

NUMERICAL STUDY OF HYDROGEN ADDITION EFFECTS ON ALUMINUM PARTICLE COMBUSTION

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ABSTRACT

In this study, the combustion of submicron-sized Al particles in air was studied numerically with a particular focus on the effect of hydrogen addition. Oxidation of the Al particles and the interaction with hydrogen-related intermediates were considered by regarding them as liquid-phase molecules initially. Zero- and One-dimensional numerical simulations were then carried out to investigate the effect of the hydrogen addition on fundamental combustion characteristics of the Al flame, by calculating properties such as ignition delay time and flame speed. Our attention was paid to how the hydrogen chemistry is coupled with the Al oxidation process. Numerical results show that the hydrogen addition generally reduces the reactivity of Al, such that the flame speed and temperature decrease, while it can greatly shorten ignition delay times of the Al flame depending on initial temperatures.

1 INTRODUCTION

Combustion of Aluminum (Al) particles has attracted attention as a promising energy conversion technology due to their high energy density. It has been proposed to use them, for instance, as additives to enhance the reactivity of hydrocarbon fuels [1], and for propulsion in underwater [2] or cosmic environments [3]. Generation of hydrogen through the reaction with water has also been considered [4]. Using the Al combustion as energy sources can also be regarded to be an environmentally friendly process. Furthermore, the Al particle combustion is also related to fire safety issues [5], and accordingly, its elucidation is extremely crucial.

In terms of the kinetic reaction, reaction chemistry of Al combustion with various reactants such as HCl [6], O₂ [7–10], H₂O [8,9,11,12], H₂ [7], CO₂ [7,8], and CH₄ [13] has been studied. These kinetic approaches often possess some limitations in including effects of the particle size or phase transition. It is also arguable whether fundamental flame characteristics such as burning velocity and ignition delay time of the heterogeneous Al flame can be defined as similar to homogeneous flames made by gaseous fuels [14]. Nevertheless, to understand fundamentals of the Al combustion, it is indispensable developing reliable reaction models through the investigation of detailed reaction pathways and accurate reaction rates.

The particle size is one of the most crucial factors governing Al particle combustion. It has been shown that decreases in the particle size lead to increases in the burning rate [15,16]. Huang *et al.* conducted combustion experiments using nano- and micron-sized Al particles [17]. The experimental results showed that increases in nano-particle addition lead to increases in both of the flame thickness and flame speed. However, the wider flame thickness is not caused by the lengthened reaction zone, but due to the overlapping between separately located reaction zones. They analytically investigated the effect of particle size on Al combustion, and showed that the flame speed is inversely proportional to the particle size [10]. It was also reported that the maximum flame speed approaches to 5.82 m/s if considering Al molecular limits, while the experimentally measured flame speed using micron-sized particles [14,17,18] has been found to be an order of magnitude smaller. Note that physical experiments using

submicron-scale Al particles are highly problematic due to their agglomeration, and accordingly, stable Al flames solely made of such particles have been hard to be achieved.

In spite of the high energy density of Al particles, Al flames obtained in physical experiments often possess high instability and ignitability. To overcome such limitations, addition of H₂ may enhance combustibility of the Al flame due to its high flame speed and small ignition energy. Risha *et al.* [18] experimentally showed that effects of the H₂ addition on Al flames, of which the seed Al particle size is 5–8 μm. It has been shown the H₂ addition decreases the flame temperature, but increases the flame speed. However, most previous kinetic studies considering hydrogen related reactions with Al oxidation have focused on production of H₂ by using H₂O as an oxidizer. Furthermore, mixing H₂ with Al particles raise concerns for safety issues regarding coupling effects caused by their high combustibility. Therefore, in the present study, we report effects of the H₂ addition on the Al particle combustion with particular attention to kinetic coupling between the Al and H oxidation chemistry.

