

Establishing a link between well-ordered Pt(100) surfaces and real systems: How do random superficial defects influence the electro-oxidation of GIOH?

Pablo S. Fernández^{a,*}, Janaina F. Gomes^{a,†}, Camilo A. Angelucci^b, Polina Tereshchuk^a, Cauê A. Martins^c, Giuseppe A. Camara^d, María E. Martins^e, Juarez L. F. Da Silva^a, Germano Tremiliosi-Filho^a.

^a São Carlos Institute of Chemistry, University of São Paulo, PO Box 780, 13560-970, São Carlos, São Paulo, Brazil.

^b Center of Natural and Human Sciences (CCNH), Federal University of ABC (UFABC), Av. dos Estados, 5001, Santo André, Brazil.

^c Faculty of Exact Sciences and Technology, Federal University of Grande Dourados, 79804-970, Dourados, MS, Brazil.

^d Institute of Chemistry, Federal University of Mato Grosso do Sul, C.P. 549, 79070-900, Campo Grande, Mato Grosso do Sul, Brazil.

^e Physical Chemistry Research Institute (INIFTA), Exact Sciences Faculty, CCT La Plata-CONICET, C.P. 1900, La Plata, Argentina.

*Corresponding Author Email: pablo.fernandez@iqm.unicamp.br (P.S.F)

Cyclic voltammetry

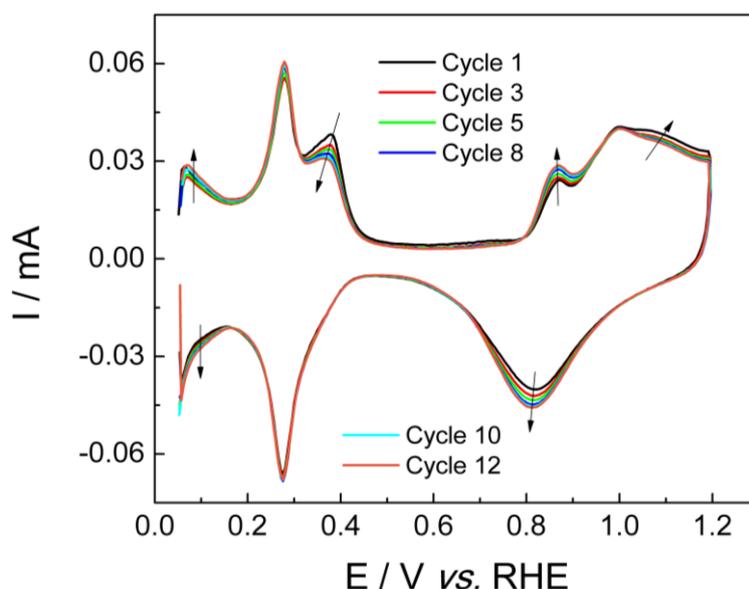


Figure S1. Pt100-0 surface is obtained after 16 cyclic voltammograms up to 1.05 V (Shown in figure 1B) and 12 cyclic voltammograms up to 1.20 V (Shown in this figure). Comparing figure 1B and S1 we can conclude that the most important surface modifications occurs during performing the cycling shown in figure 1B.

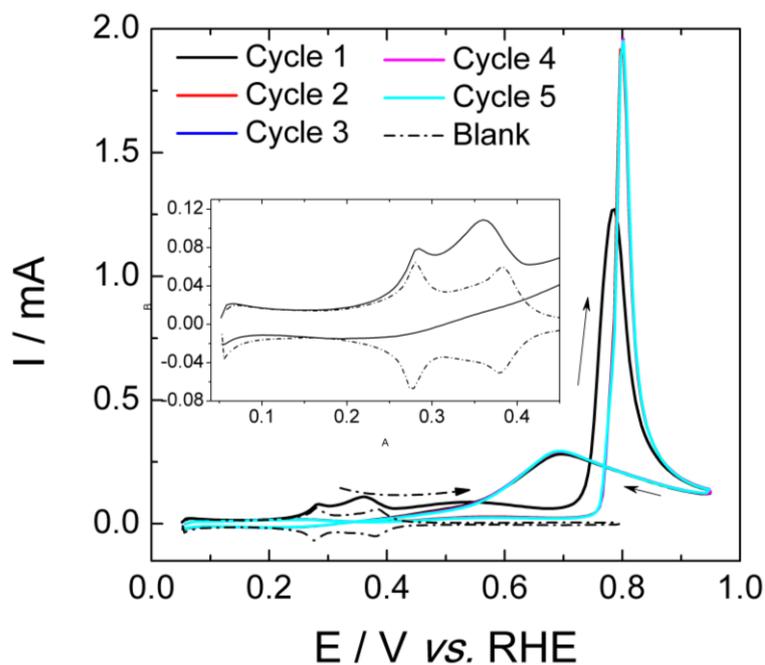


Figure S2. Voltammograms obtained in 0.2 M GIOH and 0.5 M H₂SO₄ solution with Pt50-50. $v = 0.05 \text{ Vs}^{-1}$.

