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Correction to Unraveling the role of base and catalyst polarization in alcohol oxidation on Au and Pt in water

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The authors regret that the above paper contains physically spurious data, undetected before publication. The present correction does not change the qualitative results of the original article, and the proposed role of chemisorbed OH⁻ species on the catalytic oxidation of alcohol on Au and Pt surfaces. The correction however changes the adsorption strength of OH⁻ and its coverage: Adsorption is thermodynamically stable only for a coverage below 1/16 ML. This however does not modify the role of OH⁻ to polarize the metal surface.

On January 30th, 2019, the developer of VASPsol announced an inconsistency between the electrostatic reference potential between the VASPsol module (i.e. the linear Poisson-Boltzmann model) and the standard VASP code, impacting how to obtain the physically meaningful energies based on the output. The solution of the linearized Poisson-Boltzmann equation provides a natural reference electrostatic potential by setting the potential to zero in the bulk of the electrolyte. However, plane-wave DFT codes, such as VASP, implicitly set the average electrostatic potential in the simulation cell to zero, not the potential in the electrolyte region. To keep the consistency of the reference potential between VASPsol and VASP, a shift in reference potential is needed to be added to the Kohn Sham eigenvalues and the Fermi level. The corresponding electronic energy correction is given by $\Delta E_{shift} = n_s^{tot} V_{shift}$, where n_s^{tot} is the net charge of the simulation cell and V_{shift} is the shift in reference potential, e.g., the shift to align the potential in the electrolyte region to zero. The problem hence only affects the energy of net charged electronic systems. This V_{shift} correction is in the range of 1.33-1.36eV on charged Au(111) and 1.31-1.34eV on Pt. As a consequence, this correction makes no difference in the surface chemistry described in the original communication. But when the step involves adsorption of charged species on a neutral surface, like the adsorption of OH⁻ in our study, this correction is not systematic anymore. The adsorption free energy of OH⁻ on

Au(111) surfaces on different sizes with different corrections is shown in Table A.

Table A. Adsorption free energies of OH⁻ on different sizes of Au(111) surfaces

$G_{ads}(OH^-)/eV$	p(3×3)	p(4×4)	p(5×5)
No ZPE and no ΔE_{shift}^*	-1.02	-1.26	-1.40
No ZPE and no ΔE_{shift}	-0.94	-1.18	-1.34
No ZPE but with ΔE_{shift}	+0.39	+0.14	-0.02
with ZPE and with ΔE_{shift}	+0.25	+0.01	-0.16

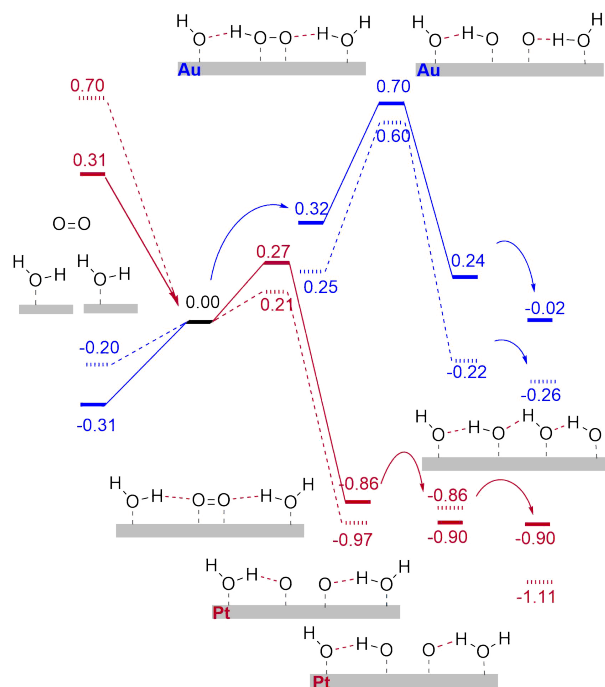
*It is noted that in the original paper, no frequency calculations were done for the adsorbed molecules, thus here the vibration entropy of adsorbates is approximated to the vibration entropy of molecules in solvent. This line is shown here to keep a consistency with the paper. In the other lines, considering the frequencies of all the species were calculated, including the adsorbed molecules and molecules in solution, we directly used the surface molecular entropy correction which is detailed in the last paragraph.

