Physical and chemical effects of phosphorus-containing compounds on laminar premixed flame*

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Phosphorus-containing compounds are the promising halon alternatives for flame inhibitions. However, some literatures suggested that the phosphorus-related inhibitors may behave as the unfavorable ones that will increase the burning velocity under lean-burn conditions, and this indeed posed potential threats to the fire prevention and fighting. To seek deeper insights into the reaction process, a numerical investigation was actualized to study the phosphorus-related effects on methane–air flames. By replacing a phosphorus-related inhibitor with the corresponding decomposed molecules, the detailed promoting and inhibiting effects of combustion were separated from the general chemical effect. A comparative study was carried out to identify the interaction between the two effects under different combustion conditions. It is observed that the promoting effect becomes the dominant factor during the reaction process when the equivalence ratio is smaller than 0.60. In this lean-burn condition, the exothermic reactions were faster than the others within the reaction chains due to the reduction of radical recombination in hydrocarbon oxidation. The results are believed to be useful for the further application and improvement of flame inhibitors.

Keywords: phosphorus-containing compounds, flame inhibition, chemical effect, burning velocity

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1. Introduction

The physical and chemical effects of halogenated fire suppressants were studied and the relative contributions of physical and chemical components on inhibitor influence were estimated.[1–4] Such researches provide the fundamental basis in selecting alternative fire suppressants to replace the halons which deplete the ozone layer,[1] and further provide the way to generate composite inhibitors composed of effective chemical inhibitors and high heat capacity diluent.[2,3] Therefore, the investigation of further insight into the physical and chemical mechanisms is of both scientific and practical magnificence.

The previous work focuses on halogenated compounds, whereas phosphorus-containing compounds (PCCs), such as dimethyl methylphosphonate (DMMP) and trimetylphosphate (TMP), are pointed out to be the effective halon alternatives which have better effects on the inhibition of hydrocarbon flame than halon,[5–7] and have been gradually used as flame inhibitors.[8,9] What the exact mechanisms of this action are has been a long standing issue. Twarowski[10–12] found that phosphine (PH_3) can accelerate radical recombination in hydrogen oxidation. Korobeinichev *et al.* tried to explain how PCCs inhibited hydrogen flames[13] and hydrocarbon flames,[14] and MacDonald *et al.* conducted a few experiments and simulations to conclude that DMMP suppresses combustion by reducing the concentration of H and OH in the flames.[15] Subsequent work by Jayaweera *et al.* confirmed that these small molecules which reduce the concentration of free radicals in the flame are mainly PO_2, $HOPO_2$, HOPO, and PO.[16] Moreover, a series of novel phosphorus-containing flame retardants which take advantage of the chemical and physical effects have been successfully synthesized.[17–19] However, recent studies[20,21] find that adding phosphorus-containing inhibitors into the lean flames could lead to an increase in the burning velocity and have a certain effect on promoting combustion. Consequently, conducting more in-depth research on the inhibition mechanisms of PCCs is expected.

Flame suppression is caused by physical and chemical effects. The physical effects are found to be a negative factor in the combustion process due to heat capacity and dilution effects, so the unexpected combustion enhancement of PCCs originates from the chemical effect which can usually inhibit combustion since it scavenges radicals in the flame reaction chains. As a consequence, considerable controversy has been focused on how the chemical effect of phosphorus-containing inhibitors promotes the combustion, what reactions work, and whether the catalytic inhibition exists in the chemical effect. In this study, we mainly focus on these issues of PCCs.

Through experiments, it is difficult to separate the physical and chemical effects, let alone decouple the chemical effect. However, the numerical simulation method is often used to study the interaction between physical and chemical properties.[22,23] Recently, a numerical method on the chemical and physical effects of halogenated fire suppressants by setting the chemical effect on or off is utilized.[3,4] When the

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flame reaches a certain temperature, the inhibitors can decompose to many small molecules, and the previous method[3,4] seems to ignore the chemical effect caused by the decomposition process of the inhibitor itself. In this work, the small molecules that play major catalytic roles in flame retardation are used to replace the original phosphorus-containing inhibitor molecule. As a result, a new numerical investigation on the methane–air premixed flames adding two phosphorus-containing inhibitors (DMMP and TMP) is carried out to further decouple the chemical effect into a phosphorus-related moiety that catalyzes the flame suppression and a carbon-related moiety that initiates the decomposition and combustion. Moreover, the relative contributions of these two chemical effects on decreasing the burning velocity are quantitatively analyzed.

2. Calculation model

2.1. The physical and chemical effects of the flame inhibitors

The burning velocity is one of the most basic parameters for the characterization of the flame propagation properties and also has been found to be an important parameter which characterizes the inhibition efficiency of halogen-containing flame retardants.[2] As the inhibitor concentration increases, the burning velocity decreases due to increased inhibitor influence. Babushok *et al.*[3] and Ren *et al.*[4] investigated the relationship between the physical and chemical effects of halon substitutes by using the laminar flame velocity. This method considered that the reason why the flame speed was reduced was the result of the chemical and physical effects, in which the physical effect consists of the dilution effect and thermal effect. These effects are independent, and this method can be mathematically expressed as

$$\Delta S = \Phi(R) + \phi(D) + \psi(T), \tag{1}$$

where $\Phi(R)$, $\phi(D)$, and $\psi(T)$ represent the chemical effect, the dilution effect, and the thermal effect, respectively. ΔS is the change of the flame speed. At the same time, the following definitions are given:

(i) When the flame inhibitor is not added, the laminar flame velocity of the flame is S_0, and the dilution effect and the thermal effect of the flame inhibitor are both zero at this time, that is,

$$\begin{aligned} &S_0 = \Phi(R)|_{t=0} + \phi(D)|_{t=0} + \psi(T)|_{t=0}, \\ &\phi(D) = \psi(T) = 0, \end{aligned}$$

$$S_0 = \Phi(R)|_{t=0} = \text{const.} \tag{2}$$

(ii) When the flame inhibitor is added, the laminar flame velocity of the flame is S_u, and

$$S_0 - S_u = \Phi(R) + \phi(D) + \psi(T). \tag{3}$$

(iii) The inhibitor in the reactants is treated as an inert polyatomic molecule which does not react chemically and only the physical effect works. We can now go through the data base and turn off the chemistry of the suppressant by arbitrarily setting all rate constants that involve it in the chemical reaction mechanism and its decomposition products to be zero. The laminar flame speed is defined as S_c at this time, and

$$S_0 - S_c = \phi(D) + \psi(T). \tag{4}$$

(iv) Compared with the inhibitor, the latent heat and specific heat capacity of N_2 are very low and negligible. It is considered that N_2 only has the dilution effect,[24] and N_2 is used to replace the additive as flame retardant. The laminar flame speed calculated in this case is expressed as S_d, and

$$S_0 - S_d = \phi(D). \tag{5}$$

Then the chemical effect, physical effect, thermal effect, and dilution effect of the inhibitor can be solved by Eqs. (3)–(5) respectively as

$$\begin{aligned} S_{\text{Che}} &= \Phi(R) = S_c - S_u, \\ S_{\text{Phy}} &= \phi(D) + \psi(T) = S_0 - S_c, \\ S_{\text{The}} &= \psi(T) = S_d - S_c, \\ S_{\text{Dil}} &= \phi(D) = S_0 - S_d. \end{aligned}$$

2.2. The catalytic and pyrolytic effects of the flame inhibitors

When the flame temperature gradually increases with the combustion, the inhibitor macromolecule decomposes into small molecules, some of which catalyze the recombination of H and OH in the flame, reducing the chain reactions and inhibiting combustion. In other words, the inhibitor is decomposed into two components of small molecules: the component of inhibiting the flame and the component of promoting combustion. Therefore, in this paper, the chemical effect of inhibitors is divided into two parts: catalytic effect and pyrolytic effect. The pyrolysis effect mentioned here includes two processes, which are the decomposition of the inhibitor into small molecules and the further reactions of such small molecules that promote combustion. Then the chemical effect of the inhibitor can be further resolved by

$$\Phi(R) = \eta(C) + \zeta(P). \tag{6}$$

In the flame inhibition mechanism of PCCs, Twarowski[10] found that PCCs produce small phosphorus-containing molecules which promote the radical recombination. Then Jayaweera[16] confirmed that these small phosphorus-containing molecules are mainly PO_2, $HOPO_2$, HOPO, and PO, while the phosphorus-containing molecules in the highest

ranking concentration are these four substances at the same time in the flame zone. Such small P-containing species promote catalytic recombination of radicals:

$$\begin{aligned}
&PO_2 + H + M \rightarrow HOPO + M,\\
&HOPO + H \rightarrow H_2 + PO_2,\\
&HOPO + H \rightarrow PO + H_2O,\\
&PO_2 + OH + (M) \rightarrow HOPO_2 + (M),\\
&HOPO_2 + H \rightarrow H_2O + PO_2.
\end{aligned}$$

These catalytic reactions actually constitute different inhibition cycles in which the phosphorus compounds are acting catalytically to recombine H and OH to form H_2O. The phosphorus-containing compounds PO(m/e 47), PO_2 (m/e 63), HOPO (m/e 64), and $HOPO_2$ (m/e 80) have been identified as the main products of the destruction of TMP and DMMP[13,25–27] in a flame. The mole balance for phosphorus in the postflame zone is

$$\alpha_{\mathrm{DMMP}} = \alpha_{\mathrm{PO}} + \alpha_{\mathrm{PO_2}} + \alpha_{\mathrm{HOPO}} + \alpha_{\mathrm{HOPO_2}}, \tag{7}$$

where α_{DMMP}, α_{PO}, $\alpha_{\mathrm{PO_2}}$, α_{HOPO}, and $\alpha_{\mathrm{HOPO_2}}$ are mole fractions.