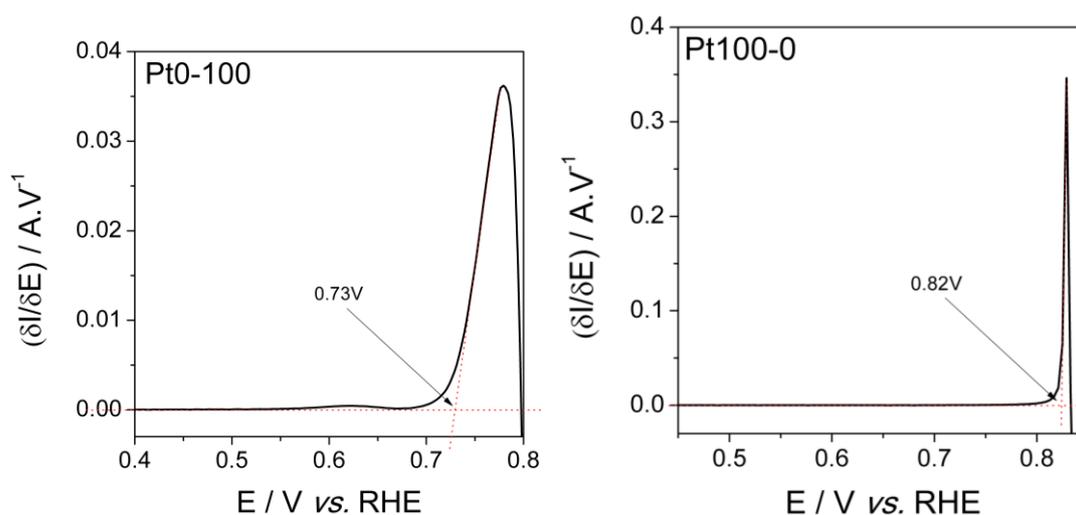


Figure S3. This figure shows the process used to calculate the onset potential for every electrode. Thus, for each case, two red pointed lines were drawn and the onset potential was extracted from intersection between them. One of the red lines was set to $(\delta I/\delta E)=0$ and the other is matching the region with the sharpest $(\delta I/\delta E)$ increasing.

FTIR

Table S1. Assignment of the most important bands in the spectra shown in figures 5 and 6.

Wavenumber (cm ⁻¹)	Chemical specie	Reference
2343	CO ₂	[1]
2040	On-top CO	[2]
1870	Bridge bonded CO	[3]
1740	Carbonil containing compounds	[4]
1200	HSO ₄ ⁻	[5]

