Supporting information to

# Elucidation of temperature-programmed desorption of high-coverage hydrogen on Pt(211), Pt(221), Pt(533) and Pt(553) based on Density Functional Theory calculations

Manuel J. Kolb<sup>1,2</sup>, Anna L. Garden<sup>3,4</sup>, Cansin Badan<sup>1</sup>, José A. Garrido Torres<sup>5</sup>, Egill Skulason<sup>3</sup>, Ludo B.F. Juurlink<sup>1</sup>, Hannes Jonsson<sup>3</sup> and Marc T. M. Koper<sup>1</sup> <sup>1</sup>Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands <sup>2</sup>Current address: SLAC National Accelerator Laboratory, 2575 Sand Hill Rd, Menlo Park, CA 94025, USA and University Stockholm, Alba Nova, Roslagstullsbacken 21, 114 21 Stockholm, Sweden <sup>3</sup>University of Iceland, Reykjavik, Iceland <sup>4</sup>University of Otago, P.O. Box 56, Dunedin 9054, New Zealand <sup>5</sup>Stanford University, Department of Chemical Engineering, Stanford, California 94305, USA & SUNCAT Center for Interface Science and Catalysis, Stanford Linear Accelerator Center, Menlo Park, California 94025, US (Dated: April 14, 2019)

## Model Surfaces used in this study

The following 4 figures show the four model surfaces that were studied in the shape as presented in figure 1, as well as a space-filling representation.



Figure 1: Left image: Surface model of the Pt(211) surface, as in figure 1 of the main paper. Surface platinum atoms are marked in silver, first sub-surface layer platinum atoms are represented in blue, while the atoms in the second subsurface layer are shown in red. Golden lines indicate the Pt-Pt connectors in the surface plane, while the purple lines indicate the Pt-Pt connectors in the step plane. Right image: Space-filling model of the stepped Pt(211) surface, with area described by the left image marked in red.



Figure 2: Left image: Surface model of the Pt(221) surface, as in figure 1 of the main paper. Surface platinum atoms are marked in silver, first sub-surface layer platinum atoms are represented in blue, while the atoms in the second subsurface layer are shown in red. Golden lines indicate the Pt-Pt connectors in the surface plane, while the purple lines indicate the Pt-Pt connectors in the step plane. Right image: Space-filling model of the stepped Pt(221) surface, with area described by the left image marked in red.



Figure 3: Left image: Surface model of the Pt(533) surface, as in figure 1 of the main paper. Surface platinum atoms are marked in silver, first subsurface layer platinum atoms are represented in blue, while the atoms in the second subsurface layer are shown in red. Golden lines indicate the Pt-Pt connectors in the surface plane, while the purple lines indicate the Pt-Pt connectors in the step plane. Right image: Space-filling model of the stepped Pt(533) surface with the same surface area shown as in the left image.



Figure 4: Left image: Surface model of the Pt(553) surface, as in figure 1 of the main paper. Surface platinum atoms are marked in silver, first subsurface layer platinum atoms are represented in blue, while the atoms in the second subsurface layer are shown in red. Golden lines indicate the Pt-Pt connectors in the surface plane, while the purple lines indicate the Pt-Pt connectors in the step plane. Right image: Space-filling model of the stepped Pt(553) surface with the same surface area shown as in the left image.

## **NEB pathways for Pt(533)**

In the following we will discuss the desorption pathways for hydrogen from the Pt(533) facet.

## 2 Hydrogen atoms per double surface unit cell

### <u>B1-B1</u>



Figure S5: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(533) at a coverage of 2 H atoms per double surface unit cell

Figure S1 shows the pathway for hydrogen desorption from two B1 sites from the Pt(533) step edge. The two hydrogen atoms approach each other with the Pt atom in the middle and then for the  $H_2$  bond. The Pt atom itself is pulled out of the step-edge plane during this reaction. We assume this is due to the temporarily increased bonding to the Pt, which then weakens the bonds with the surface.

### 4 Hydrogen atoms per double surface unit cell

### <u>B1-B1</u>



Figure S6: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(533) at a coverage of 4 H atoms per double surface unit cell

### <u>OT4-OT4</u>



Figure S7: Selected images along the NEB pathway and Energies for 2 hydrogen atoms desorbing from the OT4 and OT4 sites on Pt(533) at a coverage of 4 H atoms per double surface unit cell

Figure S3 shows the desorption pathway for 2 hydrogen atoms from the OT4 and OT4 sites on Pt(533). This pathway was not obtainable by the standard NEB method implemented by Henkelman et al. Instead, reaction barriers were determined with the machine learning surrogate model proposed by Torres et al [1] using the "one image evaluated" (OIE) method and Gaussian Process Regression (GPR) as introduced by Jonsson and coworkers [REF]. The reaction pathways for each NEB are described with 21 images. The forces on all the relaxed atoms for the initial and final end-points of the NEB were required to be smaller than 0.03 eV/Å. The uncertainty convergence criteria for the predicted NEB on the GPR model was set to 0.05 eV and the forces convergence threshold for the climbing image was set to 0.05 eV/Å.

