

Supporting Information for

Site Stability on Cobalt Nanoparticles: A Molecular Dynamics ReaxFF Reactive Force Field study

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1. Reactive force field

The optimization of the parameters in ReaxFF^{1,2} is done such that the properties predicted by ReaxFF matches with a set of quantum chemical data. More details of the optimization of the force field parameters can be found in ref³. The transferability of the ReaxFF force field determined was tested via comparing the predictions using ab-initio molecular dynamics implemented in Quantum Espresso.⁴ The results are shown in Section 4.

2. Details of Figure 3 of the text

Figure 3 of the text shows the logarithmic plot of rate of disappearance of stepped sites as a function of temperature, $\ln k$ as a function of $1/T$. k is the rate of

displacement of the step-edge atoms. The change of step-edge atoms with time follows the function of $\theta = e^{-kt}$. Therefore, $k = -\frac{\ln\theta}{t}$, where θ is the fraction of B5 sites. The number of B5 site atoms are 132, 196 and 252, for the three clusters respectively. The total number of atoms are 321, 603 and 1157. We are only interested in the change of B5 site atoms. Therefore, the fractions (shown in Table 1) are multiplied by 132/321, 196/603 and 252/1157 (for the three clusters respectively), in calculating the rates. The values of the rate k for 603-atom and 1157-atom clusters are normalized with respect to that of the 321-atom cluster with the same initial fraction.

Table 1. Change in fractions (with respect to the initial fraction of 1) of B5 sites at elevated temperatures for the three clusters studied (at time 0.25×10^{-9} s).

Temperature	321-atom (fraction)	603-atom (fraction)	1157-atom (fraction)
1000 K	0.95	0.98	0.99
1050 K	0.90	0.95	0.97
1100 K	0.88	0.94	0.94
1150 K	0.75	0.87	0.88
1200 K	0.60	0.82	0.86
1250 K	0.58	0.65	0.77
1300 K	0.46	0.49	0.68
1350K		0.40	0.55

3. Set up of Reactive force field MD and DFT calculations

Using the reactive force field parameters as determined, we carried out a series of MD simulations as a function of temperature to study the rate of disappearance of the step-edge sites. The simulations converged to non changing structure after a cut-off time of 0.5 ns. The classical MD simulations were performed by using ReaxFF (Amsterdam Density Functional (ADF) software package, version adf2012.01).¹ To optimize Cobalt surfaces and bulk systems, density functional theory (DFT) with the ultrasoft pseudopotentials (GGA) PW91 (Perdew-Wang 91) as implemented in the Vienna ab initio simulation package (VASP) was employed.⁵⁻⁸

4. Comparison with ab-initio MD

The stability of several Cobalt clusters was studied by using both Force field MD (with our developed reactive force field) and Ab-initio MD. The same initial geometries were used in both methods. The final geometries obtained at the end of the simulations are very similar, thus we show one geometry for both (except the 65-atom cluster, as explained below).

