

Article

Metal-Catalyzed Thermo-Catalytic Decomposition and Continuous Catalyst Generation

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Highlights:

- Metal dusting affords a way to generate metal catalysts in situ from cheap metal sources and a high density of catalyst particles is created, anchored to a metal support.
- The metal dusting-catalyzed carbon magnifies the second-stage TCD rate and yield by virtue of its greater active surface area.
- Complementary microscopic, spectroscopic, and thermo-gravimetric characterizations highlight the structural differences between the first (TCD)-stage metal-catalyzed carbon and the second (TCD)-stage carbon-catalyzed carbon.
- Using model carbons, the TCD carbon's nanostructure did not appear to depend on the nanostructure of the nascent carbon catalyst.

Abstract: In this study, metal dusting is utilized to initiate a two-stage thermo-catalytic decomposition (TCD) process. Stage 1 starts with metal-catalyzed TCD, and in stage 2 the metal-catalyzed carbon catalyzes additional TCD. TEM is presented of the early- versus late-stage TCD to qualitatively illustrate the second-stage TCD by the metal-catalyzed carbons. Corresponding SEM illustrates differences in growth type and surface density between early versus late reaction times, with backscattered imaging differentiating the first- versus second-stage TCD. TGA supports the microscopic inference of a second carbon phase by the presence of an early (low-temperature) reaction peak, characteristic of low-structure or disordered carbon as the second-stage TCD carbon. Raman analysis confirms that the second-stage carbon deposit is more disordered and unstructured, especially at 1000 °C, supported by the I_D/I_G and La value changes from 0.068 to 0.936 and 65 nm to 4.7 nm, respectively. To further confirm second-stage TCD occurrence upon pre-catalyzed carbons, two carbon blacks are tested. Exposing a combination of edge and basal or exclusively basal sites for the graphitized form, they afford a direct comparison of TCD carbon nanostructure dependence upon the initial carbon catalyst nanostructure. Pre-oxidation of the stainless-steel wool (SSW) prior to TCD is advantageous, accelerating TCD rates and increasing carbon yield relative to the nascent SSW for an equivalent reaction duration.

Keywords: metal dusting; metal-catalyzed carbon growth; thermo-catalytic decomposition; carbon nanostructure



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1. Introduction: Metal Dusting—Continuous Catalyst Generation

Metal dusting refers to a severe form of corrosion wherein carbon deposition is accompanied by disintegration of the substrate. Mechanistic details are yet under study, but general steps involve cementite formation with dusting resulting from the associated volumetric expansion accompanying the formation of graphite [1,2]. Presumably, the graphite forms by breakdown of the cementite, aided by graphite nucleation. While iron atoms have been proposed to migrate through the graphite, reaching the surface, coalescing

into particles that then catalyze filamentary carbon, more recently Fe_3C breakdown to nanoscale particles has been observed [3]. At higher temperatures ($>700^\circ\text{C}$), no metastable M_3C carbide phase can be developed. The alloy is destroyed by direct inward growth of graphite into the oversaturated solid-state solution. The stress generated during graphite precipitation fractures the alloy surface and dislodges metal particles, which are considerably bigger than those produced via the mechanism of M_3C decomposition [4,5]. The resulting carbon microstructures can vary widely, but in all cases depend upon the catalyst “particle” shape and composition [5]. Elsewhere, the dusting process has been considered as a method for the continuous synthesis of carbon nanotubes (CNTs), given that fresh catalyst nanoparticles can be constantly generated [6–8].

In thermo-catalytic decomposition, (TCD) metal catalysts are more active, lowering the temperature to $700\text{--}900^\circ\text{C}$, whereas carbons as catalysts generally operate from 900 to 1100°C . Metal catalysts catalyze so-called “graphitic carbon”, whereas the nanostructure of carbon catalyzed by carbons as catalysts is still largely unstudied. Based on most carbons exhibiting deactivation with continued TCD duration, it might be presumed that they, too, catalyze a less active graphitic deposit. Metal catalysts require a support to prevent sintering while aiding dispersal. Carbons, however, can be used in bulk form. While metals are sensitive to poisoning, carbons are highly tolerant of sulfur and other metals. Other differences are less comparable, yet impactful; metals can possess a wide range of compositions, whereas carbons can possess a wide range of crystallinity and porosity.

Problematically, metal catalysts deactivate by coking with cessation of activity. It would appear logical to use metal-catalyzed carbon as the catalyst for a second TCD stage, particularly given its greater amount compared to the (deactivated) metal. While possible, this does not appear to have been tested in such an integrated fashion, presumably because a higher temperature would be required for the carbon to gain sufficient activity. Even so, the issue remaining is the fixed supply of catalyzed carbon in a reactor and its potential deactivation. As a solution to these potential limitations, metal dusting was applied. A brief background on metal dusting follows next.

To date, metal dusting has received study in carburizing atmospheres at high temperatures, wherein the gas compositions often involve syn-gas or mixtures with other hydrocarbons [2,9]. For its lack of practical relevance, dusting from pure natural gas appears to have not received attention. Oppositely, CNT synthesis sets a narrow range of hydrocarbon concentrations and compositions that maintain CNT growth, maximizing yield or quality and avoiding catalyst deactivation. For this different purpose as referenced [6–8], dusting conditions (i.e., temperature, gas concentrations, and mixture composition) would be highly tailored so as to best generate nanoparticles that are as uniformly sized as possible. Generally, low hydrocarbon concentrations, $10\text{--}20\%$, possibly with additional hydrogen, CO, or water vapor in an inert carrier, work best [10,11]. In contrast to these interests, TCD would nominally operate with pure natural gas, without an inert carrier but with considerable concurrent concentration change through the reactor, with reactant loss mirrored by hydrogen concentration as conversion progressed [12]. Moreover, the temperature range (at least for carbon-catalyzed TCD) would be significantly higher too, at $900\text{--}1100^\circ\text{C}$.

The continued metal dusting is the differentiating feature from just using metal-catalyzed nanotubes, as the continued formation of new metal-catalyzed carbon forms is the means by which carbon catalytic activity is maintained, should the (depositing) TCD carbon exhibit decreased activity relative to the initial carbon structures. In fact, the continued formation of new (metal-catalyzed) carbon forms potentially could lead to an increase in the overall TCD rate as the metal-catalyzed carbon (MCC)’s surface area and active site number thereon increase.

The metal dusting approach to two-stage TCD, as illustrated in Figure 1, encompasses the following steps.

1. Metal dusting creates nanoparticles for metal-catalyzed TCD.

2. Formation and growth of carbon forms (nanotubes, fibers, coral, petals, etc.) by metal-catalyzed TCD occurs.
3. Subsequently, carbon-catalyzed TCD occurs (via metal-catalyzed carbon forms), albeit the carbon catalysts will best perform at a higher temperature. Therein lies the option to increase the operating temperature periodically until metal deactivation occurs or the reactor requires physical carbon removal.
4. The carbon-catalyzed carbon is removed. In a fluidized or related system, the carbon-catalyzed carbon could be continuously extracted, whereas in a fixed bed, removal will be required at regular intervals, wherein a dual-bed system could be implemented. Repeat steps 1–4.
5. Continued metal-catalyzed formation and growth of new carbon forms.
6. Continued carbon-catalyzed TCD (via freshly generated catalyzed carbon forms).



