Direct Evidence of Active and Inactive Phases of Fe Catalyst Nanoparticles for Carbon

Nanotube Formation

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Abstract

Iron-carbon interactions play an important role in various industrial activities such as liquid fuel production by the Fischer Tropsch process and carbon nanotube synthesis by chemical vapor deposition. In both cases, catalytic activity is confined to a subset of catalyst nanoparticles. Despite the large number of experimental and theoretical studies on the activity of Fe nanoparticles, very little is known about the difference between the active and inactive particles. We use *in situ* environmental transmission electron microscopy to elucidate the differences between active and inactive and inactive manoparticles with respect to carbon nanotube formation. We present direct evidence that nanoparticles with the cementite (Fe₃C) structure are active for nanotube growth (C-C bond

formation), while carbon rich particles Hägg (Fe_5C_2) structure are inactive. Density functional theory calculations suggest that reduced activity may be due to lower carbon mobility and higher C-C bond formation energies on the surface of nanoparticles with Fe_5C_2 structure.

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1. Introduction

Iron (Fe) is one of the most widely employed catalysts in a number of industrially valuable processes such as the low-temperature production of liquid fuel (higher hydrocarbons) from carbon monoxide and hydrogen (Fischer Tropsch process), hydrogenation of unsaturated hydrocarbons, and carbon nanotube synthesis by catalytic chemical vapor deposition (CVD) using carbon containing precursors (methane, acetylene, ethanol or carbon monoxide).[1-3] The Fischer Tropsch process and the CVD synthesis of CNTs may be considered antagonistic to each other, as Fe particles catalyze the formation of C-H bonds as the final step for the former and their breaking as the first step for the latter. In both cases, populations of active, inactive and deactivated particles co-exist during the reaction. In addition, they may be in metastable states that can be found only under reaction conditions. Despite many experimental and theoretical studies of Fe catalysts for both of these reactions, very little is known about the exact structure and chemistry of active and inactive particles, especially pertaining to the nucleation and growth mechanism of carbon nanotubes (CNTs). A better understanding of the intrinsic factors that determine catalytic activity and inactivity will lead not only to improved CNT synthesis approaches but provide fundamental

understanding of other chemical processes such as Fischer Tropsch. In order to achieve this understanding, we need to be able to characterize the dynamic behavior of nanoparticles *in situ* in the reactive environment.

Recently, *in situ* atomic-resolution observations, using environmental scanning/ transmission electron microscopy (ESTEM), have shown that Fe nanoparticles transform into cementite (Fe₃C) prior to carbon nanotube growth, implying that this metastable phase is the active catalyst structure for CNT formation.[4-6] Moreover, it is well known that only a small percentage of NPs are actually active for CNT growth, and that all active particles deactivate after some period of CNT growth. Many publications propose various hypotheses concerning CNT growth and catalyst deactivation processes, yet direct experimental evidence to corroborate any of them has been lacking. Moreover, little attention has been paid to the morphology, structure or chemistry of the large fraction of catalyst particles that remain inactive for the C-C bond formation that leads to CNT nucleation.

Here, we present direct experimental evidence of the difference in the structure and chemistry of active and inactive NPs operating under identical reaction conditions. Our experimental results are supported by kinetic and energetic data obtained from density functional theory (DFT) calculations.

2. Materials and Method

2.1 ESTEM

We have used an ESTEM column for combinatorial catalysis, i.e. to selectively deposit the Fe containing nanoparticles and use them for carbon nanotube growth via catalytic chemical vapor deposition (C-CVD). Perforated SiO_x thin films supported on a Si-TEM grid loaded on a TEM