In addition, it was noteworthy that the total amount of PO_2, $HOPO_2$, HOPO, and PO in the combustion products accounted for more than 90% of the initial inhibitor addition in the lean flame, as shown in Table 1. TMP was added into the methane–air laminar flame with an initial equivalence ratio of 0.40–0.65. It was found that when the TMP volume fraction was 1.5%, the total amount of these four substances in the combustion products accounted for 94.2%–95.2% of the sum of TMP decomposition products, and when adding 2.0%, the percentage accounted for 90.5%–93.8%. Therefore, in this paper, these four phosphorus-containing species (PO_2, $HOPO_2$, HOPO, and PO) were used to replace the original phosphorus-containing inhibitor, and the rest of the products were supplemented with N_2. In this condition, the laminar flame speed is defined as S'_u, and $\zeta(P) = 0$, indicating that the catalytic effect in the inhibitor works independently.

$$S_0 - S'_u = \eta(C) + \phi(D) + \psi(T). \tag{8}$$

Therefore, in the chemical effect of the phosphorus-containing retardants, the catalytic effect and pyrolytic effect can be expressed as

$$\begin{aligned}
S_{\mathrm{Cat}} &= \eta(C) = S_c - S'_u,\\
S_{\mathrm{Pyr}} &= \zeta(P) = S'_u - S_u.
\end{aligned}$$

Table 1. The percentage of the total quantity of PO_2, $HOPO_2$, HOPO, and PO in the products of the additive.

Addtive	Volume fraction	Equivalence ratio	Total quantity of PO_2, $HOPO_2$, HOPO, and PO	Percent
TMP	1.5%	0.40	1.43%	95.0%
TMP	1.5%	0.45	1.42%	94.9%
TMP	1.5%	0.50	1.43%	95.2%
TMP	1.5%	0.55	1.42%	94.9%
TMP	1.5%	0.60	1.42%	94.7%
TMP	1.5%	0.65	1.41%	94.2%
TMP	2.0%	0.40	1.88%	93.8%
TMP	2.0%	0.45	1.87%	93.6%
TMP	2.0%	0.50	1.86%	93.2%
TMP	2.0%	0.55	1.85%	92.7%
TMP	2.0%	0.60	1.84%	91.8%
TMP	2.0%	0.65	1.81%	90.5%

2.3. The relative contributions of various effects on the reduction of the flame speed

In terms of the laminar flame velocity, the effect of the flame retardant is manifested as reducing the flame speed. The flame speeds S_u, S_c, S_d, and S'_u in the above cases are normalized respectively to that in the situation where there is no additive, as shown in Fig. 1, so that the relative contributions of the physical effects (dilution effect and thermal effect) and the chemical effects (catalytic effect and pyrolytic effect) of the flame suppression can be obtained as

$$\begin{aligned}
Y_{\mathrm{Phy}} &= S_{\mathrm{Phy}}/S_0 = \frac{S_0 - S_c}{S_0} = 1 - \frac{S_c}{S_0},\\
Y_{\mathrm{Dil}} &= S_{\mathrm{Dil}}/S_0 = \frac{S_0 - S_d}{S_0} = 1 - \frac{S_d}{S_0},\\
Y_{\mathrm{The}} &= S_{\mathrm{The}}/S_0 = \frac{S_d - S_c}{S_0},\\
Y_{\mathrm{Che}} &= S_{\mathrm{Che}}/S_0 = \frac{S_c - S_u}{S_0},\\
Y_{\mathrm{Cat}} &= S_{\mathrm{Cat}}/S_0 = \frac{S_u - S'_u}{S_0},\\
Y_{\mathrm{Pyr}} &= S_{\mathrm{Pyr}}/S_0 = \frac{S'_u - S_u}{S_0}.
\end{aligned}$$

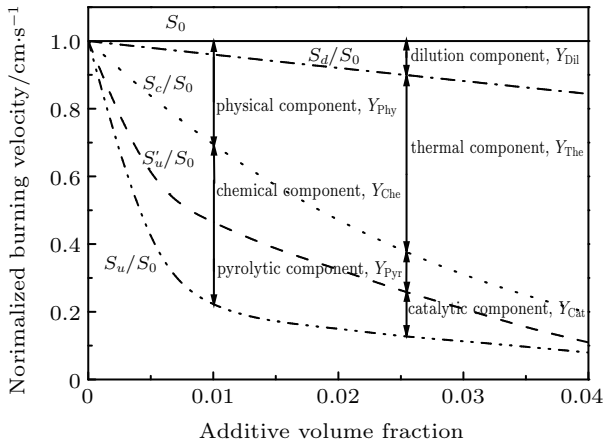


Fig. 1. Definitions of the physical component Y_{Phy} and the chemical component Y_{Che} of inhibitor influence.

3. Kinetic mechanism and initial conditions

When the inhibition of methane–air flame is studied by DMMP and TMP, the same kinetic mechanism is used. In the calculations of the burning velocity, the GRI 3.0 mechanism[28] and Curran mechanism[29,30] were used for methane oxidation. In Fig. 2, a comparative result calculated and experimental results[31,32] for the burning velocity of undoped flames and added 6000 ppm TMP flames show that the predictions obtained using GRI 3.0 mechanism are in better agreement with experimental data for near-stoichiometric flames, whereas the Curran mechanism provides the best fit for lean and rich flames. In our work, we focus on the lean flame, so we choose the Curran mechanism for methane oxidation and the mechanism of flame inhibition by PCSs, which is mainly composed of a small phosphorus-containing oxide mechanism, the DMMP mechanism, and TMP mechanism like Jayaweera *et al.*[16] The complete mechanism consists of 6 elements, 121 components, and 682 motifs. Moreover, this mechanism is in good agreement with experimental data for DMMP[16] and TMP[33] when predicting burning velocity.

The laminar flame velocity is calculated by using the PREMIX code in CHEMLIN-PRO[34] in this work. The entire calculation zone is performed in a one-dimensional region of 10 cm in length. The maximum gradient (GRAD) and maximum curvature (CURV) are set to 0.05 and 0.05, so that the final number of the generated grid is more than 500. Grid independence tests show that the absolute error of the calculated flame speed is less than 1%. Since the phenomenon of combustion promotion of phosphorus-containing inhibitors is shown in a very lean flame, the research in this work mainly focuses on the situations where the equivalence ratio ϕ is 0.40–0.65, and ϕ is selected as 0.40, 0.45, 0.50, 0.55, 0.60, 0.65, and 1.00 in initial conditions. The equivalent ratio of methane and air is calculated as

$$\Phi_i = \frac{C_{CH_4}/(C_{CH_4}/C_{O_2})_{st}}{C_{O_2}}, \tag{9}$$

where C_i represents the mole concentration of species i, and subscript st represents the value under stoichiometric conditions. In this paper, flame retardants are added to the combustible mixture, while selecting N_2 as a reference gas. The volume fraction of the inhibitor gas is defined as

$$X_a = \frac{V_{in}}{V_{in} + V_{fuel} + V_{air}}. \tag{10}$$

Selecting DMMP and TMP as additives, the volume fraction varies from 0% to 4%, and the initial temperature and pressure are set to 373 K and 1 bar.

