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Intermediates in the Formation of Graphitic Carbon on a Flat FCC-Co(111) Surface

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Possible intermediates in the formation of carbon deposits in cobalt -based Fischer−Tropsch synthesis were investigated using DFT. Larger carbon clusters are more stable than adsorbed atomic carbon, with linear carbon structures being (slightly) more stable than branched structures. The formation of aromatic structures further stabilizes the carbon cluster. A lower estimate for the barrier of diffusion of atomic carbon on flat FCC-Co(111) was estimated to be ca. 42 kJ/mol implying relative high mobility under typical Fischer−Tropsch conditions. A reaction pathway for the formation of graphene on a flat surface is proposed.

1. Introduction

Catalyst deactivation represents a loss in activity and/or selectivity over time which is a serious concern in industrial processes.[1] The nature of deactivation can vary for different systems and it is important to understand whether these deactivation pathways can be inhibited.[2] Carbon deposition has been suggested as one of the possible mechanisms of deactivation in the Fischer−Tropsch synthesis.[3] It has been reported for Fe-,[4–6] Co-,[7–10] and Ni-based systems.[11–13] Excessive carbon deposition may result in catalyst encapsulation, pore blockage, and, at extreme conditions, catalyst breakage.[2,4] The formation of deactivating carbon deposits is a problem that needs to be understood and prevented if possible, by tuning the operating conditions or catalyst parameters.

At low carbon coverage, the Co surfaces can be reconstructed by adsorption of atomic carbon,[14] while at high carbon coverage, various types of carbon have been suggested, viz. polymeric and amorphous films, filaments, fibers, whiskers, platelets, and graphite.[1]

In Ni-based reforming catalysts, encapsulating carbon and pyrolytic carbon[11] have been suggested to be a possible cause of deactivation. The deposition of carbon has been studied experimentally on Ni-based catalysts[15–17] to investigate types of carbon deposited, as well as the effect of conditions on the type of carbon deposited. Carbon structures, which can be formed on Ni catalysts, have been investigated using DFT[11,18–21] and grand canonical Monte Carlo simulation.[22,23] DFT studies suggested the formation of graphitic carbon structures to occur at the stepped surfaces as suggested by experimental work on Ru.[24] DFT studies further showed that graphene and small carbon clusters are stable on flat Ni surfaces.[20,21] Monte Carlo simulation[22,23] showed the formation chain-like structures as intermediates for graphene formation on a Ni(111) and Ni(100) surfaces.

Based on experimental and theoretical work, mechanisms have been proposed for carbon formation[25,26] suggesting that

for Ni-based catalysts, stepped surfaces play an important role in carbon deposition. As a consequence, suggestions were made that the selective poisoning of steps should reduce carbon deposition for Ni catalysts.[12,13] Selective poisoning of Co catalysts[7] has shown that the types of carbon deposits formed are different when poisoned by sulfur, but carbon deposition did not stop completely. The question therefore arises whether the elemental carbon overlayers can only form at stepped surfaces or whether a "step free" surface would also be able to form carbon deposits and overlayers. A thorough understanding of these mechanisms for formation of carbon deposits is required to be able to prevent the formation of these carbon deposits in cobalt-based Fischer−Tropsch catalysts.

Pathways for carbon formation on the flat FCC-Co(111) surface have not been proposed yet. It was recently shown[27] that C−C coupling on flat surfaces is much more facile than on stepped surfaces. Furthermore, alternative pathways on flat surfaces would become more important for small crystallites in the nanometre range where the number of steps should be minimal and consequently not play a major role in carbon overlayer formation. Studies on carbon cluster or sheet formation have not been reported for FCC-Co surfaces, where the FCC-Co is stable in small crystallites with diameter below 120 nm[28] (the surfaces for the HCP-Co(0001) and FCC-Co(111) are similar; the subsurface layers has an ABAB configuration for HCP-Co and ABCABC configuration for FCC-Co). Here we focus on the formation of carbon clusters on FCC-Co(111) to elucidate pathways for the formation of carbon overlayers.