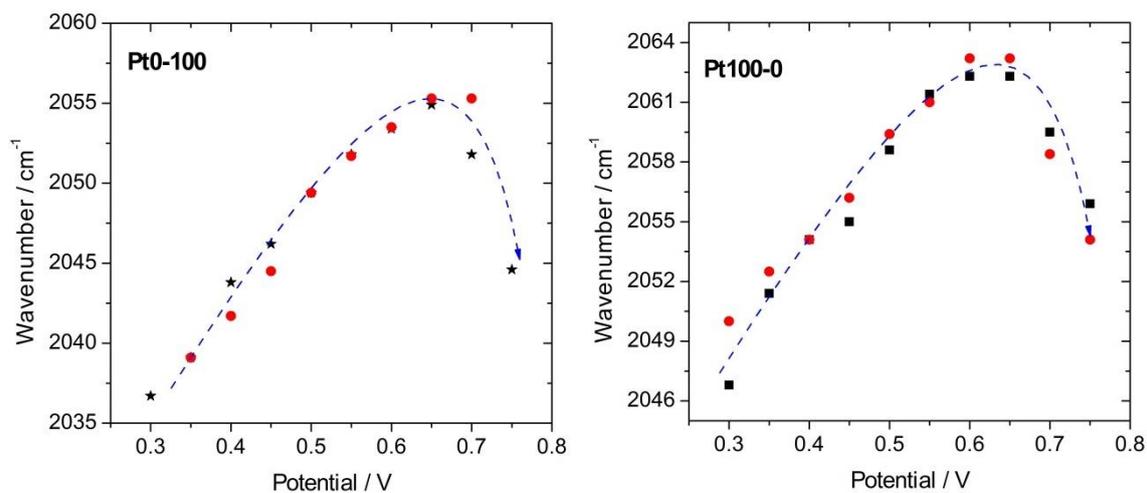


Figure S4. CO band frequency changes as a function of the working electrode potential for the well-ordered Pt0-100 and the completely disordered Pt100-0 electrode. In each figure, two independent and reproducible experiments are shown.

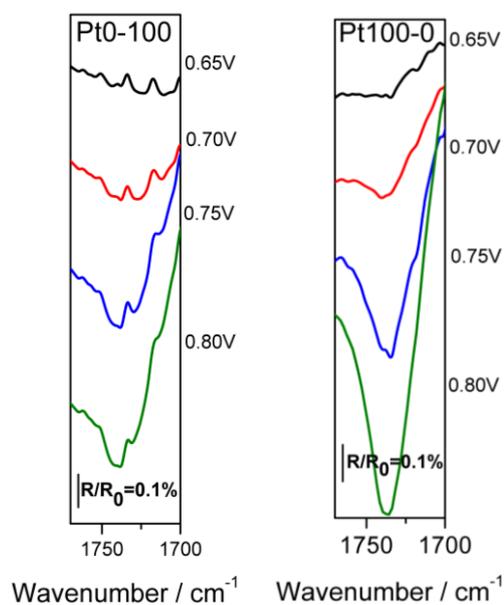


Figure S5. Detail of carbonyl bands for selected FTIR spectra extracted from Fig. 4. The illustrative potentials are indicated. Spectra obtained in 0.2 M GIOH + 0.5 M H_2SO_4 . Background spectra obtained at 0.12 V.

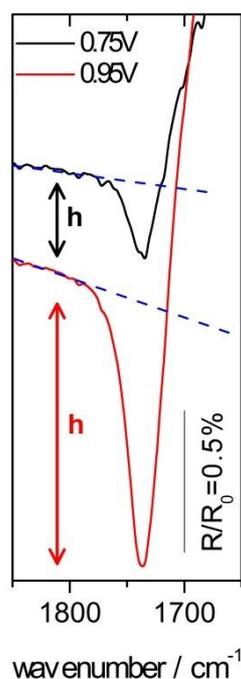


Figure S6. Two selected C=O bands are shown with the aim of clarifying the peak height measurement. The dotted blue line shows the baseline used to measure the peak height. The corresponding lines with arrows at the peaks sides show the magnitudes of each peak height.

