Abstract: Over the last two decades, our understanding of soot formation has evolved from an empirical, phenomenological description to an age of quantitative modeling for at least small fuel compounds. In this paper, we review the current state of knowledge of the fundamental sooting processes, including the chemistry of soot precursors, particle nucleation and mass/size growth. The discussion shows that though much progress has been made, critical gaps remain in many areas of our knowledge about the sooting process. We identify some of these gaps and propose the roles of certain aromatic pi radicals resulting from localized pi electron structures in particle nucleation and subsequent mass growth of nascent soot. The existence of these free radicals provides a rational explanation for the strong binding forces needed for forming initial clusters of polycyclic aromatic hydrocarbons. They may also explain a range of currently unexplained sooting phenomena, including the large amount of aliphatics observed in nascent soot formed in laminar premixed flames and the mass growth of soot in the absence of gas-phase H atoms. While the above suggestions are inspired, to an extent, by recent theoretical findings reported within the materials research community, this paper also demonstrates that the knowledge garnered through our longstanding interest in soot formation may well be carried over to flame synthesis of functional nanomaterials for clean and renewable energy applications. In particular, work on flame-synthesized thin films of nano-crystalline titania illustrates how our combustion knowledge might be useful for developing advanced yet inexpensive thin-film solar cells and chemical sensors for detecting gaseous air pollutants.
Formation of Nascent Soot and Other Condensed-Phase Materials in Flames

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Subtotal 3996

Submitted for an invited talk at the 33rd International Symposium on Combustion
and publication in the Proceedings of the Combustion Institute

Revised: September 20
Rebuttal
“Formation of Nascent Soot and Other Condensed-Phase Materials in Flames,” H. Wang

The author is grateful to reviewer 1 for carefully reading the manuscript. All of his/her comments are carefully addressed in the revised manuscript.

Reviewer 1:

The reviewer wrote:
This manuscript reviews the current status of the soot formation in flames and points to existing gaps in our understanding of the process. The author proposes that the existence of certain aromatic "pi" radicals may be responsible for the strong binding forces required for the formation of initial clusters and PAHs. Further the author argues that the knowledge generated through soot research would be more important for the nano-material synthesis for other energy applications. Although the manuscript generally written well, I am not satisfied with certain aspects of it. Specifically, issues listed below in items 1, 2, 5, and 10 should be considered by the author for a major revision of the manuscript.

My response: No response is required.

The reviewer wrote:
1. Throughout the manuscript, the author sometimes cites a large number of publications without much description. For example, on page 26, "...flame synthesis of titania has been studied extensively (e.g. [174, 175, 383-386]) with notable contributions from Pratsinis [19, 387-395]..". Unless a brief description of the contributions (and what gaps in our understanding they explain) of cited references is given, citing a large number of publications is not much help for the reader for understanding further the issue being discussed.

My response: I agree. The revised manuscript eliminated over 60 references that are not necessary. As the result, the total length of the paper is shortened by >1000 words.

The reviewer wrote:
2. Page 3, 2nd sentence of the bottom paragraph: the author boldly states that "...phenomenon is now understood at an almost quantitative level, at least for small model fuel compounds". However, in the rest of the manuscript, the discussions and arguments are in stark contradiction to this statement.

My response: A good point. In the revised paper, the statement is revised. It now reads as follows: “This exceedingly interesting combustion phenomenon is seemingly understood at a quantitative level, at least for small model fuel compounds; and as a field of combustion the science of soot may be considered to be mature. .”

The reviewer wrote:
3. Page 3, last complete sentence: "...fuel is injected in the liquid form" is a little bit vague. It might be better if it is stated as "...injected into the combustion chamber in the liquid form".

My response: Agree. The sentence has been revised.

The reviewer wrote:
4. Page 4, 10th line from the top: "...nucleation...is still illusive" should be "...nucleation... is still elusive".

My response: Done.

The reviewer wrote:
5. Page 5, last sentence of the second full paragraph: the author states that "almost all discussion is limited to studies in laminar premixed flames...". But, there are citations to a huge number of publications in which non-premixed systems have been studied. This is a very confusing situation for the reader. Either similarities and differences between soot mechanisms in premixed and non-premixed flames should be described along with the relevance of information from one to the other, or discussion should be limited to ONLY premixed flames.

My response: A good point again. The sentence in the revised manuscript now reads “This paper mostly focuses on the chemical kinetic aspects of soot formation in laminar premixed flames at or near atmospheric pressure, owing to author’s own research expertise, although many issues in high-pressure and/or diffusion flame settings are equally critical and intriguing in our overall understanding of the sooting chemistry and physics.”

The reviewer wrote:
6. Page 7, first sentence of Section 3.1: It would be more appropriate to cite the originator(s) of the HACA mechanism, in addition to those who championed it.

My response: The word “championed” is replaced by “pioneered”. To my knowledge, Michael Frenklach is the originator of the HACA mechanism. Indeed I could add my name onto the originators’ list, but I think that it’d be unfair to Michael.

The reviewer wrote:
7. Page 7, last sentence: I am not sure whether it is the right terminology to state that the H atom acts as the catalyst. It might be acceptable in everyday language, but I don’t think is is appropriate in scientific writing.

My response: This is about the only point I disagree with the reviewer. I did replace “catalyst” by “"catalyst"”

The reviewer wrote:
8. Pages 12 and 13, eqns. 3 and 4: These two equations are given without any reference to any source. Since their derivation is not in the manuscript, the reader should be referred to a source for these equations.

My response: The sentence describing the two equations now reads “With these assumptions, the approximate enthalpy and entropy of dimerization can be derived from statistical mechanical principles as:”

The reviewer wrote:
9. Acronyms should be defined when they first introduced. For example, HOMO, LUMO, UHF in page 15.

My response: Done.

The reviewer wrote:
10. Page 20, middle paragraph: The author discusses the influence if flame temperature on soot PSDF in premixed flames, then at the end of the paragraph, he cites several non-premixed flame studies to support his discussion.

My response: Agreed. Non-premixed flame discussion and references are removed.

The reviewer wrote:
11. Page 21, 2nd full paragraph. The statement related to "liquid-like" character of soot is quite strong. In view of the existence of potential alternative scenarios and explanations, the statement should be toned down (unless the author has absolute evidence).
My response: I do have strong evidence supporting the statement (as seen in Fig. 17). In the revised manuscript, the sentence is revised as

“In other words, these young particles are liquid-like rather than being carbonized and rigid, as will be discussed later.”

On p. 23, after Fig. 17 is introduced, one of the sentence is revised to read

“As it can be seen in the TEM image, the particles again spread on the substrate upon impact, forming a “sunny-side-up” structure or much like the interaction of molten wax droplet with a surface.”

The reviewer wrote:
12. Page 3, 9th line from the top. "Kennedy" is misspelled.

My response: Done.

The reviewer wrote:
13. Page 13, 4th line from the top. "Planck constant" should be "Planck’s constant".

My response: Done.

Reviewer # 2 recommends to accept the paper without changes.

Also, many comments by Professor Ronney in an unofficial review of the manuscript have been addressed in the revised manuscript.
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Submitted for an invited talk at the 33rd International Symposium on Combustion

and

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Revised: September 2010
Formation of Nascent Soot and Other Condensed-Phase Materials in Flames

Hai Wang

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Los Angeles, CA 90089, USA

Abstract

Over the last two decades, our understanding of soot formation has evolved from an empirical, phenomenological description to an age of quantitative modeling for at least small fuel compounds. In this paper, we review the current state of knowledge of the fundamental sooting processes, including the chemistry of soot precursors, particle nucleation and mass/size growth. The discussion shows that though much progress has been made, critical gaps remain in many areas of our knowledge about the sooting process. We identify some of these gaps and propose the roles of certain aromatic \( \pi \) radicals resulting from localized \( \pi \) electron structures in particle nucleation and subsequent mass growth of nascent soot. The existence of these free radicals provides a rational explanation for the strong binding forces needed for forming initial clusters of polycyclic aromatic hydrocarbons. They may also explain a range of currently unexplained sooting phenomena, including the large amount of aliphatics observed in nascent soot formed in laminar premixed flames and the mass growth of soot in the absence of gas-phase H atoms. While the above suggestions are inspired, to an extent, by recent theoretical findings reported within the materials research community, this paper also demonstrates that the knowledge garnered through our longstanding interest in soot formation may well be carried over to flame synthesis of functional nanomaterials for clean and renewable energy applications. In particular, work on flame-synthesized thin films of nano-crystalline titania illustrates how our combustion knowledge might be useful for developing advanced yet inexpensive thin-film solar cells and chemical sensors for detecting gaseous air pollutants.
1. Introduction

Formation of condensed-phase materials is ubiquitous in many flame phenomena. These materials are formed mostly as nanoparticles suspended in burned combustion gases. As a condensed-phase matter formed persistently in hydrocarbon combustion, soot found its use prehistorically as a pigment in cave paintings [1-3]. The oldest known tattoos, belonging to a Tyrolean iceman, were etched with soot [4]. Flame soot provided the black pigment for India ink—a Neolithic invention [5]. Today, the same material finds its use with versatility, including carbon black for automobile tires and a pigment in toners for laser printers. In some of the practical combustion systems, the formation of soot is critical as it facilitates radiative heat transfer [6, 7]. More recent applications include the use of soot or carbon nanoparticles as a cathode catalyst [8] in dye-sensitized solar cells [9, 10], and a catalyst support in direct methanol and other fuel cells [11].

Other condensed-phase materials form in flames often because of the presence of elements beyond the common constituents of gaseous hydrocarbon flames. As an example, metals or metal precursors can be present or added in unburned fuel-oxidizer mixtures to induce particle formation. Combustion as a method of material synthesis also has a rich history. Titania is the white pigment in paints; and silica is used for fiber optics applications. Both are produced almost exclusively by flame processes [12]. In recent years, new flame-synthesized materials and their applications are emerging at a rapid rate. Advances include specialty nanoparticles and the films produced from them for applications in catalysis [13-15], dye sensitized solar cells [16-18] and biomedical devices [19-21]. Palladium and palladium oxide nanoparticles grown in situ have shown to enable fuel ignition at low temperatures with potential applications in hypersonic combustion [22-24]. And many more exotic structures, including fullerenes, carbon nanotubes, graphenes, and metal-oxide nanowires, have been often prepared by flame methods (e.g., [25-34]).

Beyond their common origin in flames, flame soot formation and functional nanomaterial synthesis by flames share many common characteristics. Both involve the formation of condensed-phase materials from gases starting with vapor-phase nucleation, followed by mass and size growth through coalescence, coagulation, surface reactions and condensation of vapor species, and finally by aggregation into fractal structures, all of which occur over very short periods of time, typically a few milliseconds. Similar diagnostic and computational tools are employed to study the formation of both condensed-phase materials and the
long history of studies into soot formation research has yielded many useful insights into nanomaterial synthesis. Likewise, a number of combustion researchers have crisscrossed the disciplinary boundaries of combustion, nanomaterial synthesis and aerosol science; in doing so, they have made unique contributions in all these areas. Examples include Calcote’s work on carbide and nitride [35, 36], Frenklach’s work on diamond thin films and particles (e.g., [37-39]), silicon carbide [40, 41] and silicon nanoparticles [42], Harris’s work on diamond thin films [43, 44], Howard’s work on fullerenes and carbon nanotubes (e.g., [25, 34]), Roth’s work on various oxide nanoparticles [45, 46], Zachariah’s work on problems involving synthesis, characterization and fundamental theories of nanoparticles [47-49], and Kennedy’s work on yttrium and europium oxide nanoparticles and their applications as biosensors [50, 51].

Today’s scientific interest in soot formation, however, is largely unrelated to its material applications. In fact, much of the research over the last four decades has been directed towards mitigating air pollution problems that invariably result from the use of fossil fuels. It is well known that as a major contributor to anthropogenic aerosols, soot is detrimental to atmospheric visibility [52], global climate [53-61] and human health [62-67]. Soot has been fingered as a major player in global warming [61]. Evidence suggests that, as cloud condensation nuclei, soot particles participate in the formation of clouds and contrails [68-72]. As an effective light absorber, soot deposited on polar ice triggers its melting [60, 73] and may be responsible for as much as 94 % of Arctic warming [74].

The remarkable advances in the theory of soot formation have been reviewed periodically over the last fifty years [75-92] and many contemporary problems have been discussed in the proceedings of a recent workshop [93]. This exceedingly interesting combustion phenomenon is seemingly understood at a quantitative level, at least for small model fuel compounds; and as a field of combustion the science of soot may be considered to be mature. Yet because of the intricate nature, not to mention the large number of tightly coupled elementary processes involved, the science of soot formation will probably never have complete closure. In fact, we have learned that it probably will never be possible to completely mitigate soot formation in engines as long as the fuel is injected into the combustion chamber in the liquid form. Under this condition, the finite fluid-mechanic mixing rate causes the flame to invariably progress through fuel-lean and rich regions – and in those rich regions soot usually forms. Hence, the underlying problem becomes
largely a compromise of optimal combustion engine efficiency with minimal emission of particulates and other air pollutants.

Much of the work on soot formation has been driven by the need for predictive models of soot formation and oxidation arising from the principles of thermodynamics and reaction kinetics. When combined with computational fluid dynamics (CFD), a fundamental modeling approach is expected to lead to predictive design tools for the next-generation of efficient, clean-burning combustion engines [94]. Indeed there have been rapid advances in reaction models of real fuel combustion (e.g., [95-106]) and incorporation of soot formation models in CFD simulations [7, 107-115]. As these fields advance, there is a greater need to identify and fill in the gaps of current kinetic descriptions of soot formation. As will be discussed in this paper, the mechanism of soot nucleation (or particle inception) still remains elusive. We are still unable to predict the evolution of the chemical structure and composition of flame soot and to describe the gas-surface reactions at an elementary level comparable what that already accomplished in gas-phase combustion chemistry.

Beyond a predictive capability of soot formation, what is the future of soot research? On one level there is value in creating models as an integral part of engine design codes, but the largest impact perhaps will be to apply what we have learned about soot formation in flames to many different prospects for nanoparticle synthesis. Undoubtedly, that is where the greatest benefits of current knowledge will lie—not in incremental improvements in soot reduction but in the vast improvements in nanoparticle material synthesis, creating particles of value in energy, catalysis and yet unimagined fields.

The versatility of the flame synthesis method has been discussed in a number of review articles [14, 116-121]. Beyond carbon black, titania, and fused silica, flame methods for material synthesis have not been put to extensive use as chemical vapor deposition or Sol Gel methods have, even though the flame methods hold definitive economic advantages [120]. The delay in commercial flame synthesis methods lies in the difficulty of the materials research field to master the flame technique and conversely the difficulty of the combustion field to extend itself to device-level demonstration of flame-made materials. If the flame method is to see broadened uses in material synthesis, it must rely on demonstrations of its utility in constructing new, cheaper and better performing devices. Such applications will eventually lead to the formulation of fundamental
questions regarding the relationships of flame dynamics and kinetics, and the resulting material structure, properties, functionalities and performance.

Another aspect of particle research is the recognition that different vapor-phase materials have different propensity towards nucleating into particles under a given condition. Many inorganic vapors (e.g., metal oxides) have exceedingly small vapor pressure even at high temperatures or low pressures. Hence, they would nucleate out of the gas phase first in sooting flames, leading to induced soot nucleation and mass growth. For example, the addition of ferrocene in flames can lead to enhanced soot production because of the growth of carbon on iron oxide nanoparticles [122-124]. The role of silicon carbide in inducing formation of carbon in interstellar media has also been discussed by Caldwell et al. [41]. At present, the role of metal impurity in the hydrocarbon fuels and engine lubricants in soot formation remains poorly characterized.

The discussion in this paper however focuses on homogeneously nucleated soot from pure hydrocarbon flames. It highlights several critical gaps in the understanding of the early stage of soot formation. The paper will also try to convey a hope that sustained research intensity into the phenomena of condensed matter formation in flames will have to broaden its research scope to include nanomaterial synthesis and applications. The paper is organized as follows. First, the thermodynamic driving forces for condensed-phase nanomaterial formation in high-temperature flames are revisited. The discussion attempts to delineate the somewhat different thermodynamic origins of soot and metal oxide formation in flames. The problem of soot nucleation and mass/size growth is then discussed both theoretically and by examining recent experimental observations. The paper aims to fill in a critical gap between the experimental observation and mechanistic description of soot nucleation and mass growth by proposing the existence of \( \pi \)-radical aromatics in the gas phase and on nascent soot surfaces. It will be shown that this hypothesis may explain some of the experimental observations that cannot be accounted for by existing mechanisms and models of soot formation. The \( \pi \)-radical character may also explain how soot acts as cloud condensation nuclei and the wetting and water uptake by soot in combustion exhaust.

The last part of the paper will demonstrate the synthesis and characterization of nanophase titania crystals and mesoporous films for two energy-related applications: dye sensitized solar cells and chemical sensing of combustion pollutants. The flame synthesis technique utilizes well-controlled laboratory flames
and particle characterization techniques, both of which were realized through studies into soot formation. The purpose in this part of the paper is not to provide a detailed survey about flame synthesis of condensed materials, but to show how soot and basic flame theory research can yield useful yet unintended results for material synthesis with broad applications in energy conversion. This paper focuses mostly on the chemical kinetic aspects of soot formation in laminar premixed flames at or near atmospheric pressure, owing to author’s own research expertise, although many issues in high-pressure and/or diffusion flame settings are equally critical and intriguing in our overall understanding of the sooting chemistry and physics.

2. Thermodynamics

A survey of the literature often leaves one with the impression that as the first step in soot nucleation, the formation of the first aromatic ring is the most important bottleneck to soot formation. This is far from true. There are at least a handful of rate limiting steps during the formation of soot precursors and soot itself [125]. To understand why this is so, let us first examine the thermodynamics of the process. Formation of condensed phase materials or ordered structures in flames is a seemingly improbable event, because such flames are dominated by rapidly increasing entropy tending towards disorder. Yet these materials do form, and in many cases, they do so persistently. The driving force is either enthalpy release from chemical bond formation or entropy increase because of the release of gas-phase species that accompanies particle formation. Carbon forms endothermically from saturated alkanes, releasing H₂ which, in turn, causes the entropy increase that ultimately drives particle formation. In contrast, metal-oxide particles form in flames largely because of reaction exothermicity and the strong bonding between metal atoms and oxygen. The formation of condensed-phase metal oxide can be limited by entropy effects, especially when the formation of highly order structures is not accompanied by releasing molecules into the gas phase. Other examples include the formation of silicon nitride and carbide from the reactions of silane with ammonia and acetylene, respectively, which are driven or limited by both reaction exothermicity and entropy effects.

Condensed-phase material formation from gaseous species is often kinetically controlled and made more complex if, as in soot formation, the process is entropy-driven. Consider carbon formation from propane pyrolysis. The top panel of Fig. 1 shows the enthalpy and entropy contributions to the Gibbs free energy in
each step of a possible reaction sequence. The formation of acetylene as an intermediate of molecular growth is endothermic, but its formation is accompanied with a drastic increase in the system entropy because of dehydrogenation, which leads to an overall reduction in Gibbs free energy—a phenomenon directly responsible for acetylene being the dominant hydrocarbon species in fuel-rich combustion [76, 126, 127]. On the other hand, the formation of benzene from acetylene is exothermic at the expense of a reduced entropy. Molecular weight growth from benzene to polycyclic aromatic hydrocarbons (PAHs) and solid carbon is characterized by a mild but gradual reduction in Gibbs free energy. The overall sooting process is neither exceedingly exothermic nor does it release entropy significantly. It is for this reason that the kinetics for the formation of PAHs and subsequent condensed-phase soot particles can be highly reversible.

