Mechanism of the initial stages of nitrogen-doped single-walled carbon nanotube growth

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Received (in XXX, XXX) Xth XXXXXXXXXX 20XX, Accepted Xth XXXXXXXXXX 20XX
DOI: 10.1039/b000000x

We have studied the mechanism of the initial stages of nitrogen-doped single-walled carbon nanotube growth illustrated for the case of a floating catalyst chemical vapor deposition system, which uses carbon monoxide (CO) and ammonia (NH₃) as precursors and iron as catalyst. We performed first-principles electronic-structure calculations, fully incorporating the effects of spin polarization and magnetic moments, to investigate the bonding and chemistry of CO, NH₃, and their fragments on a model Fe₃₅ icosahedral cluster. A possible dissociation path for NH₃ to atomic nitrogen and hydrogen was identified, with a reaction barrier consistent with an experimentally determined value we measured by tandem infrared and mass spectrometry. Both C-C and C-N bond formation reactions were found to be barrierless and exothermic, while a parasitic reaction of HCN formation had a barrier of over 1 eV.

1. Introduction

Substitutional doping with nitrogen atoms¹⁻³ has been proposed as a possible way for controlling the electronic properties of carbon nanotubes (CNTs). A variety of methods⁴ are available for the synthesis of nitrogen-doped multiwalled carbon nanotubes (N-MWCNTs)⁵. However, synthesis of single-walled nitrogen-doped carbon nanotubes (N-SWCNTs)⁶ has struggled to overcome difficulties foreign to the synthesis of pristine material, which is nowadays produced clean in gram quantities. Efforts to master the synthesis of N-SWCNTs have been hindered by an acute lack of knowledge about the chemistry involved and the growth mechanism⁷⁻⁹, although it should also be noted that despite intensive studies, the mechanism of even pristine CNT growth is still controversial.

Furthermore, although N-MWCNTs have been widely studied, the correlation between their morphology, crystallinity and properties is not completely understood. The base growth mechanism is commonly proposed to be responsible for the characteristic bamboo-shaped structure⁸⁻⁹. This model assumes that the catalyst particles dissociate reactant molecules into N and C atoms, whose incorporation into or onto the catalyst nanoparticle results in the walls being pushed away to form a tubular structure. However, no studies have directly addressed the mechanism by which the precursors decompose. The role of nitrogen in N-MWCNTs formation is suggested to be related to the generation of pentagons along with hexagons¹⁰, because it is believed that the presence of N in the carbon deposit results in surface strain, leading to a ‘pulsed’ effect in which the C/N surface atoms detach from the metal particle intermittently, leading to the compartmentalized structure observed¹¹. However, it should be noted that this model cannot be applied to N-SWCNTs, which obviously cannot exhibit compartmentalized (bamboo-like) structures.

To our knowledge, there is only one tentative model proposed for N-SWCNT growth¹², which further does not discuss the very first stages of growth. Addressing the mechanism of chemical reactions that yield atomic carbon and nitrogen on the catalytic particle¹³ is a crucial first step towards understanding the CVD synthesis of N-SWCNTs. While a decade ago most theoretical studies tried to describe surfaces either on a qualitative level using empirical parameters or invoked rather severe approximate models, there is now a large class of surface system that can be addressed quantitatively based on first principles electronic structure calculation methods¹⁴⁻¹⁵. This progress is mainly due to advances in computer power and the development of efficient algorithms. However, only small precursor molecules can be treated at this level of accuracy, while as noted by Ewels et al.⁶, most N-CNT synthesis methods use complex molecules as their carbon and nitrogen feedstocks.

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†† Electronic Supplementary Information (ESI) available: details of the calculations of absorption geometries and of the HCN formation barrier. See DOI: 10.1039/b000000x
Recently, the synthesis of N-SWCNTs was shown\textsuperscript{16} to be feasible using a floating catalyst reactor with carbon monoxide (CO) and ammonia (NH\textsubscript{3}), with iron as catalyst. This combination of two small precursor molecules, each with only a single C or N atom, presents the simplest possible chemistry. Furthermore, in a floating catalyst approach, the particles interact with precursor molecules in the gas phase, so both the tip and base growth mechanisms are equivalent.