Figure 1. Representation of the 2-stage catalytic TCD process.

By this iterative process, the ultimate deactivation of metal catalysts is bypassed by the continued creation of new catalyst particles in the ongoing metal dusting. The potential deactivation of the metal-catalyzed carbon catalysts is bypassed by the continued formation/growth of new carbon by the newly formed metal particles. As metal catalysts have a limited lifetime and eventually become coked, generating these catalysts in situ on a continuous basis via metal dusting overcomes this limitation. Thereafter, the catalyzed carbon fibers and filaments greatly magnify the surface area and active sites thereon to not only maintain but potentially increase the TCD rate as metal dusting reactions continue, comprising the hypothesis for this study.

2. Results

2.1. SEM Time Sequence

Figure 2a shows a sequence of images from 5, 10, and 20 min to qualitatively illustrate the evolving concert of reaction processes. Once initiated, though in aggregate all occur simultaneously, microscopically they necessarily occur in sequence. The low magnification images portray an increasing density of carbon forms, while the higher magnification images illustrate the local nature: for short times there are bare patches, whereas at longer times the carbon growth density appears to densely cover the surface features. Metal dusting does not occur uniformly, likely reflecting the exposed metal facets and underlying grain structure [1,13,14]. After 1 h of time-on-stream (TOS), the stainless steel (SS) wool becomes packed with catalyzed carbon, as shown in Figure 2b. The variable structures of the catalyzed carbons and metal catalyst particles are highlighted in the higher magnification image.

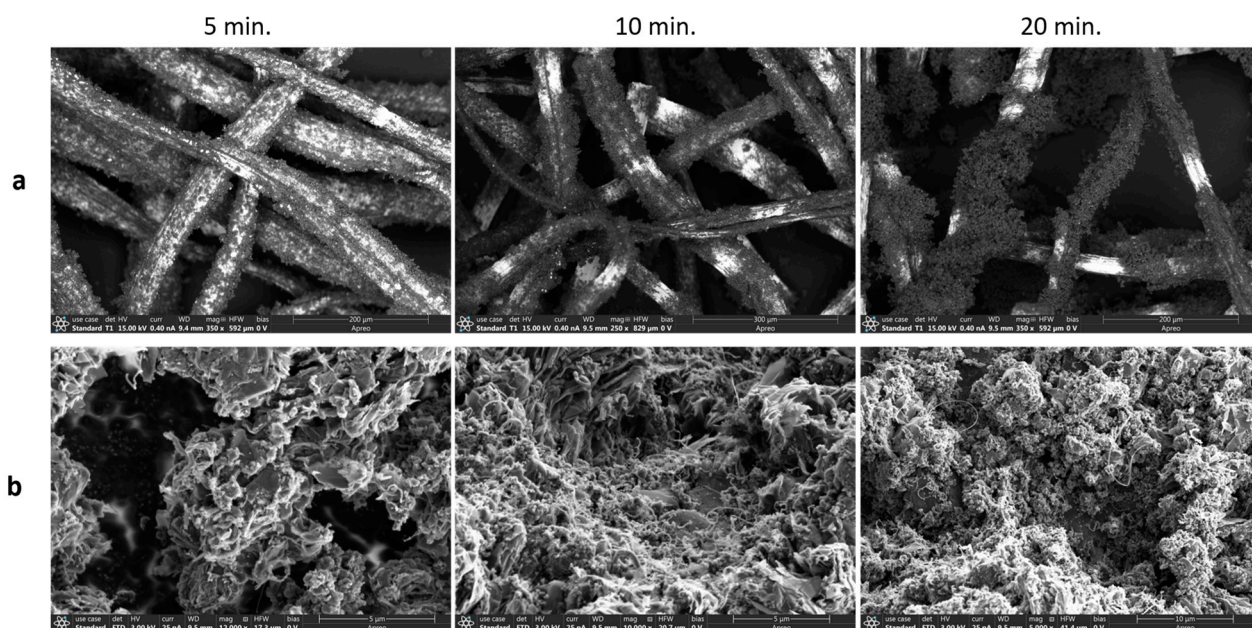


Figure 2. (a). A series of SEM images at 5, 10, and 20 min of TCD duration illustrating the collective concurrence of the sequential reaction processes. (b). SEM images of the SS mesh after 1 h of TCD with SNG, revealing the dense combination of catalyzed carbon filament growth and carbon deposition.

2.2. Secondary Carbon Deposition on Metal-Catalyzed Carbon Structures

From the standpoint of TCD, metal dusting provides a means by which to produce a packed bed using a relatively porous support material, such as the SS wool. Metal-catalyzed carbon growth can fill voids and gaps, increasing the surface area and hence active sites, boosting the TDC rate. The surface area (SA) of the nascent (#0000) mesh was $0.5 \text{ m}^2/\text{gram}$ while the SA of the deposited carbon was $\sim 150 \text{ m}^2/\text{gram}$ for the first plug, illustrating the growing capacity of the bed compared to a pre-defined fixed bed. Finally, using the exterior surfaces of nanoscale carbons offers improved mass transport compared to porous carbon catalysts—with transport-restricted internal porosity.

To determine the surface area of the metal-catalyzed carbon, adsorption isotherms were obtained for the nascent (bare) mesh pre-dusting, followed by adsorption analysis after dusting and filament/fiber formation. The difference, combined with the catalyzed carbon mass, yielded a surface area of $75 \text{ m}^2/\text{g}$ for the metal dusting-catalyzed carbon. This value is in line with similar values reported for MWNTs [15] and many carbon blacks [16].

Nominally, metal-catalyzed carbons are “graphitic”, exhibiting extended, organized lamellae, despite their formation at temperatures well below those normally required for graphitization. As “graphitic” carbons, these catalyzed forms would seemingly have poor activity towards TCD, given edge sites generally equate to active sites. Short lamellae with a higher edge-to-basal carbon ratio inherently offer greater reactivity [17]. However, these carbons are highly “defective”, given the irregular formation of lamellae and, moreover, their varied irregular shapes. In metal dusting, the catalysts are not tailored for producing carbon nanotubes (CNTs), resulting in a wide range of sizes, shapes, and compositions. Consequently, the resulting carbon structures also vary widely, with well-organized CNTs being rare. In fact, CNTs are not the primary carbon product; rather, a diverse range of carbon structures emerges, including rosebuds, ridges, fibers, and different types of CNTs, as depicted in Figure 3 below (arrows indicate the different carbon forms that are generated).