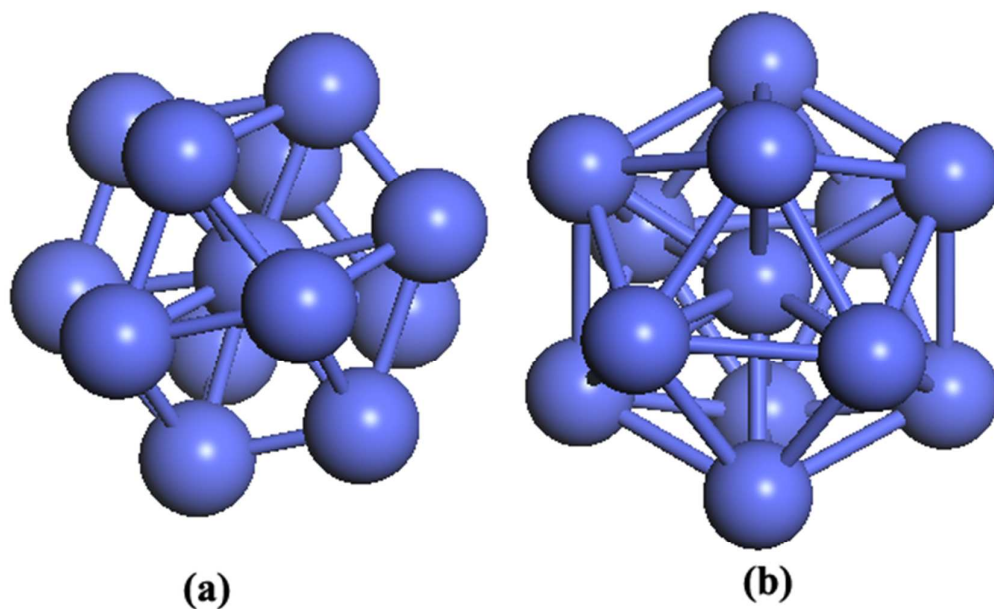


Figure 1 Transformation of Coboctahedron to Icosahedron of 13-atom Co cluster.

The stability of Coboctahedron 13-atom Co cluster is studied at room temperature. Both ReaxFF MD and Ab-initio MD demonstrate a transformation from Coboctahedron to Icosahedron. The energy difference between the initial and the final geometry are -167.0 kJ/mol and -170.6 kJ/mol for Force field MD and Ab-initio MD respectively.

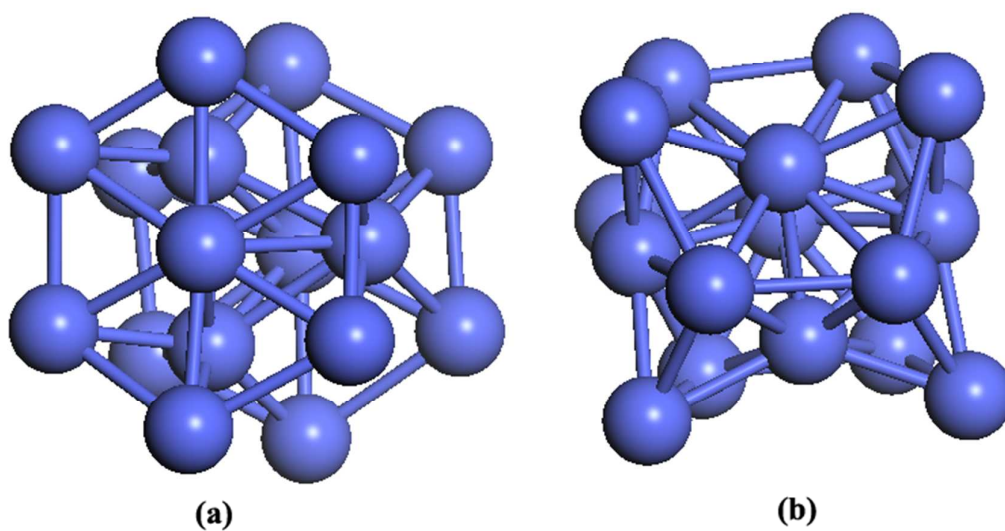


Figure 2. The initial geometry (a) and final geometry (b) of 17-atom Cobalt cluster.

The energy difference between the initial and the final geometry, shown in Figure 2, are -335.0 kJ/mol and -342.1 kJ/mol for Force field MD and Ab-initio MD respectively.

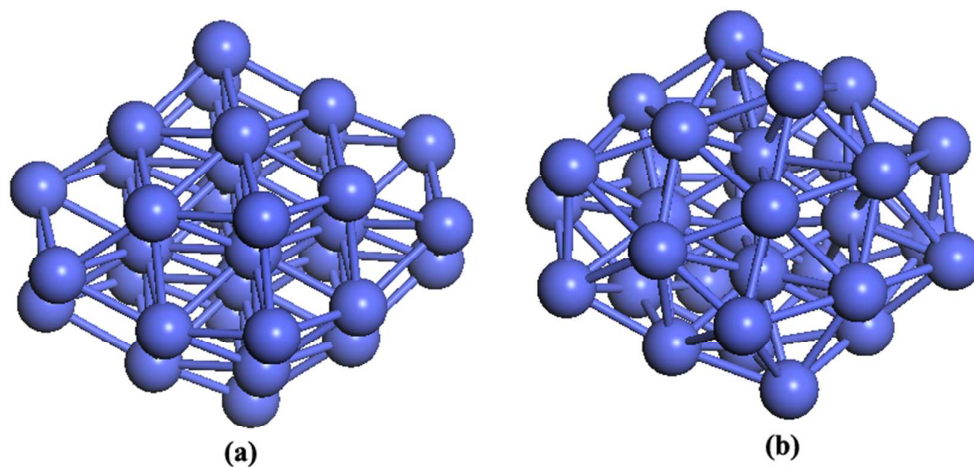


Figure 3. The initial geometry (a) and final geometry (b) of 32-atom Cobalt cluster.