2. Methods

To study the growth mechanism of N-SWCNTs motivated by the experimental system mentioned above\textsuperscript{16}, we performed first principles calculations to understand the chemistry of the precursor reactions on a model Fe\textsubscript{55} catalyst cluster\textsuperscript{14,15}. The target of the modeling was the critical very first stages of N-SWCNT growth. We believe that the adsorbed CO and NH\textsubscript{3} first dissociate into surface atomic C and N,

\[
\text{CO}_{\text{ads}} \rightarrow C_{\text{ads}} + O_{\text{ads}}
\]  
(1)

and

\[
\text{NH}_{3\text{ads}} \rightarrow \text{N}_{\text{ads}} + 3\text{H}_{\text{ads}}.
\]  
(2)

Since there is more carbon than nitrogen available on the cluster, the more numerous carbon atoms then react with each other and the nitrogen atoms to form the hexagonal carbon lattice with nitrogen dopants, starting from

\[
C_{\text{ads}} + C_{\text{ads}} \rightarrow C-C_{\text{ads}}
\]  
(3)

and

\[
C_{\text{ads}} + N_{\text{ads}} \rightarrow C-N_{\text{ads}},
\]  
(4)

while the remaining O atom reacts with additional CO to form CO\textsubscript{2} according to the well-known Boudouard reaction\textsuperscript{15,17}. The reactions above seem simple, but in reality the catalyst surface has a high coverage of the molecular precursors and their fragments, so there are complicated atom-atom interactions.

We concentrated our attention on the simplest CO and NH\textsubscript{3} reactivity and characterized the stable stationary points of the species involved in the reactions mentioned above by means of density functional theory (DFT). For the electronic structure calculations we used DFT with gradient corrections (GGA) for the exchange and correlation (RPBE functional\textsuperscript{18}). The calculations were done with the GPAW code\textsuperscript{19}, with only the valence electrons considered explicitly. Iron has a large magnetic moment, and in the cluster geometry, the spin orientation is subtle. Therefore, we fully incorporated the effects of spin polarization and collinear magnetic moments in our calculations\textsuperscript{14}. The cluster geometry was fully relaxed and free to reconstruct in the presence of adsorbates. Although the calculations were performed at zero temperature, a smearing temperature was used as a convergence parameter in the minimization of the Kohn-Sham energy. The adequacy of the computational parameters has been tested against the calculation of cluster geometry. The method has been detailed in our previous publications\textsuperscript{4,14,15}.

To improve the linking of the simulations to experiments, the reaction barriers extracted from the simulations are compared with experiential values measured using Fourier transform infrared (FTIR) spectroscopy and residual gas analysis (RGA) via mass spectrometry in tandem. Gas-phase thermal decomposition of NH\textsubscript{3} over iron nanoparticles deposited on the walls of the reactor used for N-SWCNT synthesis\textsuperscript{16} was investigated in the temperature range of 590–1090 °C. Concentrations of ammonia and water as a function of reactor maximum wall temperature were measured using FTIR (Gasmet DX-4000), and hydrogen and nitrogen using RGA (MKS Cirrus). The inlet gas consisted of 800 cm\textsuperscript{3}/min of Ar along with 500 ppm of NH\textsubscript{3}.

3. Results

As a first step, we obtained information about the stability of CO, NH\textsubscript{3} and their fragments on the Fe\textsubscript{55} cluster (comparable to earlier results obtained with the VASP code\textsuperscript{14,20}). As the second step, we considered the reaction barriers on the surface. Studying the reaction barriers is more demanding, and special transition-state search algorithms, like climbing-image nudged elastic band (CI-NEB)\textsuperscript{21,22}, were used for their determination, as detailed in previous publications\textsuperscript{4,14,15}.

Based on CO adsorption and C + O co-adsorption data (ESI), a possible dissociation path for CO was mapped out with the NEB method. The smallest activation energy (0.50 eV) was obtained starting from the optimal adsorption geometry with the CO molecule perpendicular to the cluster\textsuperscript{23} (\( \equiv \text{CO} \)). This reaction is exothermic by 0.12 eV. The barrier has been previously measured to be similar\textsuperscript{15,24}, although since the NEB method does not consider entropic effects, a direct comparison is not justified. It should also be noted that this barrier is closer to the experimental results than the previous barrier derived from VASP calculations\textsuperscript{4}.

