Direct evidence of atomic-scale structural fluctuations in catalyst nanoparticles
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nisms.

1 **ABSTRACT:** Rational catalyst design requires an atomic scale mechanistic understanding of the 2 chemical pathways involved in the catalytic process. A heterogeneous catalyst typically works by adsorb-3 ing reactants onto its surface, where the energies for specific bonds to dissociate and/or combine with 4 other species (to form desired intermediate or final products) are lower. Here, using the catalytic growth 5 of single-walled carbon nanotubes (SWCNTs) as a prototype reaction, we show that the chemical pathway may in-fact involve the entire catalyst particle, and can proceed via the fluctuations in the formation and 6 7 decomposition of metastable phases in the particle interior. We record in situ and at atomic resolution, the 8 dynamic phase transformations occurring in a Cobalt catalyst nanoparticle during SWCNT growth, using 9 a state-of-the-art environmental transmission electron microscope (ETEM). The fluctuations in catalyst 10 carbon content are quantified by the automated, atomic-scale structural analysis of the time-resolved 11 ETEM images and correlated with the SWCNT growth rate. We find the fluctuations in the carbon con-12 centration in the catalyst nanoparticle and the fluctuations in nanotube growth rates to be of complemen-13 tary character. These findings are successfully explained by reactive molecular dynamics (RMD) simulations that track the spatial and temporal evolution of the distribution of carbon atoms within and on the 14 15 surface of the catalyst particle. We anticipate that our approach combining real-time, atomic-resolution 16 image analysis and molecular dynamics simulations will facilitate catalyst design, improving reaction 17 efficiencies and selectivity towards the growth of desired structure

INTRODUCTION

1.

2 Revealing the mechanisms by which nanometer sized catalysts act in chemical reactions and ma-3 terial syntheses is essential for the precise control of reaction rate, product selectivity, and ultimately, 4 catalyst design. For example, based on the existing understanding of heterogeneous catalysis, it is assumed 5 that the role of the catalyst in the synthesis of carbon nanotubes (CNTs) by catalytic chemical vapor dep-6 osition (C-CVD), is to decompose adsorbed carbon precursors and act as a template for CNT (graphene) 7 nucleation.[1, 2] However, the detailed steps leading to graphene nucleation and subsequent nanotube 8 growth have not been experimentally established. An alternative hypothesis, suggested by Baker et al. [3], 9 and later supported by molecular dynamics simulations[4], is that the catalyst acts as a reservoir, dissolv-10 ing carbon atoms in a liquid phase that precipitates C in a solid form (carbon fibers) after reaching a 11 supersaturated concentration, analogous to the vapor-liquid-solid (VLS) mechanism proposed for silicon 12 nanowire growth [5]. However, in situ high-resolution transmission electron microscopy (HRTEM) stud-13 ies have shown that the catalyst particles are crystalline, and not liquid, during CNT growth [6-9]. These 14 results suggest a vapor-solid-solid (VSS) mechanism, where the carbon atoms may diffuse on the solid 15 catalyst surface, to form the nanotube without dissolving into the catalyst[6, 10]. However, if dissolution 16 of C into the catalyst particle were to occur, there are two possibilities: 1] formation of a stable carbide, 17 leading to inactivation of the catalyst [11], or 2] formation of a solid solution or metastable carbides that 18 allow for continued catalytic activity [12-15]. In this latter scenario, the carbon in the catalyst nanoparticle 19 represents a reactive intermediate that can combine with surface carbon.

Recently, metal catalyst particles have been reported to convert to a carbide phase prior to CNT growth [15],[13, 16]. Several theoretical studies on nucleation and growth of CNT using various simulation techniques [17] including reactive molecular dynamics [18-20], tight binding [21, 22], and timestamped force-biased Monte Carlo simulations [23] of Ni and Co catalysts have suggested that carbon

1 atoms diffusing in and out of metal particles are present at different stages of the process, thereby provid-2 ing evidence that carbon atoms indeed diffuse into the catalyst bulk prior to incorporating into SWCNTs... 3 Structural heterogeneity for cobalt catalyst nanoparticles during triple wall carbon nanotube growth has 4 also been reported [14]. The lower energy of M-C bond formation, for example, 2.6 eV for Ni-C compared 5 to 6.6 eV for C-C bonds [24, 25], and the stronger cohesion energy per formula unit of Ni-C (10.1 eV) 6 compared to Ni-Ni (4.5 eV) and C-C (7.4 e) [22] favors metal carbide formation over graphene as ex-7 plained in an earlier report [18]. However, the existence of carbide structures raises further questions 8 concerning the role of the catalyst in nucleating CNTs: does carbon diffuse on the surface of the metal 9 carbide or via the bulk, as proposed for metal particles? Or do metastable carbide structures, formed under 10 non-equilibrium conditions, play a part?

