乙炔/空气预混火焰中 CO 添加对炭黑生成影响的数值分析

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摘要: 针对乙炔/空气预混火焰中 CO 添加对炭黑生成的影响进行了详细的数值模拟. 通过对含有不同 CO 添加量的火焰的模拟结果比较, 研究 CO 添加的温度和化学作用对于炭黑形成的影响. 计算结果显示 CO 添加使炭黑的生成单调下降. 炭黑体积分数和成核速率随着温度的升高而增加, 到达一个阈值后, 再随温度的升高而减少. 从炭黑生成的 H-萃取角度来看, 由于反应 $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$ 的向右速率增加, H 原子增加以及 OH 自由基减少, CO 添加会激发炭黑生成. 从炭黑生成的 C-添加机理来看, CO 添加减小了 C_2H_2 的消耗速率, CO 添加也有助于炭黑生成, 但 CO 添加降低了燃料中 C_2H_2 的体积分数, 使得炭黑表面增长速率降低.

关键词: 炭黑; 乙炔; 一氧化碳; 燃料改进; 模化

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Numerical Analysis of the Effect of Carbon Monoxide Addition on Soot Formation in an Acetylene/Air Premixed Flame

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Abstract: The effect of carbon monoxide addition on soot formation in an acetylene/air premixed flame was investigated by detailed numerical simulation. This work focused on both the temperature effect and chemical effect of carbon monoxide addition on soot formation by comparing the results of flames with different CO contents. We find that the addition of carbon monoxide consistently reduces the formation of soot. The soot volume fraction and nucleation rate increase until a threshold temperature is reached and then decrease as the temperature increases. Considering that soot formation took place at the active site by H-abstraction mechanism, the addition of CO promotes the formation of soot. The concentration of H radicals increases and the concentration of OH radicals decreases because of the increased forward rate of the reaction $\text{OH} + \text{CO} = \text{CO}_2 + \text{H}$. For soot formation to occur by the C-addition mechanism, the degradation rates of C_2H_2 tends to decrease and this promotes the formation of soot along with CO addition. On the other hand, the addition of CO may greatly reduce the volume fraction of C_2H_2 in fuel resulting in a lower surface growth rate.

Key Words: Soot; Acetylene; Carbon monoxide; Fuel enrichment; Modeling

Acetylene is one of the most abundant intermediates in hydrocarbon combustion as well as in the combustion of halogenated hydrocarbons such as CH_3Br and CH_2Cl_2 . Acetylene is also known to play a very important role in the formation of soot^[1–2]. Soot emissions resulting from combustion have long been recog-

nized as a significant problem. Soot itself is intrinsically toxic and soot particles are strongly associated with detrimental health effects. In the earth atmosphere soot contributes to the entrapment of the solar radiation that is believed to lead to global warming. Besides, soot is present in hydrocarbon/air flames,

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where it affects flame reaction mechanisms and structure^[3-5]. Fuel enrichment combustion is a promising concept for substantial reduction in fuel consumption and pollutant emissions into the atmosphere. Guo *et al.*^[6] have shown that hydrogen enrichment can extend the flammability limit and reduce NO formation in counterflow CH₄/air premixed flames by allowing a combustor to operate at leaner condition. Ren *et al.*^[7] studied strain-rate effects on hydrogen-enhanced lean premixed combustion by experimental and numerical approaches, and verified that it can increase the lean combustion stability through addition of H₂. Coppens *et al.*^[8] focused on the effects of composition on burning velocity and nitric oxide formation in non-stretched laminar premixed flames of CH₄+H₂+O₂+N₂. By reforming hydrocarbon fuels, reformat gas contains not only H₂ but also CO. CO is a primary component of a reformat gas or a syngas which is an effective and practical enrichment additive^[9]. Assuming the reformat gas is the product of partial oxidation of methane by air which consists of H₂, CO, and N₂, Guo *et al.*^[9] studied the effect of reformat gas enrichment on extinction limits and NO_x formation in counterflow CH₄/air premixed flames. It is found that the addition of the reformat gas extends the lean flammability limit and greatly reduces the formation of NO at leaner condition without any effect on flammable range. Wu *et al.*^[10] investigated the effects of CO addition on the characteristics of premixed CH₄/air opposed-jet flames experimentally and numerically. The results show that the maximum burning velocity occurs at the rich side of stoichiometry for a fixed fuel composition. The maximum burning velocity increases with increasing CO concentration, and it reaches its highest value and then decreases along with the increase in CO concentration.

