Supporting Information:

Dynamics of Subnanometer Pt Clusters Can Break the Scaling Relationships in Catalysis

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Supporting Information

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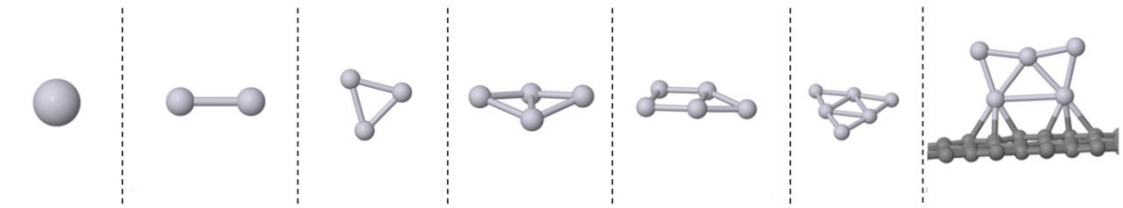

Figure S1. PBE global minima for adsorbate-free gas phase and graphene-deposited Pt_n clusters.

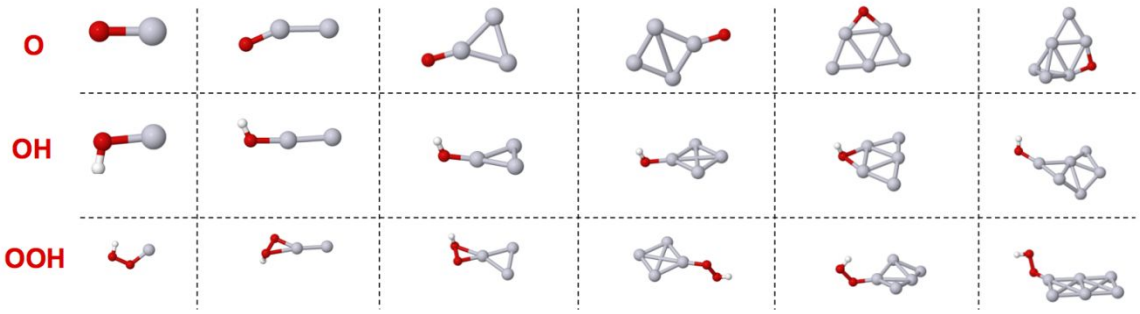

Figure S2. PBE global minima for gas phase Pt_n clusters with one bound adsorbate.

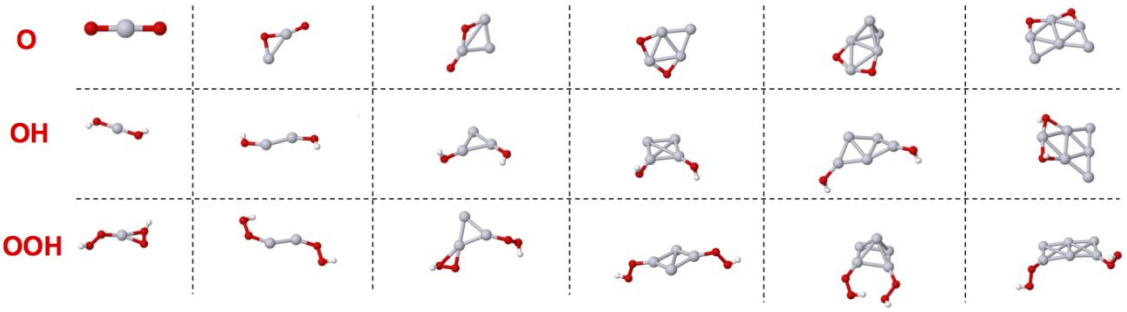

Figure S3. PBE global minima for gas phase Pt_n clusters with two bound adsorbates.