11 By employing an in situ environmental transmission electron microscope (ETEM) as an experi-12 mental platform and reactive molecular dynamics (RMD) simulations [26],[27], we resolve the entire 13 process from the nucleation and growth of a SWCNT from a single catalyst nanoparticle to termination 14 (catalyst deactivation). Here, we present the observed and simulated time-resolved structural dynamics of 15 catalyst nanoparticles under non-equilibrium conditions during SWCNT growth and compare the chemical changes associated with phase fluctuations to the carbon incorporation rate in growing nanotubes. 16 Intriguingly, we identify two sources of carbon supporting the SWCNT growth 1] Surface diffusing C 17 18 atoms that are incorporated at a constant rate 2] C atoms diffusing out of metastable carbides in the particle 19 bulk, incorporated at fluctuating time intervals. Our results hold relevance for a number of other chemical 20 reactions where Co nanoparticles are used as active catalysts for e.g. Ficsher Tropsch process for hydro-21 carbon synthesis and petroleum cracking [28]. A broader implication of this study is that our methods may 22 be employed to resolve dynamic atomic-level processes in heterogeneous catalysis.

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2. EXPERIMENTAL SECTION

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2.1. ETEM experiments.

3 Atomic-resolution videos of SWCNT growth were recorded using an environmental transmission 4 electron microscope (ETEM), operated at 300 kV and equipped with an image corrector, at a rate of 10 5 frames per s. Acetylene (C₂H₂) and Co_xMo_{1-x}/MgO (prepared by wet chemical methods) [29] were used 6 as carbon precursors and a catalyst-support system, respectively. The catalyst-support system was first 7 heated to 750 °C in oxygen (100 Pa) to remove impurities such as gaseous hydrocarbons adsorbed on the 8 surface. Then the sample was cooled to the SWCNT growth temperature of 650 °C in vacuum (0.0001 9 Pa), and was maintained at this temperature for 10 minutes before exposing to 0.01 Pa of C₂H₂. Crystalline 10 Co clusters precipitated from the support and formed 2 nm to 5 nm sized particles. These particles nucle-11 ated and grew SWCNTs. No molybdenum was found within the nanoparticles as reported earlier [15].

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2.2. Simulation Methods.

14 Classical reactive molecular dynamics (RMD) simulations as implemented in our SIMCAT code 15 [25] were employed to simulate the catalyst particle during SWCNT growth. was employed to simulate 16 the catalyst particle during SWCNT growth. The model consists of a carbide-like particle (1.8 nm diam-17 eter, 160 atoms) with Co₂C composition deposited on a rectangular monolayer substrate model in an at-18 mosphere of a C precursor gas model ($P \approx 18,000$ Pa, corresponding to 1 C atom in the box). The simu-19 lation box was 3.98 nm long, 3.88 nm wide, and 50 nm deep. The reactive empirical bond order (REBO) 20 Brenner potential [30], which is based on the Tersoff [31] and Tersoff-Brenner potentials [32], was used 21 to represent carbon-carbon interactions. Metal-carbon interactions using [25, 31] a DFT-parameterized 22 potential based on a many-body scheme based on the Tersoff potential that combines Morse-type repulsive 23 and attractive terms with an additional screening parameter; which takes into account the coordination of 24 C atoms to distinguish between surface atoms and dissolved C atoms, and different hybridization states.