For the effect of additives on soot formation, previous studies have focused on addition of H₂ or inert gases. Gülder *et al.*^[11] studied the influence of soot of hydrogen addition to the fuel in diffusion flames. They found the influence was negligible for soot formation by addition of hydrogen to the fuel side for an ethylene diffusion flame, and hydrogen addition did not show any influence on soot formation apart from the dilution effect for propane and butane flames. Glassman^[12] examined the effect of inert additives on sooting laminar coaxial diffusion flames, and it showed that temperature effect caused a logarithmic variation in soot volume fraction. Guo *et al.*^[13] investigated numerically the influence of transport properties of inert additives on soot formation in a coflow axisymmetric ethylene/air diffusion flame. They took into account the interactions between the soot and gas-phase chemistry and used a simplified two-equation soot model. The effects of adding argon and helium to either fuel or oxidant were determined, and the results showed that the effects of the additives on soot formation process were different because of the difference in their transport properties. Guo *et al.*^[14] also studied the influence of hydrogen addition to the fuel of an atmosphere pressure coflow laminar ethylene/air diffusion flame on soot formation by numerical simulation, and it indicated that the addition of hydrogen to the fuel in an ethylene/air diffusion

flame suppressed soot formation through the effects of dilution and chemistry. Pandey *et al.*^[15] investigated experimentally the effect of hydrogen addition on soot formation and soot morphology for axisymmetric coflowing acetylene/air laminar diffusion flames under different flow arrangements. Surprisingly, there is not much information available in the literature about the effect of CO addition on soot formation, especially the chemical effect of CO addition. Until recently, Guo *et al.*^[16] investigated the effect of CO addition on soot formation in an ethylene/air diffusion flame. They believed that although the addition of carbon monoxide monotonically reduced the formation of soot, the chemical effect promoted the formation of soot in an ethylene/air diffusion flame. CO is a non-sooting fuel, but it contains carbon atom. CO addition has a dilution effect in terms of soot formation on one side, but participates in reactions that may influence soot formation on the other side. Consequently, the addition of CO may have complex effect on soot formation. Measurements were made by Du *et al.*^[17]. They observed that CO addition caused a linear decrease in soot formation in an ethylene diffusion flame, and a complicated behavior in a propane diffusion flame. They explained that the addition of CO could promote soot inception chemistry, but did not provide any discussion on the sooting chemistry. For diffusion flames, Guo *et al.*^[16] argued that there existed two main reasons for CO addition causing some change in soot formation. One is that the chemical effect of CO addition may be caused by the modifications of flame temperature, the other is that the addition of CO increases the surface growth reaction rates through the reaction CO+OH=CO₂+H. In previous studies, there is almost no discussion on important sub-process of soot formation. Therefore, further investigation on the detailed mechanism of the effect of CO addition on soot formation in premixed flames is needed.

Soot formation is an extremely complex physical and chemical process which involves gas and surface phase chemistries as well as particle dynamics. Although it has been studied for several decades, models for soot formation are still at the formative stage^[18]. It is generally acknowledged that polycyclic hydrocarbons (PAHs) are the precursors to soot particles. Appel *et al.*^[19] have developed detailed PAH based soot models for laminar premixed flames of C₂ hydrocarbons which describe the formation and growth of PAHs. The H-abstraction C₂H₂-addition mechanism (HACA mechanism) along with the condensation of PAHs to soot surface are usually employed to describe the heterogeneous soot surface reactions. On the treatment of soot particles dynamics, there are several approaches: the method of moment^[19-22], the stochastic method^[23], and the sectional model^[24-26]. The method of moments is less expensive compared to sectional methods and can be solved simultaneously with the gas-phase chemistry. Additionally, information about the method of moments neglects the exact distribution of particle size, mean quantities of interest are easily determined, and it can yield encouraging results for laminar flames. As a result, the method of moments has become the focus of research for modeling soot for-

mation^[18,27–28].

This paper investigates the effect of CO addition on soot formation in an acetylene/air premixed flame by numerical simulation. Specifically, we are interested in the chemical and temperature effect of CO addition on soot formation. The moment method was used to calculate soot formation, in which kinetic modeling with detailed chemistry and physics was considered. The model combines recent developments in gas-phase reactions, aromatic chemistry, soot particle coagulation, soot particle aggregation, and soot surface growth.

