

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

Xue-Qing Zhang,^{†,‡} Eldhose Iype,[§] Silvia V. Nedeia,[§] Antonius P. J. Jansen,[‡] Bartłomiej M. Szyja,^{||} Emiel J. M. Hensen,[†] and Rutger A. van Santen^{*,†,‡}

[†]Laboratory of Inorganic Materials Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

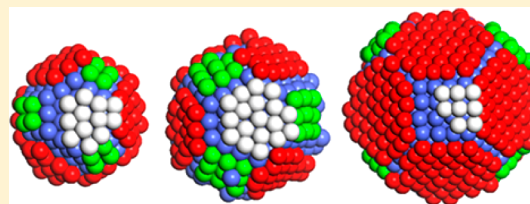
[‡]Institute for Complex Molecular Systems, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

[§]Department of Mechanical Engineering, Eindhoven University of Technology P.O. Box 513, 5600 MB Eindhoven, The Netherlands

^{||}Institute for Solid State Theory, University of Münster, Wilhelm-Klemm Str. 10, 48149 Münster, Germany

S Supporting Information

ABSTRACT: The stability of step-edge-type surface sites on cobalt nanoparticles is investigated for particles of increasing size of 1.8, 2.2, and 2.9 nm, that contain 321, 603, and 1157 atoms, respectively. The stability of surface configurations is probed by analyzing the kinetics of the disappearance of step-edge sites as a function of temperature using ReaxFF reactive force field molecular dynamics (MD) simulations. The MD simulations are based on a newly designed reactive force field. Two different activation energy regimes are identified. A low activation barrier of the order of 7 kJ/mol corresponds to single atom movement, which is independent of Co nanoparticle size. Higher activation energies (28, 37, and 22 kJ/mol for the three clusters, respectively) correspond to the shift of overlayer terraces. These concerted shifts appear to be sensitive to particle size, terrace size, and the structure of the facet. Step edges are more stable on larger particles. Shifting of the (111) surface layers leads to transformation of a thin surface layer from the initially face-centered cubic structure to hexagonal close-packed structure.



1. INTRODUCTION

The chemistry of transition metal nanoparticles^{1–18} is of great interest because their reactivity may be controlled by altering their size and shape. Such size- and shape-dependent properties are important to advances in many technologies.^{1–8,13} In this paper we will focus on structural differences of such particles relevant to heterogeneous catalysis.^{5–7}

Examples of reactions catalyzed by transition metals such as Ru or Co are ammonia synthesis from N₂⁵ and the Fischer–Tropsch reaction,¹³ which produces hydrocarbons from synthesis gas, a mixture of H₂ and CO. These reactions show a nanoparticle size dependence that is indicative of structure sensitivity. For particles larger than 1.5 nm that are typically present in catalysts used for these reactions, differences in the topology of the reactive surface site rather than changes in the particle electronic properties tend to be the dominating factors that control catalytic reactivity changes.^{14–16} Sites of low activation energy of elementary reaction steps that involve bond breaking or formation of π -type chemical bonds as in diatomic molecules such as N₂ and CO are step-edge-type sites as found on corrugated surfaces.^{5,16} A seminal early contribution that identified the effect of surface topology on the activation of N₂ was made by van Hardeveld et al.,^{17,18} who noted unique step-edge-type sites (B5 sites) on particles with the same shape as shown in Figure 1a. They proposed that such B5 sites are

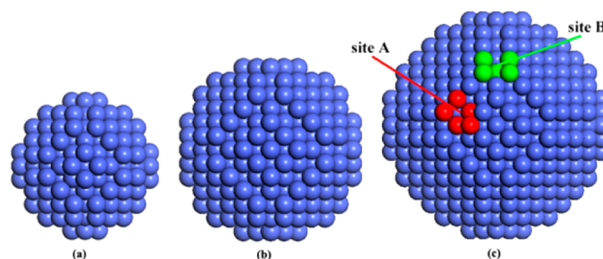


Figure 1. Initial geometry of cobalt nanoclusters. The number of atoms for these model clusters is (a) 321, (b) 603, and (c) 1157. The two different types of step-edge sites are marked on the 1157-atom cluster. Site A denotes a fcc(311) surface type B5 site, and site B denotes a fcc(110) surface type B5 surface site. The atom–atom distances are around 2.495 Å. The sizes of these clusters are (a) 1.8, (b) 2.2, and (c) 2.9 nm.

