Experimental investigation of hydrogen impact on atmospheric sooting premixed methane flames

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Abstract

The effect of hydrogen on aliphatic and aromatic species formation has been experimentally investigated in a methane "nucleation flame". The nucleation flame conditions were identified by laser induced incandescence (LII) at equivalent ratio Φ=1.82. The approach and the definition of the "nucleation flame " have been previously reported in our recent work [1,2]. Various stable species (C_1-C_6) were measured by gas chromatography while polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and pyrene were measured by jet-cooled laser induced fluorescence (JCLIF). To keep the C/O ratio and temperature values constants in the sooting flame region, all H_2-flames have been studied by replacing or adding the equivalent of 1.8%N_2. The Pt/Rh thermocouple measurements confirmed similar temperature values in the post flame region of methane/O_2/N_2 and methane/H_2/O_2/N_2flames. Moreover, additional experiments carried out in similar conditions with helium allowed to exclude the diluent affect. The new experimental results demonstrated that hydrogen can enhance significantly soot precursors (benzene, naphthalene, pyrene) even it is added at low amounts (lower than 2%). However, these aromatic compounds peak mole fraction can significantly be reduced if the experiments proceed via a low N_2- amount substitution(1.8%).The soot volume mole fraction measurements and the modeling work which are in progress should confirm the importance of H atoms in the chemical growth process of PAHs and soot formation.

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1.Introduction

Nucleation flames, which have been recently discovered in our laboratory, allow to efficiently investigate the nucleation process of soot particles from gaseous species formed in flames [3,4] because of the simplification of the soot formation mechanism they provide. Indeed, in these flames, nascent soot particles (NSP) are only generated without or very poorly undergoing surface growth all along the flame height.

Polycyclic aromatic hydrocarbons (PAHs), which are considered to be the main precursors of soot particles, have been highlighted to form and grow in size preferentially according to the HACA mechanism (H-abstraction - C_2H_2 addition) [5–7]. In the present study, we report some experimental results highlighting the hydrogen impact on the formation of PAHs and their crucial precursors in a nucleation methane flame stabilized at atmospheric pressure. Hydrogen addition to the nucleation flame is expected to affect the formation of active oxidative species such as O and OH leading to the enhancement of the PAH oxidation or to the increase of the formation of H atoms leading to the increase of the PAH formation.

Different experimental techniques have been used to carry out this work. The experimental conditions required to generate the nucleation flame have been determined by Laser Induced Incandescence (LII) while the impact of hydrogen on the formation soot precursors has been investigated by Gas Chromatography (GC) for the aliphatic species and benzene and jet-coolded laser induced fluorescence (JC-LIF) for PAHs (naphthalene and pyrene).

2.Experiment setup

2.1. Flame apparatus and conditions

The flames were stabilized on a McKenna burner (6 cm diameter) already described previously [8]. The conditions of all studied flames are summarized in Table 1.

Flame	Φ-1.82	Φ-1.82_H_2-S	Φ-1.82_H_2-A	Φ-1.82_He-S
Φ_C	1.82	1.82	1.82	1.82
Φ_{C+H}	1.83	1.83	1.83	1.82
C/O	0.445	0.445	0.445	0.445
Total flow rate (l/h)	721.4	721.4	734.6	721.4
X_{CH4}	0.184	0.184	0.181	0.184
X_{O2}	0.202	0.202	0.199	0.202
X_{N2}	0.614	0.595	0.602	0.595
X_{H2}	0	0.018	0.018	0
X_{He}	0	0	0	0.018

Table 1: Flame conditions

There are currently several approaches to investigate the impact of hydrogen in flames. In this work, we propose two different approaches to introduce hydrogen without affected the temperature profile of the reference flame (Φ-1.82). The first approach is characterized by a **hydrogen substitution**, flame Φ-1.82_H_2-S. In this case, a small amount of the nitrogen dilution, equal to 10% of the methane flow rate, is subtracted from the reference flame, and hydrogen is added into flame in order to keep constant the total flow rate. The second approach correspond to a **hydrogen addition**, flame Φ-1.82_H_2-A. This time, the small amount of hydrogen, still equal to 10% of the methane flow rate, is added, therefore slightly increasing the total flow rate of flame (less than 2%) compared to the reference flame.

