Supplementary Information for

Unveiling the Active Structure of Single Nickel Atom Catalysis: Critical Roles of Charge Capacity and Hydrogen Bonding

Xunhua Zhao, Yuanyue Liu*

Texas Materials Institute and Department of Mechanical Engineering

The University of Texas at Austin, Austin, TX, 78712

*yuanyue.liu@austin.utexas.edu

1. Computation details



Figure S1 Full-size view of the supercell used in our molecular simulations: an example of *COO adsorption at 1N site. The Ni, N and the species directly involved in the reaction are shown by balls (Ni: green; C: black; O: red; H: cyan). Hydrogen bonds are represented by dashed thin lines.

The supercell (Figure S1) is constructed from (6×6) unit cells of graphene, in which we remove one or two C atom(s) to create a mono- or di-vacancy to anchor the single nickel atom. The configuration of Ni at double vacancy is further diversified by replacing 1-4 coordinated carbon atom(s) with nitrogen. In our MD simulations, we put 72 H₂O molecules which is about the number of H₂O in 6 layers of ice on the surface. The supercell dimensions are 14.802 Å, 14.802 Å and 25 Å (surface norm direction). Nose-Hoover thermostat¹ is used to keep temperature (statistically) constant at 300 K. We started from random H₂O structure and run force-field MD using LAMMPS² for 1 nanosecond and then run AIMD for 10 pic-second to get represent the water environment around the catalytic site. Net charge is introduced into the system to include the charge effects.

Our workhorse is the plane-wave-based code Vienna Ab initio Simulation Package (VASP)^{3,4} where multiple constrained molecular dynamics are implemented. Perdew-Burke-Ernzerhof (PBE) functional⁵ together with D3 van der Waals correction⁶ are employed in most of the calculations while we compare PBE with also other functionals including Bayesian error estimation functional (BEEF),⁷ SCAN meta-GGA functional⁸ and HSE06 hybrid functional^{9,10} implemented in FHI-aims code,^{11,12} in order to check the functional dependence of the CO binding energy(see also Section 2 bout functional dependence of CO adsorption). The cutoff energy of the plane-wave basis is 400 eV in the relaxation while 300 eV is used in the MD simulations. $3\times3\times1$ Gamma-centered k-mesh is used in relaxation and MD simulations. Time step in MD is set to be 0.5 femtosecond.

To determine the surface charge for a given electrode potential, we use the VASPsol.^{13,14}, which adds implicit aqueous electrolyte into the system. We add different numbers of extra electrons (n_{extra_e}) and calculate the corresponding absolute Fermi levels (E_F) with respect to the electrostatic potential in the region far from graphene and explicit water molecules. The atomic positions are fully relaxed for each time of adding electrons. By interpolating the $n_{\text{extra}_e} - E_F$ relation, we obtain the n_{extra_e} for the target E_F (converted from the electrode potential).

In order to evaluate the kinetic barriers, we employed a constrained MD method, the "slow-growth" approach^{19,20} to obtain the free-energy profile. In this method, the value of the reaction coordinate (namely ξ) is linearly changed from the characteristic value for the initial state (IS) to that for the final state (FS) with a velocity of transformation $\dot{\xi}$. The resulting work needed to perform a transformation from IS to FS can be computed as:

$$w_{\mathrm{IS}\to\mathrm{FS}} = \int_{\xi(\mathrm{IS})}^{\xi(\mathrm{FS})} (\frac{\partial F}{\partial \xi}) \cdot \dot{\xi} \mathrm{d}t,$$