1 Model summary

The details of the model have been reported previously^[19–22,27–29]. The formation and growth for PAHs is modeled by ABF mechanism^[19]. The ABF mechanism can be split into four main components: (1) GRI-Mech.2.11 for H₂/O₂^[30], C₁ and C₂ chemistry; (2) a C₃-up section leading to the formation of benzene and phenyl, designated by A₁ and A₁[–], respectively; (3) a PAHs growth section up to pyrene, designated by A₄; (4) an oxidation section for A₁, A₁[–] and PAH. The further growth by cyclopentadienyl addition from Marinov *et al.*^[31], and combinative growth of aromatics by Skjøth-Rasmussen *et al.*^[32]. The evolution of the statistical moments M_r ($r=0, 1, 2, 3, \dots$) of the particle size distribution function (PSDF) can be derived from Smoluchowski's equation,

$$\begin{aligned}\frac{\partial M_0}{\partial t} &= R_{N0} - R_{A0} \\ \frac{\partial M_1}{\partial t} &= R_{N1} - R_{G1} - R_{O1} \\ \frac{\partial M_2}{\partial t} &= R_{N2} - R_{A2} - R_{G2} - R_{O2} \\ \frac{\partial M_3}{\partial t} &= R_{N3} - R_{A3} - R_{G3} - R_{O3}, \dots\end{aligned}\quad (1)$$

where the index N indicates nucleation (inception); A represents agglomeration; G is mass growth; O indicates oxidation; and t is the reaction time;

$$M_r = \sum_{i=1}^{\infty} m_i^r N_i \quad (2)$$

M_r is the r th concentration and size PSDF moments; m_i and N_i are the mass and number density of particles of size class i , respectively.

Nucleation is the formation of the first soot particles from PAH molecules. Nucleated soot particles are assumed to form from the collision of two dimers which are formed from the collision of two PAH molecules, and the nucleation model used here is put forward by Pitsch and his coworkers^[27]. Particle growth is considered in the free, transition and continuum regimes. Aggregates obey a fractal relationship with a dimension D_f of ca 1.8^[33], and the regimes are determined by the value of the Knudsen number. In the free molecular regime agglomeration is expressed as

$$R_{A,0} = \frac{1}{2} K_f M_0^2 f_{1/2}^{(0,0)} \quad (3)$$

$$R_{A,r} = \frac{1}{2} K_f M_0^2 \sum_{k=1}^{r-1} \left(\frac{r}{k} \right) f_{1/2}^{(k,r-k)} \quad (r=2,3, \dots) \quad (4)$$

where K_f and $f_{1/2}^{(k,r)}$ are the free molecular regime coagulation constant and the grid function, respectively, which was determined in Ref.[20]. Expressions for agglomeration in the continuum regime can be derived as

$$R_{A,0}^C = K_c [1 + \langle m_A^{1/3} N_P^{1/D_f-1/3} \rangle \langle m_A^{-1/3} N_P^{1/3-1/D_f} \rangle + K_c' (\langle m_A^{-1/3} N_P^{1/3-1/D_f} \rangle + \langle m_A^{1/3} N_P^{1/D_f-1/3} \rangle \langle m_A^{-2/3} N_P^{2/D_f-2/3} \rangle)] M_0^2 \quad (5)$$

where $K_c = 2k_B T / \eta$, k_B is the Boltzmann constant, N_P is the number density, T is the temperature, η is gas viscosity, $K_c' = K_c / 2$. There is a lack of physical models describing the transition from coalescent growth to aggregation. Kazakov and Frenklach^[20] suggested approximating the coagulation rate in the transition regime with the harmonic mean of the free molecular and continuum terms.