heating holder were introduced in TEM column. Diironnonacarbonyl (Fe₂(CO)₉) was used as precursor to form iron particles on the films. Electron beam induced decomposition (EBID) of the adsorbed precursor molecules was employed to deposit nanoparticles of desired size and spacing from this iron precursor.[4] After EBID, the samples were cleaned from residual carbon by heating to 630 °C in flowing hydrogen in the TEM column without exposing the catalyst particle to atmosphere. Fe containing nanoparticles were also observed to form by thermal decomposition of the residual precursor adsorbed on the SiO_x substrate during heating: these are smaller in size (4 nm to 8 nm in diameter).[7] Hydrogen was then replaced by 1.7 Pa of acetylene (C₂H₂), carbon source for CNT growth, while keeping the sample at 630 °C. Time resolved images were recorded at a frame rate (time resolution) of 9 s⁻¹ using digital video recorder. Occasionally, catalyst particles also nucleated and grew at 630 °C in flowing acetylene concurrently with CNT formation. These particles nucleate from the carbothermic reduction of an iron silicate, fayalite (Fe₂SiO₄) phase, most probably formed by the reaction of iron and the SiO_x substrate during heating (video-S1).

The electron dose for CNT growth observations was limited to approximately 3.7×10^5 electrons nm⁻²·s⁻¹. Although, as already described, the interaction of the electron beam with the samples is responsible for the formation of some of the catalyst nanoparticles (NPs), we do not believe it induces or hinders CNT growth, since we often found that CNTs formed *prior* to electron irradiation as well as under electron beam exposure.

(Figure 1 here)

2.2 Structure Determination of nanoparticles:

Individual frames from the videos were extracted for structural analysis using fast Fourier transformation (FFT or digital diffractogram) (Figure 1). Only the images with 2-d lattice resolution were used for structure identification. Measured d-spacing and angles were matched

with known phases containing Fe, O, Si, and carbon using a software, called Crystal Ball, developed at NIST (<u>https://gitorious.org/crystal-ball-plus</u>). The structures of known phases were retrieved from ICDD files available to us at <u>http://www-i.ncnr.nist.gov/icsd/</u>. In the first step, program uses these files to match all measured d-spacing to the same phase within specified error (under 2% for our measurement) and identifies the crystal planes (Table 1a). After that the measured angles between the planes, selected in the first step, are matched (Table 1b). In the final step, a zone axis is assigned. A structure match is assigned only if all (two or more) measured d-spacing, the angles between them, and a common zone axis matched to a known phase within 2% error (Table 1).

(Table 1a and 1b here)

2.3 Density Functional Calculations

The theoretical calculations were performed using the Vienna ab-initio simulation package $(VASP)^*$.[8-11] The interactions between valence electrons and ion cores were treated by Blöchl's all-electron-like projector augmented wave (PAW) method.[12, 13] The exchange-correlation functional was the generalized gradient approximation with the Perdew-Burke-Ernzerhof, known as GGA-PBE.[14] The wave functions at each k-point were expanded with a plane wave basis set with a kinetic cutoff energy up to 400 eV and electronic occupancies were determined according to a Fermi scheme with an energy smearing of 0.1 eV. Brillouin zone integration was approximated by a sum over special k-points chosen using the Monkhorst–Pack method[15] and they were set to $5\times5\times1$ and $3\times2\times1$ for Fe₃C (001) and Fe₅C₂ (010) (including Fe₅C₂ (010)-0.00 and Fe₅C₂ (010)-0.25), respectively. Because of the existence of magnetic atom, spin polarization was considered in all calculations. Geometries were optimized until the energy was converged to $1.0 \times 10^{-6} \text{ eV}^{-1}$ per atom and the force was converged to 0.1 eV nm⁻¹. The transition states (TSs) structures and

the reaction pathways were computed using the climbing image nudged elastic band (CI-NEB) method.[16] The minimum energy path (MEP) was optimized using a force-based conjugategradient method[17] until the maximum force was less than 0.1 eV nm⁻¹. In the TS searches, the most stable structures were set as initial states (ISs) and final states (FSs). In addition, TSs was verified by having only one imaginary frequency.

(Figure 2 here)

The models we chose are the most stable surfaces of Fe₃C (001) and Fe₅C₂ (010),[18, 19] as shown in Figure 2. Our 2D-periodic structure models consisted of eight-layer slabs, including fourlayer iron, intercalated by four layers of carbon, containing 16 and 28 atoms, respectively. The atoms in the two bottom layers were fixed in their bulk positions and others are allowed to relax. The periodic boundary condition (PBC) was considered in the x and y directions and a vacuum layer as large as 1 nm was used along the z direction normal to the surface to avoid periodic interactions.