2. Methodology

In this work a systematic study of stability of atomic carbon, carbon clusters, and semi-infinite and infinite carbon sheets was performed. This should serve as a starting point in the understanding of aspects which play a role in carbon sheet formation on cobalt-based catalysts. Intermediates under consideration might be formed by sequential addition of atomic carbon to existing carbon clusters on the surface. This analysis is therefore not an exhaustive study of all possible pathways but rather shows the stability trends of the intermediates with increase in size of the carbon clusters. The energy of carbon addition to existing clusters in the growth process can be used

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12900   *J. Phys. Chem. C, Vol. 112, No. 33, 2008*
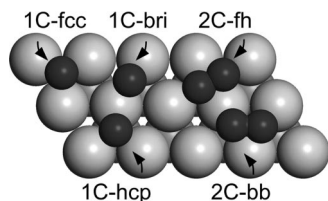
Swart et al.

Figure 1. Adsorbed atomic carbon on fcc (1C-fcc), hcp (1C-hcp) and bridge site and carbon dimers (2C-bb and 2C-fh) investigated as possible intermediates in the formation of graphene.
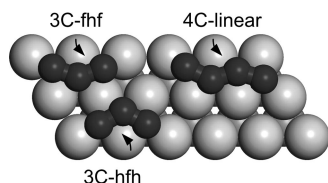

Figure 2. Trimers (3C-fhf: two carbon atoms on fcc sites one on hcp site in between; 3C-hfh: two hcp and one fcc site in between) and linear tetramer investigated as possible intermediates in the formation of graphene.
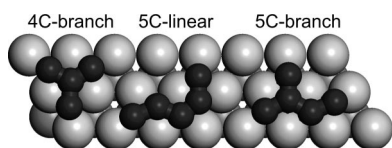

Figure 3. Larger linear and branched clusters investigated as possible intermediates in the formation of graphene.
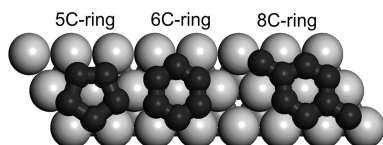

Figure 4. Ring clusters investigated as possible intermediates in the formation of graphene.
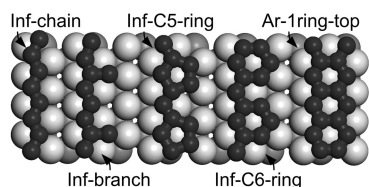

Figure 5. Infinite structures in one dimension as possible intermediates in the formation of graphene.

to propose a mechanistic pathway for carbon deposition. The stability of carbon atoms adsorbed on a FCC-Co(111) surface and small carbon clusters as shown in Figures 1–4 was determined. Nucleation of carbon clusters may take place by coupling of atomic carbon species to form dimers, trimers, and larger carbon clusters. These clusters may grow further forming branched (see Figure 3) and ring (see Figure 4) structures. Larger clusters may be represented by infinitely long chains as shown in Figure 5. Adding an atom to an infinite chain would result in branching. Subsequent addition of carbon may lead to ring formation of the surface carbon species. Further addition of carbon would result in formation of connected carbon rings (see Figure 6) and eventually form graphene or graphite.

For the small clusters, the clusters are named by the number of carbon atoms and whether the atoms are on the fcc (f), hcp (h), or bridge (b) site. For larger clusters, the number of carbon atoms is used along with the character such as linear, branched or ring. For the infinite chains, the clusters are named after the "functional" group to the chain such as a branch, C5-ring or
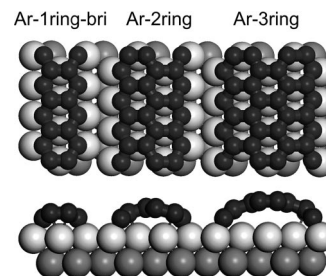

Figure 6. Optimized geometries for infinite multiple ring structures viewed from the top and side.
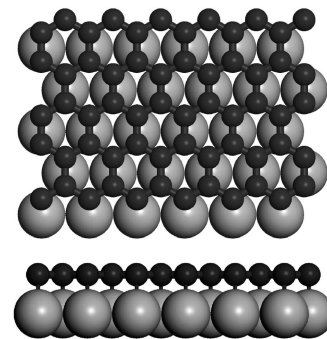

Figure 7. Optimized geometry for graphene on FCC-Co(111) with the center of the ring above the bridge position.

