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Numerical analysis of nanoaluminum combustion in steam

Alexander M. Starik^{a,*}, Pavel S. Kuleshov^a, Alexander S. Sharipov^a, Nataliya S. Titova^a, Chuen-Jinn Tsai^b

^a Central Institute of Aviation Motors, Aviamotornaya St. 2, Moscow 111116, Russia

^b Institute of Environmental Engineering, National Chiao Tung University, No. 1001, University Road, Hsinchu 30010, Taiwan

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ABSTRACT

The comprehensive analysis of chain mechanism development in the Al–H₂O system is performed on the base of novel reaction mechanism taking into account quantum chemistry studies of potential energy surfaces of the elementary reactions with Al-containing species and estimations of rate constants of corresponding reaction channels. As well the physical properties of Al-containing species involved in the reaction mechanism and needed for the calculation of their transport coefficients are reported. The developed reaction mechanism makes it possible to describe with reasonable accuracy the experimental data on ignition temperature in Al–O₂–Ar and Al–H₂O systems and obtain the qualitative agreement with measured value of laminar flame speed. The two-stage regime of ignition in the Al–H₂O reacting system was revealed both when the aluminum is in the liquid phase and when it comes into steam environment in the gas phase. It was shown that decreasing the ignition temperature one can increase the hydrogen yield in the combustion exhaust.

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1. Introduction

Water vapor is a strong oxidizer for several metals. So, the reaction of aluminum with steam yields very high energy density. The other important issue is that the combustion of Al + H₂O mixture produces a significant amount of molecular hydrogen as a combustion product, and reaction of Al with H₂O is considered as a very promising method of hydrogen production [1–3]. Though aluminum is widely utilized as a fuel ingredient in solid propellants and explosives to increase the heat release and, as a result, the specific impulse of rocket engines as well as to reduce the combustion instability [4–6], and a number of researches was addressed the study of kinetics of aluminum combustion (see, for example, [7–11]), the majority of previous works were focused on micron-sized particle burning. The main disadvantage of such particle combustion is that, in this case, large particle can burn only due to diffusion of oxidizer through the metallic oxide shell that forms on the surface of particle, and rate of combustion is limited by the rate of this process [12].

The novel very attractive topic in the combustion of energetic materials is the use of nano-sized Al particles. Such particles exhibit the distinguishing properties compared with micron-sized ones. They feature lower ignition temperature and faster burning rate [8,13–15]. It is believed that such particles undergo fast gasification, and, in this case, atomic aluminum reacts with oxidizer in

a gas phase [11]. This supposition has been recently proved by the detection of atomic aluminum during ignition of Al nanoparticles with $d = 80$ nm behind the reflected shock wave [16]. The particles with larger size can be in a liquid phase, and, frequently (see, for example, [17]), the formation of aluminum in gas phase is modeled by simple one step reaction $\text{Al}(l) \leftrightarrow \text{Al}(g)$. In line with the melt-dispersion mechanism [18], at high rate of particle heating, the melting of Al inside the particle is accompanied by volume expansion which creates large pressure in the molten Al. This leads to alumina shell dynamic spallation. As a result, Al liquid core is dispersed into small bare clusters that fly with high velocity. Oxidation of these clusters is not limited by diffusion through the initial alumina shell and occurs in a kinetic mode.

Therefore, it is of great importance to build an adequate gas phase reaction mechanism describing properly the ignition and combustion in the Al–H₂O mixture. It should be emphasized that, in past decade, only a few studies [11,17] were addressed modeling the processes in the Al–H₂O system. However, for the past years, the novel reaction paths in Al–H₂O system were revealed on the base of theoretical calculations [19–21]. This makes it possible to build a more reliable kinetic model for the ignition and combustion of aluminum in steam environment and reconsider the features of chain mechanism development in such a system. The present paper is focused on solving precisely these problems.

2. Kinetic model

The simple estimations show that, for nonoxidized particles with the radius $r < 25$ nm, the time of heating of particle core

* Corresponding author.

