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ESI for: "Ethanol electro-oxidation reaction on the Pd(111) surface in alkaline media: insights from quantum and molecular mechanics"

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Data related to DFT calculations

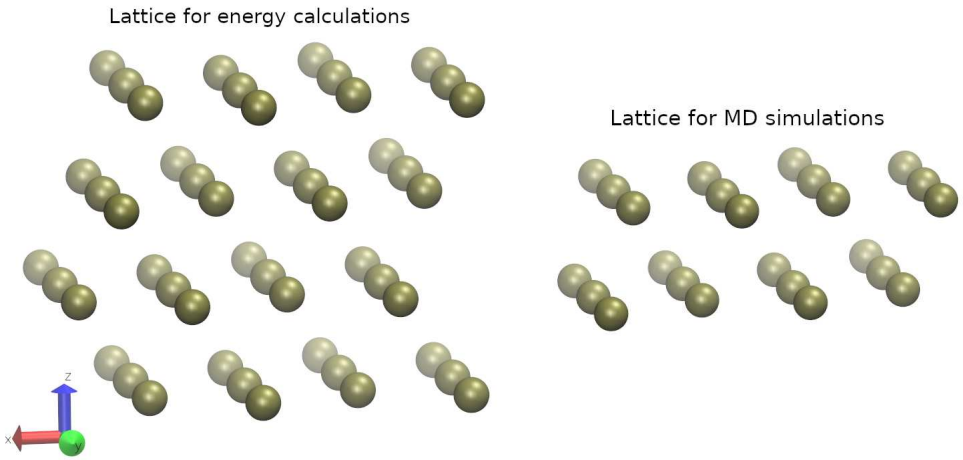

Figure S1: *Left panel:* Pd(111) lattice employed for DFT single-point energy calculations. Standard periodic boundary conditions are applied in the three axis directions. The box size along x, y and z is 9.528×8.252×30.000 Å. *Right panel:* Pd(111) lattice employed for ab initio MD simulations. Standard periodic boundary conditions are applied in the x and y directions. The box size along x and y is 9.528×8.252 Å.

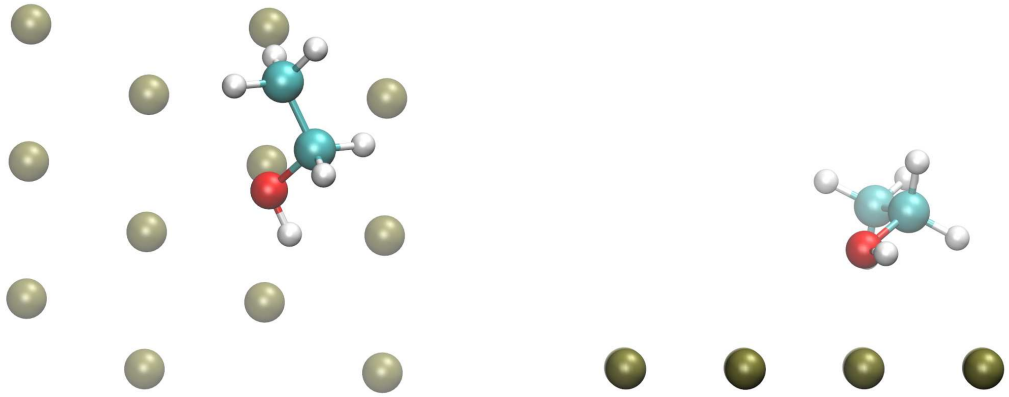

Figure S2: Top and side views of the minimum energy arrangement of the Pd(111)/EtOH system. For the sake of clarity, only the top layer of the Pd surface is reported.