In contrast, the energetics of metal oxide formation in flames are often simpler because the formation of these condensed-phase materials is usually loosely coupled to the flame chemistry owing to small concentrations of the metal precursors typically used in a synthesis process. Yet the formation of the condensed-phase oxide materials is usually highly exothermic. Taking titania as an example, the bottom panel of Fig. 1 shows its formation from titanium vapor. For a hydrocarbon flame doped with a small amount of a metal precursor compound, e.g., titanium tetrachloride or titanium tetraisopropoxide, the heat release from the flame facilitates precursor dissociation. Hence, this precursor dissociation endothermicity is usually inconsequential relative to the high exothermicity of the flame. The oxygen reacts with titanium to form vapor-phase titanium oxide, which further condenses owing to its small saturation vapor pressure. This process is highly favorable from the standpoint of enthalpy release, with exothermicity > 330 kcal/mol-TiO$_2$ at 1600 K. Unlike carbon formation, titania formation in flames is accompanied by an entropy reduction, owing to bond formation and crystallization from gas-phase species. Yet, the overall Gibbs function still progresses downhill with an overall change as large as 78 kcal/mol at 1600 K (five times that of carbon formation from acetylene). This rather large thermodynamic driving force causes titania to form with almost no kinetic complications. In fact, this analysis can be applied to a large range of flame synthesized materials with the proper precursor.
3. Nascent Soot Formation

3.1 Aromatics Formation

3.1.1 The Hydrogen-Abstraction—Carbon Addition Mechanism

The much celebrated hydrogen-abstraction—carbon-addition (HACA) mechanism, pioneered by Frenklach [89, 128-132], captures the essence of the thermodynamic and kinetic requirements for the sooting process. Soot is a ubiquitous byproduct of fuel-rich flames above a certain fuel-to-oxidizer threshold. Hence, it is a logical first postulate that the kinetic processes that drive the flame phenomenon must be related intimately to the sooting process. Factors important to both flame chemistry and soot formation are: acetylene—the most abundant hydrocarbon species—as the molecular building block, the H atom—the driving force behind chain branching and flame propagation—as the “catalyst”, and the high temperature that facilitates fast kinetics, but at the same time limits the molecular mass growth because of fragmentation of the precursor and possibly soot itself.

As precursors to soot, polycyclic aromatic hydrocarbons (PAHs) must survive from fragmentation at high temperatures. The well known Stein’s stabilomers [133] are critical to this survival [128, 129]. The most important members of the stabilomer class found in soot particles [134, 135] are pericondensed PAHs, consisting of six-membered benzenoid rings. Examples include naphthalene, phenanthrene, pyrene, and coronene. Because of their stability, the parent PAHs must be activated through H-abstraction to produce an aryl radical which in turn, allow it to react with gaseous hydrocarbon species like acetylene. All of these reactions have appreciable energy barriers and also exhibit some extent of reversibility. Hence, temperature plays a critical role in not only the rate of molecular growth, but also in the fragmentation rate.

Figure 2 shows the HACA mechanism depicted on the Gibbs free energy surface. For convenience, we chose a hypothetical mixture containing 1/7 moles of benzene, 5/7 moles of acetylene and 1/7 moles of H atom at a constant temperature of 1800 K. Molecular growth into PAHs can be seen to proceed on a rather bumpy free energy surface with a high degree of reversibility [125]. This reversibility causes aromatics formation to be highly kinetically controlled. Hence, predicting the concentrations of aromatic compounds in flames requires a rather precise knowledge about the underlying mechanism and kinetics at almost every step of the reaction sequence.
A notable advance in the kinetic development of aromatics chemistry came from the work of Dean [136] who demonstrated the importance of chemically activated reactions in combustion kinetics. This led to the work of Westmoreland et al. [137] who elucidated a number of critical chemically activated pathways to the first aromatic ring formation. Further work by Wang and Frenklach examined the thermochemical [138] and transport properties of aromatics [139], and the kinetics of chemically activated reactions for aromatics [140]. This work led to the development of a kinetic model for PAH formation [125] (which was later improved, e.g., [141]) and many variations used for the detailed modeling of soot formation.

3.1.2 Pathways Beyond the HACA Mechanism

Earlier modeling studies show that the rate of PAH formation is highly sensitive to flame temperature and more importantly, to a multitude of chemical reactions (e.g., [125]). To illustrate this point, we present in Figure 3 a sensitivity spectrum computed for pyrene production in a 90 Torr burner stabilized acetylene flame. The formation of pyrene is seen to be sensitive to a large range of elementary reactions, including those involved in the formation of the first aromatic ring, reactions governing the main flame chemistry, and aromatic ring-growth reactions. The wide spectrum of sensitivity indicates that the production of pyrene is influenced by multiple bottlenecks often because of the kinetic reversibility in the HACA mechanism. This high degree of reversibility naturally opens the HACA mechanism up to competition from other reaction pathways. In particular, it is widely accepted that resonantly stabilized free-radical species play a critical role in aromatics formation and molecular weight growth. These free radicals include propargyl, benzyl, and cyclopentadienyl. Fahr and Stein [142] suggested that the combination of propargyl radicals could lead to benzene formation. Miller and Melius [143] showed that in flames the first aromatic ring is mostly likely formed by the self-reaction of propargyl radicals. Subsequent theoretical studies by Klippenstein and Miller, spanning almost two decades [144-146], showed that the self-reaction of propargyl radicals can form a large number of rovibrationally excited complexes on the rather complicated potential energy surface shown in Fig. 4. These complexes undergo mutual isomerization eventually forming benzene through collisional stabilization or phenyl + H through C-H fission. Theoretical treatment of these reactions proves to be rather demanding. For example, the exit channel, involving the reverse of H addition to phenyl, is barrierless, and
requires use of variable reaction coordinate transition state theory [146]—an approach mastered by only a handful of experts.

Beyond the HACA mechanism and propargyl recombination, there have been a large number of reaction pathways proposed over the last decade. For example, a recent study of cyclohexane flames by Westmoreland and coworkers [147] suggests that benzene may be produced from stepwise dehydrogenation of cyclohexane, a compound and its derivatives found in many real fuels. Koshi and coworkers [148] suggested that a phenyl addition/cyclolization pathway is efficient for PAH formation and growth in benzene pyrolysis. Other recent examples include the reactions of fulvenallene with acetylene [149], cyclopentadienyl with acetylene [150, 151], and cyclopentadienyl with itself to produce naphthalene [152, 153].

3.1.3 Challenges in Accurate Prediction of Aromatics Formation

Despite all the recent advances, fundamental chemical kinetics of aromatics are in need of further research. Challenges remain especially in the context of soot precursor formation from real fuel combustion. While the HACA mechanism is likely to be the backbone in models of PAH formation, other pathways and their varying sensitivity to the fuel composition raises the question whether there can be a quantitative closure to this problem. This situation is quite unlike the kinetic knowledge needed to predict basic flame properties, such as the laminar flame speed or ignition delay, which are usually governed by just a handful number of elementary reactions common to all hydrocarbon fuels. It is not even known at present whether the number of pathways to PAHs and soot in real-fuel combustion can be treated as finite, given the large variability in fuel composition. What is troublesome additionally is the fact that the rate of PAH formation can be highly sensitive to both the main flame chemistry and the local gas temperature. An accurate prediction of PAH formation may require a more precise knowledge of flame chemistry than is currently available.

Some of the recent experimental advances will undoubtedly be instrumental in addressing the difficulties identified above. Notably, the synchrotron photoionization technique in conjunction with molecular beam mass spectrometry has proven itself to be a powerful tool for probing fuel-rich flame chemistry [147, 154-166]. Even though the molecular beam probe may perturb the flame [167], this technique allows for high molecular weight species and isomers to be probed rather quickly and accurately. As an example, Fig. 5
shows a sample series of photoionization mass spectra of flame species in the mass-to-charge ratio of 70 to 126 amu probed by Qi and coworkers [166] for burner-stabilized flames burning benzene, toluene, styrene, ethylbenzene, o-, m-, and p-xylene. Unfortunately, the data are generated at a rate faster than can be digested by theoretical and modeling studies. To better utilize these data, efficient theoretical methods beyond the approach of one-reaction-at-a-time must be developed and mastered by more than just a handful of experts.

3.2 Nucleation (Particle Inception)

3.2.1 The Three Pathways

Three conceptual pathways may be postulated for soot nucleation. As shown in Fig. 6, path A is depicted by the growth of “2-dimensional” PAHs into curved, fullerene-like structures (e.g., [85]); paths B and C involve the physical coalescence of moderate-sized PAHs into stacked clusters [131, 132, 168, 169] and the reaction or chemical coalescence of PAHs into crosslinked 3-dimensional structures [170-174], respectively. The last two paths have been discussed recently in some detail by D’Anna [92, 175]. It is known that within the HACA framework path A is too slow to account for rates observed for soot nucleation [89, 131, 132]. Ample experimental evidence shows that in premixed sooting flames the peak concentrations of PAHs drops by roughly one order of magnitude with the increment of two pericondensed rings. This dependency is illustrated in the bottom panel of Fig. 7 using data observed in several low-pressure burner-stabilized flames [159, 164, 176]. If the mole fraction of benzene is ~$10^{-3}$, those of pyrene and coronene would be roughly $10^{-5}$ and $10^{-7}$, respectively, which are of the same orders of magnitude as the number densities of soot nuclei ($10^{11}$-$10^{13}$ cm$^{-3}$) (see, e.g., [77, 177]). Hence, soot nucleation is likely to involve moderately sized PAHs [131, 132, 168, 178, 179].

There is abundant, but mostly indirect experimental evidence supporting PAH dimerization (paths B and C) as the initial nucleation step. Examples include the observation of the bimodality in the size distribution functions of nascent soot particles in premixed flames [180, 181]. In the presence of a persistent nucleation source, the kinetics process may be described by

$$\frac{dn_i}{dt} = R_0 - n_i \sum_{j=1}^{\infty} \bar{c}_{i,j} n_j,$$  \hspace{1cm} (1)
\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \varepsilon_{j,i-j} \beta_{j,i-j} n_j n_{i-j} - n_i \sum_{j=1}^{\infty} \varepsilon_{i,j} \beta_{i,j} n_j \quad (i = 2, 3, \ldots, \infty)
\]

where \(n_i\) is the number density of particle containing \(i\) number of monomers, \(t\) is the time, \(R_0\) is the rate for the formation of the “first” particle, and \(\beta_{ij}\) is the coagulation coefficient. For PAH dimerization as the initial nucleation mechanism \(R_0\) is second-order in the monomer concentration, \(R_0 = \alpha \varepsilon_0 \beta_0 C_0(t)^2\), where \(\varepsilon_0\) and \(\beta_0\) are respectively the van der Waals enhancement factor of PAH collision and the rate constant of monomer collision, \(C_0(t)\) is the concentration of the monomer, and \(\alpha\) is a parameter (0 < \(\alpha\) ≤ 1) which accounts for the reversibility. The evolution of the size distribution may be solved to show that in the presence of a persistent nucleation source the distribution function is decidedly bimodal (Fig. 8) and independent of the value chosen for \(\alpha\). If path A is dominant, nucleation kinetics is first order in monomer concentration and distribution functions with first order \(R_0\) would quickly evolve into a unimodal distribution [180]. Hence, paths B and C leave kinetic footprints that allow them to be uniquely differentiated from path A.

Experimentally, the particle size distribution functions (PSDFs) probed by a scanning mobility particle sizer indeed demonstrate a persistent bimodality, as shown in Fig. 9 for an atmospheric-pressure ethylene-oxygen-argon flame [182]. Similar observations have been made in many other flames (see, e.g., [183-191]) and also in a jet-stirred reactor [192, 193]. For flames with nucleation intensity gradually reduced as a function of distance from the main flame, a situation encountered in high-temperature flames in which PAH fragmentation is predominant in post flames, the bimodality was observed to evolve into an apparent unimodal distribution [183], but this unimodality is the result of monomer depletion, not an indication that the kinetics of particle nucleation becomes first order towards high flame temperatures. More recent studies have shown that by reducing the observable particle size from 3 nm to 1 nm, nascent soot formed in almost all flames studied are bimodal [185]. Additional experimental evidence for PAH coalescence comes from the laser ionization mass spectrometric study of Grotheer and coworkers [194]. As shown in Fig. 10, the masses of molecular fragments ablated from soot in a 100-Torr acetylene oxygen flame exhibit an interesting periodicity with frequency around 500 amu. The distinctive feature of these fragments suggests that PAH stacks are indeed the building block of nascent soot.
Theoretical aspects of PAH dimerization as the initial step to particle nucleation (path B) were recently discussed by Herdman and Miller [169]. They proposed that the electrostatic and dispersive forces between a pair of moderate sized PAHs may be strong enough to allow binding to occur even at the flame temperature (> ~1600 K). Not yet considered is the entropy resistance to binding. The macroscopic evidence illustrating this resistance is simply the boiling point or sublimation temperature. For Stein’s stabilomers as large as coronene, the boiling/sublimation temperatures are well below 1000 K (see, Fig. 7). Hence, one would expect that at the flame temperature condensed-phase PAHs should evaporate, rather than condense into particles.

Statistical mechanical analysis supports this view. Consider the dimerization of coronene, \( A_7 + A_7 \rightleftharpoons (A_7)_2 \). The process creates 6 new vibrational modes in the dimer. Let the frequencies of these modes be \( \nu_i \) (\( i = 1, \ldots, 6 \)). The rest of the vibrational frequencies in the dimer may be approximated to be equal to those in the monomers—an adequate assumption for nonbonding interactions. In addition, we approximate the rotational constants of the dimer to be one half of that of the monomer. With these assumptions, the approximate enthalpy and entropy of dimerization can be derived from statistical mechanical principles [195] as:

\[
\Delta H^\circ \approx -E_0 + \sum_{i=1}^{6} \left\{ 1 + \frac{1}{\exp \left[ \frac{\nu_i}{k_B T} \right] - 1} \right\} b \nu_i - 4 k_B T \quad (3)
\]

\[
\frac{\Delta S^\circ}{R_c} \approx \ln \left[ \frac{2B}{\mu} \right]^{1/2} \frac{b^3 \rho^0}{\pi^2 (e k_B T)^4} \frac{\sigma_1^2}{\sigma_2} + \sum_{i=1}^{6} \left[ \frac{\nu_i}{k_B T} \ln \left( \frac{1 - e^{-\nu_i/k_B T}}{e^{\nu_i/k_B T} - 1} \right) \right] \quad (4)
\]

where \( E_0 \) is the binding energy (without zero-point energy correction), \( B \) is the geometric mean of the rotational constants of the monomer, \( \sigma_1 \) and \( \sigma_2 \) are the symmetry numbers of the monomer and dimer, respectively, \( \mu \) is the monomer mass, \( b \) is Planck’s constant, and \( \rho^0 \) is the standard pressure of 1 atm. The rotational constant may be correlated empirically with the molecular weight \( MW' \) (amu) as \( \bar{B}(\text{cm}^{-1}) \approx 1510 \times MW'^{-2.125} \) using values from ref. [196]. Figure 11a shows the Gibbs free energy change for coronene dimerization as a function of temperature, where \( \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \). Here we chose a mean value of \( \bar{\nu} = 200 \text{ cm}^{-1} \) for the 6 vibrational frequencies in eqs 3 and 4, while recognizing that choosing such a
small frequency value overestimates the entropy of the dimer, and thus favoring dimerization. For example, with $\nu = 500 \text{ cm}^{-1}$, $\Delta G^\ddagger$ becomes appreciably more positive at the same binding energy, as shown in Fig. 11a. Additionally, we choose $\sigma_2 = 1$, which again favors dimerization by eliminating any symmetry in the dimer.

The self-binding energy is $E_0 = 24.5 \text{ kcal/mol}$ for a pair of coronene monomers [169]. Although this energy value may seem to be large enough, the entropy effect in fact does not allow the dimer to survive without fragmentation at combustion temperatures ($>1500 \text{ K}$). For example, at 1600 K the equilibrium constant of dimerization $(K_p = P_d/X_d^2)$ is only $4 \times 10^{-24} \text{ atm}^{-1}$. In fact, the temperature for $K_p$ to cross over the characteristic value of $10^{-6} \text{ atm}^{-1}$ is rather low† and equal to 725 K. Using $K_p \sim 10^{-6} \text{ atm}^{-1}$ as the critical condition for dimerization, the binding energy of a pair of coronene must be at least 60 kcal/mol to allow for sticking at or above 1500 K. According to Herdman and Miller [169], the binding energies of ovalene and circumcoronene are 35 and 62 kcal/mol, respectively, but even they are not strong enough to push the equilibrium constant above $10^{-6} \text{ atm}^{-1}$ at combustion temperatures. This is because an increase in mass $m$ and a decrease in the rotational constant $\tilde{B}$ cause the entropy of dimerization to decrease further. Hence, an increase in the binding energy is offset by a decrease in the entropy in the dimer. As shown in Fig. 11b, dimerization of even circumcoronene is difficult above 1335 K. Taking the binding energy for homo-molecular pairs in the limit of infinite size, 1.2 kcal per mole of C atom [169, 197, 198], we found that the monomer size must be at least C100 for dimerization to be possible at 2000 K.

The above discussion is of course subject to the assumption that dimerization is a phenomenon governed by equilibrium kinetics. To understand the non-equilibrium dynamics of PAH collision, Schuetz and Frenklach [179] carried out molecular dynamics simulation. Their results demonstrate that the collision of a pair of PAH molecules can produce a long lived, rovibrationally excited dimer. The transient binding is facilitated by the excitation of internal rotation, resulting in a dimer with lifetime much longer than the collision time scale [179, 199]. Hence, the dimer behaves as if it is a gas-phase species open to reactions with, for example, the H atom, which allows for covalent bond formation across the two PAH molecules. This

† The characteristic $K_p$ value may be estimated by assuming the partial pressures of the monomer and dimer to be equal and the partial pressure of the monomer is $10^{-6} \text{ atm}$, which is typical for atmospheric-pressure sooting flames.
hypothesis is certainly plausible, but it remains unclear whether a dimer would survive its multiple collisions with gas molecules within their lifetime, keeping in mind that the H atoms are in concentrations substantially lower than many other gas molecules. Clustering of several homo- and hetero-molecular PAHs have also been examined by Violi and coworkers using molecular dynamics [200], but again the clustering process is contingent upon the initial clusters surviving collision with flame gas molecules.

An alternative hypothesis is that the initial particles contain aromatic structures joined by aliphatic linkages (path C). These structures can be produced via a “chemical” coalescence mechanism [170-174] involving reactions between aromatic molecules with an aryl radical. This mechanism is plausible in regions close to the main flame zone where H atoms are abundant, allowing aryl radicals to be generated through the H-abstraction reactions. But it cannot explain the persistent nucleation of soot well into the post flame zone [180, 183], where the H atom concentration is too low to initiate such reactions. The above arguments leave us with the notion that the soot nuclei may be formed through a mechanism which is not yet known. This mechanism is likely to involve moderate-sized PAH-PAH interactions, but such interactions must be as strong as those seen in typical covalent bonding.