2 KINETIC MODEL FOR ALUMINUM AND HYDROGEN OXIDATION

In contrast to the oxidation of gas-phase fuels, it is not straightforward to model the reaction kinetic of solid particle combustion, because it is required to consider effects of the phase change or particle size for strict analyses. Nevertheless, submicron-sized fine Al particles have been treated as a lump of molecules [9,10,12,13]. This assumption is fairly reasonable if considering that the single Al particle with a diameter of 10 nm contains several thousands of Al atoms, and the number decreases to an order of ten when the diameter is as small as 1 nm. Furthermore, in such a case, melting points of Al particles becomes significantly lower than those of bulk material, because bonding forces in the particle are extremely weak. Note that the melting point of the nano-sized Al particle estimated by using molecular dynamics simulations could be lower than 500 K [19,20]. In addition, if the particle diameter becomes as small as submicron scales, the system is governed by the reaction kinetic rather than diffusion [10,11,17]. Accordingly, in the present study we follow the aforementioned assumption for numerical simulations. The initial phase of Al was assumed to be liquid regardless of initial temperatures, and phase changes were considered through including the Al = Al(l) reaction.

The Al-O basic mechanism involving AlO, AlO₂, Al₂O, and Al₂O₂, and Al-O-H sub-mechanism involving AlOH, AlH, AlH₂, and AlH₃ were adopted from [7,9,10]. Thermodynamic and transport data for Al-related species were taken from [21] and [12], respectively. For the O-H sub-mechanism, well-validated GRI-Mech 3.0 [22], from which C- and N-involved reactions were eliminated, was added. Total number of the species and reaction of the kinetic model used in the current study are 22 and 51, respectively. A series of numerical simulations was made using the Cantera 2.4.0 [23] code. Both the 0-D and 1-D simulations for validation reproduce the numerical results of previous studies [9,10,12] well (not shown).

3 HOMOGENEOUS IGNITION PROPERTY

Firstly, the ignition properties of the Al flame were calculated. An ideal gas reactor with a constant volume was assumed by using the IdealGasReactor class in Cantera. Conservation equations for mass, species, and energy were then solved under unsteady states. Homogeneous mixtures were composed of liquid-phase Al and air with a stoichiometric condition, and additional H₂ was mixed up to 10% in mole fraction. Initial temperatures were varied from 1000 to 3000 K under the atmospheric pressure. Ignition delay times for the Al flame were defined by a peak of AlO, which is a major intermediate of the Al oxidation process.

Figure 1 shows the calculated ignition delay time as a function of the temperature. The addition of H₂ highly accelerates the ignition of Al flames when the initial temperature is lower than 1500 K. When the initial temperature is 1200 K, the ignition delay time of the Al flame is found to be 2.04 ms. However, it decreases to 0.199 ms when 2% of H₂ is added as shown in Fig. 2. The flame temperature is slightly decreased with increasing the amount of H₂. The high blending such as 10% makes the ignition delay time almost identical to the stoichiometric H₂/air flame. On the other hand, the addition of H₂ hardly

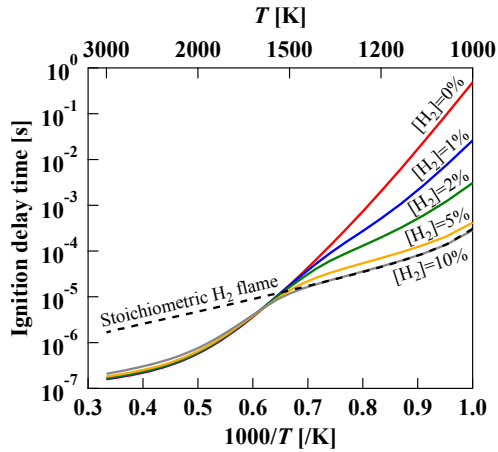


Figure 1. Ignition delay time of the Al flame blended with hydrogen.

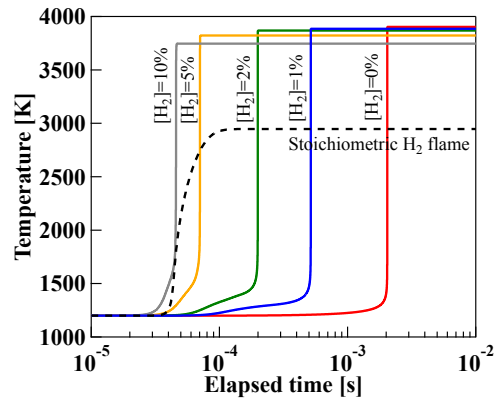


Figure 2. Ignition profiles of the Al flame when the initial temperature is 1200 K.

