INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–11

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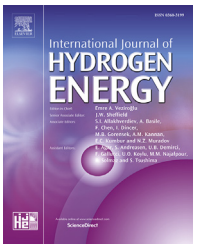

Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion

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ARTICLE INFO

Article history:
Received 15 October 2017
Received in revised form
24 November 2017
Accepted 8 December 2017
Available online xxx

Keywords:
Ammonia oxidation
Detailed kinetic modeling
Nitrogen oxide
Equivalence ratio
Ammonia–hydrogen combustion

ABSTRACT

To achieve comprehensive prediction of ammonia combustion in terms of flame speed and ignition delay time, an improved mechanism of ammonia oxidation was proposed in this work. The present model (UT-LCS) was based on a previous work [Song et al., 2016] and improved by relevant elementary reactions including NH_2, HNO, and N_2H_2. The model clearly explained reported values of laminar flame speed and ignition delay time in wide ranges of equivalence ratio and pressure. This suggests that NH_2, HNO, and N_2H_2 reactivities play a key role to improve the reaction mechanism of ammonia oxidation in the present model. The model was also applied to demonstrate NH_3/H_2/air combustion. The present model also appropriately predicted the laminar flame speed of NH_3/H_2/air combustion as a function of equivalence ratio. Using the model, we discussed the reduction of NO concentration downstream and H_2 formation via NH_3 decomposition in NH_3/H_2 fuel-rich combustion. The results provide suggestions for effective combustion of NH_3 for future applications.

Introduction

Transition to a future society that is not dependent on fossil fuels is becoming an extremely important goal for reducing CO_2 emissions. Investigations of alternatives to carbon-based liquid fuels and hydrogen carriers are thus crucial challenges. Ammonia, which is a carbon-free fuel, is a promising green energy carrier/storage medium because it has high energy density and can be easily liquefied [1–5]. In parallel, ammonia combustion has been examined for applications in gas turbines and gas engines in terms of fuel flexibility [6–13]. However, effective use of ammonia fuel remains challenging

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https://doi.org/10.1016/j.ijhydene.2017.12.066
0360-3199/

because the minimum required ignition energy is high and the burning velocity is very slow in comparison with conventional hydrocarbon fuels [3,14,15]. Recently, despite these difficulties, an essential advance in ammonia combustion with a micro gas turbine was reported [14]. Stable operation of ammonia–air power generation using a 50-kW-class micro gas turbine system was demonstrated successfully using a diffusion-flame-type combustor [14]. Therefore, application of ammonia fuel in a gas turbine is coming closer to reality. For practical use, however, further improvements in output power and efficiency, and reducing NOx emissions are indispensable.

To provide solutions to effective ammonia combustion in gas turbines and gas engines, tremendous efforts through experimental observations and kinetic modeling have been made to understand properties such as combustion temperature, flame seed, ammonia and NOx concentrations in pure ammonia combustion [16–19], ammonia/methane mixture combustion [7,20–23], and ammonia/hydrogen mixture combustion [3,24–33]. Detailed description of appropriate combustion kinetic mechanisms is important for understanding the reaction paths of ammonia decomposition and exhaust-gas formation.

Ammonia combustion models have been proposed and improved by several research groups [15,18,21,34–45]. In early studies, specific ammonia oxidation models were proposed to describe ammonia flame burning [42] and flat laminar premixed flame in ammonia combustion [43]. Later, Konnov and De Ruyck proposed a detailed mechanism to discuss ammonia oxidation decomposition, ignition, and flame structure [34,37,44]. The model of Konnov involved a full H/N/O mechanism (129 species, 1231 reactions [44]) and was tested widely and corrected in subsequent studies on ammonia combustion [3,19,27,28,36,46]. Other models were proposed by Miller-Bowman [15], GRI [38], and San Diego [47] for natural gas burning, taking into account nitrogen species such as ammonia and nitrogen monoxide. Those models were also examined for ammonia oxidation [19,32,33]. The predicted and measured flame speed were in good agreement [19,32], but some disagreements were observed for stoichiometric conditions with small ammonia concentrations and fuel-lean conditions [32]. To mitigate the discrepancies between predictions and experiments, additional discussions are ongoing [21,26,27,32,35,36,39,40,46]. To optimize operating conditions of ammonia combustion, more accurate predictions are necessary in wider ranges of temperature, pressure, and stoichiometry. To date, accurate predictions of flame speed, flame structure, and NOx concentration have not been achieved under a variety of pressurized and stoichiometric, i.e., from fuel-lean to fuel-rich conditions, but this information is indispensable. Further improvements of the models are required for practical applications to gas turbines and gas engines with high efficiency and low NOx emission concentrations.