3.2.2 The Role of Aromatic π Radicals

A series of recent theoretical materials studies predicted that many aromatic molecules have radical or diradical characteristics resulting from localized π-electron states. These studies originated from interests in polyacene as a material for a new generation of organic light emitting diodes and organic semiconductors and capacitors. If these predictions are true, they may hold the key to a satisfactory explanation of soot nucleation and some of the observations concerning soot mass growth, a topic to be discussed later. These studies show that, starting from anthracene, polyacenes with an increasing length show a vanishing HOMO-LUMO gap,* or a diminishing bandgap [201-203]. Furthermore, ground-state polyacenes with more than 5 or 6 rings are open-shell singlet diradicals [204-210] due to a disjoint diradical with partially occupied orbitals [205]. These studies are not without controversy. In a very recent paper, Haigató et al. [211] argued that the

---

* Energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital.
ground-state polyacenes are close-shell singlets, but also that the adiabatic $S_0$-$T_1$ excitation energy is small (17 and 13 kcal/mol for hexacene and heptacene, respectively). This small $S_0$-$T_1$ energy splitting suggests that triplet polyacene diradicals can form at high temperatures through vibrational excitation if intersystem crossing is allowed. The relatively high reactivity of central-ring carbon atoms in anthracene, pentacene and tetracene have also been well documented [212-218].

Another series of studies on PAHs shed an even more interesting light on the problem. It was predicted almost 20 years ago that the zigzag edges of graphene have localized $\pi$-electronic states [219, 220] and can contain significant radical characteristics. The predictions have sparked intense interests in tailored synthesis of nanographenes for nonlinear optics applications [221, 222], but they have not received enough attention in soot research. More recent studies show that graphenes with zigzag edges have an open-shell singlet ground state [223, 224]. Finite-sized graphenes are predicted to have the same radical [225-231] or even multiradical characteristics [232]. Consider a generic PAH structure given in Fig. 12. PAH(1,i) with $i=1, 2$ and 3 represents benzene, naphthalene, anthracene, respectively; and PAH(3,1) is phenanthrene. In this figure, the value of $y$ was determined from the occupation numbers of the HOMO and LUMO of unrestricted Hartree-Fock (UHF) natural orbitals and represents the diradical characteristic calculated by Nagai et al. [232]. The value ranges from 0 for closed shell singlet to 1 for a singlet diradical. As seen, PAH(4,1) (butacene) and PAH(2,3) (perylene) start to show some radical characteristics. PAH(3,3) has a significant radical character and PAH(4,3) is almost a pure diradical localized at the zigzag edges. Additional studies suggested that the diradical characteristics can be induced or promoted by functional groups. For example, bis(pyren-4-yl)ethyne, i.e., two pyrene rings bound by ethynyl, $-C\equiv C-$, also exhibited a radical characteristic similar to butacene [222]. Scanning tunneling microscopy/spectroscopy evidence appears to support the view that the electronic states for zigzag-edged graphenes are localized [233, 234]. In particular, armchair edges are generally defect free, whereas zigzag edges tend to be short and defective, and hence more reactive compared to armchair edges [221].

These $\pi$ radicals are the obvious candidates for significantly enhanced bindings in PAH clustering. Perylene can form from the reaction of a naphthyl radical with naphthalene. Likewise, PAH(3,3) can form from a pair of anthracene. The fact that these species are barely detected in flames could mean that they bind
immediately with other species upon formation. Because the radical characteristics originate from localized π-electrons, it may be speculated that these aromatic molecules can form bonds with any aromatics through π-electron interactions over a stacked geometry with strength similar to that in a covalent C-C σ bond. This mechanism would also explain why PAHs form stacks, whereas T-shaped dimer configurations are predicted to be more stable than stacked configurations for benzene and coronene (see, e.g., [235]). What remains unknown, yet critical to this hypothesis, is the binding energies of π radical bearing aromatic molecules with other PAHs. Other critical questions include whether the π radical characteristics are retained and can propagate over a stacked structure, as this would clearly enhance the binding over many PAH layers.

3.3 Mass/Size Growth, Chemical Composition and Morphology

3.3.1 The Current Understanding

The existence of π radical PAHs may also explain some of the recent and unexpected observations of soot mass growth made in premixed burner-stabilized flames. As a background, it is the current understanding that acetylene is the dominant mass growth species [76, 77, 236]. The basis of today’s modeling science for soot mass growth is formed from the work of Harris who determined the empirical rate constant of the acetylene-soot surface reaction [126, 127, 237], and more importantly the HACA mechanism of Frenklach and coworkers [89, 131, 132] in which the surface reaction rates are described at a fundamental level. The HACA mechanism describes the soot surface as composed of aromatic basal planes and edges sites. Mass growth on soot surface requires H-abstraction to form an aryl radical site, followed by acetylene attack in a manner similar to the gas-phase mechanism. Excluding soot oxidation, we have

\[
S_{-H} + H^\bullet \leftrightarrow S^\bullet + H_2 \tag{5}
\]

\[
S^\bullet + H^\bullet \rightarrow S_{-H} \tag{6}
\]

\[
S^\bullet + C_2H_2 \rightarrow S_{\mu-2-H} + H^\bullet \tag{7}
\]
In the above reactions, \( S_i \) represents an edge C atom on the surface of a particle containing \( i \) number of C atoms. Additionally, reactions or condensation of PAHs onto soot surfaces also contribute to soot mass, and the relative contributions appear to be dependent on the flame condition \([89, 131, 132]\).

A steady-state analysis of reactions 5 through 7 yields the surface radical site density as:

\[
[S_i \cdot] \approx \frac{k_{5j} [H \cdot]}{k_{5k} [H_2] + k_{6} [H \cdot] + k_{7} [C_2H_2]} [S_i-H] ,
\]

where \( k \)'s are the rate constants. The mole fractions of \( H_2 \) and \( C_2H_2 \) are generally around 0.1 and 0.05 respectively in the post flame region of typical sooting flames (see, for example, \([137, 176, 177]\)). For \( 1600 \leq T \leq 2200 \text{ K}, \frac{k_{5k}}{k_{5j}} \sim 60, 10 \leq \frac{k_{6}}{k_{5j}} \leq 100 \) and \( k_{7}/k_{5j} \sim 1 \) \([125, 140]\). Since \( [H_2] \gg [C_2H_2] \gg [H \cdot] \), we find:

\[
[S_i \cdot] \approx \frac{k_{5j}}{k_{5k}} [H \cdot] [S_i-H] .
\]

In other words, the surface radical site density is governed by the equilibrium constant of reaction 5 and by the availability of the H atom in the flame. The surface growth rate due to acetylene addition on the radical site is thus proportional to \([H \cdot]:

\[
\omega \left( \frac{\text{mol C-atom}}{\text{cm}^3 \text{s}} \right) \approx 2k_{7} \frac{k_{5j}}{k_{5k}} [H \cdot] [S_i-H] [C_2H_2] .
\]

It is well understood that while the soot mass is determined by surface reactions, the ultimate size of soot particles is governed by simultaneous particle-particle coagulation \([131]\). Transmission electron microscopy (TEM) studies of mature soot show multiple nuclei centers spaced \( \sim 5 \) to 10 nm apart within a primary particle (see, e.g., \([238, 239]\)). Primary soot particles are generally spherical because of the combined effect of surface growth and coagulation \([240, 241]\). Coagulation immediately after nucleation occurs predominantly between a pair of large and small particles because their collision frequencies are enhanced by the large cross section area of the former and the high velocities of the latter. This coagulation process forms primary particles with slightly aggregated structures (\( \text{cf}, \) the upper panels of Fig. 13). Meanwhile, surface reactions act
on these aggregated structures, “smooth” the surface and produce spherical or nearly spherical particles (the lower panels of Fig. 13). The small particles, referred to as the collector particles by Frenklach and coworkers [240-242], are essentially those that make up the small particle tails seen in Fig. 9.

3.3.2 Recent Developments in Experimental Methods

The mechanistic understanding of soot mass growth discussed above have inspired the development of a range of new experimental techniques over the last decade, allowing the mechanisms to be examined at much higher resolutions than previously possible. For example, small angle x-ray scattering (SAXS) [243-245] and small angle neutron scattering (SANS) [246] techniques have been utilized which have an advantage over light extinction and scattering techniques in that they do not require a precise knowledge of the complex refractive index of soot material in data interpretation. A variety of advanced aerosol experimental techniques have been utilized to probe soot surface properties, oxidation and reactions [247-250]. In this paper the discussion is focused primarily on findings made with inserted probes connected to mobility particle sizing devices (see, e.g., [180-189, 192, 251-260]). The technique maps the evolution of the size distribution of nascent soot particles and particles as small as 1.6 nm can be detected [185, 258]. The same technique has been applied to the analysis of metal oxide and other nanomaterial formed in flames [256, 261-263].

In general, the probe sampling technique utilizes a tubular probe crossing the flame. A gas sample from the flame zone is continuously drawn through a pin hole on the side of the probe that is in turn, delivered to a scanning mobility sizer by a carrier gas for particle sizing and counting. The technique has several limitations and requires some care in experimentation and data interpretation. For example, the PSDF could be perturbed by particle-particle coagulation in the probe. This problem has been resolved with the use of large ratios of dilution of the gas sample by a carrier gas [181, 187]. Introducing a finite-size probe into the flame inevitably disturbs the local gas temperature and perhaps more importantly, the flow field, leading to local flow stagnation. One way to handle this problem is to use the probe as the stagnation surface in a burner stabilized flame [182], so that its impact on the flow field and temperature may be quantified numerically using an axial symmetric stagnation flow code (e.g., OPPDIF [264, 265]). Figure 9 shows snap shots of the gas temperature profiles and PSDFs for a variety of burner-to-probe separations. The fact that
the experimental and computed temperature profiles are in close agreement suggest that the thus-measured PSDFs may be simulated without having to worry about mismatches between the experimental and computational boundary conditions. It eliminates the need to artificially shift the zero time for particle nucleation as often done in previous modeling efforts (see, e.g., [266]).

Another issue is that the particle size sampled is the mobility size, which can deviate from the true size. Mobility size is derived from the settling velocity of a charged particle in an electric field experiencing an electric static force in balance with fluid drag. The drag force is traditionally described by the Cunningham slip correction [267] applied to the Stokes drag force in the continuum regime [268]. The slip correction yields a relationship between the electric mobility $Z$ with the mobility diameter $\tilde{D}_p$ [269]. In the large Knudsen number limit, this relation takes the form of:

$$Z = \frac{q}{3\pi \mu \tilde{D}_p/(1.626 Kn)},$$

(11)

where $q$ is the elementary charge, $\mu$ is the viscosity, $Kn$ is the Knudsen number, and 1.626 is an empirical parameter [270].

To determine the relationship between the physical size and the mobility size, Li and Wang [271-275] carried out a gas-kinetic analysis by considering the effects of dispersive interactions between the particle and gas and the transition of specular to diffuse scattering upon gas-particle collision [275, 276]. The results show that in the large Kn limit the electric mobility $Z$ may be expressed by:

$$Z = \frac{3}{2} \frac{q}{\sqrt{2\pi m} k_B T N_g D_p \Omega_{wk}^{(1,1)*}},$$

(12)

where $m$ is the gas-particle reduced mass, $k_B$ is the Boltzmann constant, $N_g$ is the gas number density, $D_p$ is the particle diameter and $\Omega_{wk}^{(1,1)*}$ is the reduced collision integral—a parameter resulting from the dispersive force and the specular-diffuse scattering transition. For carbon particles, the physical diameter may be parameterized as a function of the mobility diameter [266]:

$$\frac{D_p}{\tilde{D}_p} = \left(1.072 - \frac{0.493}{\tilde{D}_p}\right) \times \tanh\left(1.457 + 0.0109 \tilde{D}_p\right),$$

(13)
which is valid for $2 < \tilde{D}_p \text{ (nm)} < 100$. The above equation shows that for primary soot particles the mobility diameter is quite close to the physical diameter: $D_p/\tilde{D}_p = 0.8, 0.94$ and $0.98$ for $\tilde{D}_p = 3, 10$ and $20$ nm, respectively.

3.3.3 General Feature of Particle Size Distribution Function

In general, PSDFs observed for nascent soot are bimodal. These distributions may be fitted by a bi-lognormal function [184] or by a sum of a power-decay function and a lognormal distribution [180]. As shown in Fig. 14, flame temperature has dominant effects on the shape of soot PSDF. Over the particle diameter range probed, nascent soot formed in a lower temperature, ethylene-oxygen-argon flame (1660 K) has a substantially stronger bimodal feature than that in a higher-temperature flame (1898 K) [184]. Numerical sensitivity analyses show that the PSDF shape is sensitive to the various kinetic parameters in the HACA–based soot model [266], as seen in Fig. 15. For example, the particle size at the trough increases with an increase in the nuclei or “collector” particle size, and/or in the nucleation rate. Hence, the experimental evidence suggests that the nuclei in the lower-temperature flame and/or the nucleation rates are substantially larger than those in the higher temperature flames. Though this behavior is being understood kinetically, these observations illustrate the usefulness of the detailed PSDF data in soot model development and validation. It is possible that the various model parameters, including the sticking probability of particle collision and gas-surface reaction rates, can be obtained through an inverse problem that compare detailed models against observations of a set of well characterized flames. Indeed, attempts have been made to scrutinize model parameters through comparisons of simulated PSDFs with measurements. Examples include the use of a stochastic approach by Kraft and coworkers [180, 266, 277-279], a hybrid method of moments by Blanquart, Pitsch and coworkers [280] and the various sectional methods by D’Anna [281-284], Mauss [285] and their coworkers.
3.3.4 Evidence of Aliphatics in Nascent Soot and Soot Mass Growth without H Atoms

Despite all the modeling advances, additional elements or processes must be considered to account for rather unexpected observations made in recent flame studies [246, 256, 257]. In these studies, nascent soot formation in an ethylene-oxygen-argon flame ($\phi = 2.5$) was cross-examined with a range of experimental techniques. Corroborating evidences indicate that (1) nascent soot can be rich in aliphatics; (2) soot mass can grow without the presence of gas-phase H atoms. At present, neither observation can be explained by detailed models of soot formation. Fig. 16 presents these experimental evidences, which were derived from measurements of particle size both by mobility sizing [257] and TEM [256], chemical composition by photoionization aerosol mass spectrometry (PIAMS) [257], soot volume fraction [256] by small angle neutron scattering (SANS) [246] and thermocouple particle densitometry (TPD) [257]—a method developed in Ref. [286].

The onset of soot nucleation starts in zone II as marked in Fig. 16, when the PSDF is characterized by a sharp, exponential decay curve with particles mostly below 5 nm in size. The TEM image of particles collected thermophoretically at nearly the same flame position shows that the apparent size is substantially larger than those determined by particle mobility, indicating that the particles flatten on the TEM grid upon impact. In other words, these young particles are liquid-like rather than being carbonized and rigid, as will be discussed later. Zone II ends with the appearance of doublet aggregates. At that point, the PSDF starts to segregate into two lognormal functions. By using a soft particle fragmentation technique, PIAMS measurements showed that the soot in zone II is composed of mostly PAHs from pyrene to ovalene. However the PIAMS spectrum also indicates the presence of an appreciable amount of aliphatic components. Compared with PIAMS, other techniques, including laser ablation particle mass spectrometry [287] and laser desorption/laser ionization mass spectrometry [288] are probably too destructive to the soot samples and thus insensitive to aliphatics. The presence of aliphatic components is consistent with the liquid-like character observed by TEM.

In zone III, the PSDFs are distinctively bimodal and the corresponding TEM image shows aggregates consisting of 10s' of primary particles. Interestingly, the PIAMS result shows a large amount of aliphatics compared to aromatics in soot samples collected in zone III. The atomic C-to-H ratio calculated from the
mass spectrum is around the value of unity. Under this C/H ratio, the mass density of soot material $\rho_s$ is expected to be substantially lower than that of mature soot ($\rho_s = 1.8-2.0 \text{ g/cm}^3$) [77]. Indeed, the volume fractions of soot measured by TPD and SANS can only agree with each other if the SANS data interpretation assumes $\rho_s = 1.5 \text{ g/cm}^3$ and $C/H = \sim 1$ [256]. Another important observation is that soot volume fraction continues to increase in zone III, even though the gas temperature drops to 1450 K. This is rather unexpected in the context of the HACA mechanism. Detailed modeling suggests that the concentration of the H atoms in zone III is too small to account for radical production on soot surfaces through eq 9. Hence, other mechanisms must be responsible for mass growth in this later part of the flame.

Additional studies have shown that the above observations are not limited to that specific ethylene flame. Figure 17 shows the TEM image of particles collected from a C$_2$H$_4$-O$_2$-Ar flame at equivalence ratio of 2.07 with a higher flame temperature ($T_f = 1736\pm 50 \text{ K}$) [184]. As it can be seen in the TEM image, the particles again spread on the substrate upon impact, forming a “sunny-side-up” structure or much like the interaction of molten wax droplet with a surface. Atomic force microscopy (AFM) probing of thermophoretically collected particles—a technique pioneered by D’Alessio and D’Anna [289]—shows impact crater-like morphologies typical of molten wax droplets [184]. The height ($h$) to width ($a$) ratio varies from 0.02 to 0.4, depending on the particle size [185].

The FTIR method has been employed previously to probe the chemical makeup of soot and other condensable materials from flames [290-292]. In recent studies, Cain et al. [293, 294] used this technique in conjunction with a micro-orifice uniform deposition impactor. Their results again showed aliphatic components to be dominant in nascent soot. The aliphatic-to-aromatic C-H ratios are around 4 with little dependency on the size and age of the particles [294]. With an even softer ionization method, the thermal-desorption, chemical ionization mass spectrometry technique yielded evidence in support of the PIAMS and FTIR studies. In particular, a broad range of molecular components were detected for nascent soot with molecular weight spanning from 100 to 900 amu [294]. Though some PAH stabilomer features are evident on the mass spectrum, the broad mass spectrum feature suggests that most of the PAHs in nascent soot are alkylated. Raman spectroscopic evidence [291] suggested that these aliphatic groups are bound to the particle surfaces as alkyl or alkenyl functionalities.
The experimental evidence just discussed may be summarized in Fig. 18 in a plot similar to those found in Calcote [76] and Bockhorn [82]. As shown, converging evidence indicates that nascent soot formed in laminar premixed flames has a core-shell structure: an aromatic core composed of PAHs ranging from pyrene to ovalene, and an aliphatic shell responsible for spreading into flattened structure upon thermophoretic impact. The aromatic core is produced in the early stages of the flame where the gas temperature is high, while the aliphatic shell forms later on the aromatic substrate when the gas temperature becomes somewhat lower. At present, it is unclear whether the picture presented in Fig. 18 is applicable to soot produced in other types of flames or at elevated or reduced pressures.

3.3.5 Persistent Free Radicals

The existence of aliphatics in nascent soot may well be related to their ability to undergo mass growth in the absence of gaseous H atoms. To start with, the core is aromatic in nature. Following our hypothesis about the involvement of π radical in soot nucleation, it is not difficult to speculate that these π radicals persist into young soot particles consisting of stacks of PAHs. As discussed by Cain et al. [293], the aliphatic shell will generally form in a relatively cool flame environment depleted of gas-phase H atoms, but the persistent π radicals in the aromatic core allows for reactions with unsaturated hydrocarbons (e.g., acetylene), and thus alkylating the core.

