

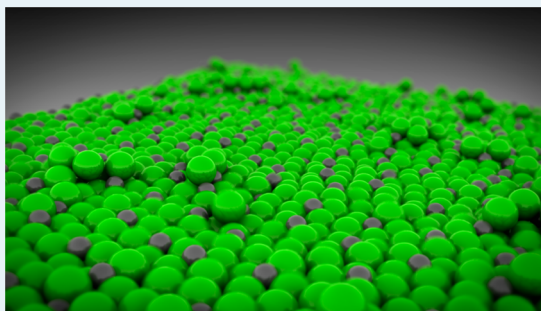
Carbon-Induced Surface Transformations of Cobalt

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Supporting Information

ABSTRACT: A reactive force field has been developed that is used in molecular dynamics (MD) studies of the surface transformation of the cobalt (0001) surface induced by an overlayer of adsorbed carbon atoms. Significant surface reconstruction is observed with movement of the Co atoms upward and part of the C atoms to positions below the surface. In a particular C ad atom coverage regime step edge type surface sites are formed, which can dissociate adsorbed CO with a low activation energy barrier. A driving force for the surface transformation is the preference of C adatoms to adsorb in 5- or 6-fold coordinated sites and the increasing strain in the surface because of the changes in surface metal atom–metal atom bond distances with the increasing surface overlayer concentration. The process is found to depend on the nanosize dimension of the surface covered with carbon. When this surface is an overlayer on top of a vacant Co surface, it can reduce stress by displacement of the Co atoms to unoccupied surface positions and the popping up process of Co atom does not occur. This explains why small nanoparticles will not reconstruct by popping up of Co atoms and do not create CO dissociation active sites even when covered with a substantial overlayer of C atoms.



KEYWORDS: catalysis, surface reconstruction, reactive force field, molecular dynamics, size dependence, step-edge sites

INTRODUCTION

In reactive environments adsorption and reaction of molecules on catalytically active surfaces may form surface overlayers, which induce surface reconstruction. This in turn affects in time surface reactivity and hence catalytic properties.^{1–5} Hence these two issues, (1) the dependence of surface reconstruction on composition and concentration of the surface overlayer and (2) the change in activity and selectivity of the restructured catalyst, must be understood for a theoretical and practical development of heterogeneous catalysis science.^{6,7} Usually overlayer formation of adsorbed O or C atoms will poison the most reactive surface sites, which will result in deactivation of the catalyst.^{8,9} Carbon atoms have been found to decorate reactive surface step-edge sites, which will inhibit their participation in reactions.^{10,11} On the other hand, the activation of a metal particle in the course of reaction is also well-known. Especially in Fischer–Tropsch catalysis such self-organization and activation of Co particles is well documented.¹² Surface reorganization induced by reactions can also lead to spatiotemporal oscillatory behavior as found for the CO oxidation reaction catalyzed by reconstructing Pt surfaces.^{5,13} Another example of reactivity enhancement is the conversion of methane to synthesis gas by oxide overlayers on Pd.^{14,15}

In this paper we will study the reconstruction of the Co(0001) surface as a function of adsorbed C atom overlayer concentration. This is relevant to the kinetics of synthesis gas conversion in the Fischer–Tropsch reaction, which produces long hydrocarbon chains useful as liquid fuels. The self-assembly of the catalyst surface into a reactive phase during

reaction is believed to be the reason for the increase in reactivity once reaction starts.¹⁶ It has also been proposed that CO, which has a high surface coverage during reaction, may be responsible. However, we have previously shown that under conditions where carbonyl formation can be excluded, not adsorbed CO but adsorbed C atoms will rearrange the surface.¹⁷ Adsorbed carbon atoms will be formed during reaction, because their formation is intrinsic to the chain growth process. Initially its overlayer concentration will be small, but in time its concentration will increase.¹⁰

We will show that reconstruction is due to the need to reduce the increasing stress within the metal atom surface layer because of the expansion of the metal atom distances by the adsorbed C atoms.