E-mail addresses: star@ciam.ru (A.M. Starik), sharipov@ciam.ru (A.S. Sharipov), titova@ciam.ru (N.S. Titova), cjtsai@mail.nctu.edu.tw (C.-J. Tsai).

caused by energy release in the course of aluminum oxidation and formation of aluminum oxide (Al_2O_3) shell is much higher than the characteristic time of phase transformation. This leads to the rapid destruction of surface layer consisting of Al_2O_3 . This conclusion was proved by molecular dynamic calculations [22]. Therefore, the model assumes that nano-sized particles boil or gasify very rapidly and aluminum comes into the environment in the gas or liquid phase. Note that, in accordance with the results of work [18], small liquid Al clusters can form during oxidation even larger sized particles. Certainly, such a model can be applied only to nonoxidized particles.

Nowadays, all developed kinetic mechanisms treated the reaction of atomic aluminum with H_2O molecule as a principal chain initiation reaction. In line with the data reported in [23], both the reaction mechanism of Huang et al. [17] and the mechanism of Washburn et al. [11] considered this reaction path as a complex processes consisting of two channels



and



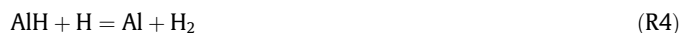
and the rate constant of R1 channel at high temperature ($T \geq 1500$ K) is more than 15 times smaller than that of R2 channel.

However, recent theoretical studies [19,20] revealed that the main reaction path of aluminum with H_2O molecule is the R1 channel, whereas the R2 reaction path is not an elementary one, and rate constant of R1 path is much higher than that of R2 one. Moreover, the reaction mechanisms of Washburn [11] and Huang et al. [17] do not include the important reaction paths with $\text{Al}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, AlO_2H and other species that were investigated theoretically in recent studies [21,24]. Note that these species were also included in the consideration upon thermodynamic analysis of the composition of combustion exhaust in the premixed $\text{Al-H}_2\text{O}_2\text{-N}_2$ flame [25]. In our reaction mechanism we included all these reactions.

In addition, we involved the novel reaction $\text{AlO} + \text{AlH} = \text{AlOH} + \text{Al}$. The rate constant for this reaction was calculated on the base of *ab initio* study of potential energy surface with the use of program package Firefly V. 7.1.G [26]. In accordance with thermochemistry, the activation energy of the reaction $\text{AlOH} + \text{Al} = \text{AlO} + \text{AlH}$ must not be lower than 21,200 K. The preliminary quantum-chemical calculations with the use of the unrestricted variant of the second-order Møller–Plesset perturbation theory (UMP2) [26] for solving the Schrödinger equation in relatively large 6-311+G(d,p) basis set revealed that the backward process $\text{AlO} + \text{AlH} \rightarrow \text{AlOH} + \text{Al}$ is nearly barrierless ($E_a \sim 670$ K). The application of more sophisticated quantum-chemical methods that treat electronic correlation more accurately proved this supposition. So, when applying the fourth-order Møller–Plesset perturbation theory in the MP4(SDQ) modification [26] with the same basis set, a slightly lower value of activation energy ($E_a \sim 440$ K) for $\text{AlO} + \text{AlH} = \text{AlOH} + \text{Al}$ was obtained. However, when utilizing the coupled-cluster method for solving the Schrödinger equation that proved to be one of the most accurate predictive tools in quantum chemistry, even zero activation barrier value was revealed. So, the calculations using the unrestricted coupled-cluster method including single, double and triple excitations (UCCSD(T)) [26] with 6-311+G(d,p) basis set, suggest that the transition state of this reaction lies more than 4000 K lower than $\text{AlO} + \text{AlH}$. Thus, it is worthwhile to include the reaction $\text{AlO} + \text{AlH} = \text{AlOH} + \text{Al}$ in the present kinetic model with the rate constant $k(T) = 2.54 \times 10^{13} T^{0.17} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ determined in accordance with methodology used for barrierless reaction [21].