In fact, the existence of persistent free radicals (PFRs) in soot has already been discussed by Dellinger and coworkers [295, 296], who attributed the origin of PFRs however to resonantly stabilized free radicals of semiquinone and phenoxyl origins. PFRs are reactive chemical species having unpaired electrons or characteristics of unpaired electrons. These free radicals can exist in substantial concentrations due to resonance and electron delocalization. They can also be stabilized by other mechanisms. For example, on the basis of density functional theory calculations, Dames et al. [297] proposed an additional source of PFRs. These are acenaphthene or hexaphenylethane derivatives with weak central carbon-carbon bonds that may be easily cleaved to yield triplet diradicals. Central C-C fission into singlet diradicals may lead to even lower bond energies, though this has not been calculated. Yet, π radicals remain to be the most plausible PFR candidate.
Regardless of the chemical origin and nature of PFRs, there is ample evidence that support its existence in soot. In ethylene-air counterflow diffusion flames, the soot volume fraction observed towards the stagnation surface can be predicted only if soot retains a radical character [298]. Electron Spin Resonance spectra of anthracite, a coal containing little to no oxygenated compounds, show a measurable concentration of free radicals [299]. Most importantly, soot formed from the pyrolysis of ethylene, acetylene, and various jet fuel surrogates also show appreciable amounts of free radicals associated with carbon atoms [300]. The Landé g-factors reported for such soot samples suggest that the radicals are of aromatic π nature and the spin concentrations can be as high as $10^{21}$ per gram of the residues insoluble in dichloromethane. Assuming the residue is made of carbon only, the number of spins is roughly 1 per 50 atoms, or one free radical for each pair of PAHs of the size of coronene.

If π radical PAHs indeed exist in nascent and mature soot, this phenomenon would hold the key to a range of health and environmental effects of soot. The uptake of persistent free radicals through the respiratory system can lead to the production of hydroxyl radicals harmful to cellular components, subsequently increasing risk of lung cancer [295, 301]. Soot exhaust from aircraft engines is thought to be responsible for contrail formation in the wake of an aircraft [69, 302, 303], thus perturbing the global and regional climate. Indeed, evidence shows that depending on the conditions in which it forms, soot has the ability to uptake substantial amounts of water on both its surface and internally [302-304]. Here, uptake of water may be facilitated by the surface radical sites [297]. Because of local electron deficiency, these radical sites allow for tight hydrogen bonding with water molecules. For example, the theoretical binding energy of hydrogen-like bonds between a methyl radical and water is 1.5 kcal/mol [305, 306] which increases to 2–4 kcal/mol for C$_1$-C$_4$ alkyl radicals [306, 307]. Hence, if PFRs exist on soot surfaces, they would make these surfaces attractive to water under atmospheric and tropospheric conditions.

3.4 Implication in Modeling and Unresolved Problems

The core-shell structures observed in nascent soot should have a notable impact on soot modeling. Because of the chemical heterogeneity of nascent soot and its possible dependence on particle size and time-
temperature history, future soot models must be able to predict the chemical composition of nascent soot and its size distribution. These models will need to delineate the differences in the mechanism and reaction kinetics of mass growth over different surfaces. This fundamental need echoes future practical needs in engine design. This is particularly true considering that current particulate emission regulations (e.g., PM2.5) are based solely on the mass of particles emitted and not on the sizes or chemical composition. However, the environmental and human health effects of soot emission are more directly related to the particle size distribution and chemical composition than particle mass [59, 308-311]. For example, ultra small particles do not contribute much to particulate mass, but they can penetrate deeper into human airways and be absorbed and transported more effectively into the blood stream. The propensity of soot to act as cloud condensation nuclei is also related to particle number density and surface chemical composition. Given these considerations, it is not difficult to foresee that future regulatory developments and thus the models of soot formation will have to take into consideration the size distribution of particles and their chemical makeup.

Indeed several research groups have embarked on detailed modeling efforts aimed to add chemical resolution to nascent soot particles [179, 240-242] and to resolve chemical composition, size distribution, and morphology at different stages of soot formation (see, e.g., [92, 174, 175, 200, 277, 278, 312-316]). Using a combined kinetic Monte Carlo and molecular dynamics approach, named Atomistic Model for Particle Inception (AMPI), Violi and coworkers [316] probe the structure of incipient soot in a benzene flame. As should be clear from the examples shown in Fig. 19, AMPI provides atomistic level structures and morphological information including density and porosity as soot precursors evolve into a three-dimensional structure. Kraft and coworkers advanced a PAH-PP (primary particle) model [278, 315] which can follow the evolution of the chemical composition of nascent soot during its growth process. As shown in Fig. 20, the method allows them to provide detailed soot composition of the type that can be observed by photoionization mass spectrometry [317]. Though still in their infancy, these numerical methods will likely lead to the next generation of soot models capable of simultaneously predicting the evolution of particle size distribution, chemical composition, and morphology.

What remain unresolved are the formation mechanisms of stacked PAHs and the aliphatic shell in nascent soot. To start, it would be useful if the molecular structures with localized π electronic states and
their mechanistic relationship to Stein’s stabilomer sequence can be identified. This will serve as a starting point for these radicals PAHs to be considered in detailed reaction models of PAH formation. Additionally, the nature and magnitude of the forces that bind these aromatic molecules to each other and with the stable Stein’s stabilomers and non-aromatic species need to be determined. While the underlying questions can be addressed by electronic structure calculations, the fundamental difficulty lies in the fact that the widely used methods such as the density functional theory is unlikely to provide accurate answers for this problem. More accurate, multiconfigurational methods may be required, but such methods are still too computationally costly for moderate-sized PAHs. Clearly, we are in need of new computational chemistry capabilities that go well beyond those currently available in standard commercial packages.

4. Metal Oxide Nanoparticle Synthesis and Applications

The thermodynamic arguments given earlier indicate that a large range of nanoparticles and nanomaterials can be synthesized in combustion flames if the initial and final thermodynamic states are chosen properly. Despite all the advances in flame synthesis, the longevity and vigor of this research area rely largely on the performance of the materials which are produced. Disciplinary barriers keeps materials scientists away from flame synthesis, as mastering the technique of flames require basic knowledge in combustion chemistry, fluid mechanics and heat transfer - subject areas not traditionally part of the materials science curriculum. Yet, it is this author’s belief that the flame process holds the key to inexpensive manufacturing of energy-conversion materials for use in photovoltaics, rechargeable batteries, and combustion pollutant sensing. As an example, this section will illustrate a flame method for producing mesoporous titania (TiO2) thin films for dye sensitized solar cells and chemical sensing.

As a versatile material, titania attracts much attention in areas critical to future energy conversion technologies, including photocatalysis [318] as in electrochemical photolysis of water (the Honda-Fujishima effect) [319], dye-sensitized solar cells (the Graetzel cell) [9], gas sensing [320, 321], and catalysis [322]. Titania has a total of eight crystal phases with rutile and anatase being the most common. In an oxygen rich environment and below a crystalline size of 14 nm, anatase is the preferred thermodynamically metastable
phase [323]. In general, anatase has properties more attractive than rutile for applications in catalysis, photocatalysis and solar cells.

Following the pioneering work of Ulrich [12, 324], flame synthesis of titania has been studied extensively (e.g., [116, 117, 325-327]) with notable contributions from Pratsinis [14, 328-331]. Hence, titania serves as a good example to illustrate the applications of combustion synthesized materials in a broad range energy science beyond combustion. For example, the applications of titania for chemical sensing and as a catalyst have been discussed by Pratsinis and coworkers [14, 332]. As in this and other cases, flame synthesized metal oxide particles are usually of higher crystallinity and phase purity, and when the flow field and particle time-history is tightly controlled, they attain exceedingly narrow size distribution when compared to other synthesis techniques [116, 333].

As discussed earlier, the thermodynamic driving force for titania formation in flames from typical precursors is rather simple. Hence, a fine control of the particle size distribution, crystal phase and purity, and crystallinity is almost entirely dependent on the flame design and particle collection method. Since the application of titania typically requires the particles to form a thin, porous film, a direct, one-step process of particle synthesis followed by film deposition would be economically beneficial. Yet, the problem is challenging because of the requirements for ultrafine particles with tunable sizes, narrow size distribution (at least for the purpose of fundamental study of the particle size effect), uniform film thickness and porosity, high crystallinity and phase purity. To obtain uniform particle size, the flame flow field must be uniform and low-dimensional. To synthesize ultrafine particles at reasonable production rates, the residence time must be kept at a few milliseconds. Deposition of a uniform particle film requires strategic substrate placement with a consideration of the flow field. Ensuring high crystallinity and phase purity requires a uniform temperature in the particle forming region and then a sharply reduced temperature near the substrate.

Studies into soot formation and laminar flames in fact have offered many critical insights into viable solutions to the above problems. Pseudo-one dimensional premixed flames have been traditionally used to follow the kinetics of soot formation with small fluid mechanic complications. These flames turn out to be advantageous for particle synthesis because of uniform time-history across the flame. In particular, flames stabilized through flow stretch by impinging a laminar flat jet against a surface satisfy all the particle synthesis
and film deposition requirements mentioned earlier. Although premixed stagnation flame was developed largely for probing flame kinetics [334-336], they prove to be ideal for particle synthesis because of their low-flow dimensionality. Another advantage is that this setup may be scaled up into an industrial process [337]. Panel (a) of Fig. 21 shows such a flame set up. The flow diverges under the stagnation surface. The flow stretch typically stabilizes the flame a few millimeters from the surface. If the unburned gas is doped with an organometallic precursor, it decomposes and is oxidized immediately in the flame region. Since most metal oxides have small vapor pressures, they condense into nanoparticles, again through nucleation, surface growth and coagulation. If the nanoparticles can be kept in the molten state, coagulation leads to production of single droplets, preventing aggregates from forming. If the stagnation surface is kept cool, the large thermophoretic force established between the flame and surface transports the particles quickly towards the surface. For the setup depicted in Fig. 21, the residence time may be kept as small as 1 ms, limiting particle growth and aggregation [333, 338]. The molten droplets crystallize adjacent to the surface as the gas cools and the particles deposited on the surface forming a thin film. This deposition process may be made continuous by translating or rotating the substrate as shown in Fig. 21. A similar technique has been developed for turbulent premixed swirl flames [339].

Particles so synthesized are narrowly distributed with a tunable median particle size, mostly single crystals, and with high phase purity, as shown in panel (b) of Fig. 21 using titania nanoparticles as an example (see, also [262, 333, 338, 340]). Also shown in the same panel is an SEM image of a mesoporous film of anatase titania grown by this approach, depicting its uniform and porous nature. These films have shown great promise for significantly enhanced gas sensing sensitivity and stability, as shown in panel (c) of Fig. 21. The titania film undergoes changes in its ohmic resistance due to the reduction of its surface by CO. The conduction band in the titania film, previously depleted of free carriers, becomes increasingly populated with free electrons as surface oxygen is removed, leading to an increase in electric conductance. As shown, exposing the film in 5 PPM CO can cause the film resistivity to drop by a factor of 2 at 500 °C [263], indicating that the film can achieve sub PPM level of detection for such combustion emitted pollutants as CO.

In addition to sensor applications, flame process may also prove to be beneficial to thin-film solar energy conversion. Recent studies have shown that dye sensitized solar cells (DSSCs) can achieve photoconversion
efficiencies well above 10% [341] and they can also be produced substantially cheaper than other types of thin-film solar cells. This progress has attracted a tremendous amount of research. One of the most important research areas is fabrication of mesoporous titania layer as the electron diffusion layer.\(^*\) The flame method may prove to be the most important and inexpensive fabrication method to achieve high surface area and good electron diffusivity, as these properties are desirable for achieving high photoefficiencies. Indeed, flame fabricated titania films have shown to provide good performance, as shown in panel (d) of Fig. 21, with photoefficiency as high as 9% [17] for cells not yet optimized.

5. Concluding Remarks

Nanoparticle formation in flames is a ubiquitous combustion phenomenon rich in its research history. Although the driving force in soot research has been to understand and predict its formation, much of the future value in this field lies in applying this knowledge beyond its disciplinary boundaries. Phenomena closely related to soot formation include its subsequent health and climate effects as they may arise from fundamental chemistry intimately related to that of soot formation in flames. They also include the inexpensive synthesis of functional materials for a broad range of traditional and renewable energy applications.

Despite the tremendous advances in the modeling science of soot formation, critical gaps and thus challenges remain in almost every one of the early steps of soot formation. In the area of soot precursor formation, the key points we have learned are: the HACA mechanism and reactions involving resonantly stabilized radicals play critical roles in the formation of pericondensed PAHs. The detailed pathways and rates in a flame are highly dependent on the local flame conditions, the fuel structure and composition. Given that a multitude of reaction pathways may exist for PAH formation, the problem cannot have a closure at the quantitative level without drastic improvement of the current one-reaction-at-a-time approach. This is true especially in the context of the recent real-fuel combustion initiatives, in that PAH formation can be

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\(^*\) Titania is a wide bandgap semiconductor (~3.2 eV), and it does not absorb visible light appreciably. To provide active electrons, a sensitizing dye is immobilized on its surface. Photoexcitation of the dye is followed by charge transfer and injection of electrons into the titania conduction band. Electrons diffuse through the titania layer and are collected on a transparent conductive substrate.
sensitive to certain compounds even if their concentrations are rather small in a fuel mixture. With data emerging from advanced experimental techniques, such as the molecular-beam synchrotron photoionization mass spectrometry, new theoretical methods are needed that can allow us to efficiently narrow down the many possible reaction pathways so that the kinetics of these reactions can be studied in some forms of chemical isolation.

Phenomenologically, the nucleation of soot in flames is decidedly second order in the monomer (PAH) concentration. Additionally, by comparing the concentrations of PAHs and soot nuclei, particle nucleation starts predominantly through clustering of moderate-size PAHs. However, we do not yet know the binding force that keeps the initial dimers, trimers, and clusters of PAHs together. There is conclusive evidence that young soot particles formed in premixed flames have a core-shell structure, with the core being aromatic in nature and the shell being aliphatic. Again, the nature of binding between aromatic and aliphatic constituents remains unclear. The mass growth of soot can proceed without the presence of gas-phase H atom, indicating that the HACA mechanism may be incomplete to describe the entire process of soot formation. It is suggested that radicals due to localized \( \pi \) electrons in PAHs may hold the key to these questions – a hypothesis inspired by recent progresses in theoretical materials research. The remaining challenges include the need to advance an alternative explanation for PAH coalescence and to find a class of PAHs with localized \( \pi \) electron structures and thus large enough binding energies. The nature and structures of these PAHs should then point to the need for further development of gas-phase reaction mechanisms and models for the formation of these peculiar aromatic radicals in flames. Such radical sites may also exist on the soot surface. Direct experimental probing of these sites remains to be performed but will be exceedingly challenging.

What have we learned and what are the value and future of research into soot and condensed-phase material formation in flame? On one level there is value in creating fundamental understanding and models of soot formation for future engine designs. What is perhaps even more valuable is the fundamental knowledge garnered from soot research and its impact on a wide range of nanoparticle synthesis problems. To this end, flame synthesis of functional nanomaterials for renewable energy utilization is expected to bring new, challenging questions to this research community. Advances in this area of research will perhaps greatly
impact the public perception about fossil-fuel combustion, from it being today’s problem to tomorrow’s solution of clean energy utilization.

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References


Figure Captions

Figure 1. Standard enthalpy ($\Delta H^\circ$) and entropy ($T \Delta S^\circ$) contributions to Gibbs function of reaction $\Delta G^\circ$ at 1600 K for carbon formation from propane and rutile-phase titania formation from titanium vapor in the presence of molecular oxygen.

Figure 2. A version of the hydrogen-abstraction—carbon addition (HACA) reaction mechanism. The standard Gibbs function per carbon atom is plotted relative to an initial system with benzene : acetylene : H atom = 1 : 5 : 1 at 1800 K. Not considered in the diagram is the combination of H atom with aryl radicals.

Figure 3. Spectral sensitivity of pyrene concentration predicted for a 90-Torr burner stabilized 0.236 C$_2$H$_2$-0.214 O$_2$–Ar flame at 0.55 cm from the burner surface [176]. The results are taken from ref [125].

Figure 4. Selected parts of potential energy surfaces of propargyl recombination leading to production of benzene and phenyl + H (from Miller and Klippenstein [145]).

Figure 5. Photoionization mass spectra of flame species in the mass-to-charge ratio of 70 to 126 for a series of burner-stabilized aromatics-oxygen-50% argon flames, all at 30 Torr pressure and with C/O = 0.68, determined by molecular beam synchrotron photoionization mass spectrometry. 1: benzene, 2: toluene, 3: styrene, 4: ethylbenzene, 5: o-xylene, 6: m-xylene, 7: p-xylene (Courtesy of F. Qi).

Figure 6. Conceptual mechanisms of soot particle nucleation.

Figure 7. Binding energies for self-interactions of a series of PAHs taken from Herdman and Miller [169] (top panel), and relative concentrations and normal boiling/sublimation temperatures of selected PAHs in the HACA sequence of reactions (bottom panel, 1-, 2-, 3-, 4- and 7-numebred aromatic rings are benzene, naphthalene, phenanthrene, pyrene, and coronene, respectively): circles: 90-Torr burner-stabilized acetylene flame [176]; triangle: 30-Torr toluene flame ($\phi = 1.9$) [164]; 30-Torr benzene flame ($\phi = 1.78$, relative to naphthalene) [159].

Figure 8. Size distribution computed by considering monomer dimerization and particle coagulation, assuming a constant, second-order nucleation strength [180]. $x$ is a dimensionless time given as $x = (8\pi k_B T / m_r)^{1/2} [4m_r / (3\pi p)]^{1/3} C_0 (0) t$. The solid and dashed lines are computed with $\alpha = 1$ and 0.1, respectively. The particle diameter (upper x-axis) is determined by assuming that the particles are spherical and the mass density of the particle material is 1.8 g/cm$^3$.

Figure 9. Snapshots of the flame, the temperature profiles determined experimentally (symbols) and numerically computed (lines), and the particle size distribution functions measured at several
burner-to-probe separation distances in a 16.3% ethylene-23.7% oxygen-argon burner-stabilized stagnation flame at atmospheric pressure (cold gas velocity = 8 cm/s) [182].

**Figure 10.** Mass spectrum of high-molecular weight species extracted from a 100-Torr acetylene-oxygen flame (φ = 3.25) by molecular beam mass spectrometry with 193 nm laser ionization (Courtesy of H.-H. Grotheer).

**Figure 11.** Gibbs function of dimerization for coronene, ovalene and circumcoronene. The shaded area corresponds to an equilibrium constant for dimerization \( K_p > 10^6 \text{ atm}^{-1} \).

**Figure 12.** PAH \((i, j)\) and radical character \((0 \leq y \leq 1)\) based on UBHandHLYP/6-31G(D) calculations of Nagai et al.[232].

**Figure 13.** Snapshots of nascent, primary soot particles simulated with a kinetic Monte Carlo procedure by Balthasar and Frenklach [240]. (Reprinted from Proc. Combust. Inst., vol. 30, Copyright 2004, with permission from Elsevier). Upper panels: particle structure resulting from coagulation of single soot nuclei. Bottom panel: particle structures after a period of mass growth through gas-surface reactions. Panel A represents a typical particle, whereas panels B and C represent extreme cases in terms of deviation from sphericity.

**Figure 14.** Evolution of PSDFs measured for two premixed 16.3% C\(_2\)H\(_4\)-23.7% O\(_2\)-Ar burner stabilized flames. Top panel: maximum flame temperature \( T_f = 1660\pm50 \text{ K} \) (cold gas-velocity \( v_0 = 5.5 \text{ cm/s} \)); bottom panel: \( T_f = 1898\pm50 \text{ K} \) (\( v_0 = 13 \text{ cm/s} \)). Data are taken from [184].