Correspondingly, based on NH\textsubscript{3,3} + xH (x=0,1,2,3) co-adsorption data (ESI), a possible dissociation path for NH\textsubscript{3} was
We believe this corresponds to the catalytic decomposition of ammonia to about 150 ppm; (II) an intermediate region (740–940 °C), where any additional decomposition of NH₃ is into N₂ and H₂. We believe this corresponds to the catalytic decomposition of NH₃ modeled in the simulations; (III) a high temperature region (990–1090 °C), possibly relevant for NH₃ self-decomposition in the gas phase. An Arrhenius plot of the mole fraction of NH₃ shows the same regions (Fig. 4). Linear least squares fits yield slopes of 28867±241 K, 4978±190 K and 1932±134 K, for the high, middle and low temperature region. These correspond to energies of -2.49±0.02 eV, -0.43±0.02 eV and -0.17±0.01 eV, respectively. Please note that because the decrease of the mole fraction of NH₃ is relevant for the decomposition reaction, the actual barriers come out with the signs reversed.

Similar measurements for the formation of HCN were performed in the same reactor using FTIR with 1000 ppm of NH₃ in a flow of 400 cm³/min CO. Analysis of the Arrhenius plot (ESI Fig. S10) yields a slope of -15689.7 K, giving an activation energy of 1.35 eV. This is consistent with the calculated value (1.65 eV).

4. Discussion

The calculated barrier for NH₃ decomposition (1.0 eV) differs significantly from the measured one (0.43 eV). The small cluster used for the simulation presents high symmetry and limited size of the facet on which the reaction is constrained. Furthermore, it
is also possible that the rate-limiting barrier for the cleaving of the final hydrogen would be slight lower if the calculation would be performed on a bigger, irregular cluster. Unfortunately the actual computational capability restricts the size of the simulated cluster to the one here used. The nitrogen in NH is tetrahedrally sp³ coordinated and the final H is pointed away from the surface, making it more difficult to reach the surface. This is an artifact of the model cluster and most likely not relevant for a real particle, where a step or a defect would lower this barrier. In the reactive conditions at high temperature in the reactor, the suspended nanoparticle could also be at least in part melted, which we could not take into account in the simulations directly. Finally, considering that the theoretical and experimental data are not directly comparable because of the inability of the NEB results to incorporate entropy change, the simulations can be said to be consistent with the experiments.

Alternatives to the HCN formation reaction pathway we identified can be considered. The pathway HN + C is not relevant for direct hydrogen cyanide formation25,26, since the hydrogen in HCN is bonded to the carbon atom, not to the nitrogen (as in hydrogen isocyanide, HNC). Our FTIR measurements specifically detected the formation of HCN, and not HNC. Furthermore, although a formation path HC + N is common for HCN formation from hydrocarbon sources25,26, we do not consider it to be likely since no CH fragments are present in the precursors. Of course, the contribution of some multi-pathways cannot be ruled out by the present work.

Thermodynamically, HCN could also be formed27,28 in a gas phase reaction between CO and NH₃. However, the formation of CH₄, N₂ and H₂O is the most favorable reaction29. Although the formation of HCN is possible in the presence of H₂, that reaction should produce CH₄ as well28, which we do not observe. We also note that the gas phase formation of HCN is typically not observed in non-hydrocarbon (CO + H₂) flames29. In any case, in the presence of a good catalyst (such as the iron nanoparticles), the assisted reaction path will most likely dominate.

