The Sensitizing Effects of NO_x on Methane Low-temperature Oxidation in a Jet Stirred Reactor

Lorena Marrodán[1], Yu Song[2], Nicolas Vin[2], Olivier Herbinet[2], Emmanuel Assaf[3], Christa Fittschen[3], Alessandro Stagni[4], Tiziano Faravelli[4], María U. Alzueta[1], Frédérique Battin-Leclerc[2]

[1]Grupo de Procesos Termoquímicos (GPT)
Instituto de Investigación en Ingeniería de Aragón (I3A)
Universidad de Zaragoza, Mariano Esquillor s/n, 50018, Zaragoza, Spain.
Tel. +34-976762707, e-mail: marrodan@unizar.es
[2]CNRS-LRGP-Nancy (France)
[3]CNRS-PC2A-Lille (France)
[4]Politecnico di Milano-Milan (Italy))

Abstract

Biogas (mainly methane and carbon dioxide) produced from biomass anaerobic digestion is considered as a potential renewable gas-phase fuel. That is why the study of the mutual effects of CH_4/NO_x have attracted considerable attention in the past decade. In this work, the oxidation of methane with and without NO_x addition has been investigated in a jet-stirred reactor.

Introduction

The limited fossil fuel resources and its harmful effects on climate, have increased the interest for environmentally friendly fuels. Biomass seems to be a promising fuel due to its sustainability, security supply and low threat to the environment. Produced from biomass anaerobic digestion, the so-called “biogas”, consists mainly of methane (CH_4) and carbon dioxide (CO_2) with trace amounts of nitrogen and sulphur compounds. Biogas can play an important role as potential renewable gas-phase fuel. The main nitrogen compound present in biogas is ammonia, which could easily convert to NO in presence of oxygen. Moreover, exhaust gas recirculation is an effective technique to reduce the pollutants by diluting reactants with exhaust gases working under high dilution and comparatively low temperature conditions. In addition to CO_2 and H_2O, exhaust gases also contain NO_x ($NO+NO_2$) which, under these conditions, may have a significant impact on ignition characteristics. Despite the abundant experimental reports concerning CH_4-NO_x interactions (for example, [1, 2]), the sensitizing effects of NO_2 on methane low-temperature oxidation in a jet-stirred reactor has not been performed yet.

In this context, the aim of the present work is to analyze the CH_4-NO_x interactions in a jet-stirred reactor (JSR) at atmospheric pressure, temperatures ranging from 650-1200 K and for different equivalence ratios (ϕ) with an intense effort in searching important intermediate species, such as HONO, CH_3NO_2 and HCN.

Methodology

The experimental setup used to perform the different methane (1%) oxidation experiments, with and without NO_x addition, was a laboratory-scale spherical fused silica JSR (volumen of 85 cm^3). A complete description can be found in [3], therefore, only the main features are mentioned here. The reactant gases are premixed and preheated before entering the reactor. The JSR has four injectors with nozzles which create high turbulence and homogenous mixing. The reactor temperature (650-1200 K) is measured by a type-K thermocouple located in the center of the reactor. The pressure inside the reactor is controlled by a needle valve positioned downstream of the reactor and kept at 107 kPa. Different NO and NO_2 concentrations in the reactant mixture have been tested: 0, 100, 500 and 1000 ppm in the case of NO, and 0, 100 and 400 ppm in the case of NO_2. Argon has been used as bath gas and the residence time inside the reactor was kept constant at a value of 1.5 s. The oxygen required to perform the different oxidation experiments has been varied to work under fuel-lean (ϕ=0.5) to fuel-rich (ϕ=2) conditions. Four different diagnostics techniques have been used to analyze the gases leaving the reactor: gas chromatography (GC), chemiluminescence NO_x analyzer, continuous wave Cavity Ring-Down Spectroscopy (cw-CRDS) and Fourier Transform Infrared spectroscopy (FTIR).

A detailed kinetic mechanism from the POLIMI group [4] has been used to interpret the experimental data. Numerical calculations have been conducted with CHEMKIN-PRO software package. Transient solver has been applied in the simulation tasks with sufficient time to allow reaching the steady state solution.

