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# Initial competing chemical pathways during floating catalyst chemical vapor deposition carbon nanotube growth

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### ABSTRACT

Ferrocene (Fc) is an effective precursor for the direct synthesis of high quality single-walled carbon nanotubes (SWCNTs) via floating catalyst chemical vapor deposition (FCCVD). However, the formation mechanism of the Fe floating catalyst and the SWNCT growth precursors, such as carbon chains, during Fc decomposition are not well understood. Here, we report first principles nonequilibrium quantum chemical molecular dynamics simulations that investigate the decomposition of Fc during FCCVD. We examine the influence of additional growth precursors including ethylene, methane, CO, and  $CO_2$  on the Fc decomposition mechanism and show that the dissociation of these species into  $C_2H_x$  radicals and C atoms provides the key growth agents for the nucleation of carbon chains from Fc-derived species such as cyclopentadienyl rings. Without an additional growth precursor, Fc decomposes via the spontaneous cleavage of Fe—C and C—H bonds, thereby enabling Fe atoms to cluster and form the floating catalyst. On the basis of these simulations, we detail the two competing chemical pathways present during the initial stages of FCCVD: Fe catalyst nanoparticle growth and carbon chain growth. The latter is accelerated in the presence of the additional growth precursors, with the identity of the precursor determining the nature of the balance between these competing pathways.

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### I. INTRODUCTION

Since their discovery,<sup>1,2</sup> single-walled carbon nanotubes (CNTs) have attracted immense research interest due to their remarkable physical and electronic properties.<sup>3–8</sup> The synthesis of single-walled CNTs (SWCNTs) via catalytic chemical vapor deposition (CVD) has matured to the point that commercial scale production is now routine.<sup>9</sup> Consequently, SWCNT-based films have recently emerged as a promising replacement for commercial transparent conductors such as indium tin oxide (ITO)<sup>8,10</sup> and are enabling related applications including flexible electronics and thin film transistors.<sup>11,12</sup>

The synthesis of SWCNT-based films can be achieved via both wet<sup>8,13</sup> and dry methods.<sup>10</sup> Of these, wet solution-based methods have been researched more extensively. Dry methods, such as floating catalyst CVD (FCCVD), however, offer a more direct synthesis capable of producing high-quality SWCNT-based films (e.g., resistance of

 $95 \,\Omega \,m^{-2}$  with 90% transmission).<sup>14</sup> FCCVD sublimates an organometallic precursor, most commonly ferrocene (Fc), in a flow of carrier gases such as N<sub>2</sub> and other gases such as H<sub>2</sub> and/or additional growth precursors. This feedstock mixture is either injected into a hot reaction chamber, typically around 1100–1300 K, or vaporized before being carried into it via a heated process line (for example, both methods have seen success for commonly used Fc-toluene solutions),<sup>15,16</sup> in which it decomposes and reacts to form SWCNTs under a laminar flow regime.<sup>15</sup>

The morphology and properties of SWCNTs synthesized via FCCVD can be controlled via the identity and concentration of the growth precursor, as well as that of the catalyst. For example, the use of CO as a FCCVD growth precursor at low concentrations significantly reduces SWCNT bundling and increases SWCNT length, both of which are important for SWCNT-based transparent conducting films.<sup>15,17,18</sup> Other oxygenated species, such as ethanol,

have been shown to enable SWCNT production in both floating<sup>14,19,20</sup> and conventional CVD.<sup>21</sup> Combining O<sub>2</sub> and S as FCCVD growth promoters also enables chirality-controlled SWCNT synthesis.<sup>22,23</sup> Incorporating ethylene in the FCCVD feedstock alleviates the need to use CO and sulfurous compounds as growth promoters, and it additionally minimizes SWCNT bundling.<sup>24</sup> Sulfurous compounds have seen success as growth promoters in the formation of SWCNT films, SWCNT aerogels, and CNT fibers.<sup>25–27</sup> In the absence of additional growth promoters and precursors, multiwalled CNTS (MWCNTs) and MWCNT arrays<sup>28</sup> often include embedded Fe nanoparticles,<sup>29</sup> a problem that can be mitigated via the use of CNT templates.<sup>30</sup> In the case of tuning the catalyst, Fe nanoparticle catalysts derived from Fc result in longer SWCNTs<sup>24</sup> than pre-made Fe catalysts.<sup>31</sup>

