



**HAL**  
open science

## The sensitizing effects of NO<sub>2</sub> and NO on methane low temperature oxidation in a jet stirred reactor

Y. Song, L. Marrodán, N. Vin, Olivier Herbinet, E. Assaf, C. Fittschen, A. Stagni, T. Faravelli, M.U. U Alzueta, F. Battin-Leclerc

### ► To cite this version:

Y. Song, L. Marrodán, N. Vin, Olivier Herbinet, E. Assaf, et al.. The sensitizing effects of NO<sub>2</sub> and NO on methane low temperature oxidation in a jet stirred reactor. Proceedings of the Combustion Institute, 2018, 37, pp.667-675. 10.1016/j.proci.2018.06.115 . hal-01922893

**HAL Id: hal-01922893**

**<https://hal.science/hal-01922893>**

Submitted on 14 Nov 2018

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# The sensitizing effects of NO<sub>2</sub> and NO on methane low temperature oxidation in a jet-stirred reactor

Y.Song<sup>a</sup>, L.Marrodán<sup>b</sup>, N.Vin<sup>a</sup>, O.Herbinet<sup>a,\*</sup>, E.Assaf<sup>c</sup>, C.Fittschen<sup>c</sup>, A.Stagni<sup>d</sup>,  
T.Faravelli<sup>d</sup>, M.U.Alzueta<sup>b</sup>, F.Battin-Leclerc<sup>a</sup>

<sup>a</sup> *Laboratoire Réactions et Génie des Procédés, CNRS-Université de Lorraine, 1 rue Grandville, 54000 Nancy, France*

<sup>b</sup> *Aragón Institute of Engineering Research (I3A), Department of Chemical and Environmental Engineering, University of Zaragoza, Mariano Esquillor s/n, 50018 Zaragoza, Spain*

<sup>c</sup> *Université Lille, CNRS, UMR 8522- PC2A-PhysicoChimie des Processus de Combustion et de l'Atmosphère, F59000 Lille, France*

<sup>d</sup> *Department of Chemistry, Materials and Chemical Engineering "G. Natta", Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

Published in Proceedings of the Combustion Institute  
<https://doi.org/10.1016/j.proci.2018.06.115>

## Abstract

The oxidation of neat methane (CH<sub>4</sub>) and CH<sub>4</sub> doped with NO<sub>2</sub> or NO in argon has been investigated in a jet-stirred reactor at 107 kPa, temperatures between 650 and 1200 K, with a fixed residence time of 1.5 s, and for different equivalence ratios ( $\phi$ ), ranging from fuel-lean to fuel-rich conditions. Four different diagnostics have been used: gas chromatography (GC), chemiluminescence NO<sub>x</sub> analyzer, continuous wave cavity ring-down spectroscopy (cw-CRDS) and Fourier transform infrared spectroscopy (FTIR). In the case of the oxidation of neat methane, the onset temperature for CH<sub>4</sub> oxidation was above 1025 K, while it is shifted to 825 K with the addition of NO<sub>2</sub> or NO, independently of equivalence ratio, indicating that the addition of NO<sub>2</sub> or NO highly promotes CH<sub>4</sub> oxidation. The consumption rate of CH<sub>4</sub> exhibits a similar trend with the presence of both NO<sub>2</sub> and NO. The amount of produced HCN has been quantified and a search for HONO and CH<sub>3</sub>NO<sub>2</sub> species has been attempted. A detailed kinetic mechanism, derived from POLIMI kinetic framework, has been used to interpret the experimental data with a good agreement between experimental data and model predictions. Reaction rate and sensitivity analysis have been conducted to illustrate the kinetic regimes. The fact that the addition of NO or NO<sub>2</sub> seems to have similar effects on promoting CH<sub>4</sub> oxidation can be explained by the fact that both species are involved in a reaction cycle interchanging them and whose result is  $2\text{CH}_3 + \text{O}_2 = 2\text{CH}_2\text{O} + 2\text{H}$ . Additionally, the direct participation of NO<sub>2</sub> in the  $\text{NO}_2 + \text{CH}_2\text{O} = \text{HONO} + \text{HCO}$  reaction has a notable accelerating effect on methane oxidation.

**Keywords:** Jet-stirred reactor; NO<sub>x</sub> methane combustion; Low-temperature oxidation

**Corresponding author:** Olivier Herbinet  
[olivier.herbinet@univ-lorraine.fr](mailto:olivier.herbinet@univ-lorraine.fr)

## 1. Introduction

The limited fossil fuel resource and its harmful effects on the climate have increased the interest for environmentally friendly fuels. Biomass seems to be a promising fuel source due to its sustainability, secure supply and low threat to the environment. Produced from the biomass anaerobic digestion, the so-called “biogas”, consists mainly of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) with trace amounts of nitrogen and sulfur compounds. Biogas plays 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 the presence of oxygen even at low temperatures. The mutual effects of CH<sub>4</sub>/NO<sub>x</sub> or CH<sub>4</sub>/NH<sub>3</sub> have attracted considerable attention in the past decade.

A large number of experimental reports concerning the hydrocarbon-NO<sub>x</sub> interactions in ideal reactors are available [1-12]. Most studies related to reburning technology were performed in tubular flow reactors (FR) for CH<sub>4</sub> high-temperature oxidation. Over a relatively low-temperature range (800–1150 K), Dagaut and Nicolle [6] demonstrated the effects of NO on methane oxidation at pressures of 1–10 atm in a jet stirred reactor. A simplified reaction path was proposed, in which the reaction NO + HO<sub>2</sub> = OH + NO<sub>2</sub> followed by OH + CH<sub>4</sub> = CH<sub>3</sub> + H<sub>2</sub>O were highlighted. In addition, the investigation of mutual effects of NO<sub>2</sub> on CH<sub>4</sub> oxidation is also of significant value. Bendtsen et al. [4] and Chan et al. [9] examined the impact of NO and NO<sub>2</sub> as promoters to CH<sub>4</sub> oxidation under fuel-lean conditions in a FR. The different key reactions at the onset for NO (CH<sub>3</sub>O<sub>2</sub> + NO = CH<sub>3</sub>O + NO<sub>2</sub>) or NO<sub>2</sub> (NO<sub>2</sub> + CH<sub>4</sub> = CH<sub>3</sub> + HONO) sensitization were identified. However, some minor reaction paths such as NO<sub>2</sub> + CH<sub>2</sub>O = HONO + HCO, which could play a role in mutual effects on CH<sub>4</sub> oxidation, have been ignored so far. Moreover, to the authors' knowledge, the sensitizing effects of NO<sub>2</sub> on methane low-temperature oxidation in a jet-stirred reactor have not been investigated yet.