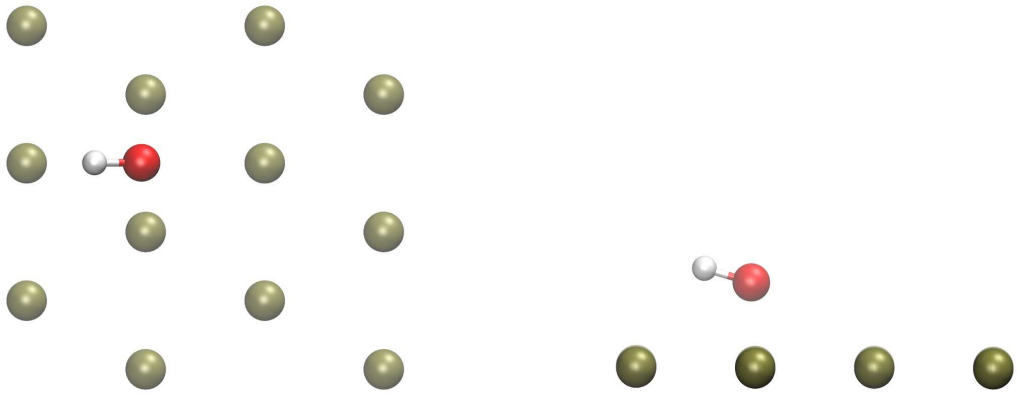

Figure S3: Top and side views of the minimum energy arrangement of the Pd(111)/OH^- system. For the sake of clarity, only the top layer of the Pd surface is reported.

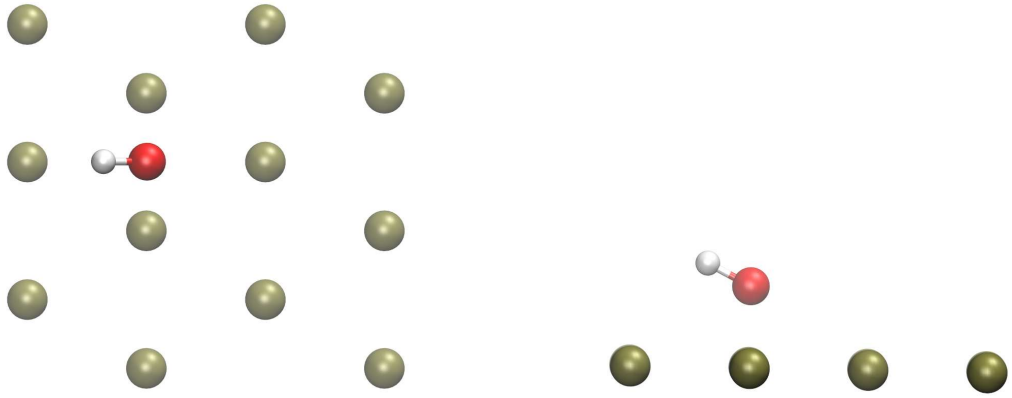

Figure S4: Top and side views of the minimum energy arrangement of the Pd(111)/OH system. For the sake of clarity, only the top layer of the Pd surface is reported.