The mechanism of SWCNT nucleation during CVD has been investigated extensively, using a combination of experiment and theory.<sup>9,32-37</sup> It is now well understood that the steps leading to SWCNT cap nucleation involve the surface diffusion of carbon and the subsequent formation of surface-bound carbon chains. These carbon chains coalesce first into a pentagon anchored to the nanoparticle by the branched carbon chains, before cross-linking to form additional pentagons and hexagons, until a "yarmulke" cap<sup>4</sup> nucleates and lifts away from the nanoparticle catalyst surface. During this process, defect healing drives the conversion of pentagons to hexagons.<sup>42</sup> The steps preceding nucleation primarily involve the decomposition of the carbonaceous growth precursor on the Fe catalyst surface. Despite CVD feedstock composition influencing SWCNT morphology,<sup>14,15,17,18,24,31,43,44</sup> the mechanistic influence of CVD growth promoters on these initial CVD reactions remains largely unexplored, except in the case of hydrogen (which has been shown to be a key modulator of the CVD process). Recently, ab initio molecular dynamics (MD) has examined the dissociation of ethanol on Fe, showing a tendency for Fe-O bond formation.<sup>51</sup> In addition, quantum chemical MD simulations showed how the presence of O in Fe catalysts can modulate the nucleation of C species from C<sub>2</sub> dimers.<sup>52</sup> Importantly, the influence of FCCVD precursors on catalyst nanoparticle formation and carbon chain growth during CVD is not yet understood.

In this work, we investigate these effects using first principles nonequilibrium MD simulations of the initial reactive stages during FCCVD decomposition of Fc. We demonstrate that, with the addition of ethylene, there is a competition between Fe clustering and carbon chain formation that kinetically hinders rapid Fe cluster formation. The decomposition of Fc via the spontaneous dissociation of hydrogen leads to Fe clustering to form the floating catalyst. With ethylene present, C2Hx radicals and C atoms formed from ethylene facilitate the opening of the Fc cyclopentadienyl rings, leading to Fe-bound carbon chains, which are the precursor to SWCNT nucleation. The addition of CO or CO2 also hinders rapid Fe clustering via the formation of Fe-O bonds, though CO/CO<sub>2</sub>-derived C radicals assist ring opening in a similar fashion to when ethylene is present. Importantly, the key growth agents in the formation of carbon chains are C2Hx radicals and lone C atoms, rather than the precursor or the Fe catalyst. Instead, the latter supports the initial nucleation of chains from Fc cyclopentadienyl rings. We also simulate the presence of premade Fe catalysts such as those formed by rod-to-tube spark discharge generators.<sup>5</sup>

We show that the premade Fe catalyst promotes further Fe clustering and provides an immediate surface on which carbon radicals adsorb and diffuse, thus facilitating the opening of cyclopentadienyl rings to form surface-bound carbon chains.

### **II. COMPUTATIONAL METHODS**

MD simulations utilized the self-consistent charge density functional tight binding (SCC-DFTB) method,<sup>54</sup> with the trans3d -0-1 parameter set<sup>55</sup> and a finite electronic temperature of 10 000 K.<sup>56–58</sup> The velocity-Verlet algorithm<sup>59</sup> was employed to integrate Newton's equations of motion with a time step of 1.0 fs. The quantum chemical potential energy and energy gradients were calculated "on-the-fly" at each MD iteration. The temperature of all simulations was held at 1323 K, i.e., a temperature relevant to FCCVD, using an NVT ensemble via the Nose–Hoover chain thermostat (chain length = 3).<sup>60,61</sup> All simulations here were performed using the DFTB+ software package.<sup>62</sup>