The reconstruction will not only cause changes within the plane but will also cause Co atoms to pop up out of the surface. These atoms can collide and, in this way, create step-edge type of sites. Such sites are well-known as low activation energy CO dissociation sites.^{18,19}

The variation in concentration of such step-edge sites has been proposed to be the main reason for the nanoparticle size dependence of the Fischer–Tropsch reaction.²⁰ This reaction has been shown to be nanoparticle size dependent. On Co particles CO and H₂ turnover frequencies (TOF) as well as the Fischer–Tropsch chain growth probability decline steeply

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when the particle size is less than a few nanometers. Smaller particles are proposed not to be able to support such step-edge sites, which are responsible for the chain growth reaction. The popping up of Co atoms induced by adsorbed C atoms can explain the increased reactivity of a Co particle as a function of reaction time and, as we will see, also the relatively large size of metal particles, that is, >6 nm, needed for high Fischer–Tropsch activity of Co nanoparticle catalysts.²¹

These substantial reconstruction effects, especially of the high-density Co(0001) surface, may lead to the apparent conclusion that the FT reaction is not structure sensitive,²² whereas the actual catalytically reactive surface has a very different structure.

There have been important advances in the theory of surface reconstruction.^{11,17,23–27} By coupling first principles with statistical mechanics, Reuter et al.²⁴ computed the surface kinetics of CO oxidation catalysis at RuO₂(110). They also presented a model of first-principles atomistic thermodynamics for oxidation catalysis.²⁵ A DFT coupled thermodynamic model, studying the H₂-induced reconstruction of supported Pt clusters, was presented by Sautet et al.²³ By using kinetic Monte Carlo (kMC), coupled with DFT, we reported the ammonia coverage dependent meandering of Pt(111).²⁷

Recently, Valero and Raybaud published a study on the C-induced reconstruction of the Co(111) surface, based on a thermodynamic approach.¹¹ They relate the surface coverage with C to the equilibrium between the adsorbed long hydrocarbon chains, which are intermediates of the Fischer–Tropsch product and adsorbed C atoms generated by dissociative adsorption of CO. DFT calculations are used to study surface reconstruction due to subsurface C incorporation. They find surface reconstruction at low carbon atom coverage. However, at high carbon coverage graphene formation becomes thermodynamically favored over C adatom induced surface reconstruction. Bond formation between the carbon atoms takes over from their interaction with transition metal surface atoms, and hence the surface relaxes to the nonreconstructed state.

The work presented here is a kinetic study that uses molecular dynamics to study the events that occur on a Co(0001) surface. This allows us to study surface reconstruction as a function of temperature and to include reaction steps with a substantial activation energy barrier. It is also useful in view of the large number of particles that have to be included in the simulation.

At the start of the molecular dynamics simulations the surface is covered with a surface concentration of C atoms and simulations are run at a high temperature to limit the time of the simulations. In agreement with Valero et al., we also observe reconstruction. Initially, only the kind of structural rearrangement is observed similar to that observed by Valero et al., but with time substantially larger displacements of the Co atoms occur as well as significant subsequent reorganization by diffusion processes. The molecular dynamics studies have been done with a newly developed reactive force field (ReaxFF). This we have earlier applied in classical molecular dynamics of Co to study the relative stability of different cluster topologies.²⁸ The ReaxFF has been originally developed by van Duin et al. and applied to a variety of materials.^{29–34} We have extended and modified the ReaxFF parameters to include also surface cobalt–carbon systems to be used in the simulations to be presented here.

The molecular dynamics studies have been executed at temperatures at which they will reach a final state within accessible computer time. From these simulations information on not only surface reconstruction but also the apparent activation energies of reconstruction is deduced.

We have used these results to propose also a solution to the question of particle size dependence of the Fischer–Tropsch catalysis.^{21,35}

At present it is generally accepted that catalytic reactions that require low activation energy dissociation of CO or N₂ and NO^{36–38} need the presence of step-edge type sites. It has been shown that such step-edge sites cannot be stabilized on nanoparticles that are too small.^{28,37,39} Our recent simulation indicates a minimum size of 1.8 nm.²⁸ However, this size is too small compared to experimental data that indicate a size of at least 6.0 nm.²¹ We propose that this larger size is needed, because otherwise relaxation of the C-induced reconstruction by spillover of metal atoms to the other surfaces of the nanoparticle takes over from the driving force to generate the step-edge sites.

To test this hypothesis, we have studied the C-induced reconstruction on Co metal atom overlayers as a function of their size. The latter enables the study of the competition between lateral Co atom displacement, which releases strain and the popping up of the Co atoms.

METHODOLOGY

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

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

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 under-coordination, respectively, of atoms with respect to their valency. The valence angle (three-body) energy is accounted for in the term 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. It is an additional penalty in energy for systems with two double bonds with an atom in the valence angle. The long-range interactions such as van der Waals interactions and effective Coulomb 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.²⁹

We developed an improved force field for the Co–C system using a recently developed Monte Carlo algorithm with simulated annealing.³³ Parameters have been deduced by fitting the many reactive force field parameters to DFT (VASP)^{40,41} calculated structures and energies of different Co surfaces.²⁸ We also include the possibility of C–C bond formation. Details on the force field parameters can be found in the [Supporting Information \(SI\)](#).