The energy difference between the initial and the final geometry, shown in Figure 3, are -167.0 kJ/mol and -165.0 kJ/mol for Force field MD and Ab-initio MD respectively.

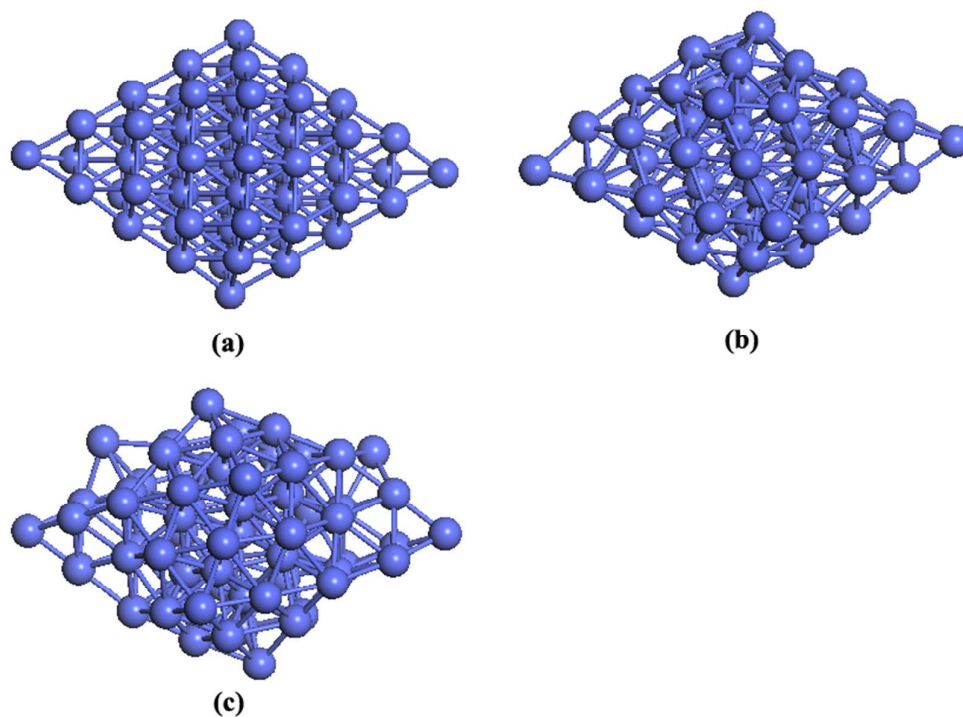


Figure 4. The initial geometry (a), intermediate metastable geometry (b), and final geometry (c) of 65-atom Cobalt cluster.

For the initial and intermediate geometry the energies are -155 kJ/mol and -139 kJ/mol for Force field MD and Ab-initio MD respectively. The Force field MD simulation shows that the intermediate is further changed to the final geometry as shown in Figure 4 (c), with the lower energy of -251 kJ/mol. However the Ab-initio MD can not predict this change. The energy of the final geometry is -251 kJ/mol,

which is lower than the intermediate. Because the central part of the 65-atom cluster transformed into an icosahedron geometry, which is much more stable than the intermediate geometry.

5. Shift of the add-layers

The shifting of (111) add-layer transformed ABC stacking into ABA stacking (3 atomic layers including the shifting layer), as shown in Figure 5 (a) and (b). The shifting of (100) layer (on 1157-atom cluster) does not lead to phase change, as shown in Figure 5 (c).