Despite the abundant kinetic studies for the CH<sub>4</sub>-NO<sub>x</sub> interactions, the knowledge of some notable intermediate nitrogen species (such as HONO) is not comprehensively understood. Chai and Goldsmith [13] calculated the rate coefficients for H<sub>2</sub> + NO<sub>2</sub> and CH<sub>4</sub> + NO<sub>2</sub> with the formation of HONO. The fate of these species is of importance to the hydrocarbon-NO<sub>x</sub> interactions during the biogas oxidation. However, until now, HONO has never been detected during fuel oxidation.

Therefore, the aim of this work is to investigate the hydrocarbon-NO<sub>x</sub> (NO and NO<sub>2</sub>) interactions in biogas oxidation at atmospheric pressure and temperatures ranging from 650 to 1200 K. A search for intermediate species HONO, CH<sub>3</sub>NO<sub>2</sub> and HCN has been made with the aid of continuous wave Cavity Ring-Down Spectroscopy (cw-CRDS) and Fourier Transform Infrared (FTIR), respectively. A detailed kinetic mechanism, recently updated according to the latest available ab initio calculations, is used to interpret the experimental data.

## 2. Experimental setup

The experimental setup was a laboratory-scale spherical fused silica JSR (volume of 85 cm<sup>3</sup>; detailed description provided elsewhere [14]). A more detailed description of the experimental setup is available in Supplementary material (SM1). The reactant gases were premixed in a preheating zone before entering the reactor center through four nozzles which create high turbulence resulting in homogeneity in composition and temperature of the gas phase. The residence time inside the preheater was only 1% with respect to the one in the reactor which was fixed at 1.5 s (±0.1 s) within all the experiments performed. Both the reactor and the preheater were heated using Thermocoax resistances. The reactor temperature was measured by a type-K

thermocouple ( $\pm 5$  K) located at the center of the reactor. The pressure in the reactor was controlled by a needle valve ( $\pm 0.2$  kPa) positioned downstream of the reactor and kept at 107 kPa. Argon, oxygen, NO, NO<sub>2</sub> and methane were provided by Messer (purities of 99.99%, respectively). The flow rates of the reactants were controlled by mass flow controllers ( $\pm 0.05\%$ ). The gases leaving the reactor were analyzed on-line using two gas chromatographs (GCs), a NO<sub>x</sub> analyzer (Thermo Scientific Model 42i), a FTIR (Thermo Scientific Antaris) spectrometer and a cw-CRDS spectroscopy cell.

- The first GC equipped with a thermal conductivity detector was used to quantify O<sub>2</sub>. The second GC equipped with flame-ionization detector preceded by a methanizer and a PlotQ capillary column was used to quantify CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>2</sub>.
- The chemiluminescence NO<sub>x</sub> analyzer was adopted to measure NO and NO<sub>2</sub>. The quantitative range is 0–5000 ppm for NO and 0–500 ppm for NO<sub>2</sub> with 0.1 ppm sensitivity, respectively. Two pumps are used for outlet and bypass channels, respectively.
- The FTIR spectrometer was used to detect the CH<sub>3</sub>NO<sub>2</sub> (if any) and HCN (calibrated using a HCN diluted (1000 ppm in N<sub>2</sub>) cylinder) species.
- cw-CRDS infrared spectroscopy was used to detect H<sub>2</sub>O, CH<sub>2</sub>O and HONO (if any) species, the description of this instrument is also provided in [15].

The uncertainty for the different diagnostic instruments is estimated to be  $\pm 5\%$  except for the FTIR and CRDS measurements which is  $\pm 10$ – $15\%$ . All the experimental data presented hereafter are detailed in a spreadsheet in SM2.

### 3. Kinetic model

The kinetic mechanism used for chemistry description and analysis of experimental results was obtained by relying on the POLIMI kinetic framework, describing the pyrolysis and oxidation of hydrocarbon fuels [16]. Its core C<sub>0</sub>–C<sub>3</sub> mechanism was recently revised by coupling the H<sub>2</sub>/O<sub>2</sub> and C<sub>1</sub>/C<sub>2</sub> subsets from Metcalfe et al. [17], C<sub>3</sub> from Burke et al. [18], and heavier fuels from Ranzi et al. [19]. For the low temperature conditions of interest in this work, particular attention was devoted to updating the (equilibrated) reaction rates of peroxy radical formation from methyl radical [20], as well as the related thermodynamic properties. They were adopted, when available, from the database of Burcat and Ruscic [21].

