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Effect of Ammonia on Chemical Vapour Deposition and Carbon Nanotube Nucleation Mechanisms

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Chemical vapour deposition (CVD) growth of carbon nanotubes is currently the most viable method for commercial-scale nanotube production. However, controlling the 'chirality', or helicity, of carbon nanotubes during CVD growth remains a challenge. Recent studies have shown that adding chemical 'etchants', such as ammonia and water, to the feedstock gas can alter the diameter and chirality of nanotubes produced with CVD. To date, this strategy for chirality control remains sub-optimal, since we have a poor understanding of how these etchants change the CVD and nucleation mechanisms. Here, we show how ammonia alters the mechanism of methane CVD and single-walled carbon nanotube nucleation on iron catalysts, using quantum chemical molecular dynamics simulations. Our simulations reveal that ammonia is selectively activated by the catalyst, and this enables ammonia to play a dual role during methane CVD. Following activation, ammonia nitrogen removes carbon from the catalyst surface exclusively via the production of hydrogen (iso)cyanide, thus impeding the growth of extended carbon chains. Simultaneously, ammonia hydrogen passivates carbon dangling bonds, which impedes nanotube nucleation and promotes defect healing. Combined, these effects lead to slower, more controllable nucleation and growth kinetics.

Introduction

Single-walled carbon nanotubes (SWCNTs) are graphene sheets rolled into cylindrical tubes. Their remarkable physical,^{1–4} electronic and optical properties,^{5, 6} have made them a cornerstone of modern nanotechnology research. The key structural characteristic of single-walled carbon nanotubes (SWCNTs) is the chirality, or helicity, of the tube; i.e. the difference between the graphene sheet's lattice vectors, and the angle at which the graphene sheet is rolled into a cylinder. Prospective SWCNT applications, such as chemical sensors,⁷ field effect transistors⁸ and transparent metal electrodes,^{9, 10} require specific (*n,m*) SWCNTs, since SWCNT electrical and optical properties are determined by the values of *n* and *m*. While SWCNTs can be separated post-synthetically (e.g. by chromatography,^{11, 12} centrifugation,^{13, 14} electrophoresis^{15, 16} and selective functionalisation^{17–19}), these approaches can be costly, suffer from limited throughput and cause irreversible damage to the SWCNT structure.²⁰ Achieving *in situ* "chirality-controlled growth", i.e. production of arbitrary (*n,m*) SWCNTs, therefore remains a key challenge for CNT growth science.

The most popular method for CNT synthesis is catalytic chemical vapour deposition (CVD), in which a carbonaceous feedstock gas is introduced to oxide-supported metal nanoparticle catalysts at high temperatures. Common

feedstock species for CVD growth of SWCNTs include methane,²¹ acetylene,²² ethanol,²³ and ferrocene.^{24–27} CVD is scalable, relatively low-cost and operable under mild conditions. It also offers control through parameters such as catalyst composition, carbon feedstock and CVD environment (i.e. temperature, pressure etc.).^{27, 28} Owing to these benefits, CVD has enabled commercial-scale production of SWCNTs.

However, chirality-controlled CVD growth of SWCNTs remains elusive at commercial scales. A number of strategies have been intensively studied over the last decade towards solving this problem including catalyst design,²⁹ 'amplification' or 'cloning' of SWCNTs from short, pre-existing open-ended SWCNTs,^{30, 31} growth from precursor organic templates,^{32–34} and vapour-phase epitaxy approaches.³⁵ The main drawbacks of the latter techniques is that they are not easily scaled up, the growth kinetics and yields are low³⁶ the synthesis of the template molecules is very challenging,^{37, 38} and the range of SWCNT chiralities that can be produced is limited by the availability of particular templates.²⁶

Etchant gases, such as H₂, O₂, CO₂, NH₃ and H₂O are typically added to the CVD feedstock to prevent 'catalyst poisoning' – the build-up of amorphous carbon on the catalyst surface – improving catalyst lifetime. Moreover, it has been demonstrated that etchants can influence the (*n,m*) distribution of SWCNTs as grown by CVD, and therefore offers a novel alternative route towards chirality-control. For instance, oxidative etchants methanol,³⁹ oxygen⁴⁰ and water⁴¹ have been shown to enable synthesis of semiconducting SWCNTs with near ~100% abundance. Hydrogen has also been used to promote growth of metallic SWCNTs.^{42, 43} More recently, the

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addition of ammonia during ferrocene CVD resulted in the production of SWCNTs with larger chiral angles; 90% displaying a chiral angle between 20–30°. ⁴⁴ We have recently proposed ⁴⁵ that this is in part due to the selective reactivity of individual (n,m) caps with nitrogenous radicals. However, the atomistic mechanism of etching during SWCNT cap formation, and its influence on (n,m) selectivity, remain unexplained.

