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Effects of ferrocene on flame temperature, formation of soot particles and growth of polycyclic aromatic hydrocarbons

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ABSTRACT

The detailed influence of ferrocene in an atmospheric pressure, fuel rich, propane/oxygen diffusion flame was investigated experimentally. Flame temperature at different heights was measured and analyzed by primary-color pyrometry. Soot particles were obtained with a quartz tube cooled by tap water above the flame. Their physico-chemical characteristics were measured by thermal gravimetric analysis, transmission electron microscopy and X-ray diffraction analysis. The organic materials in soot particles were mainly Polycyclic Aromatic Hydrocarbons (PAHs) which could be detected by gas chromatography mass spectrometer. It was found that the impact of ferrocene on flame temperature and soot characteristics occurred mainly near the terminus of the flame and their functions were interrelated. The iron from ferrocene reacted with O and OH radicals, which dropped the flame temperature and restrained smaller PAHs from growing into bigger ones. This in turn changed the characteristics of soot particles, including the reduction in crystallite size and thermal stability, as PAHs are important precursors to soot formation.

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1. Introduction

Particulate matter (PM), especially PM_{2.5} (the fraction of aerosol particles with the aerodynamic diameter less than 2.5 μm) emissions from various combustion processes negatively impact human health and global environment. They are associated with global climate change and incidences of asthma, chronic bronchitis and heart disease [1]. Therefore, it is imperative to find a cost-effective method for PM removal. Soot particles, which consist of amorphous carbon and Polycyclic Aromatic Hydrocarbons (PAHs) known to be carcinogenic, constitute a significant portion of PM_{2.5} [1,2]. Studying soot formation processes, especially PAHs growth mechanisms, helps us find ways to reduce soot formation in combustion processes.

Controlling soot particle emissions is one of the essential requirements for any combustor. However, the combustor performance can not be compromised for that purpose. Using filter is a simple way to reduce soot emissions; for example, the diesel particulate filter (DPF) is commonly used to capture and collect soot particles in the exhaust of diesel engine vehicle [3]. However, the imbalance between accumulation and oxidation of soot particles at low-temperature is a common problem to the DPF which is also vulnerable to sulfur content of the fuel [4]. Strengthening the contact between catalysts and soot particles and reducing the reaction temperature of soot catalytic combustion are two challenging solutions [5,6]. Adding fuel additives is one of the promising and effective methods for preventing and reducing the generation of soot [7,8]. Various fuel additives have been considered as a source of fuel-borne catalysts which can maximize the contact between catalysts and soot particles [9]. Ferrocene ((C₅H₅)₂Fe) and metallic-based additives as fuel-borne catalysts have been extensively studied around the world, and some promising results have been obtained [10–20].

There are some discussions on whether iron-containing compounds could increase or decrease the soot formation [11]. Based on their experimental studies, some researchers drew a conclusion that the addition of ferrocene promoted the soot formation [12]. The soot particle

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size and number density both increased after doping iron-containing compounds into the flame [1]. This was related to the solid iron oxide particles [13] which may nucleate prior to the soot inception in the flame [14,15]. In the meantime, iron oxide particles could shorten the time for soot to show in the flame [16] and decrease the critical sooting C/O ratio [17]. However, there were also opposite conclusions that the addition of ferrocene inhibited soot formation. The addition of iron-containing compounds was shown to enhance soot oxidation rates near the flame terminus and reduce overall soot yields through burnout [13,18]. Meanwhile, iron oxide particles acted as nucleation centers for soot formation and they were subsequently efficiently oxidized via reaction $\text{Fe}_x\text{O}_y + \text{C} \rightarrow \text{CO} + \text{Fe}_x\text{O}_{y-1}$ [19,20]. It is essential to understand the effects of ferrocene on the soot structure and characteristics, especially the mechanisms resulting in these phenomena.

Organic matters in soot are mainly PAHs, which are thought to be precursors to soot formation [21,22]. Soot formation usually consists of three processes: particle nucleation, surface growth and particle coagulation [23]. (a) Particle nucleation. In this process, PAHs are believed to act as the building blocks that undergo chemical reactions to form incipient soot [24]. However, the pathways of PAHs growth reactions seem to depend on the fuel. In the case of aliphatic fuels such as acetylene or methane, the first aromatic ring is usually formed from fuel decomposition products [21]. After the formation of the first ring, PAHs of large sizes are mainly formed by sequential chemical reactions of smaller PAHs with acetylene, PAHs or PAH radicals [23]. PAHs keep on growing; particle nucleation occurs. (b) Surface growth. Two major processes dominate the surface growth [25]. One is the condensation of PAHs on the surface. The other is the growth through Hydrogen-abstraction-carbon-addition (HACA), where acetylene is the source of the carbon [25]. Acetylene and PAHs are growth species whose relative contributions depend on the conditions of process [23]. (c) Particle coagulation. It can be divided into two stages: coalescence and agglomeration [26]. In coalescent growth, two roughly spherically shaped particles collide and coalesce, thereby forming a single spherically shaped particle. In agglomeration process, individual particles stick together to form fractal clusters, i.e., chainlike structures [26,27].