We model the decomposition of Fc using an ensemble of 20 Fc molecules in a periodic  $3 \times 3 \times 3$  nm simulation cell (density ~  $0.23 \text{ g cm}^{-3}$ ). This artificially high density approximates the fact the local density of a chemical species on and near the catalyst surface will be substantially higher than the ambient density in the reactor, due to surface adsorption. The influence of individual growth precursors (ethylene, methane, CO, and CO<sub>2</sub>) was studied by adding ten molecules of each species to the simulation cell in independent MD trajectories. The effect of a prenucleated  $Fe_{13}$  nanoparticle, such as those made by rod-to-tube spark discharge generators,<sup>31,43,53</sup> on these reaction dynamics was also investigated. For all simulations, data presented are an average across ten unique trajectories with randomized initial velocities satisfying a Maxwell-Boltzmann distribution at the simulation temperature; in total data presented below are obtained from 70 trajectories [10 trajectories  $\times$  4 precursors (ethylene, methane, CO, CO<sub>2</sub>)] with 10 trajectories containing only Fc, 10 trajectories containing only Fc and Fe<sub>13</sub>, and 10 trajectories containing Fc, Fe<sub>13</sub>, and ethylene. Mechanisms shown below are representative of those observed frequently for each respective condition.

### **III. RESULTS AND DISCUSSION**

The mechanism by which SWCNTs nucleate and grow is now established extensively in the literature.<sup>32–35,50</sup> It is well understood that small carbon species (e.g.,  $C_2$ - $C_5$ ) are the primary precursors of carbon network formation, whether or not a catalyst substrate is present. The key agents driving the nucleation of larger carbon structures, in either case, are extended  $C_{\rm n}$  carbon chains. In the absence of a catalyst, free reaction of these chains via cross-linking, growth, and oligomerization drives the formation of polygonal ring structures that close and shrink to form fullerene cage structures.<sup>6</sup> When a catalyst substrate mediates these interactions, they lead to polygonal ring structures with curvatures matching that of the underlying substrate; i.e., curved nanoparticle surfaces yield curved SWCNT cap structures, flat catalyst facets yield planar graphene or Haeckelite structures.<sup>39,64</sup> The hydrogen chemical potential has also been shown to be a key factor controlling the curvature of the formed carbon nanostructure.48,50,65 We, therefore, do not seek to investigate or reiterate these findings here. Instead, our aim is to

understand the chemical reaction pathways that give rise to the key agents of growth, i.e., carbon chains, during FCCVD synthesis of SWCNTs using Fc. In doing so, our results provide a new mechanistic basis explaining various experimentally observed phenomena; e.g., the fact that FCCVD catalyst diameters are on average smaller in the presence of oxygenated precursors (CO,  $CO_2$ )<sup>44</sup> and the fact that FCCVD of Fc without additional carbonaceous precursors does not result in the consistent synthesis of SWCNTs.<sup>24</sup>

### A. Ferrocene decomposition: Carbon chain formation

We begin our discussion by establishing the mechanism of Fc decomposition and carbon chain formation during FCCVD. Figure 1 presents the populations of carbon chains formed during the thermal decomposition of Fc, with and without ambient ethylene and Fe clusters. This figure shows that carbon chain formation from Fc decomposition is seldom observed within the timescales employed here. Critically, no carbon structures larger than the initial cyclopentadienyl moiety are formed. This indicates that high temperatures readily activate Fc by breaking the two Fe-cyclopentadienyl bonds, but further reaction is kinetically impeded. Figure 2(a) presents the primary mechanism by which Fc decomposition is observed, viz., initiation by the spontaneous dissociation of hydrogen from the cyclopentadienyl ring (0.02 ps). The thermal activation of these bonds rapidly destabilizes the molecule, subsequently cleaving the bonds between the Fe atom and the conjugated ring systems. An intermediate structure in which Fe atom bonds to the activated cyclopentadienyl radicals via a C-Fe-C  $\sigma$  bond system is observed momentarily (0.08 ps). Ultimately however, Fe atoms are freed into the gas-phase, thereby facilitating Fe catalyst nanoparticle formation via clustering later in the reaction (Sec. III B).44 The order of these reactive steps indicates that the C-H bonds are weaker than the Fe-C bonds, and this is in agreement with density functional bond cleavage energies reported previously (492 vs 1480 kJ mol<sup>-1</sup>).<sup>66</sup> Interestingly however, the Fe<sup>--</sup>C  $\sigma$ bonds are cleaved before the activated cyclopentadienyl radical has a chance to break, forming a five-membered carbon chain.