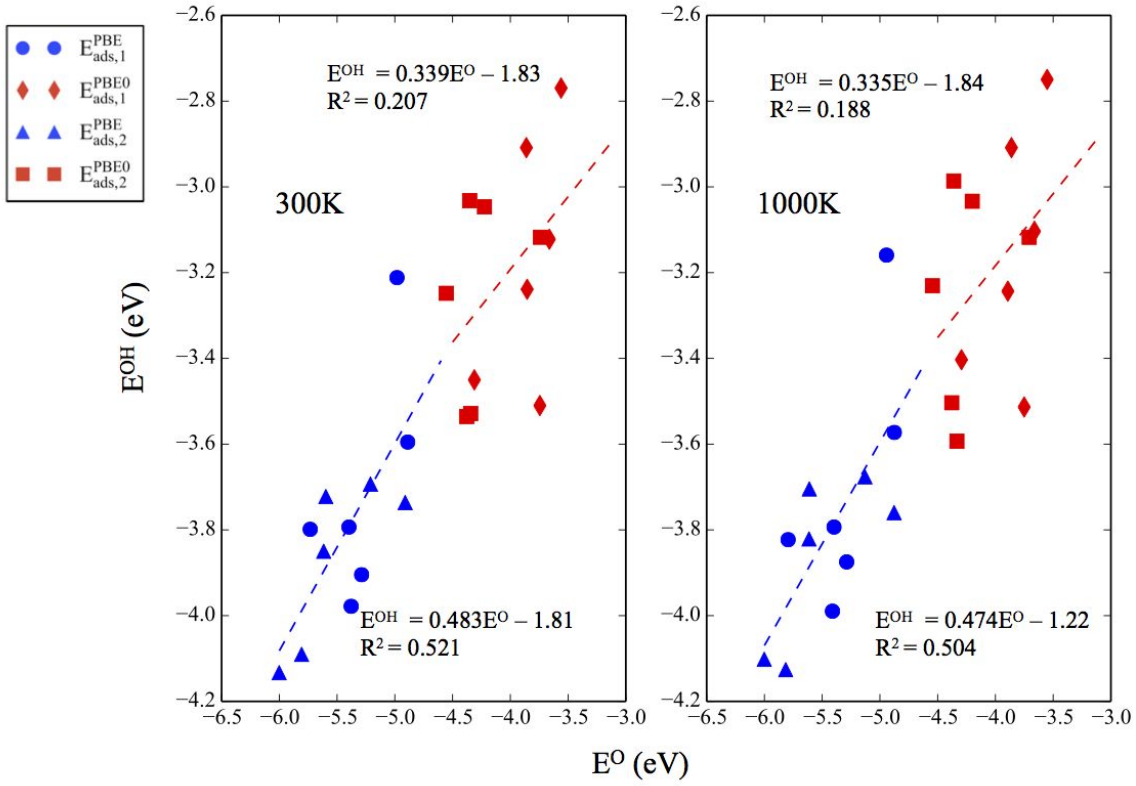

Figure S4. Correlations between the ensemble-average binding energies of O and OH on the gas phase Pt_n clusters at 300 K and 1000 K.