where *F* is the free energy calculated at general coordinate *q* which is evolving with *t*, $\frac{\partial F}{\partial \xi}$ is calculated along the track of a constrained MD through the SHAKE algorithm.¹⁵ In the limit of infinitesimally small $\partial \xi$, the work $w_{IS \to FS}$ corresponds to the free-energy difference between the final and initial state. For *COOH formation step, the reaction coordinate is chosen to be a collective variable (CV) shown in Figure S1(a) while for (*)CO formation step, CV is shown in Figure S2(b). Note that *d*1 in S2(a) is used in the CV to simulate the departure of the OH⁻ from the *COOH after which *COOH will be ready for the next step, while *d*1 in S2(b) is chosen to allow the product OH⁻ to form H₃O₂⁻ with the neighboring H₂O molecule. In practice, a $\partial \xi$ value of 0.0008 Å is used for each MD step after testing shorter step size for the "slow-growth" along the reaction coordinate. The "slow-growth" approach is available in the VASP code and we have home-made codes/scripts to post-process the output data. An example of the raw output data from VASP and the free energy profile obtained through integration are demonstrated in Figure S2(c).



Figure S2 Illustration of collective variable used as reaction coordinate in the "slow-growth" approach, for the reaction of (a) *COOH formation and (b) *CO formation. (c) shows the raw data from VASP $\left(\frac{\delta_F}{\delta_{\xi}}\right)$ and the free energy profile along the reaction coordinate for (b).

2. Functional dependence of CO adsorption



Figure S3 Functional dependence of CO adsorption energy, defined as difference in total energies $E_{\text{total}} - E_{\text{substrate}} - E_{\text{CO}}$, calculated for both neutral and charged sites.

We noticed also that the binding energy of CO on transition metal is a long-lasting challenging problem for DFT functionals,¹⁶ and conventionally used functionals such as PBE overestimates the binding energy. The comparison of functionals regarding CO adsorption on Ni is given in Figure S3. As shown in Figure S3, compared to BEEF-vdW and HSE06+D3, PBE+D3 overestimate the binding energy, while meta-GGA functional SCAN shows the largest deviation from other functionals. Since BEEF-vdW gives values close to hybrid functional HSE06+D3 and it has shown good agreement with experiments in predicting CO adsorption on transition metals.¹⁷ Therefore, we conduct the "slow-growth" MD with BEEF functional for CO desorption, with corresponding net electronic charges in the system.

3. Charge capacity comparison for other transition metal sites

Table S1. Charges (e⁻) carried by the M-xN (M=Fe, Co, Ni, Cu; x=0,1,2,3,4) sites with COOH, at potential $U_{\text{RHE}} = -0.65$ V.

M-xN	0N	1N	2N	3N	4N
Fe	1.89	1.97	1.93	1.64	1.12
Co	2.04	1.89	1.97	1.24	0.59
Ni	2.11	1.91	1.29	0.64	0.77
Cu	2.04	1.36	1.23	1.05	1.15

4. Density of states comparison

Both the work function and the density of states (DOS) can affect the charge capacity. Following the reviewer's suggestion, we have calculated the DOS for several systems as shown in Figure S4. In principle, within the rigid band approximation, the charge capacity can be understood as:

$$C(E_{\mathrm{F},\mathrm{f}}) = \int_{E_{\mathrm{F},\mathrm{n}}}^{E_{\mathrm{F},\mathrm{f}}} D(E) dE$$

where D(E) is the DOS at energy E, $E_{F,n}$ is the Fermi level at charge-neutral state (which is related with work function), and $E_{F,f}$ is the final Fermi level that the system is charged to (determined by the electrode potential). Therefore, a lower $E_{F,n}$ (i.e. higher work function), and/or a higher D(E), would result in a higher charge capacity when the $E_{F,f}$ is fixed. When comparing the D(E) across the energy range from $E_{F,n}$ to $E_{F,f}$ shown in Figure S4, it is not clear which site has a higher/lower value; while the single-value $E_{F,n}$ shows a better correlation with the C($E_{F,n}$). Therefore, we think that in these cases, the work function is a more effective descriptor.

Figure S4. Density of states of neutral and charged sites with *COOH adsorption. Vacuum is set to be the energy-zero level. The vertical dashed line labels the Fermi level.



5. Adsorption energy of CO₂ with/without H₂O molecules, and with/without charge

Table S2. Adsorption energies of CO_2 on 1N and 4N sites with/without surface charge and water molecules. The structures for 1N cases are shown below.