Figure 1 shows a comparison of quantum chemically obtained energies with those of the force field simulations. The mean average error is 0.71 kcal/mol. To further demonstrate the validity of the force field parameters, we compare the radial distribution function (RDF) of the ReaxFF fitted structures with those of the DFT calculations as shown in Figure 2.

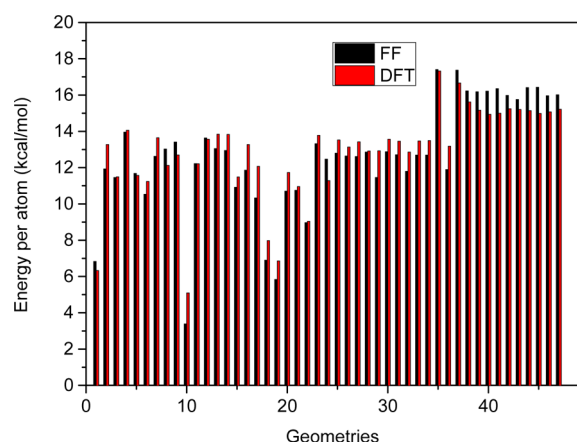


Figure 1. Comparison of the atomization energies according to the reactive force field and DFT calculations for cobalt–carbon systems.

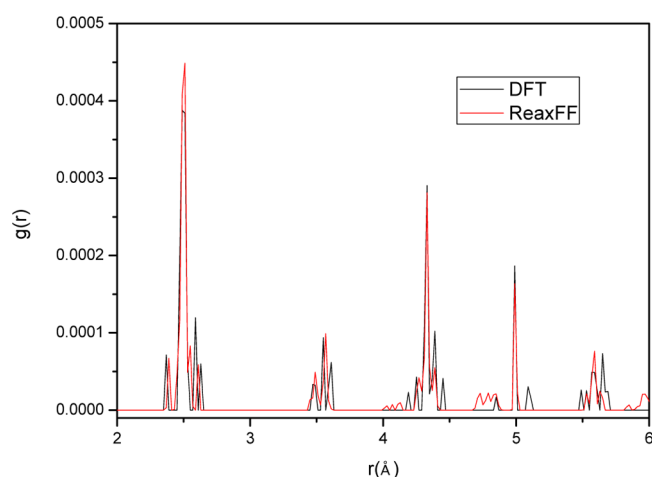


Figure 2. Comparison of the radial distribution functions (RDF) from the structures obtained by the ReaxFF calculations with those of the DFT calculated structures.

A range of calculated values for the atomic distance is shown in Table S1 in the SI. The values are in good agreement with those of Valero et al.¹¹

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 was 1.0×10^6 . Therefore, the total simulation time was 0.5 ns for each simulation. We chose high temperatures to simulate recon-

struction phenomenon that happen at longer time scales, but then can be studied at computationally accessible time scales.

RESULTS AND DISCUSSION

Initiation and Transformation. When adsorbed carbon atom induced reconstruction is studied on a Co(0001) surface, two different types of surface reconstruction are observed in different time regimes. The initial surface reconstruction initiated by the carbon atoms initially adsorbed at a 3-fold site will undergo a local transformation,^{4,11,17} which converts the C adsorption site to a more stable 4-fold coordination. The displacement of the surface metal atoms increases the distance between metal atoms and hence surface stress develops. However, at a high C atom surface coverage, the surface cannot accommodate the Co atoms anymore within the reconstructed layer. The metal atom surface density will have to change.

After some time by reaction steps with a higher activation energy than the initial local reconstruction process, a second surface transformation occurs and the Co atoms pop up as shown in Figure 3. At short time (Figure 3a) some of the surface is still converting to the initial clock reconstructed state. Once some surface atoms have popped up, a collective process starts (Figure 3b,c). Popped-up surface atoms assist additional neighboring Co atoms in popping up. This results in the formation of domains of popped-up atoms at the surface. These atoms further rearrange to form ad-layers, which at their edges form Co step-edge sites.