C6-ring. For the infinite aromatic rings (Ar), the structures with one ring in the finite dimension are named according to the adsorption site, whether the center of the ring is above the bridge or top site. The larger aromatic structures are only named by the number of rings in finite dimension (Figure 7).

All of these structures were calculated in periodic unit cells. One of the limitations of the periodic cell approach is that extremely large unit cells are required to fit the carbon structures into the unit cell with minimal lateral interactions with neighboring clusters. For this reason linear clusters with more than 5 atoms were not studied since unit cells larger than p(2 × 3) would be required. Lateral interactions must be minimized since the resulting destabilization would not provide the true stability of the cluster. The energy of the carbon cluster was found to be destabilized by at least 20 kJ/mol carbon (for atomic carbon, dimers and branched chains), if surface cobalt atoms are connected to carbon atoms of different clusters. The surface models were set up such that carbon atoms in the structures do not share surface cobalt atoms with neighboring clusters. This was found to drastically reduce lateral interaction and give a good representation of the stability of the cluster. These can be further reduced, by lowering the surface coverage from 25% to 11%. This resulted in a slight stabilization for the adsorption energy of atomic carbon on FCC-Co(111) by 3 kJ/mol carbon (a similar stabilization of the adsorption energy through lowering of the surface coverage was obtained for the infinite Ar-1ring-top structure). Therefore, surface coverage of carbon of 25% was used. A p(2 × 2) surface unit cell was used for the carbon clusters containing up to three atoms, resulting in minimal lateral interactions, but for larger clusters p(2 × 3) and p(3 × 3) surface unit cells were used. The stability of most of the structures in Figure 5 were determined using a p(2 × 3) surface unit cell. The stability of the larger structures (see Figure 6), Ar-1ring-bri and Ar-2ring-bri were determined using a r(1 × 4) surface unit cell, and for the Ar-3ring-bri and Ar-4ring-bri structures, a p(1 × 6) surface unit cell was used.

The calculated energies for the adsorbed atomic species and clusters ($E_{ads-carbon}$) are reported as the formation energy of

Intermediates in the Formation of Graphitic C

J. Phys. Chem. C, Vol. 112, No. 33, 2008 **12901**

carbon clusters from carbon monoxide (E_{CO}) and hydrogen (E_{H_2}) yielding water (E_{H_2O}) as the byproduct. The energy per carbon atom adsorbed on the slab (E_{ads-FT}) can be given by

$$CO + H_2 \leftrightarrow \frac{1}{n}C_n^* + H_2O \qquad (1)$$
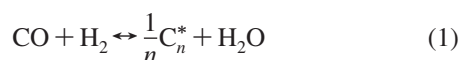
$$E_{ads-FT} = \frac{(E_{ads-carbon} + nE_{H_2O}) - (nE_{CO} + nE_{H_2} + E_{slab})}{n} \times$$

$$\text{(kJ/mol carbon)} \quad (2)$$

The energy of cluster formation can also be calculated relative to atomic carbon in the gas phase. The energy for adsorbed carbon relative to an atomic gas phase atom is 902 kJ/mol carbon lower than the energy from surface carbon formed from H_2 + CO for the equation shown above.

It should be noted that this energy would not give the strength of interaction with the surface but only the thermodynamic stability of the carbon species relative to gas phase conditions. This serves as a thermodynamic indicator for the stability of these surface species (atoms or clusters) under Fischer–Tropsch conditions. The stability of the various carbon containing clusters relative to graphene adsorbed on the surface can be compared by comparing the energy of formation of the carbon cluster to the energy of formation of graphene on FCC-Co(111) and water from synthesis gas (−192.1 kJ/mol C).