E_{ad} (eV) between CO ₂ and substrate									
	witho	ut H ₂ O	with 4H ₂ O						
site	neutral	charge=1e ⁻	neutral	charge=1e ⁻					
1N	-0.11	-0.10	-0.24	-0.55					
4N	-0.10	-0.10	-0.13	-0.27					
Structure (1N)	3.2Å	3.1Å	3.2Å	2.0Å					

6. The effects of water molecules on the charge capacity

As shown in Table S3, it is found that the water molecules increase the charge capacity of the catalyst, especially when the reaction intermediates are adsorbed on the catalyst, suggesting a synergic effect of charges and water molecules for the catalysis.

Table S3. Charge capacity of (Ni-)1N site w/ and w/o water molecules and reaction intermediates, under potential $U_{\text{RHE}} = -0.65$ V. Note that 1N-COO coordinates are adopted from charged 1N-COO+4H2O, otherwise the CO2 cannot be chemisorbed on Ni

Surface charge (e ⁻) at $U_{\rm RHE} = -0.65 \text{ V}$								
configuration	charge	configuration	charge	configuration	charge			
*	1.23	*COO	1.72	*СООН	1.76			
*+ 4H ₂ O	1.30	*COO+4H ₂ O	2.20	*COOH+4H ₂ O	1.96			

References

1. Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Phys Rev A* **31**, 1695–1697 (1985).

2. Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J Comput Phys* **117**, 1–19 (1995).

3. Kresse, G. & Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comp Mater Sci* **6**, 15–50 (1996).

4. Kresse, G. & Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys Rev B* 47, 558–561 (1993).

5. Ernzerhof, M. & Perdew, J. P. Generalized gradient approximation to the angle- and systemaveraged exchange hole. *J Chem Phys* **109**, 3313–3320 (1998).

6. Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J Chem Phys* **132**, 154104 (2010).

7. Wellendorff, J. *et al.* Density functionals for surface science: Exchange-correlation model development with Bayesian error estimation. *Phys Rev B* **85**, 235149 (2012).

8. Sun, J., Ruzsinszky, A. & Perdew, J. P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys Rev Lett* **115**, 036402 (2015).

9. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Erratum: "Hybrid functionals based on a screened Coulomb potential" [J. Chem. Phys.118, 8207 (2003)]. *J Chem Phys* **124**, 219906 (2006).

10. Heyd, J., Scuseria, G. E. & Ernzerhof, M. Hybrid functionals based on a screened Coulomb potential. *J Chem Phys* **118**, 8207–8215 (2003).

11. Blum, V. *et al.* Ab initio molecular simulations with numeric atom-centered orbitals. *Comput Phys Commun* **180**, 2175–2196 (2009).

12. Levchenko, S. V. *et al.* Hybrid functionals for large periodic systems in an all-electron, numeric atom-centered basis framework. *Comput Phys Commun* **192**, 60–69 (2015).

13. Mathew, K., Sundararaman, R., Letchworth-Weaver, K., Arias, T. & Hennig, R. G. Implicit solvation model for density-functional study of nanocrystal surfaces and reaction pathways. *J Chem Phys* **140**, 084106 (2014).

14. Mathew, K., Kolluru, C. V., nidhi Mula, Steinmann, S. N. & Hennig, R. G. Implicit self-consistent electrolyte model in plane-wave density-functional theory. (2016).

15. Ryckaert, J.-P., Ciccotti, G. & Berendsen, H. Numerical integration of the cartesian equations of motion of a system with constraints: molecular dynamics of n-alkanes. *J Comput Phys* **23**, 327–341 (1977).

16. Patra, A., Peng, H., Sun, J. & Perdew, J. P. Re-thinking CO adsorption on transition-metal surfaces: Density-driven error? *Phys Rev B* **100**, 035442 (2018).

17. Schmidt, P. S. & Thygesen, K. S. Benchmark Database of Transition Metal Surface and Adsorption Energies from Many-Body Perturbation Theory. *J Phys Chem C* **122**, 4381–4390 (2018).