This may be the mechanism of the surface corrugation and formation of nanosized particles on the Co(0001) surface after exposure to synthesis gas and Fischer–Tropsch catalysis as observed by STM in the work of Wilson and de Groot.⁴²

At intermediate C coverage in the simulations step-edge sites are generated with a topology as indicated in Figure 4, which

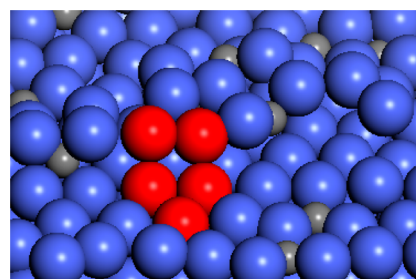


Figure 4. Representative cut from the reconstructed surface from our simulations. The carbon atoms are shown in gray, cobalt atoms in blue, and step-edge active site cobalt atoms in red.

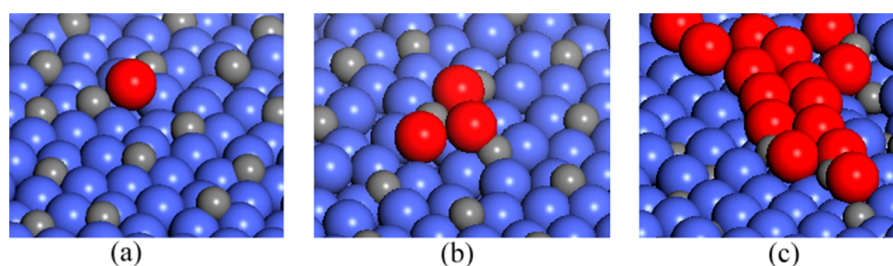


Figure 3. Molecular dynamics simulations of carbon-induced surface transformations of Co(0001) at a temperature of 1700 K: (a) short time simulation (0.01 ns); (b) longer time simulations (0.03 ns); (c) geometry after 0.5 ns of simulation. The initial C coverage is 12.5% of the 3-fold sites. The carbon atoms are shown in gray, cobalt atoms in blue, and pop-up cobalt atoms in red.

will activate CO with a low activation barrier.^{18,43} Calculations of Li et al.⁴³ have demonstrated that a surface site on a stepped Co surface with comparable configuration has an activation energy for CO dissociation of 134 kJ/mol, whereas this barrier is 229 kJ/mol at the Co(0001) surface.⁴³

When the surface coverage of C becomes too high, the carbon atoms will not only move to subsurface positions but also start to decorate the step-edge sites. This will deactivate the catalyst. We find that the maximum number of step-edge sites corresponds to a C coverage that should be <18.75%. As is illustrated by Figure 5, at coverages of 18.75 and 25% most of the surface sites are decorated by C atoms.

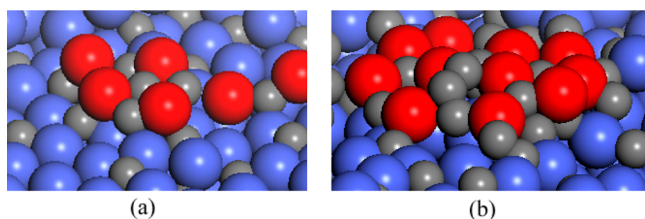


Figure 5. Snapshots of reconstructed Co surface at a simulation time of 0.04 ns for two C coverages, 18.75% (a) and 25% (b), respectively. The carbon atoms are shown in gray, cobalt atoms in blue, and pop-up cobalt atoms in red.

MD simulations executed at different temperatures can be used to provide kinetic information. Apparent activation energies can be deduced for the initial local transformation and the activation energies for the popping up of the Co atoms.

The rate of generating popped-up atoms as a function of time is shown in Figure 6. One distinguishes the two reconstruction regimes: the initiating surface reconstruction regime with local reconstruction (see Figure 7) and the activated one with the popping up of the Co atoms. The changes in the initial region are followed at longer times by the increase in the relative number of pop-up Co atoms.

