THE IMPACT OF NH_2 RADICAL ON SOOT FORMATION IN LAMINAR FLAMES

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Abstract

This study explores the impact of ammonia on reducing soot formation in ethylene laminar flames using a detailed kinetic model. It focuses on the role of the NH_2 radical and its interactions with aromatic species and soot particles. The model, benchmarked against experimental data, accurately predicts soot volume fraction and particle size evolution, especially at lower flame heights. However, it struggles to reproduce the bimodal particle size distribution at higher flame heights with ammonia addition. Kinetic analysis reveals that ammonia reduces soot by altering PAH formation pathways. Further experiments are recommended to validate nitrogen species chemistry in these flames.

1. Introduction

Ammonia (NH_3) is a promising carbon-free energy carrier, but its poor combustion properties limit its standalone use [*1*]. Blending NH_3 with hydrocarbons like ethylene improves flame stability and significantly reduces soot emissions, with studies reporting up to 87% reduction at 20% substitution [*2*]. This soot suppression is largely attributed to NH_2 radical interactions that inhibit key precursors such as C_2H_2 and C_3H_3, thereby slowing PAH and soot growth. This work employs a detailed kinetic model incorporating NH_2 reactions with gas-phase and condensed-phase aromatics to simulate ammonia/ethylene laminar flames. The model is validated against experimental data for soot volume fraction, particle size, and PSD, showing good agreement. However, further measurements of nitrogen-containing species are needed to fully resolve the mechanisms behind soot reduction in NH_3-doped flames

2. Kinetic model

A detailed kinetic model is used to study ammonia's influence on soot formation in ethylene laminar flames. Soot and PAH species are treated using a discrete sectional approach, with pseudo-species (BINs) categorized by carbon number and H/C ratio. The model includes seven soot reaction classes with rate parameters based on gas-phase analogs and updated physical interaction efficiencies. It comprises 761 species and over 131,000 reactions, covering C_0–C_4 and NH_3 chemistry, PAH growth up to five-ring species, and soot dynamics. Simulations are performed using OpenSMOKE++ with detailed transport and radiation models. Two new reaction

classes are introduced: **R1**, NH_2 addition/recombination, and **R2f/R2b**, NH_2-driven H-abstraction from aromatics and soot. In R1, NH_2 addition leads to C-atom removal as HCN, supported by theoretical [*3*] and experimental [*4*] studies showing N–C bond cleavage in high-temperature aniline decomposition, forming HNC that rapidly isomerizes to HCN—similar to phenoxy radical ring contraction.

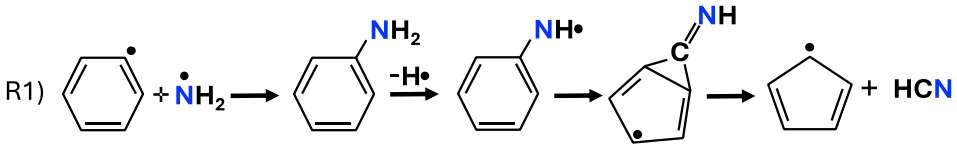

Figure 1. Decomposition mechanism of phenyl radical reacting with NH_2 radical.

Figure 1 shows the NH_2-driven decomposition of phenyl radicals via aniline formation, followed by H-loss and breakdown into cyclopentadienyl and HCN/HNC, as proposed by Altarawneh et al. [*3*]. Kinetic parameters were estimated using a lumped master equation approach with PES data from [*3*]. The recombination rate (10^{14} cm^3/mol/s) aligns with typical radical kinetics, and final rates were adapted from PAH reaction classes. H-abstraction rates (R2f/R2b) were adopted from [*3*].

3. Results and discussion

This study investigates 15 laminar ethylene/ammonia flames in both counterflow and premixed burner-stabilized stagnation configurations. The first dataset includes soot volume fraction (f_v) profiles from Bennett et al. [*2*] and Zhou et al. [*5*], shown in Figures 2a and 2b, respectively. Figure 2a compares simulations with varying ammonia content (0–25%) replacing argon at fixed $X_{C_2H_4}$ = 0.75 against PLII measurements [*2*], while Figure 2b compares simulations of ammonia substituting ethylene (up to 20%) against data from Zhou et al. [*5*] using laser extinction and scattering. The model underpredicts f_v by factors of 4.5 (addition) and 1.8 (substitution), though this aligns with known uncertainties and prior validation against 30 pure ethylene counterflow flames. Crucially, the model captures the linear reduction in peak fv with increasing ammonia, matching the ~88% experimental reduction at 25% NH_3 addition [*2*]. However, some limitations remain: the current treatment of soot particle coagulation and growth dynamics need refinement under extended residence times or varying flow conditions. Nevertheless, the model shows good consistency in capturing changes in soot morphology and structure, reinforcing the critical role of NH_2 radicals.

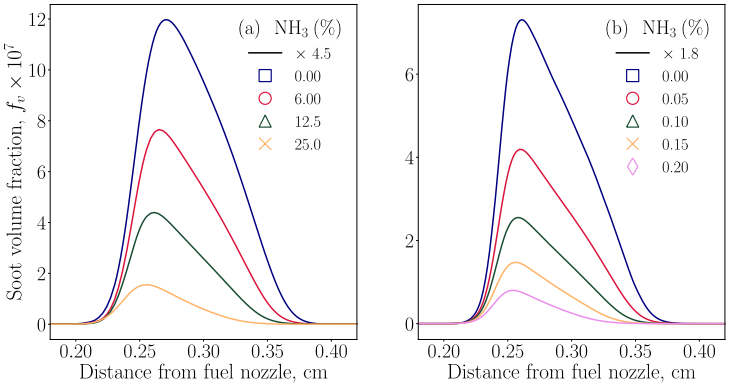

Figure 2. Soot volume fraction, f_v, profiles measured (symbols [*2*, *5*]) and simulated (lines, this work) in a)[*2*] and b)[*5*] flames.

4. Conclusion

This study highlights the pivotal role of NH_2 radical interactions with PAHs in explaining ammonia's soot-reducing effect in hydrocarbon flames. The detailed kinetic model captures key experimental trends, providing a solid foundation for further development. Due to limited theoretical data, tentative rate constants were introduced for NH_2 addition and abstraction pathways, including a proposed mechanism for carbon removal via HCN formation. Model validation against soot volume fraction data from counterflow flames shows good trend agreement, despite localized overpredictions. To strengthen the model and deepen mechanistic insight, further experimental data on nitrogen-containing species and high-level theoretical studies on NH_2-driven reactions are strongly recommended.

References

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