Results and conclusions

Figure 1 shows the results obtained for CH_4 consumption in the absence and presence of NO_x for the different equivalence ratios analyzed (ϕ). The results indicate that the onset temperature for methane oxidation (above 1025 K) is shifted to higher temperatures (825 K) by the addition of NO or NO_2, independently of the equivalence ratio. This fact indicates that CH_4 oxidation is promoted by the addition of NO_x. The consumption of CH_4 exhibits a similar trend in the presence of both NO and NO_2. New experimental data and new species detection during the low-temperature CH_4 and CH_4+NO_x jet-stirred reactor oxidation have provided insights into the understanding of the mutual effect of CH_4 and NO_x. The agreement between experimental data and model predictions is very satisfactory. With the help of the kinetic mechanism, reaction rate and sensitivity analysis were performed to identify the main reaction routes and illustrate the kinetic regimes. The analysis of the results indicates that the similar effect on promoting CH_4 oxidation by either the addition of NO or NO_2 can be explained because both species are involved in a reaction cycle interchanging them via NO_2+H/CH_3=NO+OH/CH_2O and NO+HO_2/CH_3O_2=NO_2+OH/CH_3O reactions. During this reaction sequence highly reactive OH radicals are produced, which promote methane oxidation.

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REFERENCES

[1]. DAGAUT, P. and NICOLLE, A. Experimental study and detailed kinetic modeling of the effect of exhaust gas on fuel combustion: mutual sensitization of the oxidation of nitric oxide and methane over extended temperature and pressure ranges. *Combustion and Flame*. 2005, 140(3) 161-171.

[2]. CHAN, Y.L., BARNES, F.J., BROMLY, J.H., KONNOV and A.A., ZHANG, D.K. The differentiated effect of NO and NO_2 in promoting methane oxidation. *Proceedings of the Combustion Institute*. 2011, 33(1) 441-447.

[3]. HERBINET, O. and BATTIN-LECLERC, F. Progress in understanding low-temperature organic compound oxidation using a jet-stirred reactor. *International Journal of Chemical Kinetics*. 2014, 46(10) 619-639.

[4]. SONG, Y., MARRODAN, L., VIN, N., HERBINET, O., ASSAF, E., FITTSCHEN, C., STAGNI, A., FARAVELLI, T., ALZUETA, M.U., BATTIN-LECLERC, F. The sensitizing effects of NO2 and NO on methane low temperature oxidation in a jet stirred reactor. *Submitted to Proceedings of the Combustion Institute*.

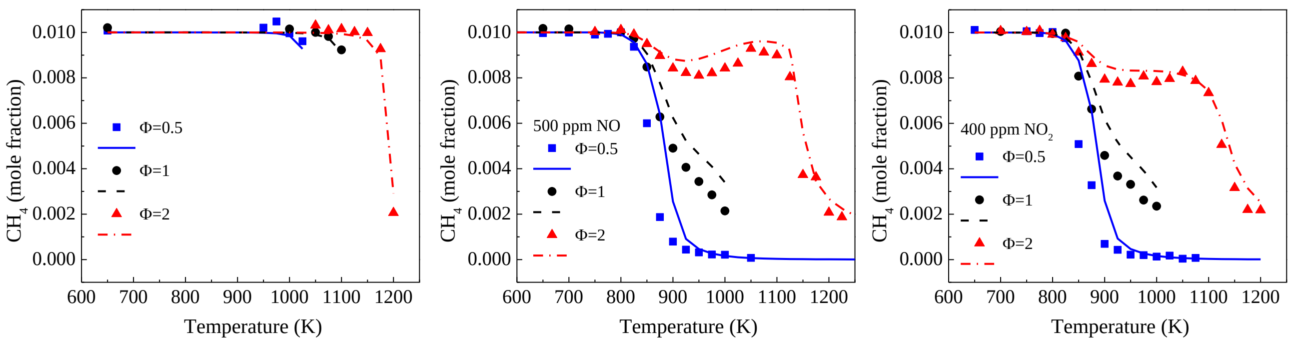

Figure 1. Experimental (symbols) and modeling calculations (lines) for CH_4 oxidation in the absence of NO_x (left), in the presence of 500 ppm of NO (middle) and in the presence of 400 ppm of NO_2 (right) for the different equivalence ratios (ϕ) considered.