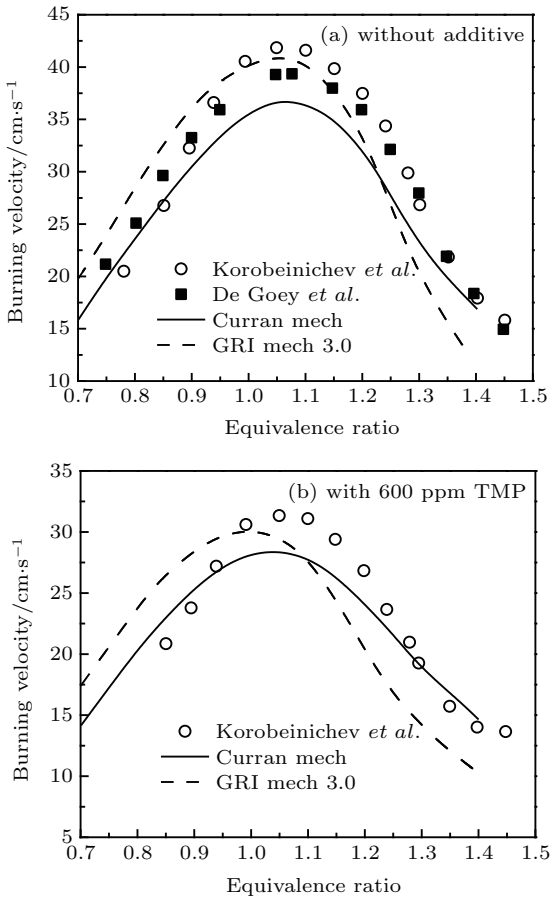


Fig. 2. (color online) Burning velocity in CH_4–air mixtures versus equivalence ratio. Symbols: experiments (circles-data from Ref. [31] and squares-data from Ref. [32]), lines: modeling (Curran mechanism[29,30] and GRI 3.0 mechanism[28]).

4. Results and discussion

4.1. The effect and reason of combustion promotion caused by PCCs

For each of the additives, DMMP and TMP, burning velocity calculations were performed under a range of equivalence ratio ϕ and an initial temperature of 373 K. Figure 3 shows the calculated burning velocity of the methane–air

flames at the indicated equivalence ratio, as a function of the agent volume fraction X_a in the mixture. Figure 3(a) shows stoichiometric flames and figure 3(b) shows lean flames. Note that the equivalence ratio here refers to that of the methane–air mixture prior to addition of the flame inhibitor. Adding different flame retardants to flammable mixtures, TMP and DMMP have the same trend, but the inhibitory effect of TMP was slightly higher by 1.6%. It can be seen from the comparison that when the initial equivalence ratio of the methane–air mixture is at $\phi \geq 0.60$, the burning velocity decreases gradually with the addition of an inhibitor. On the contrary, when $\phi < 0.60$, there is a significant increase in the process at the range of $0.005 < X_a < 0.020$ for the burning velocity. However, when the volume fraction of the inhibitor is at $X_a > 0.025$, the burning velocity decreases with the increase of the initial equivalence ratio. Thus the burning velocities at different equivalence ratios have a little difference and show a unified linear decreasing trend.

In order to observe the increase of laminar burning velocity more clearly, the situation is enlarged when $0.30 \leq \phi \leq 0.50$ and $0 \leq X_a \leq 0.02$, as shown in Fig. 4. Symbols are the calculated values and lines are the corresponding fitting curves in the diagram. It is found that when the initial equivalent ratio of methane and air is less than 0.50, the flame velocity increases and presents a significant linear incensement when adding a phosphorus inhibitor of less than 0.02 volume fractions.

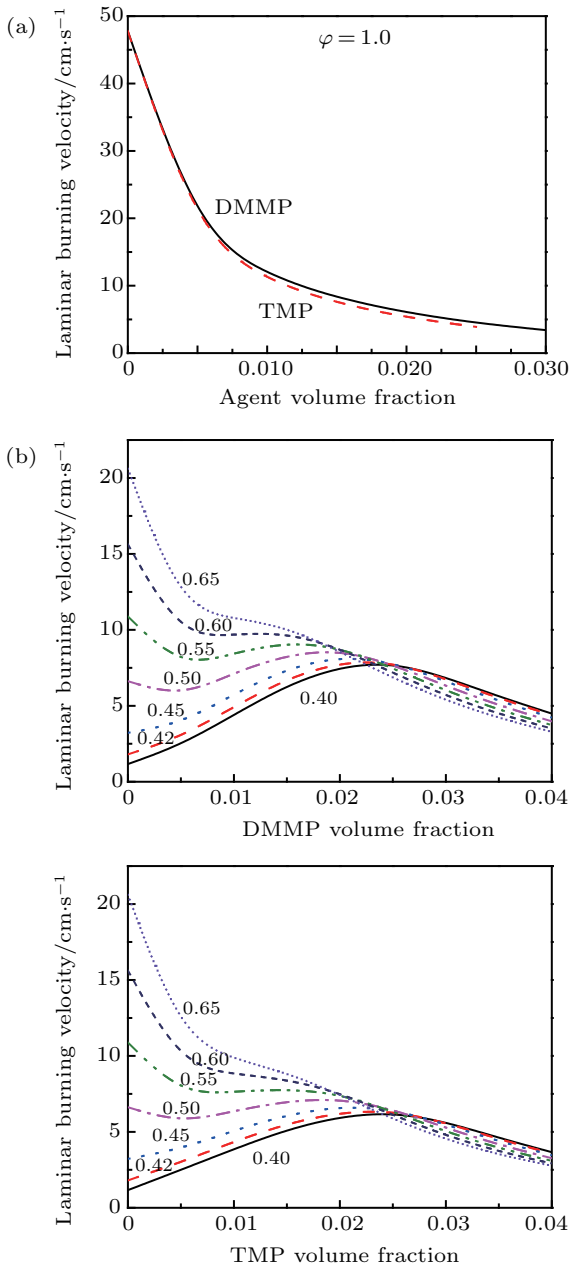


Fig. 3. (color online) Laminar burning velocity as a function of inhibitor volume fraction at different equivalence ratios (CH_4/air mixture, initial temperature 373 K). (a) Stoichiometric flames. (b) Lean flames.

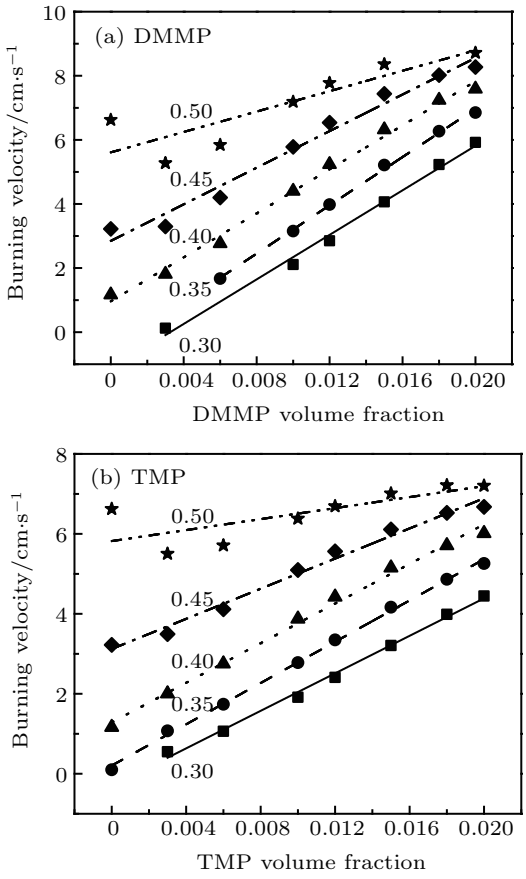


Fig. 4. Burning velocity in CH_4–air mixtures versus agent volume fraction in very lean flames.

For the initial lean mixtures, the effect of PCCs decreases severely with ϕ decreasing, and for lean enough conditions, adding DMMP and TMP can actually increase rather than decrease the flame speed. For other flame inhibitors that also have a hydrocarbon component (for example, $C_3H_2F_3Br$,[35] C_2HF_5,[35] and $C_6F_{12}O$[36]), this result has been observed and attributed to the effect of the increase in adiabatic flame temperature caused by agent-supplied fuel species addition. Figure shows the adiabatic flame temperature T_{ad} of methane–air

mixtures with different initial equivalence ratios, as a function of the agent volume fractions. As indicated, there is a critical volume fraction X_c. When the agent volume fraction is at $X_a < X_c$, the adiabatic flame temperature increases significantly, and when $X_a > X_c$, the adiabatic flame temperature decreases gradually. The smaller the equivalence ratio is, the larger X_c is, the larger the range of the growth of T_{ad} is, the greater the range of the rise of temperature is, which is consistent with the observed change in flame speed. For example, adding MMMP to a methane–air flame, when the equivalence ratio is at $\phi = 0.40$, $X_c = 0.025$ and T_{ad} is increased by up to 800 K.

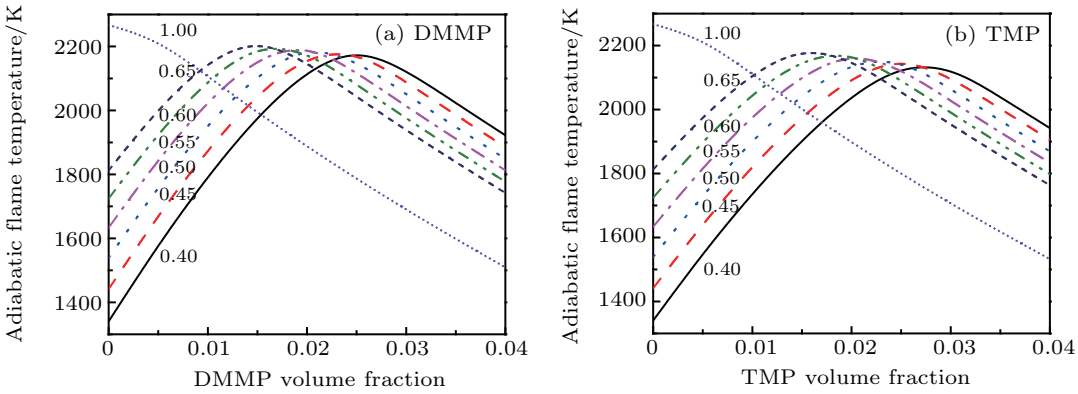


Fig. 5. (color online) Dependence of the adiabatic combustion temperature on the inhibitor concentration at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).