SWCNT nucleation and growth has been extensively modelled using a wide range of theoretical methods, as highlighted in numerous reviews. ^{26, 46} Early examples utilised the reactive empirical bond order (REBO) potential. Shibuta et al. ^{47, 48} were the first to simulate SWCNT nucleation from Ni-C vapour co-condensation using REBO in conjunction with MD, and simulations from Bolton and co-workers revealed roles for the catalyst nanoparticle and mechanistic details of SWCNT nucleation for catalysts including the effect of catalyst size, carbon concentration and metal-carbon adhesion on SWCNT growth and catalyst melting and coalescence. ^{49–54} Our own group has employed density functional tight-binding (DFTB) approaches to study SWCNT nucleation and CVD in a range of conditions. ^{55–59} However, despite this wealth of literature, few investigations have considered the roles played by hydrogen, ^{58–61} undoubtedly present from feedstock decomposition, and other etchant additives, ⁴⁵ during CVD nucleation and growth.

In this work, we address the latter shortcoming by presenting QM/MD simulations that show how ammonia influences methane CVD and SWCNT nucleation on iron nanoparticle catalysts. We show that co-adsorption of ammonia-derived radicals significantly alters the chemical pathways of CVD and SWCNT nucleation. The iron catalyst selectively activates surface-adsorbed ammonia radicals, providing an abundant source of nitrogen and hydrogen atoms. Ammonia nitrogen atoms etch surface-adsorbed carbon exclusively via the production of hydrogen (iso)-cyanide, which desorbs from the catalyst surface. Ammonia nitrogen also promotes the cleavage of polyyne chain C-C bonds, thereby impeding carbon chain growth. Ammonia hydrogen atoms passivate carbon dangling bonds on surface-adsorbed species, thereby impeding polygonal ring formation, and hence SWCNT nucleation. In light of previous investigations demonstrating that hydrogen leads to increased defect healing during SWCNT nucleation, we propose that ammonia acts as a healing agent during CVD SWCNT growth.

Computational Methods

QM/MD Methods

Newton's equations of motion were integrated using the velocity-Verlet algorithm ⁶² with a time step of 1.0 fs. An NVT ensemble was enforced at 1,500 K using a Nose-Hoover chain thermostat. ^{63, 64} The quantum chemical potential energy and energy gradients were calculated "on the fly" at each MD iteration using the SCC-DFTB method ⁶⁵ with the trans3d-0-1 parameter set ⁶⁶ and a finite electronic temperature ^{67–69} of 10,000 K. The use of a finite electronic temperature means that the occupancy of molecular orbitals near the Fermi level are

described by a Fermi-Dirac distribution function of their energy, and can take on non-integer occupations near the Fermi level.

Model Systems

SWCNT nucleation was simulated on face-centred cubic (fcc) Fe₃₈ nanoparticles. This crystal structure resembles γ -iron, a stable phase in bulk iron at the temperature employed (1,500 K). ⁷⁰ The nanoparticle was first optimised at 0 K to a local minima and then annealed at 1,500 K for 10 ps.

To determine the effect of adding ammonia as an etchant during CVD, two sets of simulations with and without ammonia were performed. Trajectories were replicated 10 times for each set of simulation conditions (total 20 trajectories). Initial velocities of all atoms were randomly generated for each trajectory to ensure statistical independence. To initiate SWCNT growth, CH_x ($x = 0, 1, 2, 3$) was supplied to the nanoparticle periodically. CH_x is supplied, as opposed to methane, since it is likely that methane partially decomposes pyrolytically under CVD conditions prior to catalyst absorption. ^{71–74} The value of x is selected randomly but weighted with a Poisson distribution to reflect the likelihood of successive dehydrogenation of methane. That is, CH₃ is chosen more often than CH₂, CH₂ more than CH, and CH more than C. CH_x was supplied in both simulations at an identical rate of 1 CH_x/ps until the number of carbon atoms on the catalyst surface was maintained at 60, consistent with previous models. ^{55, 75, 76} The feedstock molecule was positioned randomly 3.0 to 5.0 Å away from the nanoparticle, and "fired" towards the centre of mass of the nanoparticle with a velocity corresponding to 1,500 K. Ammonia is also known to decompose pyrolytically, ⁷⁷ and so NH_x is added in place of ammonia (NH₃) as described above. Every 10 ps, a single NH_x ($x = 0, 1, 2, 3$) molecule was adsorbed in the same manner, in place of a CH_x. For brevity, the set of trajectories including NH_x are denoted 1_N–10_N, and those without are denoted 1–10.