3. Results and discussion

Figure3 shows a sequence of still frames extracted from a high resolution TEM movie (video-S1). The crystal structure of particles with two-dimensional lattice resolution was obtained using fast Fourier transform (FFT) analysis described in section 2.2. The measured lattice spacing and angles obtained from the FFT's(Figure 3b, 3f, 3i) of regions marked by red boxes on the high resolution images(Figure 3a, 3d, 3e, 3h) are compared with X-ray diffraction data of iron, iron oxides, carbides and silicates to unambiguously characterize the crystal structure of the phases observed. However, this technique cannot be employed if the particle orientation results in d-spacings which are below the resolution limit of the microscope. For example, the structure of the

particle marked '1' (Figure3a), with an attached CNT that formed prior to electron-beam exposure to this area, could not be determined due to lack of lattice resolution in the video images. On the other hand, the structure of the large particle (Figure 3a) could be identified as fayalite (Fe₂SiO₄), oriented in the [010] direction, from the FFT (Figure 3b) of the red boxed region of the highresolution image (Figure3a).

(Figure 3 here)

We also observed the simultaneous evolution of active and inactive particles, marked '2', '3' and '4' in Figure 3b; (see also video-S1). The NP marked '2' formed after the carbothermic reduction of fayalite while NP '3' nucleated almost simultaneously near the edge of the original fayalite NP (Figure 3a and video-S1). Another NP'4' also became visible during this period and nucleated a CNT. Particle '2' transformed to the Fe₃C structure prior to nucleating a carbon nanotube (Figure3c; video-S1). The structural transformation process from fayalite to Fe₃C took approximately 55 s and the CNT formed immediately after the cementite formation in accordance with our earlier report.[4] However, particle '3' remained inactive for the remainder of our observation period of 60 s and the measured lattice spacing and the angles from FFT (Figure 3d) could be unambiguously matched to that of the Hägg phase (Fe_5C_2) oriented along [111].[20] Interestingly, NP's '2' and '3' are of approximately the same size (≈ 8 nm) and are exposed to identical conditions of temperature and pressure, but one is active and the other is not. This observation demonstrates that the activity of the catalyst is not only influenced by the local thermodynamics or by the catalyst diameter, but is affected by other intrinsic causes, e.g. the chemistry and crystal structure of the catalyst in the reactive environment.

We also observed the deactivation process of a catalyst NP as shown in Figure 4. Time-resolved, high-resolution images, extracted from a video (video-S2) recorded under the same conditions as in the previous example, show that the NP changes shape during the growth process (NP '2'; Figure 4a-4b). Measured one-dimensional fringe-spacing, visible for this particle is consistent with theFe₃C structure. However, after 9 s, the tube starts to detach from the particle (Figure 4c). The CNT and a portion of the NP completely detached from the original NP within the next second. The remaining NP part was then identified as having the Fe₅C₂ structure (Figure 4d and Figure 4f), and became inactive for CNT nucleation and growth. We have reported observations of a similar detachment process recorded at low magnification (no lattice resolution) earlier, where CNTs formed and detached several times from the same NP before particle deactivation.[21] Clearly, high resolution images show that the deactivation process can be correlated with the structural transformation from Fe₃C to Fe₅C₂. Lattice fringes could not be observed for NP '3', precluding structure determination.

(Figure 4 here)

The identification of an inactive phase, exhibiting a different carbide structure from that previously reported for active particles, prompted us to systematically characterize other active and inactive catalyst particles co-existing in the same reaction environment. We analyzed 40 particles from 20 videos recorded at 630 °C in 1.7Pa of acetylene. NPs, from which high-resolution images with 2-d lattice fringes could be obtained, were used for structural identification. These videos include particles formed from the precursor adsorbed on SiO_x by the three routes described

earlier. We identified three types of inactive particles: (a) un-encapsulated particles (Figure 3h and Figure 4a-particle '3'); (b) particles encapsulated within a graphitic structure (Figure 4a-particle '1'); (c) active particles becoming inactive after growth and detachment of CNTs (Video-S2, Figure 4d). In addition, we identified two particles that fluctuated between the two structures: one cementite-phase particle nucleated graphitic carbon and later transformed to Hägg phase during encapsulation, and another particle had the Fe_5C_2 structure for 0.1 s during the CNT growth. Despite of these fluctuations between the two carbide structures, the active and the inactive NPs invariably had the Fe_3C and Fe_5C_2 structures, respectively.