To demonstrate the additional fuel effect, figure 5 is reploted by the overall equivalence ratio as the X-axis instead of the additive volume fraction taking into account the fuel properties of inhibitors. It was assumed that the main combustion products of phosphorus-containing inhibitors (DMMP and TMP) are $HOPO_2$ (or $OP(OH)_3$), CO_2, and H_2O.[21] Figure 6 contains the same data as the overall equivalence ratio used in Fig. 5 as abscissa. The overall equivalence ratio of the methane–air mixture with phosphorus-containing inhibitors can be expressed as

$$\Phi_a = \frac{C_{CH_4}/(C_{CH_4}/C_{O_2}) + C_{DMMP}/(C_{DMMP}/C_{O_2}) + C_{TMP}/(C_{TMP}/C_{O_2})}{C_{O_2}}. \tag{11}$$

It shows that the mixture of methane and DMMP or TMP demonstrates the maximum adiabatic temperature close to the overall equivalence ratio 1. Differences in the maximum temperatures and some shifts from the overall equivalence ratio 1 are the result for different heats of combustion of methane and DMMP, and due to the simplified set of assumed combustion products for DMMP. However, the above phenomena still fully demonstrate the fuel effect of phosphorus-containing inhibitors, some hydrocarbon component of which are used as fuels to participate in combustion reactions.

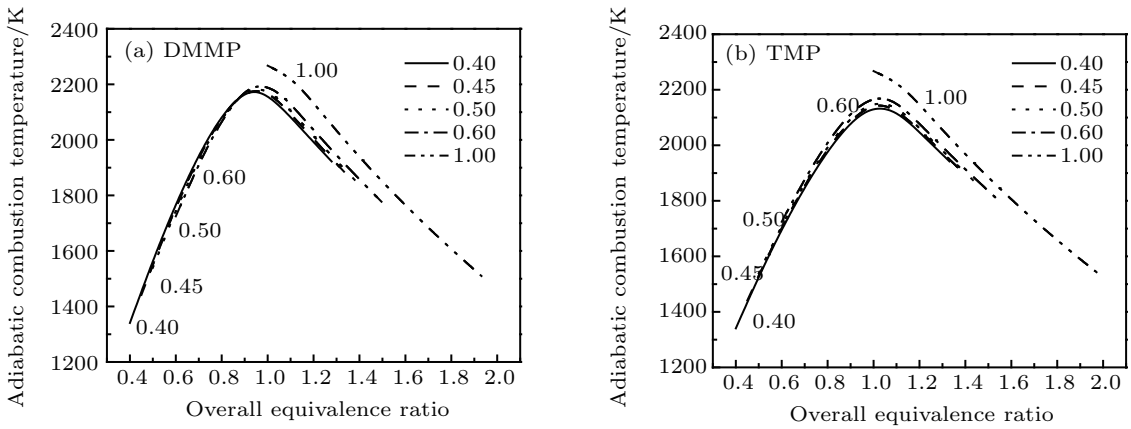


Fig. 6. Dependence of the adiabatic combustion temperature on overall equivalence ratio for CH_4–air mixture of different initial equivalence ratios.

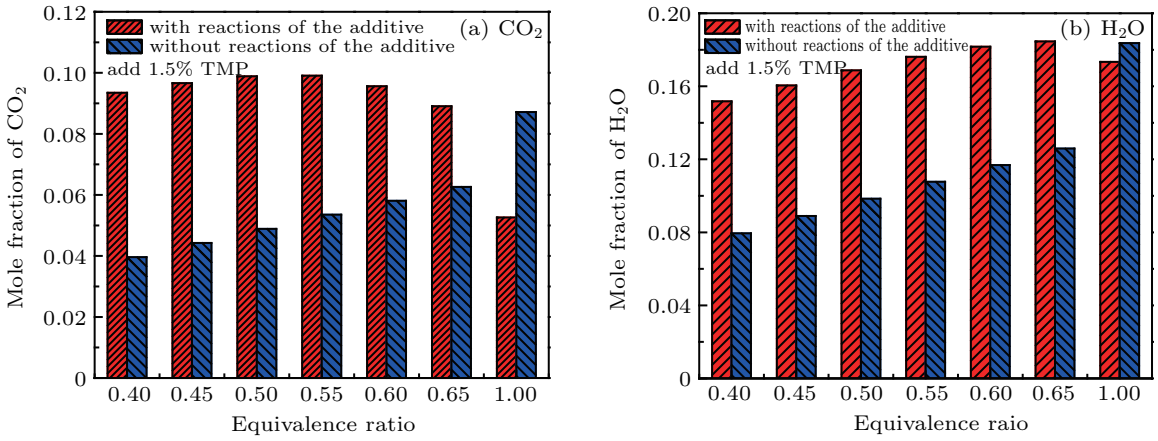


Fig. 7. (color online) The generate volume of CO_2 and H_2O in the products at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).

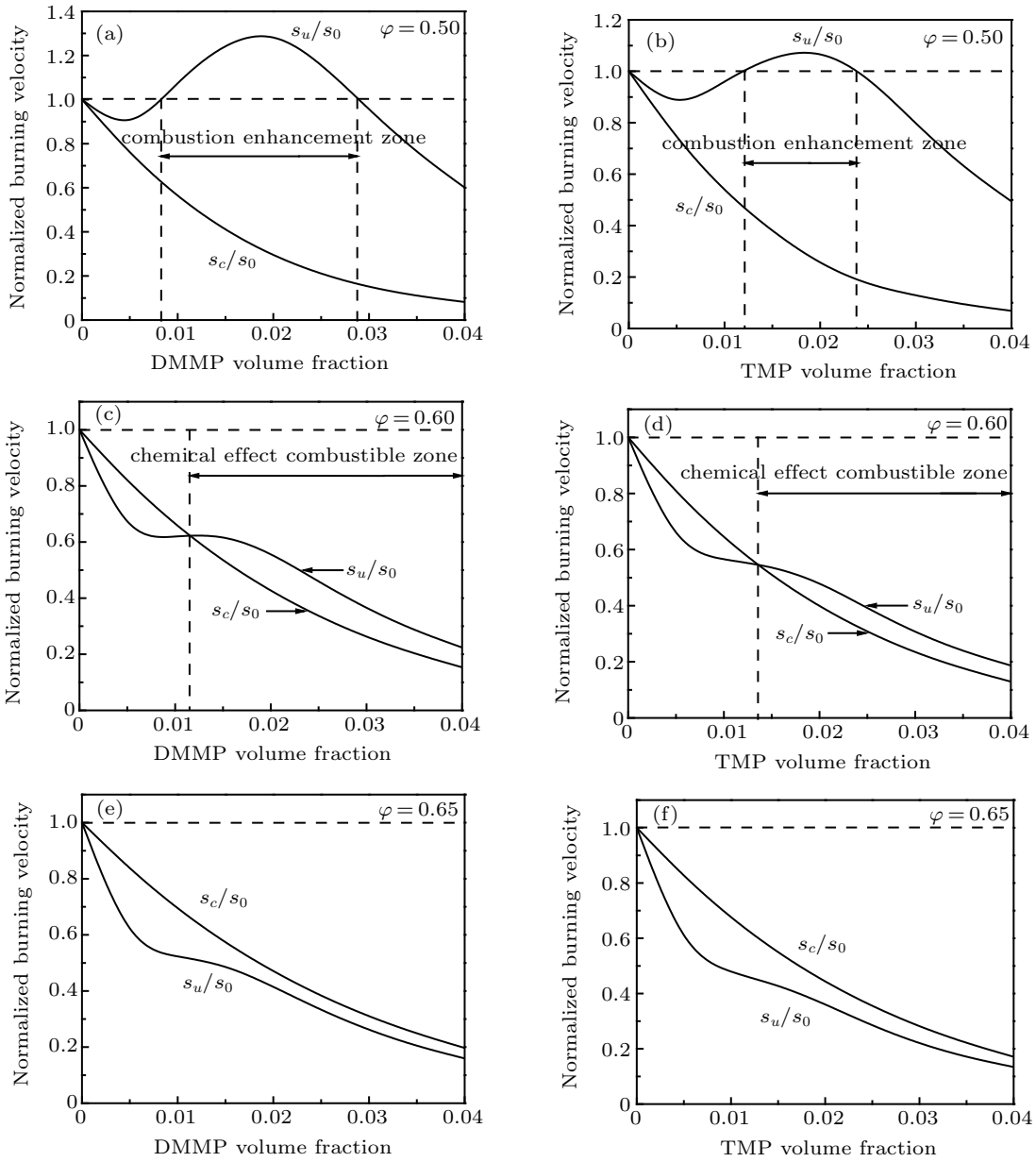


Fig. 8. Normalized burning velocity in CH_4–air mixtures with different initial equivalence ratios versus agent volume fraction.