necessary for N₂ activation. Many years later, surface science studies by Zambelli et al.¹⁹ and computational studies by the group of Norskov²⁰ confirmed the uniqueness of such sites for the dissociation of N₂ at the surface step edges of Ru(0001). A

Received: January 3, 2014

Revised: March 4, 2014

Published: March 13, 2014



similar dependence on the presence of step-edge sites for the activation energy of CO has been reported by many groups.^{21–24}

Interestingly for the reactions mentioned, the catalytic rate normalized to unit surface area of the nanoparticles is found to decrease steeply when particle size decreases below a particular size.^{20,25–27} Whereas no consensus exists on the particular reason for this decrease in activity and often also selectivity,^{13,16,28–35} an important hypothesis is a reduction in the number of catalytically reactive step-edge centers, when particle size decreases.

This study limits itself to the question of the intrinsic properties of the free nanoparticles as a reference to more complex phenomena that become important when particles are immobilized on a support. For instance, on supported catalysts particle shape and size changes may originate from the growth of particles by sintering^{36,37} or for a single particle by changes induced by adsorption of reaction intermediates during a catalytic reaction,³⁸ e.g., high coverage carbon or oxygen.^{39–41}

As a first initial step to a research effort that addresses these issues here, we will study the relative stability of step-edge sites at a single particle for three Co nanoparticles as a function of size.

2. METHODS

Because of the large number of Co atoms involved in the system, a reactive force field (ReaxFF) in combination with classical molecular dynamics is used to study the relative stability of different cluster topologies. The ReaxFF has been originally developed by van Duin et al. and has already been applied to a variety of materials.^{42–46}

ReaxFF uses hundreds of parameters to describe the interactions between atoms. The ReaxFF force field calculates the energy of the system according to eq 1

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} \quad (1)$$

where E_{bond} represents the bond energy, E_{lp} is the energy due to the presence of lone pairs, and E_{over} and E_{under} are the energies arising from over- and undercoordination, respectively, of atoms with respect to their valency. The valence angle (three-body) energy is accounted for in the terms E_{val} . E_{pen} is a penalty energy to stabilize a three-body system with the center atom having two double bonds connected to it. The long-range interactions such as van der Waals interactions and Coulombic interactions are accounted for between every pair of atoms irrespective of the presence of chemical bonds. The complete expressions for each term are given by van Duin et al.⁴²

We developed a reactive force field for Co using a recently developed Monte Carlo algorithm with simulated annealing.⁴⁷ Parameters (see Supporting Information) have been deduced by fitting the many reactive force field parameters to DFT calculated structures and energies of different Co surfaces. Details on the force field parameters can be found in the Supporting Information. Molecular dynamics simulations in the canonical ensemble (NVT) were performed using a velocity Verlet algorithm. The system temperature was controlled by a Berendsen thermostat. A time step of 0.5 fs and a temperature damping constant of 200 fs were used, and the total number of interactions is 1.0×10^6 . Therefore, the total simulation time was 0.5 ns for each simulation.

3. RESULTS AND DISCUSSION

The results in Figure 2 demonstrate that the calculations using the fitted parameters agree very well with many of the systems

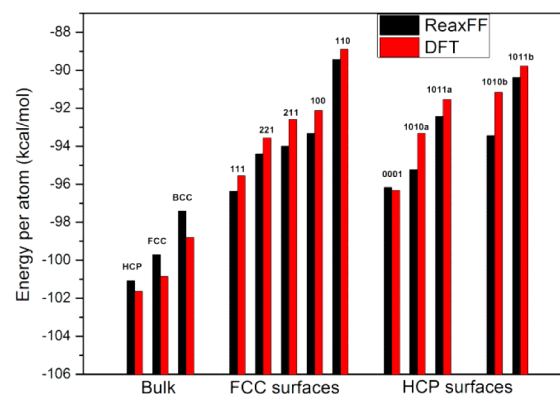


Figure 2. Comparison of the atomization energies according to the reactive force field and DFT calculations (see Supporting Information) for bulk Co systems and Co surfaces.

included. The average error bar of 1.06 kcal/mol is in the acceptable range. Transferability tests show good agreement with results of ab initio MD. This and details on the force field parameters and the simulations can be found in the Supporting Information.