Calculations were performed with only carbon on the FCC-Co(111) surface. Thus, the results are applicable to situations, in which oxygen removal via water formation on the surface is fast, ensuring no hydrogen or oxygen species originating from synthesis gas on the surface. Hydrogenated species were not considered in this study.

Spin polarized DFT calculations for these adsorbed structures have been performed on a 3D periodic slab model using VASP.[29–32] Vanderbilt type pseudopotentials[33] as generated by Kresse and Hafner[34] was used within the PW91-GGA parametrization[35] of exchange and correlation interactions. This formulation has been shown to give a good representation for the properties of transition metal surfaces; a bulk lattice parameter for cobalt of 2.501 Å[36] was determined, which was also used in this study. Different unit cells were used for efficient calculation of adsorption structures with the smallest reasonable unit cell, due to the variation in the size of the clusters. Various Monkhorst–Pack[37] k-point grids have been used for these unit cells ranging from 15 × 15 × 1 for a p(1 × 1) unit cell to 5 × 5 × 1 for a p(3 × 3) unit cell. Along with these settings, an energy cutoff of 400 eV and a Methfessel–Paxton[38] smearing with $\sigma = 0.1$ eV was used to ensure accurate energies with small errors due to smearing of less than 10 meV per unit cell for all systems (containing at least 20 metal atoms). A slab thickness of 5 layers for the FCC-Co(111) surface gave good convergence for adsorption energies (within 2 kJ/mol carbon relative to adsorption energies on a 7 layer slab for atomic carbon species and graphene sheets). Slabs were separated by 8 vacuum layers, resulting in a separation distance of at least 10 Å between adsorbed carbon structures on the surface. Geometry optimizations were performed by relaxing all atoms through minimization of the energy to within 1×10^{-4} eV for the slab and forces to within 0.02 eV/ Å.

A vibrational analysis was also performed on the 1C-hcp, 2C-fh, 3C-fhf, 4C-branched, Inf-1ring-bri, and adsorbed graphene structures to ensure that the zero point energy correction does not affect the stability trends. The zero-point vibrational energies were 9.4, 10.3, 10.4, 4.4, 2.4, and 6.7 kJ/mol carbon for these structures respectively, suggesting that the zero-point energy
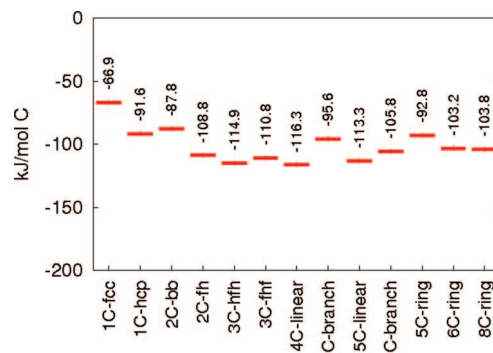

Figure 8. Energies for the finite carbon clusters (see Figures 1−4) relative to carbon monoxide and hydrogen (synthesis gas) and water.

would not affect the energy trends. The zero-point energy corrections are not included in the reported energy trends.

3. Results

Stability Trends of Carbon Species. The adsorption energies of finite carbon clusters on FCC-Co(111) relative to the gas phase molecules (CO, H_2, and H_2O) are given in Figure 8. Thermodynamically stable geometries for atomic species are such that the carbon atoms are located in the 3-fold hollow site, as previously reported before,[39,40] with Co–C distances of 1.80 Å. The energy of formation is −66.9 kJ/mol carbon on the fcc and −91.6 kJ/mol carbon on the hcp site. The energy difference suggests a substantial site preference for the hcp site, due to the interaction between adsorbed carbon and the subsurface cobalt atom. Atomic carbon species are not stable in the on-top position or on bridge sites (carbon optimized to the hollow (fcc and hcp) positions from the top and bridge starting geometries). A quasi-Newton approach minimizing only the forces yielded a stable adsorption at the bridge site with an energy of −49.6 kJ/mol carbon. A vibrational analysis showed adsorbed carbon on the bridge site to have one imaginary frequency. Thus, the bridge site is a transition state for the diffusion of atomic carbon from the fcc to the hcp site.