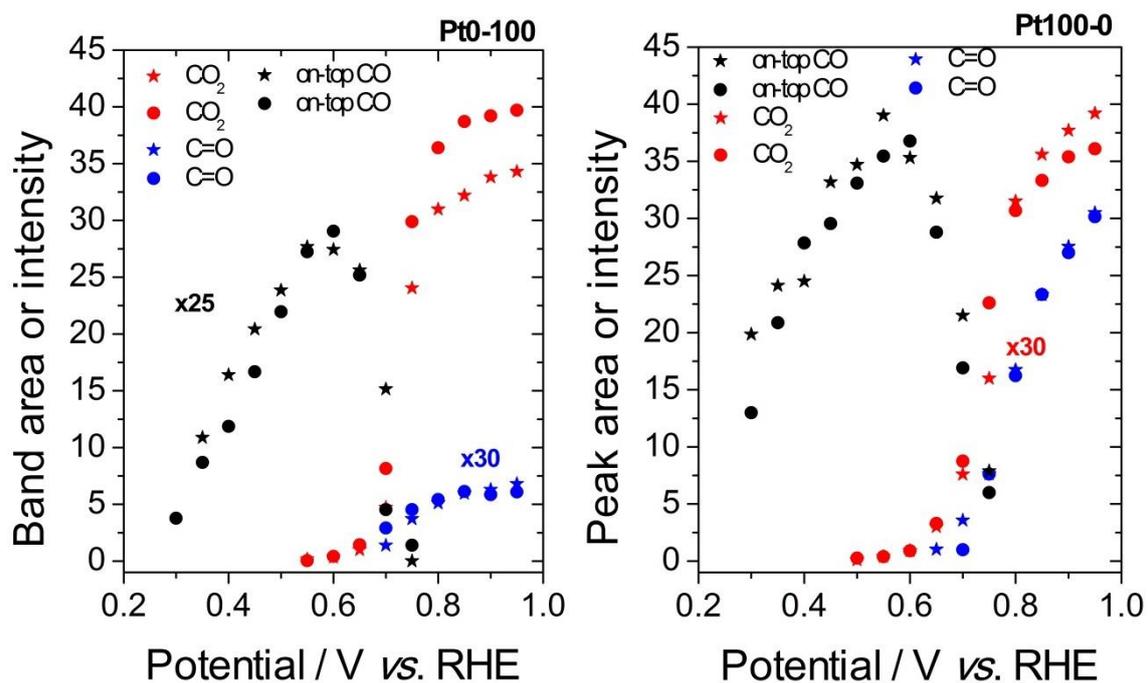


Figure S7. CO and CO₂ band intensities and C=O peak height as a function of the working electrode potential for the well-ordered Pt0-100 and the completely disordered Pt100-0 surfaces. In each figure, two independent experiments (stars and spheres) are shown.

Density functional theory calculations

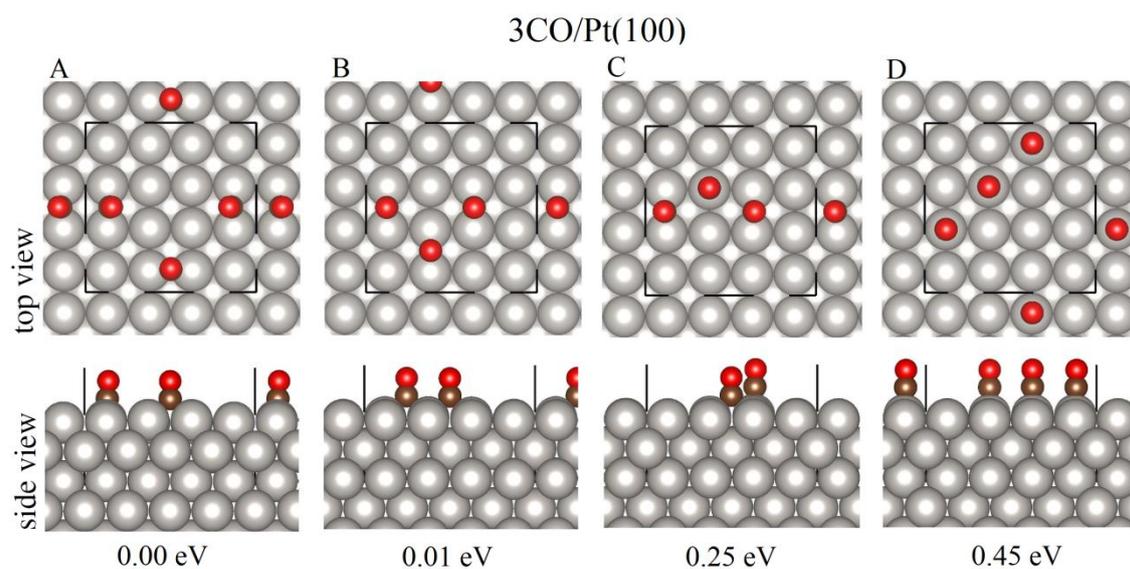


Figure S8. The lowest and high energy configurations for 3CO molecules on Pt(100). The numbers below the figures are the relative total energies.