1 The many-body Sutton-Chen potential was used to describe the metal-metal interaction [33] and the metal-substrate interaction was parameterized using an average adsorption strength of 6.11 eV·nm⁻². A 2 3 predictor-corrector algorithm and a time step of 0.5 fs were used in the integration of the equations of 4 motion and the temperature was maintained at 650 °C using the Nosé-Hoover thermostat [25]. The disso-5 lution residence time (τ_D) is the time that a C atom remains dissolved in the particle. A number of metal 6 first nearest-neighbor (MNN) greater than or equal to 5 (MNN \geq 5) was used as criterion to determine 7 whether C atoms were dissolved or not. C atoms that do not dissolve in the particle ($\tau_D = 0$ ns) are labeled 8 as SD, those remaining dissolved for less than 3 ns (0.001 ns $\leq \tau_D \leq 3$ ns) as BD, and those remaining 9 dissolved for longer ($\tau_D \ge 3$ ns) as CF.

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3. **RESULTS AND DISCUSSION**:

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3.1. Environmental TEM:

Figure 1a is a frame extracted from a video (Movie S1, frame rate of 10 s⁻¹) of SWCNT growth 14 15 from a (2.5 ± 0.04) nm diameter Co catalyst particle (uncertainties represent the deviation from a perfectly 16 spherical shape) supported on MgO. As reported earlier, the metal particle converts to a carbide phase 17 with continued exposure to C_2H_2 , before nucleating a SWCNT [15] The video sequence used here was 18 captured after the nucleation of a SWCNT with its rim anchored to the particle, enclosing approximately 19 one-third of the top portion of the particle (marked by arrows in Figure 1a and 1d). Within this individual 20 (2.5 ± 0.04) nm diameter particle, two distinct regions with different structures and a clear boundary, can 21 be visually identified (Figure 1a and 1d): a region of the particle that is mostly enclosed in the SWCNT 22 (R1), and the rest of the particle (R2). By measuring lattice spacings and angles from the fast Fourier 23 transforms (FFTs) of the high-resolution images (Figure 1b and 1c), the structures of the regions R1 and 24 R2 are identified as Co metal and Co₂C, respectively (Figure S5 and Table S1). While the co-existence of 1 Co, Co₂C and other related phases in an active catalyst particle has been reported [14], 'direct evidence' 2 in the images showing two structures with a pronounced boundary has not been reported before. *Ex situ* 3 electron diffraction studies of Co have also reported the formation of Co₃C and Co₂C at 450 °C and 500 4 °C, respectively, that decomposed to Co upon heating above 650 °C [34]. It is possible that such metasta-5 ble structures with clear boundaries co-exist in nanoparticles under non-equilibrium conditions and can 6 only be revealed by high resolution images acquired under reaction conditions.

7 In addition to the co-existence of these two distinct structures, their respective areas (R1 and R2) 8 are observed to fluctuate during SWCNT growth (Figure 1e-h). In order to quantitatively evaluate the 9 relative areas of R1 and R2, and their evolution with time, careful measurements of distances between 10 individual atomic columns in each frame are required. We establish an image processing scheme (IPS) 11 that locates the atomic-column positions in each frame, measures the average first nearest-neighbor dis-12 tance for every individual column, and then assigns atomic columns as belonging to the Co metal (0.22) 13 nm) or Co-carbide (0.25nm) phases accordingly [35] (Figure S6). The high precision of the IPS (7 pm 14 and 15 pm for Co and Co-carbide respectively) enables the accurate assignment of phases and identification of phase boundaries [35] 15

This quantification finds the size of the Co area (R1) at 4.0 s to be approximately 1.33 times larger (Figure 1e) than that at 10.0 s (Figure 1f). After 10.0 s, the size of this area increases again (Figure 1g), and then decreases at 40.0 s (Figure 1h). The variation in sizes of R1 can be attributed to the difference between the rate of carbide decomposition (r_1 , equation 1) and formation (r_2 , equation 2). This leads to a decrease (*x*C) or increase (*y*C) in the total carbon amount ($\Delta(t)$) in the particle (equation 3) under nonequilibrium conditions.