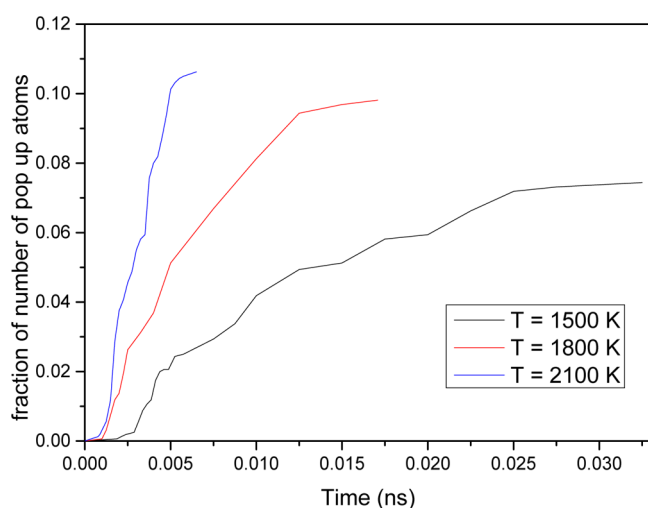


Figure 6. Molecular dynamics simulations. The fraction of Co pop-up atoms as a function of time traces the rate of the activated long time surface reconstruction process. The Co pop-up fraction is tracked for three temperatures of 1500, 1800, and 2100 K. Note the longer times of the surface reconstruction initiation regime at lower temperature in which not yet popping-up of Co atoms happens.

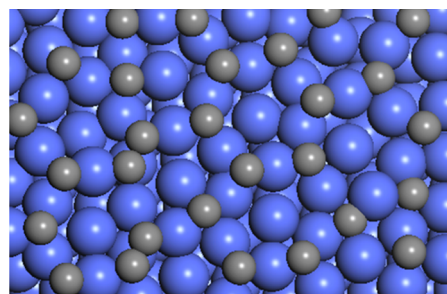


Figure 7. Snapshot of the surface reconstruction in the initiating surface reconstruction regime from the molecular dynamics study runs at 1500 K after 0.5 ps (12.5% carbon coverage). The carbon atoms are shown in gray and cobalt atoms in blue.

Figure 7 shows a snapshot of the reconstructed surface in the initial local reconstruction regime. Some of the 3-fold sites have been changed into 4-fold sites. This reconstruction structure is close to that found by Valero et al.¹¹

The activation energy (Figure 8) for the surface reconstruction initiation regime is found to be 40 kJ/mol. For the activated reconstruction regime it is 86 kJ/mol. The small activation energy of 40 kJ/mol relates to the small displacements of the metal atoms that occur. The activation energy for activated surface reconstruction of 86 kJ/mol is close to that of a C atom moving to subsurface layer (77 kJ/mol).⁴⁴

With the ReaxFF used in the present MD simulations, the activation barrier for C adatom diffusion on the Co(0001) surface is found to be 57 kJ/mol (Figure 9). This is comparable with reported calculated activation energies of C atom diffusion on metal surface terraces for Co(0001) of 44 kJ/mol⁴⁴ and 48 kJ/mol for Ni(111).³

Terrace Size Dependence. Figure 10 provides simulated results as a function of Co(0001) overlayer size on a Co(0001) substrate. The C atoms are initially deposited in the nano-sized overlayer (with 12.5% coverage of the 3-fold sites). If the terrace is small, the pop-up phenomenon of the Co atoms will not occur. Instead, the Co layer will expand. The MD simulations of the small terrace sizes (2.5 and 3.7 nm) show only expansion by lateral displacement of the Co atoms (Figure 10a,b). Only when the size of the terrace increases to 5.0 nm and larger do some Co atoms pop up as highlighted in Figure 10c,d. Thus, the critical size of an overlayer that leads to the formation of step-edge sites induced by the adsorption of C atoms is around 5.0 nm.

De Jong et al.²¹ studied the size effects of Co particle size supported on a carbon support in the Fischer–Tropsch reaction. They found a strong decrease in TOF when the Co particle already is <6 nm. This is in apparent conflict with molecular dynamics studies for carbon-free Co particles that indicate that the step-edge sites can be supported on such particles up to a size of 1.8 nm.²⁸

Instead, the simulations presented here suggest that particles smaller than 5 nm contain surfaces that are so small that strain due to coadsorbed C atoms can be released by displacement of the edge Co atoms. Therefore, no reactive step-edge sites will be generated. This possibly explains the relatively large size of the metal particles below which Fischer–Tropsch conversion rate as well selectivity to form long hydrocarbon chain molecules drops.