To investigate the dilution effect of the substituted hydrogen to the nucleation flame, a similar experiment were also carried out by replacing hydrogen by helium in the flame Φ-1.82_He-S.

2.2.LII setup

A schematic of the used LII setup is reported in Fig 1.

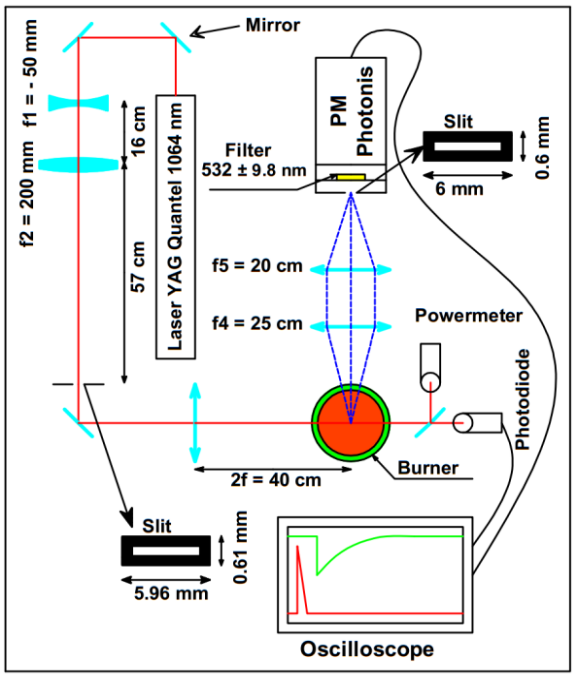

Figure 1: Experimental LII setup

LII experiments have been carried out by using a 1064 nm laser excitation wavelength generated by a Nd: YAG (Quantel) at 10Hz to heat soot particles. 1064 nm laser excitation wavelength was used to avoid the excitation of PAHs also formed in the flames. Firstly, the laser beam was expanded into a horizontal plane using two cylindrical lenses (f_1 = -50mm, f_2= 200mm). Then the laser beam passed through a rectangular slit (5.96mm (vertical) ×0.61mm (horizontal)) and a converging lens (f_3=200mm) in order to provide a top-

hat irradiance profile at the position of the LII collection volume. During these experiments, the laser energy was continuously monitored with a powermeter located after the burner. The LII signal was collected at right angle to the laser axis with two converging lenses (f_4=25cm and f_5 = 20cm) and focused on the collection slit ((0.6 mm (vertical) ×6 mm (horizontal)). LII signals were measured after the collection slit by a photomultiplier Hamamatsu E1341-01 (PM). An interference filter centered at 532 ± 9.8 nm was positioned in front of the PMT in order to limit parasite emission and scattering light from the flame. The LII signals recorded by the PMT were acquired and digitized by an oscilloscope.

2.3.Gas Chromatography (GC) setup

A schematic of the used GC setup is presented in Fig 2.

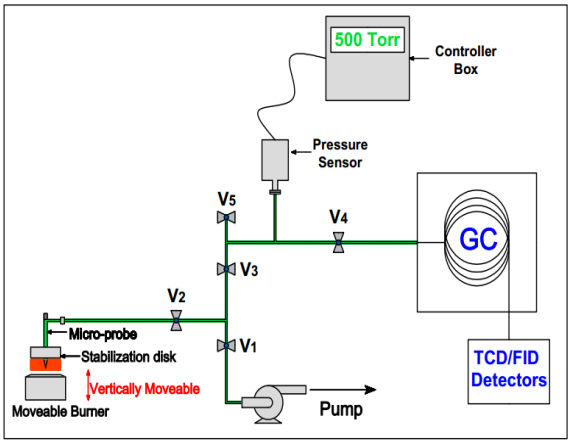

Figure 2: Experimental GC setup

Gas samples were extracted from the flames by a quartz sampling microprobe and then directly sent into a low-pressure injection system before injecting into the GC CP-3800 Varian. In this experiment, the micro-probe was fixed and the burner height adjustable along the vertical axis allowing to sampling of species from different heights above the burner. The alumina capillary and tamis molecular columns were located inside a furnace of GC and the two FID and TCD detectors located at the exit of alumina capillary and tamis column respectively allowing to detect species sampled from flame.