Our findings raise the question as to why CNT formation is favored on cementite over the carbon-rich Hägg phase. Some of the possible reasons could be (a) difference in bulk diffusion rate for C in the two structures; (b) phase stability at our reaction temperature; (c) difference in surface activity for C diffusion and polymerization (C-C bond formation). Although there is no data reported for the activation energy for bulk carbon diffusion for either phase, the reported diffusion constants at 500 °C, $D(Fe_3C) = 6.10^{-14}$ and $D(Fe_5C_2) = 8.5.10^{-14} \text{ cm}^2\text{-s}^{-1}[22]$, are too similar to explain the difference in observed activity for the CNT growth.

General understanding of the bulk Fe-C phase diagram, studied mostly for steel manufacturing, is that Fe₃C is the most stable phase, which decomposes into Fe and graphite above 700 °C, while Fe₅C₂ decomposes around 350 °C to form Fe₃C.[23] It is important to note that our experimental conditions are not comparable to the bulk phase diagram, and small iron NPs behave differently from bulk, due to their higher surface energy. Moreover, graphite formation on Fe₃C is reported to encourage carbide decomposition, which would destabilize this phase, while the newly formed Fe activates hydrocarbon decomposition, thereby encouraging CNT growth.[24] On the other hand, Fe₅C₂ is reported to be stabilized at temperatures between 400 °C to 650 °C under high

carbon chemical potential which resembles our reaction conditions.[25] Therefore it is possible that dynamic equilibrium conditions, generated under our growth conditions, allow both Fe₃C and Fe₅C₂ phases to co-exist. Consequently we can rule out the difference in the thermodynamic stability of one phase over the other as a cause for CNT formation.

(Figure 5 here)

Third possibility is confirmed by exploring the potential energy of surfaces (PESs) for carbon diffusion and C-C bond formation on the thermodynamically most stable surfaces of Fe₃C (001) and Fe₅C₂ (010) structures using DFT calculations[18, 19, 26] Despite the shape changes, the particles remain crystalline during growth and sometimes well-defined facets (surface)/surface steps are visible in 2-D images as marked by dashed lines on Figure 4a and Figure 4d. Therefore, to investigate the surface topology effect on the mechanism, we calculated the potential energy curves (PECs) of carbon migration and carbon polymerization on both Fe₅C₂(010)-0.00 and 0.25. The optimized Fe₅C₂(010)-0.25 is slightly more stable than Fe₅C₂(010)-0.00 by 0.13 eV/atom, which is consistent with the previous observation.[26] To find the most stable ISs and FSs in carbon migration/polymerization reactions, the possible configurations of C adsorption on Fe₃C (001) and Fe₅C₂ (010) (-0.00 and -0.25) were optimized, and the chemisorption energy (*E*_{ads}) was estimated as follows,

$E_{ads} = E_{nC/slab} - (E_{slab} + nE_{C})$

Where $E_{nC/slab}$ is the total energy of nC atoms on surface, E_{slab} is the total energy of the bare slab of the surface, E_C is the total energy of free C atom, n is the number of the C atoms. Starting from the most stable atomic carbon adsorption position (S₀), four and six (seven) carbon migration steps were found on Fe₃C (001) and Fe₅C₂ (010)-0.00 (0.25) surface, respectively, as shown in Figures 5a-5f. For C-C bond formation (polymerization), four reaction pathways were identified. Since they possess similar features, the rate-determining steps (those with the highest barriers) are shown in Figure 6.