Results and Discussion

Previous simulations ^{55, 60} demonstrate that SWCNT nucleation proceeds via the "pentagon-first" mechanism, which proceeds as follows. Following carbon adsorption, extended carbon polyyne chains form over the catalyst surface and fuse together to form Y-shaped structures or "Y-junctions". The sp² carbon at the junction is the "cornerstone" for the cyclization of the two branching arms. Due to high thermal energy the arms move over the surface toward each other to form a ring, the most kinetically favourable being a 5-membered pentagon ring. This first pentagon becomes the anchor site for subsequent ring condensation, ultimately leading to SWCNT cap formation. ⁵⁵

We therefore begin our discussion by analysing how co-adsorbed NH_x influences each successive step of the SWCNT nucleation process, i.e. carbon adsorption/desorption, polyyne chain formation and ring condensation.

Figure 1. Average populations of surface-adsorbed CH_x species on Fe_{38} observed in (a) trajectories 1-10, and (b) trajectories 1_N - 10_N . All data averaged over 10 trajectories.

Co-Adsorption of Carbon and Nitrogen on Iron Catalysts

Average populations of surface-adsorbed CH_x observed in trajectories 1-10 and 1_N - 10_N are shown in Figure 1.

Unsurprisingly, these populations initially reflect the relative probabilities of CH_x addition (i.e. $p(\text{CH}_3) > p(\text{CH}_2) > p(\text{CH}) > p(\text{C})$), at least prior to SWCNT nucleation. Initially, the surface population of all CH_x species increases in both sets of trajectories. This is because surface/sub-surface saturation of the catalyst with carbon is required to overcome the SWCNT nucleation barrier. Subsequently, SWCNT nucleation initially proceeds via polyene chain growth. Previous simulations⁵⁹ have shown that CH and CH_2 are the main carbon species responsible for driving polyene chain formation, due to their spare carbon dangling bonds, i.e. spare valence electrons available for additional C-C bond formation. By contrast, CH_3 adsorbed on a catalyst surface has no dangling bonds and is therefore relatively inert (unless it is activated by dehydrogenation, forming C/CH/ CH_2). Similarly, C is not as important in terms of polyene chain growth, since it is strongly bound to/within the catalyst surface, and is likely to be present at far lower surface concentrations than CH and CH_2 .

This is consistent with trends observed in Figure 1 for trajectories 1-10; surface populations of CH and CH_2 are depleted more rapidly compared to the CH_3 population. In these trajectories, CH_3 accumulates on the Fe_{38} catalyst surface until ~75 ps, and CH_2 accumulates until ~30 ps. Following this initial period, these species either desorb or are converted/incorporated into other chemical species (these phenomena are discussed further below).

The addition of NH_x has a marked influence on the adsorption behaviour of CH_3 , even at the relatively low concentrations employed here (corresponding to a partial pressure 10% of that of the carbon feedstock). Most notably, at 250 ps CH_3 begins to accumulate after its initial depletion in trajectories 1_N - 10_N , and this is not observed when NH_x is absent. CH_3 'regeneration' here is driven by the catalytic activation of surface-adsorbed NH_x , which provides a reservoir of reactive hydrogen radicals adsorbed to the catalyst surface. We note that this increase in CH_3 coincides with sudden changes carbon chain and polygonal

Figure 2. Average populations of surface-adsorbed, desorbed, and total NH_x supplied during CH_x CVD trajectories 1_N - 10_N . All data averaged over 10 trajectories.

ring populations on the catalyst surface, which we discuss in greater detail below.

Surface-adsorbed NH_x species also have a pronounced effect on the behaviour of the more reactive C and CH species. In trajectories 1-10, C and CH populations increase until ~50 ps, after which they decline. However, in trajectories 1_N - 10_N , C accumulates on the surface over a ~90 % longer time period by comparison, with the population of surface-adsorbed C beginning to decrease at ~90 ps. The average population of surface-adsorbed CH reaches a maximum at ~30 ps in trajectories 1_N - 10_N , and does not decline significantly for the remainder of the simulation. On the other hand, by 150 ps the CH population in trajectories 1-10 has decreased by 2/3 from its maximum value observed at ~50 ps. Therefore, the amounts of C and CH on the surface are being mediated by the presence of NH_x during the earliest stages of these simulations (25-80 ps). This is consistent with NH_x either (1) displacing C/CH from the catalyst surface, or (2) selectively promoting C/CH coalescence during this period.

Selective Carbon Etching via Cyanide Formation

Figure 2 shows the average populations of surface-adsorbed NH_x , desorbed NH_x , and total NH_x observed in trajectories 1_N - 10_N . Prior to 50 ps, NH_x adsorption, compared to desorption, is favoured. Following this initial period, the amount of NH_x on the catalyst surface stays essentially constant at ~20% of the concentration of surface-adsorbed carbon. Figure 2 also shows that the total amount of NH_x supplied to the catalyst interface is greater than the combined populations of adsorbed and desorbed NH_x present in the simulation after ~40 ps. This means that surface-adsorbed NH_x is being converted/incorporated into other surface-adsorbed species. Analysis of all trajectories showed that no larger nitrogenous compounds (e.g. N_2 , N_2H_2 , N_3H^- etc.) were formed catalytically. Thus, the only possible explanation for the surface-depletion of NH_x is via reaction with surface-adsorbed carbon species.