As is shown in Table A, the inclusion of the electronic energy correction ΔE_{shift} causes an increase on the adsorption energy of around 1.30 eV, which corresponds to the value of the electronic energy correction we mentioned before. Then, the adsorption of OH⁻ is not exergonic anymore on a p(3×3) cell. However, the adsorption of this anion is still feasible, but at a lower coverage. It becomes athermic for a coverage around 1/25ML if the ZPE is not included. The inclusion of the ZPE correction renders adsorption more favorable by 0.14 eV, then the adsorption of OH⁻ becomes favorable at a coverage of 1/16ML. Hence, in the following computation, the ZPE correction is taken into consideration to avoid the high CPU cost of a p(5×5) supercell and reach an improved Gibbs Free energy profile using a p(4×4) cell. The corrected schemes and tables appear below along with the accompanying caption. Also, the description of the schemes

and the table are needed to be changed in text according to the corresponding values.

Page 11717: Scheme 1.

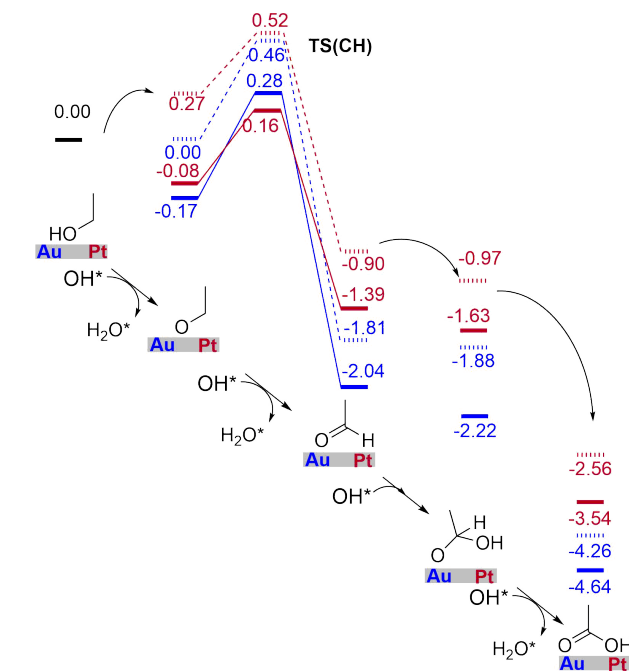
Scheme 1. O₂ activation in presence of water.



^aGibbs free energy profiles (in eV) at 25°C are shown on Au(111) (in blue) and on Pt(111) (in red) in absence (straight lines) and in presence (dashed lines) of a basic environment. All proton transfers are “barrier-less” (with the energy of transition states not higher than the reaction energy, or the barrier is lower than 0.05eV) and thus are indicated by a curved arrow. O₂ adsorption is shown with a straight arrow.

Page 11718: Scheme 2.

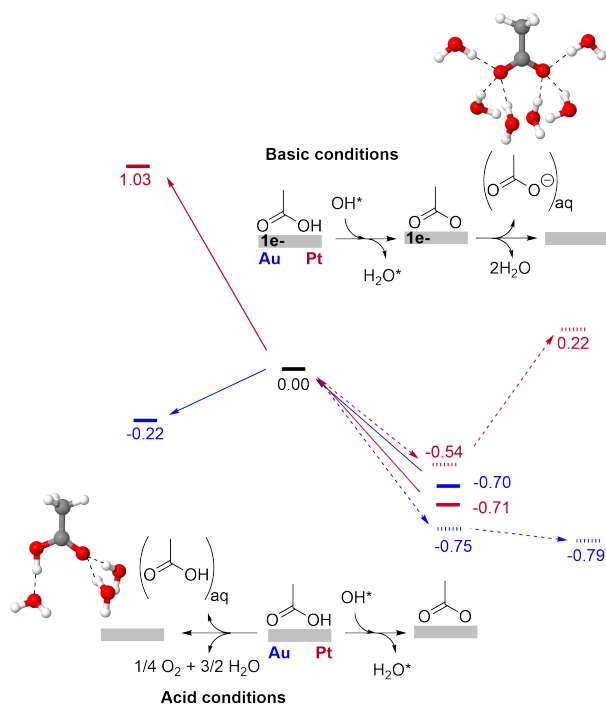
Scheme 2. Ethanol oxidation into carboxylic acid by OH*