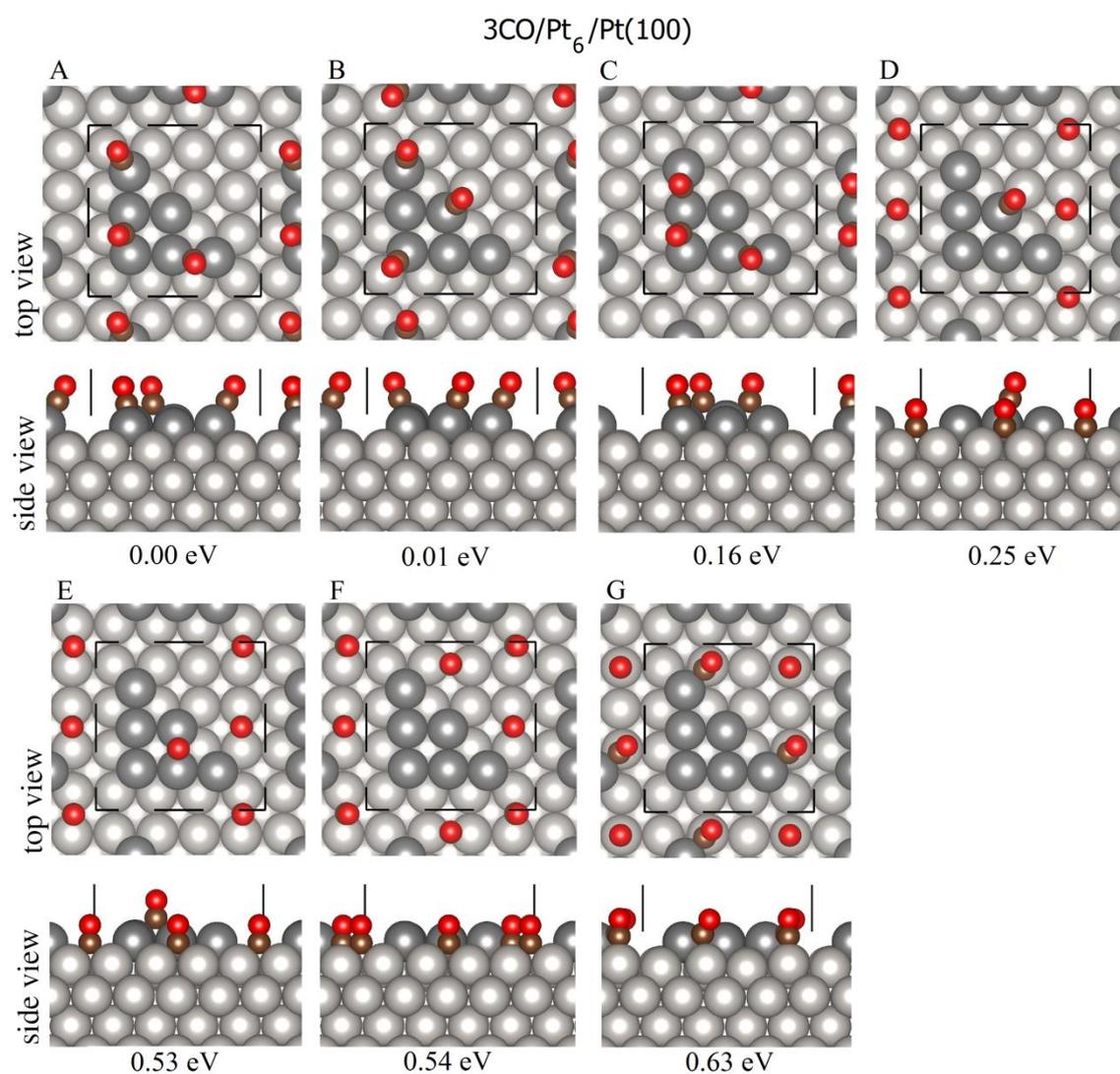


Figure S9. The lowest and high energy structures for 3CO on Pt₆/Pt(100) along with the relative total energies.