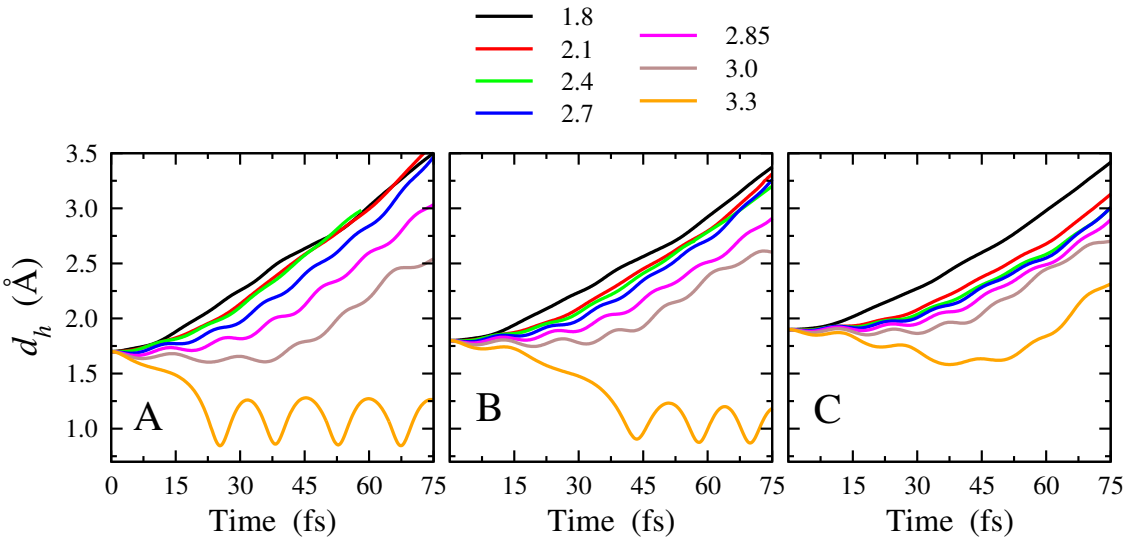

Figure S5: d_h distance as a function of time for various initial d_v distances (see legend; the values are in Å). Three sets of simulations are reported in the panels, differing for the initial d_h distance: 1.7 Å (Panel A), 1.8 Å (Panel B) and 1.9 Å (Panel C).

Data related to classical MD simulations

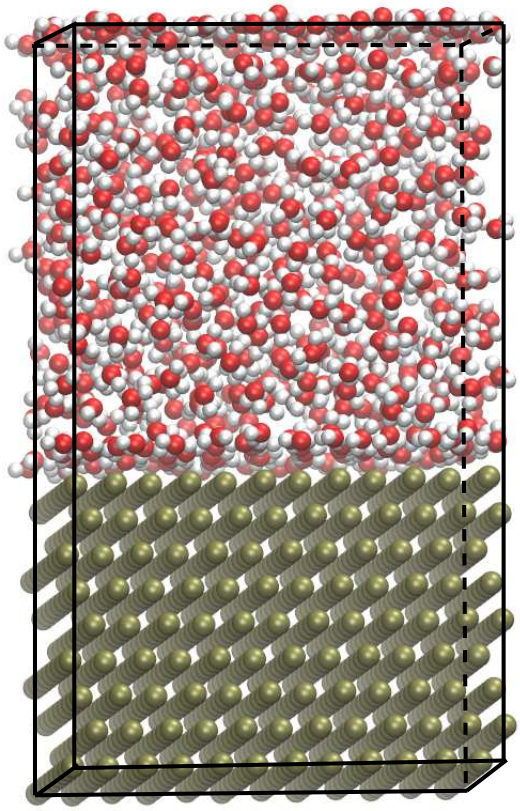

Figure S6: Snapshot of the sample employed for classical MD simulations. The simulation box (size 28.5855×24.7558×50 Å) contains 972 Pd atoms distributed into 9 lattice slabs, 714 water molecules and one target molecule (in turn, EtOH, OH^- and water). Standard periodic boundary conditions are applied along x, y and z directions.

Table S1: In MultiWindow tempering, the window potential has the harmonic functional form $k(z - z_0)^2$, where z is the current value of the collective variable, specifically the distances of C_α (Pd(111)/EtOH system) and of oxygen (Pd(111)/OH^- system) from the Pd(111) surface and z_0 is the center of the window potential characteristic of the ensemble in which the replica moves. For the Pd(111)/EtOH and Pd(111)/OH^- systems, 31 and 63 ensembles have been taken. In this table, the values of z_0 (Å units) associated to these ensembles are reported. k is the force constant of the window potentials: $k = 10$ kcal mol^{-1} Å^{-2} for Pd(111)/EtOH and $k = 20$ kcal mol^{-1} Å^{-2} for Pd(111)/OH^-.