Carbon clusters were found to be more stable than atomic carbon species (see Figure 8). All of the chain-like (linear) clusters were found to have the most stable geometries with the carbon atoms in hollow sites. Only the stable dimer geometries are shown in Figure 1. Other starting geometries optimized to either of the two stable geometries. The 2C-fh dimer has a C–C distance of 1.32 Å with Co–C distances of 1.89 and 2.05 Å, respectively. The C–C distances for the trimer (3C-fhf and 3C-hfh) are both 1.35 Å, whereas the Co–C distances range between 1.87 and 2.01 Å with the middle carbon atom slightly lifted. The C–C bond lengths are slightly distorted for the linear tetramer (4C-linear) to 1.32 and 1.35 Å and for the linear pentamer (5C-linear) to between 1.32−1.39 Å. The Co–C bond lengths for the linear tetramer (4C-linear) and pentamer (5C-linear) are similar to those observed for the trimer. The terminating carbon atoms on the cluster bind stronger to the surface than internal carbon atoms. These distances show that the interaction with the surface decreases slightly with an increase in cluster size. All linear clusters are more stable than atomic species with adsorption energies ranging between −108.8 to −116.3 kJ/mol carbon. An infinite linear chain as shown in Figure 5 also has a stability in this range and similar bond lengths (Co–C distances are 2.03 Å, whereas the C–C distances are 1.33 Å).
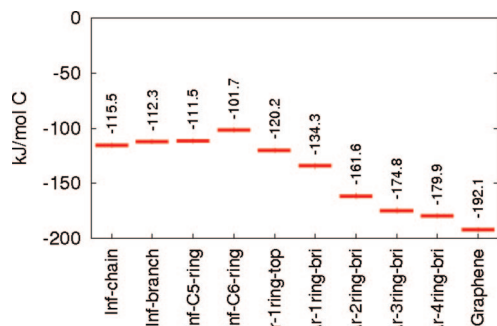
Figure 9. Energies for clusters with one or more infinite dimensions (see Figures 5 and 6) relative to carbon monoxide and hydrogen (synthesis gas) and water.

Formation of branched clusters is also possible, but calculations show that the finite branched clusters (4C-branch and 5C-branch) are less stable than linear clusters (4C-linear and 5C-linear) with the same number of atoms. The tertiary carbon atoms are lifted from the surface indicating a weaker interaction with the surface compared to linear clusters. The branched tetramer (4C-branch) has C−C distances of 1.47 Å while the Co−C distances vary from 1.87−1.95 Å for the terminating atoms and is 2.27 Å for the tertiary carbon atom. Similar bonding distances are observed for the branched pentamer (C5-branch) where the C−C bond-lengths to the tertiary carbon atom vary between 1.44 and 1.48 Å while the C−C bond-length between the internal and terminating carbon atom is 1.35 Å.

Similar results were obtained for the infinite branched chain (inf-branch) with C−C distances to the branched atoms of 1.44 Å and C−C distances between internal carbons are only 1.35 Å. The Co−C atoms for carbon connected to tertiary carbon atoms range between 1.87−1.95 Å, while the Co−C distances for internal carbon atoms range between 2.01−2.28 Å. For the tertiary carbon atoms, the Co−C bonds range between 2.26−2.38 Å. This is also the case for branched ring (8C-ring). It can thus be concluded that tertiary carbon atoms have a decreased interaction with the surface and therefore a greater Co−C distance. This can be explained by the filling of the sp$_2$-like orbitals of tertiary carbon atoms with electrons of surrounding carbon atoms. The terminating carbon atoms of the cluster would not have this stabilization and remain close to the surface for small linear clusters or move toward the surface for larger branched clusters and sheets.