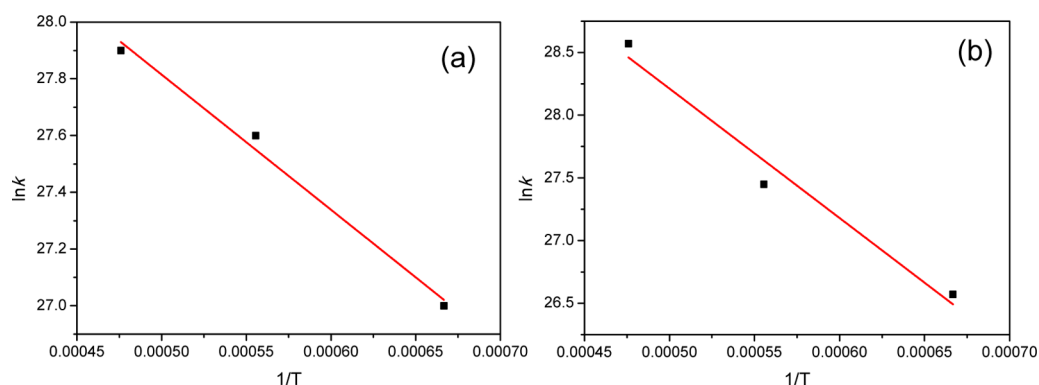


Figure 8. Arrhenius plots of activation energies of the reconstruction processes. The activation energies of the initial reconstruction regime (a) and popping-up regime (b), respectively, are shown. $\ln k$ is plotted as a function of $1/T$, where k is the rate in change of fraction of pop-up Co atoms and T is the temperature. The red line is the linear fit of the MD data.

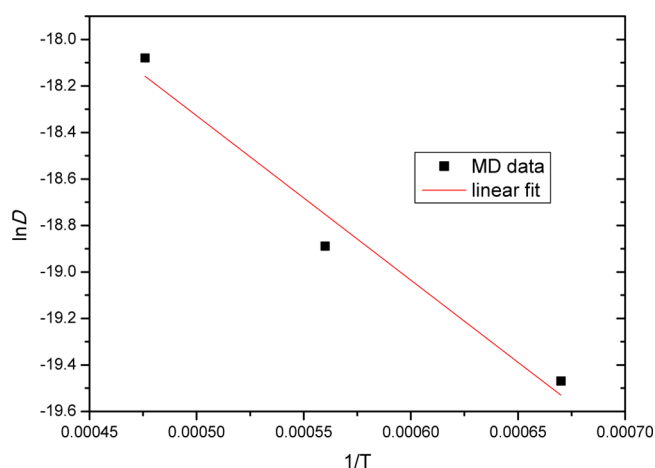


Figure 9. Arrhenius plot of C adatom diffusion over the Co(0001) surface. $\ln D$ is a function of $1/T$, where D is the diffusion constant and T is the temperature. The red line is the linear fit of the MD data.

CONCLUSIONS

A main question addressed by the studies presented is the origin of the initial activation of the Fischer–Tropsch reaction when a reduced catalyst is exposed to the reactive synthesis gas mixture. We have shown that this can be due to a self-organization of the surface topology induced by the adsorbed C atoms.

A surface of initial low activity as the terrace of the Co(0001) surface, which can dissociate CO through intermediate formyl formation,³⁵ but initially mainly produces methane, will change topology in the course of the reaction. The increasing concentration of C atoms will destabilize the surface, which will reconstruct and will generate the more reactive step-edge sites. These sites will dissociate CO with a lower activation barrier. This will not only increase the overall rate of the catalytic reaction, which is rate limited by the rate of C–O bond cleavage, but will also favor formation of long-chain hydrocarbon molecules.³⁵

However, when the concentration of surface C atoms increases further, they will tend to poison the catalytically reactive centers, which will initiate deactivation of the catalysis by carbon overlayer deposition. As Valero et al.¹¹ suggest, this may also be the consequence of graphene formation. It is well-known that step-edges also may initiate graphene formation, which then will grow over a surface terrace.^{3,8,9} In this process the initial type of surface reconstruction with incorporation of subsurface C atoms will be overtaken by graphene formation.

Molecular dynamics simulations are also presented that support the hypothesis that the particle size dependence of the Co-catalyzed Fischer–Tropsch process relates to reduced stability of reactive step-edge sites on smaller particles. It is found that adsorbed C will induce formation of step-edge sites by reconstruction of the dense Co(0001) surface, but only when the surface is sufficiently large.