Pd(111)/EtOH	Pd(111)/OH^-	
2.00	1.80	4.50
2.21	1.91	4.57
2.42	2.02	4.64
2.64	2.13	4.71
2.85	2.24	4.78
3.07	2.35	4.85
3.28	2.46	4.92
3.50	2.57	5.00
3.66	2.68	5.25
3.83	2.80	5.50
4.00	2.88	5.75
4.16	2.97	6.00
4.33	3.05	6.25
4.50	3.14	6.50
4.66	3.22	6.75
4.83	3.31	7.00
5.00	3.40	7.25
5.42	3.48	7.50
5.85	3.57	7.75
6.28	3.65	8.00
6.71	3.74	8.25
7.14	3.82	8.50
7.57	3.91	8.75
8.00	4.00	9.00
8.42	4.00	9.25
8.85	4.07	9.50
9.28	4.14	9.75
9.71	4.21	10.00
10.14	4.28	10.25
10.57	4.35	10.50
11.00	4.42	10.75
		11.00

Force field for interatomic interactions involving Pd

The empirical force field for the interactions of Pd with atoms of water, ethanol (EtOH) and OH^- has been modeled through a pairwise potential of Lennard-Jones type:

$$E(r) = \frac{A}{r^{12}} - \frac{B}{r^6} \tag{1}$$

Using this potential, with have fitted the DFT energies of the following molecule-surface configurations.

- For EtOH: configurations EtOH-1, EtOH-2, EtOH-3, EtOH-4 and EtOH-5 drawn in Fig. S7 (also shown in Fig. 1 of the main text).

- For OH^-: configurations OH-1, OH-2 and OH-3 drawn in Fig. S8 (also shown in Fig. 2 of the main text).

- For water: configurations H2O-1 and H2O-2 drawn in Fig. S9.

For each of the above configurations, the DFT energy has been computed for different molecule-surface distances, while keeping fixed the Pd(111) lattice and the molecular structures, as well as their mutual arrangement. Technical details of the DFT calculations and the setup of the Pd(111) lattice have been reported in the main text, Sec. *Methods and technical details: Quantum mechanical calculations*. The molecular structures have been obtained through an energy minimization using the DFT level also employed for single-point energy calculations. In this way, we have obtained a set of energies of configurations, only differing in the molecule-surface distance, that have been fitted with the empirical force field based on the relationship of Eq. 1. Being the molecular stuctures and the Pd lattice the same in all DFT calculations, intra-lattice and intra-molecular interactions contribute to the total energy only for an additive constant and hence they have not been accounted for.

In Figs. S7, S8 and S9, we report the DFT energies along with the Lennard-Jones potential energies obtained by the fit. Overall, the agreement is satisfactory, especially for

EtOH and water, while some deviation is observed for OH^-, probably due to the strong polarization effects arising from the net electric charge on the hydroxide ion. The A and B parameters (see Eq. 1) obtained from the fit are reported in Table S2 of this supplementary information report.