Ring structures can also be formed. The 6C-ring and 5C-ring structures are more stable than the atomic species but not as stable as the linear cluster of the same size. The branching of these ring clusters (8C-ring) does not severely affect the stability of the clusters as seen in Figure 9. The Inf-C5-ring structure formed by linking up the C5- structures (see Figure 5) is stabilized in comparison to 5C-ring, while the Inf-C6-ring has a similar stability to the finite ring structures. When an infinite aromatic ring structure (Ar-1ring-top) is formed by adding one carbon atom, a significant stabilization is obtained (see Figure 9). The Co−C bonds are slightly longer than in finite clusters with the bridged carbon atoms having a Co−C distance of 2.32 Å, whereas the bridging (internal) carbon atoms have a Co−C distance of 2.12 Å. The C−C distances are 1.50 Å between the branched atoms, whereas the other C−C bond-lengths are 1.44 Å.

This Ar-1ring-top structure can be further stabilized by ca. 10 kJ/mol carbon by shifting the structure to the ring-bridge site (Ar-1ring-bri) where the center of the ring is above the bridge site. The optimized structure on this site had C−C

distances of 1.48 Å between branched atoms and 1.44 Å for the other C−C bonds. The carbon atoms in this structure are not directly above the hollow sites anymore, but two Co−C distances are lengthened while one is shortened. The bridging/internal carbon atoms have nearest Co−C distance of 1.89 Å while the other two Co−C distances are 2.46 Å. A similar trend is observed for the branched atoms with one Co−C distance of 2.01 Å while the other two Co−C distances are between 2.81 and 2.84 Å. The bridge/internal atoms would terminate these aromatic clusters and therefore have a stronger interaction with the surface. For the aromatic structures, the carbon atoms have a sp$_2$-like orbital structure and the tilting of the terminating atom toward a metal atom would fill the sp$_2$-like orbital and stabilize the cluster. The ring-bridge site would therefore be ideal to fill the sp$_2$-like orbitals.

Larger ring structures were also calculated up to aromatic 4-ring structures where the aromatic 1-, 2-, and 3-ring structures are shown in Figure 6. All these structures are most stable on the ring-bridge type geometries. These larger aromatic structures are significantly more stable compared to the linear clusters (see Figure 9). For these structures, the branched carbon atoms start lifting from the surface forming an "arch"-like structure. The Co surface atoms can then easily fill the sp$_2$-like orbitals of the cluster terminating carbon atoms. The Co−C distances for the cluster terminating carbon atoms are 1.91 Å and 2.23 Å. The carbon atoms at the center of the cluster are approximately 2.8 Å above the surface for the Ar-2ring-bri structure. The Ar-3ring-bri cluster lifts up to 3.1 Å in the center of the cluster while the Ar-4ring-bri cluster lifts up to approximately 3.3 Å above the surface. The C−C distances for all the larger ring structures range between 1.43 and 1.45 Å, which is close to the 1.42 Å of graphene.

The energy of the flat graphene sheet on the surface was the most stable of all the aromatic structures. The graphene sheet had a Co−C distance of 2.12 Å, which is significantly less than the maximum Co−C distance observed for the arched aromatic structures. This is ascribed to the tendency of the system to accommodate both the aromaticity of the cluster and the metal−carbon interaction required to saturated the terminating sp$_2$-bonds.

Coverage Effects. Carbon clusters are stable at a high coverage, but carbon atoms are not. The interaction between adsorbed atomic carbon at coverage above 0.25 ML is repulsive, rendering a 1 ML coverage of carbon atoms unstable relative to the Fischer−Tropsch gas phase conditions due to a positive adsorption energy. The infinite chain however at an effective coverage of 1 ML is even more stable than adsorbed carbon atoms at 0.25 ML. Very stable clusters can be formed, when the local coverage is high enough to form C−C bonds. The high stability at high coverage can be attributed to formation of C−C bonds rather than interaction of the carbon atoms or clusters with the surface.