Following the modularity principle behind the POLIMI mechanism, a NO<sub>x</sub> sub-mechanism was integrated into the main framework: a complete characterization of its basic structure is provided in [22,23]. It describes the major paths leading to NO<sub>x</sub> formation. Apart from the three well-studied reactions responsible of thermal NO<sub>x</sub> mechanism [24], the mechanism underwent a major update for the prompt path, especially in relation to the NCN-route: the kinetic laws of the reactions involving NCN were updated after the ab initio calculations by Harding et al. [25] and Faßheber et al. [26]. Moreover, the chemistry of HNC and HNCN was also updated according to the modifications proposed by Lamoureux et al. [27]. On the other side, the high-temperature reburning mechanism of methane implements the rates proposed by Dean and Bozzelli [28] for the reactions of methyl with NO. The methoxy activation by NO (CH<sub>3</sub>O<sub>2</sub> + NO = CH<sub>3</sub>O + NO<sub>2</sub>) was obtained from Atkinson et al. [29], and validated in the 200–430 K temperature range, while its direct formation via NO<sub>2</sub> (CH<sub>3</sub> + NO<sub>2</sub> = CH<sub>3</sub>O + NO) was updated following Glarborg and Bendtsen [30], which is temperature independent over the range 295–1400 K. Rate coefficients of HONO and HNO<sub>2</sub> formation from methane and NO<sub>2</sub> were implemented following Chai and Goldsmith [13]. The complete mechanism (153 species and 2361 reactions) is provided as supplemental

material of this paper in CHEMKIN format, along with thermodynamic and transport properties (SM3). The present mechanism is able to reproduce experimental data from literature [6,7,9] as shown in SM1.

## 4. Results

Experiments for the oxidation of CH<sub>4</sub> doped with NO and NO<sub>2</sub> with argon as bath gas were performed under fuel-lean ( $\varphi = 0.5$ ) to fuel-rich ( $\varphi = 2$ ) conditions over the 650–1200 K temperature range. Equivalence ratios were calculated neglecting the amounts of added NO<sub>x</sub> compounds which were around 4–10% that of CH<sub>4</sub>. The experimental conditions investigated in this study are presented in Table 1. Numerical calculations were conducted with CHEMKIN-PRO software package [31]. Transient solver was applied in the simulation tasks with sufficient time allowed to reach the steady state solution.

Table 1. Experimental conditions (Inlet composition volume basis; balanced Ar).

Exp.	$X_{CH_4}$	$X_{NO}$ ppm	$X_{NO_2}$ ppm	$X_{O_2}$	$\varphi$
1	0.01	-	-	0.04	0.5
2	0.01	-	-	0.02	1
3	0.01	-	-	0.01	2
4	0.01	500	-	0.04	0.5
5	0.01	500	-	0.02	1
6	0.01	500	-	0.01	2
7	0.01	100	-	0.02	1
8	0.01	-	400	0.04	0.5
9	0.01	-	400	0.02	1
10	0.01	-	400	0.01	2
11	0.01	-	100	0.02	1
12	0.01	1000	-	0.02	1

### 4.1. Profiles of carbon compound species and water

Figure 1 shows the evolution of major products with temperature for the oxidation of CH<sub>4</sub> (left), methane doped with NO<sub>2</sub> (middle) and NO (right) for the three studied equivalence ratios ( $\varphi = 0.5$ , 1 and 2). With respect to the pure CH<sub>4</sub> oxidation, the initial oxidation temperatures are 1025 K, 1075 K and 1175 K for  $\varphi = 0.5$ , 1 and 2, respectively. Dynamic behaviors (oscillations) occur under oxidizing and stoichiometric conditions when the temperature is above 1050 K and 1100 K, respectively. This is, too, an interesting topic of research in such systems, but beyond the goals of this specific study.

In the presence of NO<sub>2</sub> (400 ppm) under fuel-lean conditions, the reaction is initiated at 825 K. The rise of consumption of CH<sub>4</sub> is extremely fast with the increase of temperature. At 950 K, 98% of the inlet methane concentration was oxidized. Under stoichiometric conditions, the onset temperature for CH<sub>4</sub> oxidation is around 825 K as well. However, CH<sub>4</sub> consumption is slower than that under fuel-lean conditions: there is still 24% CH<sub>4</sub> left in the reactor outlet at 1000 K. Similarly as under the above two conditions, the consumption of methane also starts at 825 K under fuel-rich conditions, whereas the consumption of methane is even slower compared to that under stoichiometric conditions. Differing from what is observed under stoichiometric and oxidizing conditions, the mole fraction of methane reaches a minimum at 950 K under reducing conditions, and the mole fraction of methane increases at higher temperatures until 1050 K. After that, methane is consumed again. Compared to the oxidation of neat methane (left column), the enhancing effect for the addition of NO<sub>2</sub> into the oxidizing environment system is quite obvious especially for reducing conditions.

