Supporting Information

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1 Application of an Electric Field to Density Functional Theory Simulations

Figure S1 shows a schematic of how we applied an electric field in our simulations. This method¹ avoids the need to add or remove electrons from the supercell, which can be complicated to control electric fields. Rather, it introduces a dipole sheet at the center of the vacuum region that polarizes the periodic slab and establishes an electric field in the system.



Figure S1: Schematic of the Neugebauer and Scheffler method¹ for imposing an electric field in periodic supercell calculations through the use of a dipole sheet in the vacuum.

2 Initial geometries of ethanol adsorbed on the Rh(111) surface with co-adsorbed water

The initial geometries for adsorption calculations in the presence of electric field and water were determined using one of two methods. We started with four different initial geometries for each adsorbate, similar to our previous work.² As discussed in our previous work,² the most stable geometries from vacuum calculations were used as the starting point for explicit water calculations. We then added one water molecule to interact with the surface species. Four different initial geometries were simulated for each adsorbate. For adsorbates that have both O and H atoms (like ethanol, CH₃CH₂O, CH₂CH₂O, CH₂OH, CH₂O, CH₂CO, OH) , two initial geometries had the H atom of the water molecule initially placed to interact with the O atom of the adsorbate in different ways. For the other two initial geometries, the O atom of the water molecule was initially arranged to interact with different H atoms of the adsorbate. For smaller adsorbates that only had either O or H atoms (e.g., CH_x, CO, and H), four different initial geometries were also considered in order to find the most stable adsorption structures. The first two initial geometries involved hydrogen bonding, while the second two cases did not.

Figure S2 shows four different possible initial geometries for adsorbed ethanol with water. In the first method, we first optimized these four initial geometries in the absence of an electrical field. The most stable geometry from these calculations was then used as the initial geometry for simulations in the presence of electrical field. In the second method, all four initial geometries were optimized in the presence of an electric potential. At each potential the most stable structure (i.e. lowest energy) was then chosen among these four calculations. The approach of the two methods are illustrated in Figure S3.



Figure S2: Four potential initial geometries for ethanol+water over Rh(111). (a) and (b) show the first two initial structures with water interacting with O in the adsorbate; (c) and (d) show the other two initial structures with water interacting with H in the adsorbate. Grey spheres represent carbon atoms, red spheres represent oxygen atoms, white spheres represent hydrogen atoms, and blue spheres represent rhodium atoms.



Figure S3: Illustration of the two methods used in this work when modeling water with an adsorbate in an electric field.

3 Comparison of calculated adsorption energies with literature values in the absence of electric fields

The calculated adsorption energies in the absence of an external electric field were compared with literature values as shown in Table S1. Our results agree well with previous calculations.

Table S1: Comparison of our calculated adsorption energies over Rh(111) with literature values. All energies were calculated in the absence of an electric field.

$\Delta E_{ads} \ (eV)$								
Species	This work	Literature values						
$*CH_3CH_2OH$	-0.374	$-0.46;^3$ $-0.51;^4$ -0.28^5						
$*CH_3CH_2O$	-2.328	-2.30^{4}						
$*CH_2CH_2O$	-1.220	-1.29^{4}						
$*CH_2OH$	-2.115	$-1.74;^{5}$ -2.27^{6}						
$*CH_2O$	-0.890	$-0.68;^{5}$ -1.07^{6}						
$*CH_3CO$	-2.414	-2.41^{5}						
$*CH_2CO$	-1.437	-1.41^{4}						
*CHCO	-3.429	-3.32^4						
$*CH_3$	-1.843	$-1.90;^{5}$ $-1.97;^{4}$ $-1.32;^{7}$						
$*CH_2$	-4.162	$-4.14;^{5}$ -4.15^{4}						
*CH	-6.811	$-6.62;^{5}-6.55^{4}$						
*CO	-1.949	-1.93 ; ⁴ -2.04 ; ⁷ -1.77^5						
H^*	-2.781	$-2.79;^{4} -2.79;^{7} -2.74;^{5} 2.79^{8}$						

4 Calculated adsorption energies in a potential

We show in Figure S4 the adsorption energies in vacuum and potentials between -1 V/Å and 1 V/Å. Three different types of adsorption energy changes were observed. For the first set of species (CH₃CH₂OH, CH₃CH₂O, CH₂CH₂O, CH₂OH, CH₃CO, CH₃, CH₂, CH₃COOH and OH), their adsorption energies decreased (i.e., became more stable) with increasing field strength. For the second set of species (CHCO and CO), their adsorption energies increased with increasing field strength. For the third set of species (CH₂O, CH₂O, CH₂CO and H), their adsorption energies first decreased then increased.



Figure S4: Adsorption energies of species relevant to ethanol oxidation in the presence of electric fields. All calculations were in vacuum (no water present).

5 Geometries in vacuum (no water present)

Figure S5 shows an example of the optimized geometries of CH_3CH_2O on Rh(111) surface in vacuum and with an electric field. In the case of CH_3CH_2O , the geometries only changed very slightly. This result is common for adsorbates with no water molecule present, or that geometries only changed slightly in positive/negative potentials, as discussed further in the following Section.