By contrast, when ethylene is present in the reaction, large carbon chains (up to  $C_{11}$  in these simulations) immediately form





in the initial stages of the FCCVD process. Figure 1 also shows that the population of shorter chains (e.g., C2 and C3) is also higher, as one might expect. Figures 2(b) and 2(c) demonstrate the typical origins of these carbon chains. Figure 2(b) shows that ethylene undergoes spontaneous (<10 fs) pyrolytic activation under the conditions employed in these simulations, yielding highly reactive H and C radicals. The latter combine directly with the Fc cyclopentadienyl ring via C-C bond formation (0.20 ps); this destabilizes the aromatic system, leading to ring C-C bond cleavage (0.22 ps) and ring opening to form a six-membered carbon chain. Figure 2(b) shows that the interaction between this chain and the Fe atom disrupts the remaining Fe-cyclopentadienyl bond. Fc decomposition in this case thus results in a Fe-C<sub>6</sub> chain moiety and a cyclopentadienyl radical as intermediate structures (0.25 ps). Figure 2(c) shows an alternative mechanism of Fc decomposition in the presence of ethylene. In this case, ethylene derived radicals, C2Hx, successively attack the Fc Fe atom via Fe-C bond formation (0.45, 3.2 ps), causing the displacement of a cyclopentadienyl radical (21.01 ps). Ultimately, the Fe atom here acts as a catalytic substrate supporting carbon chain growth. Pyrolytic activation of a cyclopentadienyl C-H bond (30.09 ps) destabilizes the ring system to yield a C<sub>9</sub> chain (34 ps).

The catalytic action of the Fc Fe atom evident in Fig. 2 is consistent with the role played by larger Fe clusters, depicted in Fig. 3. While Fig. 1 shows that Fe<sub>13</sub> clusters do not appreciably change the distribution of carbon chains formed, Fig. 3 demonstrates that they influence the mechanism by which carbon chains grow into larger structures. Specifically, Fe clusters mediate the reaction of Fc with ethylene and ethylene-derived species. Figure 3 details an example in which Fc and an ethylene-derived C2 radical adsorb (0.05, 5.71 ps, respectively) and subsequently react to form a C<sub>7</sub> carbon chain. Here, the Fe catalyst facilitates the opening of the cyclopentadienyl ring to afford a five-membered surface-bound carbon chain in a manner analogous to that observed with a single Fe atom [Figs. 2(b) and 2(c)]. FCCVD using Fc without additional C-based precursors does not result in the consistent synthesis of SWCNTs;<sup>24</sup> our simulations provide one potential mechanistic basis for this experimental observation. Without ethylene, Fig. 1 shows that chain growth (beyond C<sub>5</sub>) on the Fe cluster surface is not a prominent chemical pathway in the initial stages of reaction.