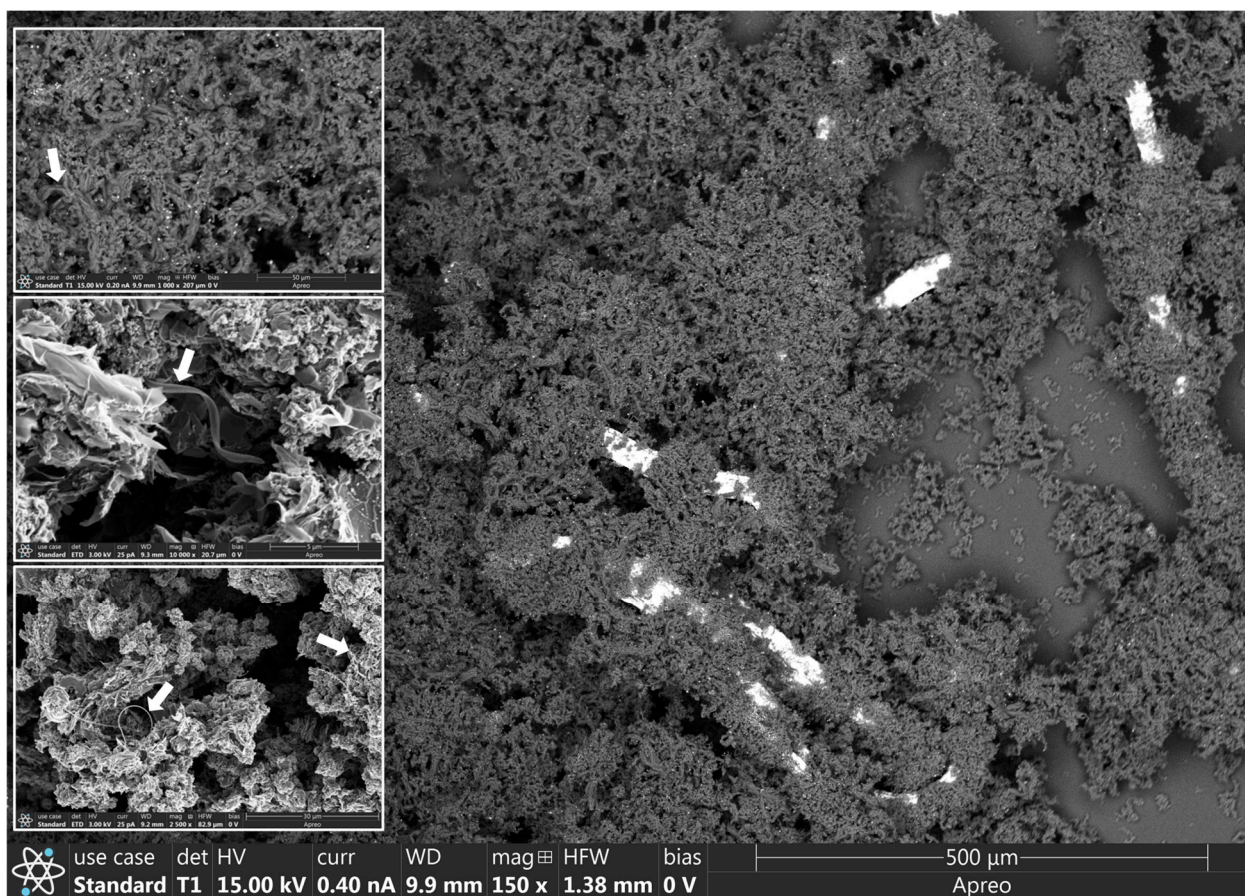


Figure 3. Metal dusting array of carbon flora, ranging from rosebuds to ridges to fibers to CNTs of varied types. Arrows indicate the different carbon forms that are generated.

Though SEM provides an overview of carbon coverage, it is not well suited for gauging small changes in diameter or size due to secondary carbon deposition; TEM is far better suited. Figure 4 compares HRTEM images of a CNT and a graphene stack at an early and later stage of TCD. At early stages, the continuity of the lamellae structure in the CNT suggests no secondary carbon deposition. At later times, different observations point to significant secondary deposition upon the metal-catalyzed carbons. Overall, the nanotubes and nanofibers appear larger in diameter. Reciprocally, the small and numerous CNTs that were apparent in the SEM of early-stage TCD were absent after the later-stage continuation, a sign of carbon burial (by TCD). HRTEM of nanofibers revealed a different texture for the outer carbon, indicative of its deposition origin rather than it being metal catalyzed. Additionally, protrusions often appear in this carbon layer, but are much more noticeable on or near ends. These protrusions are consistent with island nucleation and growth in CVD deposition [18].

During the initial phase of the reaction, the graphene sheets that are produced tend to be less stacked. The low stacking is also consistent with the minimal contrast of the sheet, as seen in Figure 4b. The graphene sheets have distinct, well-defined edges. This characteristic suggests a high degree of order of well-defined graphenic sheets during this stage. In contrast, the graphene sheets produced during the secondary deposition exhibit greater contrast. This means they do not have the internal voids and discontinuities seen in the first stage. The stacks exhibit greater contrast with substantial coverage by amorphous carbon. Moreover, these second-stage graphene sheets are irregular, consistent with carbon deposition along exposed edges (illustrated by the arrows in Figure 4b).

