



A soot particle surface reactivity model applied to a wide range of laminar ethylene/air flames



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ABSTRACT

The effect of soot surface reactivity, in terms of the evolution of sites on the soot particles' surface available for reaction with gas phase species, is investigated via modeling numerous ethylene/air flames, using a detailed combustion and sectional soot particle dynamics model. A new definition of a particles' age is introduced. A methodology has been developed to study soot particle surface reactivity. Subsequently, it is investigated if the surface reactivity can be correlated with the particle age. An exponential function giving a smooth transition of surface activity with particle age is employed to model a variety of ethylene/air flames, which differ in fuel stream dilution levels, fuel stream premixing, and burner configurations. Excellent agreement with measured soot volume fractions of a variety of flames, burners, and datasets could be obtained with this approach. The newly developed function based on particle age eliminates the need to fit soot surface growth parameters to each experimental condition. Finally, the applicability and limitation of the new surface reactivity function for use in detailed soot formation models is discussed.

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1. Introduction

Several stages have been identified during soot formation and oxidation. Soot formation starts with inception, which is the appearance of the first nano-scale soot particles. The newly incipient soot particles can grow through surface growth via surface chemical reaction and polycyclic aromatic hydrocarbons (PAH) condensation, and through particle coagulation. Finally, the soot particles lose mass and size during oxidation and fragmentation processes.

Among all the different processes, surface growth is known to be responsible for most of the soot mass yield in many systems [1]. As a soot particle traverses hot fuel rich regions, the surface of the particle reacts with the gas phase. The chemical kinetics of the soot surface has been examined by several studies. These studies concluded that acetylene is the primary growth species independent of the fuel type [1,2]. Based on this observation and the fact that the formation of soot proceeds via PAHs, it has been proposed that the reaction sequence for the build-up of PAHs and soot should be analogous. The most widely used theoretical model to describe the formation and growth of the aromatics is

the Hydrogen–Abstraction–Carbon–Addition (HACA) mechanism [2,3]. The HACA mechanism consists of a repetitive sequence of radical site formation by hydrogen abstraction, followed by carbon addition, most often by acetylene bonding, forming an additional aromatic ring. It is proposed that soot growth in flames also occurs at active sites.

The reaction scheme used to account for surface growth and oxidation is detailed in Table 1. The kinetics of the surface reactions are described using the concept of surface sites (an armchair site, which is a site with four carbon atoms as illustrated in Fig. 1), which are carbon atoms either saturated ($C_{\text{soot}}-H$) (or dehydrogenated (C_{soot}°) on the surface of soot particles. The concentration of saturated sites, $[C_{\text{soot}}-H]$ (mole/cc), is calculated by Eq. (1):

$$[C_{\text{soot}}-H] = \frac{A_s}{A_v} \chi_{C_{\text{soot}}-H} \quad (1)$$

where $\chi_{C_{\text{soot}}-H}$ is the number of sites per unit soot surface area; A_s (cm^2/cc) is the surface density of soot particles and A_v is Avogadro's number. The concentration of dehydrogenated sites $[C_{\text{soot}}^{\circ}]$ is similarly calculated with $\chi_{C_{\text{soot}}^{\circ}}$ as the number of dehydrogenated sites (C_{soot}°) per unit surface area. Finally by assuming a steady state for C_{soot}° , $\chi_{C_{\text{soot}}^{\circ}}$ can be calculated from Eq. (2) and substituted to find the individual rate of each of the soot reactions listed in Table 1.

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Table 1
HACA-based soot surface growth and oxidation reactions [10], $k = AT^b e^{-E_a/RT}$.