Thus, despite the abundance of Fc in the reaction, these results implicate smaller carbonaceous fragments, principally C<sub>2</sub>H<sub>x</sub> radicals, as the key agents of carbon chain growth, in agreement with prior simulations<sup>65</sup> and experimental measurements of SWCNT growth kinetics.<sup>67,68</sup> Our results indicate that Fc should instead be considered as a substrate, or feedstock, consumed by these reactive C<sub>2</sub>H<sub>x</sub> growth agents to form larger carbon structures. This is consistent with organometallic analogs of ferrocene, e.g., cobaltocene, yielding SWCNTs with average diameters of 1.06 and 1.05 nm, respectively, via FCCVD with ethylene in the absence of an additional growth promoter.<sup>43</sup> More recently, ethylene was used as a precursor to simultaneously synthesize fullerenes, SWCNTs, and graphene in the gas-phase, and the use of either ferrocene, cobaltocene, or nickelocene did not affect the synthesized product in any way, aside from yield.<sup>69</sup> Moreover, while Fc-derived Fe catalysts have been shown to produce a higher SWCNT yield via FCCVD, compared to derived Co and Ni catalyst particles, the



FIG. 2. Fc decomposition mechanism via the spontaneous dissociation of hydrogen from the cyclopentadienyl ring. (b) Fc decomposition with ethylene present is influenced by C radicals formed via ethylene decomposition (0.05 ps), leading to the cyclopentadienyl ring opening to form a chain. (c) Fc decomposition following the reaction with ethylene, leading to a disubstituted cyclopentadienyl ring that opens to form a carbon chain. Orange, gray, and white spheres represent Fe, C, and H atoms, respectively.

structural properties of the SWCNTS are due to catalyst size and not composition.<sup>31</sup> This is further evidence indicating that the key growth agents driving SWCNT formation themselves are independent of the organometallic precursor.

## B. Ferrocene decomposition: Catalyst growth

The preceding section established how Fc plays the role of a catalytic substrate, or feedstock, during the initial stages of FCCVD with respect to carbon chain formation. Figure 3 highlights a competing



FIG. 3. Fc and ethylene adsorb to the Fe<sub>13</sub> catalyst. The Fe<sub>13</sub> catalyst abstracts the Fe atom from the Fc precursor and facilitates the opening of the cyclopentadienyl ring to form a carbon chain. Atom colors as in Fig. 2.

key role played by Fc during this phase of the FCCVD reaction, i.e., Fe catalyst nanoparticle growth. In this case, catalyst nanoparticle growth is illustrated via the catalytic disproportionation of Fc on an Fe<sub>13</sub> cluster, which releases the Fe atom that remains adsorbed to the Fe cluster surface. In effect, the formation of carbon chains that is facilitated by the Fe cluster surface triggers its incremental growth. In this section, we examine the mechanism of Fe cluster formation observed during Fc FCCVD more closely.

Figure 4 compares the growth of Fe clusters observed during simulated Fc FCCVD with and without ethylene. This figure shows that two competing reaction pathways exist during the initial stages of Fc FCCVD: carbon chain formation and Fe catalyst growth. In the absence of ethylene, the latter wins out, i.e., chain formation impedes initial Fe catalyst growth. Figure 4(a) shows that Fe catalyst formation is rapid without ethylene, with Fc disproportionation completed in the first ~50 ps of reaction. This is also the case when methane, a less reactive carbon precursor compared to ethylene, is included (Fig. S1 in the supplementary material). The rapid drop in Fe—C bonds [Fig. 4(b)] shows that Fc-cyclopentadienyl bond cleavage is the driver of this process. The small number of Fe-C bonds remaining is evidence of a small amount of carbon adsorbed to the cluster surface.

On the other hand, incorporating ethylene into the reaction brings balance to these two competing pathways by altering their kinetics. In this case, Fe nanoparticle formation is  $\sim$ 3-4 times slower [Fig. 4(a)], while the population of Fe-C bonds is proportionally higher throughout the reaction. Considering the preceding discussion, we attribute this to ethylene-derived radicals producing a higher population of longer carbon chains, which passivate the catalyst cluster and hence slow its growth. In the presence of a higher density of Fe nanoparticles, achieved here via the incorporation of an additional Fe13 cluster in the simulation, this passivation effect is further exaggerated, with Fig. 4(a) showing that Fe catalyst growth is hindered completely in this case. This (somewhat counterintuitive) result is due to the Fe13 cluster itself facilitating more rapid chain growth earlier in the reaction; the higher proportion of surface-bound chains thus formed on the Fe<sub>13</sub> cluster effectively prevents it from adsorbing Fc and growing via the mechanism shown in Fig. 3.