Appel *et al.*^[19] proposed the following soot growth and oxidation mechanism, based on the corresponding gaseous reactions of aromatic species:

- (i) $C_{\text{soot}}H + H \rightleftharpoons C_{\text{soot}}^* + H_2$
- (ii) $C_{\text{soot}}H + OH \rightleftharpoons C_{\text{soot}}^* + H_2O$
- (iii) $C_{\text{soot}}^* + H \rightarrow C_{\text{soot}}H$
- (iv) $C_{\text{soot}}^* + C_2H_2 \rightarrow C_{\text{soot}}H + H$
- (v) $C_{\text{soot}}^* + O_2 \rightarrow 2CO + \text{products}$
- (vi) $C_{\text{soot}}H + OH \rightarrow CO + \text{products}$

where $C_{\text{soot}}H$ and C_{soot}^* represent the arm-chair site and the radical site on the soot particle surface, respectively. The H abstraction reaction could also occur *via* reactions with methyl (CH₃), ethynyl (C₂H), and propargyl (C₃H₃) radicals:

- (vii) $C_{\text{soot}}H + C_2H \rightleftharpoons C_{\text{soot}}^* + C_2H_2$
- (viii) $C_{\text{soot}}H + CH_3 \rightleftharpoons C_{\text{soot}}^* + CH_4$
- (ix) $C_{\text{soot}}H + C_3H_3 \rightleftharpoons C_{\text{soot}}^* + C_3H_4$

2 Model validation

In this section, the above presented soot model is validated in simulations of high temperature premixed ethylene and acetylene as well as benzene flames with the C/O molar ratio varied between 0.6 and 1.3. All simulations presented in this work were performed with our developed code based on PREMIX program^[34–35], and the code has soot subroutines which contain the above particle dynamics. Wang and Frenklach^[36] studied the formation and growth of PAHs in laminar premixed acetylene and ethylene flames, and suggested a detailed reaction mechanism (WF mechanism) consisting of 99 chemical species and 531 reactions. Appel *et al.*^[19] augmented WF mechanism and developed ABF mechanism for PAHs mass growth and oxidation. In the current article, ABF mechanism is used to describe gas-phase chemistry for soot formation.

The flames examined numerically were those investigated experimentally in five different laboratories, thus providing a diversity of different techniques and individual characteristics. The properties of these flames are summarized in Table 1^[5,19,37–39]. The above present soot model can reproduce the existing experiment results in the literature with good accuracy. Most of the flames reached a maximum flame temperature from 1700 to 2100 K, with an exception of the ethane flame, CS1_0.748, with the reported maximum flame temperature of 1270 K. These

Table 1 Summary of flame conditions

Flame designation	$10^{-5}p/\text{Pa}$	Fuel	$x(\text{fuel})$	$x(\text{O}_2)$	$x(\text{N}_2)$	$x(\text{Ar})$	$v/(\text{cm}\cdot\text{s}^{-1})$	$x(\text{C})/x(\text{O})$	T_{max}/K	Ref.
XSF1_0.78	1	C_2H_4	14.00	18.00	68.00	—	4.0	0.780	2104	[5]
XSF1_0.88	1	C_2H_4	15.50	17.40	67.10	—	6.5	0.880	1957	[5]
XSF1_0.98	1	C_2H_4	17.00	17.40	65.60	—	5.4	0.980	1908	[5]
JW1_0.69	1	C_2H_4	12.66	18.34	69.00	—	5.9	0.690	1711	[19]
JW10_0.60	10	C_2H_4	11.20	18.65	70.15	—	6.0	0.600	2017	[19]
JW10_0.673	10	C_2H_4	12.38	18.40	69.22	—	3.0	0.673	1895	[19]
JW10_0.68	10	C_2H_4	12.50	18.40	69.10	—	6.0	0.680	1880	[19]
WBF0.12_1.3	0.12	C_2H_2	22.60	12.40	—	55.00	20.1	1.300	1980	[37]
CS1_0.748	1	C_2H_6	24.12	32.25	—	43.36	7.0	0.748	1270	[38]
TCB1_0.72	1	C_6H_6	4.80	19.99	75.21	—	4.0	0.720	1821	[39]
TCB1_0.77	1	C_6H_6	5.11	19.93	74.96	—	4.0	0.770	1754	[39]

v : cold gas velocity

flames contain the information required to test various parts of the numerical model, and collectively the data taken together can test many of the critical aspects of the soot formation model: the major combustion products and intermediates, single-ring aromatics and their precursors, polycyclic aromatics, soot volume fraction, particle size, and particle aggregation.