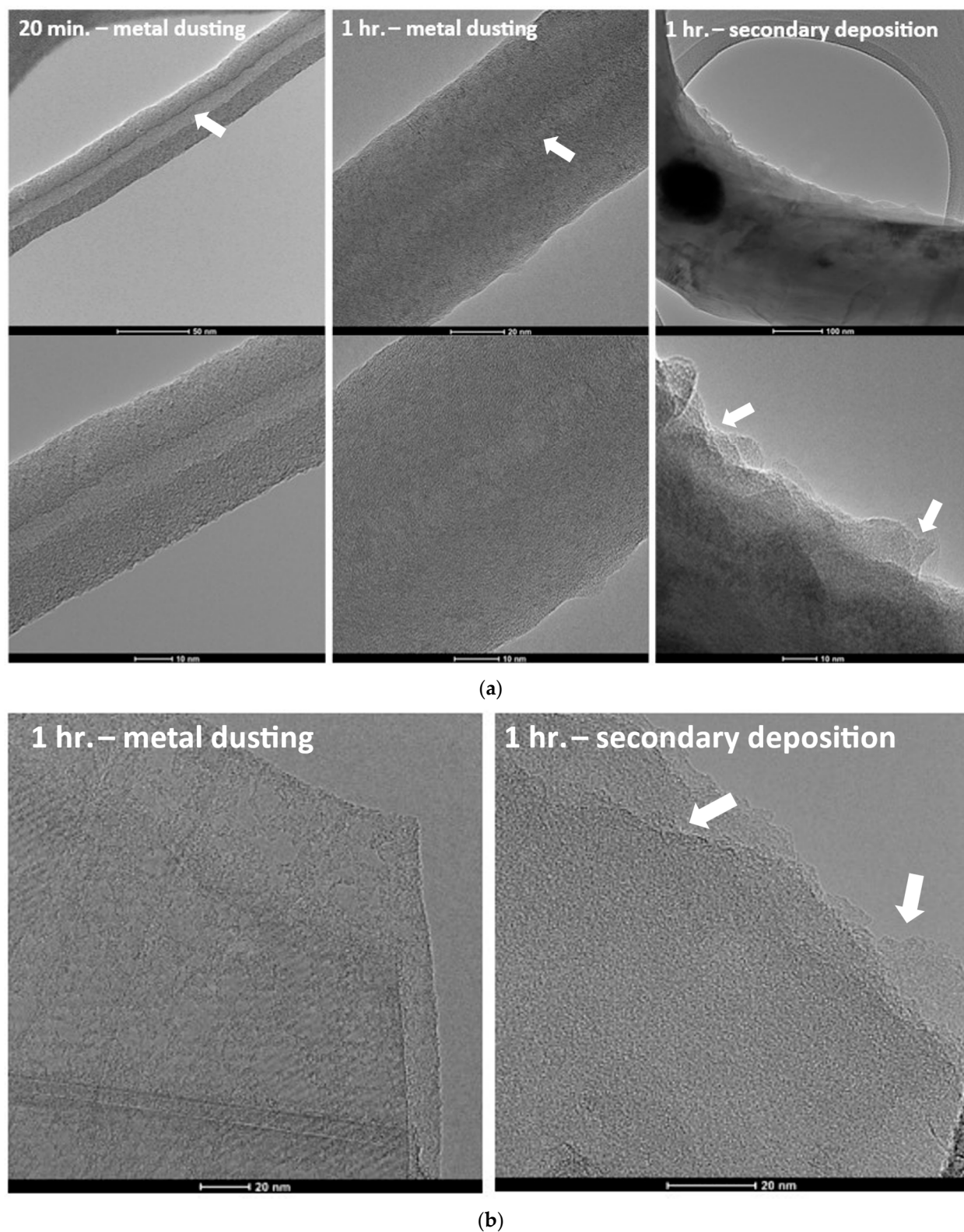


Figure 4. (a) Spotlighting secondary carbon deposition by contrasting HRTEM images of a CNT at early and later stages of TCD. (b) Spotlighting secondary carbon deposition by contrasting HRTEM images of a graphene stack at an early and later stage of TCD. Arrows indicate the different carbon forms that are generated.

2.3. TGA of Later-Stage TCD Carbons

Thermogravimetric oxidation was conducted on the first plug after the second reaction (TCD) deposition, testing for different carbon phases. If the TCD carbon (catalyzed by the metal-catalyzed carbon) is more amorphous/unstructured than the MCC forms, then this difference might register as an early initial mass loss in the TGA.

TGA oxidation tests were performed on the carbon deposit (MCC) after the first reaction and the subsequent second stage (carbon-catalyzed TCD at 900 °C and 1000 °C). The TGA analysis indicated that there are two separate phases of carbon deposition, each with distinct oxidative reactivity. Figure 5 shows the oxidation profiles of the different carbon deposits as represented by their weight loss and weight loss rates. These different carbon phases burn off at different temperatures (second-stage TCD at 1000 °C < second-stage TCD 900 °C < first-stage MCC at 900 °C). This difference in reactivity suggests variations in the structural properties and bonding of the carbon phases.

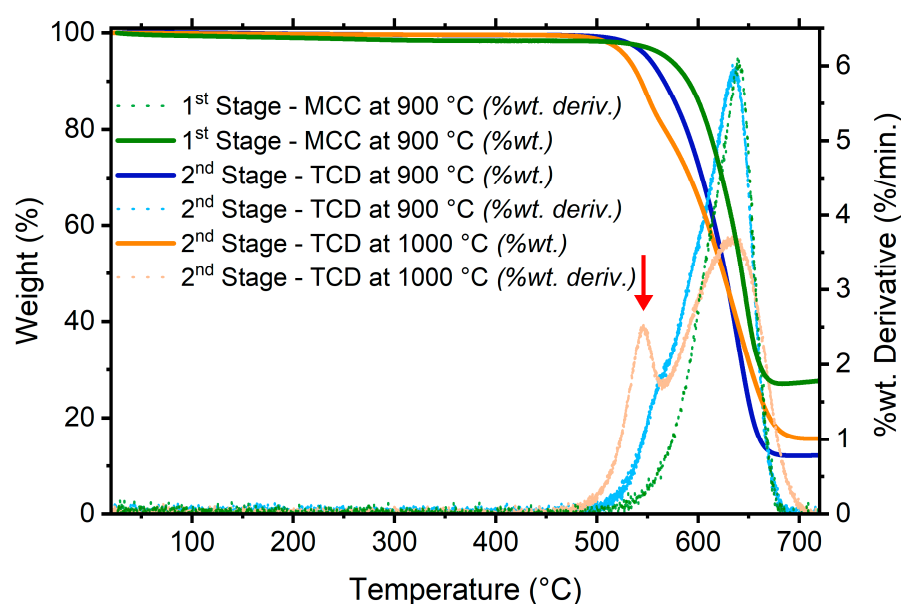


Figure 5. TGA oxidation of 1st- and 2nd-stage depositions, illustrating the different carbon phases through the different inset temperatures and derivatives.

The presence of two distinct carbon phases at later stages, but not at early stages, reinforces the picture of a two-stage TCD process. In the first stage, the deposited carbon is relatively ordered and structured. In the second stage, as deposition continues, a more disordered/amorphous phase begins to develop alongside the existing graphitic carbon produced by metal dusting. This transition aligns with the proposed two-stage mechanism, where initial metal-catalyzed deposition creates a flora of carbon forms, and subsequent deposition is catalyzed by the newly formed carbon. Surprisingly, the TCD at 1000 °C appears to be less structured than that formed at 900 °C. A possible explanation is that the more rapid deposition at the higher temperature produces a more disordered deposit. More likely is that at 900 °C, the deposited carbon was more ordered due to templating on the metal-catalyzed carbons but became buried by the greater amount of disordered carbon deposited at 1000 °C.

2.4. Raman of Initial Metal Dusting and Later-Stage TCD Carbons

The Raman spectrum of carbon provides valuable insights into the structural changes from graphitic to disordered/amorphous forms. These changes are primarily observed in the positions, intensities, and widths of the characteristic D and G bands, as well as the emergence of additional features, such as the appearance of the 2D band. In the first-stage MCC (Figure 6a), the D band (1344 cm^{-1}) is weak while the G band (1576 cm^{-1})

is very sharp and intense, indicating a high degree of graphenic integrity and crystalline order. Additionally, the presence of a strong 2D band (2715 cm^{-1}) is further indicative of a graphitic carbon nanostructure.