FIG. 4. Average Fe–Fe bond count observed during the initial Fc FCCVD reaction, not including those within the initial Fe<sub>13</sub> cluster. (b) Average Fe–C bond count observed during the initial Fc FCCVD reaction; the inset highlights Fe–C bond count 50 and less. (c) Fe clustering via the disproportionation and aggregation of Fc. (d) Fe clustering hindered by the presence of ethylene and the competition between clustering and carbon chain formation. Atom colors as in Fig. 2.

The competition between carbon chain growth and Fe cluster growth is illustrated further in Figs. 4(c) and 4(d) and Fig. S2 in the supplementary material. Figure 4(c) shows how the Fe atoms of two separate Fc moieties combine (0.57 ps) to form Fe-Fe bonds through the exclusion of their Fc cyclopentadienyl rings (0.83 ps). Adsorbed cyclopentadienyl rings initially prevent the inclusion of nearby Fe atoms (1.26 ps), though dissociate from the growing cluster through Fe-cyclopentadienyl ring bond cleavage to allow for further incremental growth of the Fe cluster (5.35, 8.39 ps). With ethylene present in the reaction [Fig. 4(d)], the initial cluster nucleation due to cyclopentadienyl ring exclusion is not impeded. However, in this case, carbon chains, formed on the surface of Fe atoms following cyclopentadienyl ring opening (0.44 ps), impede agglomeration of Fe atoms via bridging chain motifs (6.23 ps) and surface-bound chains (14.02 ps). Comparison of Fig. 4(c) (8.39 ps) and Fig. 4(d) (14.02 ps) is indicative of the relative kinetics here; the higher population of surface-bound chains in the presence of ethylene effectively halves the clustering rate in this case.

### C. Ferrocene decomposition: Influence of CO and CO<sub>2</sub>

The preceding discussion has established how ethylene facilitates the growth of carbon chains during Fc FCCVD through cyclopentadienyl ring opening, and that this chemical pathway kinetically hinders the growth of Fe catalyst nanoparticles that would naturally occur during thermal Fc decomposition. We conclude our discussion by considering how pertinent oxygenated FCCVD feedstock additives  $\rm CO^{15,17-18}$  and  $\rm CO_2^{44,70}$  influence these chemical pathways.

Figure 5(a) shows the population of carbon chains formed via thermal decomposition of Fc, with and without CO or CO2. It is immediate from this figure that CO and CO<sub>2</sub> both facilitate chain growth during Fc FCCVD. In the absence of these species, Fc decomposition leads to predominantly stable cyclopentadienyl moieties adsorbed to the growing Fe cluster, as detailed above. In the presence of both CO and CO<sub>2</sub>, however, the population of other carbon fragments increases. Notably, carbon atoms [i.e., C1 in Fig. 5(a)] are formed in greatest abundance via catalytic activation of CO and CO<sub>2</sub>. Upon adsorption to the growing catalyst cluster, CO and CO<sub>2</sub> both readily split to yield C and O atoms. In the case of CO<sub>2</sub>, this activation process is sequential (i.e.,  $CO_2^* \rightarrow CO^* + O^* \rightarrow C^* + 2O^*$ ). In this respect, CO and CO<sub>2</sub> both simply act as additional sources of carbon on the growing catalyst surface, which facilitate the formation of the larger carbon chains [up to  $C_{10}$ , Fig. 5(a)], via cyclopentadienyl ring opening. A typical ring-opening mechanism is illustrated by the example in Fig. 5(b), which shows the adsorption of CO to a small Fe cluster via a Fe-O bond (5.05 ps). The nearby adsorbed cyclopentadienyl ring is opened following the formation of a C-C bond with CO (5.71, 5.75 ps). On the same cluster, this process can be repeated with multiple adsorbed CO molecules, often as they dissociate on the surface (6.71 ps). Carbon chain growth [Fig. 5(c)] follows ring opening that is facilitated by Fe-adsorbed C (10.8 ps). Chains grow either by further surface diffusion of C atoms or by the addition of nearby gasphase C atoms after they form from CO/CO<sub>2</sub> activation (113.2 ps), resulting in C<sub>10</sub> carbon chains on the timescales employed here (244.6 ps). Either mechanism of chain growth involves the C atoms derived from the CO or CO<sub>2</sub> precursor, rather than the precursor itself. O here does not contribute to the growth of carbon chains, interacting instead with the Fe cluster.