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$$Co_2C \xrightarrow{r_1} Co_2C_{1-x} + xC$$
 (1)

23
$$yC + Co_2C_{1-y} \xrightarrow{r_2} Co_2C$$
 (2)

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$$\Delta(t) = r_1(t) - r_2(t)$$
 (3)

The data-rich IPS results are also employed to evaluate the carbon content in the particle at any given time. We first carefully measure the carbon distribution within the particle in one frame (Figure 2a). The ratios of carbon to Co (C:Co) in each atomic layer are shown in Figure 2b, where layer 1 is in contact with the MgO support and layer 10 is the top surface that is enclosed by the growing SWCNT (red arrow). We find that the C:Co ratio is 0.5 in the first three atomic layers, and then gradually drops down to 0.31 in the next five layers. For the 9th and 10th atomic layers, the ratios for are approximately 0.16 (Figure 2b).



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10 **Figure 1.** Co and Co₂C domains in catalyst nanoparticle and dynamic fluctuations in their relative areas. (a) A high-resolution image of a catalyst particle during SWCNT growth that contains two distinct regions, 11 R1 and R2. (b) and (c) FFT from R1 and R2 showing the structures in R1 and R2 as Co and Co₂C, 12 13 respectively. (d) A simplified illustration of Figure 1a identifying the catalyst particle with the two struc-14 tures R1 and R2, in contact along one edge with the MgO substrate, which is in the same plane (dark 15 green). MgO planes below the particle, are marked as lighter shades of green. (e-h) High-resolution snap-16 shots of CNT growth at 4.0 s (e), 10.0 s (f), 20.0 s (g), and 40.0 s (h). Co (R1) and Co-carbide (R2) areas 17 are colored red and blue, respectively, to highlight the change in respective areas with time. All scale bars

18 represent 1 nm.

1 Experimentally, the number of carbon atoms in the nanoparticle at time t (C_p(t)) can be obtained 2 from individual frames of the growth video by measuring the volume of the Co_2C region, relative to the 3 volume of the catalyst particle (Figure S6). Figure 2c shows the variation in $C_p(t)$ as a function of time. 4 The amount of carbon inside the particle fluctuates aperiodically until the supply of carbon precursor is 5 ended. For instance, the amount of carbon drops to (163 ± 3) atoms at 3.6 s, increases again to (210 ± 3) 6 atoms at 9.8 s, and then drops to (162 ± 3) atoms at 16.5 s. The uncertainty in C_p(t) is derived by propa-7 gating the uncertainty in atomic position identification (15 pm) through equations shown in the Supple-8 mentary Information. In order to elucidate the role of carbide phase for the SWCNT growth, we measure 9 relative change in the length of the growing SWCNT with time. Since the diameter of the growing 10 SWCNT remains relatively unchanged during this observation period, we obtain number of the carbon 11 atoms added during a specific time period by measuring the increase in the arc length of the tube profile 12 (Figure S7) in each frame. The plot in Figure 2d shows the variation in the number of carbon atoms added 13 to the SWCNT as a function of time. A stochastic fluctuation in the growth periods and intervals between 14 growth periods is observed and is in agreement with earlier reports.[36, 37]





Figure 2. Experimentally measured, spatial (layer-wise) and temporal variations in carbon content in the nanoparticle and the growing SWCNT. (a) A single high resolution frame after applying IPS showing the location of atomic columns, where inter-atomic column distances ranging 0.20 nm to 0.22 nm or 0.23 nm to 0.26 nm correspond to Co or Co_2C , respectively. 1st atomic layer of the catalyst particle is in contact with MgO support (green dashed line), and the 10th layer is inside the SWCNT. Atomic layers are numbered 1 to 10 away from the green line. The scale bar represents 1 nm. (b) Corresponding local ratios of carbon and Co as a function of atomic layer. (c) Number of carbon atoms in the catalyst particle $C_p(t)$; and (d) the number of carbon atoms added to growing nanotube plotted as a function of time. A moving average of 10 frames is applied to smooth the data (raw data in Figure S8).

The carbon amount in the catalyst particle and in the tube at specific time intervals can be compared from the data provided in Figure 2c and 2d. As the number of carbon atoms added to the tube increases in the time period between 10.0 s to 15 s (Figure 2d), $C_p(t)$ decreases (Figure 2c). On the other hand, $C_p(t)$ increases until 23.8 s while the tube growth rate decreases to a local minimum. These comparisons suggest that the variations in the particle composition, i.e. low and high carbon concentration, in the measured time period might be inversely related to SWCNT growth rate (Figure 2c-d). The complementary character of the fluctuations in SWCNT growth rate and particle carbon content implies that fluctuations in the SWCNT growth could be related to the periods of carbide formation and carbide de composition.