Here, we describe the current status of predictions of ammonia combustion properties. In Fig. S1 of the supplementary material, laminar flame speed is shown as a function of fuel–air equivalence ratio using previous experimental [19,48–51] and numerical calculation [18,21,37,40,52,53] results. The fuel–air equivalence ratio is defined by overall reaction, $NH_3 + 3/4O_2 \rightarrow 1/2N_2 + 3/2H_2O$, in this study. The calculated values of laminar flame speed were higher than experimental values. Although recently calculated values, such as those reported by Song et al. [40], were improved in comparison with the early work by Konnov [37], the deviation between experiments and calculations remains.

In Fig. S2 of the supplementary material, we compare the shock tube ignition delay times of experimental values (Mathieu and Petersen [18]) and calculated values (Song et al. [40], Tian et al. [21], Dagaut et al. [52], Klippenstein et al. [53], and Mathieu and Petersen [18]). Models proposed by Song et al. [40], Tian et al. [21] and Klippenstein et al. [53] resulted in similar results, i.e., calculated values were smaller than the experimental values, as shown in Fig. S2. However, good agreement between experiments and calculations was achieved by Dagaut et al. [52], as previously indicated by Klippenstein et al. [53], and Mathieu and Petersen [18]. Thus, these models explained the ignition delay time well, but did not reproduce experimental results for flame speed, as shown in Fig. S1. Thus, all previous works have overestimated ammonia combustion in terms of flame speed. Mathieu and Petersen [18] refined the model of Dagaut et al. [52]. They added relevant elementary reactions and changed reaction rate constants to improve the model Mathieu and Petersen [18] in Fig. S2. This model explained the ignition delay time very well, but also overestimated the flame speed of ammonia combustion, as shown in Fig. S1. In the present study, therefore, we propose an ammonia combustion model to explain both flame speed and ignition delay time satisfactorily.

In the present study, we improve a chemical kinetic model of ammonia combustion through a preliminary sensitivity analysis based on a previous model [40]. We propose a modified model of ammonia combustion, which provides more accurate predictions of flame speed, ignition delay, and concentrations of ammonia and NOx in an exhaust gas in a wide range of operating conditions, including pressure and stoichiometry (i.e., equivalence ratio of ammonia/oxygen and ammonia/hydrogen/oxygen). Using the modified model, we discuss conditions for effective ammonia combustion to achieve low NOx emission, which can provide strategies for developing future applications of NH_3 combustors.

Computational details

In this study, the improved reaction model of ammonia oxidation (UT-LCS model) was made using a base model developed by Song et al. (32 species, 204 reactions) [40], which was, in turn, a modified model based on the model of Klippenstein (31 species, 202 reactions) [53]. The proposed reaction model in this study was examined using CHEMKIN PRO software package [54].

The details of improvements of an ammonia combustion model are as follows. As Song and co-researchers have suggested, reactions of amino radical are important in ammonia combustion. We thus developed the model, taking into this point. First, we conducted a sensitivity analysis of elementary reactions for laminar flame seed using the model of Song et al. (see Table S1 in the supplementary material) with equivalence ratio $\phi = 1.1$ at atmospheric pressure. The definition of a sensitivity coefficient for laminar flame speed of reaction j, S_j, is as follows.

Please cite this article in press as: Otomo J, et al., Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion, International Journal of Hydrogen Energy (2017), https://doi.org/10.1016/j.ijhydene.2017.12.066