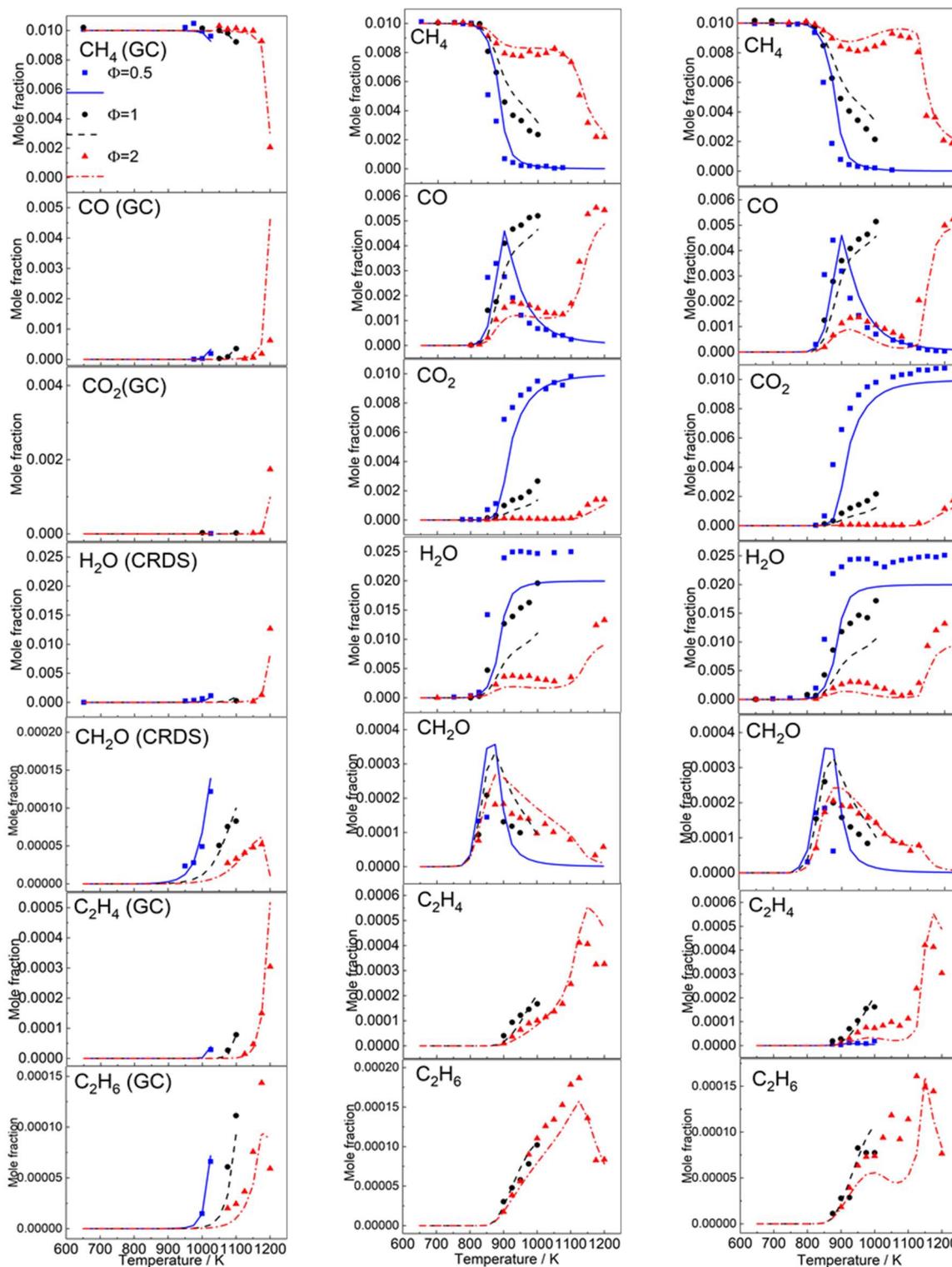


Figure 1. Species profile comparison between experimental data and model predictions. The left column is for the oxidation of neat methane; the middle column is for the oxidation of methane doped with  $\text{NO}_2$  (400 ppm); the right column is for the oxidation of methane doped with  $\text{NO}$  (500 ppm). Here and in further figures in this paper, symbols represent experiments and lines denote simulations. Experiments and simulations are not presented for conditions where oscillations were observed.

In the presence of NO (500 ppm), the evolution of methane profiles is quite similar to what is obtained in the presence of NO<sub>2</sub>. This indicates that the promoting effects of NO and NO<sub>2</sub> on methane oxidation is almost the same although the amount of the addition of NO and NO<sub>2</sub> is a little different.

Note that oscillations even occur under stoichiometric ( $T > 1000$  K) and oxidizing conditions ( $T > 1100$  K, with NO<sub>2</sub> addition) in the presence of NO and NO<sub>2</sub>. The present model could reproduce the above mentioned dynamic behavior as shown in SM1.

The peak mole fraction of CH<sub>2</sub>O profile occurs at a temperature of 850 K, which is independent of equivalence ratios in the presence of both NO and NO<sub>2</sub>. Likewise, the mole fraction of CO reaches its utmost value at 850 K under fuel-lean conditions, which indicates that the methane oxidation is very fast at this specific temperature. Under fuel-rich conditions, the temperature for the peak CO mole fraction shifts to 900 K. C<sub>2</sub> species (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) mainly appear under stoichiometric and reducing conditions at higher temperature ( $T > 900$  K). Under oxidizing conditions, the mole fraction of C<sub>2</sub> species are below the detection limit and this behavior is well captured by the model as is shown in SM1. The global carbon balance has been checked and the deviation is below 5% (SM2).

The agreement between the experimental data and simulated results is generally good within all the investigated conditions except for that the model underestimates the experimental profile of H<sub>2</sub>O under stoichiometric and fuel-lean conditions, which was also observed by Bugler et al. [32]. It might be ascribed to the uncertainty in cw-CRDS measurements derived from its significant concentrations. Also, the performance of different literature models against present experimental data is displayed in SM1. It is found that the current POLIMI model is better capturing the experimental data than the other models.

In order to evaluate the effect of the amount of added NO<sub>2</sub> and NO on the methane oxidation, three more sets of experiments with addition of 100 ppm NO<sub>2</sub> or NO and addition of 1000 ppm NO (sets 7, 11 and 12 in Table 1), respectively, were conducted. Figure 2 shows both the experimental and model results. It was found that the onset temperature for methane oxidation is independent of the added amount of NO<sub>2</sub> and NO. Moreover, with the lower added amount of NO<sub>2</sub> or NO, the methane conversion is slower. When 1000 ppm of NO is present, methane conversion shows a trend similar to that with 500 ppm NO addition. Furthermore, the consumption rate for methane also exhibits the similar trend in the presence of both NO<sub>2</sub> (100 ppm) and NO (100 ppm) which differs from what was previously observed by Chan et al. [9] in a FR.

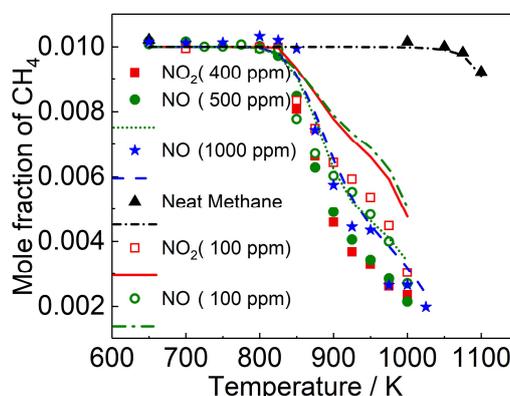


Figure 2. Mole fractions of methane with various additions of NO<sub>2</sub> (400 and 100 ppm) and NO (1000, 500 and 100 ppm) under stoichiometric condition.