Figure S5: Optimized CH_3CH_2O structures adsorbed on Rh(111) in vacuum and in an electric field.

6 Structural fluxionality of adsorbed species in vacuum

We calculated the structural fluxionality of adsorbates using the approach discussed by Yang et al.⁹ They defined a displacement to describe the extent of the structural fluxionality using the following formula:

$$Displacement = \frac{\sum_{n} \sqrt{(X_{nf} - X_{ni})^2 - (Y_{nf} - Y_{ni})^2 - (Z_{nf} - Z_{ni})^2}}{N}.$$
 (S1)

Here X, Y, and Z represent the coordinates (in x-, y-, z-directions) of the n-th atom in the system, i and f represent the initial and final states, and N equals the number of atoms in the slab. The initial states were the geometries with no field, while the final states were the geometries with an electric field present. Table S2 provides the structural fluxionality values of adsorbates in vacuum. As indicated, displacement values are all very small.

Table S2: Structural fluxionality of ethanol component species on Rh(111) in the vacuum.

Displacement (Å)											
Electric Field (V/Å)	-1	-0.8	-0.6	-0.4	-0.2	0	0.2	0.4	0.6	0.8	1
*CH ₃ CH ₂ OH	0.0114	0.0144	0.0082	0.0045	0.0018	0	0.0014	0.0036	0.0063	0.0108	0.013
$*CH_3CH_2O$	0.0016	0.0021	0.0015	0.0009	0.0004	0	0.0004	0.0008	0.0012	0.0016	0.0022
$*CH_2CH_2O$	0.0014	0.0017	0.0012	0.0008	0.0004	0	0.0003	0.0006	0.001	0.0013	0.0018
$*CH_2OH$	0.0088	0.0105	0.007	0.0042	0.0015	0	0.0004	0.0035	0.0076	0.0133	0.0186
$*CH_2O$	0.0017	0.0015	0.001	0.0006	0.0003	0	0.0002	0.0006	0.001	0.0017	0.0027
$*CH_3CO$	0.0016	0.0018	0.0013	0.0008	0.0005	0	0.0003	0.0007	0.0013	0.0018	0.0024
$*CH_2CO$	0.0021	0.0019	0.0011	0.0007	0.0003	0	0.0003	0.0006	0.001	0.002	0.0026
*CHCO	0.0062	0.0045	0.0023	0.0019	0.0004	0	0.0006	0.0016	0.0036	0.0042	0.0065
$*CH_3$	0.001	0.0013	0.0009	0.0005	0.0002	0	0.0002	0.0004	0.0006	0.0008	0.0009
$*CH_2$	0.0007	0.0009	0.0006	0.0003	0	0	0	0.0002	0.0003	0.0005	0.0006
*CH	0.0005	0.0004	0	0	0	0	0	0	0.0002	0.0003	0.0003
*CO	0.0023	0.0011	0.0008	0.0005	0.0002	0	0.0002	0.0005	0.0008	0.0012	0.0014
$^{*}\mathrm{H}$	0.0004	0.0004	0.0004	0	0	0	0.0003	0.0003	0.0003	0.0009	0.0008
*CH ₃ COOH	0.0074	0.0067	0.0058	0.0038	0.0011	0	0.0034	0.0035	0.0035	0.0061	0.0075
*OH	0.0023	0.0021	0.0017	0.0011	0.0006	0	0.0004	0.0007	0.0010	0.0014	0.0018

7 Bader charge analysis of adsorbed species in vacuum

We present Bader charge analysis in Figures S6 and S7. Additionally, Figure S7 illustrates the relationship between Rh charges and adsorption energies, with varying electric fields applied. Figure S7 illustrates a correlation between the adsorption energies and the total Bader charges of the bonded Rh atoms. For the species characterized by positive effective dipole moments, an increase in adsorption energy is observed as the Rh atoms become more positively charged, while the atoms in the adsorbates exhibit increased negative charges.







Figure S6: Bader charges of reaction intermediates as a function of an electric field in vacuum: (a) CH_3CH_2OH , (b) CH_3CH_2O , (c) CH_2CH_2O , (d) CH_2OH , (e) CH_2O , (f) CH_3CO , (g) CH_2CO , (h) CHCO, (i) CH_3 , (j) CH_2 , (k) CH, (l) CO, (m) H, (n) CH_3CHOOH , and (o) OH. Red and blue numbers represent the positive and negative charges of the atoms, respectively. Occasionally, an Rh atom may appear isolated from the adsorbate due to periodic boundary conditions.



Figure S7: The relationship between the adsorption energies and the sum of the Bader charges of all the Rh atoms bound to the adsorbate. Results are shown in a negative electric field ((-1 V/Å), in no electric field ((0 V/Å), and in a positive electric field ((1 V/Å)). Indicated with each plot are the effective dipole moments (see Equation 5) of each species. All results are presented in vacuum.