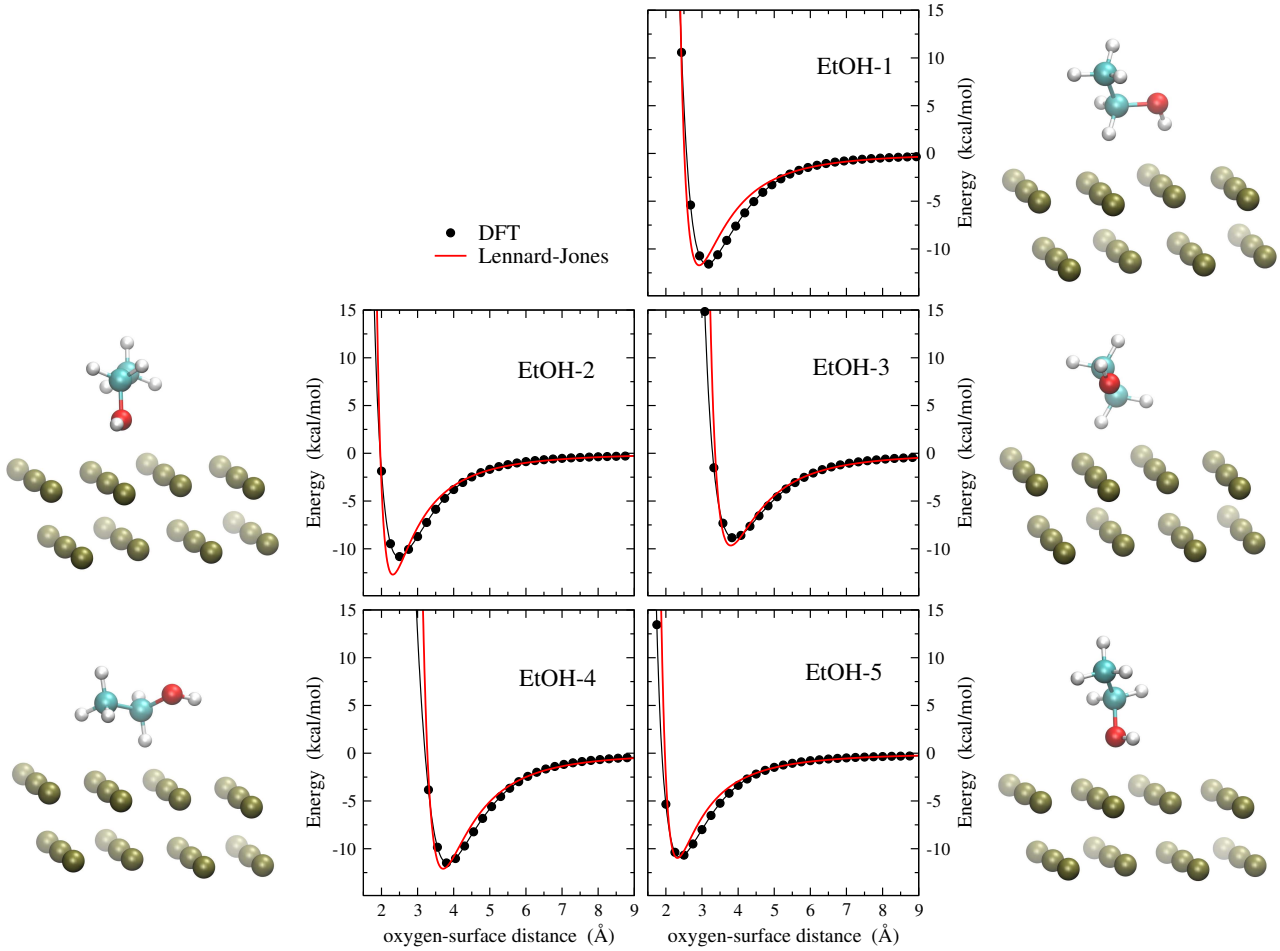

Figure S7: DFT energy of the Pd(111)/EtOH configurations as a function of the oxygen-surface distance (filled circles; the black lines are guide for the eyes). The energy plot for a given configuration is recovered by using structures where the atomic coordinates are obtained translating rigidly the molecule along the normal to the surface, while keeping fixed the arrangement as shown in the pictures. For the sake of clarity, only a limited portion of the surface is reported. The zero energy is taken at the largest oxygen-surface distance. The red lines represent the energy obtained by fitting the DFT energy via Eq. 1.