The combustion promotion of DMMP and TMP under lean conditions is fully demonstrated by the anomalous phenomenon that the flame speed and temperature increase rather than decrease. The reason for this phenomenon is that the addition of the flame inhibitor provides a new combustible material, among which the hydrocarbon component of the flame inhibitor is served as replenishment fuel for combustion. The concentrations of CO_2 and H_2O in the combustion products were analyzed for both cases with and without the addition of 1.5% TMP, as shown in Fig. 7. TMP decomposes and produces more CO_2 and H_2O with reactions of the additive than that without reactions of the additive after combustion in lean flames, which fully proves the agent-supplied fuel effect of phosphorus-containing flame inhibitor under lean conditions. It also indicates that OH and H in the flame take priority reaction with the hydrocarbon moiety decomposing from DMMP and TMP in lean flames.

4.2. The physical and chemical effects of phosphorus-containing inhibitors

The effect of a flame inhibitor on a flame is composed of two parts: the physical effect, which is determined by the thermal effect and the dilution effect, and the chemical effect that is determined by the catalytic cycle reactions. Figure 8 gives the flame velocities before and after the elementary reactions when the corresponding phosphorus-containing inhibitors are closed as the equivalence ratio is 0.50, 0.60, and 0.65, respectively. It can be seen from the diagram that when the initial equivalent ratio is 0.50, there is a region that makes the normal normalized flame velocity larger than 1. In this region, the phosphorous inhibitor increases the velocity and promotes combustion, so this region belongs to the combustion enhancement area. For example, the combustion enhancement area of DMMP is $0.008 \leq X_a \leq 0.028$, and the combustion enhancement area of TMP is $0.012 \leq X_a \leq 0.024$. When $\phi \geq 0.60$, the phosphorus-containing inhibitor inhibits the combustion of the methane–air flame as a whole, and the combustion enhancement area no longer exists. However, when $\phi = 0.60$, there is also a region where the normal normalized velocity is larger than that of the elementary reactions when the corresponding phosphorus-containing inhibitor are closed. This region belongs to the chemical effect combustible zone, where the chemical effect is negatively promoting flame combustion, and the physical effect and the chemical effect are antagonistic to each other in the confrontation zone. The chemical effect combustible zone contains the combustion enhancement zone. In the stoichiometric methane–air flame, the physical and chemical effects are both in the flame suppression area, and both of them synergistically inhibit the combustion.

To further explore the interrelation between the physical effect and the chemical effect, the relative contributions of them are calculated in Table 2. "+" represents decreasing the burning velocity and inhibiting the combustion, and "−" represents increasing the burning velocity and promoting the combustion. Figure corresponds to Table 2. As can be seen, the physical effect has always been in the flame suppression area, and its relative effect on the velocity first increases then decreases with the increase of equivalence ratio. DMMP reaches the strongest near $\phi = 0.65$, while TMP near $\phi = 0.60$. In the chemical effect, the thermal effect is dominant, while the relative effect of the dilution

Table 2. The relative contributions of the physical and chemical effects for 1.5% DMMP and TMP in CH_4–air flames.

Agents	ϕ	Y_{Phy}	$\frac{Y_{Phy}}{\lvert Y_{Phy}\rvert+\lvert Y_{Che}\rvert}$	Y_{Che}	$\frac{Y_{Che}}{\lvert Y_{Phy}\rvert+\lvert Y_{Che}\rvert}$
DMMP	0.40	0.657	+11.43%	-5.093	-88.57%
DMMP	0.50	0.595	+40.98%	-0.857	-59.02%
DMMP	0.60	0.468	+82.98%	-0.096	-17.02%
DMMP	0.65	0.429	+84.78%	0.077	+15.22%
DMMP	1.00	0.321	+38.72%	0.508	+61.28%
TMP	0.40	0.690	+14.43%	-4.091	-85.57%
TMP	0.50	0.624	+47.67%	-0.685	-52.33%
TMP	0.60	0.494	+93.21%	-0.036	-6.79%
TMP	0.65	0.453	+79.75%	0.115	+20.25%
TMP	1.00	0.340	+40.21%	0.505	+59.79%

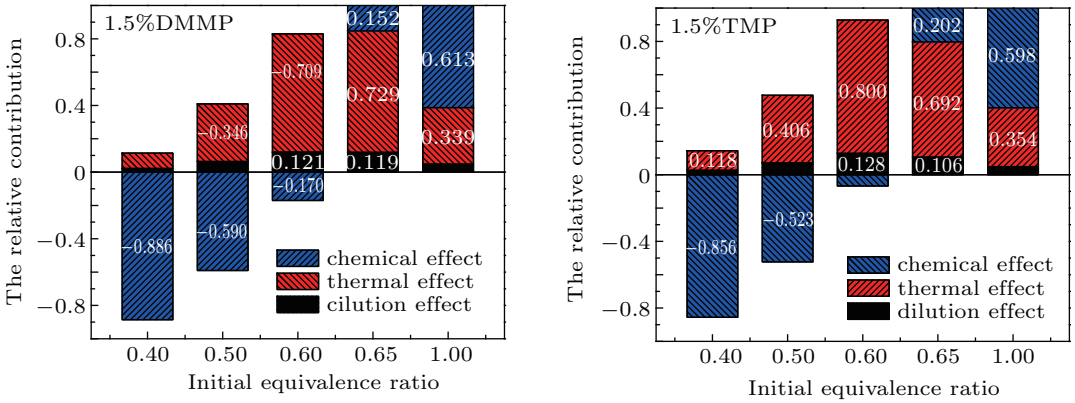


Fig. 9. (color online) The relative contributions of the physical and chemical effects for 1.5% phosphorus-containing inhibitors in CH_4–air flames.

effect is very low. The chemical effect is in the combustion enhancement zone under lower equivalent ratios. With the increase of the equivalent ratio, the effect of the chemical effect on inhibiting the flame is gradually enhanced. When $\phi \leq 0.50$, the chemical effect on promoting combustion dominates all effects. When $0.5 < \phi \leq 1.0$, the physical effect on inhibiting combustion is dominant. When $\phi > 1.0$, the chemical effect on inhibiting combustion is dominant.

4.3. Decoupling catalytic and pyrolytic effects in the chemical effect

Phosphorus-containing inhibitors decompose into the phosphorus-related component and the carbon-related component. From the analysis above, it can be seen that the carbon-related component served as a supplementary fuel promotes combustion under very lean conditions, whereas the phosphorus-related component (PO, PO_2, HOPO, and $HOPO_2$) catalyzes H and OH radical recombination for flame inhibition. In this work, the effect of the thermal decomposition of PCCs and the combustion of the decomposed hydrocarbon component is called the pyrolytic effect. Therefore, the chemical effect of phosphorus-containing inhibitors is caused by the coupling of catalytic and pyrolytic effects.

By varying the rate constant, an analysis of speed sensitivity coefficients of TMP-doped CH_4–air flames for the reactions involving P-containing species is shown in Fig. 10. The left part of Fig. 10 is the diagram when the phosphorus-related inhibitor is replaced by the decomposed molecules, whereas the right part shows the diagram without replacement. It is encouraging that figure 10 shows that the sensitivities of speed coefficient to the rate constants for decomposition of TMP become zero when the phosphorus-related inhibitor is replaced, indicating that the replacement modelling of TMP works well. Most of these speed sensitivity coefficients are positive, which suggests that these reactions promote the combustion process. In either the replaced or non-replaced processes, the dominant inhibition reactions are the same. Reaction pathways $HOPO_2 + H = PO_2 + H_2O$, $PO_2 + OH + M = HOPO_2 + M$, $HOPO + OH = PO_2 + H_2O$, and $PO_2 + H + M = HOPO + M$ make up the two most important cycles: $HOPO_2 \Leftrightarrow O_2$ and $HOPO \Leftrightarrow PO_2$. Therefore, the decomposition reactions of TMP indeed promote the flame speed, and correspondingly the radical recombination reactions inhibit the flame speed.

