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Supporting information

DFT Insights into Competing Mechanisms of Guaiacol Hydrodeoxygenation on a Platinum Cluster

Chiara Nania,[a] Marco Bertini,[a] Laura Gueci,[a]
Francesco Ferrante,*[a] Dario Duca[a]

[a] *Dipartimento di Fisica e Chimica "E. Segrè", Università degli Studi di Palermo, Viale delle Scienze - 90128 Palermo, Italy.*

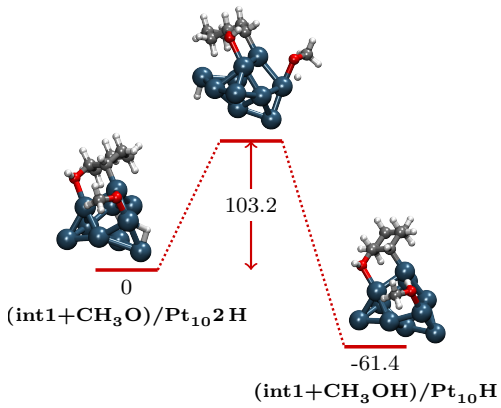

Figure S1: Hydrogenation of OCH_3, following fragmentation of an H_2 molecule, leads to the formation of chemisorbed methanol.

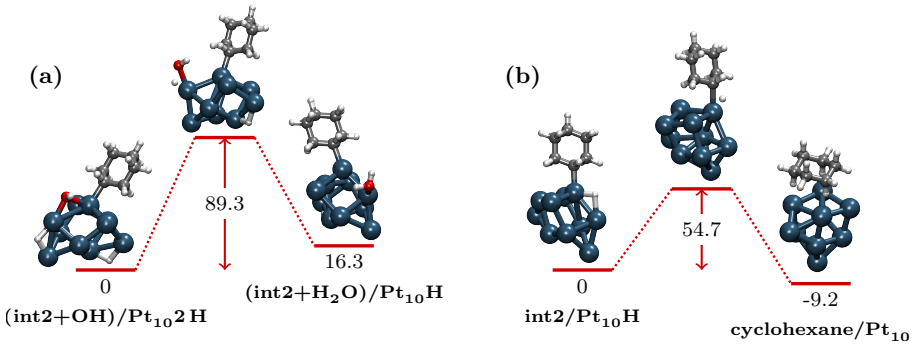

Figure S2: The reaction profiles shows (a) the formation of the adsorbed H_2O molecule through transfer of an H atom to the OH fragment and, after desorption of the H_2O molecule and diffusion of an H atom through the cluster, and (b) the cyclohexane generation.

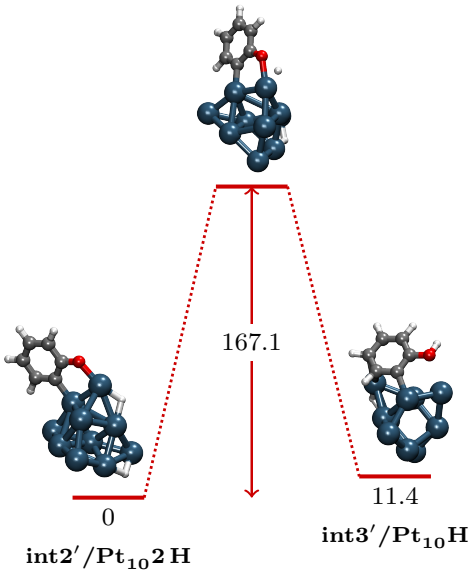

Figure S3: Hydrogenation of the dangling O of int2′ in the absence of CH_3OH.

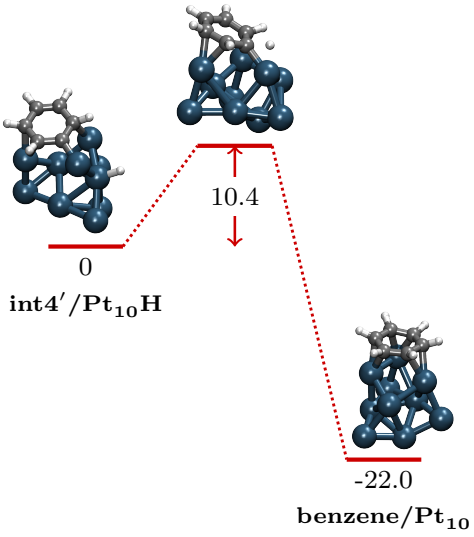

Figure S4: Hydrogenation of the unsaturated ring to form adsorbed benzene.