Considering the findings as a whole, we believe that the precursor decomposition reactions happen on the nanocluster itself, not at the open edge of the growing N-SWCNT (as proposed by Sumpter et al.15). At least in the case of CO and NH₃, the calculated reaction barriers strongly suggest that the precursors cannot significantly self-decompose without catalyst at the middle temperature region relevant for nanotube growth. Thus nitrogen is incorporated continuously into the nanotube at the root, not at the leading edge. Cap nucleation and detachment are likely similar to what has been proposed for SWCNTs30,31, as are the dynamics of the steady-state growth32-34. However, peculiar to the N-doped case, if the nitrogen feedrate is too large, nanotube growth has been found to terminate16. This can be either due to a saturation and breakdown of the hexagonal carbon network by nitrogen, or to nitrogen blocking the adsorption sites on the cluster and preventing the sufficient input of further carbon35, slowing down and eventually stopping the growth. Another possibility is that NH₃ accelerates the production of active gaseous compounds, which compete with sp² bond formation (etching effect). If the feedrate is suitable, growth continues in the steady state, with the nanotube being continuously doped with nitrogen until the particle leaves the active zone of the reactor16.

The next step would be to study the formation of larger fragments, such as C₂N, C₃N, and beyond. However, this would require larger facets than the Fe₃₅ cluster enables. A larger cluster would in turn require at least a doubling of the number of iron atoms in the simulations, entailing an enormous increase in the computational resources required. Nonetheless, this study marks the first explicit study of the initial stages of N-SWCNT growth. Since no fundamental differences were found in the chemistry of the C and N precursors, we believe that the observed difficulties in synthesizing nitrogen-doped SWCNTs can be explained by the fact that N-MWCNTs can tolerate much larger amounts of N and the defects they entail for the graphitic lattice, while N-SWCNTs are more likely severely disturbed by even relatively small amounts of N during their nucleation and growth.

5. Conclusions

The mechanism of the initial stages of nitrogen-doped single-walled carbon nanotube growth was studied in a system with the simplest possible experimentally feasible chemistry with CO and NH₃ as precursors. The dissociation reaction of NH₃ to atomic nitrogen and hydrogen was identified, with a reaction barrier comparable to an experimentally determined value measured by tandem infrared and mass spectrometry. It was found that the chemistry involving C and N is rather similar. The formation of a C–N bond between atomic carbon and nitrogen was also found to be barrierless and exothermic, while there is a large barrier for parasitic HCN formation. Thus there seems to be no fundamental differences in the mechanism of the precursor reactions.

Acknowledgements

We acknowledge the generous computational resources provided by CSC (Center for Scientific Computing, Finland). This work has been supported by the Academy of Finland (project No 128445), Finnish TEKES GROCO Project (1298/31/08), and the Aalto University MIDE-program project CNB-E. P.A. acknowledges an individual Marie Curie Intra-European Fellowship within the 7th European Community Framework Programme.

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Supplementary information

Mechanism of the initial stages on single-walled nitrogen-doped carbon nanotube growth

DOI: 10.1039/c1cp20454h

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**Supplementary information**

First-principles DFT calculations were used to study CO, NH$_3$, NH$_2$, NH, atomic C and N adsorption on icosahedral Fe$_{55}$ cluster. The geometry optimization was started from the high symmetry adsorption sites of one the 20 triangular face of the cluster. The high symmetry adsorption sites are the top site, octahedral hollow site and tetrahedral bridge sites. In our simulation, the bridge and top site can be in-plane on the cluster face or on its edge/vertices. For CO, interaction geometries presenting the molecular bond both coplanar (=) and perpendicular (\(\perp\)) to the cluster surface were considered. When the CO molecule is placed flat on the cluster, during the geometry optimizations oxygen atoms are not bonding to the surface and the molecule flips up.

Perpendicular adsorption is not favorable when oxygen is toward the surface (\(\perp\) OC). During the relaxations with the molecule adsorbed through the carbon (\(\perp\) CO), it spontaneously moves, migrating on the B, D and F sites (Fig. S1) of the surface. To describe quantitatively the energetics of the adsorbed species on the surface, we introduce the interaction energy term (I.E.), defined as

\[
\text{I.E.} = E_{\text{Fe}_{55}/\text{CO}} - (E_{\text{Fe}_{55}} + E_{\text{CO}}),
\]

where \(E_{\text{Fe}_{55}/\text{CO}}\) is the total energy of the adsorbate-substrate system, \(E_{\text{Fe}_{55}}\) of the Fe$_{55}$ cluster, and \(E_{\text{CO}}\) of the free CO molecule. I.E. describes the strength of the adsorbate-substrate interaction. In Fig. S1 the I.E. values are reported for the optimized geometries.