(Figure 6 here)

From this data, we find that all pathways involving the Fe₃C (001) surface have lower energies (lower barrier heights) for C migration and C-C bond formation (C polymerization), relative to Fe₅C₂ (010) regardless of 0.00 and 0.25, especially for the latter. The DFT calculations indicate that the C migration and C polymerization are both kinetically and thermodynamically favored on the Fe₃C (001) surface, promising further carbon nanotubes growth. However, Hägg carbide particles are inactive and do not appear to be associated with the growth of the carbon nanotubes due to higher migration and polymerization barrier, in agreement with the experimental findings described above.

We also note that Fe converts into carbide structures (Fe₃C and Fe₅C₂) during the Fischer Tropsch reaction to form higher hydrocarbons (synthetic fuel) from a mixture of CO and H₂.[1] It is the carbon-rich Hägg phase that is active for H-C bond formation.[27] The surface stability, CO dissociation and hydrocarbon formation on different surfaces of Fe₅C₂ has been explored extensively. In agreement with our results, Cao *et al.*[28] have shown that the C-C coupling energy barrier is 0.55 eV higher than the C-H bond formation for the Hägg phase, implying that C polymerization leading to a large sp² network on the Fe₅C₂ (001) surface is not favored.

4. Conclusions

In summary, our observations, made under conditions leading to CNT growth, provide direct evidence that the structure and chemistry of the NPs may change under reaction conditions and play a critical role in catalytic activity and the related deactivation processes. For example, we show that the Fe catalyst transforms into two distinct carbide phases, cementite (Fe₃C) and Hägg (Fe₅C₂) under CNT growth conditions. Whereas the carbon-rich Hägg carbide has been shown to be an active phase for hydrocarbon formation in the Fischer Tropsch process, it is invariably inactive for the competitive process, namely CNT formation, in contrast to the less carbon-rich cementite phase. Our studies provide new insights into the intrinsic differences in the catalytic activity of Fe-C NPs which can help designing new experimental strategies that aim to select the appropriate phase for the desired synthesis process (CNT or FT). Our methods can be extended to identify the structure and chemistry of catalyst nanoparticles for other processes.

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REFERENCES

[1] M.E. Dry, The Fischer–Tropsch process: 1950–2000, Catalysis Today, 71 (2002) 227-241.

[2] A. Kukovecz, Z. Konya, N. Nagaraju, I. Willems, A. Tamasi, A. Fonseca, J.B. Nagy, I. Kiricsi, Catalytic synthesis of carbon nanotubes over Co, Fe and Ni containing conventional and sol-gel silica-aluminas, Physical Chemistry Chemical Physics, 2 (2000) 3071-3076.

[3] C.P. Casey, Guan, H., An Efficient and Chemoselective Iron Catalyst for the Hydrogenation of Ketones, Journal of The American Chemical Society, 129 (2007) 5816-5817.

[4] R. Sharma, Moore, E.S., Rez, P, Treacy M.M.J., Site-specific fabrication of Fe particles for carbon nanotube growth, Nano Letters, 9 (2009) 689-694.

[5] H. Yoshida, Takeda, Seiji, Uchiyama, Tetsuya, Kohno, Hideo, Homma, Yoshikazu, Atomic-Scale In-situ Observation of Carbon Nanotube Growth from Solid State Iron Carbide Nanoparticles, Nano Letters, 9 (2008) 3810-3815.

[6] C.T. Wirth, B.C. Bayer, A.D. Gamalski, S. Esconjauregui, R.S. Weatherup, C. Ducati, C. Baehtz, J. Robertson, S. Hofmann, The Phase of Iron Catalyst Nanoparticles during Carbon Nanotube Growth, Chemistry of Materials, 24 (2012) 4633-4640.

[7] S.-W. Chee, Sharma, R., Fabricating Fe Nanoparticles for Carbon Nanotube Growth Using Electron Beam Induced Deposition, Micron, 43 (2011) 1181-1187.

[8] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, Computational Materials Science, 6 (1996) 15-50.

[9] G. Kresse, J. Hafner, Ab initio molecular dynamics for liquid metals, Physical Review B, 47 (1993) 558-561.