Table S1: Gibbs free energies of desorption (T = 298.15 K, p = 1 atm) for the stable intermediates and products occurring in the investigated HYD and DDO pathways. Each molecule is intended adsorbed on the Pt_{10} cluster.

compound	$\mathbf{\Delta G_{des}}$ **(kJ mol−1)**
guaiacol	78.7
2-methoxy-cyclohexan-1-ol	41.4
cyclohexanol	51.0
methoxycyclohexane	59.6
cyclohexane-1,2-diol	27.0
2-methoxycyclohex-2,4-dien-1-ol	199.4
2-methoxycyclohexa-3-en-1-ol	93.3
phenol	63.2
benzene	97.8
anisole	59.7
cathecol	91.8
cyclohexa-1,3-dien	121.8
cyclohexene	87.1
cyclohexane	29.7
methanol	61.9
water	31.3
methane	-12.0

Table S2: Elementary stage reactions in the HYD mechanism with the corresponding free energy barrier and reaction ΔG expressed in kJ mol^{-1} (T = 298.15 K, p = 1 atm). The last column indicates the figure number in the main manuscript where the elementary process is displayed.

Elementary process	$\Delta G^{\#}$	ΔG	**Figure**
guaiacol/Pt_{10} → I	64.7	17.0	2
I → II	85.3	-35.9	2
II+2H → III	57.1	-8.3	2
III → IV	85.6	58.3	2
IV+2H → V	28.3	-14.0	2
V → VI	100.6	25.4	2
2-methoxycyclohexan-1-ol/Pt_{10} → (int1+OCH_3)/Pt_{10}	140.3	-57.0	3
(int1+CH_3O)/Pt_{10}2 H → (int1+CH_3OH)/Pt_{10}H	99.5	-60.6	S1
int1/Pt_{10}H → cyclohexanol/Pt_{10}	106.2	38.1	3
cyclohexanol/Pt_{10} → (int2+OH)/Pt_{10}	188.2	11.1	3
int2/Pt_{10}H → cyclohexane	59.4	-4.4	S2
2-methoxycyclohexan-1-ol/Pt_{10} → (int3+OH)/Pt_{10}	151.2	-112.1	4
int3/Pt_{10}H → methoxycyclohexane/Pt_{10}	101.8	43.3	4
methoxycyclohexane/Pt_{10} → (int4+OCH_3)/Pt_{10}	183.6	11.7	4
methoxycyclohexane/Pt_{10} → (int5+CH_3)/Pt_{10}	204.8	47.5	4
2-methoxycyclohexan-1-ol/Pt_{10} → (int6+CH_3)/Pt_{10}	165.1	6.7	5
int6/Pt_{10}H → cyclohexane-1,2-diol/Pt_{10}	168.5	47.2	5
cyclohexane-1,2-diol/Pt_{10} → (int7+OH)/Pt_{10}	161.9	-102.4	5

Table S3: Elementary stage reactions in the DDO mechanism with the corresponding free energy barrier and reaction ΔG expressed in kJ mol^{-1} (T = 298.15 K, p = 1 atm). The last column indicates the figure number in the main manuscript where the elementary process is displayed.

Elementary process	$\Delta G^{\#}$	ΔG	**Figure**
guaiacol/Pt_{10} $\rightarrow$ (int1′+OCH_3)/Pt_{10}	132.4	0.2	6
(int1′+OCH_3)/Pt_{10} $\rightarrow$ (int2′+CH_3OH)/Pt_{10}	26.1	-7.4	6
(int2′+CH_3OH)/Pt_{10}2 H $\rightarrow$ (int3′+CH_3OH)/Pt_{10}H	47.9	-28.4	6
int3′/Pt_{10}H $\rightarrow$ phenol/Pt_{10}	61.2	-31.9	6
phenol/Pt_{10} $\rightarrow$ (int4′+OH)/Pt_{10}	103.6	-26.6	6
guaiacol/Pt_{10} $\rightarrow$ (int5′+OH)/Pt_{10}	167.0	59.7	7
int5′/Pt_{10}H $\rightarrow$ anisole/Pt_{10}	62.4	-30.2	7
anisole/Pt_{10} $\rightarrow$ (int6′+OCH_3)/Pt_{10}	83.0	-35.1	7
anisole/Pt_{10} $\rightarrow$ (int7′+CH_3)/Pt_{10}	145.4	-33.9	7
int7′/Pt_{10}H $\rightarrow$ phenol/Pt_{10}	88.1	42.0	7
guaiacol/Pt_{10} $\rightarrow$ (int8′+CH_3)/Pt_{10}	149.3	-43.2	8
int8′/Pt_{10}H $\rightarrow$ catechol/Pt_{10}	151.6	64.6	8
catechol/Pt_{10} $\rightarrow$ (int3′+OH)/Pt_{10}	203.3	-14.6	8
benzene/Pt_{10} $\rightarrow$ Ia	89.3	-24.7	9
Ia $\rightarrow$ IIa	85.0	61.5	9
IIa+2H $\rightarrow$ IIIa	27.0	-24.7	9
IIIa $\rightarrow$ IVa	65.2	56.9	9
IVa+2H $\rightarrow$ Va	40.8	19.5	9
Va $\rightarrow$ cyclohexane/Pt_{10}	84.1	13.0	9
int2′/Pt_{10}2 H $\rightarrow$ int3′/Pt_{10}H	166.2	18.1	S3
int5′/Pt_{10}H $\rightarrow$ benzene/Pt_{10}	12.7	-20.7	S4