We used the gaseous commercial cylinder calibration mixture (Air Product) with uncertainty of mole fraction ± 0.5 - 2% to calibrate the GC.

2.4.JC-LIF setup

A schematic of the used JC-LIF setup is shown in Fig 3. JC-LIF was also carried out after the sampling of the species from the flame thanks to the same micro-probe used for the GC experiments. Then species samples were directly cooled down in an expanded free jet generated inside the analysis chamber. LIF measurements were done directly in the free jet in this low-pressure chamber. In these very low temperature conditions provided by the free jet expansion (around 100 K), the spectra of the sampling PAHs simplify and highlight specific spectral structures enabling their selective measurements by LIF. In the absence of collision inside the free jet, LIF signal can be calibrated by studying the LIF signal issued from pure compounds with known concentrations sent and cooled down inside the free jet.

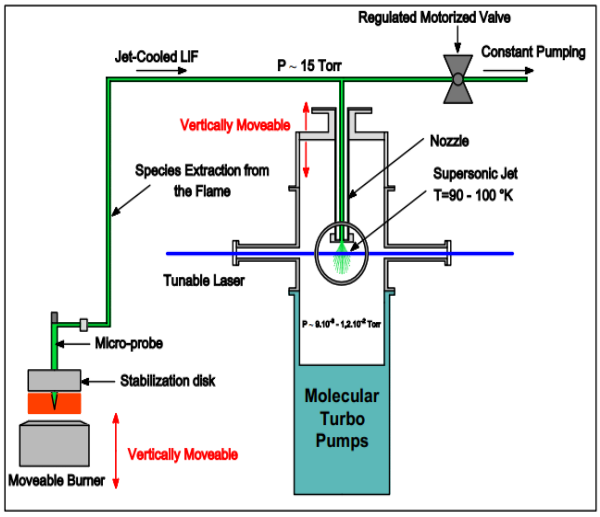

Figure 3: Experimental JC-LIF setup

The laser system we used consisted of a Quantel Nd:YAG laser, pumping a dye laser (TDL70 Quantel) with the 2nd harmonic at 532 nm. Tunable wavelengths covering different spectral ranges could be generated by using different dyes to match the spectral excitation range of naphthalene and pyrene. The laser beam was spatially reduced to a diameter of approximately 1 mm with a pinhole and sent into the analysis chamber. The energy was adjusted around 0.048 J/cm^2 to be linear regime of fluorescence. Fluorescence emission spectra were recorded via spectrometer iHR 320 (300 mm focal length - gratings with 300 gr/mm) which can be coupled either to a 16 bit intensified charge coupled device camera (Roper Pimax II) or to a photomultiplier (Photonis XP2020Q). The conditions of excitation and collection wavelengths for the measurement of naphthalene and pyrene are reported in Table 2.

	Naphthalene	Pyrene
Transition	$S_1 \leftarrow S_0$	$S_2 \leftarrow S_0$
Excitation	λ_{ex}= 308 mm	λ_{ex}= 321 mm
Collection	$320<\lambda_{collec}<340$	$370<\lambda_{collec}<390$

Table 2: Spectroscopic data

3.Results and discussion

3.1. Nucleation condition identification

The equivalence ratio enabling the generation of the nucleation flame has been obtained by following the evolution of the LII temporal decays along the flame height. The relationship between the LII temporal decay and the soot size distribution is rather complex [9,10], and requires the use of LII modeling to interpret the signals in terms of primary particle diameter. However, it is established that this temporal decay is correlated to the diameter of the soot particles. The nucleation flame conditions can therefore be obtained by adjusting the flow rate of the reactants so that we do not observe any growth of the temporal LII decay rate all along the flame height as reported in Fig 4. By this way, we defined the equivalence ratio conditions equal to Φ-1.82 to generate a methane nucleation flame at atmospheric pressure.

