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1st Symposium on Ammonia Energy

OH and NO measurements in ammonia flames at low-pressure using LIF and absorption

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Introduction

To face the Green-House Gas emission impact and the climate global change, wind or solar energies are envisaged by most of the countries [1]. To circumvent the problem of the intermittency supply, energy can be stored as e-fuels like hydrogen or ammonia. Ammonia can be envisaged either as H₂-carrier or as fuel supply to combustion devices. The use of NH₃ as fuel is quite challenging because of its low laminar burning velocity and high ignition temperature, and requires to be blended with another fuel, H₂ being carbon-free is preferable. One of the main issue comes from the expected high levels of NO_x and N₂O emissions. In order to better understand the conditions in which these emissions could be limited, it is necessary to develop reliable detailed kinetic models. They are already many of them, mostly validated against global kinetic parameters; laminar burning velocities [2–4], and ignition delay times [5–7]. Recently few models have been validated thanks to experimental data obtained in Jet-Stirred Reactors in a temperature ranging 700-1300K [8–11]. To improve the models, it is important to broaden the range of conditions in which species measurements are performed. Only few chemical flame structure analysis have been performed in low-pressure [12,13] or atmospheric pressure [14,15] flames. Using laser spectroscopic diagnostics, Brackmann et al. [14] obtained NH, OH and NO species profiles in NH₃/air premixed flames. To help the flame stabilization, a disk at 16.2 mm above the burner surface serves as stagnation plate. Species concentration profiles were measured using Molecular Beam Mass Spectrometry in premixed flames either in pure NH₃/O₂ [12] or in Ar diluted [13,15] along the flame axis. With the addition of H₂ in the premixed gases, a synergic effect with a regeneration/recovery mechanism is described in [10,16,17]. In laminar flames studies [13,15], it seems that the addition of H₂ does not impact the NO formation in stoichiometric condition. The present work aims to complete these scarce experimental data by measuring OH and NO species using spectroscopic laser diagnostics in four premixed flames stabilized at 10 kPa. The experimental results are compared to four kinetic models [4,10,16,18].

Materials and Methods

Premixed flames were stabilized above a stainless-steel porous burner (Holthuis). The burner is enclosed in a stainless-steel enclosure maintained at a constant pressure ($p=10\text{kPa}$) thanks to a vacuum pump and a regulating valve. The porous burner is water cooled at 323 K. It is vertically mobile in order to describe the species and temperature profiles as function of the height above the burner (HAB). The premixed gases mixtures are supplied through mass flow controllers, while the flow of the shroud N₂ gas is maintained constant through a rotameter. The equivalence ratio of 1 is calculated according to a full conversion into N₂ and H₂O as products. Three flames are NH₃/O₂ diluted

with 24% N₂ (with an equivalence ratio (ϕ) equal to 0.87, 1.10 and 1.33), and the fourth one is NH₃/H₂ blend (90%/10%) ($\phi=0.87$) diluted with 40%N₂. The flame conditions are given in Table 1.

Table 1. Flame composition (in slpm).

Flame #	NH ₃	H ₂	O ₂	N ₂
NH3(087)	1.07		0.92	0.64
NH3(110)	1.23		0.84	0.64
NH3(133)	1.29		0.73	0.64
NH3-10H2(087)	1.16	0.13	1.07	1.58

Four optical access allowed for the laser diagnostics arrangement. Laser Induced Fluorescence and absorption measurements were performed using a Nd/YAG laser pumping a tunable dye laser. The laser beam diameter was restricted through a diaphragm of 2 mm and was strictly parallel to the burner surface. For both species, measurements were obtained in the linear regime of LIF. LIF signals were collected at right angle through a spectrometer and a photomultiplier tube (PMT). Fluorescence was collected through a two-lenses arrangement, and the entrance slit of the spectrometer was limited to obtain a spatial vertical resolution of 250 μm in the flame.

The mole fraction profiles of OH and NO were measured by LIF calibrated respectively by single pass absorption or by the method of the added values as previously performed in methane flames [19]. The temperature was measured by single-pass absorption across the lean NH3(087) flame: by scanning the laser wavelength from 306.8

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to 307.1 nm, 7 isolated absorption lines of OH could be selected from which the temperature was determined at different HAB. From the spectral integrated absorption measurement along the $R_2(7)$ line, the OH mole fraction was measured at 30 mm in the lean $NH_3(087)$ flame and used to calibrate the relative LIF profiles measured in the 4 flames.

