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Kinetic modeling of ammonia/air weak flames in a micro flow reactor with a controlled temperature profile

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ABSTRACT

Ammonia is considered to be one of the promising energy carriers in the future and reliable chemical kinetics to accurately predict ignition characteristics of ammonia/air mixtures is necessary for developing ammonia combustors. However, ignition characteristics of ammonia/air mixtures at low temperatures have not been well studied. The present study employed weak flames in a micro flow reactor with a controlled temperature profile, which have been extensively employed to examine ignition characteristics of hydrocarbons, to investigate ignition characteristics of ammonia/air mixtures at low temperatures. Species measurements for weak flames of ammonia/air mixtures at atmospheric pressure and equivalence ratios of 0.8, 1.0 and 1.2 under a maximum wall temperature of 1400 K were conducted using a mass spectrometer and profiles of the NH_3, O_2, H_2O NO, and N_2O mole fractions were obtained. Chemical kinetic modeling was conducted with extensive updates mainly for the N_2H_x chemistry because N_2Hx species were expected to be produced from the $NH_2 + NH_2$ reactions at low temperatures. The mechanism developed in the present study well predicted species profiles of NH_3, O_2 and H_2O for weak flames measured in experiments. The present mechanism also well predicted the final values of the NO and N_2O mole fractions behind the reaction zone of weak flames but overestimated these mole fractions in the reaction zone of weak flames. To confirm the existence of N_2H_x species in the reaction zone of weak flames, signals from N_2H_4 were distinguished from measured signals. Sensitivity analysis and reaction flux analysis were conducted and the importance of the N_2H_x chemistry in the reaction zone of weak flames at low temperatures was identified. Validation of the present mechanism with literature data on ignition delays and flame speeds were conducted and reasonable agreements with literature data were confirmed. For N_2O and NO in the reaction zone of weak flames, however, there was discrepancy between measured and computational mole fractions and further improvements of chemical kinetics related to ammonia ignition are still necessary.

1. Introduction

Ammonia (NH_3) is considered to be one of promising energy carriers [1,2] and ammonia direct combustion has a great potential as an energy utilization method without carbon emission to compensate rapid and huge variation of energy demand due to renewable energy sources. Although the reactivity of ammonia is much lower than those of hydrocarbons, AIST (National Institute of Advanced Industrial Science and Technology) has successfully demonstrated power generation using a small gas turbine of ammonia/air combustion [3] and it has been shown that recent advanced combustion technologies combined with heat regeneration and swirl burners enables to overcome the low reactivity of ammonia. For further development of large-scale, high-efficiency ammonia combustors, reliable reaction mechanisms validated with various ammonia combustion characteristics are necessary to be developed.

Ammonia reaction mechanisms have been developed with extensive validation using experimental and theoretical studies on oxidation and pyrolysis reactions of ammonia [4–9] as well as NO_x reduction reactions with ammonia [10–13] and NO_x formation reactions from ammonia [14–17] because the NO_x reaction system is a sub-mechanism of the ammonia oxidation. The developed ammonia reaction mechanisms have also been validated with flame and ignition characteristics. As flame characteristics, laminar flame speeds [18–22], flammability limits [19,22], flame structures [23] and extinction stretch rates [24] of ammonia/air

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mixtures have been obtained. As ignition characteristics, shock tube experiments for highly-diluted ammonia/oxygen/argon or ammonia/oxygen/nitrogen mixtures at high temperatures (mostly higher than 1800 K) have been conducted [25–30]. However, there have been no studies on ignition delay times of ammonia/air mixtures at lower temperatures. Ignition characteristics at low temperatures are practically important in the base of premixed turbulent jet flames [31]. Longer residence time by introducing swirl and recirculation near the base of premixed turbulent jet flames successfully attained stable combustion with ammonia/air mixtures [3]. To examine ignition characteristics of ammonia/air mixtures at low temperatures (around 1300 K), weak flames in a micro flow reactor with a controlled temperature profile were employed in our previous study [32].

The micro flow reactor was originally employed to investigate flame dynamics in a heated microchannel of a premixture and weak flames were observed in low flow velocity conditions [33]. A weak flame branch was found to be on the ignition branch of the Fendell curve in a theoretical study [34] and weak flames have successfully been applied to investigate ignition characteristics of given premixtures. The transient, two-stage ignition of high hydrocarbons has been observed as steady, three-stage weak flames for dimethyl ether [35] and *n*-heptane [36]. Fuel reactivity has been evaluated using the weak flame position as an index, namely, weak flames of lower/higher reactivity fuels are placed in a higher/lower temperature region of the reactor for syngas [37], C1–C4 alkanes[38], C2–C5 alkenes [39], gasoline primary reference fuels (PRFs) [40] and diesel PRFs [41]. The gas-phase temperature profile is nearly equal to the given wall-temperature profile even in the reaction zone in the weak flame regime [42] and the steady, 1-D numerical model of the micro flow reactor has enabled the validation of the employed reaction mechanisms under a well-defined temperature profile by comparison with experimental weak flame responses [38,40].

