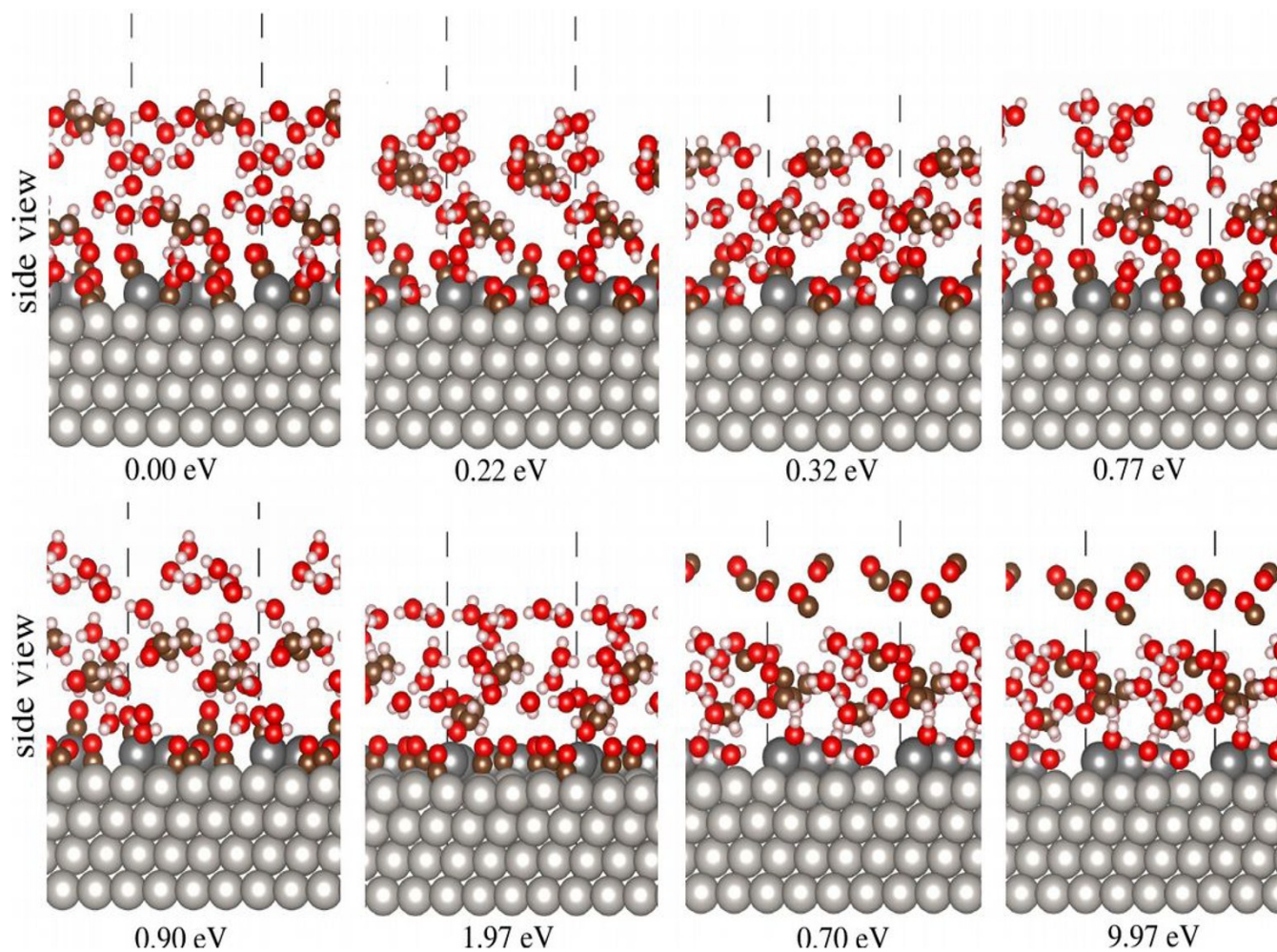

Figure S12. 2Glycerol+12Water+6CO molecules on Pt6/Pt15/Pt(111): the lowest energy and higher energy structures with the relative total energy.

The role of vdW interactions.

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We found that vdW correction affects the atomic structure slightly. For example, it contributes to increase the O-Pt bond lengths for GlOH and water, i.e. by 0.03–0.04 Å and 0.01–0.06 Å, respectively, however, it does not affect the C-Pt bond lengths of CO molecules, which is supported by our previous studies[1,2]. As also expected, vdW correction results in the enhancement of the adsorption energy of the investigated systems. As shown in our previous works, the enhancement factor for vdW correction, $\alpha = E_{ad}^{vdW}/E_{ad}$, depends on the element, surface structure and molecule[1,3]. Our results show the increase of the adsorption energy by 2.09 and 1.27 eV for 1 GlOH and 1 Water, respectively. Once we increase the number of molecules on the surface, α also increases, i.e. by 2.16 and 1.47 eV, for 2 GlOH and 12 Waters, respectively, which implies that the enhancement factor for vdW correction depends on the number of molecules as well, however it applies only for the system with the same type of molecules. For the mixture of the molecules, 2GlOH+12Water+ 6CO/Pt, α enhances only slightly, i.e. by 1.11 eV, which is close the enhancement for the chemisorbed CO molecule, i.e. 1.09 eV.

The work function change.

The calculated work function for the $Pt_6/Pt_{15}/Pt(111)$ surface ($\Phi^{clean\ Pt}$) found to be 5.69 eV, which is similar to the value for the clean Pt(111) surface[1]. Using vdW correction slightly decreases $\Phi^{clean\ Pt}$ up to 5.66 eV. Upon molecular adsorption the work function was reduced, so that the work function change became negative, implying the effective charge transfer from the Pt surface to the region of molecules. The increase of the number of molecules on the surface incrfeases the work function change, i.e. from −1.07 to −1.29 eV for 1GlOH and 2 GlOH on $Pt_6/Pt_{15}/Pt(111)$, respectively, which is due to the increased charge redistribution on the surface area. However, $\Delta\Phi$ becomes positive for 6CO on $Pt_6/Pt_{15}/Pt(111)$, (i.e. 0.24 eV), which can indicate donation-back-donation mechanism of the charge between CO molecule and the surface. Such finding is in accordance with our previous results[3] and can be explained by the model developed by Blyholder[4]. For the molecular mixture (2GlOH +12Water+6CO/Pt) it has negative sign due to the contribution of the large number of GlOH and Water molecules on the surface. The vdW correction made a slight effect on $\Delta\Phi$ in most cases, which is expected, as vdW does not lead to structural changes.

References

(1) P. Tereshchuk and J. L. F. Da Silva, *J. Phys. Chem. C*, 2014, **118**, 15251-15259.
(2) P. Tereshchuk and J. L. F. Da Silva, *J. Phys. Chem. C*, 2012, **116**, (46), 24695–24705.
(3) S. Gautier, S.N. Steinmann, C. Michel, P. Fleurat-Lessard, P. Sautet. *Phys. Chem. Chem. Phys*. 2015, **17**, 28921-28930.
(4) G.J. Blyholder. *J. Phys. Chem.* 1964, **68**, 2772-2777.