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- **3.2.** Reactive Molecular Dynamics.

5 In order to better relate the carbide formation and decomposition reactions to the tube growth, we 6 examine the trajectories of individual C atoms in a Co nanoparticle by reactive molecular dynamics sim-7 ulations (RMD) and identify the role of different types of C atoms and their contribution to the growth 8 process. The RMD simulations were performed on a model 1.8 nm diameter Co₂C particle deposited on 9 a rectangular monolayer substrate in an atmosphere of a C precursor gas model ($P \approx 18,000$ Pa, Figure 10 3a). The particle size was intentionally kept smaller and the reaction conditions, such as carbon precursor 11 pressure, more aggressive in the simulations than in the experiment in order to decrease the calculation 12 time needed to observe complete events from the simulations. We note that recent advances on accelerated 13 molecular dynamics and hyperdynamics simulations have been reported and new methodologies are cur-14 rently being developed such as collective variable-driven hyperdynamics (CVHD) [38] or hybrid approaches that combine reactive molecular dynamics with time-stamp force-bias Monte Carlo simulations 15 [39], both of which could satisfactorily reproduce the dynamic behavior of reactive systems up to time 16 17 scales of seconds without altering reaction conditions [38]. Previous studies using the current approach 18 have shown that the mechanisms of nucleation and growth are the same for different particle sizes [18]. 19 The kinetics are also analogous for different particle sizes [40] and the carbon precursor concentration 20 [41]. Thus, we can qualitatively compare our simulations to the experiment results. Using a dissolution 21 residence-time criterion, as reported previously [40], C atoms can be classified into three types: 1] atoms 22 that are predominantly involved in diffusion on the particle surface (SD), or 2] in the bulk (BD) before 23 becoming part of the growing nanotube structure or 3] atoms that remain dissolved in the nanoparticle for prolonged periods of time, which makes them candidates for participation in carbide formation (CF) (Fig ure S1).

3 After the nanotube cap is formed and the nucleation stage concluded, the carbon concentration 4 in each atomic layer is obtained by calculating the ratio of z-density profiles for each atomic species (Co 5 and C) in each layer (Figure S2). The C:Co ratios from each atomic layer are averaged over 5 ns in three 6 different reaction time zones (35 ns to 40 ns, 40 ns to 45 ns and 45 ns to 50 ns). In each time zone, the 7 ratio decreases linearly along the normal away from the substrate plane (direction guided by the arrow in Figure 3a) from 0.8 to 0.2, and stabilizes in the 4th layer at approximately 0.2 (Figure 3b). It is noted that 8 9 the carbon concentration profile corresponding to the growth stage (Figure 3b) has similarity with that of the nucleation stage reported in our earlier work [27], which indicates that such carbon gradient starts to 10 11 be generated at earlier times and consolidates at the growth stage. This analysis does not include the pure 12 metal layer in contact with the support, as C atoms undergo repulsion from the support and the first peak 13 of C atoms from the z-density profiles is located closer to the second Co peak than to the first one (Fig. 14 S2). Although the particle size is smaller in the simulation than in the experiments, both of them show that carbon stays inside the particle, and the C:Co ratio drops moving perpendicularly away from the 15 16 substrate plane and remains at ≈ 0.2 in the particle region located inside the growing SWCNT (Figure 2b) 17 and 3b). For the layer that is in contact with the substrate, the C:Co ratio can be as high as 0.75 in the simulation, which includes SD, BD and CF types of C atoms. This ratio is restricted to a maximum value 18 19 of 0.5 in the experimental measurements, as from the images we can only identify the carbon amount 20 associated with the Co₂C phase and not the dissolved C atoms, if present. Moreover, the C:Co ratio for 21 each atomic layer in time zone 45 ns to 50 ns is generally lower than those for the other two time zones; 22 especially the ratio in layer 4 (≈ 0.1 in 45 ns to 50 ns time zone) implying that the total carbon amount in 23 the particle varies during SWCNT growth, which agrees with our experimental results.



