



A model of particle nucleation in premixed ethylene flames

Andrea D'Anna^{a,*}, Mariano Sirignano^a, John Kent^b

^a *Dipartimento di Ingegneria Chimica, Università di Napoli "Federico II", Napoli, Italy*

^b *School of Aerospace, Mechanical & Mechatronic Engineering, University of Sydney, Australia*

ARTICLE INFO

Article history:

Received 8 February 2010

Received in revised form 12 April 2010

Accepted 29 April 2010

Available online 23 May 2010

Keywords:

Modelling

Combustion-formed particles

Particle size distribution functions

Particle internal structure

ABSTRACT

A detailed model of particle inception is proposed to delve into the physical structure and chemistry of combustion-formed particles. A sectional method is used, from a previously developed kinetic mechanism of particle formation with a double discretization of the particle phase in terms of C and H atom number. The present model also distinguishes between different particle structures based on their state of aggregation; single high molecular mass molecules, cluster of molecules and aggregates of clusters. The model predicts the mass of particles, hydrogen content and internal structure. It represents a first approach in following the chemical evolution and internal structure of the particles formed in flames, coupled with the main pyrolysis and oxidation of the fuel.

The model is tested in atmospheric premixed flat flames of ethylene and the effect of fuel equivalence ratio on particle morphology is analyzed. Molecular weight growth of aromatic compounds and the inception of particles are predicted. The morphology of the particles and the number of molecules in the clusters at particle inception are also indicated.

© 2010 The Combustion Institute. Published by Elsevier Inc. All rights reserved.

1. Introduction

The formation of nano-sized soot particles in combustion is receiving increasing attention. Combustion-formed nanoparticles are of particular concern for their health and environmental effects. They contribute significantly to the composition of atmospheric particulate and to the formation of secondary particles and are known to cause increased morbidity and mortality [1–5]. By contrast, engineered carbon-based nanoparticles of tailored composition and structures produced in combustion reactors are widely used in many practical applications including drug delivery, coating for photovoltaic cells, new nano-sized materials and they are playing a major role in today's science and technology [6]. In order to reduce or enhance the production of carbon-based nanoparticles in combustion reactors, it is important to gain insight into their formation and growth pathways as well as their morphology and internal structure.

In recent years, several experimental investigations have been conducted in order to understand the mechanism of particle nucleation and the internal structure of the particles in high temperature environments [7–9]. Morphological studies conducted on particles collected from flames have revealed that ordered and disordered carbons coexist in incipient soot particles. The order arises due to stacking of planar polycyclic aromatic hydrocarbons (PAHs) to form parallel atomic layers; the disordered part is due to the

presence of randomly oriented and/or non-planar PAHs [10]. The combustion environment in which the particles are formed determines the final concentration of the particles as well as the organization at atomic scale; low temperatures and short residence times in the flame favor the formation of particles with disordered structures; the higher temperatures and longer residence times favor the formation of ordered structures with wide regions containing parallel stacks of PAHs [7,8]. As a consequence it appears that PAH molecules have an important role as a soot precursor, and their chemical structure and the combustion environment in which they are formed may control the nature of the particles.

Many experimental studies have been performed to analyze the structure and the sizes of the PAHs formed from different fuels under different operating conditions, with the aim of filling the gap between gas-phase compounds and the first particle nuclei [11–26]. A number of detailed chemical mechanisms of PAH formation have been proposed to study PAH growth in flame environments [27–40]. Kinetic mechanisms are based on the reactions of the abundant gaseous species such as C_2H_2 and small aromatic compounds activated by H and OH radicals. Along with the chemical growth reactions, the simultaneously physical process of coagulation of PAHs to form particle nuclei is considered [27–29,36–43]. The presence of PAH stacks in experimental HR-TEM images of soot particles is proof of coagulation of PAHs [7,8,44].

Particle nuclei can continue to add molecules to increase their sizes or they can coagulate with other particles maintaining invariant total mass. Two different kinds of coagulation can be considered: coalescence and agglomeration. Coalescence occurs when a

* Corresponding author. Fax: +39 081 593 6936.

E-mail address: andrea.danna@unina.it (A. D'Anna).

molecule from the gas-phase or a small particle collides with a particle and the formed entity tends to reduce free surface to minimize free energy. This results in the inclusion of the colliding molecules or small particles in the larger ones. In larger particles, the timescale of the molecule or small particle inclusion into the particle is larger than the timescale of the coagulation process. In that case the colliding entities maintain their own structure and they aggregate to form agglomerate of particles [45–49].

Although the coagulation processes (coalescence and agglomeration) have been widely observed for large PAH molecules and for small particles, their rates and the exact pathway in which they occur are still debated [42,50]. The ability of PAHs to coagulate depends on dispersion forces. Planar pericondensed aromatic molecules have a high tendency to coagulate; the higher the molecular mass, i.e. the number of aromatic cycles in the molecule, the higher is the binding energy. Non-planar aromatic molecules show a different behavior. They exhibit lower binding energies also at high molecular mass because of the steric conformation of the molecules, which hinders the molecules from reaching an interaction distance. Therefore, the chemical structure of the PAHs and their sizes are controlling factors in determining the rate of particle inception and the internal structure of the incipient particles. The coagulation of planar pericondensed PAH may be responsible for the formation of ordered stacks of aromatics, whereas the coagulation of non-planar aromatics results in less ordered clusters.