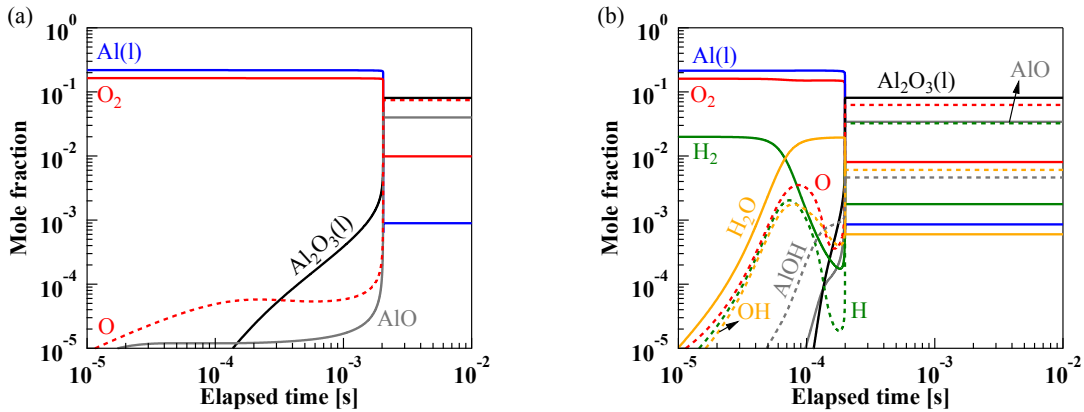


Figure 3. Temporal changes of the major species concentration in the Al flame when (a) 0% and (b) 2% of H_2 is added.

affects the ignition at temperatures above 1500 K, and it is fully governed by the Al oxidation chemistry.

For further discussions, developments of major intermediate species with reactants and products were investigated as shown in Fig. 3 when the initial temperature is 1200 K. The H_2 addition shortens the ignition delay time, but has little effect on composition of the final product. Active radicals such as OH and atomic O/H are produced by the mild oxidation of H_2 , and they advance the oxidation of Al. It is interesting that H_2 is oxidized with producing H_2O via $H_2 + OH/O = H + H_2O/OH$ reactions at the early stage, but resynthesized after the ignition by $Al + H_2O = AlO + H_2$.

4 FLAME STRUCTURE

One-dimensional numerical simulations were made to explore effects of H_2 addition on the Al flame structure. Freely propagating flat flames were assumed under the atmospheric pressure and adiabatic condition by using the FreeFlame class in Cantera. The inlet temperature was set to 300 K. The calculation domain width was initially set to 1 mm, but it could be extended according to the flame

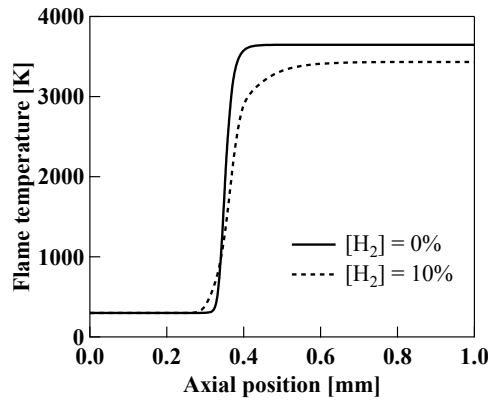


Figure 4. Comparison of the flame temperature with and without the H₂ addition.

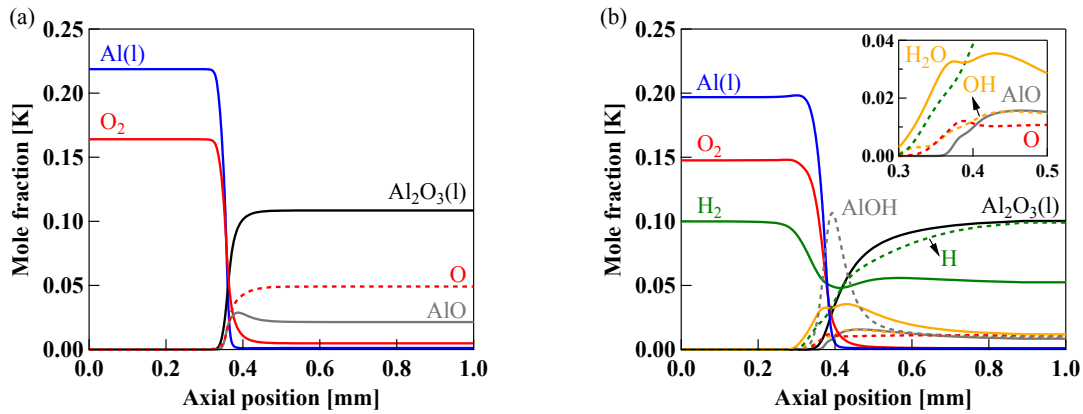


Figure 5. Species distributions in the Al flame when (a) 0% and (b) 10% of H₂ is added. The inset graph in (b) shows the distribution at the axial position from 0.3 to 0.5 mm.