As shown in Fig.1, the prediction results for the soot volume fraction are excellent, and the soot density, expressed as the total mass of soot particles per unit volume, is reasonably well predicted for both premixed benzene flames shown in Fig.2. In the experiments, soot particles were collected in the flames and then extracted in dichloromethane (DCM) to isolate them from condensed species (CS). We turned to flame CS1_0.748 which reported experiment data for both small hydrocarbons and one- to multi-ring PAHs, thus allows the examination of the transition from the small-hydrocarbon chemistry to PAH formation. As demonstrated in Fig.3, most of the measured small species (where a- C_3H_4 is allene, $\text{A}_1\text{C}_2\text{H}_3$ represents styrene, $\text{A}_1\text{C}_2\text{H}$ is the species in which a hydrogen atom from the benzene ring has been substituted by an ethynyl group C_2H , P_2 is biphenyl) were predicted well, and the aromatic species (A_1 – A_4) were also predicted reasonably close.

Eleven of the flames considered here report soot measure-

Fig.1 Soot volume fraction (F_v) in the eight sooting laminar premixed flames

line: simulation result, symbol: experiment result

Fig.2 Soot density for the premixed benzene flames

line: simulation result, symbol: experiment result

ments, and all of these data are reproduced by the model within a factor of 2.5 (defined in Ref.[19]). This level of agreement is very encouraging, considering the difficulties associated with experimental measurements for polyaromatics and soot, and the current uncertainties in the thermodynamics and kinetics of the aromatics chemistry as well as soot particle nucleation and surface reactions. It implies that the above soot formation model can be used to predict soot formation in laminar premixed flames for research purpose in this paper.

3 Results and discussion

In the present, some parameters used are defined as follows: ratio of carbon monoxide addition a , $a = x_{\text{CO}}/(x_{\text{CO}} + x_{\text{C}_2\text{H}_2})$; dilution factor D , $D = x_{\text{O}_2}/(x_{\text{O}_2} + x_{\text{N}_2})$ (D is taken to be 0.21 as constant in this work); fuel-equivalence ratio φ ,

$$\varphi = [(x_{\text{C}_2\text{H}_2} + x_{\text{CO}})/x_{\text{O}_2}]_{\text{actual}} / [(x_{\text{C}_2\text{H}_2} + x_{\text{CO}})/x_{\text{O}_2}]_{\text{stoichiometric}}$$

where x_k represents mole fraction of the species k . The problem is modelled to solve burner-stabilized flame, and temperature profile was obtained by the coupled energy-species equations. Multi-component diffusion and thermal diffusion options were taken into account. Due to the complexity of numerical model about soot formation, the CNTN option was used in order to converge more easily or speed up iteration, which made the adaptive grid parameters GRAD and CURV vary from 1.0 and 1.0 to 0.1 and 0.5, respectively. Relative and absolute error crite-

Fig.3 Species profiles for flame CS1_0.748

line: simulation result, symbol: experiment result

ria were $RTOL=1 \times 10^{-5}$ and $ATOL=1 \times 10^{-10}$, respectively, and total number of grid points was typically 100–200.

Firstly, we give a glimpse at profiles of temperature and soot volume fraction as well as primary particle diameter for CO addition in acetylene/air premixed flame shown in Fig.4. The parameters of this flame condition are: CO addition $a=50\%$; fuel-

Fig.4 Profiles of temperature and soot volume fraction as well as primary particle diameter (d) for $a=50\%$ at $\varphi=2.7$
drawing for skipping 2 points

equivalence ratio $\varphi=2.7$; mass flow rate through the burner $FLRT=0.005 \text{ g} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, the maximum temperature will rise along with the increase of $FLRT$ while other parameters are the same. As shown in Fig.4, the maximum temperature in flame stability zone reaches 1556 K, the temperature rises rapidly during the height of 0.01–0.1 cm and temperature already reaches 1295 K in the height of 0.1 cm. Soot volume fraction F_v and primary particle diameter d increase as the temperature rises, and the trend is similar to the temperature curve, but d declines during the initial phase of rapid temperature rising. F_v and d read 2.06×10^{-9} and $1.40 \times 10^{-7} \text{ cm}$ respectively in the height of 0.1 cm above the burner.