Figure 3. Average populations of adsorbed/desorbed CN, HNC, and CH_3N fragments in trajectories 1_N - 10_N . All data averaged over 10 trajectories.

In total, 13 different $\text{C}_x\text{N}_y\text{H}_z$ fragments (CN, CNH, CNH_2 , CNH_3 , CNH_4 , C_2NH_2 , C_2NH_3 , C_3NH_1 , C_3NH_2 , C_3NH_5 , C_4NH_6 , C_7NH_7 , and CN_2H) were observed to desorb from the catalyst surface by 300 ps. Of these, the only species that were consistently produced in an appreciable quantity were cyanide (CN^-), hydrogen (iso)-cyanide (HCN/HNC), and methanimine (CH_3N). Populations of these species are presented in Figure 3. It is therefore evident that the more populous species such as NH_3 and NH_2 are activated by the iron catalyst before playing any significant role with respect to carbon etching.

In trajectories 1_N - 10_N , carbon and nitrogen predominantly desorb from the surface together as hydrogen (iso)cyanide, as shown in Figure 4. However, HCN and HNC are not the most common $\text{C}_x\text{N}_y\text{H}_z$ species on the catalyst surface at any time. Other desorbed CNH_x fragments were only seldom observed, and very few of the desorbed fragments contained multiple carbon atoms. This indicates that NH_x selectively etches singular C atoms or CH molecules, rather than more H-saturated CH_x species, longer polyyne chains or polygonal carbon rings. This is somewhat counter-intuitive, since C and CH are the most strongly adsorbed CH_x species on the catalyst. The hydrogen in HNC moiety can be bonded to the N atom (hydrogen isocyanide), or the C atom (hydrogen cyanide). Approximately 60% of the time, HNC desorbs as hydrogen isocyanide and 40% as hydrogen cyanide. The addition of NH_x clearly accelerates the desorption of CH and C.

We turn now to describe various pathways to hydrogen (iso)cyanide formation observed in trajectories 1_N - 10_N . In Figure 3(a), a NH molecule approaches the catalyst surface and in doing so strips a H atom from an adsorbed CH molecule at 40.06 ps. The NH_2 molecule formed immediately binds to the surface C atom, which triggers the dissociation of one of its hydrogen atoms (40.11 ps). Approximately 2 ps later, the hydrogen isocyanide molecule desorbs from the surface. In Figure 5(b) hydrogen isocyanide forms via a H-C=N-H moiety that is formed on the surface from CH and NH species at 63.07 ps in trajectory 1_N . Between 63.08 and 63.10 ps the H-C=N-H moiety rearranges

Figure 4. Populations of desorbed C, CH, and HCN/HNC species observed in trajectories 1_N - 10_N . All data averaged over 10 trajectories.

Figure 5. Mechanisms of (a)-(c) HNC formation and (d) HCN formation observed in trajectories 1_N - 10_N . (a) depicts the formation of HNC in trajectory 1_N by NH addition, (b) formation of HNC by CH addition in trajectory 8_N , (c) coalescence of surface-adsorbed C and NH in trajectory 8_N , and (d) production of HCN from larger polyyne chain cleavage in trajectory 6_N . Amber spheres represent iron, cyan spheres represent carbon, blue spheres represent nitrogen and white spheres represent hydrogen atoms.

such that it adsorbs to the catalyst *via* the C atom. This atom is then dehydrogenated by the catalyst at 63.12 ps and immediately desorbs from the surface as hydrogen isocyanide at 63.14 ps. A more direct route to hydrogen isocyanide formation is shown in Figure 5(c), which depicts the formation of HNC observed in trajectory 8_N via coalescence of surface-adsorbed C and NH species. In this case, desorption of HNC occurs within 3 ps. Hydrogen cyanide can also be created when a larger surface-adsorbed molecules fragment, as shown in Figure 5(d). At 116.49 ps, a surface-adsorbed C_2H_4 molecule is nitrogenated, which causes a CH_3 moiety to desorb. The hydrogen cyanide thus formed almost instantaneously desorbs from the catalyst surface.

Prior to desorption, most often HNC or CN^- moieties are bound to the iron catalyst surface *via* the carbon atom. This suggests that nitrogen etches surface C/CH species by weakening the Fe-C bond, which subsequently breaks due to the high thermal energy present in the simulation (representative of typical CVD conditions). CH_2 and CH_3 desorption is virtually unaffected by this self-sacrificial process of N removing singular CH_x molecules as $N-CH_x$; desorption of N_x-CH_3 is not observed to the same extent as HNC or CN^- , whereas desorption of and N_x-CH_2 is not observed whatsoever in trajectories 1_N-10_N (Figure 3). This is due to two factors; firstly, surface adsorbed nitrogen does not disrupt the catalyst-carbon bond, but instead attacks carbon dangling bonds, which are less accessible in CH_2 and CH_3 ; and secondly, compared to C and CH, CH_2 and CH_3 are more weakly bound to the catalyst surface, and desorb more readily (Figure 1). Supposing the concentration of NH_x was increased in these simulations, etching of CH_2 and CH_3 by NH_x nitrogen may presumably be accelerated.