**Figure 15.** Sensitivity of the features of a bimodal PSDF with respect to model parameters [266].

**Figure 16.** Temperature profile and soot volume fraction of a burner-stabilized laminar premixed ethylene-oxygen-argon flame (φ = 2.5). For volume fraction, open symbols were measured by thermocouple particle densitometry; filled symbols were obtained from a re-interpretation of the small angle neutron scattering data [246] by Zhao et al. [256]; line is drawn to guide the eye. The PSDFs and mass spectra are taken from Oktem et al. [257]. The TEM images are taken from ref [256].

**Figure 17.** Panel (i) TEM micrograph [184], panel (ii) AFM images [184] and aspect ratio [185], and panel (iii) micro-FTIR characterization of aliphatic-to-aromatic C-H ratios, and thermal-desorption chemical ionization mass spectrometry [294] of nascent soot collected from a 16.3% C\(_2\)H\(_4\)-23.7% O\(_2\)-Ar flame at distances of 0.5, 0.7 or 1.0 cm above the burner surface (cold gas velocity \( v_0 = 8 \text{ cm/s} \), maximum flame temperature \( T_f = 1736\pm50 \text{ K} \)).

**Figure 18.** A conceptual model of soot formation. Stacks of lines represent stacked aromatic structures and the wiggly lines represent aliphatic components.
Figure 19. Examples of incipient soot formed in a premixed benzene flame as simulated by AMPI (courtesy of A. Violi).

Figure 20. Left panel: PAH mass spectrum of soot in a burner-stabilized laminar 50%\(\text{C}_2\text{H}_4\)-50%\(\text{O}_2\) at 120 mbar by Happold and Grotheer [317]. Right panel: Mass spectra computed by the PAH-PP model. (Courtesy of M. Kraft).

Figure 21. Panel (a) illustration of the method of flame stabilized at a few millimeters under a rotating stagnation surface (also as a particle collection surface). The laminar premixed flame is stabilized by flow stretch. The rotation causes the plate to cool by convection, thus creating a large temperature gradient and pushing the particles towards the collection plate for thermophoretic film deposition. Panel (b): particle size distribution of nanocrystalline titania synthesized, as measured by probe sampling/mobility sizing [256]; TEM images showing the crystal structures and scanning electron microscopy image of a porous particle film of titania [333]. Panel (c): Ohmic response of a chemical sensor, prepared by the flame technique, to exposure of trace CO in air, (1) 280 PPM, (2) 140 PPM, (3) 93 PPM, (4) 46 PPM, (5) 18 PPM and (6) 5 PPM (taken from [263]). Panel (d): polarization and power density curves measured for a dye sensitized solar cell with the photoanode prepared by the method of stagnation flame stabilized on a rotating surface (taken from [17]).
Figure 1. Standard enthalpy ($\Delta H^\circ$) and entropy ($T\Delta S^\circ$) contributions to Gibbs function of reaction $\Delta G^\circ$ at 1600 K for carbon formation from propane and rutile-phase titania formation from titanium vapor in the presence of molecular oxygen.

Figure 2. A version of the hydrogen-abstraction—carbon addition (HACA) reaction mechanism. The standard Gibbs function per carbon atom is plotted relative to an initial system with benzene : acetylene : H atom = 1 : 5 : 1 at 1800 K. Not included in diagram is the combination of H atom with aryl radicals.
Figure 3. Spectral sensitivity of pyrene concentration predicted for a 90-Torr burner stabilized 0.236 C\textsubscript{2}H\textsubscript{2}-0.214 O\textsubscript{2} -Ar flame at 0.55 cm from the burner surface [176]. The results are taken from ref [125].

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Figure 14. Evolution of PSDFs measured for two premixed 16.3% C2H4-23.7% O2-Ar burner stabilized flames. Top panel: maximum flame temperature $T_f = 1660\pm50$ K (cold gas-velocity $v_0 = 5.5$ cm/s); bottom panel: $T_f = 1898\pm50$ K ($v_0 = 13$ cm/s). Data are taken from [184].
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Formation of Nascent Soot and Other Condensed-Phase Materials in Flames

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Formation of Nascent Soot and Other Condensed-Phase Materials in Flames

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Abstract

Over the last two decades, our understanding of soot formation has evolved from an empirical, phenomenological description to an age of quantitative modeling for at least small fuel compounds. In this paper, we review the current state of knowledge of the fundamental sooting processes, including the chemistry of soot precursors, particle nucleation and mass/size growth. The discussion shows that though much progress has been made, critical gaps remain in many areas of our knowledge about the sooting process. We identify some of these gaps and propose the roles of certain aromatic $\pi$ radicals resulting from localized $\pi$ electron structures in particle nucleation and subsequent mass growth of nascent soot. The existence of these free radicals provides a rational explanation for the strong binding forces needed for forming initial clusters of polycyclic aromatic hydrocarbons. They may also explain a range of currently unexplained sooting phenomena, including the large amount of aliphatics observed in nascent soot formed in laminar premixed flames and the mass growth of soot in the absence of gas-phase H atoms. While the above suggestions are inspired, to an extent, by recent theoretical findings reported within the materials research community, this paper also demonstrates that the knowledge garnered through our longstanding interest in soot formation may well be carried over to flame synthesis of functional nanomaterials for clean and renewable energy applications. In particular, work on flame-synthesized thin films of nano-crystalline titania illustrates how our combustion knowledge might be useful for developing advanced yet inexpensive thin-film solar cells and chemical sensors for detecting gaseous air pollutants.
1. Introduction

Formation of condensed-phase materials is ubiquitous in many flame phenomena. These materials are formed mostly as nanoparticles suspended in burned combustion gases. As a condensed-phase matter formed persistently in hydrocarbon combustion, soot found its use prehistorically as a pigment in cave paintings [1-3]. The oldest known tattoos, belonging to a Tyrolean iceman, were etched with soot [4]. Flame soot provided the black pigment for India ink—a Neolithic invention [5]. Today, the same material finds its use with versatility, including carbon black for automobile tires and a pigment in toners for laser printers. In some of the practical combustion systems, the formation of soot is critical as it facilitates radiative heat transfer [6, 7]. More recent applications include the use of soot or carbon nanoparticles as a cathode catalyst [8] in dye-sensitized solar cells [9, 10], and a catalyst support in direct methanol and other fuel cells [11].

Other condensed-phase materials form in flames often because of the presence of elements beyond the common constituents of gaseous hydrocarbon flames. As an example, metals or metal precursors can be present or added in unburned fuel-oxidizer mixtures to induce particle formation. Combustion as a method of material synthesis also has a rich history. Titania is the white pigment in paints; and silica is used for fiber optics applications. Both are produced almost exclusively by flame processes [12]. In recent years, new flame-synthesized materials and their applications are emerging at a rapid rate. Advances include specialty nanoparticles and the films produced from them for applications in catalysis [13-15], dye-sensitized solar cells [16-18] and biomedical devices [19-21]. Palladium and palladium oxide nanoparticles grown in situ have shown to enable fuel ignition at low temperatures with potential applications in hypersonic combustion [22-24]. And many more exotic structures, including fullerenes, carbon nanotubes, graphenes, and metal-oxide nanowires, have been often prepared by flame methods (e.g., [25-34]).

Beyond their common origin in flames, flame soot formation and functional nanomaterial synthesis by flames share many common characteristics. Both involve the formation of condensed-phase materials from gases starting with vapor-phase nucleation, followed by mass and size growth through coalescence, coagulation, surface reactions and condensation of vapor species, and finally by aggregation into fractal structures, all of which occur over very short periods of time, typically a few milliseconds. Similar diagnostic and computational tools are employed to study the formation of both condensed-phase materials and the
long history of studies into soot formation research has yielded many useful insights into nanomaterial synthesis. Likewise, a number of combustion researchers have crisscrossed the disciplinary boundaries of combustion, nanomaterial synthesis and aerosol science; in doing so, they have made unique contributions in all these areas. Examples include Calcote’s work on carbide and nitride [35, 36], Frenklach’s work on diamond thin films and particles (e.g., [37-39]), silicon carbide [40, 41] and silicon nanoparticles [42], Harris’s work on diamond thin films [43, 44], Howard’s work on fullerenes and carbon nanotubes (e.g., [25, 34]), Roth’s work on various oxide nanoparticles [45, 46], Zachariah’s work on problems involving synthesis, characterization and fundamental theories of nanoparticles [47-49], and Kennedy’s work on yttrium and europium oxide nanoparticles and their applications as biosensors [50, 51].

Today’s scientific interest in soot formation, however, is largely unrelated to its material applications. In fact, much of the research over the last four decades has been directed towards mitigating air pollution problems that invariably result from the use of fossil fuels. It is well known that as a major contributor to anthropogenic aerosols, soot is detrimental to atmospheric visibility [52], global climate [53-61] and human health [62-67]. Soot has been fingered as a major player in global warming [61]. Evidence suggests that, as cloud condensation nuclei, soot particles participate in the formation of clouds and contrails [68-72]. As an effective light absorber, soot deposited on polar ice triggers its melting [60, 73] and may be responsible for as much as 94% of Arctic warming [74].

The remarkable advances in the theory of soot formation have been reviewed periodically over the last fifty years [75-92] and many contemporary problems have been discussed in the proceedings of a recent workshop [93]. This exceedingly interesting combustion phenomenon is seemingly understood at a quantitative level, at least for small model fuel compounds; and as a field of combustion the science of soot may be considered to be mature. Yet because of the intricate nature, not to mention the large number of tightly coupled elementary processes involved, the science of soot formation will probably never have complete closure. In fact, we have learned that it probably will never be possible to completely mitigate soot formation in engines as long as the fuel is injected into the combustion chamber in the liquid form. Under this condition, the finite fluid-mechanic mixing rate causes the flame to invariably progress through fuel-lean and rich regions – and in those rich regions soot usually forms. Hence, the underlying problem becomes
largely a compromise of optimal combustion engine efficiency with minimal emission of particulates and other air pollutants.

Much of the work on soot formation has been driven by the need for predictive models of soot formation and oxidation arising from the principles of thermodynamics and reaction kinetics. When combined with computational fluid dynamics (CFD), a fundamental modeling approach is expected to lead to predictive design tools for the next-generation of efficient, clean-burning combustion engines [94]. Indeed there have been rapid advances in reaction models of real fuel combustion (e.g., [95-106]) and incorporation of soot formation models in CFD simulations [7, 107-115]. As these fields advance, there is a greater need to identify and fill in the gaps of current kinetic descriptions of soot formation. As will be discussed in this paper, the mechanism of soot nucleation (or particle inception) still remains elusive. We are still unable to predict the evolution of the chemical structure and composition of flame soot and to describe the gas-surface reactions at an elementary level comparable what that already accomplished in gas-phase combustion chemistry.

Beyond a predictive capability of soot formation, what is the future of soot research? On one level there is value in creating models as an integral part of engine design codes, but the largest impact perhaps will be to apply what we have learned about soot formation in flames to many different prospects for nanoparticle synthesis. Undoubtedly, that is where the greatest benefits of current knowledge will lie—not in incremental improvements in soot reduction but in the vast improvements in nanoparticle material synthesis, creating particles of value in energy, catalysis and yet unimagined fields.

The versatility of the flame synthesis method has been discussed in a number of review articles [14, 116-121]. Beyond carbon black, titania, and fused silica, flame methods for material synthesis have not been put to extensive use as chemical vapor deposition or Sol Gel methods have, even though the flame methods hold definitive economic advantages [120]. The delay in commercial flame synthesis methods lies in the difficulty of the materials research field to master the flame technique and conversely the difficulty of the combustion field to extend itself to device-level demonstration of flame-made materials. If the flame method is to see broadened uses in material synthesis, it must rely on demonstrations of its utility in constructing new, cheaper and better performing devices. Such applications will eventually lead to the formulation of fundamental
questions regarding the relationships of flame dynamics and kinetics, and the resulting material structure, properties, functionalities and performance.

Another aspect of particle research is the recognition that different vapor-phase materials have different propensity towards nucleating into particles under a given condition. Many inorganic vapors (e.g., metal oxides) have exceedingly small vapor pressure even at high temperatures or low pressures. Hence, they would nucleate out of the gas phase first in sooting flames, leading to induced soot nucleation and mass growth. For example, the addition of ferrocene in flames can lead to enhanced soot production because of the growth of carbon on iron oxide nanoparticles [122-124]. The role of silicon carbide in inducing formation of carbon in interstellar media has also been discussed by Caldwell et al. [41]. At present, the role of metal impurity in the hydrocarbon fuels and engine lubricants in soot formation remains poorly characterized.

The discussion in this paper however focuses on homogeneously nucleated soot from pure hydrocarbon flames. It highlights several critical gaps in the understanding of the early stage of soot formation. The paper will also try to convey a hope that sustained research intensity into the phenomena of condensed matter formation in flames will have to broaden its research scope to include nanomaterial synthesis and applications. The paper is organized as follows. First, the thermodynamic driving forces for condensed-phase nanomaterial formation in high-temperature flames are revisited. The discussion attempts to delineate the somewhat different thermodynamic origins of soot and metal oxide formation in flames. The problem of soot nucleation and mass/size growth is then discussed both theoretically and by examining recent experimental observations. The paper aims to fill in a critical gap between the experimental observation and mechanistic description of soot nucleation and mass growth by proposing the existence of π-radical aromatics in the gas phase and on nascent soot surfaces. It will be shown that this hypothesis may explain some of the experimental observations that cannot be accounted for by existing mechanisms and models of soot formation. The π-radical character may also explain how soot acts as cloud condensation nuclei and the wetting and water uptake by soot in combustion exhaust.

The last part of the paper will demonstrate the synthesis and characterization of nanophase titania crystals and mesoporous films for two energy-related applications: dye sensitized solar cells and chemical sensing of combustion pollutants. The flame synthesis technique utilizes well-controlled laboratory flames
and particle characterization techniques, both of which were realized through studies into soot formation. The purpose in this part of the paper is not to provide a detailed survey about flame synthesis of condensed materials, but to show how soot and basic flame theory research can yield useful yet unintended results for material synthesis with broad applications in energy conversion. This paper focuses mostly on the chemical kinetic aspects of soot formation in laminar premixed flames at or near atmospheric pressure, owing to author’s own research expertise, although many issues in high-pressure and/or diffusion flame settings are equally critical and intriguing in our overall understanding of the sooting chemistry and physics.

2. Thermodynamics

A survey of the literature often leaves one with the impression that as the first step in soot nucleation, the formation of the first aromatic ring is the most important bottleneck to soot formation. This is far from true. There are at least of a handful of rate limiting steps during the formation of soot precursors and soot itself [125]. To understand why this is so, let us first examine the thermodynamics of the process. Formation of condensed phase materials or ordered structures in flames is a seemingly improbable event, because such flames are dominated by rapidly increasing entropy tending towards disorder. Yet these materials do form, and in many cases, they do so persistently. The driving force is either enthalpy release from chemical bond formation or entropy increase because of the release of gas-phase species that accompanies particle formation. Carbon forms endothermically from saturated alkanes, releasing H₂ which, in turn, causes the entropy increase that ultimately drives particle formation. In contrast, metal-oxide particles form in flames largely because of reaction exothermicity and the strong bonding between metal atoms and oxygen. The formation of condensed-phase metal oxide can be limited by entropy effects, especially when the formation of highly order structures is not accompanied by releasing molecules into the gas phase. Other examples include the formation of silicon nitride and carbide from the reactions of silane with ammonia and acetylene, respectively, which are driven or limited by both reaction exothermicity and entropy effects.

Condensed-phase material formation from gaseous species is often kinetically controlled and made more complex if, as in soot formation, the process is entropy-driven. Consider carbon formation from propane pyrolysis. The top panel of Fig. 1 shows the enthalpy and entropy contributions to the Gibbs free energy in
each step of a possible reaction sequence. The formation of acetylene as an intermediate of molecular growth is endothermic, but its formation is accompanied with a drastic increase in the system entropy because of dehydrogenation, which leads to an overall reduction in Gibbs free energy—a phenomenon directly responsible for acetylene being the dominant hydrocarbon species in fuel-rich combustion [76, 126, 127]. On the other hand, the formation of benzene from acetylene is exothermic at the expense of a reduced entropy. Molecular weight growth from benzene to polycyclic aromatic hydrocarbons (PAHs) and solid carbon is characterized by a mild but gradual reduction in Gibbs free energy. The overall sooting process is neither exceedingly exothermic nor does it release entropy significantly. It is for this reason that the kinetics for the formation of PAHs and subsequent condensed-phase soot particles can be highly reversible.

In contrast, the energetics of metal oxide formation in flames are often simpler because the formation of these condensed-phase materials is usually loosely coupled to the flame chemistry owing to small concentrations of the metal precursors typically used in a synthesis process. Yet the formation of the condensed-phase oxide materials is usually highly exothermic. Taking titania as an example, the bottom panel of Fig. 1 shows its formation from titanium vapor. For a hydrocarbon flame doped with a small amount of a metal precursor compound, e.g., titanium tetrachloride or titanium tetraisopropoxide, the heat release from the flame facilitates precursor dissociation. Hence, this precursor dissociation endothermicity is usually inconsequential relative to the high exothermicity of the flame. The oxygen reacts with titanium to form vapor-phase titanium oxide, which further condenses owing to its small saturation vapor pressure. This process is highly favorable from the standpoint of enthalpy release, with exothermicity > 330 kcal/mol-TiO₂ at 1600 K. Unlike carbon formation, titania formation in flames is accompanied by an entropy reduction, owing to bond formation and crystallization from gas-phase species. Yet, the overall Gibbs function still progresses downhill with an overall change as large as 78 kcal/mol at 1600 K (five times that of carbon formation from acetylene). This rather large thermodynamic driving force causes titania to form with almost no kinetic complications. In fact, this analysis can be applied to a large range of flame synthesized materials with the proper precursor.
3. Nascent Soot Formation

3.1 Aromatics Formation

3.1.1 The Hydrogen-Abstraction—Carbon Addition Mechanism

The much celebrated hydrogen-abstraction—carbon-addition (HACA) mechanism, pioneered by Frenklach [89, 128-132], captures the essence of the thermodynamic and kinetic requirements for the sooting process. Soot is a ubiquitous byproduct of fuel-rich flames above a certain fuel-to-oxidizer threshold. Hence, it is a logical first postulate that the kinetic processes that drive the flame phenomenon must be related intimately to the sooting process. Factors important to both flame chemistry and soot formation are: acetylene—the most abundant hydrocarbon species—as the molecular building block, the H atom—the driving force behind chain branching and flame propagation—as the “catalyst”, and the high temperature that facilitates fast kinetics, but at the same time limits the molecular mass growth because of fragmentation of the precursor and possibly soot itself.

As precursors to soot, polycyclic aromatic hydrocarbons (PAHs) must survive from fragmentation at high temperatures. The well known Stein’s stabilomers [133] are critical to this survival [128, 129]. The most important members of the stabilomer class found in soot particles [134, 135] are pericondensed PAHs, consisting of six-membered benzenoid rings. Examples include naphthalene, phenanthrene, pyrene, and coronene. Because of their stability, the parent PAHs must be activated through H-abstraction to produce an aryl radical which in turn, allow it to react with gaseous hydrocarbon species like acetylene. All of these reactions have appreciable energy barriers and also exhibit some extent of reversibility. Hence, temperature plays a critical role in not only the rate of molecular growth, but also in the fragmentation rate.