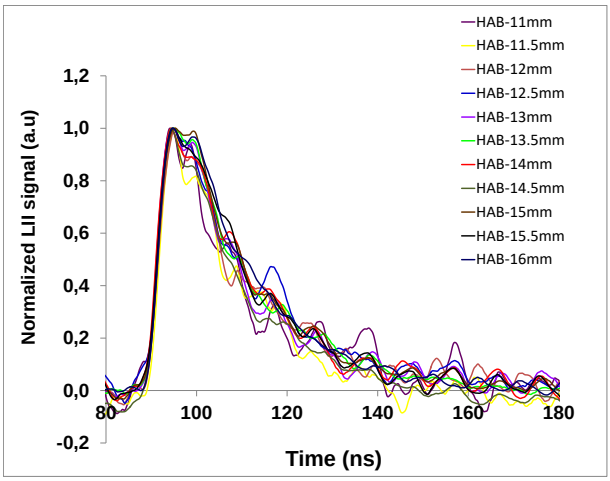

Figure 4 :LII temporal decays measured at different HAB for the flame Φ-1.82. Peak LII signals have been normalised to 1. Laser fluence set at 0.41J/cm

3.2. Impact of hydrogen on formation of soot precursors

Fig 5 reports the effect of hydrogen substitution on the formation of acetylene, propyne, benzene, naphthalene, and pyrene in the nucleation flame. The mole fraction profiles of all species shift about 2 mm toward the burner surface comparing to the reference flame because the hydrogen substitution enhances the laminar flame speed [11]. The above unsaturated aliphatic species play a significant role in first aromatic ring and PAHs formation. Acetylene (C_2H_2) can produce benzene by its reaction with butadienyl radicals and contributes significantly to the PAHs and soot growth processes [5,12]. Propyne (P-C_3H_4) is a main source propargyl (C_3H_3) radicals which self-recombination yields benzene [13].

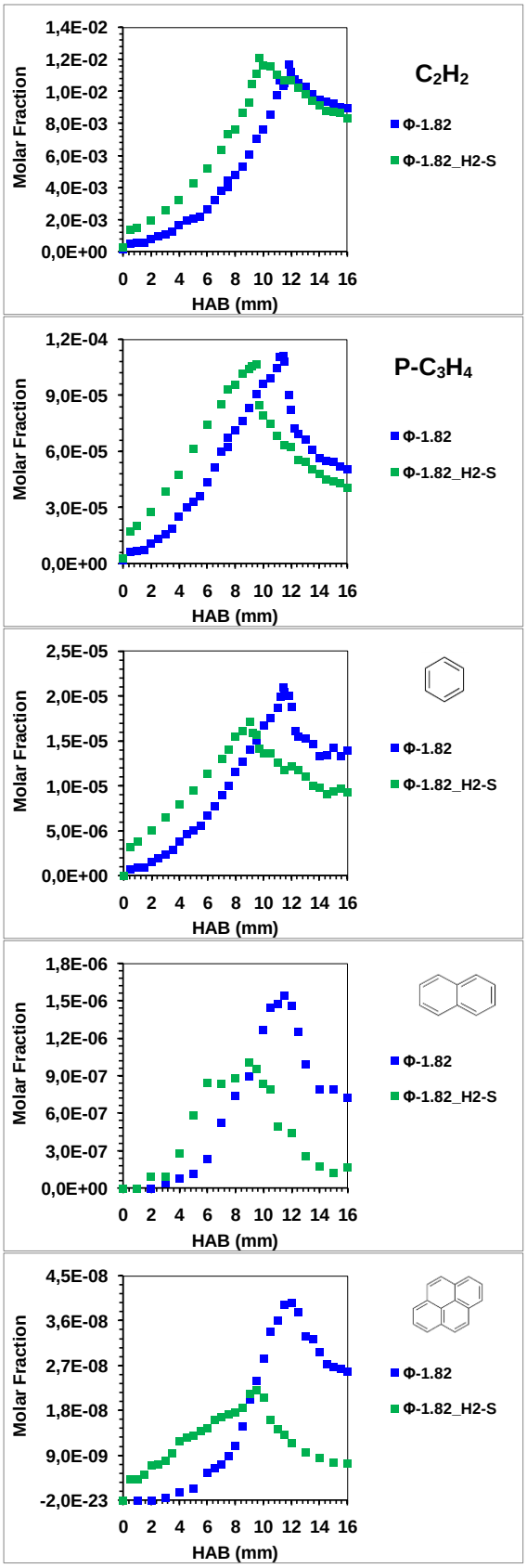

Figure 5: Impact of hydrogen substitution on formation of acetylene C_2H_2, propyne P-C_3H_4, benzene, naphthalene and pyrene in the nucleation flame - Hydrogen Substitution