The relative stability of B5-type sites constructed on a truncated octahedron has been followed by calculating the disappearance rate of the step-edge sites (all the step-edge atoms are B5 site atoms) of the three Co particles as a function of temperature. This allowed for the identification of activation energies of the rates of the successive atom rearrangement reactions.

As initial configuration we choose the analogues of the 321-atom nanocluster (Figure 1a) proposed by van Hardeveld et al.^{17,18} Two other clusters were chosen with similar shape but larger size and similar surface termination: the 603-atom cluster (Figure 1b) and 1157-atom cluster (Figure 1c). The geometries of the clusters are obtained via removal of the edge atoms of perfect truncated octahedron nanoclusters. The Co particles have the FCC structure consistent with this preferred phase stability for nanosized Co particles.^{13,18}

The nanoclusters undergo reconstruction as the temperature increases. As a result, the step-edge sites become unstable at high temperature, and they start to disappear. The changes in concentration of sites A and sites B are related, since they often share a same metal atom.

Table 1 shows the decrease of the fraction of B5 sites at the end of the simulation with respect to the initial fraction with temperature. The findings clearly show that larger clusters are

Table 1. Relative Change in Fraction of B5 Sites at a Particular Temperature for the Three Clusters Studied

temp (K)	321-atom (fraction)	603-atom (fraction)	1157-atom (fraction)
1000	0.94	0.98	0.99
1100	0.80	0.92	0.93
1200	0.57	0.77	0.85
1300	0.42	0.46	0.66
1400	0.08	0.29	0.44
1500		0.12	0.31

more resistant to disappearance of B5 sites. Initially, at low temperatures there is only a small decrease. At higher temperatures, the rate of disappearance strongly increases.

Figure 3 shows an Arrhenius plot of the calculated rate of displacement of the step-edge atoms, from which the activation

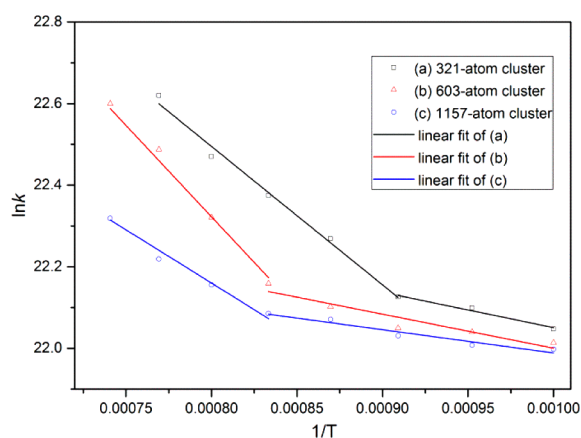


Figure 3. Arrhenius plots of the disappearance of stepped sites as a function of temperature for the two kinetically distinguishable regimes: single atom movement and cooperative movement. The solid lines are linear fits to the simulated data.

energy of displacement of step-edge atoms can be determined. On the smallest Co particle containing 321 atoms the initial fraction of B5 site atoms is 41.1% and on the larger particle (1157-atom) that fraction is 21.8%. Whereas on the larger particle the total fraction of B5 sites remains smaller than that on the smaller particle up to a temperature of 1400 K, the rates of change of the fraction show a clear trend. The rate of change is faster on the smaller particle. Two kinetically distinct regimes can be identified.

Careful analysis of the molecular dynamics simulations show that changes with the lower activation energy (low temperature) correspond to single atom movements. The average activation energy is around 7 kJ/mol. The second higher activation energy regime (higher temperature) corresponds to that of cooperative atomic movements by the shifting of layers. In this regime, for the three clusters shifting of surface layers occurs with activation energies of 28, 37, and 22 kJ/mol, respectively. At temperatures higher than the onset temperature (1100, 1200, and 1200 K for the three clusters, respectively) surface layers start to shift.

Cooperative movement of bulk layers, which occurs at higher temperatures has also been observed by Landman et al.^{48,49} in simulations of the melting of gold clusters.

Figure 4 illustrates for three clusters the single atom movements as well layer shifts. At selected temperatures a representative structure is shown.