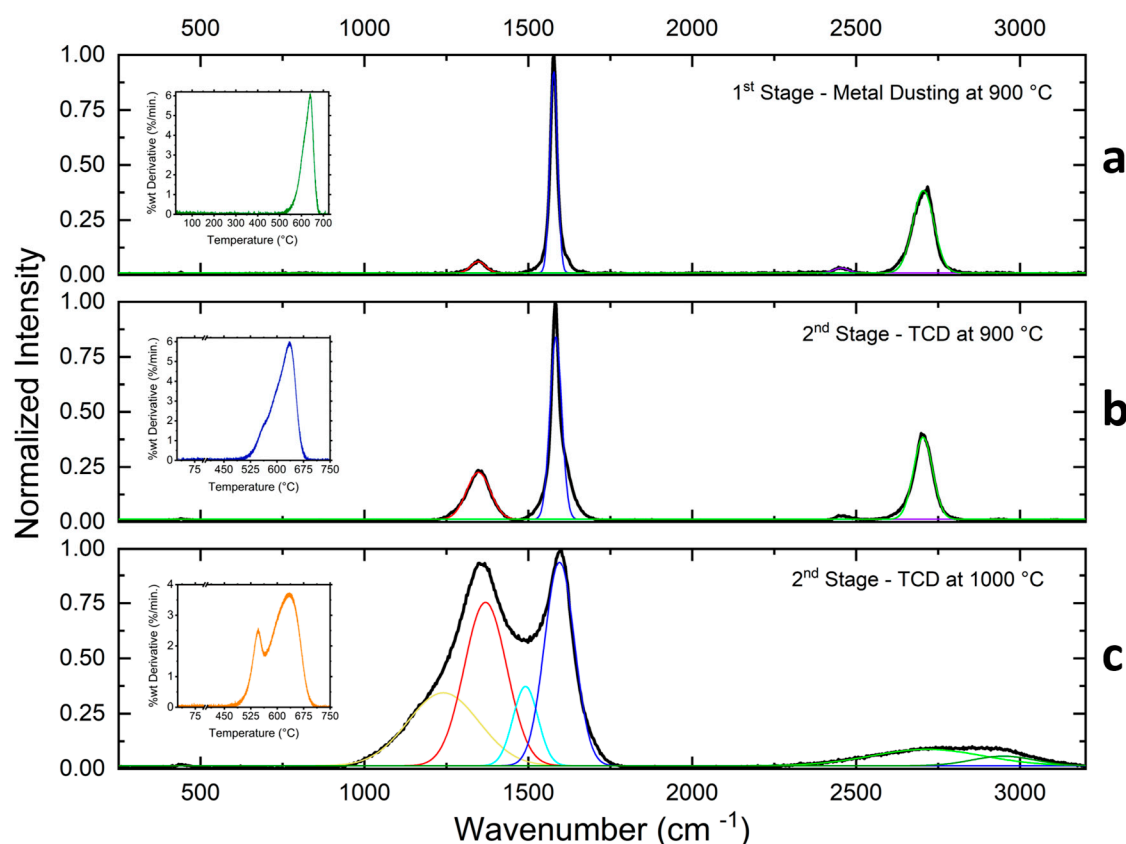


Figure 6. Raman spectroscopy highlighting the different nanostructures of the TCD carbon (increasingly disordered—2nd stages (b,c)) and initial carbon deposit by metal dusting (ordered/graphitic—1st stage (a)) with inserts illustrating the different carbon phases through TGA weight loss derivatives.

In the second stage, especially with increased deposition rates at 1000 $^{\circ}\text{C}$ (Figure 6c), the structure of the deposited carbon is evidenced by more disorder; the D band becomes broader and more intense. More significantly, the intensity ratio of the D band to the G band (I_D/I_G) increases from 0.068 to 0.936 consistent with a high level of disorder. Additionally, as the carbon-catalyzed carbon deposition intensifies, the 2D band becomes broader and less intense. The values for the lateral extent of crystallinity (L_a) reflect this change, decreasing from 65 nm to 18.7 nm and ultimately to 4.7 nm for the first and second (900 $^{\circ}\text{C}$ and 1000 $^{\circ}\text{C}$) deposition stages, respectively, by applying the Tuinstra–Koenig relation [19]. The large L_a value indicates better crystallinity and larger graphitic domains, while the smaller value implies a higher degree of disorder, limiting the sp^2 domains for phonon propagation [20,21]. Figure 6b marks the transition from metal-catalyzed carbon at 900 $^{\circ}\text{C}$ and the carbon-catalyzed carbon deposition, also at 900 $^{\circ}\text{C}$. This transition is illustrated by the intensification and broadening of the D peak, as evidenced by the I_D/I_G ratio increase from 0.068 to 0.235 and subsequently to 0.936 at 1000 $^{\circ}\text{C}$. In highly amorphous carbon, this band can become almost indiscernible due to the significant loss of long-range order. Overall, these spectral changes reflect the transition from an ordered sp^2 structure to a more disordered network with increasing sp^3 content and varied bond angles and lengths, typical of amorphous carbon, as manifested by the emergence of the D3 peak at $\sim 1500\text{ cm}^{-1}$ seen in Figure 6c [22]. The changing structure of the carbon is further confirmed by the derivative TGA (DTG) spectra, shown as insets in the panels of Figure 6, where lower peak oxidation temperatures are observed.

2.5. Backscattered Electron Imaging of Initial Metal Dusting and Later-Stage TCD Carbons

Direct backscatter imaging functions as a qualitative measure for energy-dispersive X-ray spectroscopy (EDS) because the intensity of backscatter is directly proportional to the atomic number (Z) up to about $Z = 50$. Consequently, elements with higher atomic numbers appear brighter in the scanning electron microscope (SEM) images, providing an integrated map based on Z . Essentially, the backscatter intensity offers an EDS measure that is weighted by the atomic number. This Z -dependence is significant because lighter elements like carbon generate a weak backscatter signal compared to heavier transition metals such as those found in steel wool catalysts. The catalyst particles produced by metal dusting will be compounds of iron (Fe) and nickel (Ni), with their specific composition varying among particles, but this variability is not critical for catalyzing the first stage of thermo-catalytic decomposition (TCD). It is important to note that similar compositional variability is also observed in particles produced by standard methods such as incipient wetness and wet impregnation. A notable portion of the catalyst particles formed by metal dusting will develop into structures like filaments, fibers, and nanotubes through tip-growth which can be detected via backscatter imaging. These particles are visible as numerous bright spots in the SEM images, such as those shown in Figure 7a.

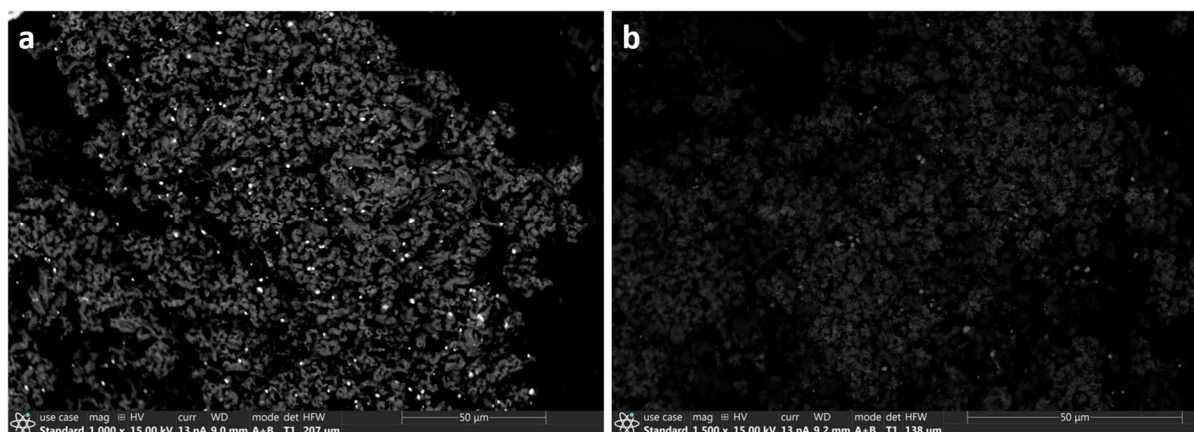


Figure 7. SEM backscattered electron imaging showing (a) the presence of metal particles (bright spots) during the first-stage metal dusting reaction at 900 °C and (b) the near absence of observable metal particles during the second-stage deposition at 1000 °C.