Carbon Chain Formation: Influence of Ammonia

Etching of surface carbon is driven almost exclusively via the formation and desorption of hydrogen (iso)cyanide from the Fe_{38} catalyst surface. Nevertheless, there remains a small but constant amount of NH_x adsorbed on the catalyst surface, which is gradually incorporated into polyyne chains and Y junction structures. There is therefore the potential for nitrogen to be incorporated into polygonal carbon rings, and hence become part of the ultimate SWCNT structure, potentially effecting chirality-alteration during nucleation and/or growth. In this section we discuss the effect of nitrogen on carbon polyyne chain formation.

The formation of carbon polyyne chains with and without surface-adsorbed NH_x is compared in Figure 6. The discussion is limited to the formation of C_3 – C_6 chains, since longer chains are not produced in appreciable quantities (at these lengths, polyyne chains prefer to oligomerise into polygonal ring structures⁵⁵).

The time at which particular polyyne chain lengths emerge is the same in both sets of simulations, therefore, NH_x does not slow or accelerate polyyne chain growth appreciably under the present conditions. Carbon polyyne chain growth begins at 15-

Figure 6. Average populations of non-linear C_2 , C_3 , C_4 , C_5 and C_6 polyyne chains observed in trajectories 1-10 and 1_N-10_N . All data averaged over 10 trajectories.

25 ps with the appearance of C_3 chains. From 50-125 ps there are double the number of C_3 chains in trajectories 1-10. After 125 ps, the amount of C_3 in these trajectories decreases, but continues to increase in trajectories 1_N-10_N . By 180 ps, trajectories 1_N-10_N have ~30% more C_3 chains than trajectories 1-10. Both sets of trajectories witness a notable drop in the population of C_3 chains at ~200-250 ps. This coincides with the initiation of polygonal ring formation, discussed in the subsequent section. At 40 ps, C_4 and C_5 chains begin to form in both sets of trajectories. More C_4 chains are initially formed in trajectories 1_N-10_N , before 75 ps. Between 75 – 140 ps, the population of C_4 chains in these trajectories is effectively constant. On the other hand, C_4 chains are rapidly formed in trajectories 1-10 during this same period, and by 90-115 ps the number of C_4 chains in both simulations become equal. The number of C_4 chains in trajectories 1-10 continues to increase until 170 ps at which point the population is roughly double that in trajectories 1_N-10_N , then decreases immediately after resulting in the C_4 populations in the two sets of simulations becoming equivalent again. The number of C_5 chains in both simulations is comparable in the early stages of the simulation. Following 110 ps however, ~40-300% more C_5 chains are observed in trajectories 1-10, compared to trajectories 1_N-10_N . The populations become equal briefly from 150-185 ps, though, the number of C_5 chains in trajectories 1-10 begins to accelerate more rapidly once again. C_6 chains become visible from 50 ps onwards in both sets of trajectories, with populations approximately equal in the first 180 ps. From 180-300 ps, trajectories 1_N-10_N have ~200% more C_6 chains, however, it is noted that at all times during the simulation C_6 populations remain low.

The presence of ammonia during CH_4 CVD on iron catalysts therefore does not significantly alter polyyne chain growth during the early stages of nucleation. Nevertheless, analysis of trajectories 1_N-10_N demonstrated that surface-adsorbed nitrogen promoted C-C bond cleavage during the polyyne chain growth phase of nucleation. Individual examples of interactions between NH_x and C_n chains on the Fe_{38} catalyst surface are depicted in Figure 7. Nitrogen induces C-C bond cleavage in both terminal and non-terminal (e.g. branching) positions in the growing chains. For instance, Figure 7(a) depicts a $N + C_3 \rightarrow NC_3 \rightarrow C + NC_2$ cleavage process in trajectory 4_N , in which a surface

Figure 7. Surface-adsorbed nitrogen drives C-C bond cleavage during polyyne chain growth. (a) $\text{N} + \text{C}_3 \rightarrow \text{NC}_3 \rightarrow \text{C} + \text{NC}_2$ cleavage mechanism observed in trajectory 4_{N} , resulting in a C_3 chain being broken into a C_2 chain and atomic carbon by NH . (b) $\text{N} + \text{C}_5 \rightarrow \text{C}_3 + \text{NC}_2$ cleavage mechanism observed in trajectory 2_{N} showing C_5N chain cleavage upon NH_2 addition, forming C_2 and C_3 chains. (c) Sequential cleavage of a non-linear C_6N chain observed in trajectory 4_{N} , forming CNH via C_4N and C_3 chain intermediates. (d) Cleavage of a $\text{C}_2\text{-N-C}_2$ linear chain observed in trajectory 5_{N} via the disruption of the central C-N bond. Amber spheres represent iron, cyan spheres represent carbon, blue spheres represent nitrogen and white spheres represent hydrogen atoms.

