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Detailed, sterically-resolved modeling of soot oxidation: Role of O atoms, interplay with particle nanostructure, and emergence of inner particle burning

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ABSTRACT

A newly-developed detailed mechanism of soot oxidation was tested against experimental observations. The computations were performed at an atomistic level and with a detailed consideration of soot particle surface sites. Several additional reactions were investigated theoretically and one of them, oxidation of embedded five-member rings by O atoms, was included in the model. The primary focus of the study was on the high-temperature shock-tube experiments of Roth et al. (1991). The reaction model was able to reproduce the experimental results, but required coupling to particle nanostructure: partial oxidation of PAH molecules and the decrease in PAH initial sizes along the oxidation path. The principle reaction mechanism was identified to be the formation of oxyradicals, their decomposition, formation of hard-to-oxidize embedded five-member rings, and oxidation of the latter predominantly by O atoms. The analysis identified O as the most effective oxidizer of the embedded five-member rings, which thus controls the rate of the overall oxidation. The model thus predicts fast oxidation during a brief initial period followed by a slow-oxidation one. The model of partial oxidation of an aromatic molecule and switching to the next intact molecule suggests pore formation and subsequent inner particle burning. We also investigated the ability of the present model to reproduce recent measurements of soot oxidation rates performed by Camacho et al. (2015) at about 1000 K. The initial reaction model failed to predict these results, and no adjustment could reconcile the differences. The only way to bring the model to experimental values was by assuming a catalytic decomposition of water on the reactor wall supplying additional radicals, H and OH, to the reacting gas mixture. Additional chemistry, oxidation through complex formation at neighboring surface sites, was required to fully reproduce the experimental observations. These additional reactions were found to play no role in the high-temperature simulations, nor were they sufficient to reproduce the low-temperature experiment on their own, without the assumed catalytic decomposition of water.

1. Introduction

Oxidation of soot is one of the key processes of soot particle phenomena in hydrocarbon combustion; it counterbalances the growth and, ultimately, is responsible for the removal of soot from exhaust. There is essentially a unanimous consensus that the oxidizing agents in flames are primarily O_2 and OH with minor contributions of O, H_2O, CO_2, NO_2, etc. (e.g., [1–9]). Early models of soot oxidation by O_2 were based on studies of carbon oxidation, most notably those of Nagle and Strickland-Constable (NSC), who postulated two empirical sites: less reactive and more reactive [10–12]. The NSC model has been commonly used in practical applications and has become a benchmark for comparison when new experimental measurements (e.g., 7,13–20]) or computational studies (e.g., [8,9,21–25]) are performed. With some exceptions (e.g., [19]), most experimental studies found their oxidation rates to agree or being close to those of the NSC model. The oxidation of soot by OH, suggested by Fenimore and Jones [26], has been

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commonly described by OH collision efficiency with soot particle surface, initially measured by Neoh et al. [27] and re-measured in subsequent studies [3,28–33].

In the late 1980s–early 1990s, Frenklach and co-workers [21,34–36] suggested a reaction model for soot growth and oxidation based on physically resolved surface sites. The growth is now known as HACA [36], and the oxidation was postulated to proceed by two reactions: (1) O_2 reacting with radical sites of aromatic molecules that comprise a soot particle, with the rate coefficient assigned by analogy to phenyl oxidation [37], and (2) OH reacting with “generic” surface (C–H) sites, described by the collision-efficiency model of Neoh et al. [27]. This simple kinetic model has been broadly employed in numerical studies of soot formation in hydrocarbon flames (e.g., there are 910 citations to one of such models [22] identified by the Google Scholar as of this writing).

While the simple reaction model based on chemical analogy for surface oxidation and growth was successful in achieving an order-of-magnitude agreement with experiment [21,22,31,32,38], subsequent research revealed richer chemistry of both growth [39–48] and oxidation [23–25,49–60]. Sterically-resolved modeling of the growth, which included newly identified reaction pathways and performed employing a kinetic Monte-Carlo with molecular mechanics relaxation (KMC-MMR) technique, exhibited curving of the initially planar aromatics [45,61,62]. The curving is a result of surface migration of five-member rings along zigzag edges of aromatics [39], embedding of the five member rings into the growing surface [42], and capping of such embedded sites [47].

Recent KMC-MMR modeling of the oxidation of soot by O_2 [23] indicated that the addition of oxygen promotes the formation of five-member rings embedded in the aromatic edge. The results exhibited deceleration of oxidation with reaction time, in accord with experimental observations of Vander Wal et al. [63] who found reactivity to decrease as oxidation progresses. Yet, the site-resolved modeling [23] identified the cause for the decrease in the oxidation rate to be accumulation of five-member rings in the edges of aromatics, seemingly in contrast with the earlier study of Vander Wal et al. [64] observing that increased curvature leads to increased, not decreased reactivity. The follow-up analysis [65] reconciled this apparent conflict by the difference in the reactivity and thermal stability of the five-member rings forming in the aromatics edges.