No.	Reaction	A ($\frac{\text{cm}^3}{\text{mol s}}$)	b	E_a ($\frac{\text{kcal}}{\text{mol}}$)
S1	$C_{\text{soot}} - \text{H} + \text{H} \rightleftharpoons C_{\text{soot}} \circ + \text{H}_2$	4.2×10^{13}	0.0	13.0
S2	$C_{\text{soot}} - \text{H} + \text{OH} \rightleftharpoons C_{\text{soot}} \circ + \text{H}_2\text{O}$	1.0×10^{10}	0.73	1.43
S3	$C_{\text{soot}} \circ + \text{H} \rightarrow C_{\text{soot}} - \text{H}$	2.0×10^{13}	0.0	0.0
S4	$C_{\text{soot}} \circ + \text{C}_2\text{H}_2 \rightarrow C_{\text{soot}} - \text{H} + \text{H}$	8.0×10^7	1.56	3.8
S5	$C_{\text{soot}} \circ + \text{O}_2 \rightarrow 2\text{CO} + \text{product}$	2.2×10^{12}	0.0	7.5
S6	$C_{\text{soot}} - \text{H} + \text{OH} \rightarrow \text{CO} + \text{product}$		$\gamma_{\text{OH}}=0.13$	

$$\chi_{C_{\text{soot}} \circ} = \frac{(k_1[\text{H}] + k_2[\text{OH}])\chi_{C_{\text{soot}} - \text{H}}}{k_{-1}[\text{H}_2] + k_{-2}[\text{H}_2\text{O}] + k_4[\text{C}_2\text{H}_2] + k_5[\text{O}_2]} \quad (2)$$

It was experimentally observed that the reactivity of surface sites changes with increasing particle growth or age [1,2,4,5]. Hence, this process is often called surface ageing. It was attributed to a decrease of active surface sites, i.e., sites that are accessible for reaction. Other experimental studies [1,6–8] showed the dependency of soot ageing on temperature. More recently, by analyzing surface growth pathways, Kronholm and Howard [9] cast doubt on the monotonically decreasing behavior of soot reactivity with residence time if C_2H_2 is assumed to be the dominant soot surface growth reactant.

The notion of active sites on the soot particle surface was introduced into kinetic soot modeling by Frenklach and Wang [3]. In conjunction with a decrease in concentration of C–H sites [1,3], it was used as an explanation for the experimental observation of surface ageing. On a mechanistic basis, Frenklach and co-workers [14–16] attributed surface ageing to the formation of defects on the particles' surface generated during surface growth. Surface ageing was also attributed to the reversibility of the HACA surface growth scheme [17–19]. The surface ageing effect was embedded into the HACA surface reaction scheme by introducing a steric parameter, α , which is positive and less than unity. Therefore the reaction rate for an individual reaction, for example S4, becomes:

$$R_4 = \alpha k_4 [\text{C}_2\text{H}_2] [\text{C}_{\text{soot}} \circ] \quad (3)$$

A review of the assumptions made in the soot surface growth scheme clarifies the necessity of the α parameter. The number density of the $C_{\text{soot}} - \text{H}$ sites, $\chi_{C_{\text{soot}} - \text{H}}$, was estimated based on the assumption that the surface is covered with stacks of benzene rings [10]. The distance between the stacks is 3.51 Å and it was assumed that 2 C–H bonds are available per benzene ring length (2.46 Å). Thus $\chi_{C_{\text{soot}} - \text{H}}$ was calculated to be $2/(3.51 \times 2.46) = 0.23 \text{ site}/\text{Å}^2$. Considering that all of these sites are accounted for as armchair sites, this value is the theoretical maximum value of soot surface site density. The nanostructure of soot particles has been experimentally studied in [13,21,22]. All of these studies concluded that soot particles are composed of stacks of 4 to 8-ring PAHs. If for estimation of $\chi_{C_{\text{soot}} - \text{H}}$ it was assumed that the surface of the soot particles is covered with a 5-ring PAH such as benzopyrene (A5) in accordance with the recent findings, the number of C–H bonds available per unit length on average would be 0.5 site/Å which results in $\chi_{C_{\text{soot}} - \text{H}} = 0.5/3.51 = 0.14 \text{ site}/\text{Å}^2$. Similarly, if it were