Based on the above considerations, a detailed mechanism of particle inception is proposed here to delve into the physical structure and chemistry of combustion-formed particles. A sectional method is used; it is based on a previously developed kinetic mechanism of particle formation with a double discretization of the particle phase in terms of C and H atom number [43]. The present model also distinguishes between different particle structures based on their state of aggregation, i.e. single high molecular mass molecules, particles (clusters of molecules) and agglomerates of particles. This allows to follow not only the mass of particles, but also the hydrogen content and internal structure. The model is a first approach to follow the chemical evolution and internal structure of particles formed in flames, fully coupled with the main pyrolysis and oxidation of the fuel. The coupling between gas- and particle-phase is very important because of the role of abundant gaseous species such as C_2H_2 , aromatic compounds and small radicals such as H and OH in the nucleation and the chemical growth processes.

The model is tested in atmospheric premixed flat flames of ethylene at different equivalence ratios for which a large set of experimental data exists [51–54]. The effect of fuel equivalence ratio on particle morphology is also investigated.

2. Kinetic mechanism

2.1. Gas-phase reactions

Hydrocarbon oxidation and pyrolysis is modeled with a detailed kinetic mechanism built onto the GRI mechanism for C1 and C2 species [55]. The mechanism has been used to model several premixed flames at atmospheric pressure. It has shown reasonable ability to predict the structures of aliphatic and aromatic hydrocarbons in rich flames [35,56].

Fuel rich conditions promote molecular growth and hydrogen loss. In aliphatic fuel flames acetylene and methane are the most abundant, gaseous, unburned hydrocarbons and benzene is the first product of the molecular growth process. Benzene formation is considered to occur by the addition of n-C4 radicals to C_2H_2 and the self-combination of propargyl radicals [35]. The sequential addition of C_2H_2 to phenyl radical (HACA mechanism) [27–30] and the com-

bination of resonantly stabilized radicals, i.e. the combination of two cyclopentadienyl radicals and the combination of benzyl and propargyl radicals, first proposed as possible reaction routes by Marinov et al. [57] and Bohm et al. [58], are the pathways considered for the growth of aromatic cycles up to pyrene [30,35]. Starting from pyrene, all of the compounds with larger molecular masses are considered as lumped species. The gas-phase kinetic mechanism consists of 460 reactions involving 120 species. Details of the gas-phase kinetic mechanisms are reported elsewhere [35,56].

2.2. Lumped species reactions

As the molecular mass of the aromatic compounds increases a wide number of compounds are formed. Although it is almost impossible to follow each of these species, some classifications are possible. Two broad classes of aromatic molecules can be considered: aromatics in which only π -bonds among C atoms exist, named pericondensed aromatic hydrocarbons (PCAH) and aromatics having both σ - and π -bonds between C atoms consisting of incompletely-condensed oligomers of PCAH. Formation of PCAH is modeled by the H-Abstraction-Acetylene Addition mechanism [27–30]. The molecular growth process is initiated by an H atom loss and continues by addition of acetylene. There are a high number of sites where acetylene can be attached and so it is possible to hypothesize that each acetylene addition sequence forms a closed aromatic ring. Usually six-member ring structures are formed which lead to the formation of PCAH. The formation of a five-member ring is also possible as in the case of acenaphthylene-like compounds, but it can easily be converted into PCAHs as demonstrated by Frenklach and coworkers [59].

PCAHs with a fixed number of C atoms exist in a large number of isomers having different H atoms. The PCAHs having the lowest amount of H atoms are maximally condensed six-member ring structures. Their H/C ratio decreases to very low values as the molecular size increases; the largest of these compounds is a graphene sheet.

PCAHs which grow preferentially along one direction have a higher numbers of H atoms for fixed C atoms than the maximally condensed aromatics, i.e. those PCAHs which grow in both directions. The limit of the oblong structures is the series of acenes (growth only in one direction). The H/C ratio of these molecules decreases to values of the order of 0.5 as the molecular size increases. If only six-member ring structures constitute the aromatic species, the molecules are planar. When five-member rings are included in the molecule and are bordered by more than two adjacent edges a molecular distortion is induced and the molecule assumes a fair curvature.

When an aromatic compound, or its radical add to the radical site instead of acetylene, incompletely-condensed oligomers of aromatics are formed. The formation of an incompletely-condensed aromatic can occur either by H atom substitutions by a pericondensed structure, such as in the formation of bi-phenyl or bi-naphthyl, and by aromatic radical addition to non aromatic double bonds, such as those of pentagons condensed peripherally with hexagons (acenaphthylene type), and those of compounds like phenanthrene. The H/C ratio of the oligomers remains comparable to those of the aromatic molecules involved in the addition reactions and it remains quite unchanged as the molecular weight of the oligomers increases. Due to the less rigid structure of the σ -bond connecting the aromatic molecules, oligomers usually assume a non-planar structure. Both pericondensed and incompletely-condensed aromatics can grow indefinitely forming extremely large molecules. The molecular growth process competes with molecule oxidation by hydroxyl radical and O_2 molecules.

Whereas PCAH can only add acetylene or other gaseous hydrocarbons (if an aromatic molecule is added an incompletely-con-

Download English Version:

<https://daneshyari.com/en/article/166683>

Download Persian Version:

<https://daneshyari.com/article/166683>

[Daneshyari.com](https://daneshyari.com)