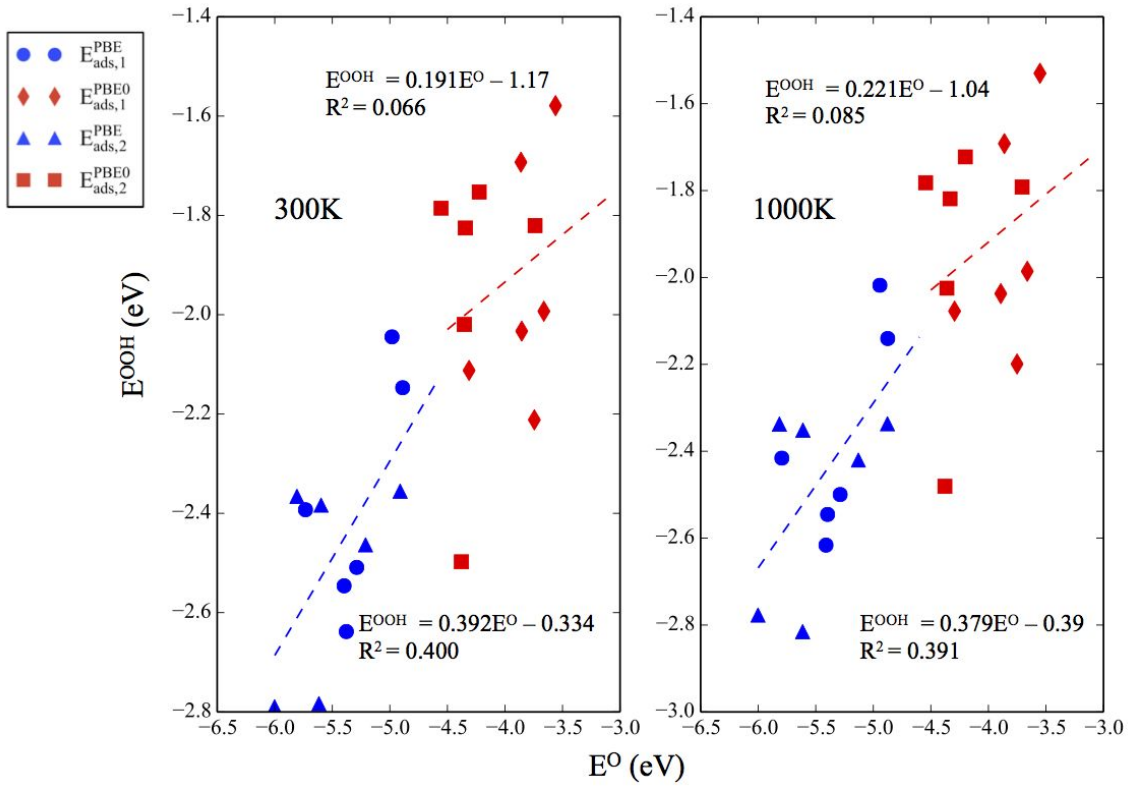

Figure S5. Correlations between the ensemble-average binding energies of O and OOH on the gas phase Pt_n clusters at 300 K and 1000 K.

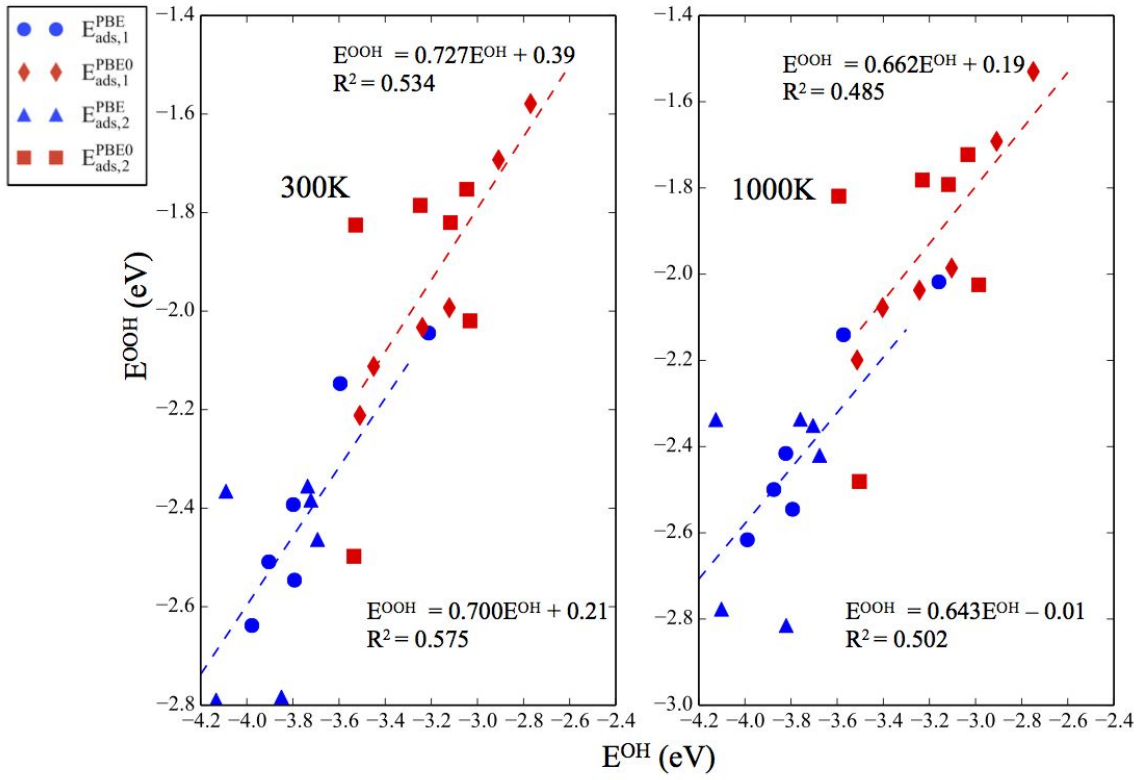

Figure S6. Correlations between the ensemble-average binding energies of OH and OOH on the gas phase Pt_n clusters at 300 K and 1000 K.

