

Identification of ammonia oxidation regimes in a JSFR reactor. A survey on available kinetic schemes performance.

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Introduction

The search for alternative to fossil fuels is an important concern of our society and many studies are focused on low-carbon or non-carbon fuels. Ammonia is a non-carbon molecule that could be used as a clean energy carrier in combustion systems since it can be oxidized without CO₂ emissions. Furthermore, ammonia can be produced by traditional or innovative processes integrated with renewable sources. Its storage and delivery are particularly feasible if compared with hydrogen. However, physical and chemical proprieties of ammonia (high ignition temperature, low laminar flame velocity and low heating value) are not promising to burn ammonia by traditional technologies and, peculiar attention should be paid for its high potentiality to produce NO_x in oxidation processes. For these reasons, the successful application of ammonia as an alternative fuel requires a detailed understanding of its oxidation mechanism and NO_x pollutant formation routes. Such targets are hindered by the lack of experimental data in simple systems with controlled operating parameters. In fact, most models are developed as an adjustment of NO_x formation/reducing mechanisms. Given this background, this work aims at collecting data by performing experimental tests in a Jet Stirred Flow Reactor.

Methodology

The oxidation process of ammonia mixtures was studied in a JSFR. This reactor enables to systematically study the dependence of the chemical species distribution as a function of a range of combustion parameters, such as fuel mixture composition and temperature. It consists of a fused silica sphere of 113 cm³. The main flow is composed of oxygen and diluent. It passes through a quartz tube located within two cylindrical electrically heated ceramic fiber ovens. It subsequently mixes with the secondary flow, composed by fuel and diluent, in a premixing chamber. Then the pre-mixed mixture enters the reactor through four nozzles of 1 mm diameter located at its center. To detect and follow accurately the temperature changes during gaseous reactions, a type R thermocouple (40 µm bead size) was used.

Experiments were performed setting the follow operative conditions: inlet temperature 950-1300 K, pressure 1.227 atm, dilution level 96 % using nitrogen as diluent agent, residence time 0.21 s, equivalence ratio from 0.8 to 1.2.

To provide a detailed chemical analysis, the outlet stable species O₂, N₂, H₂ were analyzed by gas chromatography (µ-GC AGILENT), O₂ and NO_x concentrations were measured by TESTO 350. In addition, O₂ was also analyzed by an oxygen analyzer supplied by ADEV s.r.l.. Gas outlet flow was cooled down to 1-2 °C by a chiller to condense water and obtain concentrations on a dry base.

The experimental results obtained in the JSFR were simulated using the PSR code of the CHEMKIN PRO software package [1]. Four different detailed gas-phase chemical kinetic models were used (tab. 1).

| Kinetic mechanism | Number of Reactions | Number of Species |
|---------------------------|---------------------|-------------------|
| Song et al. (2016) | 204 | 34 |
| Konnov (2018) | 286 | 36 |
| Frassoldati et al. (2006) | 173 | 32 |
| Nakamura et al. (2017) | 232 | 38 |

Tab. 1. Kinetic mechanisms and details.

Experimental tests and simulations

Tests were performed for ammonia/oxygen/nitrogen mixtures, changing the mixture inlet temperature (T_{in}) and equivalence ratio (ϕ).

From temperature profiles (not reported here) the ignition temperature is independent of equivalence ratio and its value is about 1225 K. Figure 1 shows the experimental profiles of hydrogen and NO for different mixture equivalence ratio as a function of pre-heated temperature. For temperature under 1225 K hydrogen profiles do not depend on equivalence ratio. H_2 mole fraction increases until 1150 K, then it decreases increasing the temperature towards the ignition one. Above $T_{in} = 1225$ K, significant differences between the three mixtures analyzed occur: for fuel lean and stoichiometric conditions, H_2 mole fraction increases as a function of temperature and the maximum values are detected at $\phi = 0.8$, instead hydrogen concentration decreases for the fuel rich mixture. Similarly to H_2 , NO profiles are slightly dependent on equivalence ratio below the ignition temperature. They exhibit a relative minimum around 1080 - 1110 K, which occurs at higher T_{in} for the rich condition, and a minimum at around 1225 K independently of the initial composition. NO trends are strongly dependent on equivalence ratio at high temperatures. NO mole fraction is approximatively constant at $\phi = 1.2$ while, for lean and stoichiometric conditions, it increases with temperature. The higher values are found at $\phi = 0.8$ where NO concentration reaches about 120 ppm.

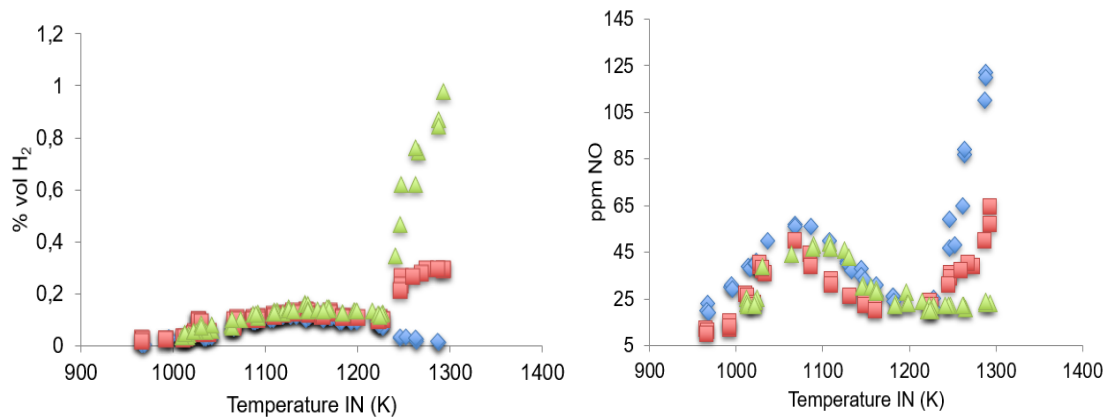
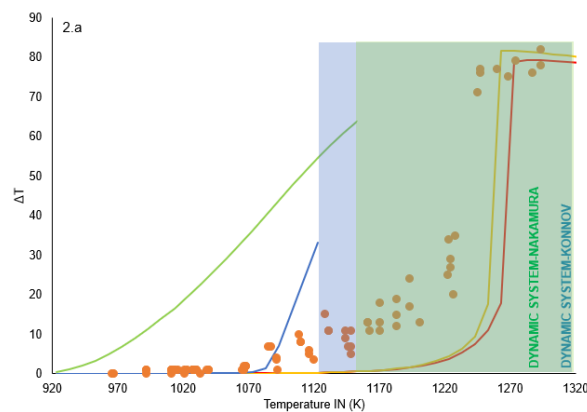