bound NH moiety bonds to the central carbon of a C_3 polyyne chain to form a small Y-junction (128.33 ps). 7 ps later the structure is anchored to the nanoparticle through one carbon, and the bond between that carbon and the rest of the structure is broken, resulting in the desorption of C_2NH_3 . The malleability of the Fe_{38} surface here is also important, since the C atom formed is stabilised by the formation of two new Fe-C bonds. A similar situation is presented in Figure 7(b), which depicts trajectory 2_{N} . Here, an incoming NH_2 radical adds at the C_2 position of a C_5 chain. Within 0.1 ps, this bond formation leads to the cleavage of the $\text{C}_2\text{-C}_3$ bond, forming C_3H and C_2NH_2 moieties that both remain on the surface. Figure 7(b) shows that this reaction is essentially unmediated by the catalyst surface. It is therefore likely that this C-C bond cleavage is triggered by nitrogen withdrawing electron density from the $\text{C}_2\text{-C}_3$ bond, making it more amenable to breaking due to thermal vibrations in the chain. Figure 7(c) demonstrates a mechanism of CNH formation from an extended polyyne chain observed in trajectory 4_{N} . At 180.08 ps, a NH radical adsorbs to the iron surface and loses its hydrogen to a neighbouring C atom before terminating a C_5 polyyne chain. At 187.09 ps the now branched C_4 chain (due to CH_2 addition at 184.07 ps, not shown) is broken at the junction to give C_2H_3 and C_4NH_4 chains. Over 1 ps later, the C_4NH_4 chain is further broken into NCH and C_3H_2 , with NCH ultimately desorbing from the catalyst nanoparticle. Nitrogen can also reside in the middle of polyyne chains, as shown in Figure 7(d) which depicts trajectory 5_{N} . At 179.86 ps a CN molecule and ring fragment join together *via* the N atom. By 190.54 ps the polyyne chain arm containing the nitrogen has grown by one carbon. At 190.55 ps the fragment is broken at the N atom, leaving C_2N and the larger ring fragment on the catalyst surface.

The smaller chains produced by this accelerated C-C bond cleavage may persist on the surface, whereby they participate in further oligomerisation reactions, or desorb (i.e. are etched) and removed from the SWCNT nucleation reaction. Polyyne chains terminated with nitrogen can also be broken down into smaller chains.

While C-C bond cleavage, illustrated by Figure 7, is prevalent through trajectories $1_{\text{N}}\text{-}10_{\text{N}}$, they are still relatively rare compared to the rate of C-C bond formation. This is a simple result of the surface nitrogen concentration being $\ll 10\%$ of the surface carbon concentration. Thus, the effectiveness of NH_x radicals as a carbon etchant would be markedly increased at higher surface concentrations than those used here. Potentially, nitrogen atoms could be incorporated into the SWCNT structure. The CVD conditions applied in these simulations are similar to those used for the production of nitrogen-doped CNTs.^{78, 79} However, no rings containing nitrogen are observed in trajectories $1_{\text{N}}\text{-}10_{\text{N}}$. We attribute this to the timescale employed in these simulations, and this possibility is the subject of ongoing research in our group.

Figure 8. Populations of polygonal carbon rings formed in trajectories (a) 1-10, and (b) 1_N-10_N. All data averaged over 10 trajectories.

Carbon Ring Condensation: Influence of Ammonia

SWCNT nucleation occurs via the formation of carbon polyyne chains on the catalyst surface, followed by the oligomerisation of these chains to form polygonal carbon rings according to the pentagon first mechanism. The mechanism and kinetics of SWCNT nucleation can be effectively monitored via the population of 4, 5, 6 and 7-membered rings on the catalyst surface, which are shown in Figure 8.

In trajectories 1-10 (Figure 8(a)), pentagon rings begin to form at ~55 ps. Subsequent ring formation is dominated by further pentagon addition.^{55, 80} Hexagon addition during this period is more limited and delayed by comparison. Both pentagon and hexagon addition here are consistent with previous reports.^{55, 81} The mechanism of polygonal ring formation in comparable conditions is now well-established, and so we do not discuss it further here.