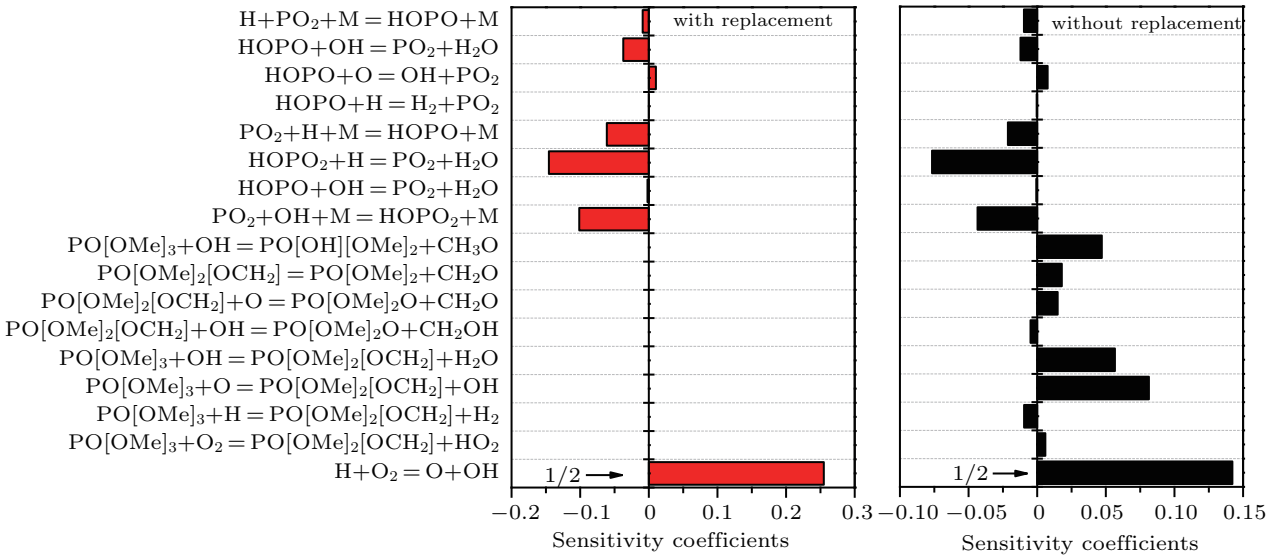


Fig. 10. (color online) Sensitivity coefficients of the speed of CH_4–air flame (ϕ=0.5) doped with 1.5% TMP to rate constants of 17 key reactions of the inhibition mechanism involving P-containing species.

Figure 11 plots the profiles of the key phosphorus-containing reactions involved in the production/destruction of PO_2 (using the rate of production (ROP) in $mol \cdot cm^{-3} \cdot s^{-1}$, values from the postprocessor of PREMIX) in CH_4–air flame ($\phi = 0.5$), doped with 1.5% TMP. For clarity, only the pronounced reactions are included. In Fig. 11, the dominant reaction for PO_2 production is $HOPO_2 + H = PO_2 + H_2O$, whereas the most negative reaction for PO_2 consumption is $PO_2 + OH + M = HOPO_2 + M$. These two reactions constitute a catalytic cycle resulting in $H + OH = H_2O$. In the same way, the second primary reaction cycle belongs to HOPO and PO_2, which also suppress the combustion process significantly.

To further evaluate the effect of the replacing model, the reaction pathways of TMP decomposition for premixed CH_4–air flame ($\phi = 0.5$) with 1.5% added agents are plotted in Fig. 12. In Fig. 12(a), the destruction of TMP is primarily by thermal decomposition and reaction with chain-carrier rad-

icals:

$$\mathrm{PO[OMe]_3 + OH = PO[OMe]_2[OCH_2] + H_2O},$$
$$\mathrm{PO[OMe]_3 + O = PO[OMe]_2[OCH_2] + OH},$$
$$\mathrm{PO[OMe]_3 + OH = PO[OH][OMe]_2 + CH_3O},$$
$$\mathrm{PO[OMe]_2[OCH_2] = PO[OMe]_2 + CH_2O}.$$

The further thermal decomposition of $PO[OMe]_2$ leads to the formation of CH_3OPO_2, which is the main decomposed compound of TMP, and the HOPO and $HOPO_2$ generated by CH_3OPO_2 are responsible for the inhibiting species in a hydrocarbon flame. As the phosphorus-related inhibitor is replaced, the major inhibition pathways involved H and OH radicals are the same as that shown in Fig. 12(b).

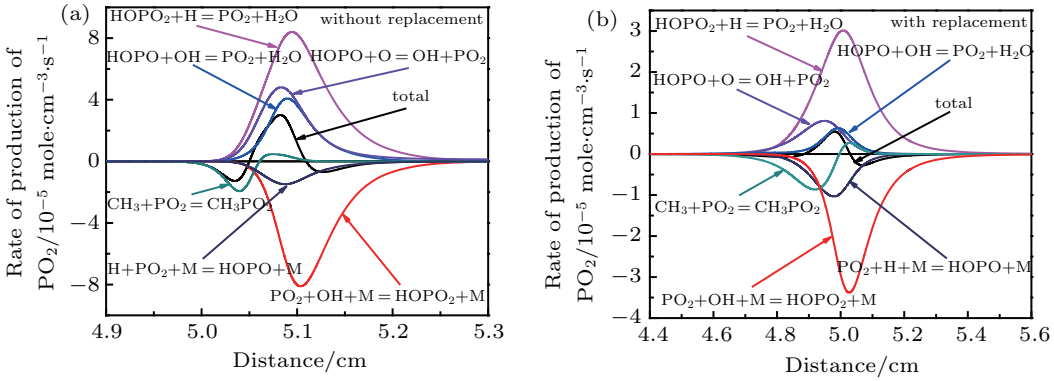


Fig. 11. (color online) Rate of production of PO_2 due to various reactions in CH_4–air flame ($\phi = 0.5$) doped with 1.5% TMP.

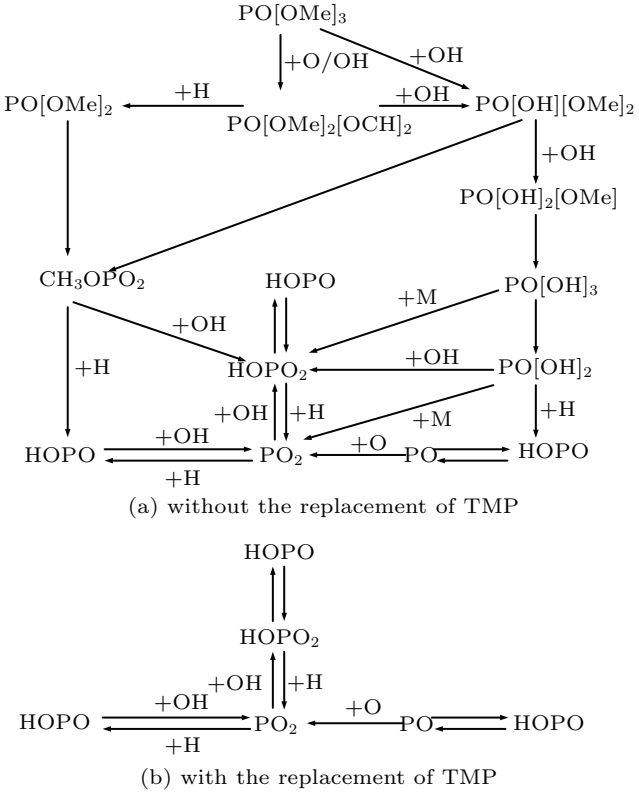


Fig. 12. Reaction pathways for decomposition of TMP in CH_4–air flame ($\phi = 0.5$) doped with 1.5% TMP.

Figure 13 shows the effects of the catalytic effect and pyrolytic effect of DMMP and TMP on the flame speed of the methane–air flame as a function of additive concentration when the equivalence ratio is at $\phi = 0.50$, 0.65, and 1.00. It can be seen that for $\phi = 0.50$, the catalytic effect and the pyrolytic effect are in the antagonistic zone, and the combustion pyrolytic effect is the dominant effect, so that the overall chemical effect promotes the combustion and increases the flame speed, and the flame radicals take the priority reaction with the hydrocarbon moiety decomposing from DMMP and TMP in lean flames. For $\phi = 0.65$, the catalytic effect and pyrolytic effect are also in the antagonistic zone, the influence of the catalytic effect is about 2 times that of the pyrolytic effect, and the catalytic effect is dominated, so that the chemical effect inhibits the combustion and decreases the flame speed. For $\phi = 1.00$, the catalytic effect and the pyrolytic effect are in the coordinated influence zone and show combustion inhibition. The chemical effect is close to the catalytic effect with a significant reduction of the flame speed because of the strong catalytic effect and weak pyrolytic effect.

Table 3 illustrates the relative contributions of the catalytic and pyrolytic effects for 1.5% DMMP and TMP in CH_4–air flames. The relative effect of the catalytic effect on the velocity first increases then decreases with the increase of the equivalence ratio. The relative effect of the pyrolytic effect reaches a negative maximum near $\phi = 0.60$, where the combustion is promoted to the strongest. When $\phi \geq 1.0$, the pyrolytic effect no longer promotes the combustion, and the hydrocarbon component of the phosphorus inhibitor no longer provides additional fuel. Therefore, the endothermic reactions are greater than the exothermic reactions. By analyzing the proportion of the catalytic effect in the chemical effect, it is found that the catalytic effect becomes stronger and stronger in the chemical effect with the increase of the equivalent ratio.

