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A mechanistic study of the influence of graphene curvature on the rate of high-temperature oxidation by molecular oxygen

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ABSTRACT

Kinetic Monte-Carlo (KMC) simulations of the evolution of a graphene sheet in combustion-like environments were performed using a set of newly established elementary reactions of graphene-edge oxidation by O_2. The KMC results revealed two principal pathways for an oxyradical site: oxidation and regeneration of an aromatic radical site. The two pathways compete for oxyradicals, but exclusion of the regeneration pathway does not significantly affect the oxidation rate. Examination of the morphology of the evolving graphene edges indicated that the addition of O_2 promotes the formation of five-member rings embedded in the graphene. The overall oxidation rate of the graphene was computed to be time dependent, with reactivity decreasing over time as the ratio of reactive edge sites decreases relative to the number of basal-plane carbon atoms. At the same time, the oxidation rate was found to be higher for graphene with a higher initial curvature. Both results are in accord with experimental observations. Analysis showed that distinct aspects of graphene-edge morphology are responsible for curvature either raising or reducing the oxidative reactivity of the graphene edge.

1. Introduction

Oxidation of carbon by molecular oxygen has been studied for a long time, in various disciplines and contexts. One of the primary interests is mechanistic understanding of the process. It is not straightforward to decipher experimental observations into mechanistic details, and theoretical tools provide increasingly reliable approaches in this direction. Formation of carbon at high temperatures, such as soot formation in flames, is especially amenable to theoretical studies. Indeed, the overall reaction time at high temperatures is on the order of milliseconds and hence only fast reactions should be accounted for. Furthermore, at these conditions the gas-surface reactions follow the direct, Eley-Rideal mechanism [1] that allows a simpler theoretical treatment, as compared to the Langmuir–Hinshelwood [1,2] and mobile-precursor [3,4] mechanisms at lower temperatures that increase the complexity of molecular interactions and enlarge the number of possible reactions. The past few decades of theoretical studies of high-temperature carbon growth have brought us to mechanistic understanding of the process [5] that is being currently exploited not only for combustion soot [6,7] but also for carbon-black processes [8] as well as gas-phase synthesis of graphene [9]. These accomplishments motivate employing a similar strategy for unravelling details of carbon oxidation, and hence we begin with soot oxidation at high temperatures.

Oxidation of soot by molecular oxygen has received substantial attention over the years (see, e.g., a recent review [10] and accounts given in recent articles [11–16]). Early conception was based on an empirical model of Nagle and Strickland-Constable (NSC) [17], who represented the carbon surface by two empirical sites: less reactive and more reactive. In the early 1990's, Frenklach and co-workers [5,18,19] suggested a physically-resolved model, postulating that oxidation by molecular oxygen occurs on radical sites of aromatic molecules comprising a soot particle, i.e.,

$$C_{surface}\bullet + O_2 \rightarrow \text{products} \tag{1}$$

The rate coefficient of this reaction was assigned by analogy to phenyl oxidation [20]. This simple, one-step kinetic model has been broadly employed in numerical studies of soot formation in hydrocarbon flames.

While the simple reaction model based on chemical analogy, for both surface oxidation and growth, was successful in achieving an order-of-magnitude agreement with experiment [5,19,21,22], the

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follow-up research revealed richer chemistry of the growth (see, e.g. [23–31], and references cited therein). One of the main features is surface migration of five-membered rings along zigzag edges of aromatics [23,26]. Being in itself intriguing, this process opens numerous reaction possibilities [26,27,29–31]. Modeling that included all such identified different reactions exhibited curving of the initially planar aromatics [29]. Recent experimental studies suggested a substantial dependence of soot oxidation rate on soot particle curvature [11]. Clearly, a simple model such as (1) is insufficient to explain this observation.

A more detailed look at soot and carbon oxidation has been given within the past decade (see, e.g. [14,15,32–42], and references cited therein). Some of the recent interest is motivated by the use of filters to capture soot from diesel engines and their regeneration through oxidation of the captured soot [15,43]. The attention of the present study is on oxidation of soot at high temperatures, i.e., at conditions realized in flames of hydrocarbon fuels and inside combustion engines. Here we explore the kinetic implications of a newly developed detailed reaction mechanism for these conditions [40] by performing sterically-resolved kinetic Monte-Carlo (KMC) simulations of graphene-sheet evolution in O_2-rich environments. Our ultimate goal is to compare the prediction of theory with available experimental data. Here we focus on examining mechanistic factors affecting such comparison.

The central issue investigated in the present study is the role played by graphene-sheet curvature in oxidation. Performing initial KMC simulations [40] we noticed deceleration of oxidation with reaction time, in accord with experimental observations of Vander Wal et al. [12] who found reactivity to decrease as oxidation progresses. The site-resolved modeling [40] identified the cause for the decrease in the oxidation rate to be accumulation of five-member rings in the graphene edge, seemingly in contrast with the earlier study of Vander Wal et al. [11] observing that increased curvature leads to increased, not decreased reactivity. The present analysis resolves this apparent conflict.