## 4.2. Profiles of nitrogen containing species

### 4.2.1. $\text{NO}_2$ and $\text{NO}$

Figure 3 shows the evolution of  $\text{NO}_2$  and  $\text{NO}$  profiles as a function of temperature for methane oxidation in the presence of  $\text{NO}_2$  (left) and  $\text{NO}$  (right), respectively. In the presence of 400 ppm  $\text{NO}_2$ , the consumption of  $\text{NO}_2$  is approximately similar for all investigated equivalence ratios. The increase of the  $\text{NO}$  mole fraction is quite sharp over the range 800–900 K, and is independent of equivalence ratio. After that, it attains a “plateau” level of 280 ppm in stoichiometric and oxidizing conditions and 300 ppm in reducing conditions, with the increase of temperature. Only under rich conditions the  $\text{NO}$  concentration drops from 300 to 100 ppm when the temperature increases from 1100 K to 1200 K. The model accurately predicts the onset for both the consumption of  $\text{NO}_2$  and production of  $\text{NO}$ . It overestimates the amount of  $\text{NO}$  when the temperature is above 800 K.

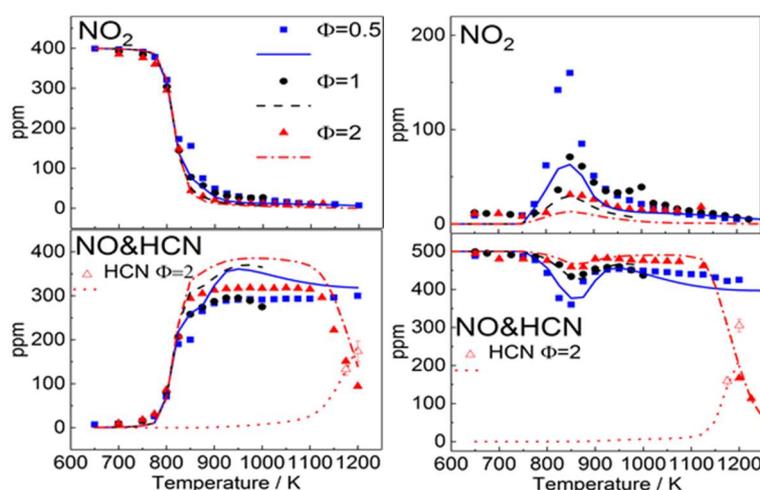


Figure 3. The comparison of  $\text{NO}_2$ ,  $\text{NO}$  and  $\text{HCN}$  profiles between experimental data and model predictions. Left: the oxidation of methane doped with  $\text{NO}_2$  (400 ppm). Right: the oxidation of methane doped with  $\text{NO}$  (500 ppm).

In the presence of  $\text{NO}$  (500 ppm), the mole fraction of  $\text{NO}_2$  peaks at 850 K, which corresponds to the maximum consumption of  $\text{NO}$  with all equivalence ratios. The amount of  $\text{NO}_2$  drops gradually as the temperature is above 850 K, meanwhile, the mole fraction of  $\text{NO}$  increases to a stable value until the temperature is beyond 900 K. Under reducing conditions, the mole fraction of  $\text{NO}$  decreases dramatically over the temperature range 1100–1200 K. Although the model underestimates the formation of  $\text{NO}_2$ , the initiation temperature for  $\text{NO}$ - $\text{NO}_2$  conversion is well captured.

### 4.2.2. $\text{HCN}$

$\text{HCN}$  has been quantified by FTIR at the highest temperatures (1175–1200 K) studied in this work for both  $\text{NO}_2$  and  $\text{NO}$  additions as shown in Figure 3. The measured  $\text{HCN}$  spectrum is displayed in SM1. At a same temperature, the amount of  $\text{HCN}$  is higher in the presence of  $\text{NO}$  than with  $\text{NO}_2$  addition. Moreover, the quantification of  $\text{HCN}$  could somewhat help to close the nitrogen balance at the highest temperatures. The model predicts the formation of  $\text{HCN}$  quite well in the presence of  $\text{NO}_2$ , although it underestimates the amount of  $\text{HCN}$  in the presence of  $\text{NO}$  at 1200 K.

The mass balance of nitrogen deteriorates with the increase of temperature when temperature is above 850 K in the presence of NO<sub>2</sub> condition. The reason could be ascribed to the detection failure for some nitrogenated species with the currently available diagnostic instruments. Also, the overprediction of NO in the presence of NO<sub>2</sub> indicates that the NO<sub>2</sub> conversion channel needs to be further investigated.

#### 4.2.3. A search for HONO and CH<sub>3</sub>NO<sub>2</sub> species

The absorption spectrum of HONO has been previously measured by Jain et al. [33]. This previous work indicates that HONO, if any, should be detected in the present study. In our study, the cw-CRDS product analyses were conducted in the near infrared at wavenumbers in the 6638.0–6643.5 cm<sup>-1</sup> range. The absorption line at 6643.17 cm<sup>-1</sup> was chosen as the most suitable for the quantification of HONO with an absorption cross-section of  $4.2 \pm 1.7 \times 10^{-21}$  cm<sup>2</sup> [33] due to the fact that there are no interferences at this specific absorption line. There were obvious signals at this absorption line in the spectrum around a temperature of 850 K. However, for some less intense absorption lines, such as 6642.45 cm<sup>-1</sup>, no signals could be observed in our spectra. Therefore, the maximum produced HONO mole fraction is then below the estimated detection limit of 3 ppm. No obvious FTIR absorption lines for CH<sub>3</sub>NO<sub>2</sub> could be observed. The maximum produced CH<sub>3</sub>NO<sub>2</sub> mole fraction is then below the estimated detection limit of 5 ppm. The measured spectra of HONO and CH<sub>3</sub>NO<sub>2</sub> of this study can be found in SM1. Modeling calculations (see SM1) predict low mole fraction (1–2 ppm) of HONO, which is consistent with what is observed in these experimental data. Note that the discrepancy between experimental and modeling calculations found in the 800–1000 K range for NO<sub>2</sub> (right upper in Figure 3), can be explained by the too high predicted formation of CH<sub>3</sub>NO<sub>2</sub>. However, no experimental detection of this species by FTIR was achieved although it could be done.