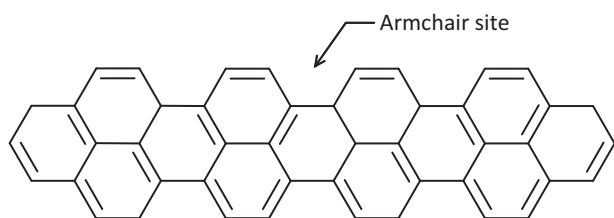


Fig. 1. Illustration of armchair sites on the surface of a soot particle.

assumed that the surface is covered with layers of coronene (A7) as opposed to the classical benzene-surface assumption, the number of C–H bonds available per unit length on average would be 0.4 site/Å and subsequently the number density of the $C_{\text{soot}} - \text{H}$ sites, $\chi_{C_{\text{soot}} - \text{H}} = 0.115 \text{ site}/\text{Å}^2$. Thus, the estimated value of $\chi_{C_{\text{soot}} - \text{H}}$ would be 25–50% less than the originally proposed value if the surface of the soot particles is assumed to be covered by the layers of 4 to 8-ring PAHs. The rate coefficients of the heterogeneous reactions, presented in Table 1, were estimated based on analogous gas phase reactions of one-ring aromatics. The rate coefficient steric factor (A) of each of the $C_{\text{soot}} - \text{H}$ sites is assumed to be one sixth of the benzene molecule. Also the activation energy is chosen to be constant for all the soot particles and 3 (kcal/mol) less than the corresponding gas phase analogous reaction of one-ring aromatics. However, it has been shown by [2,11,13,23] that the C/H ratio of soot particles which represents the carbonization or graphitization of soot increases with residence time of the soot particles and results in less chemical reactivity. In conclusion, the empirical ageing parameter, α , reconciles the inaccuracies of treating sites on the soot surface as corresponding sites on gaseous PAH molecules.

While initially a constant fraction of active sites was used with the kinetic soot model [1,3], it was later expressed as a function of flame temperature [20], and subsequently as a function of flame temperature and mean particle size [10]. Several studies measured the ageing parameter, α , based on the HACA surface growth scheme in laminar premixed and diffusion flames with different fuels, pressures, and flame temperatures, and proposed a temperature dependent function for the ageing parameter [23–29]. However, the predicted value of α yielded by those forms is 1.0 for most of the sooting region of laminar diffusion flames, which is quite close to the theoretical maximum value of available soot surface sites, and unrealistically high.

Dworkin et al. [30] shows that if particle inception is enhanced by accurate prediction of PAH molecules in the gas phase, α could be kept within a more realistic range to achieve physically accurate values of soot volume fraction. By calculation of particle age distributions in simulated premixed flames, Singh et al. [31] proposed two correlations for the fraction of active sites. However, their attempt to relate particle ageing with flame temperature in order to find a general expression for α was unsuccessful. The various forms of α proposed in the literature are summarized in Table 2. The value for α that is predicted for each of these functions at 1700 K, which is close to the local temperature in most of the sooting region in the diffusion flames, is included in this table. These values show a great discrepancy among different proposed functions for α . In some of these studies, such as [29,30], despite the similarities in the flames studied and soot surface growth models implemented, different values for α have been employed to achieve the same soot volume fraction predictions. This discrepancy is a

Table 2
Proposed functional forms of α for models based on the HACA mechanism.

Proposed by	Function	α at 1700 K
Frenklach and Wang [3]	0.1	0.1
Appel et al. [10]	$\tan h(a/\log \mu_1 + b)^a$	0.93
El-Leathy et al. [28]	$0.0017 \exp(12100/T)$	1.0
Guo et al. [29]	$0.0045 \exp(900/T)$	0.9
Dworkin et al. [30]	0.078	0.078
Singh et al. [31]	$\begin{cases} 1 & \text{for } A_p \leq 0.012 \\ 0.2 & \text{for } A_p > 0.012 \end{cases}$	1.0
Singh et al. [31]	$0.02 + 0.8 \exp(-CA_p)^c$	0.71

^a Where μ_1 is the first size moment of the soot particle distribution, and a and b are fitted parameters and found to be $12.56 - 0.00563T$, and $-1.38 + 0.00068T$, respectively.

^b Where A_p is particle residence time.

^c Different values for C have been used for each of the flames studied.

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