Figure 2 shows the HACA mechanism depicted on the Gibbs free energy surface. For convenience, we chose a hypothetical mixture containing 1/7 moles of benzene, 5/7 moles of acetylene and 1/7 moles of H atom at a constant temperature of 1800 K. Molecular growth into PAHs can be seen to proceed on a rather bumpy free energy surface with a high degree of reversibility [125]. This reversibility causes aromatics formation to be highly kinetically controlled. Hence, predicting the concentrations of aromatic compounds in flames requires a rather precise knowledge about the underlying mechanism and kinetics at almost every step of the reaction sequence.
A notable advance in the kinetic development of aromatics chemistry came from the work of Dean [136] who demonstrated the importance of chemically activated reactions in combustion kinetics. This led to the work of Westmoreland et al. [137] who elucidated a number of critical chemically activated pathways to the first aromatic ring formation. Further work by Wang and Frenklach examined the thermochemical [138] and transport properties of aromatics [139], and the kinetics of chemically activated reactions for aromatics [140]. This work led to the development of a kinetic model for PAH formation [125] (which was later improved, e.g., [141]) and many variations used for the detailed modeling of soot formation.

3.1.2 Pathways Beyond the HACA Mechanism

Earlier modeling studies show that the rate of PAH formation is highly sensitive to flame temperature and more importantly, to a multitude of chemical reactions (e.g., [125]). To illustrate this point, we present in Figure 3 a sensitivity spectrum computed for pyrene production in a 90 Torr burner stabilized acetylene flame. The formation of pyrene is seen to be sensitive to a large range of elementary reactions, including those involved in the formation of the first aromatic ring, reactions governing the main flame chemistry, and aromatic ring-growth reactions. The wide spectrum of sensitivity indicates that the production of pyrene is influenced by multiple bottlenecks often because of the kinetic reversibility in the HACA mechanism. This high degree of reversibility naturally opens the HACA mechanism up to competition from other reaction pathways. In particular, it is widely accepted that resonantly stabilized free-radical species play a critical role in aromatics formation and molecular weight growth. These free radicals include propargyl, benzyl, and cyclopentadienyl. Fahr and Stein [142] suggested that the combination of propargyl radicals could lead to benzene formation. Miller and Melius [143] showed that in flames the first aromatic ring is mostly likely formed by the self-reaction of propargyl radicals. Subsequent theoretical studies by Klippenstein and Miller, spanning almost two decades [144-146], showed that the self-reaction of propargyl radicals can form a large number of rovibrationally excited complexes on the rather complicated potential energy surface shown in Fig. 4. These complexes undergo mutual isomerization eventually forming benzene through collisional stabilization or phenyl + H through C-H fission. Theoretical treatment of these reactions proves to be rather demanding. For example, the exit channel, involving the reverse of H addition to phenyl, is barrierless, and
requires use of variable reaction coordinate transition state theory [146]—an approach mastered by only a handful of experts.

Beyond the HACA mechanism and propargyl recombination, there have been a large number of reaction pathways proposed over the last decade. For example, a recent study of cyclohexane flames by Westmoreland and coworkers [147] suggests that benzene may be produced from stepwise dehydrogenation of cyclohexane, a compound and its derivatives found in many real fuels. Koshi and coworkers [148] suggested that a phenyl addition/cyclolization pathway is efficient for PAH formation and growth in benzene pyrolysis. Other recent examples include the reactions of fulvenallene with acetylene [149], cyclopentadienyl with acetylene [150, 151], and cyclopentadienyl with itself to produce naphthalene [152, 153].

3.1.3 Challenges in Accurate Prediction of Aromatics Formation

Despite all the recent advances, fundamental chemical kinetics of aromatics are in need of further research. Challenges remain especially in the context of soot precursor formation from real fuel combustion. While the HACA mechanism is likely to be the backbone in models of PAH formation, other pathways and their varying sensitivity to the fuel composition raises the question whether there can be a quantitative closure to this problem. This situation is quite unlike the kinetic knowledge needed to predict basic flame properties, such as the laminar flame speed or ignition delay, which are usually governed by just a handful number of elementary reactions common to all hydrocarbon fuels. It is not even known at present whether the number of pathways to PAHs and soot in real-fuel combustion can be treated as finite, given the large variability in fuel composition. What is troublesome additionally is the fact that the rate of PAH formation can be highly sensitive to both the main flame chemistry and the local gas temperature. An accurate prediction of PAH formation may require a more precise knowledge of flame chemistry than is currently available.

Some of the recent experimental advances will undoubtedly be instrumental in addressing the difficulties identified above. Notably, the synchrotron photoionization technique in conjunction with molecular beam mass spectrometry has proven itself to be a powerful tool for probing fuel-rich flame chemistry [147, 154-166]. Even though the molecular beam probe may perturb the flame [167], this technique allows for high molecular weight species and isomers to be probed rather quickly and accurately. As an example, Fig. 5
shows a sample series of photoionization mass spectra of flame species in the mass-to-charge ratio of 70 to 126 amu probed by Qi and coworkers [166] for burner-stabilized flames burning benzene, toluene, styrene, ethylbenzene, \(o\), \(m\), and \(p\)-xylene. Unfortunately, the data are generated at a rate faster than can be digested by theoretical and modeling studies. To better utilize these data, efficient theoretical methods beyond the approach of one-reaction-at-a-time must be developed and mastered by more than just a handful of experts.

3.2 Nucleation (Particle Inception)

3.2.1 The Three Pathways

Three conceptual pathways may be postulated for soot nucleation. As shown in Fig. 6, path A is depicted by the growth of “2-dimensional” PAHs into curved, fullerene-like structures (e.g., [85]); paths B and C involve the physical coalescence of moderate-sized PAHs into stacked clusters [131, 132, 168, 169] and the reaction or chemical coalescence of PAHs into crosslinked 3-dimensional structures [170-174], respectively. The last two paths have been discussed recently in some detail by D’Anna [92, 175]. It is known that within the HACA framework path A is too slow to account for rates observed for soot nucleation [89, 131, 132]. Ample experimental evidence shows that in premixed sooting flames the peak concentrations of PAHs drops by roughly one order of magnitude with the increment of two pericondensed rings. This dependency is illustrated in the bottom panel of Fig. 7 using data observed in several low-pressure burner-stabilized flames [159, 164, 176]. If the mole fraction of benzene is \(\sim 10^{-3}\), those of pyrene and coronene would be roughly \(10^{-5}\) and \(10^{-7}\), respectively, which are of the same orders of magnitude as the number densities of soot nuclei \((10^{11}-10^{13} \text{ cm}^{-3})\) (see, e.g., [77, 177]). Hence, soot nucleation is likely to involve moderately sized PAHs [131, 132, 168, 178, 179].

There is abundant, but mostly indirect experimental evidence supporting PAH dimerization (paths B and C) as the initial nucleation step. Examples include the observation of the bimodality in the size distribution functions of nascent soot particles in premixed flames [180, 181]. In the presence of a persistent nucleation source, the kinetics process may be described by

\[
\frac{dn}{dt} = R_0 - n_i \sum_{j=1}^{\infty} q_{i,j} \beta_{i,j} n_j ,
\]  

(1)
\[
\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} \varepsilon_{j,i-j} \beta_{j,j-i} n_j n_{i-j} - n_i \sum_{j=1}^{\infty} \varepsilon_{i,j} \beta_{i,j} n_j \quad (i = 2, 3, \ldots, \infty)
\]

where \(n_i\) is the number density of particle containing \(i\) number of monomers, \(t\) is the time, \(R_0\) is the rate for the formation of the “first” particle, and \(\beta_j\) is the coagulation coefficient. For PAH dimerization as the initial nucleation mechanism \(R_0\) is second-order in the monomer concentration, \(R_0 = \alpha \varepsilon_0 \beta_0 C_0(t)^2\), where \(\varepsilon_0\) and \(\beta_0\) are respectively the van der Waals enhancement factor of PAH collision and the rate constant of monomer collision, \(C_0(t)\) is the concentration of the monomer, and \(\alpha\) is a parameter \((0 < \alpha \leq 1)\) which accounts for the reversibility. The evolution of the size distribution may be solved to show that in the presence of a persistent nucleation source the distribution function is decidedly bimodal (Fig. 8) and independent of the value chosen for \(\alpha\). If path A is dominant, nucleation kinetics is first order in monomer concentration and distribution functions with first order \(R_0\) would quickly evolve into a unimodal distribution [180]. Hence, paths B and C leave kinetic footprints that allow them to be uniquely differentiated from path A.

Experimentally, the particle size distribution functions (PSDFs) probed by a scanning mobility particle sizer indeed demonstrate a persistent bimodality, as shown in Fig. 9 for an atmospheric-pressure ethylene-oxygen-argon flame [182]. Similar observations have been made in many other flames (see, e.g., [183-191]) and also in a jet-stirred reactor [192, 193]. For flames with nucleation intensity gradually reduced as a function of distance from the main flame, a situation encountered in high-temperature flames in which PAH fragmentation is predominant in post flames, the bimodality was observed to evolve into an apparent unimodal distribution [183], but this unimodality is the result of monomer depletion, not an indication that the kinetics of particle nucleation becomes first order towards high flame temperatures. More recent studies have shown that by reducing the observable particle size from 3 nm to 1 nm, nascent soot formed in almost all flames studied are bimodal [185]. Additional experimental evidence for PAH coalescence comes from the laser ionization mass spectrometric study of Grotheer and coworkers [194]. As shown in Fig. 10, the masses of molecular fragments ablated from soot in a 100-Torr acetylene oxygen flame exhibit an interesting periodicity with frequency around 500 amu. The distinctive feature of these fragments suggests that PAH stacks are indeed the building block of nascent soot.
Theoretical aspects of PAH dimerization as the initial step to particle nucleation (path B) were recently discussed by Herdman and Miller [169]. They proposed that the electrostatic and dispersive forces between a pair of moderate sized PAHs may be strong enough to allow binding to occur even at the flame temperature (> ~1600 K). Not yet considered is the entropy resistance to binding. The macroscopic evidence illustrating this resistance is simply the boiling point or sublimation temperature. For Stein’s stabilomers as large as coronene, the boiling/sublimation temperatures are well below 1000 K (see, Fig. 7). Hence, one would expect that at the flame temperature condensed-phase PAHs should evaporate, rather than condense into particles.

Statistical mechanical analysis supports this view. Consider the dimerization of coronene, A_7 + A_7 \rightleftharpoons (A_7)_2. The process creates 6 new vibrational modes in the dimer. Let the frequencies of these modes be \nu_i (i = 1,...,6). The rest of the vibrational frequencies in the dimer may be approximated to be equal to those in the monomers—an adequate assumption for nonbonding interactions. In addition, we approximate the rotational constants of the dimer to be one half of that of the monomer. With these assumptions, the approximate enthalpy and entropy of dimerization can be derived from statistical mechanical principles [195] as:

$$\Delta H^\circ \simeq -E_0 + \sum_{i=1}^{6} \left\{1 + \frac{1}{\exp\left[\frac{\nu_i}{k_BT}\right]} - 1\right\} \nu_i - 4k_BT$$

(3)

$$\frac{\Delta S^\circ}{R^*} \simeq \ln \left\{ \frac{2\overline{B}}{\pi \mu} \right\}^{1/2} \frac{\hbar^3 b^0}{\pi^2 (k_BT)^{1/2}} \frac{\sigma_1^2}{\sigma_2^2} + \sum_{i=1}^{6} \left[ \frac{\nu_i}{k_BT} - 1 - \ln\left(1 - e^{-\nu_i/k_BT}\right) \right]$$

(4)

where $E_0$ is the binding energy (without zero-point energy correction), $\overline{B}$ is the geometric mean of the rotational constants of the monomer, $\sigma_1$ and $\sigma_2$ are the symmetry numbers of the monomer and dimer, respectively, $\mu$ is the monomer mass, $h$ is Planck’s constant, and $p^0$ is the standard pressure of 1 atm. The rotational constant may be correlated empirically with the molecular weight $MW^\circ$ (amu) as $\overline{B}(\text{cm}^{-1}) \simeq 1510 \times MW^\circ^{-2.125}$ using values from ref. [196]. Figure 11a shows the Gibbs free energy change for coronene dimerization as a function of temperature, where $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Here we chose a mean value of $\overline{\nu} = 200$ cm$^{-1}$ for the 6 vibrational frequencies in eqs 3 and 4, while recognizing that choosing such a
small frequency value overestimates the entropy of the dimer, and thus favoring dimerization. For example, with $\nu = 500 \text{ cm}^{-1}$, $\Delta G^\text{r}$ becomes appreciably more positive at the same binding energy, as shown in Fig. 11a. Additionally, we choose $\sigma_2 = 1$, which again favors dimerization by eliminating any symmetry in the dimer.

The self-binding energy is $E_0 = 24.5 \text{ kcal/mol}$ for a pair of coronene monomers [169]. Although this energy value may seem to be large enough, the entropy effect in fact does not allow the dimer to survive without fragmentation at combustion temperatures ($>1500 \text{ K}$). For example, at 1600 K the equilibrium constant of dimerization ($K_p = \frac{p_{A,A}}{p_{A}^2}$) is only $4 \times 10^{-24} \text{ atm}^{-1}$. In fact, the temperature for $K_p$ to cross over the characteristic value of $10^{-6} \text{ atm}^{-1}$ is rather low† and equal to 725 K. Using $K_p \sim 10^{-6} \text{ atm}^{-1}$ as the critical condition for dimerization, the binding energy of a pair of coronene must be at least 60 kcal/mol to allow for sticking at or above 1500 K. According to Herdman and Miller [169], the binding energies of ovalene and circumcoronene are 35 and 62 kcal/mol, respectively, but even they are not strong enough to push the equilibrium constant above $10^{-6} \text{ atm}^{-1}$ at combustion temperatures. This is because an increase in mass $m$ and a decrease in the rotational constant $B$ cause the entropy of dimerization to decrease further. Hence, an increase in the binding energy is offset by a decrease in the entropy in the dimer. As shown in Fig. 11b, dimerization of even circumcoronene is difficult above 1335 K. Taking the binding energy for homo-molecular pairs in the limit of infinite size, 1.2 kcal per mol of C atom [169, 197, 198], we found that the monomer size must be at least C$_{100}$ for dimerization to be possible at 2000 K.

The above discussion is of course subject to the assumption that dimerization is a phenomenon governed by equilibrium kinetics. To understand the non-equilibrium dynamics of PAH collision, Schuetz and Frenklach [179] carried out molecular dynamics simulation. Their results demonstrate that the collision of a pair of PAH molecules can produce a long lived, rovibrationally excited dimer. The transient binding is facilitated by the excitation of internal rotation, resulting in a dimer with lifetime much longer than the collision time scale [179, 199]. Hence, the dimer behaves as if it is a gas-phase species open to reactions with, for example, the H atom, which allows for covalent bond formation across the two PAH molecules. This

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† The characteristic $K_p$ value may be estimated by assuming the partial pressures of the monomer and dimer to be equal and the partial pressure of the monomer is $10^{-6} \text{ atm}$, which is typical for atmospheric-pressure sooting flames.
hypothesis is certainly plausible, but it remains unclear whether a dimer would survive its multiple collisions with gas molecules within their lifetime, keeping in mind that the H atoms are in concentrations substantially lower than many other gas molecules. Clustering of several homo- and hetero-molecular PAHs have also been examined by Violi and coworkers using molecular dynamics [200], but again the clustering process is contingent upon the initial clusters surviving collision with flame gas molecules.

An alternative hypothesis is that the initial particles contain aromatic structures joined by aliphatic linkages (path C). These structures can be produced via a “chemical” coalescence mechanism [170-174] involving reactions between aromatic molecules with an aryl radical. This mechanism is plausible in regions close to the main flame zone where H atoms are abundant, allowing aryl radicals to be generated through the H-abstraction reactions. But it cannot explain the persistent nucleation of soot well into the post flame zone [180, 183], where the H atom concentration is too low to initiate such reactions. The above arguments leave us with the notion that the soot nuclei may be formed through a mechanism which is not yet known. This mechanism is likely to involve moderate-sized PAH-PAH interactions, but such interactions must be as strong as those seen in typical covalent bonding.

3.2.2 The Role of Aromatic π Radicals

A series of recent theoretical materials studies predicted that many aromatic molecules have radical or diradical characteristics resulting from localized π-electron states. These studies originated from interests in polyacene as a material for a new generation of organic light emitting diodes and organic semiconductors and capacitors. If these predictions are true, they may hold the key to a satisfactory explanation of soot nucleation and some of the observations concerning soot mass growth, a topic to be discussed later. These studies show that, starting from anthracene, polyacenes with an increasing length show a vanishing HOMO-LUMO gap,* or a diminishing bandgap [201-203]. Furthermore, ground-state polyacenes with more than 5 or 6 rings are open-shell singlet diradicals [204-210] due to a disjoint diradical with partially occupied orbitals [205]. These studies are not without controversy. In a very recent paper, Haigató et al. [211] argued that the

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* Energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital.
ground-state polyacenes are close-shell singlets, but also that the adiabatic $S_0$-$T_1$ excitation energy is small (17 and 13 kcal/mol for hexacene and heptacene, respectively). This small $S_0$-$T_1$ energy splitting suggests that triplet polyacene diradicals can form at high temperatures through vibrational excitation if intersystem crossing is allowed. The relatively high reactivity of central-ring carbon atoms in anthracene, pentacene and tetracene have also been well documented [212-218].

Another series of studies on PAHs shed an even more interesting light on the problem. It was predicted almost 20 years ago that the zigzag edges of graphene have localized $\pi$-electronic states [219, 220] and can contain significant radical characteristics. The predictions have sparked intense interests in tailored synthesis of nanographenes for nonlinear optics applications [221, 222], but they have not received enough attention in soot research. More recent studies show that graphenes with zigzag edges have an open-shell singlet ground state [223, 224]. Finite-sized graphenes are predicted to have the same radical [225-231] or even multiradical characteristics [232]. Consider a generic PAH structure given in Fig. 12. PAH(1,0) with $i_1=1$, 2 and 3 represents benzene, naphthalene, anthracene, respectively; and PAH(3,1) is phenanthrene. In this figure, the value of $y$ was determined from the occupation numbers of the HOMO and LUMO of unrestricted Hartree-Fock (UHF) natural orbitals and represents the diradical characteristic calculated by Nagai et al. [232]. The value ranges from 0 for closed shell singlet to 1 for a singlet diradical. As seen, PAH(4,1) (butacene) and PAH(2,3) (perylene) start to show some radical characteristics. PAH(3,3) has a significant radical character and PAH(4,3) is almost a pure diradical localized at the zigzag edges. Additional studies suggested that the diradical characteristics can be induced or promoted by functional groups. For example, bis(pyren-4-yl)ethyne, i.e., two pyrene rings bound by ethynyl, $-C≡C-$, also exhibited a radical characteristic similar to butacene [222]. Scanning tunneling microscopy/spectroscopy evidence appears to support the view that the electronic states for zigzag-edged graphenes are localized [233, 234]. In particular, armchair edges are generally defect free, whereas zigzag edges tend to be short and defective, and hence more reactive compared to armchair edges [221].