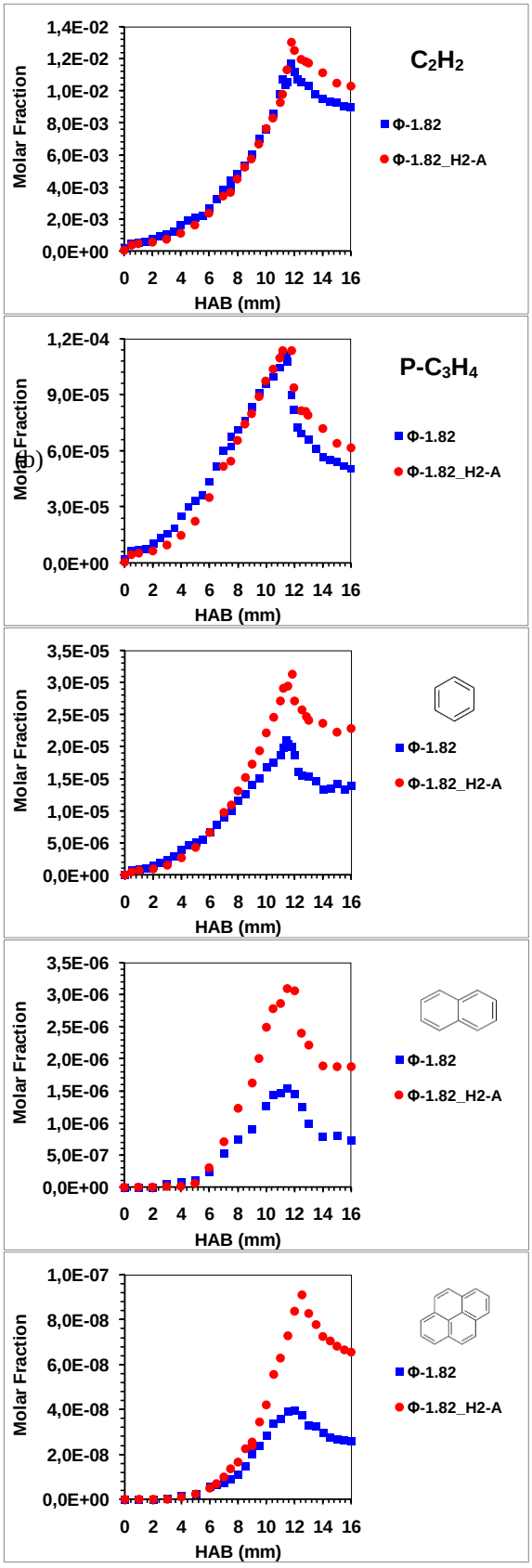

Figure 6: Impact of hydrogen addition on formation of acetylene (C_2H_2), propyne ($P\text{-}C_3H_4$), benzene, naphthalene and pyrene in the nucleation flame – Hydrogen Addition

According to Figs. 5 and 6, hydrogen strongly affects benzene, naphthalene and pyrene formation while it only slightly influences acetylene and propyne formation. The observed hydrogen effect depends strongly on the operating flame conditions. The results of Fig.6 exhibits that hydrogen can enhance significantly soot precursors (benzene, naphthalene, pyrene) even it is added at low amounts (lower than 2%). However as shown in fig.5, these aromatic compounds peak mole fraction can significantly be reduced if the experiments proceed via a low N_2-amount substitution (1.8%).

As can be seen from Fig. 7, helium substitution/addition does not affect the formation of acetylene, propyne and benzene. Therefore, aromatic compounds peak mole fraction differences observed in methane and methane-H_2 flames is probably due to the chemical effect. Note that the Helium and Hydrogen effect are very close[14] .