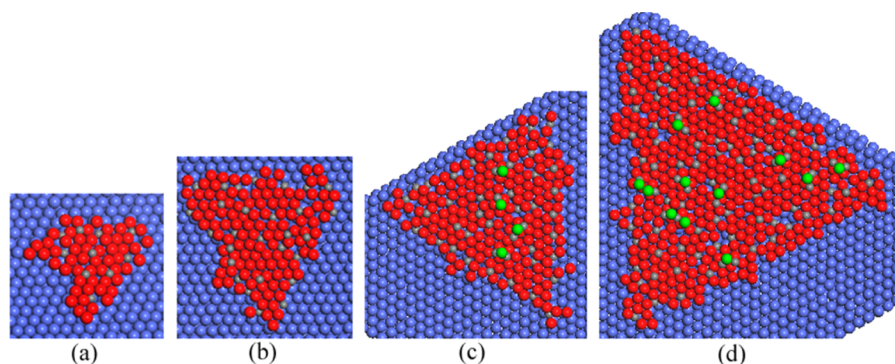


Figure 10. Snapshots of four different terrace sizes (after a simulation time of 0.5 ns). The initial C coverage (12.5%) is the same as used in the full-layer simulations. The terrace sizes are 2.5, 3.7, 5.0, and 7.6 nm for panels a, b, c, and d, respectively. The edges are due to periodic boundary conditions. The carbon atoms are shown in gray, cobalt bottom terrace atoms in blue, ad-layer cobalt atoms in red, and pop-up atoms in green.

A newly developed reactive force field (ReaxFF) is demonstrated to be suitable for molecular dynamics simulations of such surface transformations of the Co surface induced by C atoms. The activation energy for the induction period that gives local surface atom displacements without formation of step-edge sites is typical for metal atom diffusion, whereas the activation energy for the Co atom popping up process is similar to that for diffusion of a C atom into a subsurface layer.

■ ASSOCIATED CONTENT

Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/cs501484c.

Details of simulations, radial distribution function of MD simulated structures, interatomic distances, and force field parameters ([PDF](#))