In order to describe the formation of liquid Al_2O_3 , in according with [8,17] we treated the reaction of the transformation of

gaseous Al_2O_3 to the liquid phase $\text{Al}_2\text{O}_3(\text{g}) \leftrightarrow \text{Al}_2\text{O}_3(\text{l})$ with the rate constant of 10^{14} s^{-1} . Besides these reaction paths, the developed kinetic model must comprise the submechanism that describes the reactions in the $\text{H}_2\text{-O}_2$ system. Earlier, the authors built the kinetic mechanism, which reproduces the large set of experimental data in $\text{H}_2\text{-O}_2\text{-Ar}$ and $\text{H}_2\text{-air}$ mixtures with rather high accuracy [27,28]. Precisely this reaction mechanism was utilized as a submechanism in the kinetic model for the ignition and combustion in the $\text{Al-H}_2\text{O}$ system. Thus, the developed reaction mechanism comprises 59 reversible reactions with following species: O, O_2 , H, H_2 , OH, H_2O , HO_2 , H_2O_2 , Al, AlO, AlO_2 , Al_2O , Al_2O_2 , Al_2O_3 , $\text{Al}_2\text{O}_3(\text{l})$, AlH, AlH_2 , AlH_3 , AlOH, $\text{Al}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, AlO_2H . Table 1 lists the elementary reactions involved in the model and coefficients needed for the calculations of forward reaction rate constants k_q^+ in line with Arrhenius formula $k_q = A_q T^{n_q} \exp(-E_q/T)$, where A_q is the Arrhenius coefficient, E_q is the activation energy of q th reaction and n_q is the power coefficient. The coefficients for the reactions with Al-containing species presented in Table 1 were chosen on the base of recommendations [8,11,20,21,29]. It should be emphasized that we reconsidered the rate constants for the reactions



reported previously by Swihart et al. [29]. The rate constants were estimated on the base of the simplified model of triple collisions for the reaction (R3) and in accordance with methodology used for barrierless reaction for the reaction (R4) [21]. The rate constants of backward reactions k_q^- were calculated with the use of detailed balancing principle. Thermodynamic properties of Al-containing species were taken from the databases reported in [21,30].

It should be emphasized that for some species there are no data on their transport properties. These data are strongly needed to model the deflagrative mode of combustion and the speed of laminar flame propagation. In this work, the coefficients of molecular diffusion, thermal conductivity and viscosity were estimated with the usage of known formulas [31]. The ionization energy E_i , dipole moment μ_i , polarizability α_i and Van-der-Waals collision diameters σ_i , needed for these estimations, were taken from [21,32] or obtained on the base of density functional theory (DFT) calculations at the B3LYP/6-311+G(d,p) level of theory [26]. These parameters as well as the estimated well depth of Lennard-Jones potential for Al-containing species are presented in Table 2.

As in [8,17], we supposed that transport properties of condensed phase of Al and Al_2O_3 are identical to their gas phase counterparts. Though, it should be emphasized that this supposition can be invalid, and the transport properties of rather large clusters $(\text{Al})_n$ and $(\text{Al}_2\text{O}_3)_n$ with $n > 4$, that form the liquid phase, can differ substantially from those of Al and Al_2O_3 monomers. This issue requires special consideration on the basis of *ab initio* calculations of structure and physical properties of such clusters.

3. Results and discussions

Despite the long history of the studies of aluminum particle burning, the researches of the features of reaction in aluminum–air and aluminum–steam mixtures with the use of detailed gas phase reaction mechanism are fairly limited. These researches allow one to gain an insight both in nano- and in micro-sized aluminum particle combustion. Because the behavior of reaction in Al–air and Al– H_2O mixtures was examined earlier by Huang et al. [8,17], it is reasonable to consider the features of chain mechanism development in such systems, investigated on the base of updated kinetic model, in comparison with that reported in

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