Supplementary Information for "On the Mechanism of High Product Selectivity for HCOOH using Pb in CO_2 Electroreduction"

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Supplementary Note:

Correction terms (zero-point energy, enthalpic temperature, entropy corrections) for adsorbates were calculated using the harmonic oscillator approximation with all degrees of freedoms displaced within 0.01 Å and temperature set to 298.15 K. Those values were taken from our previous publications and were used to convert electronic energies into free energies.[1, 2] For free molecules (CO_2, H_2, H_2O, and HCOOH), electronic energies were calculated in the 10 × 10 × 10 $Å^3$ box, and then converted into free energies with their fugacity set to 101325 Pa, 101325 Pa, 3534 Pa and 2.0 Pa, respectively. The fugacity for liquid water and formic acid corresponds to the vapor pressure of water and activity of 0.01, respectively.[3] As the gas-phase thermochemical energies calculated by RPBE are known to be somewhat inconsistent with experimental values, +0.45 eV corrections were added for –OCO– containing molecules (HCOOH and CO_2).[3] For *COOH adsorbates, an approximate solvation correction was applied, where G(*COOH) is assumed to be stabilized by 0.25 eV due to an existence of water layer. We note that these corrections yielded results that are in good agreements with experiment or previous theoretical calculations.[1, 2]

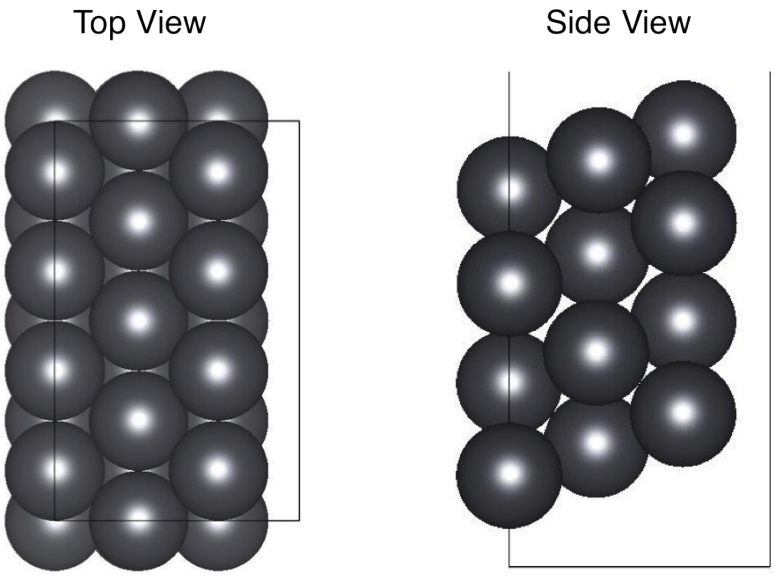

Figure S.1. Top view and side view of (3×4) surface unit cell of Pb (211).

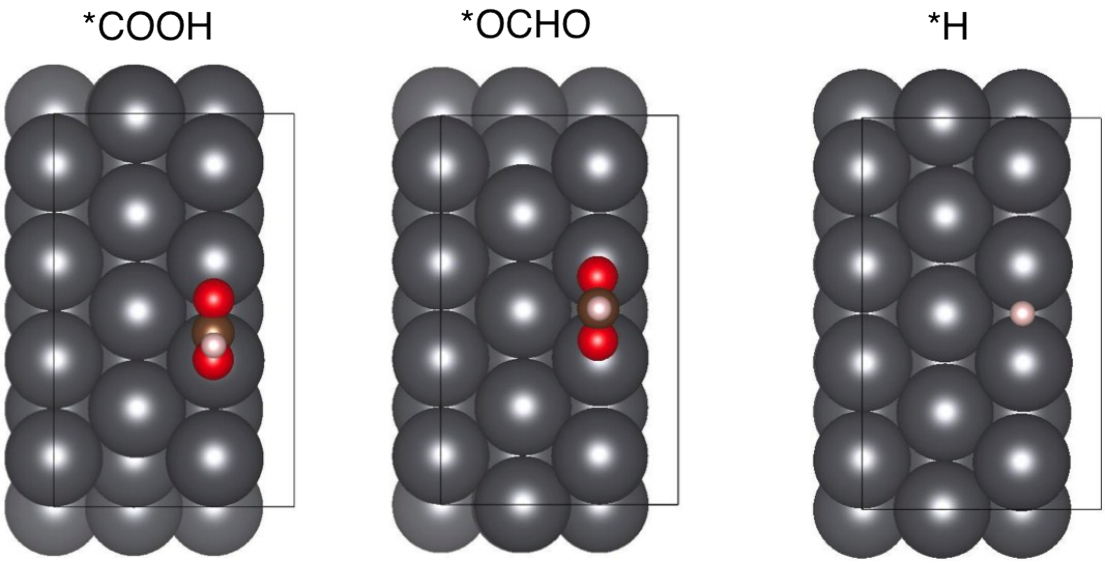

Figure S.2. Top views of optimized geometries for various adsorbates.