While Fig. 5(a) shows that CO and CO<sub>2</sub> increase the distribution of longer carbon chains compared to when only Fc is present, the population and diversity of long carbon chains are both greater in the presence of ethylene (Fig. 1). Interestingly, CO and CO<sub>2</sub> also fail to produce  $C_2H_x$  (i.e.,  $C_2$  chains), despite there being a sufficiently high density of reactive carbon atoms on the cluster surface for such species to be formed. This provides additional evidence implicating  $C_2H_x$  as the key agents driving chain growth at the beginning of SWCNT nucleation in FCCVD.

We consider the role of CO/CO<sub>2</sub> derived oxygen on Fe catalyst growth in Fig. 6. The addition of CO or CO<sub>2</sub> to the reaction significantly impedes the Fe clustering process, as indicated by the reduction in the number of Fe-Fe bonds in both cases [Fig. 6(a)]. Principally, this is due to the presence of oxygen. Ultimately, CO and CO2 limit the size of the Fe cluster to  ${\sim}66\%$  and 50% of the size formed naturally via thermal decomposition of Fc. Figure 6(c) shows that the principal mechanism preventing Fe catalyst growth here is Fe-O bond formation; adsorption and activation of  $CO/CO_2$  on the growing cluster release oxygen atoms that partially saturate its surface, presenting a barrier to further Fe aggregation. These Fe-O bonds, once formed from CO/CO<sub>2</sub>, remain in the simulation [Fig. 6(c)]. This is anticipated since the Fe–O bond is strong and is known to form readily under these conditions.<sup>44</sup> We note that the 2:1 ratio in the Fe-O bond populations for CO<sub>2</sub> and CO matches the natural stoichiometry of these compounds. This indicates that CO/CO2 C-O bond activation is effectively 100%, and means that C-O bond activation is almost exclusively driven via the Fe cluster surface (although thermal activation of CO and  $CO_2$  in the gas-phase is also observed on occasion). With a reduction in initial Fe-Fe clustering, the Fe nanoparticles formed in the presence of CO/CO2-derived oxygen are on average smaller, consistent with recent experiments.<sup>4</sup>

Cluster growth is also impeded via  $CO/CO_2$ -derived carbon. As shown in Fig. 5(a), both CO and  $CO_2$  yield more long carbon chains on the growing catalyst surface. We note that the formation of these surface-bound carbon chains is also more prevalent for CO than it is for  $CO_2$  [Fig. 6(b)]. In this respect, the effect of CO is comparable to that of ethylene [Fig. 4(d)]. As the dissociation products of CO and  $CO_2$  are the key agents driving cyclopentadienyl ring-opening, discussed above, the increase in chain formation is observed for CO rather than  $CO_2$ , as there is less oxygen impeding the active C-based radicals on the Fe cluster surface. Within the timescales of our simulations, further C—O bond formation on the catalyst surface is not observed [Fig. 6(d)], suggesting that the release of carbon into the Fc decomposition chemistry by  $CO/CO_2$  is irreversible.