The LIF profiles of OH and NO were measured by probing the transition $R_{21}(7)$ and $Q_2(27)$ lines, at 307.0 and 205.6 nm respectively. The LIF signal is proportional to the absolute rotational population of the probed species. Knowing the temperature, and the absolute concentration species at a given location in $NH_3(087)$ flame, the rotational population is converted into absolute species concentration, and mole fraction. Probing NO around 225 nm, a broadband absorption due to NH_3 [20,21] along the laser axis in the flame (mostly close to the burner surface) was observed. The LIF signal was corrected for the laser energy (including the absorption) to get the rotational population along the flame axis.

Results and Discussions

The temperature profile along the flame axis was measured from absorption OH spectra. The determination of T relies on the Boltzmann distribution of the rotational OH population and is derived by plotting the Boltzmann plot. T profile close to burner surface was completed by measurements obtained directly from commercial thermocouple. During this on-going work, the full profile was obtained in the lean NH_3 flame only, and was assumed identical for all flames.

From the experimental results, OH mole fraction profiles present similar shape in all flames with a peak value around 6-8 mm followed by a decrease in the burned gases. It is shown that both OH peak mole fractions and NO mole fractions in the burned gases region decrease with the increase of ϕ . In the two lean flames (with and w/o H_2), the NO mole fraction profiles show an increase at $HAB > 17$ mm. The addition of H_2 in the lean flames affects moderately the OH and NO with an increase of 15% of the mole fractions (within the experimental uncertainties). Kinetic modeling of the four flames was performed using four different kinetic models from the literature. The simulated OH mole fraction profiles agree well with the experimental ones (shape and quantitatively) as shown in Fig. 1. Small deviations are noticed between the kinetic models. The predicted NO mole fraction profiles show important discrepancies between the models with a mole fraction of NO equal to 1.6% ($\pm 20\%$) in the burned gases of the lean $NH_3(087)$ flame. Moreover, the simulated NO mole fraction profiles are at least 5 times larger than the experimental data whatever the equivalence ratio. In the lean flames, the simulated NO mole fraction profiles remain flat in the burned gases contrary the experimental increase.

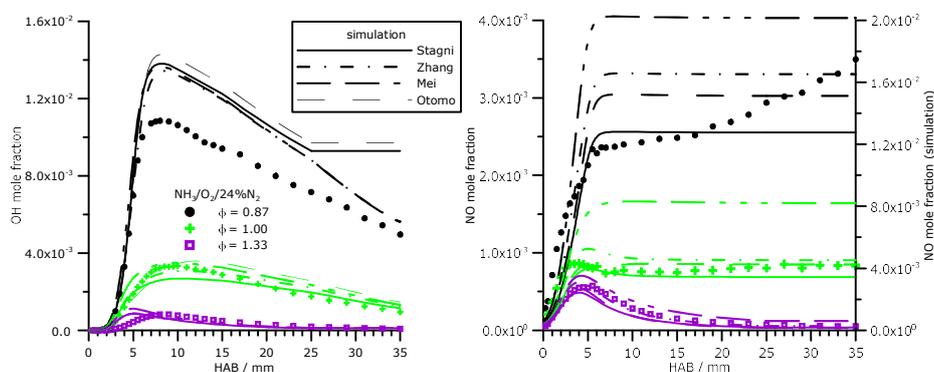


Fig. 1. Experimental and simulated NO and OH mole fraction profiles in $NH_3/O_2/N_2$ flames at $p=10$ kPa

Conclusions

OH and NO mole fraction profiles along four laminar low-pressure flames were measured using in situ LIF. The results indicate that the H_2 addition does not affect the OH and NO mole fraction (within 15%). Comparison with simulated species profiles using different kinetic models indicate a good prediction of the experimental OH profiles. However, the simulated NO profiles indicate significant over-prediction of the experimental ones (a factor of 5 at least), and a large divergence from one model to the other. These experimental results highlight the importance of pursuing effort for a better understanding of the NO formation in order to improve its formation during NH_3 oxidation.

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