8 Electronic properties analysis of adsorbed species in vacuum and water

To further our understanding of how electric fields affect the electronic interactions between adsorbates and the Rh surface, we analyzed the density of states (DOS) and charge density difference (CDD) of selected species. These species, include CH_3CH_2OH , CH_2CO , and CHCO as shown in Figure 3 of the main paper. Figures 4 and 5 of the main paper show DOS and CDD for CH_3CH_2OH . The DOS and CDD for adsorbed (a) CH_2CO and (b) CHCO, both in vacuum and in the presence of water under different electric fields, are shown in Figures S8 and S9.



Figure S8: Density of states analysis of adsorbed (a) CH_2CO and (b) CHCO species in vacuum and the presence of water under different electric fields.



Figure S9: Charge density difference analysis of adsorbed (a) CH_2CO and (b) CHCO species in vacuum and the presence of water under different electric fields. The isosurface level of the differential charge densities of is 0.01 e/bohr^3 .

9 Comparison of Methods 1 and 2 for modeling the presence of water

The adsorption energies with Methods 1 and 2 for all species we modeled are shown in Figure S10. The hydrogen bond distances for select species using different modeling approaches are given in Table S3. Also given is a comparison of different geometries using Methods 1 and 2 (Figures S11, S12 and S13).



Figure S10: Adsorption energies of several species relevant to ethanol oxidation under external electric fields and with water present. Two different approaches (Method 1 and 2 as discussed in the Methodology) were used for selecting initial geometries for the optimizations.

Table S3: Comparison of hydrogen bond distances for select adsorbates using Methods 1 and 2. Bond distances are given in Å and are calculated as the distance between O/H pairs. The bond distance may be calculated from the water O or H atom and the corresponding O or H atom in the adsorbate, whichever is appropriate.

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	Electric Potential (V/A)											
	Method	-1	-0.8	-0.6	-0.4	-0.2	0	0.2	0.4	0.6	0.8	1
CH_3CH_2O	1	2.53	2.60	2.40	2.75	2.77	2.78	2.79	2.80	2.86	2.95	3.05
	2	2.53	2.53	2.53	2.50	2.32	2.54	2.47	2.49	2.55	2.54	2.52
CH_2CH_2O	1	1.47	1.47	1.47	1.47	1.48	1.49	1.49	1.49	1.50	1.51	1.52
	2	1.45	1.45	1.45	1.45	1.45	1.45	1.45	1.46	1.46	1.51	1.52
CO	1	1.90	1.90	1.90	1.90	1.91	1.92	1.92	1.94	1.96	1.98	2.01
	2	1.91	1.91	1.91	1.91	1.92	1.92	1.92	1.94	1.96	1.98	2.01



Figure S11: Geometries of adsorbed CH_3CH_2O and water in the presence of electrical fields. The top graphic corresponds to Method 1, while the bottom graphic corresponds to Method 2.



Figure S12: Geometries of adsorbed CO and water in the presence of electrical fields. The top graphic corresponds to Method 1, while the bottom graphic corresponds to Method 2.



Figure S13: Geometries of adsorbed CH_2CH_2O and water in the presence of electrical fields. The top graphic corresponds to Method 1, while the bottom graphic corresponds to Method 2.



Figure S14: Optimized geometries and calculated energies of C-C bond cleavage reactions in CH_2CH_2O using different solvation methods and electric fields. These results illustrate how different solvation approaches can lead to different reactant and product geometries, and hence different reaction energies.

10 Comparison of results in vacuum and with water present

A direct comparison of adsorption energies and reaction energies in vacuum and with water present (Method 2) are also given below (Figures S15 to S17). The same data are presented in the main text in various Figures (e.g., Figure 1).



Figure S15: Adsorption energies of species relevant to ethanol oxidation under external electric fields. Shown is a comparison of adsorption energies in vacuum and with water present using Method 2.



Figure S16: Comparison of reaction energies for C-C bond breaking in vacuum and in the presence of water (Method 2) under an electric potential. Reactions involved: (1) $CH_3CH_2OH \rightarrow CH_3 + CH_2OH$; (2) $CH_3CH_2O \rightarrow CH_3 + CH_2O$; (3) $CH_2CH_2O \rightarrow CH_2$ $+ CH_2O$; (4) $CH_3CO \rightarrow CH_3 + CO$; (5) $CH_2CO \rightarrow CH_2 + CO$; (6) $CHCO \rightarrow CH + CO$.



Figure S17: Comparison of reaction energies for C-H bond breaking and C-O bond formation in vacuum and in the presence of water (Method 2) under an electric potential. Reactions involved: (1) CH₃CO \rightarrow CH₂CO + H; (2) CH₂CO \rightarrow CHCO + H; (3) CH₃CO + OH \rightarrow CH₃COOH.

11 Simulation Files

We have included input and output files for the simulations in our paper at the site: https://github.com/Deskins-group/Structure-Files/tree/master/Ethanol%200xidation%20-% 20Potential.

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