Interestingly however, the presence of  $CO/CO_2$  does not kinetically hinder the clustering of Fe atoms in the same manner as ethylene. With ethylene present, there is a balance between Fe clustering and carbon chain formation, where, initially, carbon chain formation dominates and Fe clustering is hindered. After ~150 ps, the number of Fe–Fe bonds present in this case is equal to that observed without ethylene. On the other hand, when CO or CO<sub>2</sub> are present, the initial rate of Fe clustering is unchanged (compared to Fc decomposition), due to the dissociation of CO



FIG. 5. Average carbon chain count after 250 ps of simulation across ten trajectories for the simulations of Fc, CO, and CO<sub>2</sub>. (b) Fc cyclopentadienyl rings and CO adsorbed to a Fe cluster formed following Fc decomposition and Fe aggregation (5.05 ps). Interaction between the adsorbed CO group and the cyclopentadienyl ring facilitates the opening of the ring to form a polypne chain (5.71 to 5.75 ps). Subsequently, CO dissociates into surface-bound C and O (6.71 ps). (c) Growth of Fe-adsorbed carbon chain via C–C bond formation with Fe-adsorbed C (10.8 ps) followed by the C–C bond formation with the gas-phase C (113.2 ps). Atom colors as in Fig. 2; red spheres represent O atoms.

and  $CO_2$  and the formation of Fe-O-Fe bonding motifs. However, surface-bound O quickly saturates the Fe cluster surface, thereby effectively limiting the achievable Fe cluster size on the time-scales employed here. This is most observable in the presence of

CO<sub>2</sub>. Ultimately, these results indicate that the identity of the growth precursor determines the nature of the balance between carbon chain formation and catalyst growth during the initial stages of FCCVD.



FIG. 6. Average bond populations observed during simulated FCCVD of Fc with ethylene, CO, or CO<sub>2</sub>. (a) Fe-Fe, (b) Fe-C, (c) Fe-O, (d) C-O.

### **IV. CONCLUSIONS**

We have reported the initial reactive pathways during FCCVD decomposition of Fc with and without the presence of additional growth precursors such as ethylene, CO, and CO<sub>2</sub>. These simulations demonstrate how Fc decomposes during FCCVD via the spontaneous dissociation of H and the subsequent release of Fe atoms to allow for Fe clustering. Critically, Fc decomposition and carbon chain formation is accelerated significantly in the presence of these additional growth precursors, notably ethylene. The key growth agents in the ring opening mechanism are the products of the growth precursor dissociation, viz.,  $C_2H_x$  radicals and C atoms from ethylene, and C atoms from CO and CO<sub>2</sub>. The formation of carbon chains predominantly occurs on the surface of the growing Fe clusters, and this gives

rise to two competing chemical pathways—carbon chain growth and Fe catalyst nanoparticle growth. The presence of ethylene kinetically hinders the rapid formation of Fe clusters as carbon chain formation is favored, with carbon chains up to  $C_{11}$  observed over 250 ps of simulation. Moreover, the addition of a Fe<sub>13</sub> cluster (simulating a pre-made FCCVD catalyst) promotes the formation of larger Fe clusters without ethylene present. However, with ethylene present in the reaction,  $C_2H_x$  radicals and C atoms deposit on the surface of the larger cluster growth. The presence of CO and CO<sub>2</sub> does not hinder rapid Fe clustering in the same fashion but instead limits the amount of Fe—Fe bonding due to the formation of strong saturating Fe—O bonds. The increased oxygen chemical potential with CO<sub>2</sub> over CO

leads to a preferential increase in Fe—O bonds and a general reduction in chain growth kinetics. It is worth noting that sulfur-containing compounds, often added as growth promoters, may assist in balancing Fe clustering and Fe—O bond formation by reacting with excess O. We believe the results reported here offer key insights into the initial stages of FCCVD growth of SWCNTs and the influence of tuning the growth precursor on the critical balance between FCCVD catalyst growth and key reactive intermediates formed during SWCNT nucleation, notably carbon chains.

### SUPPLEMENTARY MATERIAL

See the supplementary material for Fe—Fe bond population analysis, mechanism of competition between carbon chain growth and Fe cluster growth, and initial simulation configurations.

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### DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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