After the second stage of TCD, the deposited carbon covers the metal-catalyzed carbon structures and their catalyst particles, significantly reducing their backscatter signal. As a result, these particles blend into the surrounding carbon and become nearly indistinguishable. The lack of high-intensity backscatter in the SEM images after this stage serves as evidence of the carbon-deposited layer, explaining the near absence of such particles in Figure 7b. For an acceleration voltage of 15 kV, the nominal electron penetration depth into carbon is ~300 nm. The absence of high backscatter intensity suggests that this is the minimum second-stage TCD carbon thickness.

2.6. Confirming Secondary Deposition: Comparison of TCD Carbon Dependence upon Initial Carbon Nanostructure

In order to confirm the poorly structured carbon's origin, two carbon blacks were also tested for secondary TCD carbon structure. Notably, their different nanostructures enable a direct comparison of TCD carbon structure dependence upon the initial carbon (catalyst) nanostructure. An ordinary carbon black, R250, and its graphitized form, G-R250, were used as catalysts under the same TCD conditions as the SS wool. As Figure 8 shows, the R250 surface lamellae exposes both edge and basal carbons while the G-R250 surface presents exclusively basal planes without edge sites.

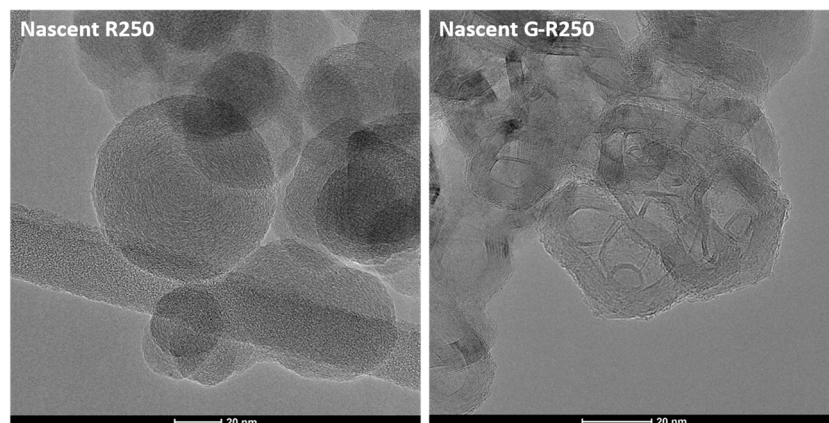


Figure 8. HRTEM images of nascent R250 and its graphitized analogue (G-R250) contrasting their different nanostructures.

As Figure 9 shows, HRTEM of these carbons post-TCD reveals similarities in the carbon deposits. A particular advantage of the R250 and G-R250 forms is their distinct particle and aggregate morphology. Notably, the graphitization preserves this structure. Additionally, the recognizable lamellae nanostructure in both forms facilitates the differentiation of deposited TCD carbon. As the HRTEM images show, the deposited carbon consisted of twisted, seemingly folded graphene stacks and amorphous carbon deposits lacking a definitive shape or form, the lamellae structures therein appearing random. These images support the identification of the second-stage TCD carbon made previously while also demonstrating an insensitivity of the TCD carbon deposits to the initial carbon nanostructure. This latter observation is particularly surprising, as active sites responsible for TCD are considered tied to nanostructure. Basal planes without edge exposure in principle offer no active sites, yet supported substantial TCD deposition. The percentage mass gains for R250 and G-R250 were 120% and 84%, respectively. This rough equivalency further supports the independence of the deposition rate upon the initial carbon nanostructure for the reaction conditions employed here.

2.7. Two-Stage Metal Dusting

A second way of fostering metal dusting yet still relying upon carbide-induced breakup is to first oxidize the surface, forming a “rust”. This familiar oxidation process also breaks up the metal surface, given the volumetric mismatch between the iron oxide (Fe_2O_3) and the underlying metal. This facilitates the breakup during the reduction of the iron III oxide to reduced metal and by the subsequent carbide formation. It was observed that the rusted SS wool had higher carbon deposition per mass of catalyst compared to its nascent counterpart, with a 56.4% weight increase compared to 39.9% for the rusted and nascent samples, respectively. Figure 10 shows that the carbon flora generated by the nascent and the oxidized SS wool were similar.

2.8. Carbon Yield and Deposition Rates

For each stage, the initial mass of the catalyst was known, allowing for accurate determination of the total yield of the deposited carbon. The deposition rates were evaluated in terms of catalyst mass and reaction time, ensuring a comprehensive understanding of the deposition process. From Table 1, the total yield (%) change is the fractional deposit mass increase in relation to the initial catalyst mass. The mass deposition rate is the rate of carbon generation per unit time, normalized by the catalyst mass.

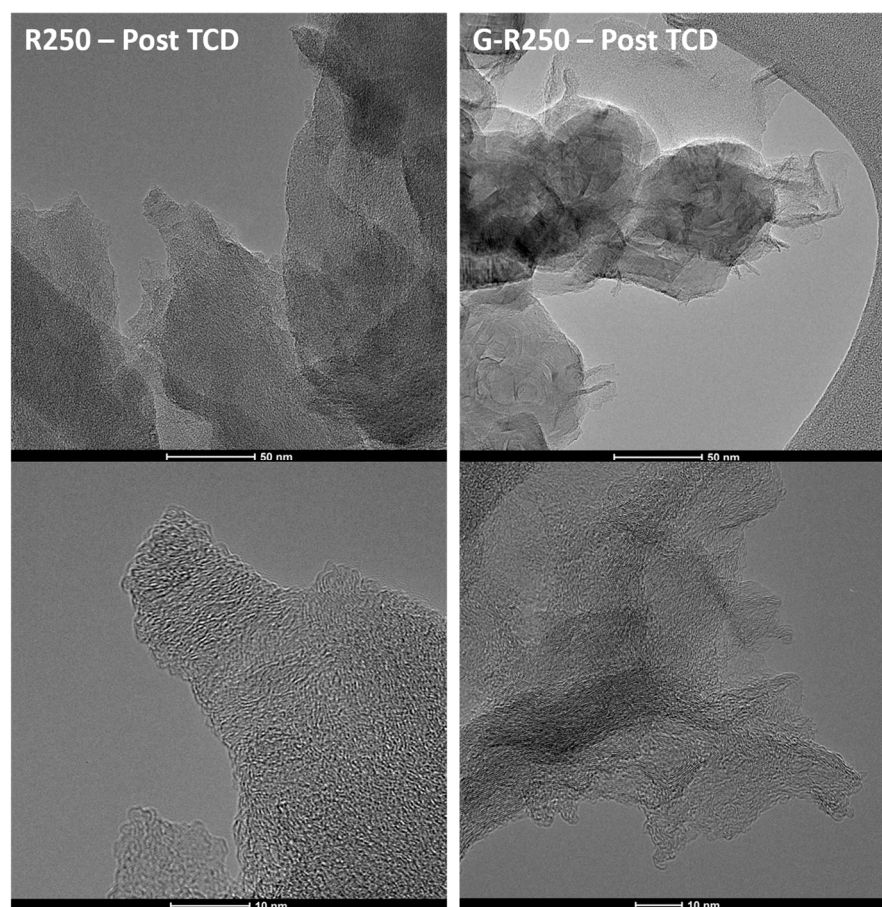


Figure 9. HRTEM images of the carbon deposits upon the carbon black catalysts post-TCD. The irregular morphology, resembling sea coral, and disordered lamellae therein appear common to both catalysts, despite their very different nanostructures.

