



A modeling study of the effect of surface reactions on methanol–air oxidation at low temperatures



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ABSTRACT

A detailed modeling study was performed to investigate the inhibitory effect of the interior surface of a reactor in the process of low-temperature oxidation of methanol–air mixture. By using the reduction technique, which is for the gas-phase kinetic mechanism, a modified nine-step skeletal mechanism for the low-temperature methanol oxidation was developed. Important quenching species as well as surface reactions which have great influences on gas-phase branching reactions were identified. The adsorption of the species such as hydroxyl, hydroperoxyl, hydrogen peroxide and formaldehyde and the desorption of stable molecules generated by the recombination of the above adsorbents have constituted the surface kinetic model for methanol–air mixture. Computations based on the established heterogeneous radical quenching mechanism show excellent agreement with the experimental results from literatures, demonstrating that the radical quenching not only has significant inhibitory impact on slow oxidation, but also enables the retardation of ignition delay time. For the purpose of evaluating the inhibitory influence of the surface reactions on auto-ignition, a more in-depth five-step reduced mechanism combining the gas-phase reactions and the surface reactions was developed. Based on this mechanism, an explicit expression for the auto-ignition prediction was derived with the activation-energy asymptotic treatment. The formula can predict the ignition delay time with sufficient accuracy for both inert and high-reactive surfaces.

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1. Introduction

With the development of fabrication technologies of micro-electro-mechanical systems (MEMS), the miniaturization of combustors and internal combustion engines have become research hotspots in recent years. The effect of radical quenching on the interior surface for micro-scale combustion is getting concerned increasingly [1,2]. On account of the frequent collision of radicals to the interior surface in a small volume, considerable amount of radicals may get adsorbed by the chamber surface resulting in the lack of homogeneous chemistry [3]. Consequently, the ignition delay time of fuel-oxidant mixture would be extended, which is, however, required to be short in the combustion process so as to maintain sufficient power output and high efficiency [3–6]. For instance, the physical length scale of combustion chambers of micro-engines is usually below 1 mm [1], and large surface-to-volume ratio of these chambers may cause significant radical quenching. Therefore, the auto-ignition phenomena may be determined by not only homogeneous gas-phase reactions but also heterogeneous reactions.

The interior surfaces of combustors were found to be having significant influence on auto-ignition boundaries of premixed fuel-oxygen mixtures and various oxidation phenomena [7,8]. Early studies on the surface radical extinction were often conducted experimentally in static reactors. In this type of experiments, low-temperature oxidation mechanisms of hydrocarbons were studied with isothermal boundary condition in a closed quartz or silica vessel. Norrish and Foord [8] reported that the reaction rates of methane–oxygen mixtures were evidently lower in smaller vessels under the same operating conditions. It was demonstrated that the existence of radical loss on the interior wall had significant inhibitory influence on the gas-phase oxidation. Bowman and Wilk [9] investigated the correlation between the surface-to-volume ratio of a vessel and the ignition delay time of methanol–air mixture. Their experimental results showed that the ignition delay time, also was called the induction period, extended as the surface-to-volume ratio increased, indicating that the radical loss on the wall could not be ignored during this period. In addition, the ignition delay time was also found to be sensitive to the interior surface conditions in experiments that were with shock tube and jet-stirred reactor [10,11]. However, the surface reaction mechanism for radical quenching which should had considerable impact on micro-scale combustion was not so clear yet [2].

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Rational selection of gas-phase species which are likely to be adsorbed by the surface is an essential factor for the surface-reaction modeling. However, there is still no consensus among researchers on which kinds of gas-phase species should be considered as capable of being adsorbed and which ones can be neglected. The recombination of several reactive molecules on the surface, such as H, O, OH and CH₃, has been verified by various experiments [12,13]. For modeling studies, Raimondeau et al. [14] established a surface kinetic model by only considering the adsorption and the recombination of these four species to study high-temperature methane–air premixed flames. H atom was found to be the dominant species and the quenching of it caused significant inhibitory effect on the combustion process. This conclusion was also supported by Andrae et al. [15] in their two-dimension computational work. Konnov et al. [16] counted in H and O atoms for surface reactions and deduced that the influence of surface reactions on methane oxidation at 823 K was less pronounced than that at 1100 K. In low-temperature region (generally less than 900 K), however, it is known that HO₂ and H₂O₂ are important species for the oxidation of hydrocarbons [17] and their concentrations during the induction period are much larger than small radicals like H atom. Thus, the effect of surface reactions at low temperature may be underestimated due to such incomprehensive assumption. Considering the adsorption of hydroperoxyl and hydrogen peroxide, fine agreement was obtained between the modeling and the experimental results of low-temperature oxidation [18–20].