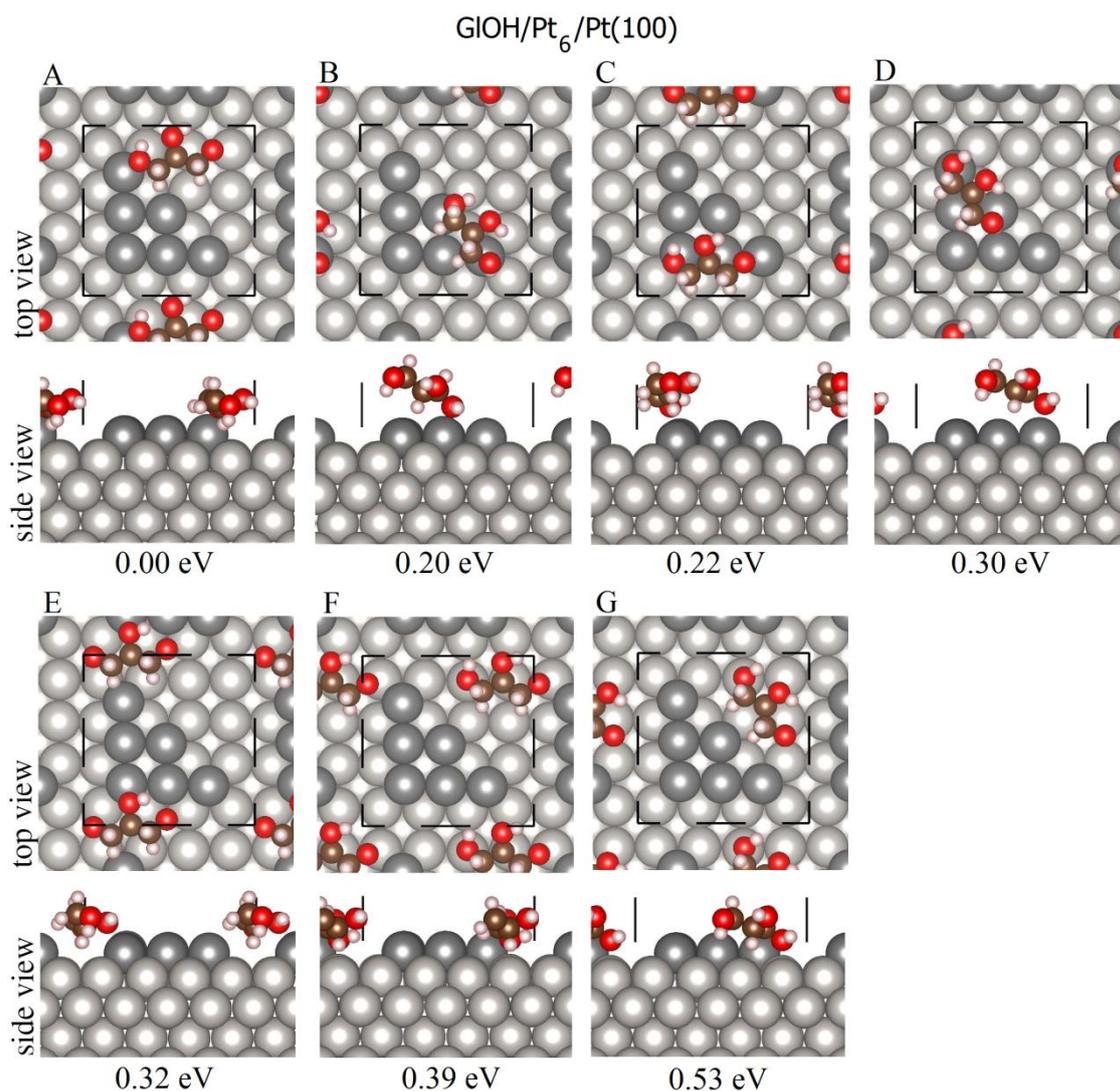


Figure S10. Lowest and high energy structures for GIOH on Pt₆/Pt(100). The numbers below the figures are the relative total energies.

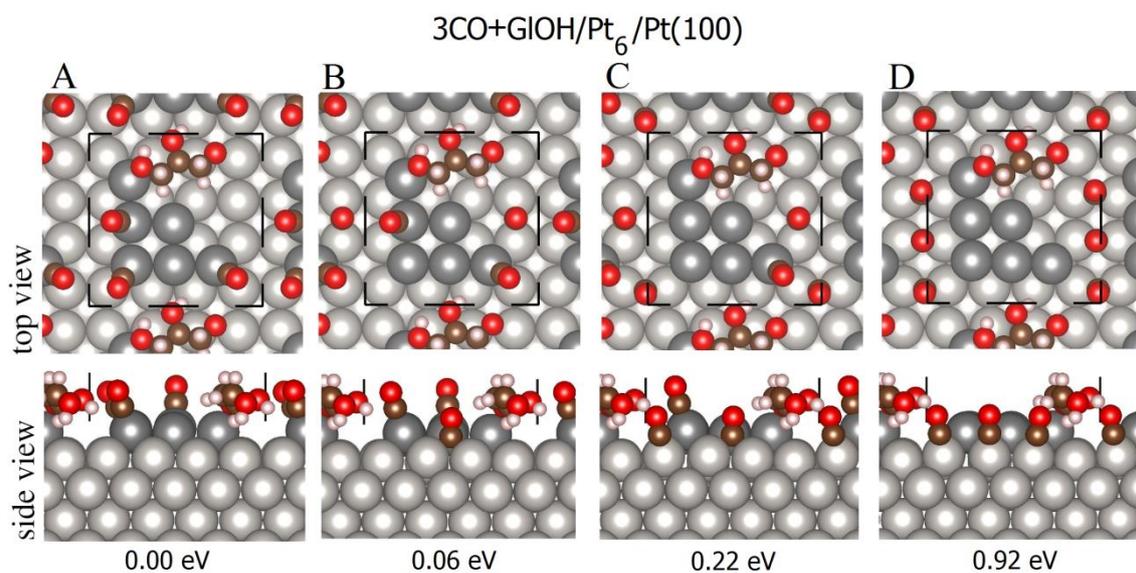


Figure S11. The lowest and high energy structures for 3CO + GIOH molecules on Pt₆/Pt(100) and their relative total energies are given below.

