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Formation and destruction of nitric oxide in methane flames doped with NO at atmospheric pressure

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Abstract

A study of formation and destruction of NO in adiabatic laminar premixed flames of $CH_4 + O_2$ mixtures diluted with N_2 or Ar (with various dilution ratios) in a range of equivalence ratios at atmospheric pressure is presented. Nitric oxide was seeded into the flames using mixtures of diluent gas + 100 ppm of NO. The heat flux method was employed to measure adiabatic burning velocities of these flames. Nitric oxide concentrations in the post-flame zone at 10, 15 and 20 mm above the burner surface were measured using probe sampling. Burning velocities and NO concentrations simulated using a previously developed chemical kinetic mechanism were compared with the experimental results. The conversion ratio of NO seeded into the flames was determined. The kinetic mechanism accurately predicts burning velocities over the range of equivalence ratios and NO conversion in the rich flames. Significant discrepancies between measured and calculated NO conversion in the lean and near-stoichiometric flames were observed and discussed.

Keywords: Burning velocity; Nitric oxide; Laminar flame; NO conversion

1. Introduction

Exhaust Gas Recirculation (EGR) is considered as the basic method to control Homogeneous Charge Compression Ignition (HCCI) combustion [1]. The application of EGR in HCCI engines has a number of effects on the combustion process and emissions:

- preheating effect: the inlet charge temperature increases due to hot EGR gases;
- dilution effect: the introduction of the EGR gases leads to a reduction of the oxygen concentration;
- heat capacity effect: the total heat capacity of the mixture of the EGR gases, air, and fuel will be higher owing to the higher heat capacity of carbon dioxide and water vapor;
- chemical effect: unburned hydrocarbons, CO, CO_2, NO, H_2O, etc. in the EGR gases are chemically active and could moderately affect reaction rates.

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To address these effects and also NO reburning processes in flames, a number of studies have been performed in methane flames with admixture of NO at sub-atmospheric pressures [2–16] as well as at atmospheric and higher pressures [17–22].

A summary of experimental results obtained in premixed $CH_4 + O_2 + N_2 + NO$ flames at various conditions is given in Fig. 1, where conversion ratio of NO versus initial concentration of NO in the flames is plotted. Here, conversion ratio was determined as the ratio of destroyed [NO] to [NO] added initially to the fresh mixture. One can see that all experimental data were obtained in the flames with initial [NO] additive higher than 1000 ppm. Lean ($\phi = 0.86$) premixed $CH_4/O_2/N_2$ and $H_2/O_2/N_2$ flames stabilized on a McKenna burner at atmospheric pressure with addition of 0.11–0.33% of NH_3, NO and N_2O were studied by Martin and Brown [21]. Using microprobe gas sampling, relationships between NO and N_2O formation in the post-flame zone and addition of NH_3, NO and N_2O to combustion mixture were determined. The relative error of the measurements of NO concentration in the post-flame zone was about ±10–50%. The effect of addition of 1000 ppm of NO on the structure of premixed CH_4/air flames in a range of equivalence ratios 0.8–1.7 was studied by Jansohn et al. [18]. A nozzle burner was used for flame stabilization and concentrations of stable species were determined. A comparison of the measurements and modeling using the mechanism of Miller and Bowman [24] in the rich ($\phi = 1.25$) undoped flame showed an under-prediction of NO concentration in the post-flame zone by a factor of 2. On the other hand, in the flame seeded with 1000 ppm of NO the modeling over-predicted the NO concentration by a factor of 1.2 at the same experimental conditions. Feng et al. [22] studied the structure of burner-stabilized $CH_4/O_2/Ar$ flames doped with NO (960–1070 ppm) using a quartz microprobe sampling and subsequent chemiluminescence analysis. They found that the modeling using the mechanism of Lindstedt et al. [25] under-predicts NO concentrations in the post-flame zone at rich conditions ($\phi = 1.3$–1.4) by a factor of 1.5–2. In very rich flames ($\phi = 1.4$–1.7) and in lean ones ($\phi = 0.8$–1.0) the modeling however satisfactory predicts NO concentration.

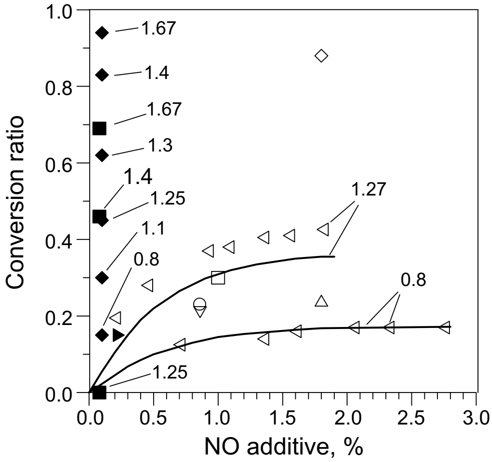

Fig. 1. Conversion ratio of nitric oxide in a number of $CH_4 + O_2 + N_2 + NO$ flames at various conditions derived from measurements obtained by different research groups. Filled squares: [18], equivalence ratios $\phi = 0.8$–1.66 (specified on the plot), pressure $p = 1$ atm; filled right triangle: [21], $\phi = 0.85$, $p = 1$ atm; filled diamonds: [22], $\phi = 0.8$–1.66 (specified on the plot), $p = 1$ atm; open diamond: [2], $\phi = 1$, $p = 10$ torr; open circle: [3], $\phi = 1$, $p = 10$ torr; open up triangle: [4], $\phi = 1$, $p = 10$ torr; open down triangle: [5], $\phi = 1$, $p = 10$ torr; open square: [6], $\phi = 1$, $p = 10$ torr; open left triangle: [23] (lines indicate modeling results obtained in this work), $\phi = 0.8$ and 1.27, $p = 25$–30 torr.

Measurements of NO conversion in the flames doped with lower concentration of nitric oxide were not reported. Numerical simulations, e.g. [7,17,19,23,26] based on the GRI-Mech. 2.11 [27], 3.0 [28], and Miller–Bowman kinetic mechanism [24] showed that in the lean flames doped with low concentration of NO (on the average less than ~600 ppm) its consumption does not exceed 10%. This fact was used for calibration of NO fluorescence signals in flames at atmospheric and higher [17,19], as well as at sub-atmospheric pressures [7,23,26]. Thomsen et al. [19] calibrated NO fluorescence signal in premixed lean ($\phi = 0.6$) $CH_4/O_2/N_2$ flames stabilized on a McKenna burner at pressures 1–14 atm with addition of 157 ppm of NO. They assumed that no NO is destroyed in the flame front of these flames, and validated their assumption by computer modeling, which predicted less than 5% NO destruction. Bessler et al. [17] performed their calibration using a lean premixed flame ($\phi = 0.95$) stabilized on a McKenna burner doped with NO (300–600 ppm). It was concluded that in this flame decomposition of NO additive was less than 10%.

Thus, the literature showed that the degree of NO reburning in flames depends on the stoichiometry and on initial concentration of NO seeded into fresh mixture. Although there was no direct experimental proof, it was generally accepted that small amounts of NO seeded into lean flames are not consumed (within ±10 %) and can be used for, e.g., LIF signal calibration.

The original goal of the present work was therefore to investigate NO reburning mostly in rich premixed methane flames at atmospheric pressure for validation of the Konnov detailed kinetic mechanism [29]. The heat flux method was used for flame stabilization. This method allows accurate measurements of the laminar burning velocities and facilitates comparison of