The identification of controlling gas-phase species quenched on surface is crucially important for developing surface kinetic mechanism. Therefore, in this work, a modeling study was conducted to identify influential quenching species and heterogeneous reactions by using the gas-phase kinetic mechanism reduction technique associated with surface reactions. Methanol is one of the desirable transport fuels for small scale applications due to its higher volumetric energy density than hydrogen and its fast burning rate [2]. In order to investigate the radical quenching effects on auto-ignition of methanol–air mixtures at low temperatures, a surface reaction mechanism for methanol oxidation was developed. Combining the reduced gas-phase mechanism and the surface reaction model, quantitative study on the effect of radical quenching was carried out. Consequently, an explicit formula for the ignition delay time evaluation which involved the consideration of surface reactions was deduced. The computation was intended to reveal the auto-ignition behavior in scale-down combustor applications

2. Surface kinetic mechanism development

The surface kinetic mechanism consists of adsorption reactions of radical species and desorption reactions of stable species which are formed by recombination reactions of adsorbed species [21]. According to Langmuir theory [22], for species *i*, the surface adsorption reaction rate $\omega_{\text{surf},i}$ (mol s⁻¹ cm⁻²), can be expressed as

$$\omega_{\text{surf},i} = \gamma \theta \sqrt{\frac{RT}{2\pi M_i}} C_i \quad (1)$$

where γ , θ , R , M_i , T , C_i are the surface sticking coefficient, the site fraction of bare site, the universal gas constant, the molecular weight, the gas-phase temperature and the concentration of the species *i*, respectively. The influence of surface reactions may depend not only on the scale and the surface activity of reactor but also gas-phase concentrations of species. Surface reactions compete with gas-phase reactions for radicals. Heterogeneous consumption of species which is crucial to chain propagation or chain branching may have significant impact on the homogeneous chemistry. In this section, the reduction technique for gas-phase kinetic mechanism is utilized to define whether the species is influential or negligible for surface reactions.

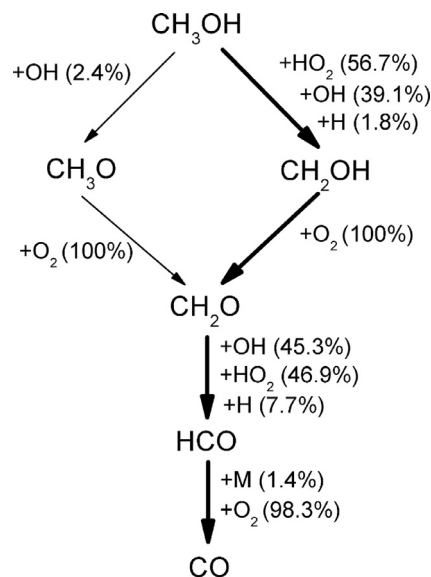


Fig. 1. Integrated methanol consumption pathway before homogeneous ignition in the condition of $T = 800$ K, $P = 1$ atm and $\Phi = 1$. AramcoMech 1.3 [24] was applied in the simulation.

2.1. Skeletal kinetic mechanism

There are several notable comprehensive oxidation models of methanol [18,23–27], among which Li model [23] is commonly used. However, some researchers reported that it failed to predict the ignition delay time for rapid compression machine (RCM) experiments [29]. Due to potential limitations of Li model, the mechanism developed by Metcalfe et al. [24], namely AramcoMech 1.3, was chosen in this work. This mechanism got comprehensive development and test for methanol combustion. It has been proved to be an accurate kinetic model for methanol oxidation by validating against various experimental data.

Based on AramcoMech 1.3 [24], a skeletal kinetic mechanism for methanol oxidation at low temperatures was developed in this work via sensitivity analysis on the ignition delay and the reaction path study with CHEMKIN-Pro [28]. As shown in Fig. 1, the gas-phase reaction path of methanol–air mixture during the low-temperature induction period is quite simple. During the initial period of the induction time, HO₂ is the most important chain carrier accounting for most methanol consumption. With the increase of the gas temperature and the H₂O₂ concentration, methanol molecules are increasingly consumed by OH, which is generated mostly via the decomposition of H₂O₂. As Fig. 2 shows, the formation of CH₃O isomer contributes less than 2.5% methanol consumption. And the simulations revealed that the omitting of this consumption path had little impact on the ignition time prediction. The decomposition of H₂O₂ is considered as the main chain branching reaction which accelerates the gas-phase reaction significantly and finally leads to ignition. Therefore, a nine-step skeletal mechanism was obtained, listed in Table 1. Detailed explanations on the derivation of this skeletal model can be found in the Supplementary material.

The homogeneous ignition delay of methanol–oxidizer has been well studied at high temperatures, but theoretical calculations at low temperatures have not yet reached a consensus [29]. It is worth noting that reaction R9 was neglected in the description of the low-temperature mechanism developed by Held and Dryer [18]. However, due to a very small activation energy, R9 contributes approximately 10–20% of HO₂ consumption during the induction period. The ignorance of R9, the chain termination reaction, would result in overestimating the reaction rate of R2 for the skeletal mechanism. Consequently, a much shorter ignition time would be predicted. Therefore,

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