Fig.5 shows the profiles of temperature, soot volume fraction and primary particle diameter as well as nucleation rate for different CO additions at fuel-equivalence ratio $\varphi=2.3$. It seems that the addition of CO inhibits soot formation. The temperature in flame stability zone reaches above 1900 K, for example 1909 K in the height of 0.3 cm above the burner. The temperature decreases by 22 and 63 K, respectively, for 25% and 50% CO addition at 0.3 cm above the burner. In this location, soot volume fractions fall to 5.57×10^{-8} and 2.18×10^{-8} respectively for 25% and 50% CO addition from original 8.17×10^{-8} , and with the increase of CO addition primary particle diameters drop to 2.635×10^{-7} and $2.349 \times 10^{-7} \text{ cm}$ respectively from $2.856 \times 10^{-7} \text{ cm}$. It can be found that a rapid increase in nucleation rate during ignition stage, then the nucleation rate declines in the stability zone of flame. The addition of CO can greatly reduce the nucleation rate as shown in Fig.5. It needs to point out that Guo *et al.*^[16] suggested CO addition promotes the formation of soot in the ethylene/air diffusion flame, but this conclusion was drawn from the comparison of CO and N_2 diluted flames, that is, CO addition promotes more soot formation than that of N_2 dilution. In fact, the experiments by Guo *et al.* show that the addition of both CO and N_2 monotonically reduces the formation of soot, and addition of

Fig.5 Profiles of temperature (a), soot volume fraction (b), primary particle diameter (c), and nucleation rate (v_n) (d) for different CO additions (a) at $\varphi=2.3$

Fig.6 Soot volume fraction and primary particle diameter with temperature at height of 0.6 cm above the burner in flame stability zone for different conditions

Fig.7 Nucleation (v_n) and coagulation (v_c) rates at height of 0.6 cm above the burner in flame stability zone for different conditions

N_2 is more effective than that of CO in suppressing soot formation.

As mentioned above, the addition of CO decreases the temperature in the flame, but it is still unknown whether the decreases of soot volume fraction and primary particle diameter are due to temperature drop, the chemical effects by CO addition also influence soot formation. Guo *et al.*^[16] suggested that the chemical effect of CO addition might be caused by the modifications of the flame temperature, soot surface growth, and oxidation reactions. They argued that flame temperature increases relative to a nitrogen diluted flame, which results in a higher surface growth rate, when CO is added. So it is very important to analyze the effects of temperature on the formation of soot. Fig.6 and Fig.7 show profiles of soot volume fraction, primary particle diameter, nucleation and coagulation rates with temperature in height of 0.6 cm above the burner in flame stability zone in different conditions. Each legend represents a set of numerical results, therefore, Fig.6 and Fig.7 are got through calculations for 72 rounds. Keeping fuel-equivalence ratio φ and CO addition

constant, it makes temperature at the height varies by changing the mass flow rate through the burner, the purpose of doing that is decoupling the influence of C/O ratio on soot formation. Soot volume fraction and nucleation rate increase until a threshold temperature and then decrease as the temperature further increases. Primary particle diameter increases along with the temperature rising, and there is an approximate mirror symmetry relation between the nucleation rates and the coagulation rates. Along with increase of CO addition, soot volume fraction and nucleation rate fall rapidly, while primary particle diameter has a slight decline in the low or medium temperature area. Under the condition of the same CO addition a , soot volume fraction and nucleation rate rise greatly with the fuel-equivalence ratio φ increases, while primary particle diameter keeps almost unchanged in the low or medium temperature area.

Fig.8 shows mole fraction changes of H and OH and Fig.9 illustrates profiles of surface growth/oxidation rates due to effect by OH for different CO additions at $\varphi=2.3$. The addition of CO increases the concentration of H radical in the lower flame re-

Fig.8 Mole fractions of H and OH for different CO additions at $\varphi=2.3$

Fig.9 Profiles of surface growth/oxidation rates (SG) due to effect by OH for different CO additions at $\varphi=2.3$

gion owing to the intensified forward rate of the reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$ and therefore increases the soot surface growth rates. The addition of CO also slows the oxidation rate of soot because the same reaction $\text{CO}+\text{OH}=\text{CO}_2+\text{H}$ results in a lower concentration of OH and a higher concentration of H, then it causes the higher active site formation rate of the key reaction $\text{C}_{\text{soot}}\text{H}+\text{H}\rightleftharpoons\text{C}_{\text{soot}}+\text{H}_2$ (soot formation of active site by H-abstraction). This implies that the addition of CO chemically promotes the formation of soot, which is different from the chemical effect

Fig.10 Profiles of production rates of C_2H_2 for different CO additions at $\varphi=2.3$

Fig.11 Profiles of surface growth/oxidation rates due to effect by C_2H_2 for different CO additions at $\varphi=2.3$

of CO_2 or H_2 addition.

