Surface Reaction Barriometry: Methane Dissociation on Flat and Stepped Transition-Metal Surfaces (Correction)

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Addition/Correction

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Correction to "Surface Reaction Barriometry: Methane Dissociation on Flat and Stepped Transition-Metal Surfaces"

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Two different projector augmented wave (PAW) pseudopotentials issued with VASP[1−5] were used for the calculations presented in the Letter for the Pt(211) slab. An older version (here named for simplicity paw2001) was used to relax the slab in its 0 K geometry, and a newer version (named paw2005) was used in all the other calculations (including the determination of the transition state, the AIMD simulations, and also all the calculations on Pt(111)). Despite the similarity between the two (i.e., both treat explicitly 10 valence electrons) the paw2001 gives a slightly more expanded Pt(211) slab compared to the one obtained using paw2005. As a result the barrier height for Pt(211) reported in the Letter is not correct. Computing the barrier using paw2005 on the slab relaxed using the same pseudopotential gives the correct value of 53.9 kJ/mol, which is 1.3 kJ/mol larger than that reported in the Letter (i.e., 52.6 kJ/mol). The interlayer distances of the relaxed 0 K slab computed with the two different pseudopotentials and the transition state geometry details are reported in Table 1.

This problem does not affect the AIMD calculations as the 10 slabs used as initial conditions for the surface in the dynamics have been relaxed for at least 1 ps using paw2005 (which is the same pseudopotential used to carry out the AIMD trajectories). To prove that the paw2001 slabs are fully equilibrated to the paw2005 geometry, we relaxed another 10 different slabs starting from the paw2005 relaxed geometry. Comparing the results of the equilibration of 10 different slabs using paw2005 but starting from either the paw2001 or the paw2005 relaxed geometry, we find that the first two interlayer distances and the angle between the normal to the (111)-like terrace and z are the same within 0.003 Å and 0.1°, respectively. The results, averaged over 1000 time steps for 10 equilibrations for each setup, are reported in Table 2 together with their associated standard error (computed as $\sigma/\sqrt{N}$, where σ is the standard deviation and N is the sample size). The error bars on the differences are propagated from the data.

A few of the results reported in the Supporting Information depend on the relaxed geometry of the slab and therefore need to be updated. Here below we comment on these results and report the minor differences obtained using the correct 0 K relaxed slab geometry.

In order to double check the validity of our convergence test reported in Table S5 of the Supporting Information, we recomputed the barrier for the fully converged setup used as a reference using the correctly relaxed slab. The fully converged setup used has 5 layers and a 4-atom wide terrace and includes 2 steps. The energy is computed using 500 eV of cutoff and a 8 × 8 × 1 K-point grid. The setup used in the AIMD calculations returns the same minimum barrier height of the fully converged setup within 1.1 kJ/mol.

The results reported in Table S6 have been recomputed on the slab equilibrated with the correct pseudopotentials and are reported here in Table 3. The barrier computed with 13 Å of vacuum and corrected by the residual energy (see original Letter for definition) differs only by 1.0 kJ/mol from the barrier computed with a converged 30 Å vacuum size.

The largest adsorption energy reported in Table S7 of the Supporting Information has also changed. The correct numbers are reported here in Table 4. Note that we take the occasion to correct also the results for Pt(111), which have been incorrectly reported.

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Table 1. First and the Second Interlayer Distances Reported for the Slab Optimized with the Two Pseudopotentials[a]

PAW used for slab relaxation	first interlayer distance (Å)	second interlayer distance (Å)	(111) terrace angle (deg)	E_b (kJ/mol)	r_b (Å)	Z_b (Å)	θ_{CH} (deg)
paw2001	2.4980	2.4541	15.97	52.6	1.53	2.27	133
paw2005	2.4867	2.4411	15.82	53.9	1.53	2.27	133
difference	−0.0113	−0.0130	−0.015	1.3	0.00	0	0

[a]The TS geometrical properties (calculated always with paw2005) on the two differently optimized slabs are reported including the activation barrier, E_b; dissociative bond length, r_b,; distance from the carbon atom to the surface, Z_b; and angle between the dissociating bond and the surface normal, θ_{CH}. The last line reports the differences between the quantities reported in the columns.

Table 2. Data in Reference to the Slabs Equilibrated Using paw2005 Starting from the Geometry Relaxed with Either paw2001 or paw2005[a]

PAW used for slab relaxation	PAW for slab equilibration	first interlayer distance (Å)	second interlayer distance (Å)	(111) terrace angle (deg)
paw2001	paw2005	2.5285 ± 0.0005	2.4723 ± 0.0004	15.61 ± 0.01
paw2005	paw2005	2.5263 ± 0.0003	2.4695 ± 0.0003	15.50 ± 0.01
difference		−0.0022 ± 0.0006	−0.0028 ± 0.0005	−0.11 ± 0.01

[a]The results are reported as averages over 1000 time steps and 10 surfaces. The quantities are reported together with the standard error. The last line reports the differences between the quantities reported in the columns.

Table 3. Data Reported in Table S6 of the Supporting Information Recomputed with the Correct Slab Geometry[a]

	Pt(211)
$E_b^{13Å}$ (kJ/mol)	56.1 (54.6)
$E_b^{30Å}$ (kJ/mol)	52.9 (51.4)
E_R (kJ/mol)	2.1 (2.0)
E_b^e (kJ/mol)	53.9 (52.6)
$E_b^e - E_b^{30Å}$ (kJ/mol)	1.0 (1.2)

[a]Previous results are in brackets.

Table 4. Data Reported in Table S7 of the Supporting Information Recomputed with the Correct Slab Geometry[a]

system	largest E_{ads}^c (kJ/mol)	Z_C (Å)
Pt(111)	21.8 (21.9)	3.527 (3.648)
Pt(211)	24.9 (24.8)	2.733 (3.380)

[a]Previous results are in brackets.

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