From a thermodynamic point of view, high carbon coverages will result in the formation of carbon clusters. Cluster growth can be seen as a surface phase segregation or "island" formation where it is more favorable to have a region of high carbon coverage (carbon cluster with coverage of up to 2 ML) and a region of low coverage than an even distribution of atomic carbon on the surface.

Carbon clusters being much more stable than adsorbed, individual atoms at high coverage are destabilized at high coverages when they are to close to other clusters. Similar to the atoms at high coverage, the lateral interaction between clusters can become large enough to have a destabilizing effect.

Intermediates in the Formation of Graphitic C

J. Phys. Chem. C, Vol. 112, No. 33, 2008 **12903**

This destabilizing effect can be overcome by forming bonds between the clusters to form a larger surface cluster.

4. Discussion

All proposed carbon clusters on FCC-Co(111) are stable with respect to the conditions of the Fischer−Tropsch synthesis and can thus be formed under these conditions. Furthermore, carbon clusters are more stable than adsorbed atomic carbon demonstrating the stabilizing effect obtained through C−C coupling. The carbon clusters are less stable than adsorbed graphene on FCC-Co(111). Formation of graphene starting from atomic carbon adsorbed in FCC-Co(111) is energetically a downhill process, which may lead to catalyst deactivation through the formation of a carbon overlayer (although this depends also on the crystallite size).

Growth of carbon clusters may occur through surface carbon−carbon coupling. This may happen faster on flat surfaces than on stepped surfaces. It has been shown that carbon−carbon coupling on flat Co(0001) surface is much more facile than on a stepped Co(0001) surface.[27] Carbon−carbon coupling not only requires a facile transition state but also adsorbed atomic carbon species in close proximity. Atomic carbon is favored at low coverage. Diffusion of atomic carbon is thus an important subprocess in the carbon−carbon coupling. Atomic carbon on stepped surfaces is expected to have a lower mobility than carbon atoms adsorbed on a flat surface, due to the stronger bond to low coordination surface atoms located in a step.[18] The mobility of atomic carbon adsorbed on FCC-Co(111) can be estimated from the energy of formation of atomic carbon on the bridge and top sites. These geometries are not stable, but can be used to suggest a lower limit to the barrier of diffusion of atomic carbon on the surface. The energy of formation of carbon on the bridge site is found to be ca. −49 kJ/mol suggesting a barrier for diffusion of atomic carbon from the hcp to fcc site of ca. 42 kJ/mol carbon. The barrier for diffusion of carbon from the fcc to the hcp site is ca. 18 kJ/mol carbon giving a total barrier of diffusion from the hcp to hcp site over the FCC-Co(111) surface of ca. 42 kJ/mol carbon. This agrees well with the barrier of 52 kJ/mol carbon suggested for Ni.[18] The diffusion of atomic carbon on FCC-Co(111) should therefore be possible under typical Fischer−Tropsch conditions of ca. 500 K. The mobility of larger carbon clusters is expected to be much less that that of the smaller clusters, and especially atomic carbon. A translation of larger clusters would require a concerted movement over the surface since the C−C bonds is very strong. Such a concerted movement would also lead to all the atoms being destabilized over the bridge sites simultaneously.

Growth of carbon clusters is therefore thought to occur initially from the attachment of adsorbed atomic carbon to the larger structures, resulting in a stabilization of the larger structures. The formation of linear chains by sequential addition of adsorbed atomic carbon is favored over the formation of branched and cyclic. Hence, the formation of chain-like structures on the FCC-Co(111) surface can be expected, as was shown for nickel using Monte Carlo simulation.[22] Branches can be formed and are more likely to form with longer chains, since the energy difference between the addition of atomic carbon to the terminal carbon atom and the formation of a branch is only ca. 3−4.5 kJ/mol C added to a chain. The formation of larger carbon clusters is even favored at relative high coverage of the surface. Linkage between adjacent chains may lead to the formation of more stable aromatic structures, such as Ar-1ring-top. This may further stabilize through a shift in the adsorption position, i.e., Ar-1ring-bri. Further linkage with long chains or

sequential addition of carbon may lead to growth of the aromatic structure and in the end lead to the formation of graphene on the surface.