Another key reaction for soot formation is the C-addition reaction $\text{C}_{\text{soot}}+\text{C}_2\text{H}_2\rightarrow\text{C}_{\text{soot}}\text{H}+\text{H}$. One of the primary destruction reactions of C_2H_2 in which there exists carbon monoxide species is $\text{C}_2\text{H}_2+\text{O}=\text{CO}+\text{CH}_2$. The reverse rate of this reaction is intensified by the addition of CO, resulting in the lower C_2H_2 destruction rate and thus higher concentration of C_2H_2 , and it seems that CO addition promotes the formation of soot. Guo *et al.*^[16] found that in the upper flame region, the difference in C_2H_2 of the different flames in the peak surface growth region is negligible in a laminar ethylene/air coflow diffusion flame, so they believed

Fig.12 Rates of progress for some key reactions for different CO additions at $\varphi=2.3$

that C_2H_2 may not be a factor that results in the higher surface growth rate due to the chemical effect of CO addition. Profiles of production rates of C_2H_2 for different CO additions at $\varphi=2.3$ can be seen in Fig.10, and Fig.11 shows the profiles of surface growth/oxidation rates due to C_2H_2 for different CO additions at $\varphi=2.3$. The addition of CO weakens production rates for C_2H_2 , but the addition of CO greatly reduces the volume fraction of C_2H_2 in fuel and then reduces the soot surface growth due to C_2H_2 . One of the key production reactions of C_2H_2 is $C_2H_3+O_2=C_2H_2+HO_2$. In addition, it is important about PAH chemistry in soot formation. Two main routes for the formation of benzene and phenyl are combination of propargyl $C_3H_3+C_3H_3\rightarrow A_1$ and reaction of $n-C_4H_3+C_2H_2=A_1$ -(phenyl). Fig.12 shows rates of progress for these reactions for different CO additions at $\varphi=2.3$, it can be found that the rates of progress for these reactions decrease with the increase of CO addition.

4 Concluding remarks

A detailed numerical study has been conducted on the effect of CO addition on soot formation in an acetylene/air premixed flame, and it shows that the addition of CO monotonically reduces the formation of soot. The formation of soot particles depends on a wide range of parameters, in which temperature and chemical effects play particularly important roles. There is a strong coupling between the chemical effect and thermal effect in soot formation. The changed rates of the reactions due to variations in temperature can cause different heat releases, and feed back to modify the temperature. The effect of temperature is isolated from the chemical effect by comparing the results of CO diluted flames at fixed height above the burner, and the fuel-equivalence ratio φ and CO addition a remain constant, it makes temperature at the fixed height vary by changing the mass flow rate through the burner. The soot volume fraction and nucleation rate increase until a threshold temperature and then decrease as the temperature further increases. Primary particle diameter increases along with the increase of temperature, and there is an approximate mirror symmetry relation between the nucleation rates and the coagulation rates. The analysis of the details from numerical simulation suggests that there are mainly three factors for chemical effect of CO addition on the formation of soot. (1) The concentration of H radical is increased due to the intensified forward rate of the reaction $OH+CO=CO_2+H$, which results in the higher surface growth rate for soot formation known as formation of active site by H-abstraction. Meanwhile, the addition of CO reduces the concentration of OH radical due to the same reaction and consequently slows the oxidation rates of soot. (2) The rates of progress for the primary destruction and production reactions of C_2H_2 ($C_2H_2+O=CO+CH_2$ and $C_2H_3+O_2=C_2H_2+HO_2$) tend to decrease with CO addition, while the addition of CO can greatly reduce the volume fraction of C_2H_2 in fuel, resulting in lower concentration of C_2H_2 . So we draw a different conclusion with Guo *et al.* that C_2H_2 may be a factor that results in the lower surface growth rate due to the CO addition. (3)

In PAH chemistry, two main routes for the formation of benzene and phenyl ($C_3H_3+C_3H_3\rightarrow A_1$ and $n-C_4H_3+C_2H_2=A_1$ -(phenyl)) were also analyzed, it shows that the formation of soot is suppressed by CO addition.

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