### 4.3. Discussion

Reaction rate and sensitivity analyses have been performed to identify the main reaction routes and the utmost sensitive reactions for CH<sub>4</sub> consumption in the presence of NO<sub>x</sub>, respectively, as shown in Figure 4. The characteristic temperature of 850 K is selected because the consumption of methane is quite significant and the formation of carbon species peaks at this specific temperature.

In the case of neat CH<sub>4</sub>, the reaction path analysis is conducted at 1100 K, its consumption proceeds through methyl radicals (CH<sub>3</sub>) which can continue reacting following 4 different routes: (a) a self-reaction forming ethane; reactions with O<sub>2</sub>, (b) forming directly CH<sub>2</sub>O + OH radicals, (c) giving CH<sub>3</sub>O radicals which also lead to formaldehyde via reaction (1) CH<sub>3</sub>O(+ M) = CH<sub>2</sub>O + H(+ M) or (d) producing CH<sub>3</sub>O<sub>2</sub> radical via reaction (2) CH<sub>3</sub>+ O<sub>2</sub>(+ M) = CH<sub>3</sub>O<sub>2</sub>(+ M), which is also a minor source of formaldehyde.

At 850 K, in the presence of NO<sub>x</sub>, methoxy radical formation through reaction (3) CH<sub>3</sub> + NO<sub>2</sub> = CH<sub>3</sub>O + NO is the most sensitive as shown in sensitivity analysis except for the addition of NO under reducing condition, when reaction (3) is slightly less sensitive than chain branching reaction H + O<sub>2</sub> = O + OH. In this case, CH<sub>3</sub>O radicals are also formed in large extent by the reaction of NO with CH<sub>3</sub>O<sub>2</sub> radicals: reaction (4) CH<sub>3</sub>O<sub>2</sub>+ NO = CH<sub>3</sub>O + NO<sub>2</sub>. The whole reaction cycle (1)–(4) results in an overall balance: 2CH<sub>3</sub>+ O<sub>2</sub>= 2CH<sub>2</sub>O + 2H and produces a strong acceleration of methane oxidation, since 2 H atoms are obtained from 2 CH<sub>3</sub> radicals and one O<sub>2</sub> molecule. The

reaction route involving C<sub>2</sub> species becomes more relevant as the temperature is increased being almost negligible at 850 K.

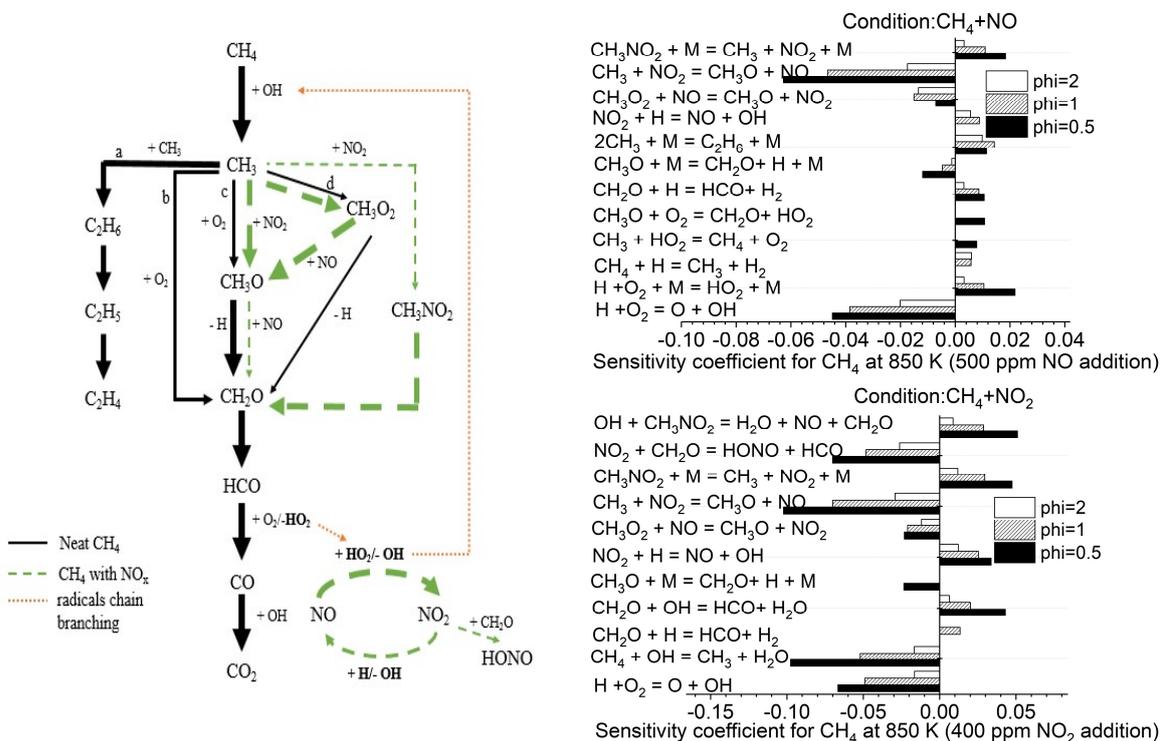


Figure 4. Left: Reaction path diagram for CH<sub>4</sub> oxidation in presence of NO<sub>x</sub> ( $\varphi = 1$ ,  $T = 850$  K).