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) *Introduction to Surface Chemistry and Catalysis*; Somorjai, G. A., Ed.; Wiley-Interscience: New York, 1994.
- (2) *Reactions at Solid Surfaces*; Ertl, G., Ed.; Wiley: Hoboken, NJ, USA, 2009.
- (3) Abild-Pedersen, F.; Nørskov, J. K.; Rostrup-Nielsen, J. R.; Sehested, J.; Helveg, S. *Phys. Rev. B* **2006**, *73*, No. 115419.
- (4) Somorjai, G. A.; van Hove, M. A. *Prog. Surf. Sci.* **1989**, *30*, 201–231.
- (5) Ertl, G. *Science* **1991**, *254*, 1750–1755.
- (6) Bowker, M. *Top. Catal.* **1996**, *3*, 461–468.
- (7) Armbrüster, M.; Behrens, M.; Cinquini, F.; Föttinger, K.; Grin, Y.; Haghofer, A.; Klötzer, B.; Knop-Gericke, A.; Lorenz, H.; Ota, A.; Penner, S.; Prinz, J.; Rameshan, C.; Révay, Z.; Rosenthal, D.; Rupprechter, G.; Sautet, P.; Schlögl, R.; Shao, L.; Szentmiklósi, L.; Teschner, D.; Torres, D.; Wagner, R.; Widmer, R.; Wownsick, G. *ChemCatChem* **2012**, *4*, 1048–1063.
- (8) Wu, M.; Goodman, D. W. *J. Am. Chem. Soc.* **1994**, *116*, 1364–1371.
- (9) Wu, M.; Goodman, D. W.; Zajac, G. W. *Catal. Lett.* **1994**, *24*, 23–30.
- (10) Weststrate, C. J.; Kızılkaya, A. C.; Rossen, E. T. R.; Verhoeven, M. W. G. M.; Ciobica, I. M.; Saib, A. M.; Niemantsverdriet, J. W. *J. Phys. Chem. C* **2012**, *116*, 11575–11583.
- (11) Valero, M. C.; Raybaud, P. *J. Phys. Chem. C* **2014**, *118*, 22479–22490.
- (12) Schulz, H.; Nie, Z.; Ousmanov, F. *Catal. Today* **2002**, *71*, 351–360.
- (13) Gelten, R. J.; Jansen, A. P. J.; van Santen, R. A.; Lukkien, J. J.; Segers, J. P. L.; Hilbers, P. A. J. *J. Chem. Phys.* **1998**, *108*, 5921.
- (14) Hellman, A.; Resta, A.; Martin, N. M.; Gustafson, J.; Trincherro, A.; Carlsson, P.-A.; Balmes, O.; Felici, R.; van Rijn, R.; Frenken, J. W. M.; Andersen, J. N.; Lundgren, E.; Grönbeck, H. *J. Phys. Chem. Lett.* **2012**, *3*, 678–682.
- (15) Chin, Y.; Buda, C.; Neurock, M.; Iglesia, E. *J. Am. Chem. Soc.* **2013**, *135*, 15425–15442.
- (16) Schulz, H.; Nie, Z.; Ousmanov, F. *Catal. Today* **2002**, *71*, 351–360.
- (17) Ciobica, I. M.; van Santen, R. A.; van Bergec, P. J.; van de Loosdrecht, J. *Surf. Sci.* **2008**, *602*, 17.
- (18) Ge, Q.; Neurock, M. *J. Phys. Chem. B* **2005**, *109*, 22341–22350.
- (19) Zhao, Y.-H.; Liu, J.-X.; Su, J.-X.; Sun, K.; Li, W.-X. *ChemCatChem* **2014**, *6*, 1755–1762.
- (20) van Santen, R. A. *Acc. Chem. Res.* **2009**, *42*, 57–66.
- (21) den Breejen, J. P.; Radstake, P. B.; Bezemer, G. L.; Bitter, J. H.; Froseth, V.; Holmen, A.; de Jong, K. P. *J. Am. Chem. Soc.* **2009**, *131*, 7197–7203.
- (22) Loveless, B. T.; Buda, C.; Neurock, M.; Iglesia, E. *J. Am. Chem. Soc.* **2013**, *135*, 6107–6121.
- (23) Mager-Maury, C.; Bonnard, G.; Sautet, P.; Raybaud, P. *ChemCatChem* **2011**, *3*, 200.
- (24) Reuter, K.; Frenkel, D.; Scheffler, M. *Phys. Rev. Lett.* **2004**, *93*, No. 116105.
- (25) Reuter, K.; Scheffler, M. *Phys. Rev. Lett.* **2003**, *90*, No. 046103.
- (26) van Beurden, P.; Bunnik, B. S.; Kramer, G. J.; Borg, A. *Phys. Rev. Lett.* **2003**, *90*, No. 066106.
- (27) Zhang, X. Q.; Offermans, W. K.; van Santen, R. A.; Jansen, A. P. J.; Scheibe, A.; Lins, U.; Imbühl, U. *Phys. Rev. B* **2010**, *82*, No. 113401.
- (28) Zhang, X. Q.; Iype, E.; Nedea, S. V.; Jansen, A. P. J.; Szyja, B. M.; Hensen, E. J. M.; van Santen, R. A. *J. Phys. Chem. C* **2014**, *118*, 6882–6886.
- (29) van Duin, A. C. T.; Dasgupta, S.; Lorant, F.; Goddard, W. A. J. *Phys. Chem. A* **2001**, *105*, 9396–9409.
- (30) Joshi, K.; van Duin, A. C. T.; Jacob, T. *J. Mater. Chem.* **2010**, *20*, 10431–10437.
- (31) LaBrosse, M. R.; Johnson, J. K.; van Duin, A. C. T. *J. Phys. Chem. A* **2010**, *114*, 5855–5861.
- (32) Neyts, E. C.; Shibuta, Y.; van Duin, A. C. T.; Bogaerts, A. *ACS Nano* **2010**, *4*, 6665–6672.
- (33) Iype, E.; Hutter, M.; Jansen, A. P. J.; Nedea, S. V.; Rindt, C. C. M. *J. Comput. Chem.* **2013**, *34*, 1143–1154.
- (34) Available at <http://www.scm.com>.
- (35) van Santen, R. A.; Markvoort, A. J.; Filot, I. A. W.; Ghouri, M. M.; Hensen, E. J. M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 17038–17063.
- (36) van Santen, R. A.; Neurock, M.; Shetty, S. G. *Chem. Rev.* **2010**, *110*, 2005–2048.
- (37) Honkala, K.; Hellman, A.; Remediakis, I. N.; Logadottir, A.; Carlsson, A.; Dahl, S.; Christensen, C. H.; Nørskov, J. K. *Science* **2005**, *307*, 555–558.
- (38) Loffreda, D.; Simon, D.; Sautet, P. *J. Catal.* **2003**, *213*, 211.
- (39) van Harveld, R.; van Montfoort, A. *Surf. Sci.* **1966**, *4*, 396–430.
- (40) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *48*, 13115–13118.
- (41) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169–11186.
- (42) Wilson, J.; de Groot, C. J. *J. Phys. Chem.* **1995**, *99*, 7860–7866.
- (43) Zhao, Y.-H.; Liu, J.-X.; Su, H.-Y.; Sun, K.; Li, W.-X. *ChemCatChem* **2014**, *6*, 1755–1762.
- (44) Li, B.; Zhang, Q.; Chen, L.; Cui, P.; Pan, X. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7848–7855.