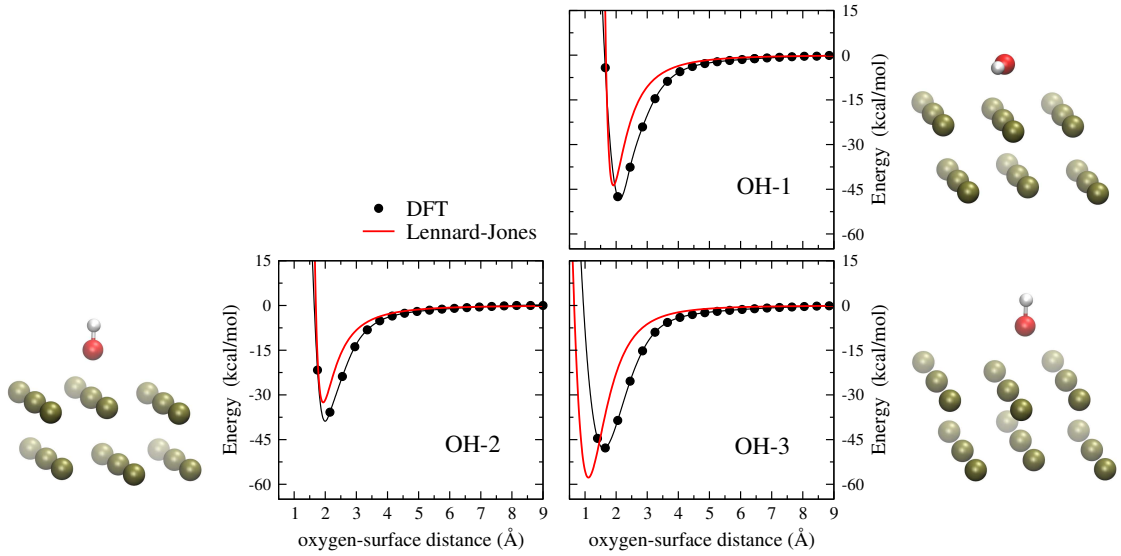

Figure S8: DFT energy of the Pd(111)/OH^- configurations as a function of the oxygen-surface distance (filled circles; the black lines are guide for the eyes). The energy plot for a given configuration is recovered by using structures where the atomic coordinates are obtained translating rigidly the molecule along the normal to the surface, while keeping fixed the arrangement as shown in the pictures. For the sake of clarity, only a limited portion of the surface is reported. The zero energy is taken at the largest oxygen-surface distance. The red lines represent the energy obtained by fitting the DFT energy via Eq. 1.

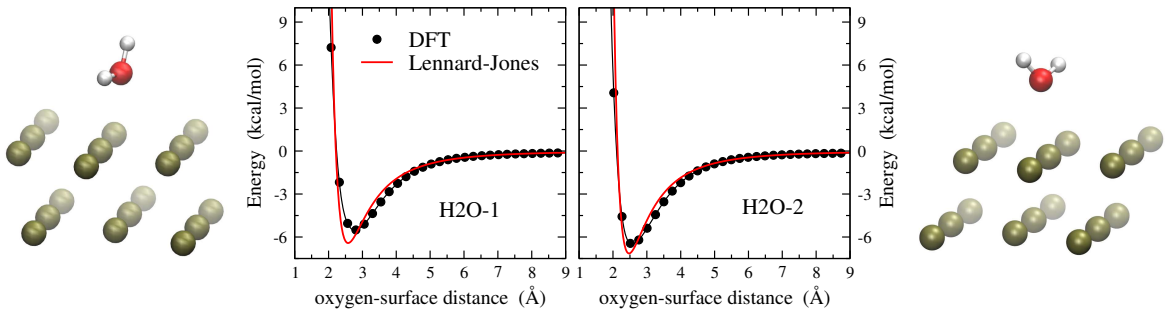

Figure S9: DFT energy of the Pd(111)/water configurations as a function of the oxygen-surface distance (filled circles; the black lines are guide for the eyes). The energy plot for a given configuration is recovered by using structures where the atomic coordinates are obtained translating rigidly the molecule along the normal to the surface, while keeping fixed the arrangement as shown in the pictures. For the sake of clarity, only a limited portion of the surface is reported. The zero energy is taken at the largest oxygen-surface distance. The red lines represent the energy obtained by fitting the DFT energy via Eq. 1.

Table S2: Force field parameters related to the interactions of Pd with atoms belonging to EtOH, OH^- and water obtained by fitting the DFT energies with a Lennard-Jones type potential (Eq. 1).

	B (kcal Å^6/mol)	A (kcal Å^{12}/mol)
EtOH		
C	2808.60	2831211.61
H	35.39	4504.15
O	983.79	153885.05
OH^-		
O	2004.80	59570.30
H	1106.37	37205.36
H_2O		
O	1172.24	186025.67
H	359.10	231981.07