Solid lines represent the main reaction routes occurring during the oxidation of neat CH<sub>4</sub> (1100 K); dashed lines highlight the main changes due to the presence of NO<sub>x</sub>. The size of the arrow is proportional to the flow rate of the given reactions. Right: CH<sub>4</sub> sensitivity coefficient at 850 K in the presence of NO<sub>2</sub> (upper: 400 ppm) and NO (bottom: 500 ppm).

The above mentioned reaction loop (1)–(4) acts as a “catalytic” cycle and it can explain the fact that the addition of NO or NO<sub>2</sub> seems to have similar effects on promoting methane oxidation. Note that NO/NO<sub>2</sub> interchanging occurs via the reaction of NO and HO<sub>2</sub> radicals giving NO<sub>2</sub> and OH radicals and the reaction of NO<sub>2</sub> with H radicals reforming NO and OH radicals. The OH radicals produced during the NO-NO<sub>2</sub> interchanging cycle interact with CH<sub>4</sub> promoting its conversion, whereas the H and HO<sub>2</sub> radicals produced during the conversion of CH<sub>4</sub> (i.e. mainly through CH<sub>3</sub>O(+M) = CH<sub>2</sub>O(+M) + H and HCO + O<sub>2</sub> = CO + HO<sub>2</sub>) promote the NONO<sub>2</sub> conversion as described earlier. The role of the radicals in the mutual sensitization of the oxidation of CH<sub>4</sub> and NO<sub>x</sub> has been highlighted in Figure 4.

Moreover, in the presence of NO or NO<sub>2</sub>, CH<sub>3</sub> radical is consumed by an alternative route, leading to the formation of nitromethane, CH<sub>3</sub>NO<sub>2</sub>. This acts as an inhibitor of the whole system for two different reasons: (i) it traps both CH<sub>3</sub> and NO<sub>2</sub>, slowing down their successive reactions and the formation of the very reactive methoxy radical (CH<sub>3</sub>O), and (ii) it also acts as an OH scavenger via OH + CH<sub>3</sub>NO<sub>2</sub> = H<sub>2</sub>O + NO + CH<sub>2</sub>O.

The main formation route for HONO is from NO<sub>2</sub> by reactions NO<sub>2</sub> + CH<sub>2</sub>O = HONO + HCO and NO<sub>2</sub> + HNO = HONO + NO. It only represents 4% in the total NO<sub>2</sub> consumption at 850 K and  $\varphi = 0.5$ , hence the expected HONO mole fraction is small, which agrees with the experimental data.

However, these reactions play an essential role for the consumption of methane because the unstable HONO can readily convert to OH radical. In turn this favors the abstraction reaction  $\text{CH}_4 + \text{OH} = \text{CH}_3 + \text{H}_2\text{O}$ , which is the second most sensitive reaction for methane depletion in the conditions with  $\text{NO}_2$  addition. Note that the sensitivity analysis in Figure 4 shows a strong promoting effect of the reaction  $\text{NO}_2 + \text{CH}_2\text{O} = \text{HONO} + \text{HCO}$ .

At high temperatures, when HCN has been experimentally detected, NO reacts with HCCO and  $\text{CH}_3$  radicals to form HCNO and  $\text{H}_2\text{CN}$ , respectively, and later HCN is obtained; thus, NO is reduced by means of well-known reburn type reactions [3].

## 5. Conclusions

In this work, the oxidation of neat methane and methane doped with  $\text{NO}_2$  or NO at 107 kPa and temperatures of 650–1200 K with a fixed residence time of 1.5 s has been investigated in a jet-stirred reactor under oxidizing to reducing conditions from both experimental and modeling points of view. In general, there is a good agreement between experimental results and modeling calculations. New experimental data and new species detection, along with the confirmation of a detailed kinetic model under these new conditions, have provided insights into understanding the mutual effect of  $\text{CH}_4/\text{NO}_x$  interaction. The addition of  $\text{NO}_2$  or NO produces comparable results on methane oxidation, anticipating the onset temperature for  $\text{CH}_4$  consumption to lower temperatures (825 K) regardless of the equivalence ratio. Kinetic analysis showed that the parallel behavior of NO and  $\text{NO}_2$  is connected to their interchanging via  $\text{NO}_2 + \text{H}/\text{CH}_3 = \text{NO} + \text{OH}/\text{CH}_2\text{O}$  and  $\text{NO} + \text{HO}_2/\text{CH}_3\text{O}_2 = \text{NO}_2 + \text{OH}/\text{CH}_3\text{O}$  reactions. This allows relating both actions to a common, oxidation-sensitizing mechanism, activated by methoxy radical formation, whilst counteracted by the parallel formation of nitromethane. The mole fraction of HCN has been quantified with FTIR, and the agreement between the experimental data and model prediction is generally good. Modeling calculations predict the formation of  $\text{CH}_3\text{NO}_2$ , which was not detected experimentally although it could be, partially explaining the discrepancy between experimental and modeling results in the  $\text{NO}_2$  profile at 800–1000 K. The contribution of HONO in the activation of the system was pointed out, too. The amount of HONO was under the detection limit, consistently with the modeling predictions.

## Acknowledgments

This work has received funding from the European Union H2020 (H2020-SPIRE-04-2016) under Grant agreement no. 723706 and from the COST Action CM1404 “Chemistry of smart energy carriers and technologies”. Ms. Marrodán acknowledges Aragón Government for the predoctoral grant awarded.

## Supplementary materials

- Supplemental information:
  - Additional description of the experimental setup.
  - Comparison of simulations using the present mechanism (POLIMI mechanism) with literature data.
  - The evolution profiles of methane as a function of time at both steady and oscillation states.
  - Evolution with temperature of mole fractions of the different species according to model calculations with POLIMI mechanism.
  - The performance of literature models against the experimental data.