The activation energies for single atom movements are independent of particle size and have the low value typically found for surface atom diffusion.^{25,26} The activation energies to shift a layer are different as the size and type of the layers to be shifted are different. The activation energy of the second regime of 321-atom is lower than that of the 603-atom cluster. This is reasonable as this cluster is smaller, and the shifting (111) surface layer is also smaller. However, the layer shift activation energy of the 1157-atom cluster is lower than that of the smaller 603-atom cluster. This decrease in layer shift activation energy for the larger cluster is due to a shift of a different and

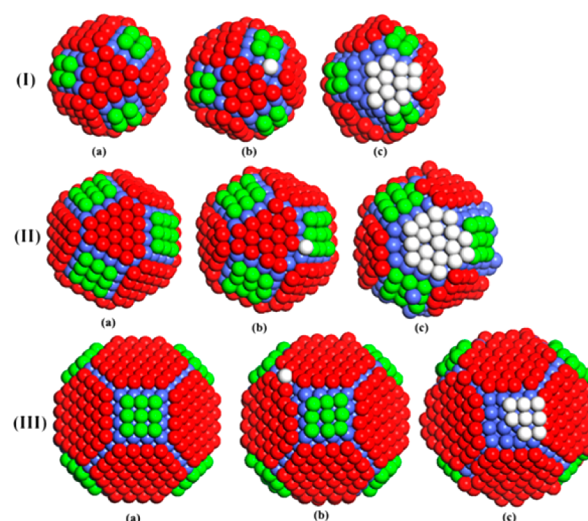


Figure 4. Representative geometries for the three clusters studied: (a) the initial geometries of the 321-, 603-, and 1157-atom clusters used in the simulations, (b) intermediate geometries showing single atom movements, and (c) the final geometries of the three clusters, which shows layer shifts. The (111) surface layer is colored in red and the (100) surface layer in green. The one atom displacements and layer shifts are colored in white. (I) 321-atom cluster at temperature of 1150 K, (II) 603-atom cluster at temperature of 1250 K, and (III) 1157-atom cluster at temperature of 1250 K.

smaller layer in the 1157-atom cluster compared to that of the 321-atom and 603-atom clusters. It is because the (111) layer, which has the lower surface energy becomes larger for increasingly large clusters. Instead, the 1157-atom cluster shifts the smaller layers, in this case that of the higher surface energy (100) layer (see Figure 4(III)), which according to Wulff's law²⁷ has a smaller surface area. Its smaller size makes that its shift costs less energy. For even larger clusters such overtaking of particle shape change mechanism by the smaller surfaces area layers will be repeated.

The shifting of (111) adlayer transformed the fcc stacking of surface layers to a HCP stacking (see Supporting Information).

4. CONCLUSIONS

In summary, the temperature dependence of the stability of step-edge sites has been investigated with a newly developed reactive force field on three Co nanoparticles of different size. With increasing temperature the fraction of step-edge sites becomes lower due to the displacement of atoms or assemblies of atoms. We found two distinct dynamical movements responsible for the disappearance of the step-edge sites: single atom movements and shifts of surface layers. There is only a significant dependence in activation energy of the latter movement with particle size. This relates to changing size of the layers with particle size and shape. The corresponding activation energy increases with the surface area of the shifted layer. On the 321- and 603-atom clusters there is shift of (111) surface layers and activation energy increases with particle size. On the larger 1157-atom particle the (111) layers become too large, and at this size shifts occur in the (100) surface layers. Since its surface area is smaller, the corresponding activation energy is lower. One therefore expects generally an increase in site stability on the larger particles, but the changes will be nonuniform.

The increase in relative stability of the stepped surface sites with increasing nanoparticle size is in line with the catalytic observation that reactivity ascribed to the presence of such sites decreases when nanoparticle size decreases beyond a limiting size.

■ ASSOCIATED CONTENT

■ Supporting Information

Computational details; transferability tests; force field parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Ph +31 402473082; e-mail r.a.v.santen@tue.nl (R.A.v.S.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank I. M. Ciobica for providing VASP computed data and C. Popa and W. Song for fruitful discussions. Funding has been provided by National Research School (catalysis controlled by chemical design). Supercomputing facilities were funded by The Netherlands Organization for Scientific Research (SH-256-13).

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