2 Figure 3. Simulated spatial (layer-wise) and temporal variations in carbon content in the nanopar-3 ticle and the growing SWCNT. (a) Simulated catalyst particle (on a support) that nucleates a SWCNT 4 with atomic layers from 1 to 4 numbered in the direction of the red arrow. (b) Corresponding ratios of 5 carbon and metal as a function of each atomic layer at different time intervals (35 ns to 40 ns, 40 ns to 45 6 ns, 45 ns to 50 ns). The values are obtained from z-density profiles reported in supplementary information 7 (Figure S2). (c) Variation in the number of carbon atoms in the particle with time. (d) Carbide decompo-8 sition rate, r₁, estimated from an atomic balance of carbon atoms in the particle (equation 4) *versus* time. 9 Yellow or light blue regions indicate an increase or decrease, respectively, in either growth rate or carbon 10 concentration in the particle. (e) Nanotube growth rate (surface diffusion contribution not included) estimated directly from the total number of atoms that leave the particle versus time. 11

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To further examine the role of carbide in nanotube growth, a thorough atomic balance of C atoms from the RMD trajectories is performed. The C atomic balance equation (equation 4) shows that the carbide decomposition rate, r_1 , is a function of three components. They are the carbon dissolution (carbide formation) rate, r_2 , (Figure S3), the variation of C content in the particle with time, dC/dt, and C diffusion across the C gradient in the particle, $D_c(\nabla^2 C)$ (Figure S3).

$$r_1 = r_2 + \frac{dC}{dt} - D_C \cdot (\nabla^2 C) \tag{4}$$

2 As estimated from the RMD trajectories, the carbon atoms rate (r_2) is 1.50 $\cdot ns^{-1}$ (Figure S4a, we 3 note that rates reported from RMD calculations are much larger than actual experimental rates due to the 4 accelerated nature of these simulations). In contrast, dC/dt exhibits a fluctuating behavior in agreement 5 with experimental observations (Figure 3c and 2c, respectively). Molecular transport of C atoms inside 6 the particle is described in equation 4 as the product of the diffusion coefficient of atomic carbon in the 7 particle multiplied by the variation of the carbon concentration gradient across the nanoparticle. The dif-8 fusion term (D_c) is estimated from the mean-squared displacement and Einstein's diffusivity equation 9 (Figure S4b). The variation of the carbon gradient in the direction perpendicular to the substrate is esti-10 mated from the C composition profiles by fitting the curves in Figure 3b to a quadratic function and 11 analytically calculating the second derivative with respect to position in the z-direction. We find that the diffusion coefficient is $(1.29 \pm 0.07) \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$, which is in agreement with reported diffusion coeffi-12 cients of C dissolved in transition metals such as Ni (ranging between $10^{-11} \text{m}^2 \cdot \text{s}^{-1}$ and $10^{-10} \text{m}^2 \cdot \text{s}^{-1}$) [18], 13 and the second derivative of the carbon concentration per nm² varies between 0.14 carbon atoms and 14 0.23 C atoms. Thus, by knowing r_2 , dC/dt and $D_c(\nabla^2 C)$, r_1 is obtained via equation 4 as a function of time 15 16 (Figure 3d). In addition to obtaining the rates of carbide decomposition (r_1) , the overall tube growth rate 17 is also determined by monitoring independently the carbon atoms that leave the particle (Figure 3e). De-18 spite the accelerated dynamics intrinsic to our simulation model, the results obtained are in qualitative 19 agreement with experimental measurements. The calculated r_1 has the same fluctuations as the tube 20 growth and its value is consistently lower than that of the tube growth by approximately 2 carbon atoms 21 per ns. This observation is in qualitative agreement with experimental results (Table S2), which find the 22 number of carbon atoms integrated into the SWCNT to be larger than the number of carbon atoms ejected 23 from the bulk of the particle by a factor of 2. This implies that the carbon from the carbide decomposition 24 is forming the tube and the difference suggests that another C source is contributing to the tube growth.

1 RMD simulations show that a considerable percentage of C atoms in the catalytic process partic-2 ipate in surface diffusion, which fluctuates between 15 % and 55 % (Figure S1). Some of these carbon 3 atoms diffusing on the surface may become part of the nanotube as a function of time as illustrated in 4 Figure 4. The growth rate due to surface diffusion is estimated to be 1.03 carbon atoms·ns⁻¹ from the slope 5 of the straight line that fits the data. These results indicate a constant addition of C atoms to the nanotube 6 from C atoms diffusing on the surface, in contrast to the fluctuating behavior originating from C atoms 7 diffusing out of the particle bulk.



