Effect of surface reactions on ignition delay of methanol/air mixture

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Abstract. A surface reaction kinetic model for the combustion of methanol/air mixture was developed in order to investigate the ignition inhibitory mechanism of wall on the premixed gas in a micro closed volume. In this model, except for H, O, OH and CH$_3$ radicals, the absorption of hydrogen peroxide and hydroperoxyl on the surface were also considered. By applying CHEMKIN-Pro software, the model was integrated into the calculation of homogeneous combustion process of gas mixture. Surface reactions were found resulting in the increase of ignition delay time. The sensitivity analysis showed that the loss of hydrogen peroxide on the wall was the main reason, due to the direct suppression effect on the generation and accumulation of OH in the radical pool. However, the loss of hydroperoxyl would take the place of hydrogen peroxide as the main inhibitory factor when the sticking coefficient became as large as the order of 10$^{-3}$. In addition, the ignition delay time increased with sticking coefficient or surface-area-to-volume ratio. Enhancing the initial temperature of premixed gas was able to reduce the inhibitory effect of surface reactions.

1. Introduction

Micro-scale internal combustion engine is considered as an ideal power source for unmanned vehicles and portable electronic instruments, owing to large energy density and long lifetimes. The fabrication and assembly of micro-engines have got fast development due to the major improvement of MEMS technology. The physical length scale of micro-engine is usually below 1 mm. Therefore, the surface-area-to-volume ratio become so large that great heat loss and radical loss on the internal wall show non-ignorable or even significant inhibitory effect on the ignition and flame propagation of gas mixture. Fundamental studies on micro-combustion inside a small closed vessel were carried out by researchers worldwide [1].

Norrish and Reagh [2] measured the slow oxidation reaction rate of several hydrocarbons in some cylindrical silica reaction vessel varying different diameters. It was found that the reaction rate dropped abruptly as the diameter of the vessel was sufficient reduced. The major reason was that more percentage of radicals was destroyed by internal surface with decreasing scale of the vessel. A number of similar oxidation experiments at low temperature were described in reference [3], and their results indicated that the surface had inhibitory influence on gas phase oxidation, especially strong when the internal diameter was less than 5 mm. Bowman and Wilk [4] investigated methanol auto-ignition including surface effect with three spherical glass reaction vessels of different sizes. The experimental results showed that heterogeneous surface effect would retard the ignition of the system and the ignition delay time increased with surface-area-to-volume ratio. Besides silica and quartz, other
different materials like stainless steel, alumina and zirconia ceramics, were adopted as wall material to study the surface effect on combustion process in a narrow channel [5, 6]. The results implied that stainless steel has the largest radical removal ability in the quenching process.

Metallic material, e.g. stainless steel, is favored as the manufacturing material for micro-combustor. The inhibitory effect of radical loss at wall on the ignition of hydrocarbons may not be neglected as micro-combustor has large surface-area-to-volume ratio. However, the mechanism of radical loss at wall is still unclear. In this study, a surface reaction kinetic model for the combustion of methanol/air mixture is developed and the heterogeneous surface effects on ignition delay are examined.

2. Model

2.1. Model setup

The surface kinetic mechanism consists of absorption reactions of radical species by the surface and desorption reactions of stable species which are formed by recombination reactions of absorbed species [7]. However, there is no consensus among researchers on which radical species should be considered as they are capable of being absorbed and which can be neglected. Aghalayam et al [7] first built a surface reaction model for premixed hydrogen-air impinging on a flat surface. The model consisted of five radical species including H, O, OH, HO\(_2\), and H\(_2\)O. A similar surface reaction model for methane-air was setup by Raimondeau et al [8], in which only CH\(_3\), H, O, OH was considered, exclusive of HO\(_2\) and H\(_2\)O. However, Held and Dryer [9] indicated that the low temperature oxidation rate of methanol/oxygen in a closed vessel was determined by H\(_2\)O (wall) \(\rightarrow\) H\(_2\)O + 1/2O\(_2\). But the loss of HO\(_2\) at wall has a very small impact on the reaction rate.

| Absorbed species | Reactions \(a\) | Sticking Coefficient \(\gamma\) or Pre-Exponential (s\(^{-1}\)) |
|------------------|-----------------|----------------------------------------------------------|
| H                | H + * \(\rightarrow\) H* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |
| O                | O + * \(\rightarrow\) O* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |
| OH               | OH + * \(\rightarrow\) OH* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |
| HO\(_2\)         | HO\(_2\) + 2* \(\rightarrow\) OH* + O* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |
| H\(_2\)O         | H\(_2\)O + 2* \(\rightarrow\) 2OH* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |
| CH\(_3\)         | CH\(_3\) + * \(\rightarrow\) CH\(_3\)* | 0 \(\sim\) 1 \(\times\) \(10^{13}\) |

\(a\) * denotes reactive surface site and for example H* means an adsorbed H radical.