Figure 1. Experimental profiles of hydrogen (on the left) and NO (on the right), for different equivalence ratio Φ . Symbols: $\Phi=0.8$, blue rhombus; $\Phi=1.0$, red square; $\Phi=1.2$, green triangle.

Experimental data suggest that it is possible to identify three different kinetics regimes: low, intermediate and high temperatures.

Figure 2 reports the comparison between experimental trends and numerical predictions.



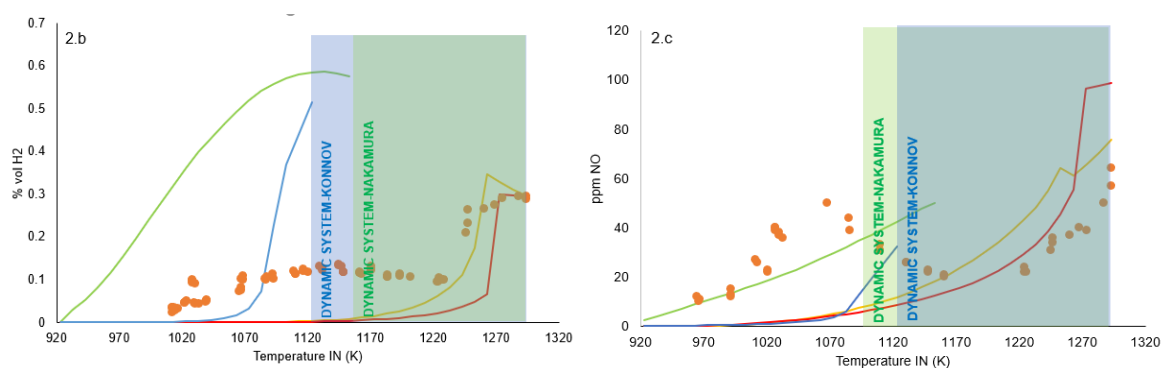


Figure 2. Comparison between experimental profiles and numerical predictions. Symbols: experiments, points; Konnov et al. mechanism, blue line; Nakamura et al. mechanism, green line, Song et al. mechanism, red line; Frassoldati et al. mechanism, yellow line.

As shown in figure 2.a, two of the considered models (Konnov et al. [2], Nakamura et al. [3]) predict a higher reactivity at low temperatures with respect to the experimental data and suggest the occurrence of dynamic behaviors at intermediate ones. The other two kinetic schemes (Song et al. [4], Frassoldati et al. [5]) predict no reactivity at low and intermediate temperatures. At high temperatures, all the models envisage a similar reactivity. H_2 and NO profiles obtained by the Nakamura et al. [3] mechanism predict experimental trends at low temperatures, instead the same profiles obtained by the Song et al. [4] mechanism reproduce experimental trends at high temperatures (figures 2.b and 2.c). For these reasons these two mechanisms have been considered for a detailed analysis of reaction paths.

In order to identify the reactions that control the ammonia oxidation process, flux diagrams, Reaction Rates and first-order temperature sensitivity analyses were realized. Results suggested that the most important reactions at high temperature (above 1350 K) are the same for both mechanism and they involve NH radical. Instead more differences are noticed at low and intermediate temperatures. According to Nakamura et al. [3] mechanism, N_2H_2 and N_2H_4 species play a key role at low temperature (below 1110 K), while N_2H_4 becomes insignificant at intermediate temperatures (1110÷1150 K). These two species are not considered by Song et al. mechanisms [4]. According to this model, at low and intermediate temperatures the reactivity is controlled by H_2NO . In fact, the lower reactivity exhibited by the Song et al. [4] mechanism is partially due to the marginal role of N_2H_2 .

Conclusions

The present work experimentally characterizes the oxidation process of diluted and pre-heated ammonia/oxygen mixtures in a perfectly stirred reactor under a wide range of operative conditions (inlet temperatures and mixture equivalence ratios). Results suggest the existence of three different kinetic regimes: low, intermediate and high temperature. Ammonia reactivity and the key species concentrations are independent on equivalence ratio at low and intermediate temperature, while at high temperatures species profiles are significantly different. Particularly, fuel lean and stoichiometric mixtures produce a high amount of NO, instead fuel rich mixtures provide higher concentration of H_2 and small amounts of NO.

The comparison between experimental data and numerical predictions obtained by four different kinetic mechanisms shows that models cannot correctly reproduce experimental points at low and intermediate temperature, while they better perform experimental data for fuel rich mixtures (not reported here). Reaction rate analysis suggests that the differences found at low and intermediate temperatures are essentially due to the different description of N_2H_2 chemistry.

This study highlights that kinetic mechanisms should be improved especially for low and intermediate temperatures and for fuel lean and stoichiometric conditions.

References

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