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Figure 4. Simulated number of surface diffusing carbon atoms added to SWCNT versus time. The rate of growth due to surface diffusion is estimated to be the slope of a straight line fit to the data relating the number of surface carbon atoms incorporated into the nanotube and time. The fit has a coefficient of determination of 0.98.

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14 **4. CONCLUSIONS:**

To summarize, both atomic-resolution images and RMD simulations show that two distinct phases; Co and Co-carbide phases co-exist in a single catalyst particle during SWCNT growth. The carbon-rich phase (carbide) is generally in contact with the support (MgO), and the carbon-poor Co is away from the support and in contact with the SWCNT rim. We propose that the carbon feedstock from the

precursor decomposes at the catalyst surface, and part of the resulting carbon diffuses into the particle to 1 2 form metal carbide. Once the tube forms and partially covers the particle surface, the carbon may not be 3 able to diffuse into the particle efficiently, making the carbide phase unstable. Therefore, a carbon-de-4 pleted region that is covered by the tube rim is present during growth. Such a carbon gradient acts as a 5 driving force causing carbon atoms to diffuse over the particle towards the surface. This resolves the 6 mechanism of carbon diffusion in particle sizes below 5 nm. This mechanism is in contrast with the one 7 previously proposed by Baker et al., who suggest that the driving force of carbon diffusion is due to a 8 temperature gradient, despite the fact that it is very difficult to sustain any significant temperature gradient 9 in such small particles [42] In the real-time videos, volume ratios of these two phases change as a function 10 of time, consistent with the fluctuating measured SWCNT growth rate. The simulations indicate that the 11 rate of tube formation from surface diffusion is constant, while the fluctuating growth observed both ex-12 perimentally and in simulation suggests that bulk processes within the particle are important. By employ-13 ing automated image analysis of the large data set (generated by the real-time atomic-resolution videos), 14 we provide first quantitative experimental evidence that the carbon concentration profile developed inside 15 the catalyst is a critical determinant in tube formation, and that the tube growth rate depends on the rates 16 of carbide formation and decomposition. These results are further corroborated by RMD simulations. We 17 also show that this new approach to probe the atomic scale mechanisms for heterogeneous catalysis.

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Appendix A. Supplementary material. A detailed presentation of RMD results, description of mecha nisms contributing to SWCNT growth, structure determination method and a detailed description of image
 analysis.

- 4 Appendix B: Movie S1 contains the high resolution video of SWCNT growth from Co catalyst supported
 5 on MgO.
- 6

2 SYNOPSIS TOC: Rational catalyst design requires an atomic scale mechanistic understanding of the 3 chemical pathways involved in the catalytic process. A heterogeneous catalyst typically works by adsorb-4 ing reactants onto its surface, where the energies for specific bonds to dissociate and/or combine with 5 other species (to form desired intermediate or final products) are lower. Here, using the catalytic growth 6 of single-walled carbon nanotubes (SWCNTs) as a prototype reaction, we show that the chemical pathway 7 may in-fact involve the entire catalyst particle, and can proceed via the fluctuations in the formation and 8 decomposition of metastable phases in the particle interior. We record in situ and at atomic resolution, the 9 dynamic phase transformations occurring in a Cobalt catalyst nanoparticle during SWCNT growth, using a state-of-the-art environmental transmission electron microscope (ETEM). The fluctuations in catalyst 10 11 carbon content are quantified by the automated, atomic-scale structural analysis of the time-resolved ETEM images and correlated with the SWCNT growth rate. We find the fluctuations in the carbon con-12 13 centration in the catalyst nanoparticle and the fluctuations in nanotube growth rates to be of complemen-14 tary character. These findings are successfully explained by reactive molecular dynamics (RMD) simulations that track the spatial and temporal evolution of the distribution of carbon atoms within and on the 15 surface of the catalyst particle. We anticipate that our approach combining real-time, atomic-resolution 16 17 image analysis and molecular dynamics simulations will facilitate catalyst design, improving reaction 18 efficiencies and selectivity towards the growth of desired structures.

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