Base on the fundamental research of referred groups, a new surface reaction model for methanol/air mixture is established in this study. Table 1 tabulates the model, which has several basic assumptions: (1) Six radical species can be destroyed at wall, including H, O, OH, HO\(_2\), H\(_2\)O and CH\(_3\). (2) The sticking coefficient \(\gamma\) of each radical species is identical. (3) The surface recombination reactions are taken to have zero activation energy and their pre-exponential are estimated at \(10^{13}\) s\(^{-1}\) [7].

2.2. Model validation

The effect of surface reaction on the ignition and the oxidation process were study numerically using CHEMKIN-Pro software [10]. The detail gas phase kinetic mechanism of methanol/air has been
developed by Li et al [11]. The surface kinetic mechanism was integrated into the calculation of homogeneous combustion process of gas mixture in order to investigate the inhibitory effect of surface.

Experimental verifications for the heterogeneous surface effect on the ignition delay of mixtures in an adiabatic system are quite rare, but various static reactor experiments have been conducted to study the surface effect. The calculated results have fine agreement with both experimental data [12, 13] for $4.2 \times 10^{-6} - 8 \times 10^{-6}$ of $\gamma$, shown in figure 1 and figure 2.

![Figure 1](image1.png)

**Figure 1.** Experimental (scatters) and calculated pressure profile (lines) of reference [12]. The $\gamma$ are $6 \times 10^{-6}$, $8 \times 10^{-6}$ and $8 \times 10^{-5}$ respectively for 404 torr, 350 torr and 200 torr cases under 710 K.

The developed surface reaction model for methanol oxidation is demonstrated to be applied to predict the influence of surface on gas phase reaction rate. The sticking coefficients $\gamma$ is a crucial parameter that determines the absorption intensity of the internal surface. However, it is difficult to measure the value of $\gamma$ as it has correlation with surface material, microscopic surface texture and physical property of the surface, etc. Therefore, a certain discrepancy of $\gamma$ may occur in the estimation for reaction vessels that are even made of the same material. The value of $\gamma$ is at the order of $10^{-6}$ for quartz. For stainless steel, $\gamma$ may be of more than 100 times larger than quartz [14].

**3. Numerical method**

In order to investigate the effect of surface reaction on the ignition delay of methanol/air mixture in an adiabatic system, surface reaction mechanism of methanol in this study has been integrated into the calculation of homogeneous reactions using CHEMKIN-Pro software. The ignition delay time $\tau_{\text{ign}}$ was defined by the maximum molar concentration of OH. The calculations were performed for initial pressure of 3 atm and a stoichiometric equivalence ratio. In this study, the main interest is to find out the dominant surface reaction affecting the ignition of mixture at initial temperature $T_{0}$ below 1000 K. In addition, the sticking coefficient $\gamma$ and surface-area-to-volume-ratio $S/V$ are two important parameters for surface reactions, and their effects on ignition delay are also analyzed.

**4. Results and discussions**

The gas phase kinetic mechanism of methanol/air has got comprehensive study by Held and Dryer [9]. At low temperature, OH is mainly produced by the decomposition of H$_2$O$_2$ during the induction time.

In the numerical simulations, the cases of inert surface and reactive surface were compared. For inert surface, the system proceeds homogeneous combustion and no radical is absorbed. For reactive one, the surface can be regard as the sink of radicals, reducing the radical concentration in the gas phase. In figure 3, the growth rate of H$_2$O mole fraction in the gas phase is lower for reactive-surface case, resulting in slower production of OH as the reaction rate of R6 is lower. Since the absorbed H$_2$O$_2$ by the surface converges to H$_2$O and O$_2$ eventually, less OH is produced by the decomposition H$_2$O$_2$. This is the main reason why the reactive-surface case has longer ignition delay time.
surface effect is determined by the absorption of H$_2$O$_2$ which produces most of the H due to the larger radical loss on the gas-phase chain reactions increase quickly. The effect of absorption of HO produces large and the effect of absorption of HO$_2$ through R1 and is removed rapidly by R2 and R4, and absorption reaction of HO produces radicals. Figure 6 illustrates that the ignition delay time increases with SOF when T$_0$=800 K. Therefore, they are not shown in figure 4, which gives out seven largest sensitivities among the sensitivity of absorption reactions for H, O, OH and CH. The normalized sensitivity was computed using the formula as Zhang et al [15]. It was found that the sensitivity of absorption reactions for H, O, OH and CH$_3$ were so small that can be neglected. Therefore, they are not shown in figure 4, which gives out seven largest sensitivities among gas phase reactions and surface reactions. When γ=7.0×10$^{-4}$, the absolute values of the sensitivity for the absorption of HO$_2$ and H$_2$O$_2$ were much smaller than gas phase reactions. It means that the ignition delay time is mainly determined by gas phase reactions when γ is small. But the inhibitory effect of surface reaction is still significant. The main cause of this inhibitory effect is the absorption of H$_2$O$_2$ and the absorption of HO$_2$ can be ignored, the same conclusion deduced in reference [9]. However, the sensitivity of R1 increases abruptly when γ increases to 4.0×10$^{-3}$ and the sensitivity for the absorption of HO$_2$ surpasses the one of H$_2$O$_2$. Since HO$_2$ is an important chain carrier, it comes out through R1 and is removed rapidly by R2 and R4, and absorption reaction of HO$_2$. When γ is quite large and the effect of absorption of HO$_2$ cannot be ignored, less HO$_2$ is consumed by R2, which produces most of the H$_2$O$_2$, resulting in lower concentration of H$_2$O$_2$ shown in figure 3. Therefore, the surface effect is determined by the absorption of H$_2$O$_2$ when γ is small. But when γ is as large as the order of 10$^{-3}$, the absorption of HO$_2$ should be considered.