In the meantime, during soot formation processes, soot particles can be destroyed through two partially parallel processes: oxidation and fragmentation [28]. Oxidation is the removal of mass from soot through chemical reactions with O_2 and OH, continuously competing with soot formation processes [29]. Fragmentation is the break-up of large particle aggregates into smaller pieces, usually after structures have been weakened by oxidation [30]. Finally, these two processes lead to the destruction of soot particles and the decrease in particle size [30,31].

Ferrocene as the catalyst added to the fuel not only influences the soot formation but also changes the flame speed and temperature. When vaporized ferrocene concentration reaches 200 ppm, the methane/air premixed flame speed reduces two orders of magnitudes [32,33]. In K. Tian's study, they examined the relationship between flame temperature and species concentration in the flame, and suggested that the two C_5H_5 rings in ferrocene were more important than the iron [11]. However, the effects of iron from ferrocene on flame temperature and soot formation should not be ignored and need to be discussed.

The above-mentioned studies of the influences of ferrocene on flame, soot particles and PAHs were performed separately. Hence the main aim of the current work was to study the chemical effects of ferrocene on flame temperature, PAHs growth and soot formation and find their relationships with flame structure. In this work, ferrocene as the fuel-borne catalyst was doped in propane, and its influence in a fuel-rich propane/oxygen diffusion flame was investigated. The charge coupled device (CCD) image technique was used in flame temperature field measurements in an effort to examine the effect of ferrocene on the temperature. Transmission electron microscope (TEM), thermal gravimetric analysis (TGA) and X-ray diffraction (XRD) were applied to analyze the characteristics of soot particles including their shape, size, thermal stability and crystallite size. Energy dispersive spectroscopy (EDS) was used to reveal the existence of iron in soot particles. The diversification of PAHs was measured with a gas chromatography-mass spectrometer (GC/MS).

2. Experimental apparatus and procedures

2.1. Experimental apparatus

The effects of ferrocene on flame temperature, soot formation and PAHs growth were studied in a fuel-rich propane/oxygen diffusion flame. Fig. 1 shows the schematic of the flame burner system, which consists of a burner, four tubes, a reservoir, two controllers, a digital color camera and a computer. During the experiments, ferrocene was introduced to the flame by flowing the propane gas through a reservoir filled with ferrocene, according to Ref. [20]. The reservoir was immersed in a thermal bath to heat ferrocene and increase the vapor pressure of ferrocene, because ferrocene was sublimed when heated. The ferrocene-saturated vapor pressure is given as follow: $\ln P_{sv} = \frac{1}{R} \left[15.186 + 74290 \left(\frac{1}{\theta} - \frac{1}{T} \right) - 71 \left(\frac{\theta}{T} - 1 + \ln \frac{T}{\theta} \right) \right]$ with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $\theta = 317.20 \text{ K}$, T is the temperature, and P_{sv} is the vapor pressure [20]. The addition level of ferrocene in the fuel was adjusted by controlling the temperature of the thermal bath. At 353.2 K, the evaluated vapor pressure was 104.6 Pa, which corresponded within the mixture a percentage volume fraction of 0.1%. At 363.2 K, the volume fraction of ferrocene in the mixture was 0.2%. In order to prevent ferrocene re-condensation, the fuel-ferrocene mixture flowed through a heated line to the burner. The flow rates of gases (propane and oxygen) were controlled by mass flow controllers. The diameters of outer tube and inner tube are 12 mm and 2 mm respectively, and the diameters of the 12 array tubes are 1.5 mm.

Experiment 1: the relationship between flame temperature and heights above the burner (HABs) with different concentrations of ferrocene in the fuel. Full temperature profiles of flames without and with ferrocene doped in the fuel were measured by primary-color pyrometry. When ferrocene was doped in the fuel, its volume fractions in the mixture were 0.1% and 0.2%, respectively. In order to keep flames with the same structure, the equivalent ratio of propane/oxygen was maintained at 2.52 during the test, and the propane flow rate (1.10 L/min) and oxygen flow rate (2.18 L/min) were maintained by the mass flow controllers.

Experiment 2: the relationship between flame structure and characteristics of soot and diversification of PAHs. As shown in Fig. 1, a quartz tube cooled by water was placed horizontally above the burner for sampling of the soot particles. Soot particles were obtained at 7 cm and 14 cm flame heights without and with ferrocene doped in the fuel, respectively. When ferrocene was doped, its volume fraction in the mixture was 0.2%. In order to make sure that soot particles were sampled at the same sooting stage across these two flames, the length and structure of flames were kept unchanged. During the test, the flow rates of gases (propane and oxygen) were held constant; the propane flow rate was 1.10 L/min and oxygen flow rate was 2.18 L/min.

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