^aGibbs free energy profile (in eV) at 25°C are shown on Au(111) (in blue) and Pt(111) (in red) in absence (straight lines) and in presence (dashed lines) of a basic environment. Most steps are barrier-less except the C-H bond breaking in the ethoxy inter-mediate.

Page 11719: Scheme 3.

Scheme 3. Competition between over-oxidation of acetic acid by OH* and desorption into the water solution.



³Gibbs free energy profile (in eV) at 25°C are shown in absence (straight line) and in presence (dashed line) of basic conditions, using CH₃COO* acid and OH* as a reference.

Page 11719: Table 1.

Table 1. Energetic Span (δG , eV), reaction Gibbs Free energy at 25°C (ΔG , eV) TOF-Determining intermediate (TD-Int) and TOF-Determining Transition State (TD-TS) in different conditions.

Conditions	Metal	δG	ΔG	TD-Int ^a	TD-TS ^b
Neutral	Au	1.58	-	CH ₃ COO*	TS(O-OH)
			4.47		
	Pt	1.74	-	CH ₃ COO*	Desorption
			4.47		
Basic	Au	0.97	-	solutes	TS(O-OH)
			4.92		
	Pt	0.78	-	CH ₃ COO*	Desorption
			4.92		

^aCH₃COO*: chemisorbed carboxylate; solutes = unadsorbed species in solution ^bTS(O-OH): O-O scission in the OOH fragment

Due to the change of surface cell size (from p3×3 to p4×4), there appears some changes in the energy profiles and energetic span above even when only surface reactions taken into consideration, but the main conclusion that alcohol oxidation works better in the basic environment than in the neutral environment has not been affected.

Page 11717, paragraph 1, line 3: the adsorption energy should be corrected to 0.01 eV.

Page 11717, paragraph 1, line 13: should be corrected as follows “Careful tests demonstrated that a p(4×4) surface should be used for the system of interest here.”

Page 11717, paragraph 3, line 7: the O-O distance should be 1.88 Å.

Page 11717, paragraph 3, line 12: the electron concentration should be changed to “one electron per 16 surface atoms”.

Page 11717, paragraph 3, line 17: the barrier range be changed to 0.6-0.7 eV.

Page 11717, paragraph 4, line 5: should be corrected as follows “On Au, this reaction is strongly endergonic (1.47 eV) and is associated with a larger barrier (1.77 eV).”

Page 11719, paragraph 2, line 7: the sentence “In the absence of any hydroxide anion, Au is much less active than Pt with an energetic span of 1.38 eV vs 1.28 eV.” should be corrected as follows “In the absence of any hydroxide anion, reactions are both difficult on Au and Pt.”

Page 11719, paragraph 3, line 7: It should be corrected as follows “Then, the cost of desorption is only 1.04 eV (see Figure S9 in the SI), instead of 1.74 eV on Pt under acidic conditions.”

The vibrational contribution to the Gibbs Free energy were fully taken into account using frequencies computed in the harmonic approximation for the molecules and the adsorbate. For linear molecules, there are in total 3N-5 normal modes, and for non-linear molecules the numbers of normal modes are in total 3N-6, where N represents the numbers of atoms in the molecule. A cut-off of 50 cm⁻¹ is used to limit the evaluation of vibrational entropy to large enough wavenumbers. For molecules on surface, the ZPE correction is only done on the molecular part with the surface atoms frozen. Similar to the molecules in solution, the vibrational entropy of an adsorbate like OH*_e is given by:

$$S_{aq(vib)}(OH*_e) \approx 0.54 \times S_{gas(vib)}(OH*_e)$$

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