From this growth model, the formation of carbon sheets on cobalt does not require a stepped surface or defects for nucleation and occurs fairly easily on the flat FCC-Co(111) surface (it has been proposed that steps act as preferential nucleation sites,[11] but the relative high mobility of adsorbed atomic carbon negates the presence of these special nucleation sites). Selective poisoning of the step defects would thus not necessarily inhibit the formation of graphene, since stable intermediates can be formed on flat surfaces. A certain minimum number of adjacent Co surface atoms on the flat surface are required to nucleate carbon clusters and grow the graphitic ring structures. It might thus be postulated that, if a sufficient number of adjacent surface metal atoms is not available, carbon structures can not be formed. This could be the case if immobile atoms such as gold or sulfur are present on the surface, limiting the space on the surface available for cluster growth and "poisoning" the surface for cluster growth. It was postulated that these poisoning atoms would have a greater inhibiting effect on the formation of carbon deposits which require a large surface ensemble than, e.g., methanation which requires a smaller ensemble of surface atoms.[13] Sulfur poisoning by Kim et al.[7] showed the formation of less "graphitic" carbon and more "amorphous" carbon. This was postulated to be due to the fact that small clusters can not grow to sheets but rather form a nanocrystalline agglomeration of amorphous carbon.

Step defects may stabilize the aromatic clusters further and thus facilitating carbon overlayer formation. It was shown, that in aromatic structures the clusters start bending to accommodate the sp2-like orbitals of the terminating carbon atoms of the cluster. This termination can also easily occur at a step defect in the surface. This might prevent bending of the part of the cluster down to the surface in order to fill the sp2-like orbitals of the cluster terminating atoms. It was shown that carbon sheets connected to step defects would remain flat on the surface as shown on Ni.[17] For relatively small carbon structures, having one side of the aromatic cluster attached to a step does not necessarily result in a flat sheet, as seen for Ni[18] where bent structures were observed in order to saturate the sp2 bonds of the terminating carbon atoms. Cluster termination may also occur with hydrogen which would allow the aromatic cluster to remain "flat" on the surface.

The bent structures have only been calculated with one infinite dimension. The behavior of a two-dimensional cluster would probably be slightly different since the sp2-like bonds must then be saturated in two dimensions. The compensation for the sp2-like orbitals of the carbon should be more difficult for a two-dimensional cluster since this would require the formation of a "blister" on the surface as reported for Ni.[16]

5. Conclusions

DFT calculations on FCC-Co(111) show that graphene can be formed via stable, smaller carbon clusters on the flat Co surface starting from adsorbed atomic carbon. The preferential adsorption site of atomic carbon is the hcp-site. The formation of linear carbon structures is slightly favored over the formation of branched carbon structures with the same carbon atoms, due to a reduced metal−carbon interaction and carbon−carbon interaction on the tertiary carbon atom. Aromatic clusters were seen to lift off from the flat surface resulting in Co−C distances substantially larger than the Co−C distance for graphene adsorbed on a flat FCC-Co(111)-surface. This is caused by the

need to saturate the terminating sp_2-bonds by forming Co−C-bonds and the need to maintain aromaticity of the system.

Sequential addition of atomic carbon is proposed as the initial step for the formation of carbon overlayers resulting in the formation of (branched) carbon chains. Linkage of carbon chains at high coverage will give rise to the formation of the more stable aromatic clusters. Further growth of these structures, either through addition of atomic carbon or linking-up of longer chains will result in the formation of graphene on the surface. A prerequisite for this mechanism is a relative high mobility of adsorbed atomic carbon, which can be expected on flat surfaces and low coverage, since the barrier of diffusion seems to be in the order of 40−50 kJ/mol.

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