Table S4: The shorthand notation used in the following for the main species involved in guaiacol hydrodeoxygenation reaction.

compound	**abbreviation**
guaiacol	**G**
2-methoxy-cyclohexan-1-ol	**MOCEO**
cyclohexanol	**CEO**
cyclohexane	**CE**
methoxycyclohexane	**MOCE**
cyclohexane-1,2-diol	**CEDO**
phenol	**P**
benzene	**B**
anisole	**AN**
cathecol	**CA**

Table S5: Summary of the eight most important mechanisms found for the guaiacol hydrodeoxygenation reaction on Pt_{10}, according to the scheme reported in Figures 2 and 10 of the main text.

mechanism	**sequence**	**other products**
HYD-1	**G–MOCEO–CEO–CE**	CH_3OH, H_2O
HYD-2	**G–MOCEO–MOCE–CE**	CH_3OH, H_2O
HYD-3	**G–MOCEO–MOCE–CEO–CE**	CH_4, $2\,H_2O$
HYD-4	**G–MOCEO–CEDO–CEO–CE**	CH_4, $2\,H_2O$
DDO-1	**G–P–B–CE**	CH_3OH, H_2O
DDO-2	**G–AN–B–CE**	CH_3OH, H_2O
DDO-3	**G–AN–P–B–CE**	CH_4, $2\,H_2O$
DDO-4	**G–CA–P–B–CE**	CH_4, $2\,H_2O$

Table S6: Reaction rates (s^{-1}) of the eight guaiacol HDO mechanisms (M) at various temperature (K). The power of 10 of scientific notation is given in parenthesis. Gibbs free energies (as a function of temperature, at p = 1 atm) have been considered for the kinetic analysis.

M \ T	**473**	**573**	**673**	**773**	**873**	**973**	**1073**
HYD-1	1.6(-13)	9.3(-9)	1.8(-5)	8.5(-4)	3.2(-3)	4.8(-3)	1.5(-2)
HYD-2	1.9(-12)	5.3(-8)	5.8(-5)	2.0(-3)	5.0(-3)	5.2(-3)	1.3(-2)
HYD-3	6.9(-15)	8.6(-10)	3.0(-6)	8.0(-4)	4.6(-3)	5.0(-3)	1.2(-2)
HYD-4	1.7(-18)	9.8(-13)	9.4(-9)	1.5(-6)	1.4(-5)	4.3(-5)	2.5(-4)
DDO-1	4.9(-9)	3.7(-5)	1.9(-2)	1.7(0)	3.6(+1)	6.2(+2)	1.1(+3)
DDO-2	4.9(-9)	3.7(-5)	1.9(-2)	1.0(0)	3.2(0)	3.1(0)	7.3(0)
DDO-3	4.9(-9)	3.7(-5)	1.8(-2)	6.6(-1)	1.9(0)	1.9(0)	4.5(0)
DDO-4	1.2(-16)	3.2(-11)	2.1(-7)	2.0(-4)	1.0(-2)	4.5(-2)	2.2(-1)

Table S7: Reaction rates (s^{-1}) of the eight guaiacol HDO mechanisms (M) at various temperature (K). The power of 10 of scientific notation is given in parenthesis. Energy values with vibrational zero point contribution have been considered for the kinetic analysis.

M \ T	**473**	**573**	**673**	**773**	**873**	**973**	**1073**
HYD-1	4.8(-15)	3.1(-10)	7.3(-7)	2.3(-4)	2.0(-2)	6.9(-1)	1.2(+1)
HYD-2	5.6(-14)	2.2(-9)	3.8(-6)	9.6(-4)	6.9(-2)	2.1(0)	3.3(+1)
HYD-3	3.1(-19)	1.2(-13)	9.9(-10)	8.2(-7)	1.5(-4)	9.1(-3)	2.6(-1)
HYD-4	3.4(-20)	1.8(-14)	1.9(-10)	1.8(-7)	3.6(-5)	2.4(-3)	7.6(-2)
DDO-1	8.1(-13)	2.3(-8)	3.2(-5)	6.9(-3)	4.3(-1)	1.2(+1)	1.7(+2)
DDO-2	8.1(-13)	2.3(-8)	3.2(-5)	6.9(-3)	4.3(-1)	1.2(+1)	1.7(+2)
DDO-3	8.1(-13)	2.3(-8)	3.1(-5)	6.8(-3)	4.3(-1)	1.2(+1)	1.7(+2)
DDO-4	3.9(-18)	9.5(-13)	6.0(-9)	4.0(-6)	6.1(-4)	3.3(-2)	8.7(-1)