These $\pi$ radicals are the obvious candidates for significantly enhanced bindings in PAH clustering. Perylene can form from the reaction of a naphthyl radical with naphthalene. Likewise, PAH(3,3) can form from a pair of anthracene. The fact that these species are barely detected in flames could mean that they bind
immediately with other species upon formation. Because the radical characteristics originate from localized \pi\text{-}electrons, it may be speculated that these aromatic molecules can form bonds with any aromatics through \pi\text{-}electron interactions over a stacked geometry with strength similar to that in a covalent C-C \sigma\text{-}bond. This mechanism would also explain why PAHs form stacks, whereas T-shaped dimer configurations are predicted to be more stable than stacked configurations for benzene and coronene (see, e.g., [235]). What remains unknown, yet critical to this hypothesis, is the binding energies of \pi\ radical bearing aromatic molecules with other PAHs. Other critical questions include whether the \pi\ radical characteristics are retained and can propagate over a stacked structure, as this would clearly enhance the binding over many PAH layers.

3.3 Mass/Size Growth, Chemical Composition and Morphology

3.3.1 The Current Understanding

The existence of \pi\ radical PAHs may also explain some of the recent and unexpected observations of soot mass growth made in premixed burner-stabilized flames. As a background, it is the current understanding that acetylene is the dominant mass growth species [76, 77, 236]. The basis of today’s modeling science for soot mass growth is formed from the work of Harris who determined the empirical rate constant of the acetylene-soot surface reaction [126, 127, 237], and more importantly the HACA mechanism of Frenklach and coworkers [89, 131, 132] in which the surface reaction rates are described at a fundamental level. The HACA mechanism describes the soot surface as composed of aromatic basal planes and edges sites. Mass growth on soot surface requires H-abstraction to form an aryl radical site, followed by acetylene attack in a manner similar to the gas-phase mechanism. Excluding soot oxidation, we have

\[
S_-H + H^* \leftrightarrow S^* + H_2 \quad (5)
\]
\[
S^* + H^* \rightarrow S_-H \quad (6)
\]
\[
S^* + C_2H_2 \rightarrow S_{n+2}^-H + H^* \quad (7)
\]
In the above reactions, Si represents an edge C atom on the surface of a particle containing i number of C atoms. Additionally, reactions or condensation of PAHs onto soot surfaces also contribute to soot mass, and the relative contributions appear to be dependent on the flame condition [89, 131, 132].

A steady-state analysis of reactions 5 through 7 yields the surface radical site density as:

\[
[S_r \cdot] = \frac{k_{5, r} [H \cdot]}{k_{5, b} [H_2] + k_{6} [H \cdot] + k_{7} [C_2H_2]} [S_r \cdot-H],
\]

(8)

where k’s are the rate constants. The mole fractions of H_2 and C_2H_2 are generally around 0.1 and 0.05 respectively in the post flame region of typical sooting flames (see, for example, [137, 176, 177]). For 1600 ≤ T ≤ 2200 K, \( k_{5, b} / k_{5, r} \sim 60 \), 10 ≤ \( k_{6} / k_{5, r} \) ≤ 100 and \( k_{7} / k_{5, r} \sim 1 \) [125, 140]. Since \([H_2] \sim [C_2H_2] \gg [H \cdot]\), we find:

\[
[S_r \cdot] \approx \frac{k_{5, r} [H \cdot]}{k_{5, b} [H_2]} [S_r \cdot-H].
\]

(9)

In other words, the surface radical site density is governed by the equilibrium constant of reaction 5 and by the availability of the H atom in the flame. The surface growth rate due to acetylene addition on the radical site is thus proportional to \([H \cdot]\):

\[
\omega_s \left( \frac{\text{mol C-atom}}{\text{cm}^3 \cdot \text{s}} \right) \approx 2k_r \frac{k_{5, r} [H \cdot]}{k_{5, b} [H_2]} [S_r \cdot-H] [C_2H_2].
\]

(10)

It is well understood that while the soot mass is determined by surface reactions, the ultimate size of soot particles is governed by simultaneous particle-particle coagulation [131]. Transmission electron microscopy (TEM) studies of mature soot show multiple nuclei centers spaced ~5 to 10 nm apart within a primary particle (see, e.g., [238, 239]). Primary soot particles are generally spherical because of the combined effect of surface growth and coagulation [240, 241]. Coagulation immediately after nucleation occurs predominantly between a pair of large and small particles because their collision frequencies are enhanced by the large cross section area of the former and the high velocities of the latter. This coagulation process forms primary particles with slightly aggregated structures (cf, the upper panels of Fig. 13). Meanwhile, surface reactions act
on these aggregated structures, “smooth” the surface and produce spherical or nearly spherical particles (the lower panels of Fig. 13). The small particles, referred to as the collector particles by Frenklach and coworkers [240-242], are essentially those that make up the small particle tails seen in Fig. 9.

3.3.2 Recent Developments in Experimental Methods

The mechanistic understanding of soot mass growth discussed above have inspired the development of a range of new experimental techniques over the last decade, allowing the mechanisms to be examined at much higher resolutions than previously possible. For example, small angle x-ray scattering (SAXS) [243-245] and small angle neutron scattering (SANS) [246] techniques have been utilized which have an advantage over light extinction and scattering techniques in that they do not require a precise knowledge of the complex refractive index of soot material in data interpretation. A variety of advanced aerosol experimental techniques have been utilized to probe soot surface properties, oxidation and reactions [247-250]. In this paper the discussion is focused primarily on findings made with inserted probes connected to mobility particle sizing devices (see, e.g., [180-189, 192, 251-260]). The technique maps the evolution of the size distribution of nascent soot particles and particles as small as 1.6 nm can be detected [185, 258]. The same technique has been applied to the analysis of metal oxide and other nanomaterial formed in flames [256, 261-263].

In general, the probe sampling technique utilizes a tubular probe crossing the flame. A gas sample from the flame zone is continuously drawn through a pin hole on the side of the probe that is in turn, delivered to a scanning mobility sizer by a carrier gas for particle sizing and counting. The technique has several limitations and requires some care in experimentation and data interpretation. For example, the PSDF could be perturbed by particle-particle coagulation in the probe. This problem has been resolved with the use of large ratios of dilution of the gas sample by a carrier gas [181, 187]. Introducing a finite-size probe into the flame inevitably disturbs the local gas temperature and perhaps more importantly, the flow field, leading to local flow stagnation. One way to handle this problem is to use the probe as the stagnation surface in a burner stabilized flame [182], so that its impact on the flow field and temperature may be quantified numerically using an axial symmetric stagnation flow code (e.g., OPPDIF [264, 265]). Figure 9 shows snap shots of the gas temperature profiles and PSDFs for a variety of burner-to-probe separations. The fact that
the experimental and computed temperature profiles are in close agreement suggest that the thus-measured PSDFs may be simulated without having to worry about mismatches between the experimental and computational boundary conditions. It eliminates the need to artificially shift the zero time for particle nucleation as often done in previous modeling efforts (see, e.g., [266]).

Another issue is that the particle size sampled is the mobility size, which can deviate from the true size. Mobility size is derived from the settling velocity of a charged particle in an electric field experiencing an electric static force in balance with fluid drag. The drag force is traditionally described by the Cunningham slip correction [267] applied to the Stokes drag force in the continuum regime [268]. The slip correction yields a relationship between the electric mobility $Z$ with the mobility diameter $\bar{D}_p$ [269]. In the large Knudsen number limit, this relation takes the form of:

$$ Z = \frac{q}{3\pi\mu\bar{D}_p/(1.626\text{Kn})}, $$

where $q$ is the elementary charge, $\mu$ is the viscosity, Kn is the Knudsen number, and 1.626 is an empirical parameter [270].

To determine the relationship between the physical size and the mobility size, Li and Wang [271-275] carried out a gas-kinetic analysis by considering the effects of dispersive interactions between the particle and gas and the transition of specular to diffuse scattering upon gas-particle collision [275, 276]. The results show that in the large Kn limit the electric mobility $Z$ may be expressed by:

$$ Z = \frac{3}{2} \frac{q}{\sqrt{2\pi m_r k_B T N_g D_p^2 \tilde{\Omega}_r^{(1,1)r}}}, $$

where $m_r$ is the gas-particle reduced mass, $k_B$ is the Boltzmann constant, $N_g$ is the gas number density, $D_p$ is the particle diameter and $\tilde{\Omega}_r^{(1,1)r}$ is the reduced collision integral—a parameter resulting from the dispersive force and the specular-diffuse scattering transition. For carbon particles, the physical diameter may be parameterized as a function of the mobility diameter [266]:

$$ \frac{D_p}{\bar{D}_p} = \left(1.072 - \frac{0.493}{\bar{D}_p}\right) \times \tanh\left(1.457 + 0.0109\bar{D}_p\right), $$

21
which is valid for $2 < \bar{D}_p \text{ (nm)} < 100$. The above equation shows that for primary soot particles the mobility diameter is quite close to the physical diameter: $D_p/\bar{D}_p = 0.8, 0.94$ and $0.98$ for $\bar{D}_p = 3, 10$ and $20 \text{ nm}$, respectively.

3.3.3 General Feature of Particle Size Distribution Function

In general, PSDFs observed for nascent soot are bimodal. These distributions may be fitted by a bi-lognormal function [184] or by a sum of a power-decay function and a lognormal distribution [180]. As shown in Fig. 14, flame temperature has dominant effects on the shape of soot PSDF. Over the particle diameter range probed, nascent soot formed in a lower temperature, ethylene-oxygen-argon flame (1660 K) has a substantially stronger bimodal feature than that in a higher-temperature flame (1898 K) [184]. Numerical sensitivity analyses show that the PSDF shape is sensitive to the various kinetic parameters in the HACA–based soot model [266], as seen in Fig. 15. For example, the particle size at the trough increases with an increase in the nuclei or “collector” particle size, and/or in the nucleation rate. Hence, the experimental evidence suggests that the nuclei in the lower-temperature flame and/or the nucleation rates are substantially larger than those in the higher temperature flames. Though this behavior is being understood kinetically, these observations illustrate the usefulness of the detailed PSDF data in soot model development and validation. It is possible that the various model parameters, including the sticking probability of particle collision and gas-surface reaction rates, can be obtained through an inverse problem that compare detailed models against observations of a set of well characterized flames. Indeed, attempts have been made to scrutinize model parameters through comparisons of simulated PSDFs with measurements. Examples include the use of a stochastic approach by Kraft and coworkers [180, 266, 277-279], a hybrid method of moments by Blanquart, Pitsch and coworkers [280] and the various sectional methods by D’Anna [281-284], Mauss [285] and their coworkers.
3.3.4 Evidence of Aliphatics in Nascent Soot and Soot Mass Growth without H Atoms

Despite all the modeling advances, additional elements or processes must be considered to account for rather unexpected observations made in recent flame studies [246, 256, 257]. In these studies, nascent soot formation in an ethylene-oxygen-argon flame ($\phi = 2.5$) was cross-examined with a range of experimental techniques. Corroborating evidences indicate that (1) nascent soot can be rich in aliphatics; (2) soot mass can grow without the presence of gas-phase H atoms. At present, neither observation can be explained by detailed models of soot formation. Fig. 16 presents these experimental evidences, which were derived from measurements of particle size both by mobility sizing [257] and TEM [256], chemical composition by photoionization aerosol mass spectrometry (PIAMS) [257], soot volume fraction [256] by small angle neutron scattering (SANS) [246] and thermocouple particle densitometry (TPD) [257]—a method developed in Ref. [286].

The onset of soot nucleation starts in zone II as marked in Fig. 16, when the PSDF is characterized by a sharp, exponential decay curve with particles mostly below 5 nm in size. The TEM image of particles collected thermophoretically at nearly the same flame position shows that the apparent size is substantially larger than those determined by particle mobility, indicating that the particles flatten on the TEM grid upon impact. In other words, these young particles are liquid-like rather than being carbonized and rigid, as will be discussed later. Zone II ends with the appearance of doublet aggregates. At that point, the PSDF starts to segregate into two lognormal functions. By using a soft particle fragmentation technique, PIAMS measurements showed that the soot in zone II is composed of mostly PAHs from pyrene to ovalene. However the PIAMS spectrum also indicates the presence of an appreciable amount of aliphatic components. Compared with PIAMS, other techniques, including laser ablation particle mass spectrometry [287] and laser desorption/laser ionization mass spectrometry [288] are probably too destructive to the soot samples and thus insensitive to aliphatics. The presence of aliphatic components is consistent with the liquid-like character observed by TEM.

In zone III, the PSDFs are distinctively bimodal and the corresponding TEM image shows aggregates consisting of 10s’ of primary particles. Interestingly, the PIAMS result shows a large amount of aliphatics compared to aromatics in soot samples collected in zone III. The atomic C-to-H ratio calculated from the
mass spectrum is around the value of unity. Under this C/H ratio, the mass density of soot material $\rho_i$ is expected to be substantially lower than that of mature soot ($\rho_i = 1.8$-$2.0$ g/cm$^3$) [77]. Indeed, the volume fractions of soot measured by TPD and SANS can only agree with each other if the SANS data interpretation assumes $\rho_i = 1.5$ g/cm$^3$ and $C/H = \sim 1$ [256]. Another important observation is that soot volume fraction continues to increase in zone III, even though the gas temperature drops to 1450 K. This is rather unexpected in the context of the HACA mechanism. Detailed modeling suggests that the concentration of the H atoms in zone III is too small to account for radical production on soot surfaces through eq 9. Hence, other mechanisms must be responsible for mass growth in this later part of the flame.

Additional studies have shown that the above observations are not limited to that specific ethylene flame. Figure 17 shows the TEM image of particles collected from a C$_2$H$_4$-O$_2$-Ar flame at equivalence ratio of 2.07 with a higher flame temperature ($T_f = 1736\pm50$ K) [184]. As it can be seen in the TEM image, the particles again spread on the substrate upon impact, forming a “sunny-side-up” structure or much like the interaction of molten wax droplet with a surface. Atomic force microscopy (AFM) probing of thermophoretically collected particles—a technique pioneered by D’Alessio and D’Anna [289]—shows impact crater-like morphologies typical of molten wax droplets [184]. The height ($h$) to width ($a$) ratio varies from 0.02 to 0.4, depending on the particle size [185].

The FTIR method has been employed previously to probe the chemical makeup of soot and other condensable materials from flames [290-292]. In recent studies, Cain et al. [293, 294] used this technique in conjunction with a micro-orifice uniform deposition impactor. Their results again showed aliphatic components to be dominant in nascent soot. The aliphatic-to-aromatic C-H ratios are around 4 with little dependency on the size and age of the particles [294]. With an even softer ionization method, the thermal-desorption, chemical ionization mass spectrometry technique yielded evidence in support of the PIAMS and FTIR studies. In particular, a broad range of molecular components were detected for nascent soot with molecular weight spanning from 100 to 900 amu [294]. Though some PAH stabilomer features are evident on the mass spectrum, the broad mass spectrum feature suggests that most of the PAHs in nascent soot are alkylated. Raman spectroscopic evidence [291] suggested that these aliphatic groups are bound to the particle surfaces as alkyl or alkenyl functionalities.
The experimental evidence just discussed may be summarized in Fig. 18 in a plot similar to those found in Calcote [76] and Bockhorn [82]. As shown, converging evidence indicates that nascent soot formed in laminar premixed flames has a core-shell structure: an aromatic core composed of PAHs ranging from pyrene to ovalene, and an aliphatic shell responsible for spreading into flattened structure upon thermophoretic impact. The aromatic core is produced in the early stages of the flame where the gas temperature is high, while the aliphatic shell forms later on the aromatic substrate when the gas temperature becomes somewhat lower. At present, it is unclear whether the picture presented in Fig. 18 is applicable to soot produced in other types of flames or at elevated or reduced pressures.

3.3.5 Persistent Free Radicals

The existence of aliphatics in nascent soot may well be related to their ability to undergo mass growth in the absence of gaseous H atoms. To start with, the core is aromatic in nature. Following our hypothesis about the involvement of $\pi$ radical in soot nucleation, it is not difficult to speculate that these $\pi$ radicals persist into young soot particles consisting of stacks of PAHs. As discussed by Cain et al. [293], the aliphatic shell will generally form in a relatively cool flame environment depleted of gas-phase H atoms, but the persistent $\pi$ radicals in the aromatic core allows for reactions with unsaturated hydrocarbons (e.g., acetylene), and thus alkylating the core.

In fact, the existence of persistent free radicals (PFRs) in soot has already been discussed by Dellinger and coworkers [295, 296], who attributed the origin of PFRs however to resonantly stabilized free radicals of semiquinone and phenoxy origins. PFRs are reactive chemical species having unpaired electrons or characteristics of unpaired electrons. These free radicals can exist in substantial concentrations due to resonance and electron delocalization. They can also be stabilized by other mechanisms. For example, on the basis of density functional theory calculations, Dames et al. [297] proposed an additional source of PFRs. These are acenaphthene or hexaphenylethane derivatives with weak central carbon-carbon bonds that may be easily cleaved to yield triplet diradicals. Central C-C fission into singlet diradicals may lead to even lower bond energies, though this has not been calculated. Yet, $\pi$ radicals remain to be the most plausible PFR candidate.
Regardless of the chemical origin and nature of PFRs, there is ample evidence that support its existence in soot. In ethylene-air counterflow diffusion flames, the soot volume fraction observed towards the stagnation surface can be predicted only if soot retains a radical character [298]. Electron Spin Resonance spectra of anthracite, a coal containing little to no oxygenated compounds, show a measurable concentration of free radicals [299]. Most importantly, soot formed from the pyrolysis of ethylene, acetylene, and various jet fuel surrogates also show appreciable amounts of free radicals associated with carbon atoms [300]. The Landé g-factors reported for such soot samples suggest that the radicals are of aromatic π nature and the spin concentrations can be as high as $10^{21}$ per gram of the residues insoluble in dichloromethane. Assuming the residue is made of carbon only, the number of spins is roughly 1 per 50 atoms, or one free radical for each pair of PAHs of the size of coronene.

If π radical PAHs indeed exist in nascent and mature soot, this phenomenon would hold the key to a range of health and environmental effects of soot. The uptake of persistent free radicals through the respiratory system can lead to the production of hydroxyl radicals harmful to cellular components, subsequently increasing risk of lung cancer [295, 301]. Soot exhaust from aircraft engines is thought to be responsible for contrail formation in the wake of an aircraft [69, 302, 303], thus perturbing the global and regional climate. Indeed, evidence shows that depending on the conditions in which it forms, soot has the ability to uptake substantial amounts of water on both its surface and internally [302-304]. Here, uptake of water may be facilitated by the surface radical sites [297]. Because of local electron deficiency, these radical sites allow for tight hydrogen bonding with water molecules. For example, the theoretical binding energy of hydrogen-like bonds between a methyl radical and water is 1.5 kcal/mol [305, 306] which increases to 2–4 kcal/mol for C$_1$-C$_4$ alkyl radicals [306, 307]. Hence, if PFRs exist on soot surfaces, they would make these surfaces attractive to water under atmospheric and tropospheric conditions.