The effects of γ and SOF on ignition delay were also explored. As figure 5 shows, for T$_0$=800 K, the ignition delay time has slightly change when γ<1.0×10$^{-4}$, but increasing rapidly when γ>1.0×10$^{-4}$ because of the surface effect. When T$_0$ is up to 900 K, the rapid increase just emerged after γ>1.0×10$^{-3}$. And for T$_0$=1000 K, the ignition delay time increases quite slightly. It illustrates that the enlargement of T$_0$ greatly help weaken the inhibitory effect caused by surface reaction because the reaction rate of the gas-phase chain reactions increase quickly and more radicals are produced, compensating the radical loss on surface. Figure 6 illustrates that the ignition delay time increases with SOF, which associates with the shape and the internal volume of reaction vessel. The larger of the SOF, the more

Table 2. Low temperature kinetic mechanism of methanol/air [9]

| No. | Reactions | Reaction type |
|-----|-----------|---------------|
| R1  | CH$_3$OH + O$_2$ = CH$_2$OH + HO$_2$ | Chain initiation |
| R2  | CH$_3$OH + HO$_2$ = CH$_2$OH + H$_2$O$_2$ | Chain propagation |
| R3  | CH$_2$OH + O$_2$ = CH$_2$O + HO$_2$ | Chain propagation |
| R4  | CH$_2$O + HO$_2$ = HCO + H$_2$O$_2$ | Chain propagation |
| R5  | HCO + O$_2$ = CO + HO$_2$ | Chain propagation |
| R6  | H$_2$O$_2$(+M) = 2OH(+M) | Chain branching |
| R7  | CH$_3$OH + OH = CH$_2$OH + H$_2$O | Chain propagation |
| R8  | CH$_2$O + OH = HCO + H$_2$O | Chain propagation |

Figure 3. Mole fraction profiles of OH and H$_2$O$_2$ radicals for inert-surface and reactive-surface. (SOF=10 cm$^{-1}$, γ=7×10$^{-4}$).

Figure 4. Normalized sensitivity of ignition delay time with respect to reaction rate (T$_0$=900 K, SOF=10 cm$^{-1}$)
possibility of radicals impinge to the surface and get absorbed. In addition, as $SV$ becomes larger, the
growth rate of ignition delay time is faster when $\gamma$ is large. Therefore, besides $\gamma$, $SV$ also is one of
important surface parameters that describe the intensity of inhibitory effect of surface on ignition delay.

![Figure 5](image1.png)  ![Figure 6](image2.png)

**Figure 5.** Comparison of ignition delay times for different temperatures versus sticking coefficients ($SV=10$ cm$^{-1}$)

**Figure 6.** Comparison of ignition delay times for different sticking coefficients versus surface-area-to-volume ratios ($T_0=900$ K)

5. Conclusions
In this paper, a surface kinetic reaction mechanism for methanol oxidation in a small closed volume
was developed. Using the surface model, the inhibitory effect of surface reaction on ignition delay was
also investigated. It was found that the absorption of H$_2$O$_2$ on the surface was the main reason, due to
the direct suppression effect on the concentration of OH in the radical pool. However, the absorption
of HO$_2$ would take the place of H$_2$O$_2$ as the main inhibitory factor when the sticking coefficient
became as large as the order of $10^{-3}$. Both the sticking coefficient and surface-area-to-volume ratio
were two important parameters that determined the intensity of surface effect. And the ignition delay
time increased with sticking coefficient or surface-area-to-volume ratio. In addition, enhancing the
initial temperature of the mixture was able to reduce the inhibitory effect of surface reactions.

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