The influence of ammonia on the kinetics of ring formation are immediate from Figure 8(b). When ammonia is introduced, pentagon ring formation is delayed by 50 ps, and the frequency of pentagon formation events is effectively zero up until 175 ps. Those pentagons that are formed are soon removed again. After 175 ps, pentagon formation accelerates, with an average of one pentagon ring in each trajectory by 300 ps. The extent and kinetics of hexagon formation is comparable with and without ammonia, and the removal of hexagons in trajectories 1_N-10_N is not observed during the timescale employed here (300

ps). This is consistent with the greater thermodynamic stability of a carbon hexagon, versus a carbon pentagon on a catalyst surface (due to lower ring strain).^{55, 57} Hexagon formation is concordant with pentagon formation in trajectories 1_N-10_N prior to 225 ps, after which pentagon rings dominate.

We note here that SWCNT caps do not nucleate in trajectories 1-10 within the timescale employed here (300 ps) (Figure S1). This is a direct consequence of the presence of hydrogen; removal of hydrogen would undoubtedly lead to cap nucleation and growth here, as it has done in a number of prior investigations of SWCNT cap nucleation,^{59, 60, 82} polycyclic aromatic hydrocarbon growth⁸³ and fullerene formation.^{84, 85} Hydrogen plays a dual role during condensation of sp²-hybridized carbon networks.^{60, 83} Firstly, hydrogen inhibits ring condensation via the passivation of carbon dangling bonds and thus prevention of C-C bond formation. Secondly, hydrogen promotes healing mechanisms that convert defective carbon structures (such as pentagon and heptagon defects) into higher-quality hexagon structures. The latter effect is due in part to slower growth rates observed with higher hydrogen concentrations.

In the preceding section it was shown that NH_x-derived nitrogen accelerates C-C bond cleavage during carbon chain growth. Interestingly however, analysis of trajectories 1_N-10_N demonstrated that analogous C-C bond cleavage during ring condensation did *not* occur. Instead, NH_x-derived hydrogen, was responsible for impeding ring formation in trajectories 1_N-10_N. This phenomenon is elucidated further via analysis of the populations of C-H, N-H and Fe-H during the CVD process, shown in Figure 9.

CH_x is actively dehydrogenated in trajectories 1-10 between 0-20 ps by the Fe₃₈ catalyst surface (Figure 9(a)). This catalytic activation continues until 20 ps, at which point hydrogen transfer between adsorbed CH_x and the catalyst surface ceases (or, perhaps less likely, the rates of CH_x → Fe and Fe → CH_x hydrogen transfer become the same). This is attributed to surface saturation, which will be far lower than the theoretical maximum (100%, i.e. 38 adsorbed species) in the case of CH_x due to steric repulsion between neighbouring CH_x adsorbates on the relatively small nanoparticle. Considering the adsorption rate of CH_x (1 / ps), at 20 ps a maximum of 20 CH_x species will be adsorbed to the surface. The extent of catalytic activation of these species, according to Figure 9(a), is therefore ~10%, since only 2 Fe-H bonds are formed during this period. Between 20 - 120 ps, hydrogen transfer between the catalyst and adsorbed CH_x either ceases, or reaches an apparent equilibrium. At ~120 ps Δ(C-H) begins to drop, becoming increasingly negative, while Δ(Fe-H) remains constant. This can only be explained by surface-adsorbed CH_x being dehydrogenated by the catalyst surface, and surface hydrogen atoms desorbing into the vacuum. This coincides with the point at which the catalyst surface is carbon-saturated. Since carbon-iron adhesion is stronger than hydrogen-iron adhesion, hydrogen is displaced from the catalyst surface following abstraction from CH_x, and is forced to desorb on a thermochemical basis. At 200 ps Δ(C-H) becomes constant once again. This is a consequence of CH_x

Figure 9. The extent of dehydrogenation (X-H bond breaking) or hydrogenation (X-H bond formation) of the Fe_{38} surface, carbon, and nitrogen in trajectories (a) 1-10 and (b) 1_N-10_N . $\Delta(\text{X-H}) < 0$ indicates X-H bond cleavage, while $\Delta(\text{X-H}) > 0$ indicates X-H bond formation. In both (a) and (b) the green line is zero when hydrogen is only being exchanged between the adsorbates and the catalyst surface. All data averaged over 10 trajectories.

supply temporarily ceasing (at this point the desired surface carbon density is reached in the simulation). This is also observed in Figure 9(b) at 250 ps.

In the presence of ammonia, this surface chemistry changes markedly, as shown in Figure 9(b). In trajectories 1_N-10_N , carbon feedstock is initially dehydrogenated by the catalyst (0-35 ps), and the catalyst becomes partially hydrogen-passivated. Hydrogen transfer from CH_x to NH_x is not observed during this period, since $\Delta(\text{N-H})$ is slightly negative, which means that N-H bonds are being broken, not formed. The extent of NH_x activation is however very limited, compared to the extent of CH_x activation, which is now approximately double that observed without ammonia. The adsorption of NH_x evidently enhances the catalytic activity of the nanoparticle in this case.