The stability of NH$_3$ on the cluster was considered as well. The molecule was set on the vertices, on the edge and on the centre of the icosahedral face of the cluster. For every adsorption site the possible effect of the orientation was considered, though only the interaction N-Fe was favorable, and only the top sites are stable (-0.73 eV < B.E.(NH$_3$) < -0.60 eV). The obtained stable geometries and I.E.s (calculated with respect to \(E_{\text{NH}_3}\)) are reported in Fig. S2.

In order to study CO and NH$_3$ dissociation with the CI-NEB method, we need to know the preferred adsorption sites for NH$_2$, NH, N, C and O atoms on the cluster. Considering NH$_2$, during relaxation the molecule spontaneously moves, migrating to the bridge sites on the facet of the surface (-3.10 eV < B.E.(NH$_2$) < -2.52 eV) (Fig. S3). The arrangement presenting the nitrogen
tetrahedrally coordinated to two hydrogens and two iron atoms is clearly preferred. Similar behavior has been observed considering the interaction of NH at the high symmetry adsorption site (-4.64 eV < B.E.(NH) < -3.18 eV) (Fig. S4). During geometry optimization, the fragment rearranges, moving to the hollow site, where N can easily interact with three metal atoms.

Considering atomic carbon and nitrogen, all possible adsorption sites on the surface (Figs. S5 and S6) and below (Figs. S7 and S8) were considered, but only few stable sites for individually adsorbed C and N were located. Both of the atoms present similar behavior: the hollow sites on and below the surface are most stable. I.E. values are reported in the figures; for comparisons remember that the reference energy for a non-adsorbed carbon is that of the isolated atom.

Fig. S9 shows a possible formation path for HCN was calculated with the NEB method. The obtained reaction barrier is 1.65 eV. Fig. S10 shows an Arrhenius plot of the mole fraction of HCN as a function of reactor wall temperature. A fit to the linear region yields a slope of -15689.7 K, which corresponds to an activation energy of 1.35 eV.

Fig. S1 Behavior observed during geometry relaxation of CO, started from the molecule adsorbed perpendicular at the cluster surface. During optimization, the molecule spontaneously moves to the edge of the facet or to the border of the hollow cavity.
**Fig. S2** Behavior observed during geometry relaxation of NH$_3$, started from the molecule adsorbed on the cluster surface. NH$_3$ prefers to interact with the most exposed metal atoms, and after the first H dissociation, the molecule spontaneously moves to the top sites during geometry optimization.

**Fig. S3** Behavior observed during geometry relaxation of NH$_2$, started from the molecule adsorbed on the cluster surface. In order to optimize the interaction with the surface and maintain tetrahedral coordination, NH$_2$ spontaneously move to the bridge sites (C and B) during the optimization.
**Fig. S4** Behavior observed during geometry relaxation of NH, started from the molecule adsorbed on the cluster surface. In order to optimize interaction with the surface and maintain tetrahedral coordination, NH spontaneously moves to the hollow sites (A and E) during the optimization.

**Fig. S5** Behavior observed during geometry relaxation of atomic C adsorbed on the high symmetry adsorption sites of the cluster surface. The hollow sites (A and E) are the only stable ones, and from the others, the adsorbed C migrates to the nearest hollow site.
**Fig. S6** Behavior observed during geometry relaxation of atomic N adsorbed on the high symmetry adsorption sites of the cluster surface. The hollow sites (A and E) are the only stable ones, and from the bridge sites, the adsorbed N migrates on the nearest hollow site.

**Fig. S7** Behavior observed during geometry relaxation of subsurface atomic C adsorbed on the high symmetry adsorption sites of the cluster surface. In the majority of cases, the C atom moves spontaneously to the octahedral cavity below the A site during the geometry optimization.
**Fig. S8** Behavior observed during geometry relaxation of subsurface atomic N adsorbed on the high symmetry sites of the cluster surface. The behavior is similar to what is observed for atomic C.

**Fig. S9** Proposed reaction path for HCN formation reaction on the cluster.
**Fig. S10** Arrhenius plot of the mole fraction of HCN measured using FTIR as a function of reactor maximum wall temperature.