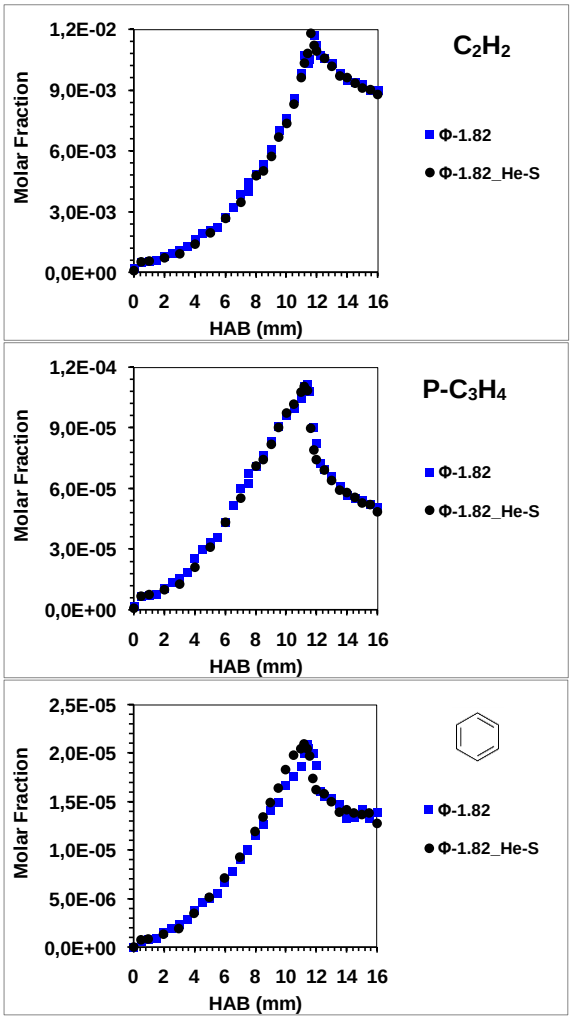

Figure 7: Impact of helium substitution on the formation of acetylene (C_2H_2), propyne ($P\text{-}C_3H_4$), and benzene in the nucleation flame – Helium Substitution

The modelling of these new experimental results using our recent mechanisms is in progress [1,15]. It should provide more precise information on H_2 effects. As

discussed above, our experimental results show clearly that substitution hydrogen enhances the overall reactivity indicating an increase of the laminar flame speed. The substitution should then enhance the branching reaction converting H atoms to oxidative active species OH and O. However, the addition of 1.8% H_2 does not seem to disturb the reaction flame zone indicating that the laminar flame speed remains probably unchanged. It also means that the branching reaction proceeds with the same efficiency under these conditions. Accordingly, hydrogen atoms preferentially used for H-transfer reactions and termination reactions involving aromatic radicals.

4. Conclusion

In this work, we have studied the impact of hydrogen on the formation of important soot precursors (e.g. benzene, naphthalene, and pyrene) in a nucleation flame of methane at atmospheric pressure. Two approaches of hydrogen introduction to the nucleation flame have been examined. In these two approaches, hydrogen strongly influences on the formation of benzene, naphthalene and pyrene whereas it slightly impacts the formation of aliphatic species.

Hydrogen substitution enhances the flame speed, hence favoring the formation of oxidation active species. Thus, it strongly inhibits the formation of benzene, naphthalene, and pyrene.

Hydrogen addition does not modify the mole fraction profiles of all the measured species. It notably strongly enhances the formation of benzene, naphthalene and pyrene before their peak mole fraction while it only slightly increases the formation of acetylene and propyne in post combustion region. Thus, hydrogen addition favors the formation of active species which takes an important role in the PAHs growth mechanims.

In the two approaches, the most important impacts of hydrogen was observed for the pyrene formation. Therefore, hydrogen appears as an excellent additive in the studied nucleation flame to investigate the transition step leading to the primary soot particles in flame.

The effects of hydrogen on the formation of PAHs in the nucleation flames are very different according to the different investigated approaches. Therefore, we have to be careful when studying the impact of additives in sooting flames.

Acknowledgments

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