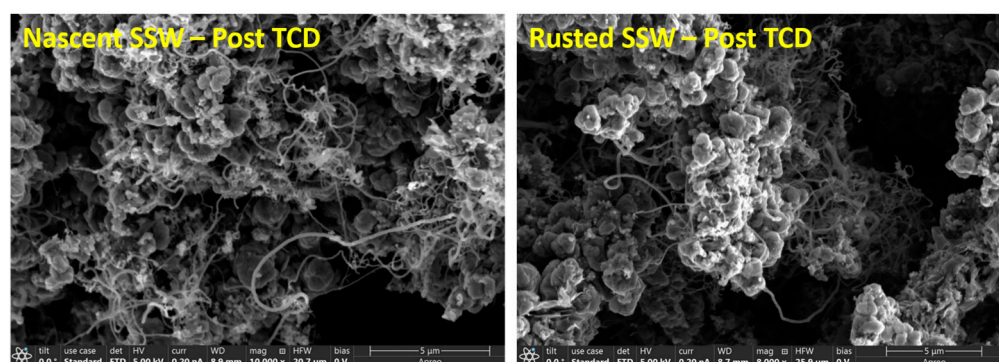


Figure 10. SEM images of nascent and rusted SSW post-TCD deposits using a mixture of 25% SNG with balance argon at 900 °C for 30 min.

Table 1. Carbon yield and deposition rates.

	1st Stage—MCC (900 °C)	2nd Stage—TCD (900 °C)	2nd Stage—TCD (1000 °C)
Deposition rate (mg/s·mg cat)	2.4×10^{-4}	1.97×10^{-3}	8.75×10^{-4}
Total yield change (%)	86.5%	707.7%	315.0%

The second-stage values in Table 1 show that the amount of carbon deposited during the second stage of TCD is significantly higher than in the first stage. The increased mass

addition rates and yield (%) suggest that the conditions in the second stage are more favorable for rapid carbon growth. As explanation, the increased carbon surface area in the second stage enhances the catalytic decomposition of methane, therein highlighting the primary feature of two-stage TCD.

The deposition rate significantly increases in the second stage at 900 °C (1.97×10^{-3} mg/s·mg cat.) compared to the first stage (2.4×10^{-4} mg/s·mg cat.), largely reflecting the difference between MCC versus TCD between the two stages. However, when using 1000 °C in the second stage, the deposition rate (8.75×10^{-4} mg/s·mg cat.) is lower than in the second stage at 900 °C. Conducting the second stage at 900 °C results in the highest carbon yield change, as well as the highest deposition rate. This indicates that the conditions at 900 °C are particularly effective for the process, leading to substantial carbon deposition. The effectiveness at this temperature can be attributed to the optimal space velocity and catalyst mass used, which ensure that the carbon deposition is maximized.

In contrast, when the temperature is increased to 1000 °C in the second stage, the total carbon yield change (%) and deposition rate decrease. This reduction is likely due to an oversupply of the catalyst that was used at the higher temperature, resulting in its less effective use and a lower deposition rate per unit of catalyst mass. Similarly, the excess catalyst at 1000 °C results in a lower yield change compared to the second stage at 900 °C. As evidence of the excess catalyst used in the second-stage TCD at 1000 °C, the (%) yield decreased by a factor of two at 1000 °C, reflecting the $\sim 2\times$ larger amount of starting carbon catalyst used. Overall, these tests demonstrate the critical role of carefully controlled catalyst mass and space velocity in achieving high mass-specific deposition rates and yields. Nonetheless, the value at 1000 °C represents a conservative lower limit of the second-stage deposition process.

3. Discussion

The high similarity between metal-catalyzed TCD and carbon nanotube synthesis should be noted. Unfortunately, many of the options available to promote CNT formation or increase catalyst longevity are not desirable in the context of TCD. For example, to maintain catalytic activity in CNT synthesis, hydrogen would be co-fed along with the hydrocarbon feed. Indeed, recent studies have demonstrated the efficacy of added hydrogen in maintaining TCD activity [23]. Presumably, in operation, some portion of the produced hydrogen could be recycled to the input.

Another popular approach for maintaining catalyst activity in CNT synthesis is to add water to the reactant stream [24]. As a mild oxidant, it can act to remove carbon buildup on the catalysts, thereby preventing their coking and deactivation. Similar approaches use alcohols as oxygen carriers added to the feed, or substitute for the C_xH_y feed [25]. However, oxygen will form CO and CO₂, negating one of the primary advantages of TCD—clean hydrogen unburdened by a need for WGS stages and CO removal.

If metal catalyst particle generation was the only motivation, metal dusting would seemingly be a poor approach, and would be in fact less desirable than the controlled synthesis of metal nanoparticles with a controlled size and composition. However, the abundant carbon that forms provides an evolving and growing surface that can catalyze further TCD via secondary deposition.

In reality, any study forming carbon nanotubes or other catalyzed form of carbon could realize the same opportunity for second-stage, carbon-catalyzed TCD. However, given the specific conditions to maintain CNT formation and reaction rate continuity, operational temperatures are too low to significantly promote carbon-catalyzed TCD. Here, without worry about metal particle sintering or ripening at reaction temperatures, metal dusting can be conducted at higher temperatures, being sufficient to activate the catalyzed carbons as TCD catalysts. Common to metal catalysts is their deactivation, yet metal dusting can continue to generate new catalyst particles and fresh carbon structures that can promote TCD.

Ultimately, carbon growth could become sufficiently dense to impede further reactant transport to drive continued dusting versus secondary deposition upon the metal-catalyzed carbon forms. One option would be simple mechanical removal of both MCC and TCD carbons just by a simple abrasion or scraping action (using suitable support structures). Such an approach could be envisioned even while at temperature in the reactor to maintain continuity of operation, compared to a batch process. Another solution would be to gasify the deposited carbon in a swing-bed system, generating dry CO by the Boudouard reaction in the regeneration stage. Notably, this also would accomplish CO₂ reuse from some other source. Operating in tandem with the TCD bed, separate sources of H₂ and CO would be available in any desired ratio for synthesis of liquid fuels and chemicals via the Fischer–Tropsch process. Notably, these syn-gas components would be clean and separated, unlike the blend generated by steam methane reforming (SMR). After gasification, the same metal framework could remain in place for subsequent TCD during the swing (i.e., switch) of reactions between the parallel beds for renewed two-stage TCD. These elements constitute future work.