The calculation shown here is performed with a newer version of VASP, a different pseudopotential for hydrogen as well as the algorithm for the calculation of forces as implemented in ASE rather than the native VASP algorithm. All this will mean that there are minor differences expected for the total energies and adsorption energies along the pathway. However, the reaction pathway presented here and its overall barrier will still be qualitatively significant, as in that the barrier is over 1eV higher than all other barriers that were observed. The pathway obtained is one of the most complicated hydrogen desorption pathways that we are aware of, which is also reflected in the very high barrier of over 1.3eV. The pathway consists of two main components: The OT4-bound hydrogen atoms move up the step edge and then meet to form the H2-bond. However, to enable this movement, one of the B1-bound hydrogen atoms is required to move the an HCP1 site behind the step edge, which we assume to be a large contribution to the high observed barrier. Figure S4 is an animation of the desorption pathway, which we added in order to clarify the process.



Figure S8: NEB Pathway as animation for added clarity (available in the ESI)

### 6 Hydrogen atoms per double surface unit cell

<u>B1-B1</u>



Figure S9: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(533) at a coverage of 6 H atoms per double surface unit cell

Figure S5 shows the desorption pathway from two B1 sites at a coverage of 6 hydrogen atoms per double unit cell. The reaction pathway is visually and energetically very similar to the ones observed for 2 and 4 adsorbed hydrogen atoms per double unit cell.

### FCC1-FCC1



Figure S10: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the FCC1 and FCC1 sites on Pt(533) at a coverage of 6 H atoms per double surface unit cell

Figure S6 shows the desorption pathway from two hydrogen atoms bound to the terrace FCC1 FCC1 sites. The desorption pathway is conceptually very similar to the B1-B1 mechanism, with two hydrogen atoms approaching each other with a Pt atom in between. We assume the Pt-Pt bonding in the surface plane to be stronger, which in turn causes a slightly elevated barrier compared to the step-edge-related mechanism.

### 8 Hydrogen atoms per double surface unit cell

### <u>B1-B1</u>



Figure S11: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(533) at a coverage of 8 H atoms per double surface unit cell

Figure S7 shows the desorption pathway for the combination of two B1 sites from Pt(533) at a coverage of 8 hydrogen atoms per double surface unit cell. The reaction pathway is again very similar to the other pathways observed for B1-B1 combinations at other coverages.

### FCC2-FCC2



Figure S12: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the FCC2 and FCC2 sites on Pt(533) at a coverage of 8 H atoms per double surface unit cell

Figure S8 shows the desorption pathway for two hydrogen atoms desorbing from the terrace on Pt(533) at a coverage of 8 hydrogen atoms per double surface unit cell. The pathway is

visually and energetically very similar to the ones observed at a coverage of 6 hydrogen atoms per double unit cell.

# NEB pathways for Pt(553)

## 2 Hydrogen atoms per double surface unit cell

<u>B1-B1</u>



Figure S13: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(553) at a coverage of 2 H atoms per double surface unit cell

Figure S9 shows the desorption pathway of 2 hydrogen atoms from the step edge B1 sites on Pt(553). Note the slightly asymmetric behaviour at the beginning of the pathway, which also leads to the small plateau in the reaction pathway energy diagram.

## 4 Hydrogen atoms per double surface unit cell

<u>B1-B1</u>



Figure S14: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(553) at a coverage of 4 H atoms per double surface unit cell

Figure S10 shows the desorption pathway for 2 step-bound hydrogen atoms at a coverage of 4 hydrogen atoms per double unit cell. The resulting pathway is virtually identical to the one for

the lower coverage shown in figure S9, due to the negligible interaction between the FCC3 and the B1 sites.

### FCC3-FCC3



Figure S15: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the FCC3 and FCC3 sites on Pt(553) at a coverage of 4 H atoms per double surface unit cell

Figure S11 shows the desorption pathway for the terrace-bound hydrogen atoms in the FCC3 sites. The pathway is qualitatively very similar to the terrace-bound hydrogen atoms on Pt(533).

### 6 Hydrogen atoms per double surface unit cell

### <u>B1-B1</u>



Figure S16: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(553) at a coverage of 6 H atoms per double surface unit cell

Figure S12 shows the desorption pathway for two step-bound hydrogen atoms in the B1 sites at a coverage of 6H per double unit cell. The pathway again is almost identical to the one observed for the B1-B1 combination at lower coverages.

### FCC2-FCC2



Figure S17: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the FCC2 and FCC2 sites on Pt(553) at a coverage of 6 H atoms per double surface unit cell

Figure S13 shows the reaction pathway for the desorption of two FCC2-bound hydrogen atoms at a coverage of 6 hydrogen atoms per double unit cell. The pathway shows a similar behavior as the one observed for the FCC3 sites.

### 8 Hydrogen atoms per double surface unit cell

#### <u>B1-B1</u>



Figure S18: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the B1 and B1 sites on Pt(553) at a coverage of 8 H atoms per double surface unit cell

Figure S14 shows the reaction pathway for the desorption of two step-bound hydrogen atoms at a coverage of 8 hydrogen per double unit cell. We, again, observe a very similar behaviour as for the pathways at lower coverages.

### FCC4-FCC4



FigureS 19: NEB Pathway and Energies for 2 hydrogen atoms desorbing from the FCC4 and FCC4 sites on Pt(553) at a coverage of 8 H atoms per double surface unit cell

Lastly, Figure S15 shows the desorption pathway for two hydrogen atoms from the terrace FCC4 sites. The pathway, again, shows a very similar behaviour as for the other two terrace sites at lower coverages.

## References

[1] Low-Scaling Algorithm for Nudged Elastic Band Calculations Using a Surrogate Machine Learning Model, José A. Garrido Torres, Paul C. Jennings, Martin H. Hansen, Jacob R. Boes, Thomas Bligaard; arXiv:1811.08022