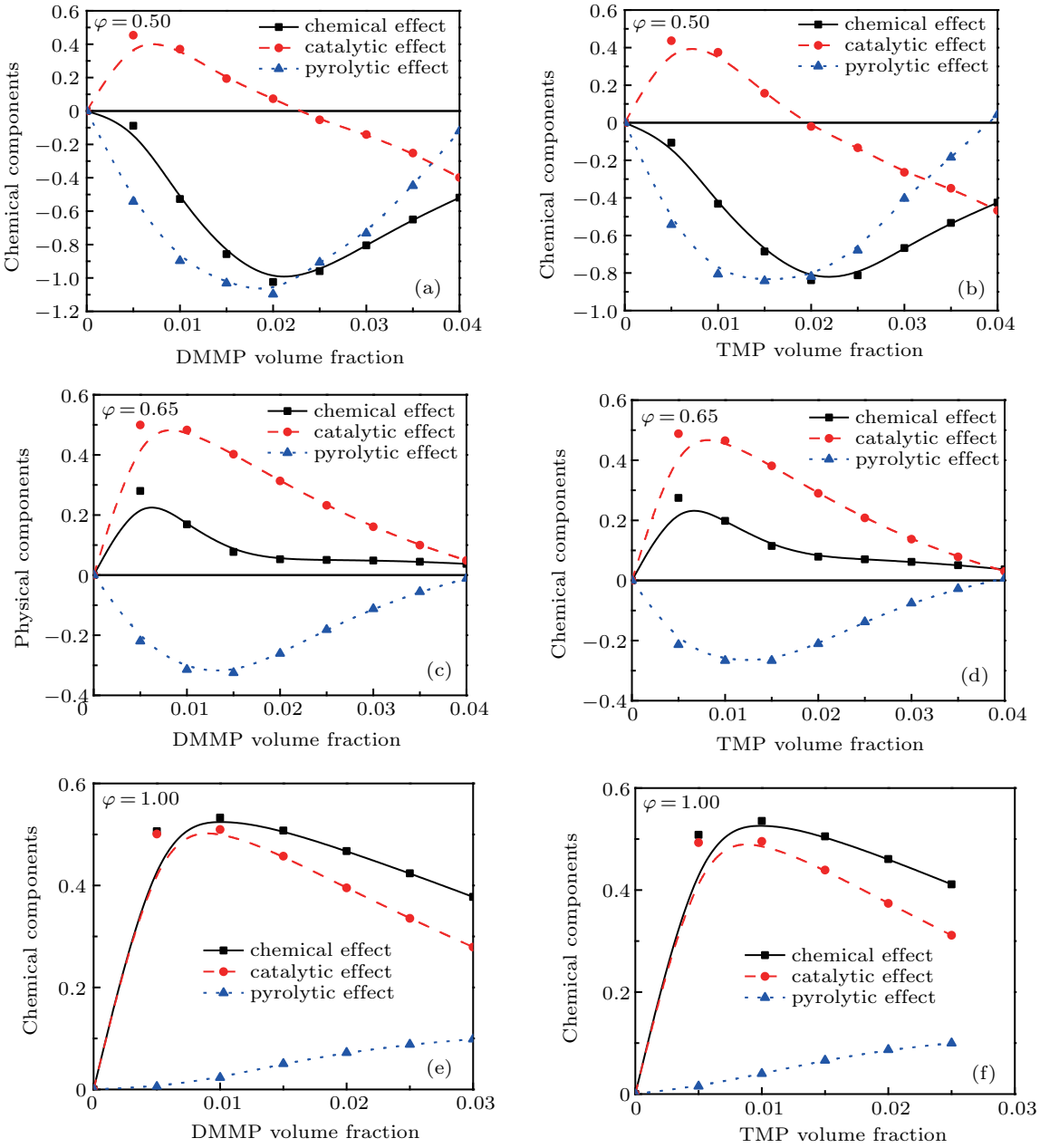


Fig. 13. (color online) The catalytic and pyrolytic effects of phosphorus-containing fire suppressants.

Table 3. The relative contributions of the catalytic and pyrolytic effects for 1.5% DMMP and TMP in CH_4–air flames.

Agents	ϕ	Y_{Cat}	$\frac{Y_{Cat}}{\lvert Y_{Phy}\rvert+\lvert Y_{Che}\rvert}$	Y_{Pyr}	$\frac{Y_{Pyr}}{\lvert Y_{Phy}\rvert+\lvert Y_{Che}\rvert}$	$\frac{Y_{Cat}}{\lvert Y_{Cat}\rvert+\lvert Y_{Pyr}\rvert}$
DMMP	0.50	0.174	+11.98%	–1.03	–70.94%	+14.45%
DMMP	0.60	0.355	+62.94%	–0.45	–79.79%	+44.10%
DMMP	0.65	0.402	+79.45%	–0.325	–64.24%	+55.30%
DMMP	1.00	0.457	+55.13%	0.050	+6.08%	+90.07%
TMP	0.50	0.157	+11.99%	–0.842	–64.32%	+15.72%
TMP	0.60	0.354	+66.79%	–0.39	–73.58%	+47.58%
TMP	0.65	0.387	+68.13%	–0.267	–47.01%	+57.17%
TMP	1.00	0.439	+51.95%	0.066	+7.82%	+86.91%

When $\phi \leq 0.60$, the pyrolysis effect dominates the chemical effect and the chemical effect promotes the combustion, whereas when $\phi > 0.60$ the catalytic effect is in the dominant position and the chemical effect inhibits the combustion.

4.4. The comparisons among components of the physical and chemical effects

Figure 14 shows the specific physical and chemical effects of methane–air laminar flames on burning velocities by taking various equivalence ratios as a function of the TMP additive concentration. A positive number indicates a decrease in burning velocity, inhibiting combustion. Conversely, a negative number indicates an increase in burning velocity, promoting combustion. As predicted, the physical component of the inhibition action, in which the dilution effect increases linearly and the growth rate of the thermal effect becomes smaller and smaller, is increased with increasing additive concentration. It can be seen from Figs. 14(d)–14(f) that the chemical component is negative when equivalence ratio $\phi < 0.65$, indicating

that TMP plays a role in promoting combustion in this range of equivalence ratio. There is a negative maximum value near $X_a = 0.022$, that is to say, the effect of combustion promotion is strongest when the volume fraction of TMP is 2.2%. For $\phi \geq 0.65$, the chemical component of TMP shows a flame retardant effect. The inhibition influence increases first, then decreases, and reaches maximum when the volume fraction is at $X_a = 0.007$, because the catalytic effect of TMP is strongest at $X_a = 0.007$ and has the same trend with the chemical component. The relative contribution of the catalytic effect on flame suppression gradually increases with an equivalent ratio. The value of heat released from the combustion of the hydrocarbon component is greater than that of heat absorption to promote the decomposition of TMP, so that the pyrolytic component of phosphorus-containing inhibitors is negative and reaches maximum when $X_a = 0.015$, which shows a strong combustion promotion when the equivalence ratio is at $\phi \leq 0.65$. For $\phi \geq 1.00$, the fuel is sufficient, so that the combustion of the hydrocarbon component does not occur. However, the decomposition process needs to absorb heat. Therefore, the pyrolytic effect is positive and increases with the addition amount.

Figure 15 shows the relative contributions of the pyrolytic effect, catalytic effect, thermal effect, and dilution effects of DMMP and TMP, to the flame inhibition adding 1% and 2% agent. The total effect of the inhibitors is the sum of these four effects. At the same amount of addition, the dilution effect and thermal effect on the flame speed decrease with the increase of