[10] G. Kresse, J. Hafner, Ab initio molecular-dynamics simulation of the liquid-metal-amorphous-semiconductor transition in germanium, Physical Review B, 49 (1994) 14251-14269.

[11] G. Kresse, J. Furthmüller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B, 54 (1996) 11169-11186.

[12] P.E. Blöchl, Projector augmented-wave method, Physical Review B, 50 (1994) 17953-17979.

[13] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method, Physical Review B, 59 (1999) 1758-1775.

[14] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Physical Review Letters, 77 (1996) 3865-3868.

[15] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, Physical Review B, 13 (1976) 5188-5192.

[16] G. Henkelman, B.P. Uberuaga, H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, The Journal of Chemical Physics, 113 (2000) 9901-9904.

[17] G.F. Kresse, J., Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B, 54 (1996) 11169-11186.

[18] W.C. Chiou, E.A. Carter, Structure and stability of Fe₃C-cementite surfaces from first principles, Surface Science, 530 (2003) 87-100.

[19] P.J. Steynberg, van den Berg, J.A., Janse van Rensburg, W., Bulk and Surface Analysis of Hagg Fe carbide (Fe_5C_2): a density functional theory study, Journal of Physics Condensed Matter, 20 (2008) 11.

[20] J.J. Retief, Powder diffraction data and Rietveld refinement of Haegg-carbide, chi-(Fe₅C₂), Powder Diffraction, 14 (1999) 130-132.

[21] A. Gamalski, E.S. Moore, M.M.J. Treacy, R. Sharma, P. Rez, Diffusion-gradient-induced length instabilities in the catalytic growth of carbon nanotubes, Applied Physics Letters, 95 (2009).

[22] A. Schneider, G. Inden, Carbon diffusion in cementite (Fe₃C) and Hagg carbide (Fe₅C₂), Calphad-Computer Coupling of Phase Diagrams and Thermochemistry, 31 (2007) 141-147.

[23] http://web.utk.edu/~prack/MSE%20300/FeC.pdf, in.

[24] F. Tsui, Ryan P.A., Self-organization of carbide superlattice and nucleation of carbon nanotubes, Journal Of Nanoscience And Nanotechnology, 4 (2004) 408-413.

[25] Q. Wei, Pippel, E., Woltersdorf, J., Grabbke, H.J., Microprocesses of coke formation in metal dusting, Materials and Corrosion, 50 (1999) 628-633.

[26] D.C. Sorescu, Plane-Wave Density Functional Theory Investigations of the Adsorption and Activation of CO on Fe5C2 Surfaces, Journal of Physical Chemistry C, 113 (2009) 9256-9274.

[27] T. Herranz, S. Rojas, F.J. Perez-Alonso, M. Ojeda, P. Terreros, J.L.G. Fierro, Genesis of iron carbides and their role in the synthesis of hydrocarbons from synthesis gas, Journal of Catalysis, 243 (2006) 199-211.

[28] D.B. Cao, Y.W. Li, J.G. Wang, H.J. Jiao, Adsorption and reaction of surface carbon species on $Fe_5C_2(001)$, Journal of Physical Chemistry C, 112 (2008) 14883-14890.

Figure Caption

Figure1. HRTEM image and corresponding FFT used to measure the d-spacing and angles for structural identification. This particle was identified as Fe_5C_2 oriented in [111] direction.

Figure 2.The Models of $Fe_3C(001)$ and $Fe_5C_2(010)$ (including 0.00 and 0.25). Blue and gray spheres indicate the Fe and C atoms in the top two layers. Green and Orange spheres indicate the Fe and C atoms in the bottom two layers, respectively.

Figure 3. High resolution images extracted from a video (S1) showing the progression of NP structure transformation during observation. (a) A large NP (unmarked) and small active NP, marked '1', with CNT attached. (b)FFT from red boxed region of larger particle in A; (c) cartoon showing the indices of planes matching fayalite structure, (d) particle '2', '3' and '4' form after 36 s of observation period. Note a CNT formed from NP'4'. (e) NP'2' transformed into Fe₃C (cementite) as CNT's nucleated from it. (f) FFT of the red boxed region marked in E. (g) cartoon of FFT showing the indices matching to Fe₃C structure. (h) High magnification image of inactive NP '3', (i) FFT of red boxed region in H, (j) cartoon of FFT showing the indices matching Fe₅C₂ (Hägg) structure. Bar is 5 nm.