4. Materials and Methods

Two approaches are conceivable for combining metal- and carbon-catalyzed TCD. The first is where the metal dusting- and subsequent carbon-catalyzed TCD reactions are conducted at one common temperature. Higher temperatures accelerate the metal dusting and metal-catalyzed TCD, with the potential limitation of faster deactivation of the metal catalyst by coking, in part due to accelerated gas phase pyrolysis reactions forming deactivating PAHs. The second is a two-stage process wherein metal dusting and metal-catalyzed carbon formation are conducted at one temperature and, after sufficient carbon is formed, the temperature is increased to where the carbon itself then catalyzes TCD. It should be noted that in this approach, the second temperature stage is somewhat artificial, as metal dusting and catalyzed carbon will continue during the second stage at the higher temperature. A Rhoades American stainless steel wool grade #000 was used as the metal catalyst in the first-stage metal dusting reaction. This process is demonstrated in Figure 11 below.

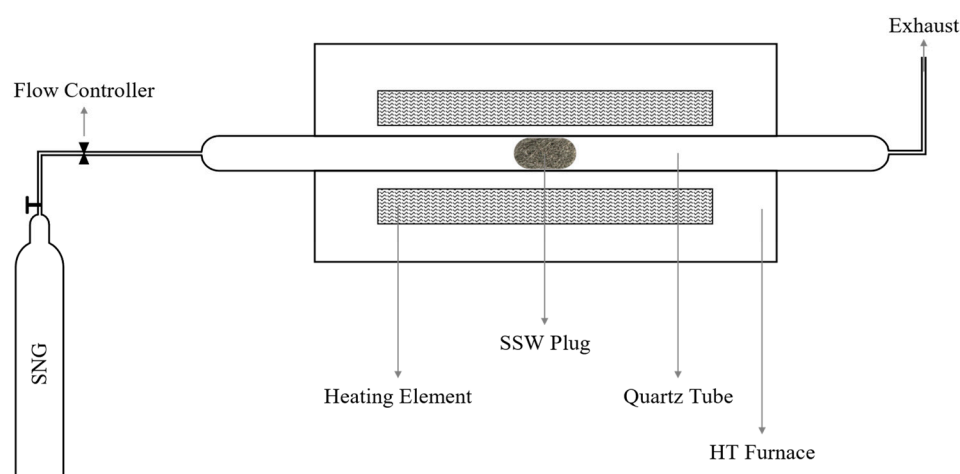


Figure 11. Metal dusting apparatus.

4.1. Transmission Electron Microscopy

TEM was performed using an FEI Talos F200X (ThermoFisher Scientific, Waltham, MA 02451, USA) equipped with a 200 keV FEG source and a resolution of 0.12 Å. Samples were dispersed and sonicated in methanol for increased dispersion before being dropped onto 300 mesh C/Cu lacey TEM grids.

4.2. Thermogravimetric Analysis

A TA instruments (TA Instruments, New Castle, DE 19720, USA) Thermogravimetric Analyzer (TGA) with simultaneous Differential Scanning Calorimetry (DSC) TGA-SDT Q600 is used as a bulk material characterization technique to study the response of the material to thermal treatment under oxidizing conditions. The carbon blacks were heated at a ramp rate of 10 °C/min until a complete weight loss was reached.

4.3. Raman Spectroscopy

A Horiba (Horiba Scientific, Austin, TX 78754, USA) LabRAM HR Evolution equipped with a 600 groove/mm grating and a 532 nm laser was used to obtain the Raman spectra for the samples. Laser power was maintained at 1 mW to avoid oxidation or changes in nanostructure because of localized heating. To make the analysis more representative, at least three measurements were collected for each sample.

4.4. Scanning Electron Microscopy

SEM images were obtained using a ThermoFisher Scientific field-emission SEM Apreo 2 (ThermoFisher Scientific, Waltham, MA 02451, USA). Samples were prepared by placing a few milligrams on a carbon-taped pin stub holder. To obtain FESEM images, an acceleration voltage of 1–15 kV and a working distance between 10 mm to 9 mm was maintained. The Trinity Detection System allowed the simultaneous acquisition of backscattered electrons which highlighted a clear compositional contrast of the metal catalyst particles over the carbon deposit.

5. Conclusions

Long considered an industrial problem and potential hazard, metal dusting can be exploited to create metal catalyst particles from inexpensive bulk precursors, such as SSW. A particular advantage of this flexibility is to mold or otherwise conform the substrate to nearly any desired geometry. Once metal-catalyzed carbons form, they too can contribute to TCD. Although the metal particles will eventually deactivate, the metal dusting reaction can continue to create new catalyst particles that in turn catalyze varied carbon forms which can be exploited as secondary catalysts for TCD.

With many benefits, metal dusting is compatible with a packed-bed reactor. Secondary carbon growth continues as long as the metal dusting reactions/processes continue; therein, “fresh” or new carbon catalyst is formed continuously. Ideally, the deposited carbon and underlying carbon fibers and filaments could be readily removed, enabling “regeneration” by mechanical action and the reuse of the metal substrate, given an appropriately designed support. Similar to a fixed-bed system, the nanostructure of the TCD carbon can be used to identify the degree/mode of carbon deposition, while the TCD rate can be determined from the mass of the catalyzed carbon deposit. The two-stage metal-catalyzed TCD process includes the following additional benefits: metal dusting affords a way to generate metal catalysts in situ from cheap metal sources and a high density of catalyst particles is created, anchored to a metal support. Additionally, no prior catalyst preparation is required, nor its dispersal upon a support. Catalyst particles are continuously created, as are the catalyzed carbons in the second-stage TCD.

Comparison of SEM images of carbons between early versus later stages reveals larger diameter filaments and a general absence of smaller ones. Backscattered electron imaging shows the presence of metal catalyst particles during the first-stage metal dusting reaction, while they were near absent after secondary deposition. This absence of high intensity backscatter provides further confirmation of the carbon-catalyzed deposited carbon in the second-stage TCD. TEM images of sampled carbons show that the exterior carbon exhibited a discontinuity in nanostructure from that of the internal carbon while often presenting twisted and folded graphene stack morphologies. Similarly, the graphene sheets formed during the initial metal dusting stage are internally hollow/discontinuous, less layered, and contain straight edges. Conversely, graphene sheets generated during the secondary

deposition appear denser with fuzzy edges. TGA reveals two carbon phases differing significantly in their oxidative reactivity while TGA analysis of early-stage TCD carbon does not, further supporting the proposed two-stage TCD (by the associated unstructured carbon). Additionally, the carbon mass additions during the second TCD stage are far greater than those observed in the first stage, consistent with the far greater carbon surface area catalyzing methane decomposition during the second stage. When the reaction temperature is raised from 900 °C to 1000 °C in the second stage, both the total carbon yield and deposition rate decrease. This decline reflects an excess of catalyst at the higher temperature, artificially reducing the (%) yield and normalized mass deposition rate. The TCD carbon on two carbon blacks possessed similar structure and morphology. Despite the very different lamellae exposure between the two carbon blacks (edge plus basal for the nascent R250, while only basal for the G-R250), the TCD carbon's structure and morphology were not observably different with regard to secondary deposition. For the reaction conditions here and these carbon blacks, the TCD carbon's nanostructure appeared independent of that of the nascent carbon catalysts.

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