- Comparison of FTIR spectra for HCN with the spectra obtained during the oxidation of methane doped with NO.
  - Comparison of FTIR spectra for CH<sub>3</sub>NO<sub>2</sub> with the spectra obtained during the oxidation of methane doped with NO<sub>2</sub>.
  - Comparison of cw-CRDS spectra for HONO with the spectra obtained during the oxidation of methane doped with NO<sub>2</sub>.
  - Comparisons between the original POLIMI model and POLIMI model with CH<sub>3</sub>+NO<sub>2</sub>=CH<sub>2</sub>O+NO modified against the experimental data under different conditions.
- Experimental results (excel spreadsheet)
  - Detailed kinetic model (reactions, thermodynamic properties, transport data)

## References

- [1] J.H. Bromly, F.J. Barnes, S. Muris, X. You, B.S. Haynes, *Combust. Sci. Technol.*, 115 (1996) 259-296.
- [2] M.U. Alzueta, P. Glarborg, K. Dam-Johansen, *Combust. Flame*, 109 (1997) 25-36.
- [3] Glarborg, P., Alzueta, M.U., Dam-Johansen, K., Miller, J.A. *Combust Flame*, 115 (1998) 1-27.
- [4] A.B. Bendtsen, P. Glarborg, K.I.M. Dam-Johansen, *Combust. Sci. Technol.*, 151 (2000) 31-71.
- [5] P. Dagaut, J. Luche, M. Cathonnet, *Proceedings of the Combustion Institute*, 28 (2000) 2459-2465.
- [6] P. Dagaut, A. Nicolle, *Combust. Flame*, 140 (2005) 161-171.
- [7] C.L. Rasmussen, A.E. Rasmussen, P. Glarborg, *Combust. Flame*, 154 (2008) 529-545.
- [8] T. Mendiara, P. Glarborg, *Energy Fuels*, 23 (2009) 3565-3572.
- [9] Y.L. Chan, F.J. Barnes, J.H. Bromly, A.A. Konnov, D.K. Zhang, *Proc. Combust. Inst.*, 33 (2011) 441-447.
- [10] J. Giménez-López, V. Aranda, A. Millera, R. Bilbao, M.U. Alzueta, *Fuel Process. Technol.*, 92 (2011) 582-589.
- [11] Y. Chan, J. Bromly, A. Konnov, D. Zhang, *Combust. Sci. Technol.*, 184 (2012) 114-132.
- [12] J. Zhang, V. Burklé-Vitzthum, P.-M. Marquaire, *Combust. Sci. Technol.*, 187 (2015) 1139-1156.
- [13] J. Chai, C.F. Goldsmith, *Proc. Combust. Inst.*, 36 (2017) 617-626.
- [14] O. Herbinet, F. Battin-Leclerc, *Int. J. Chem. Kinet.*, 46 (2014) 619-639.
- [15] C. Bahrini, O. Herbinet, P.-A. Glaude, C. Schoemaeker, C. Fittschen, F. Battin-Leclerc, *Chem. Phys. Lett.*, 534 (2012) 1-7.
- [16] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A. Kelley, C. Law, *Prog. Energy Combust. Sci.*, 38 (2012) 468-501.
- [17] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, *Int. J. Chem. Kinet.*, 45 (2013) 638-675.
- [18] S.M. Burke, U. Burke, R. Mc Donagh, O. Mathieu, I. Osorio, C. Keesee, A. Morones, E.L. Petersen, W. Wang, T.A. DeVerter, *Combust. Flame*, 162 (2015) 296-314.
- [19] E. Ranzi, A. Frassoldati, A. Stagni, M. Pelucchi, A. Cuoci, T. Faravelli, *Int. J. Chem. Kinet.*, 46 (2014) 512-542.
- [20] R.X. Fernandes, K. Luther, J. Troe, *J. Phys. Chem. A*, 110 (2006) 4442-4449.
- [21] A. Burcat, B. Ruscic, *Third millenium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables*, Argonne National Laboratory Argonne, IL, 2005.
- [22] T. Faravelli, A. Frassoldati, E. Ranzi, *Combust. Flame*, 132 (2003) 188-207.
- [23] A. Frassoldati, T. Faravelli, E. Ranzi, *Combust. Flame*, 135 (2003) 97-112.
- [24] J.A. Miller, C.T. Bowman, *Prog. Energy Combust. Sci.*, 15 (1989) 287-338.
- [25] L.B. Harding, S.J. Klippenstein, J.A. Miller, *J. Phys. Chem. A*, 112 (2008) 522-532.

- [26] N. Faßheber, J. Dammeier, G. Friedrichs, *Phys. Chem. Chem. Phys.*, 16 (2014) 11647-11657.
- [27] N. Lamoureux, H. El Merhubi, L. Pillier, S. de Persis, P. Desgroux, *Combust. Flame*, 163 (2016) 557-575.
- [28] A.M. Dean, J.W. Bozzelli, *Combustion chemistry of nitrogen*, in: *Gas-phase combustion chemistry*, Springer, 2000, pp. 125-341.
- [29] R. Atkinson, D. Baulch, R. Cox, J. Crowley, R. Hampson, R. Hynes, M. Jenkin, M. Rossi, J. Troe, I. Subcommittee, *Atmos. Chem. Phys.*, 6 (2006) 3625-4055.
- [30] P. Glarborg, A.B. Bendtsen, J.A. Miller, *Int. J. Chem. Kinet.*, 31 (1999) 591-602.
- [31] CHEMKIN-PRO 15151, Reaction Design, San Diego, (2013).
- [32] J. Bugler, A. Rodriguez, O. Herbinet, F. Battin-Leclerc, C. Togbé, G. Dayma, P. Dagaut, H.J. Curran, *Proc. Combust. Inst.*, 36 (2017) 441-448.
- [33] C. Jain, P. Morajkar, C. Schoemaeker, B. Viskolcz, C. Fittschen, *J. Phys. Chem. A*, 115 (2011) 10720-10728.