One of the important characteristics of the micro flow reactor is its capability for investigating ignition characteristics of low reactivity premixtures in low temperature conditions [43] because of long residence time and the well-defined temperature profile. Weak flames of ammonia/air mixtures, which have quite low reactivity, were successfully observed in our previous study and species measurements in the stoichiometric condition showed complete consumptions of ammonia and oxygen and the formation of near-equilibrium water vapor in the reaction zone [32]. However, most existing reaction mechanisms did not predict the formation of weak flame. Only the reaction mechanism developed by Konnov [44] predicted the formation of weak flame but its position was on the far upstream side (low temperature side) compared with the experimental weak flame position. These results indicated that the Konnov mechanism predicted too high reactivity, whereas the other mechanisms predicted too low reactivity, which were also confirmed by ignition delay simulation at relevant temperatures (around 1300 K). On the other hand, all the mechanisms showed similar ignition delay times at high temperatures (around 2000 K). Therefore, modeling studies based on species profiles of ammonia/air weak flames are expected to develop a more reliable ammonia reaction mechanism, especially for the validity of ignition characteristics at low temperatures.

The objective of the present study is to develop an ammonia reaction mechanism which correctly predicts species profiles of ammonia/air weak flames. Numerical simulations with the developed mechanism for predicting ignition delay times and laminar flame speeds were conducted and the comparisons with literature data were made to confirm the comprehensive performance of the developed mechanism. Hereafter, low temperatures indicate those around 1300 K relevant to temperatures of weak flames in the present experiments and high temperatures indicate those around 2000 K relevant to temperatures of shock tube experiments.

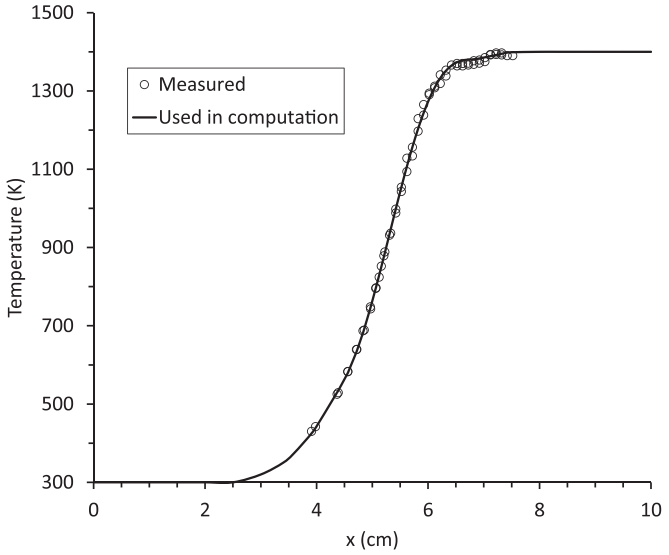

Fig. 1. Wall-temperature profile measured in experiment and used in computation.

2. Experimental setup and computational method

The same experimental setup and computational method as those employed in a previous study [32] were employed in the present study. Details can be found in [32] and only a short summary is given here.

A quartz tube with an inner diameter of 2 mm was used as the reactor channel and heated by a hydrogen/air flat-flame burner to give a stationary temperature ramp along the inner surface of the reactor channel in the flow direction. Hereafter, "wall temperature" means the temperature on the inner surface of the reactor channel. The present study set the maximum wall temperature of 1400 K and measured wall temperature profile is shown in Fig. 1. Ammonia/air mixtures with an inlet mean flow velocity of 10 cm/s were supplied from the low temperature side of the reactor channel at atmospheric pressure and weak flames were formed in the high temperature region of the reactor channel. A quartz micro-probe (inner diameter: 0.1 mm; outer diameter of the edge: 0.25 mm; outer diameter of the root: 1.6 mm) was fused on the side wall of the reactor channel and a T-shaped reactor was fabricated. Gas in the reactor channel was sampled from the micro-probe and introduced to a quadrupole mass spectrometer (QMS) through a fused-silica capillary. The temperature of the sampling line was kept at 373 K by electric heaters to prevent condensation of water vapor. This setup attained rapid reductions of pressure and temperatures of sampled gas at a sufficiently low flow rate so that the disturbance of the flow in the reactor channel by the sampling and chemical reaction in the sampling line were negligibly small [32]. The sampled gas was analyzed by the QMS, and NH_3, O_2, H_2O, N_2O and NO were identified and quantified. Electron ionization of 13 eV was chosen to minimize the fragmentation effects. Voltage of an electron multiplier was set to be 1000 V for NH_3, O_2 and H_2O, whereas that was set to be 1400 V for N_2O and NO. Overall error of the measured mole fraction was estimated to be 10–15%. All experiments were conducted at atmospheric pressure in the present study.

To simulate weak flames in the micro flow reactor, the flow field in the reactor channel was modeled as a one-dimensional steady-state reactive flow without a boundary layer. Computations were conducted using PREMIX in ANSYS Chemkin-Pro v17.2 and a