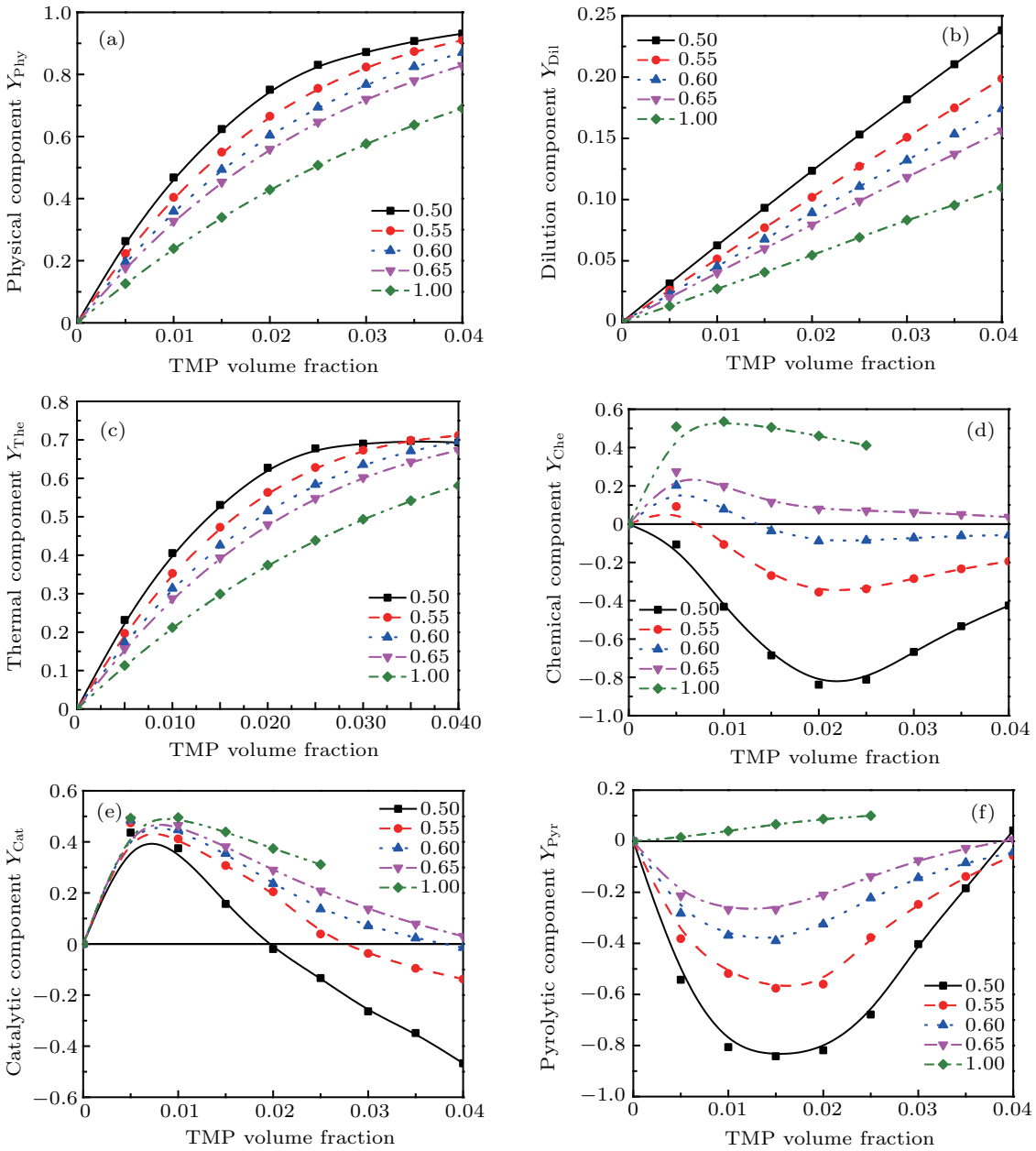


Fig. 14. (color online) The physical and chemical components as a function of TMP concentration at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).

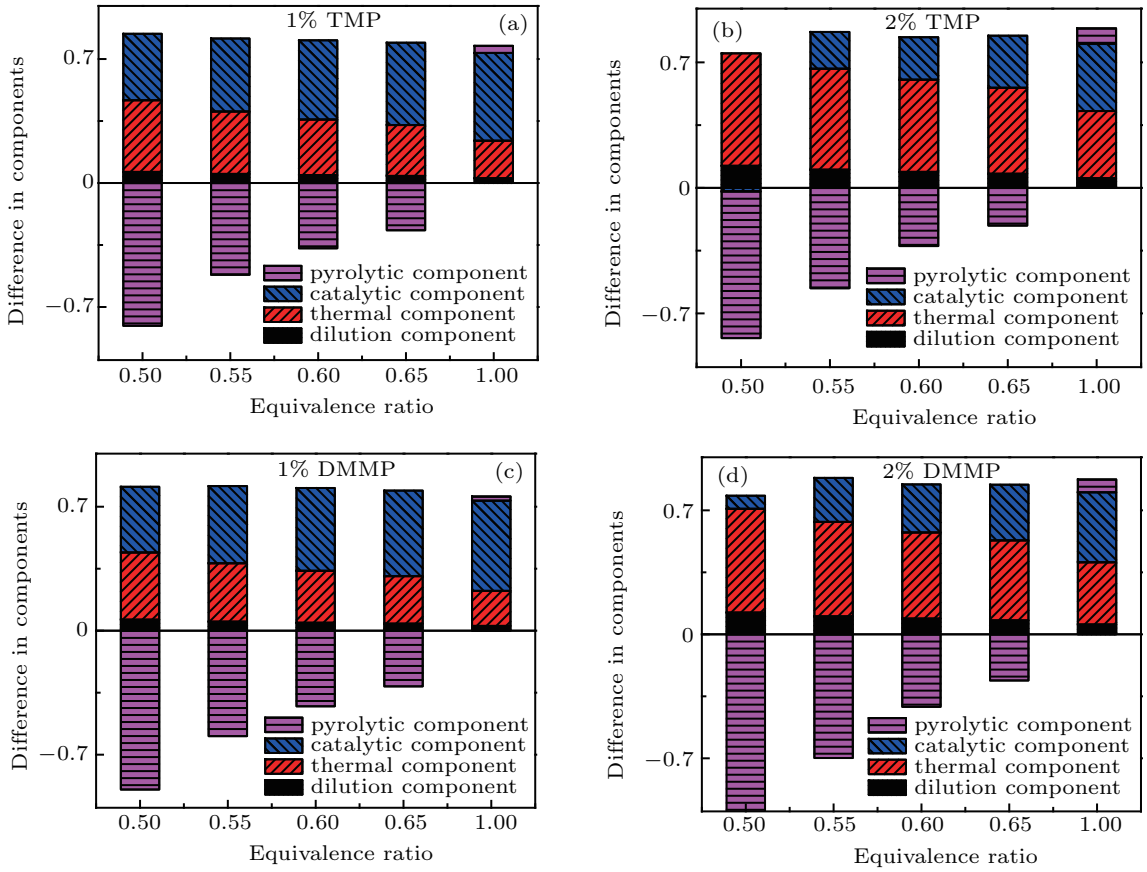


Fig. 15. (color online) The relative contributions of the physical and chemical components as a function of TMP concentration at different equivalence ratios (CH_4/air mixture, initial temperature 373 K).

equivalence ratio, so that the total physical effect decreases gradually. Similarly, the catalytic effect gradually increases, and the influence of combustion promotion of the pyrolytic effect, which becomes an inhibitory effect when the equivalence ratio $\phi \geq 1.00$, is gradually reduced. Under extremely lean conditions, the pyrolytic effect dominates the chemical effect, resulting in an increase in the overall flame speed. For example, when $\phi = 0.50$, adding 1% DMMP, the pyrolytic effect, catalytic effect, thermal effect, and dilution effect on the flame speed in methane–air flame are 37.0%, −89.7%, 38.0%, and 6.3% respectively, and the total effect was −8.4%, with the overall performance to promote the combustion of the flame. When $\phi = 0.65$ and 1% DMMP addition, the pyrolytic component, catalytic component, thermal component, and dilution component are 48.3%, 31.4% 26.8%, and 4.0% respectively, with a total effect of 47.7%. The overall performance is to suppress the flame combustion and the catalytic effect is in the dominant position.

5. Conclusion

PCCs exhibits a significant but undesirable promoting effect on the burning velocity in lean flames due to the chemical effect, so the physical and chemical effects are separated. To take a deeper insight into the chemical effect, this work definitely divides the initial decomposition products of phosphorus inhibitors into two components, which include the carbon-related component that supplies additional fuel to the mixture promoting combustion, and the phosphorus-related component that catalyzes radials recombination inhibiting combustion. A new approach in which the original phosphorus-containing inhibitors (DMMP and TMP) is replaced by the small P-containing molecules (PO, PO_2, HOPO, and $HOPO_2$) after decomposition turning the reactions with the carbon-related component off is proposed in the study. In this way, the chemical effect is decoupled into the pyrolytic effect and catalytic effect, and the relative contributions of these two effects to flame suppression are quantified. A numerical investigation for methane–air premixed flame with initial equivalence ratio at $0.40 \leq \phi \leq 1.20$ and the addition of DMMP and TMP at $0 \leq X_a \leq 0.04$ is carried out. The results indicate that when $\phi < 0.60$, the pyrolytic effect of DMMP and TMP is stronger than the catalytic effect, so that the chemical effect promotes the combustion since the flame radicals behave as the primary reaction with the hydrocarbon component of DMMP and TMP. When $0.60 \leq \phi < 1.00$, the catalytic effect dominates the chemical effect, since the flame radicals act as the primary reaction with PO, PO_2, HOPO, and $HOPO_2$. For $\phi \geq 1.00$, the catalytic and pyrolytic effects show a syn-

ergistic effect on flame inhibition with few reactions with the hydrocarbon moiety of phosphorus-containing inhibitors.

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