One puzzling aspect of the KMC-MMR results remains unanswered: as mentioned above, current models of soot oxidation assume a “steady” oxidation reaction kinetics [22,66], yet the detailed, KMC-MMR modeling shows a rather sharp decline, on a sub-millisecond time scale, in the oxidation rate [23,65]. Such a rapidly decreasing oxidation rate was observed experimentally [67], but at conditions substantially different from those used in the KMC-MMR simulations [23,65]: the experiment was carried out at temperatures below 1000 K, whereas the modeling, focusing on combustion, was performed at temperatures above 1500 K.

The objective of the present study is to examine quantitatively predictions of the newly developed detailed model of soot oxidation against experimental observations. While many studies have measured the oxidation rates of carbon, including chars, coals, and graphite, there have been considerably fewer studies directly measuring the oxidation rate of soot (e.g., [3,13–19,26,68,69]), especially at temperatures relevant to combustion. With our immediate interest being combustion, we chose to focus on the experiments of Roth et al. [16], the most recent studies of soot oxidation rates at high temperatures that employed non-intrusive laser diagnostics. We also investigated the ability of the present model to reproduce recent measurements of soot oxidation rates performed by Camacho et al. [19] at about 1000 K.

To account for the oxidative experimental environments, several additional reactions were included in the model. Thus, our presentation begins with a section, Section 2, on the reaction model description of the additional reactions, theoretical calculations of the rate coefficient for one of them, namely, the oxidation of embedded five-member rings by O atoms. The latter reaction was included to test a possible acceleration of the overall oxidation. At the end of Section 2, we describe exploration of other possible reaction channels. Section 3 is devoted to the simulations of the high-temperature oxidation rates of Roth et al. [16]; this section also presents an extension of the KMC method, coupling the gas-phase and surface reactions. In Section 4 we report our simulation results of the oxidation rates of Camacho et al. [19]. We conclude with a section summarizing the key findings of the present study and outlining implications of the present results to current practices and future efforts.

2. Surface oxidation model

2.1. Reaction model

The surface reaction model employed in the present study is presented in Table 1. The initial set of 45 growth [45,61] and 45 oxidation [23,65] reactions, Reactions (S1)–(S45) and (S46)–(S90), respectively, are taken from our prior studies, those cited above. This reaction mechanism was constructed for high temperatures, 1500–2500 K, assuming the gas-surface reactions to follow the direct, Eley–Rideal mechanism [65,70]. It was also presumed that active soot-particle surface is comprised of H-saturated aromatic edges and an active, reactive site for the oxidation is an aromatic radical, created by H-atom abstraction [21,36]. This is so not only for the reaction with O_2, as in the initial proposal [21,34], but also for the reaction with OH, as follows from recent theory [55]. At high temperatures and gaseous environments containing hydrogen, the probability of having two adjacent radical sites is relatively low and hence reactions occurring on such diradical sites were neglected; yet, their possibility was tested for the low-temperature simulations. Also, the employed KMC-MMR simulations consider evolution of a single graphene “flake”, and hence no particle-dynamics processes, such as particle aggregation [2] and oxidation-induced particle fragmentation [27,71–74], were included in the model. Yet, the present results support a notion of internal particle burning [27,75,76], as will be discussed in Section 3.

The rate coefficients of reactions (S1)–(S45) and (S46)–(S90) are taken from [45,61] and [23,65], respectively. Those of the reactions added in the present study to account for the oxidative environments of the examined environments are as follows:

- abstraction of surface aromatic H by O_2, reaction (S91) in Table 1, with the rate coefficient assigned by analogy to that of reaction benzene + O_2 → phenyl + HO_2 determined in shock-tube experiments by Asaba and Fujii [77];
- abstraction of surface aromatic H by OH, reaction (S92), with the coefficient assigned by analogy to that of reaction benzene + OH → phenyl + H_2O of Seta et al. [78];
- addition of O atoms to aromatic C–H bonds, Aryl-H + O → Aryl-O• + H, reactions (S93)–(S95), with the rate coefficient assigned by analogy to that of reaction of O with benzene studied by Leidreiter and Wagner [79];
- oxidation of aromatic radicals by OH, reactions (S96)–(S99), with the rate coefficient determined in a recent theoretical study of Edwards at al. [55];
- oxidation of aromatic radicals by H_2O, reactions (S100)–(S103), with the coefficient assigned from [80];
- embedded five-member ring oxidation by O, reaction (S104), with the rate coefficient determined in the present study (Section 2.2).