2. Methodology

The KMC methodology followed that used previously [29,40,44]. Briefly, the KMC simulations tracked a single graphene "molecule" evolving in a flame-like environment, but maintaining the gas phase in a constant state, i.e., at constant values of temperature, pressure, and species mole fractions, which allowed us to investigate unambiguously the influence of individual factors on the simulation outcome. At each time step, a reaction event was selected stochastically and then applied.

The processes of surface growth and oxidation were modeled as a Markovian sequence of reaction events. There are two types of reactions that comprise the present model: bimolecular reactions between the gaseous species and surface sites, and unimolecular "decompositions" of surface species. All stochastic events were treated as first-order processes, with the respective per-site rates. The second-order reactions produced pseudo-first-order rate constants through multiplication of the gas-surface rate coefficient by the concentration of the gaseous reactant. The selection of the reaction event and specific graphene-edge site was done by application of the Gillespie algorithm [45,46] adapted for surface processes [47,48]. Briefly, given an instant of a current reaction event, t_n, the time of the next reaction event to occur at substrate site i is $t_{n+1,i} = t_n - (\ln u)/k_{\text{total},i}$, where u is a random number distributed uniformly from 0 to 1 and $k_{\text{total},i} = \Sigma_j k_{j,i}$ is the sum of the per-site rates of reactions possible at site i. The smallest among the $t_{n+1,i}$ values, computed for all surface reaction sites, becomes the time instant of the next reaction event, t_{n+1}, and the particular reaction to occur at that time is chosen according its probability $p_{j,i} = k_{j,i}/k_{\text{total},i}$ upon drawing another random number u. Once a reaction event is implemented, the process repeats itself.

The set of surface reactions employed in the KMC model contains 45 growth and 45 oxidation reactions. The surface growth reactions and their corresponding rate coefficients are taken from Whitesides and Frenklach [29,44] and 45 of the surface oxidation reactions and their corresponding rate coefficients are from our recent study [40]. This reaction mechanism is constructed for high temperatures, 1500–2500 K; in doing so, it has been presumed that active soot-particle surface is comprised of H-saturated graphene edges and an active, reactive site for the O_2 attack is an aromatic radical, created by H-atom abstraction [5,19]. At high temperatures and gaseous environments containing hydrogen, the probability of having two adjacent radical sites is relatively low and hence we neglected reactions occurring on such diradical sites. Furthermore, considering the millisecond time scale of the high-temperature processes, we neglected slow reactions, such as edge reconstruction and nascent site deactivation [14,49]. With these considerations, the primary product of carbon oxidation is CO [15,39–41] and the O atoms released in the surface reactions enter into the gas phase. The gaseous concentration of O atoms and their contribution to soot oxidation is relatively low in flame environments [50,51], as compared to OH and O_2, and hence the oxidative attack of graphene carbons by O atoms were not included in the present study. Also, the present simulations consider evolution of a single graphene "flake", and hence no particle-dynamics processes, such as oxidation-induced particle fragmentation [51,52], were included in the model. The reaction mechanism employed in the present study is provided in Table S1 of the Supplementary Data.

To properly account for the evolving curvature, the KMC model was coupled to molecular-mechanics geometry optimization using the MM3 potential [53] with the TINKER molecular mechanics package [54]. The MM3 potential has been found to produce geometries for fullerenes in good agreement with the ab initio Hartree-Fock method [55] as well as experimental and DFT results for fullerenic fragments [56]. Optimization of the structure geometry was performed after each structure-changing event. The geometry optimization step properly accounted for substrate curvature while maintaining physically accurate bonding and geometric configuration of the evolving structures. A check was made after each geometry optimization to ensure that the geometry produced by the molecular mechanics code was consistent with the bonding implied by the KMC model. Specifically, the code tested if the geometry optimization left all carbon atoms within a specified distance of the other atoms to which they were bonded in the KMC description. If any two carbon bonds were found to be separated by more than two angstroms, the simulation was ended.

The evolution of the graphene structure, referred to hereafter as substrate, was monitored by computing the numbers of reaction events, instantaneous structure size, and its five-member ring fraction, f_{R5}, the latter defined as [44].

$$f_{R5} = \frac{32}{12}\frac{N_{R5}}{N_{R5} + N_{R6}}, \tag{2}$$

where N_{R5} and N_{R6} are the number of five- and six-member rings, respectively, and the 32/12 coefficient normalizes Eq. (2) to have $f_{R5} = 1$ for buckminsterfullerene, C_{60}.

To collect better statistics, simulations for each set of initial conditions were repeated 100 times, each with a different starting random seed. The results reported in this work are averages over these ensembles of simulations. In the previous study [40] we repeated the entire sequence of calculations, comprised of the initial period of substrate growth followed by a period of substrate