Figure 4. Individual frames extracted from a video (S2) showing MWCNT growth, (a-b) catalyst particle, marked 2, changes shape during the growth process. (c)After 9 s, the tube starts to detach from the particle and (d) residual particle remains inactive. (e) FFT for red boxed region marked in d and (f) cartoon of FFT with indices matching Fe₅C₂ structure. Dotted red lines I (a) and (d) indicate the facets on active and inactive particles respectively.

Figure 5. The schematic pathways (a, c, and e) and potential energy curves (b, d, and f) of carbon migration on Fe₃C(001), Fe₅C₂(010)-0.00, and Fe₅C₂(010)-0.25; Here, S_CX and S_HX'(S_HX) (X=0

to 6) are the stable structures of single carbon atom adsorption on Fe_3C (Cementite) and Fe_5C_2 (Hägg Fe carbide 0.00 and 0.25), respectively. The surface-adsorbed carbon atoms are highlighted in pink.

Figure 6. The rate-determining steps (with the highest barrier) of the 4 possible pathways for C-C polymerization (See Figure S2for more information). Blue and gray spheres indicate the Fe and C atoms in the top two layers. Arrows indicate C diffusion paths. Green and orange spheres indicate the Fe and C atoms in the bottom two layers, respectively. Here, D_CX, D_HX'(D_HX), and TS_CX, TS_HX'(TS_HX) are the reactants/products and transition states involved in the elementary reactions. The surface-adsorbed two carbon atoms are highlighted in pink.

| Spot Number | Measured Spacing (nm)* | Reference spacing (nm) | % error | Plane |
|----------------|------------------------------|------------------------------|------------|-----------|
| 1 | 0.2411±0.0114 | 0.2419 | 0.347 | (-2 0 2) |
| 2 | 0.4819±0.0067 | 0.4839 | 0.409 | (-1 0 1) |
| 3 | 0.2152±0.011 | 0.2122 | 1.395 | (-2 2 0) |
| 4 | 0.2054±0.011 | 0.2025 | 1.457 | (-1 2 -1) |

Table 1a. Matching and assigning d-spacing using CrystalBall

Table 2.1b. Matching angles and assigning zone axis.

| 1 st Spot | 2 nd Spot | 1 st plane | 2 nd plane | Measured Angle (deg.) | Referen ce Angle (deg.) | % error | Zone Axis |
|-------------------------|-------------------------|-----------------------|-----------------------|-----------------------------|-------------------------------|------------|--------------|
| 1 | 4 | (-2 0 2) | (-1 2 -1) | 108.68±1.9 | 108.473 | 0.191 | [1 1 1] |
| 1 | 3 | (-2 0 2) | (-2 2 0) | 83.73±1.8 | 83.889 | 0.190 | [1 1 1] |
| 3 | 4 | (-2 2 0) | (-1 2 -1) | 24.95±0.2 | 24.584 | 1.491 | [1 1 1] |
| 2 | 4 | (-1 0 1) | (-1 2 -1) | 108.47±1.9 | 108.473 | 0.002 | [1 1 1] |

*measurement errors estimated from the pixel resolution.



Figure 1.



Figure 2.



Figure 3.



Figure 4.



Figure 5



Figure 6

Supporting Information:

Video-S1.High resolution digital video recorded with time resolution of 9 frames s-1 at 630 °C in 1.7 Pa of flowing acetylene showing (a) structural transformation of iron silicate (fayalite), (b) nucleation of particle 2, 3, and 4 and (c) nanotube growth from particle 2 and 4 but not from 3.

Video S2

High resolution digital video, recorded under same conditions video S1, showing the shape change and deactivation of the catalyst NP after CNT detachment.