By 35 ps the catalyst surface is saturated in trajectories 1_N-10_N , at which point C-H bonds are reformed via $\text{Fe} \rightarrow \text{CH}_x$ hydrogen transfer. This continues until ~75 ps, at which point the number of C-H bonds stabilises. This coincides with the time

polyne chains coalesce to form rings in the absence of NH_x (Figure 8(a)). $\Delta(\text{C-H})$ from 75 to 150 ps is ~0 or slightly positive, indicating that there are more C-H bonds present than observed without NH_x (Figure 9(a)). For $\Delta(\text{C-H})$ to be positive, CH_x must be receiving hydrogen from an additional source, i.e. surface-adsorbed NH_x . This is corroborated by $\Delta(\text{N-H})$ during this period, which becomes increasingly negative, indicating continual N-H bond cleavage. Hydrogen abstracted from NH_x that is not taken up by CH_x desorbs from the catalyst surface according to the same mechanism detailed above. Following carbon saturation of the Fe_{38} nanoparticle at ~150 ps, $\Delta(\text{C-H})$ becomes negative as in trajectories 1-10.

Thus, the addition of NH_x to the CVD reaction effectively inhibits ring condensation, and hence SWCNT nucleation, by saturating the reaction with hydrogen. The sustained activation of NH_x by the catalyst (hydrogen transfer from $\text{NH}_x \rightarrow \text{Fe}$), as opposed to hydrogen exchange between the catalyst and CH_x , also provides a source of more reactive N and NH radicals which are involved in the etching processes described above. In essence, the catalyst selectively and continually activates NH_x , thereby enabling etching of surface carbon species by nitrogenous radicals.

As noted above, hydrogen not only inhibits ring condensation and sp^2 carbon network growth,^{60, 84, 86, 87} but also catalyses defect healing during growth, leading to higher-quality carbon nanotube structures. This is consistent with the rates of pentagon formation observed with and without NH_x shown in Figure 9. We therefore propose that NH_3 can yield higher quality SWCNTs during CVD growth, as it provides a supplementary hydrogen source at the growth interface that actively removes defects, which is known to change (n,m) chirality during growth.^{88, 89} This is consistent with shifts in (n,m) SWCNT chirality distributions observed in recent experiments.⁴⁴ However, our results do not preclude NH_3 working as a chirality-control agent in a number of other ways. For instance, Hofmann and co-workers^{90, 91} have also shown that exposing catalyst nanoparticles to NH_3 prior to CVD growth narrows (n,m) SWCNT chirality distributions and decreases tube diameters. This was attributed to phase-control of the iron nanoparticle catalyst, by NH_3 , before growth took place. Our own recent investigation⁴⁵ also demonstrated how NH_3 etchant can preferentially remove particular (n,m) SWCNT caps during CVD growth. We also note that the addition of acetonitrile during ethanol CVD growth of SWCNTs leads to a reduction in SWCNT diameters,^{92, 93} which is the opposite trend observed using NH_3 .⁴⁴ This suggests that acetonitrile influences CVD and the SWCNT nucleation/growth processes in a different manner to NH_3 . These possibilities are the subject of further research within our group.

Conclusions

We have presented the first investigation detailing how the co-adsorption of a chemical etchant, ammonia, influences the chemical pathways that underpin hydrocarbon CVD and SWCNT nucleation on a transition metal catalyst. QM/MD simulations

show that ammonia-derived radicals exclusively etch carbon from an iron catalyst surface *via* the desorption of hydrogen-(iso)-cyanide (HNC). Nitrogen etches surface C/CH species by attacking the carbon dangling bonds thereby weakening the catalyst-carbon bond. The dissociation of N-CH₂ and N-CH₃ species is rarely observed owing to the increased inaccessibility of carbon dangling bonds in CH₂, and the absence of dangling bonds in CH₃.

The addition of ammonia during CH₄ CVD on iron catalysts accelerates C-C bond cleavage during the chain growth process. Ring condensation is also severely impeded in the presence of ammonia. However, ammonia nitrogen itself does not play a central role in the inhibition of ring formation. Instead, ammonia provides an additional source of hydrogen, which, by virtue of the weaker N-H bond, is readily activated by the iron catalyst surface. Once on the surface, adsorbed hydrogen species passivates carbon dangling bonds present in extended polyyne chains. This effectively prevents chain oligomerisation, which is the key step in the SWCNT nucleation process, converting sp-hybridised carbon species into a single sp² carbon network. Continued NH_x activation by the catalyst affords the source of more reactive N and NH radicals involved in the etching of surface carbon species. In effect, the catalyst selectively activates NH_x and this enables the etching of carbon by nitrogenous species. The simulations presented here demonstrate that ammonia-derived hydrogen, which is abundant at the SWCNT growth interface, is a potential component of ammonia's experimentally-observed capacity to alter (*n,m*) chirality during CVD SWCNT growth.⁴⁴

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