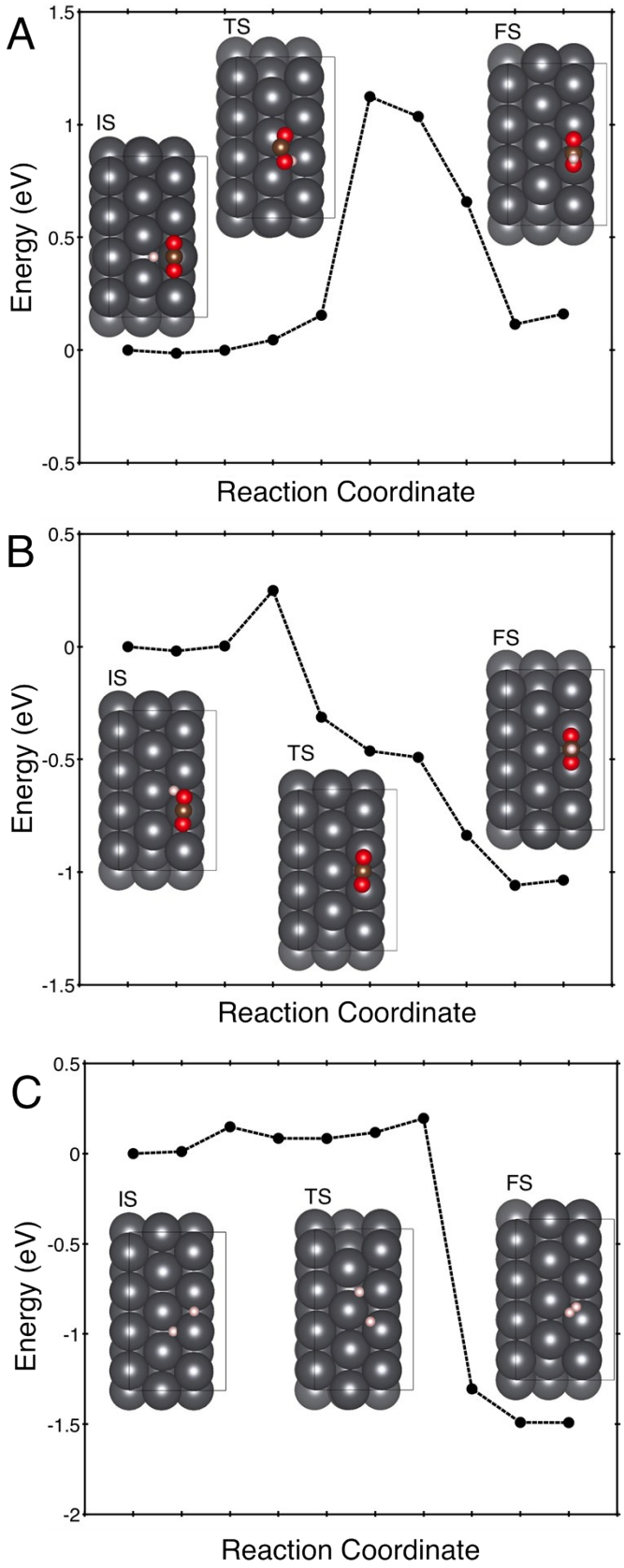

Figure S.2. The NEB results of activation barriers for the coupling of *H (A) with CO_2 to produce *COOH, (B) with CO_2 to produce *OCHO and (C) with *H to produce H_2.

References

1. S. Back, M. S. Yeom and Y. Jung, *ACS Catal.*, 2015, **5**, 5089-5096.
2. S. Back, H. Kim and Y. Jung, *ACS Catal.*, 2015, **5**, 965-971.
3. A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy Environ. Sci.*, 2010, **3**, 1311-1315.