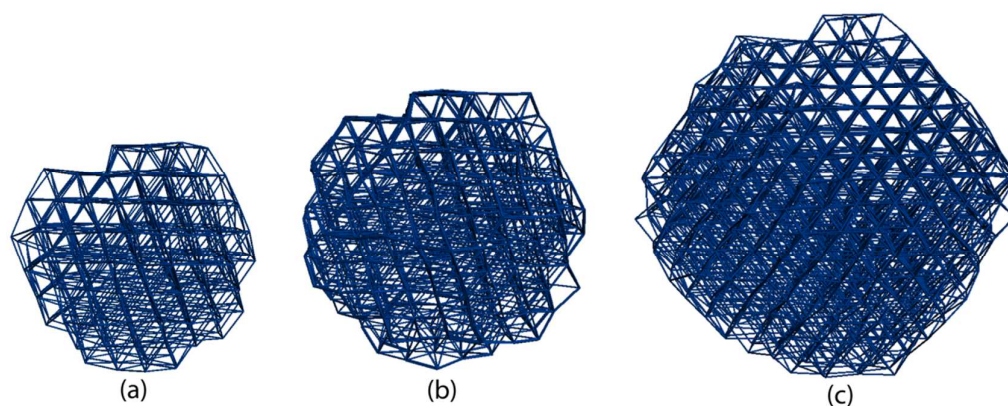


Figure 5. Wireframe show of the shifts of the add-layers. (a) the 321-atom cluster with ABA stacking of the top three layers, (b) 603-atom cluster with ABA stacking of the top three layers, and (c) 1157-atom cluster, with ABC stacking.

6. Force field parameters

Reactive force field: Co

39 ! Number of general parameters
 50.0000 !Overcoordination parameter
 9.5469 !Overcoordination parameter

26.5405 !Valency angle conjugation parameter
 1.7224 !Triple bond stabilisation parameter
 6.8702 !Triple bond stabilisation parameter
 60.4850 !C2-correction
 1.0588 !Undercoordination parameter
 4.6000 !Triple bond stabilisation parameter
 12.1176 !Undercoordination parameter
 13.3056 !Undercoordination parameter
 -70.5044 !Triple bond stabilization energy
 0.0000 !Lower Taper-radius
 10.0000 !Upper Taper-radius
 2.8793 !Not used
 33.8667 !Valency undercoordination
 6.0891 !Valency angle/lone pair parameter
 1.0563 !Valency angle
 2.0384 !Valency angle parameter
 6.1431 !Not used
 6.9290 !Double bond/angle parameter
 0.3989 !Double bond/angle parameter: overcoord
 3.9954 !Double bond/angle parameter: overcoord
 -2.4837 !Not used
 5.7796 !Torsion/BO parameter
 10.0000 !Torsion overcoordination
 1.9487 !Torsion overcoordination
 -1.2327 !Conjugation 0 (not used)
 2.1645 !Conjugation
 1.5591 !vdWaals shielding
 0.1000 !Cutoff for bond order (*100)
 2.1365 !Valency angle conjugation parameter
 0.6991 !Overcoordination parameter
 50.0000 !Overcoordination parameter
 1.8512 !Valency/lone pair parameter
 0.5000 !Not used
 20.0000 !Not used
 5.0000 !Molecular energy (not used)
 0.0000 !Molecular energy (not used)
 2.6962 !Valency angle conjugation parameter
 1 !Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;
 alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.; cov r3;Elp;Heat
 inc.;n.u.;n.u.;n.u.;n.u.; ov/un;val1;n.u.;val3,vval4
 Co 2.0121 3.0000 58.9330 1.8331 0.1981 0.8139 0.2089 3.0000
 12.3004 3.9173 3.0000 0.0000 0.0000 4.8038 7.3852 0.0000
 -0.9623 0.0000 96.9473 1.6928 4.3501 0.4034 0.8563 0.0000
 -3.3875 2.9330 1.0338 2.8790 2.5791 0.0000 0.0000 0.0000


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1      ! Nr of bonds; Edisl;LPpen;n.u.;pbe1;pbo5;l3corr;pbo6
      pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
1  1  60.1966   0.0000   0.0000  -0.4558  -0.2000   0.0000  16.0000   0.3065
      0.8040  -0.2000  15.0000   1.0000  -0.0522   8.2012   0.0000   0.0000
0      ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
0      ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
0      ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n
0      ! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1

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7. Complete references

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