To improve our understanding of the binding mechanism of the molecules with the defected $\text{Pt}_6/\text{Pt}(111)$ surface, we calculated the following properties of the systems: local density of states, the changes in the substrate work function ($\Delta\Phi = \Phi^{\text{molecule/Pt}} - \Phi^{\text{clean Pt}}$), which reflects electron density rearrangement on the surfaces upon the adsorption of molecules, and an effective charge of every atom on the systems using Bader charge analysis ($Q = Z_{\text{val}} - Q_{\text{Bader}}$, where $Z_{\text{val}} = 4, 6, 1,$ and 10 for C, O, H, and Pt atoms, respectively).

Figure 10 shows the local density of states (LDOS) averaged over different chemical species for the clean $\text{Pt}_6/\text{Pt}(111)$ surface, and for the 3CO, GIOH and 3CO+GIOH adsorbed on the $\text{Pt}_6/\text{Pt}(111)$ surface. The LDOS of Pt_6 atoms demonstrate very tiny differences with the LDOS of the terrace $\text{Pt}(111)$ due to the low-coordinated atoms. Furthermore, the position of the center of the d-band of the topmost surface layer with respect to the Fermi level is also affected by the presence of the low coordinated atoms on the surface, e.g. the centers of the d-band are -2.48 eV and -2.76 eV, for $\text{Pt}_6/\text{Pt}(111)$ and $\text{Pt}(111)$ surface, respectively. As expected and supported by the d-band model proposed by Norskov [6], the center of the d-bands correlates with the magnitude of the adsorption energy of the molecules (e.g. -0.79 eV and -0.45 eV for GIOH on $\text{Pt}_6/\text{Pt}(111)$ and $\text{Pt}(111)$, respectively), i.e. the adsorption energy is larger for adsorption sites with a d-band center near to the Fermi.

Upon the molecular adsorption, the LDOS of Pt atoms is slightly affected compared with the LDOS of the clean Pt_6 , which is due to the interaction with the molecules. Moreover, p-states derived from the O and C p-states of the GIOH molecule are closer to the Fermi level than the corresponding states of CO molecules, however, there is a tail of the O p-states belong to CO molecule, which implies the different interaction mechanisms between the molecules and the surface.

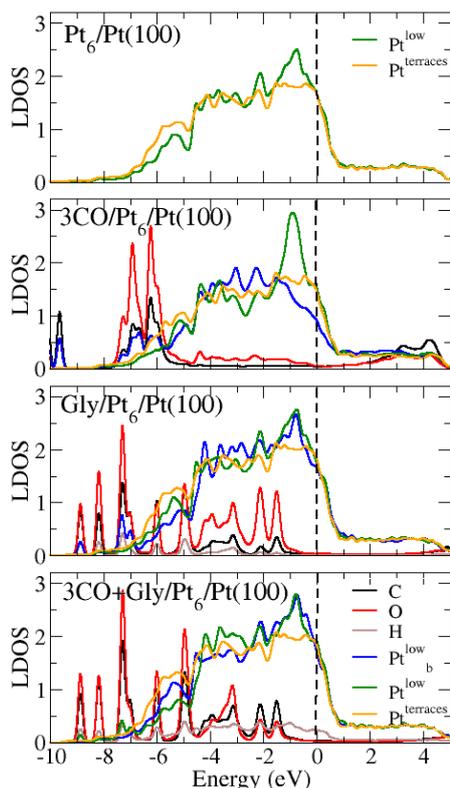


Figure S12. Local density of states for the clean $\text{Pt}_6/\text{Pt}(111)$ surface, and 3CO, GIOH and 3CO+GIOH adsorbed on the $\text{Pt}_6/\text{Pt}(111)$ surface.