thickness. Note that for the calculation of pure H₂ flames, much wider domain is desirable. Without the H₂ addition, the flame speed and adiabatic flame temperature for the stoichiometric Al/air flame are found to be 5.6 m/s and 3648 K, respectively, which are highly agreeing with the values reported in the previous studies [10,12]. It should be noted that the estimated flame speed is much higher than the experimentally obtained values using micron-scale Al particles due to the molecular treatment of Al particles as mentioned in the introduction section.

Figure 4 compares streamwise distributions of the flame temperature when 10% H₂ is added. By adding H₂, the adiabatic flame temperature and flame speed are decreased to 3433 K and 3.9 m/s, respectively. The flame thickness, showing the opposite tendency to the flame speed, is almost doubled. Again, the trend in the flame speed is opposed to the experimental results reported by Risha *et al.* [18], showing the H₂ addition positively increases the flame speed, which is attributed to high thermal conductivity and low molecular weight of H₂.

Distributions of the major species are shown in Fig. 5. When H₂ exists, formation of final products such as Al₂O₃(l) proceeds gradually. As similar to the result shown in Fig. 3b, H₂ is synthesized at downstream once after consumed near the inlet side. In addition, two peaks are shown in the distributions of H₂O, which is caused by competition between H₂ + OH = H + H₂O and Al + H₂O = AlO + H₂. Regardless of

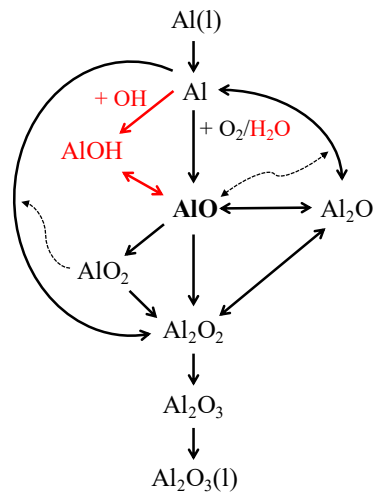


Figure 6. Reaction pathway of the Al oxidation process, and its change by adding H₂.

the H₂ addition, AlO appears as a key intermediate, which also has been confirmed in the 0-D ignition delay calculation. But when H₂ is added AlOH also plays an important role in the oxidation process. As revealed from the pathway analysis shown in Fig. 6, it is simultaneously produced from Al and AlO in the upstream. But it decomposes again with producing AlO, and rarely exists in the exhaust as shown in Fig. 5. The H₂ addition producing abundant H₂O molecules also interferes with the Al oxidation, by producing AlO through Al + H₂O reactions. In addition, the reaction system becomes sensitive to OH radical-involved gas-phase reactions such as H₂ + O = H + OH and H + O₂ = O + OH, which also possessing the high sensitivity to the H₂ flame.

5 CONCLUSION

Effects of H₂ addition on Al flames have been studied numerically. A series of 0-D and 1-D simulations was made to investigate flame characteristics such as ignition delay time and flame structure. The H₂ addition significantly advances the ignition of Al flames when initial temperatures are lower than 1500 K. For instance, when the initial temperature is 1200 K and 2% of H₂ is added, the ignition delay time is reduced to be 0.2 ms, which is one tenth of the pure Al case. It decreases the flame temperature and flame speed, and increases the flame thickness. In the Al/H₂/air combustion system, H₂ is initially consumed by OH and O radicals with producing H₂O, but it oxidizes Al with resynthesizing H₂ afterward. Regardless of the presence of H₂, AlO is a key intermediate species in the Al oxidation process. AlOH also appears as a major intermediate when H₂ is added.

In terms of kinetic effects, the addition of H₂ to Al/air reaction systems causes significant coupling with Al oxidation pathways. Further investigations such as numerical approaches considering effects of the Al particle size and experimental verification under well-defined boundary conditions have to be followed.

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