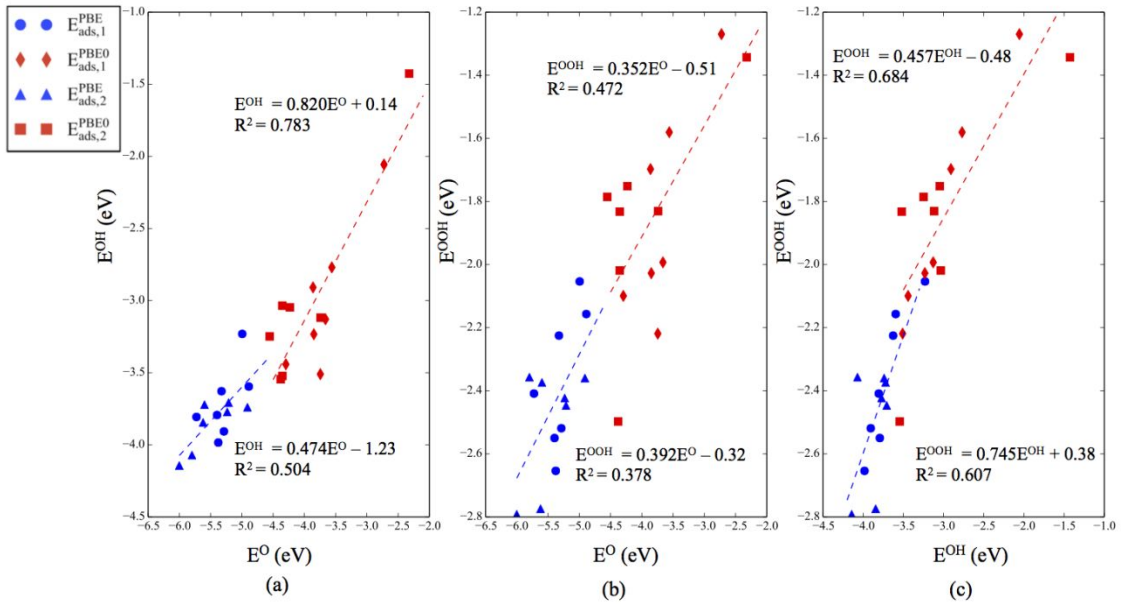

Figure S7. Scaling relations combining the results for the gas phase and surface-deposited clusters: (a) OH vs. O, (b) OOH vs. O, (c) OOH vs. OH.

The effect of exchange-correlation functional

The effect of exchange-correlation functional can be important in determining the global minimum structure of metal clusters. It is clear from Figures 4, S1-S3 that PBE0 gives different global minimum geometries from the ones obtained from PBE. For example, PBE calculations predict Pt_4 cluster to be almost flat in Pt_4OH and Pt_4OOH. On the other hand, PBE0 predicts Pt_4 to have a 3D geometry and to be more globular. Other clusters whose geometry is functional dependent include $Pt_5(OH)$, $Pt_6(OH)$, $Pt_5(OOH)$, $Pt_6(OOH)$, $Pt_5(OH)_2$, and $Pt_6(OOH)_2$. One should also pay attention to the fact that the binding site can also change by changing the functional, although it is not as sensitive as the geometry. $Pt_5(OH)$ can be used as an example in which OH prefers bridge and atop site according to PBE and PBE0 respectively. This is fully unexpected since the geometry, and, therefore, binding site preference changes.

All in all, although one should be cautious when choosing the functional in DFT calculations, we should emphasize that the final message is independent of the choice of functional in this case.

Bond Length Distribution Algorithm (BLDA) and Birmingham Parallel Genetic Algorithm (BPGA)

Initial structures for the global optimization should be created in such a way that they are less prone to suffer from a Self-Consistent Field (SCF) convergence problem. Furthermore, by generating initial structures wisely, the computational cost to search in a chemically unfavorable configuration space can be significantly reduced. Briefly speaking, one way to do so is by restricting the distance of atoms to their closest and second closest atoms to follow a normal distribution. This means that both distances are fitted to normal distribution and the initial structures are generated based on that. This generation algorithm based on the statistical restriction is called Bond Length Distribution Algorithm (BLDA).

On the other hand, BPGA employs a pool methodology to evaluate structures in parallel rather than generating a large number of structures. A few number of random structures are generated initially and relaxed in order to form a population. Then the

crossover and mutation operations of the genetic algorithm begin for each instance. The new structures, which are called offspring structures, are produced through weighted crossover according. Mutated clusters are either obtained by displacing some of the atoms randomly or swapping different types of atoms in alloy clusters. These newly generated structures are minimized thereafter to compare with existing structures in the pool to update the pool.