To obtain a further insight into the nature of the interaction between the molecules and the surface, we calculate the work function (Φ) for the clean $\text{Pt}_6/\text{Pt}(100)$ and $\text{Pt}(100)$. We found that Φ is smaller in the case of $\text{Pt}_6/\text{Pt}(100)$ by 0.55 eV (5.41 eV and 5.96 eV, respectively) due to the low coordinated Pt_6 atoms. Upon molecular adsorption we found the reduction of the work function in the case of GIOH adsorption, and the enhancement of the work function in the case of CO adsorption, e.g. $\Delta\Phi = -0.29$ eV and 0.53 eV for $\text{Gly}/\text{Pt}_6/\text{Pt}(100)$ and $3\text{CO}/\text{Pt}_6/\text{Pt}(100)$, respectively, which indicates the different interaction mechanisms, i.e. an effective charge transfer from the substrate to GIOH, and donation-back-donation of the charge in the case of

CO molecule, which is supported by our previous results [7] and the model developed by Blyholder [8], respectively. As expected, for the whole system involving both molecules, 3CO+Gly/Pt₆/Pt(100), $\Delta\Phi$ has the value which is between those findings, i.e. -0.12 eV, due to the combination of those models, i.e. small charge transfer from Pt₆ to GIOH and donation back donation of the charge for CO molecules.

To obtain the quantitative results of the charge on the systems, we calculated the average effective charge for the C, O, H and Pt atoms separated by the low coordinated Pt atoms and terraces in the lowest energy configurations (Table 1). The low coordinated Pt₆ atoms of the clean Pt₆/Pt(100) surface possess tiny negative effective charge (-0.05 e), while the charge on terraces is almost zero. The adsorption of the molecules results in slight changes in the charges of the surface Pt₆/Pt(100), for example, the charge at the low coordinated Pt atoms that bind directly with the molecules is slightly positive (e.g. 0.07 eV for CO on Pt₆/Pt(100)) due to the charge transfer, while other Pt atoms at the low coordinated sites as well as on the terrace remain slightly negative (e.g. -0.03 eV for CO on Pt₆/Pt(100)) which is similar to the clean Pt₆/Pt(100) surface. Moreover, the positive charge of Pt_{low}^b is slightly larger for the case of GIOH than for CO (by almost 0.05 eV) indicating the different interaction mechanisms, i.e. an effective charge transfer to GIOH, the donation-back-donation mechanism between the CO molecules and the Pt₆/Pt(100) surface. The trends remain the same for the case of the 3CO and GIOH mixture, i.e. larger for GIOH and smaller for 3CO on the Pt₆/Pt(100) surface (see table 2).

Table 2. The average effective charge (in e) for the C, O, H and Pt atoms for the lowest energy configurations. The charge for the Pt atoms is separated by the charge in the low coordinated sites of Pt atoms directly bound with the molecules, Pt_{low}^b, and do not bound, Pt_{low}^a, and terrace sites, Pt^{terraces}.

	Pt ₆ /Pt(100)	3CO/Pt ₆ /Pt(100)	Gly/Pt ₆ /Pt(100)	3CO+Gly/Pt ₆ /Pt(100)
C		0.94	0.42	1.03 ^a ; 0.43 ^b
O		-1.05	-1.08	-1.08
H			0.61 ^c ; 0.05 ^d	0.61 ^c ; 0.05 ^d
Pt_{low}^b		0.07	0.12	0.09 ^e ; 0.13 ^f
Pt_{low}^a	-0.05	-0.03	-0.07	-0.09
Pt^{terraces}	0.00	-0.03	-0.01	-0.03

Here C^a and C^b show the charge of C atoms belonging to CO and GIOH molecules, respectively. H^c and H^d indicate the charge for H atoms belonging to O and C, respectively. Pt^e and Pt^f are the charges on Pt atoms, which bind to CO and GIOH, respectively.

References

- (1) Martins, C. A.; Giz, M. J.; Camara, G. A. *Electrochim. Acta* **2011**, *56*, 4549-4553.
- (2) Avramovic, M.; Leger, J. M.; Beden, B.; Hahn, F.; Lamy, C. *J. Electroanal. Chem.* **1993**, *351*, 285-297.
- (3) Iwasita, T.; Nart, F. C.; López, B.; Vielstich, W. *Electrochim. Acta* **1992**, *37*, 2361-2367.
- (4) Socrates, G.; *Infrared and Raman Characteristic Group Frequencies*, WileyInterscience, New York, 1980.
- (5) Parry, D. B.; Samant, M. G.; Seki, H.; Philpott, M. R.; Ashley, K. *Langmuir* **1993**, *9*, 1878-1887.
- (6) Bligaard, T.; Norskov, J. K. *Electrochim. Acta* **2007**, *52*, 5512-5516.
- (7) Tereshchuk P.; Da Silva J. L. F. *J. Phys. Chem. C* **2014**, *118*, 15251-15259.
- (8) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772-2777.