3.4 Implication in Modeling and Unresolved Problems

The core-shell structures observed in nascent soot should have a notable impact on soot modeling. Because of the chemical heterogeneity of nascent soot and its possible dependence on particle size and time-
temperature history, future soot models must be able to predict the chemical composition of nascent soot and its size distribution. These models will need to delineate the differences in the mechanism and reaction kinetics of mass growth over different surfaces. This fundamental need echoes future practical needs in engine design. This is particularly true considering that current particulate emission regulations (e.g., PM2.5) are based solely on the mass of particles emitted and not on the sizes or chemical composition. However, the environmental and human health effects of soot emission are more directly related to the particle size distribution and chemical composition than particle mass [59, 308-311]. For example, ultra small particles do not contribute much to particulate mass, but they can penetrate deeper into human airways and be absorbed and transported more effectively into the blood stream. The propensity of soot to act as cloud condensation nuclei is also related to particle number density and surface chemical composition. Given these considerations, it is not difficult to foresee that future regulatory developments and thus the models of soot formation will have to take into consideration the size distribution of particles and their chemical makeup.

Indeed several research groups have embarked on detailed modeling efforts aimed to add chemical resolution to nascent soot particles [179, 240-242] and to resolve chemical composition, size distribution, and morphology at different stages of soot formation (see, e.g., [92, 174, 175, 200, 277, 278, 312-316]). Using a combined kinetic Monte Carlo and molecular dynamics approach, named Atomistic Model for Particle Inception (AMPI), Violi and coworkers [316] probe the structure of incipient soot in a benzene flame. As should be clear from the examples shown in Fig. 19, AMPI provides atomistic level structures and morphological information including density and porosity as soot precursors evolve into a three-dimensional structure. Kraft and coworkers advanced a PAH-PP (primary particle) model [278, 315] which can follow the evolution of the chemical composition of nascent soot during its growth process. As shown in Fig. 20, the method allows them to provide detailed soot composition of the type that can be observed by photoionization mass spectrometry [317]. Though still in their infancy, these numerical methods will likely lead to the next generation of soot models capable of simultaneously predicting the evolution of particle size distribution, chemical composition, and morphology.

What remain unresolved are the formation mechanisms of stacked PAHs and the aliphatic shell in nascent soot. To start, it would be useful if the molecular structures with localized \( \pi \) electronic states and
their mechanistic relationship to Stein’s stabilomer sequence can be identified. This will serve as a starting point for these π radical PAHs to be considered in detailed reaction models of PAH formation. Additionally, the nature and magnitude of the forces that bind these aromatic molecules to each other and with the stable Stein’s stabilomers and non-aromatic species need to be determined. While the underlying questions can be addressed by electronic structure calculations, the fundamental difficulty lies in the fact that the widely used methods such as the density functional theory is unlikely to provide accurate answers for this problem. More accurate, multiconfigurational methods may be required, but such methods are still too computationally costly for moderate-sized PAHs. Clearly, we are in need of new computational chemistry capabilities that go well beyond those currently available in standard commercial packages.

4. Metal Oxide Nanoparticle Synthesis and Applications

The thermodynamic arguments given earlier indicate that a large range of nanoparticles and nanomaterials can be synthesized in combustion flames if the initial and final thermodynamic states are chosen properly. Despite all the advances in flame synthesis, the longevity and vigor of this research area rely largely on the performance of the materials which are produced. Disciplinary barriers keeps materials scientists away from flame synthesis, as mastering the technique of flames require basic knowledge in combustion chemistry, fluid mechanics and heat transfer - subject areas not traditionally part of the materials science curriculum. Yet, it is this author’s belief that the flame process holds the key to inexpensive manufacturing of energy-conversion materials for use in photovoltaics, rechargeable batteries, and combustion pollutant sensing. As an example, this section will illustrate a flame method for producing mesoporous titania (TiO2) thin films for dye sensitized solar cells and chemical sensing.

As a versatile material, titania attracts much attention in areas critical to future energy conversion technologies, including photocatalysis [318] as in electrochemical photolysis of water (the Honda-Fujishima effect) [319], dye-sensitized solar cells (the Graetzel cell) [9], gas sensing [320, 321], and catalysis [322]. Titania has a total of eight crystal phases with rutile and anatase being the most common. In an oxygen rich environment and below a crystalline size of 14 nm, anatase is the preferred thermodynamically metastable
phase [323]. In general, anatase has properties more attractive than rutile for applications in catalysis, photocatalysis and solar cells.

Following the pioneering work of Ulrich [12, 324], flame synthesis of titania has been studied extensively (e.g., [116, 117, 325-327]) with notable contributions from Pratsinis [14, 328-331]. Hence, titania serves as a good example to illustrate the applications of combustion synthesized materials in a broad range of energy science beyond combustion. For example, the applications of titania for chemical sensing and as a catalyst have been discussed by Pratsinis and coworkers [14, 332]. As in this and other cases, flame synthesized metal oxide particles are usually of higher crystallinity and phase purity, and when the flow field and particle time-history is tightly controlled, they attain exceedingly narrow size distribution when compared to other synthesis techniques [116, 333].

As discussed earlier, the thermodynamic driving force for titania formation in flames from typical precursors is rather simple. Hence, a fine control of the particle size distribution, crystal phase and purity, and crystallinity is almost entirely dependent on the flame design and particle collection method. Since the application of titania typically requires the particles to form a thin, porous film, a direct, one-step process of particle synthesis followed by film deposition would be economically beneficial. Yet, the problem is challenging because of the requirements for ultrafine particles with tunable sizes, narrow size distribution (at least for the purpose of fundamental study of the particle size effect), uniform film thickness and porosity, high crystallinity and phase purity. To obtain uniform particle size, the flame flow field must be uniform and low-dimensional. To synthesize ultrafine particles at reasonable production rates, the residence time must be kept at a few milliseconds. Deposition of a uniform particle film requires strategic substrate placement with a consideration of the flow field. Ensuring high crystallinity and phase purity requires a uniform temperature in the particle forming region and then a sharply reduced temperature near the substrate.

Studies into soot formation and laminar flames in fact have offered many critical insights into viable solutions to the above problems. Pseudo-one dimensional premixed flames have been traditionally used to follow the kinetics of soot formation with small fluid mechanic complications. These flames turn out to be advantageous for particle synthesis because of uniform time-history across the flame. In particular, flames stabilized through flow stretch by impinging a laminar flat jet against a surface satisfy all the particle synthesis
and film deposition requirements mentioned earlier. Although premixed stagnation flame was developed largely for probing flame kinetics [334-336], they prove to be ideal for particle synthesis because of their low-flow dimensionality. Another advantage is that this setup may be scaled up into an industrial process [337]. Panel (a) of Fig. 21 shows such a flame set up. The flow diverges under the stagnation surface. The flow stretch typically stabilizes the flame a few millimeters from the surface. If the unburned gas is doped with an organometalic precursor, it decomposes and is oxidized immediately in the flame region. Since most metal oxides have small vapor pressures, they condense into nanoparticles, again through nucleation, surface growth and coagulation. If the nanoparticles can be kept in the molten state, coagulation leads to production of single droplets, preventing aggregates from forming. If the stagnation surface is kept cool, the large thermophoretic force established between the flame and surface transports the particles quickly towards the surface. For the setup depicted in Fig. 21, the residence time may be kept as small as 1 ms, limiting particle growth and aggregation [333, 338]. The molten droplets crystallize adjacent to the surface as the gas cools and the particles deposited on the surface forming a thin film. This deposition process may be made continuous by translating or rotating the substrate as shown in Fig. 21. A similar technique has been developed for turbulent premixed swirl flames [339].

Particles so synthesized are narrowly distributed with a tunable median particle size, mostly single crystals, and with high phase purity, as shown in panel (b) of Fig. 21 using titania nanoparticles as an example (see, also [262, 333, 338, 340]). Also shown in the same panel is an SEM image of a mesoporous film of anatase titania grown by this approach, depicting its uniform and porous nature. These films have shown great promise for significantly enhanced gas sensing sensitivity and stability, as shown in panel (c) of Fig. 21. The titania film undergoes changes in its ohmic resistance due to the reduction of its surface by CO. The conduction band in the titania film, previously depleted of free carriers, becomes increasingly populated with free electrons as surface oxygen is removed, leading to an increase in electric conductance. As shown, exposing the film in 5 PPM CO can cause the film resistivity to drop by a factor of 2 at 500 °C [263], indicating that the film can achieve sub PPM level of detection for such combustion emitted pollutants as CO.

In addition to sensor applications, flame process may also prove to be beneficial to thin-film solar energy conversion. Recent studies have shown that dye sensitized solar cells (DSSCs) can achieve photoconversion
efficiencies well above 10% [341] and they can also be produced substantially cheaper than other types of thin-film solar cells. This progress has attracted a tremendous amount of research. One of the most important research areas is fabrication of mesoporous titania layer as the electron diffusion layer.* The flame method may prove to be the most important and inexpensive fabrication method to achieve high surface area and good electron diffusivity, as these properties are desirable for achieving high photoefficiencies. Indeed, flame fabricated titania films have shown to provide good performance, as shown in panel (d) of Fig. 21, with photoefficiency as high as 9% [17] for cells not yet optimized.

5. Concluding Remarks

Nanoparticle formation in flames is a ubiquitous combustion phenomenon rich in its research history. Although the driving force in soot research has been to understand and predict its formation, much of the future value in this field lies in applying this knowledge beyond its disciplinary boundaries. Phenomena closely related to soot formation include its subsequent health and climate effects as they may arise from fundamental chemistry intimately related to that of soot formation in flames. They also include the inexpensive synthesis of functional materials for a broad range of traditional and renewable energy applications.

Despite the tremendous advances in the modeling science of soot formation, critical gaps and thus challenges remain in almost every one of the early steps of soot formation. In the area of soot precursor formation, the key points we have learned are: the HACA mechanism and reactions involving resonantly stabilized radicals play critical roles in the formation of pericondensed PAHs. The detailed pathways and rates in a flame are highly dependent on the local flame conditions, the fuel structure and composition. Given that a multitude of reaction pathways may exist for PAH formation, the problem cannot have a closure at the quantitative level without drastic improvement of the current one-reaction-at-a-time approach. This is true especially in the context of the recent real-fuel combustion initiatives, in that PAH formation can be

* Titania is a wide bandgap semiconductor (~3.2 eV), and it does not absorb visible light appreciably. To provide active electrons, a sensitizing dye is immobilized on its surface. Photoexcitation of the dye is followed by charge transfer and injection of electrons into the titania conduction band. Electrons diffuse through the titania layer and are collected on a transparent conductive substrate.
sensitive to certain compounds even if their concentrations are rather small in a fuel mixture. With data emerging from advanced experimental techniques, such as the molecular-beam synchrotron photoionization mass spectrometry, new theoretical methods are needed that can allow us to efficiently narrow down the many possible reaction pathways so that the kinetics of these reactions can be studied in some forms of chemical isolation.

Phenomenologically, the nucleation of soot in flames is decidedly second order in the monomer (PAH) concentration. Additionally, by comparing the concentrations of PAHs and soot nuclei, particle nucleation starts predominantly through clustering of moderate-size PAHs. However, we do not yet know the binding force that keeps the initial dimers, trimers, and clusters of PAHs together. There is conclusive evidence that young soot particles formed in premixed flames have a core-shell structure, with the core being aromatic in nature and the shell being aliphatic. Again, the nature of binding between aromatic and aliphatic constituents remains unclear. The mass growth of soot can proceed without the presence of gas-phase H atom, indicating that the HACA mechanism may be incomplete to describe the entire process of soot formation. It is suggested that radicals due to localized $\pi$ electrons in PAHs may hold the key to these questions – a hypothesis inspired by recent progresses in theoretical materials research. The remaining challenges include the need to advance an alternative explanation for PAH coalescence and to find a class of PAHs with localized $\pi$ electron structures and thus large enough binding energies. The nature and structures of these PAHs should then point to the need for further development of gas-phase reaction mechanisms and models for the formation of these peculiar aromatic radicals in flames. Such radical sites may also exist on the soot surface. Direct experimental probing of these sites remains to be performed but will be exceedingly challenging.

What have we learned and what are the value and future of research into soot and condensed-phase material formation in flame? On one level there is value in creating fundamental understanding and models of soot formation for future engine designs. What is perhaps even more valuable is the fundamental knowledge garnered from soot research and its impact on a wide range of nanoparticle synthesis problems. To this end, flame synthesis of functional nanomaterials for renewable energy utilization is expected to bring new, challenging questions to this research community. Advances in this area of research will perhaps greatly
impact the public perception about fossil-fuel combustion, from it being today’s problem to tomorrow’s solution of clean energy utilization.

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References


Figure Captions

Figure 1. Standard enthalpy ($\Delta H^\circ$) and entropy ($T\Delta S^\circ$) contributions to Gibbs function of reaction $\Delta G^\circ$ at 1600 K for carbon formation from propane and rutile-phase titania formation from titanium vapor in the presence of molecular oxygen.

Figure 2. A version of the hydrogen-abstraction—carbon addition (HACA) reaction mechanism. The standard Gibbs function per carbon atom is plotted relative to an initial system with benzene : acetylene : H atom = 1 : 5 : 1 at 1800 K. Not considered in the diagram is the combination of H atom with aryl radicals.

Figure 3. Spectral sensitivity of pyrene concentration predicted for a 90-Torr burner stabilized 0.236 C$_2$H$_2$-0.214 O$_2$–Ar flame at 0.55 cm from the burner surface [176]. The results are taken from ref [125].

Figure 4. Selected parts of potential energy surfaces of propargyl recombination leading to production of benzene and phenyl + H (from Miller and Klippenstein [145]).

Figure 5. Photoionization mass spectra of flame species in the mass-to-charge ratio of 70 to 126 for a series of burner-stabilized aromatics-oxygen-50% argon flames, all at 30 Torr pressure and with C/O = 0.68, determined by molecular beam synchrotron photoionization mass spectrometry. 1: benzene, 2: toluene, 3: styrene, 4: ethylbenzene, 5: o-xylene, 6: m-xylene, 7: p-xylene (Courtesy of F. Qi).

Figure 6. Conceptual mechanisms of soot particle nucleation.

Figure 7. Binding energies for self-interactions of a series of PAHs taken from Herdman and Miller [169] (top panel), and relative concentrations and normal boiling/sublimation temperatures of selected PAHs in the HACA sequence of reactions (bottom panel, 1-, 2-, 3-, 4- and 7-numered aromatic rings are benzene, naphthalene, phenanthrene, pyrene, and coronene, respectively): circles: 90-Torr burner-stabilized acetylene flame [176]; triangle: 30-Torr toluene flame ($\phi$ = 1.9) [164]; 30-Torr benzene flame ($\phi$ = 1.78, relative to naphthalene) [159].

Figure 8. Size distribution computed by considering monomer dimerization and particle coagulation, assuming a constant, second-order nucleation strength [180]. $x$ is a dimensionless time given as $x = (8\pi k_B T/m_r)^{\frac{3}{2}} [4m_r/(3\pi p)]^{\frac{3}{2}} C_0(0) t$. The solid and dashed lines are computed with $\alpha = 1$ and 0.1, respectively. The particle diameter (upper x-axis) is determined by assuming that the particles are spherical and the mass density of the particle material is 1.8 g/cm$^3$.

Figure 9. Snapshots of the flame, the temperature profiles determined experimentally (symbols) and numerically computed (lines), and the particle size distribution functions measured at several
burner-to-probe separation distances in a 16.3% ethylene-23.7% oxygen-argon burner-stabilized stagnation flame at atmospheric pressure (cold gas velocity = 8 cm/s) [182].

**Figure 10.** Mass spectrum of high-molecular weight species extracted from a 100-Torr acetylene-oxygen flame (ϕ = 3.25) by molecular beam mass spectrometry with 193 nm laser ionization (Courtesy of H.-H. Grotheer).

**Figure 11.** Gibbs function of dimerization for coronene, ovalene and circumcoronene. The shaded area corresponds to an equilibrium constant for dimerization $K_p > 10^6$ atm$^{-1}$.

**Figure 12.** PAH$(i,j)$ and radical character ($0 \leq y \leq 1$) based on UBHandHLYP/6-31G(D) calculations of Nagai et al.[232].

**Figure 13.** Snapshots of nascent, primary soot particles simulated with a kinetic Monte Carlo procedure by Balthasar and Frenklach [240]. (Reprinted from Proc. Combust. Inst., vol. 30, Copyright 2004, with permission from Elsevier). Upper panels: particle structure resulting from coagulation of single soot nuclei. Bottom panel: particle structures after a period of mass growth through gas-surface reactions. Panel A represents a typical particle, whereas panels B and C represent extreme cases in terms of deviation from sphericity.

**Figure 14.** Evolution of PSDFs measured for two premixed 16.3% C$_2$H$_4$-23.7% O$_2$-Ar burner stabilized flames. Top panel: maximum flame temperature $T_f = 1660\pm 50$ K (cold gas-velocity $v_0 = 5.5$ cm/s); bottom panel: $T_f = 1898\pm 50$ K ($v_0 = 13$ cm/s). Data are taken from [184].

**Figure 15.** Sensitivity of the features of a bimodal PSDF with respect to model parameters [266].

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Figure 19. Examples of incipient soot formed in a premixed benzene flame as simulated by AMPI (courtesy of A. Violi).

Figure 20. Left panel: PAH mass spectrum of soot in a burner-stabilized laminar 50% C2H4-50% O2 at 120 mbar by Happold and Grotheer [317]. Right panel: Mass spectra computed by the PAH-PP model. (Courtesy of M. Kraft).

Figure 21. Panel (a) illustration of the method of flame stabilized at a few millimeters under a rotating stagnation surface (also as a particle collection surface). The laminar premixed flame is stabilized by flow stretch. The rotation causes the plate to cool by convection, thus creating a large temperature gradient and pushing the particles towards the collection plate for thermophoretic film deposition. Panel (b): particle size distribution of nanocrystalline titania synthesized, as measured by probe sampling/mobility sizing [256]; TEM images showing the crystal structures and scanning electron microscopy image of a porous particle film of titania [333]. Panel (c): Ohmic response of a chemical sensor, prepared by the flame technique, to exposure of trace CO in air, (1) 280 PPM, (2) 140 PPM, (3) 93 PPM, (4) 46 PPM, (5) 18 PPM and (6) 5 PPM (taken from [263]). Panel (d): polarization and power density curves measured for a dye sensitized solar cell with the photoanode prepared by the method of stagnation flame stabilized on a rotating surface (taken from [17]).
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Figure 18. A conceptual model of soot formation [293]. Stacks of lines represent stacked aromatic structures and the wiggly lines represent aliphatic components.

Figure 19. Examples of incipient soot formed in a premixed benzene flame as simulated by AMPI (courtesy of A. Violi).
Figure 20. Left panel: PAH mass spectrum of soot in a burner-stabilized laminar 50%C₂H₄-50%O₂ at 120 mbar by Happold and Grotheer [317]. Right panel: Mass spectra computed by the PAH-PP model. (Courtesy of M. Kraft).

Figure 21. Panel (a) illustration of the method of flame stabilized at a few millimeters under a rotating stagnation surface (also as a particle collection surface). The laminar premixed flame is stabilized by flow stretch. The rotation causes the plate to cool by convection, thus creating a large temperature gradient and pushing the particles towards the collection plate for thermophoretic film deposition. Panel (b): particle size distribution of nanocrystalline titania synthesized, as measured by probe sampling/mobility sizing [256]; TEM images showing the crystal structures and scanning electron microscopy image of a porous particle film of titania [333]. Panel (c): Ohmic response of a chemical sensor, prepared by the flame technique, to exposure of trace CO in air, (1) 280, (2) 140, (3) 93, (4) 46, (5) 18 and (6) 5 PPM (taken from [263]). Panel (d): polarization and power density curves measured for a dye sensitized solar cell with the photoanode prepared by the method of stagnation flame stabilized on a rotating surface (taken from [17]).