An experimental and kinetic modeling study of NH_3 oxidation in a Jet Stirred Reactor

A. Stagni[1], Y. Song[2], O. Herbinet[2], F. Battin-Leclerc[2], T. Faravelli[1]

1. CRECK Modeling Lab - Dipartimento di Chimica, Materiali e Ing. Chimica "G. Natta" – Politecnico di Milano – Milano, Italy.
2. Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, Nancy Cedex, France

Introduction

The increasing interest towards renewable, and more sustainable energy sources imposes a wide-range analysis of the underlying chemistry, in order to maximize the efficiency of combustion devices and reduce pollutant emissions. In this context, ammonia chemistry has recently gained major attention: it is present in biogas and bio-oil, in trace amounts. Investigating ammonia chemistry can benefit from several studies carried out in the past decades on its pyrolysis and oxidation behavior. However, scarce literature is available on the conditions of interest previously mentioned, since the presence of ammonia in trace amounts results in superoxidative conditions. The available kinetic models of ammonia have been built up by mostly relying on high-temperature data, obtained in ideal reactors [1]. On the other side, few work has been carried out to investigate its oxidation at lower temperatures.

In order to further investigate this topic, and to provide a stronger support for kinetic model validation, in this study the oxidation of ammonia in diluted conditions, at relatively low temperatures (T < 1200 K) and a pressure close to atmospheric, is investigated by using a Jet Stirred Reactor. In addition to ammonia conversion, the formation of Nitrogen Oxides (NO_x) is also analyzed. At the same time, a detailed kinetic mechanism for ammonia oxidation is developed by leveraging the most recently available kinetic data on experimental and theoretical reaction rates, and is used to analyze the obtained data, after being validated against the literature data in similar conditions.

Experimental details

The experimental device consisted of a quartz Jet Stirred Reactor, having a volume of 85 cm^3, kept at constant temperature. Such setup had been extensively used in the past to study the low-temperature oxidation of organic species [2]. Its residence time was set to 1.5 s, pressure was fixed at 107 kPa, and temperatures from 500 K to 1200 K were investigated. Helium was used as balance gas, with all gases having a 99.99% purity. The quantification of ammonia was conducted with the aid of continuous-wave cavity ring-down spectroscopy (cw-CRDS). Intense signals of ammonia were observed at spectrum ranging from 6638 to 6643 cm^{-1}. Two wavenumbers (6641.33 and 6642.57 cm^{-1}), which showed a very good consistency, were selected for ammonia quantification. A chemiluminescence NO_x analyzer was employed to measure NO and NO_2. The uncertainty for NO_x analyzer and cw-CRDS is estimated to be ± 5 and ±10-15%.

Kinetic Model and validation

The kinetic mechanism of ammonia combustion was built upon the POLIMI kinetic framework, which in its full version describes the pyrolysis and oxidation of hydrocarbon fuels up to C_{16}. A complete characterization of the mechanism is provided elsewhere [3]. For the purposes of this

corresponding author: Alessandro Stagni

study, it is worth mentioning that, due to its intrinsic hierarchical dependence, ammonia sub-mechanism was directly connected to the NO_x module, which had been recently updated following the same rationale, and successfully validated [4].

Due to its rather high stability, initiation reactions play a major role in its decomposition: the rate constant of its scission with and without oxygen were taken Baulch [5] and Dean and Bozzelli [6], respectively. The pyrolysis mechanism was taken from Davidson et al. [7], complemented by the experimental and theoretical calculations of Klippenstein et al. [8] for the reactions of ammonia radicals ($NH_x + NH_y$ = Products). The remainder of the H-abstractions via O, H and OH was mostly taken from Dean and Bozzelli [6]. Reduction mechanism of NO and via NH_2 (thermal DeNOx) was identified as a critical step in the oxidation mechanism: the overall reaction rate and branching ratio were taken from the theoretical calculations of Klippenstein and coworkers [9].

The overall mechanism is constituted of 159 species and 2463 reactions, and describes ammonia pyrolysis and oxidation as well as its interaction with hydrocarbons up to C_3. The kinetic mechanism underwent extensive validation against available datasets obtained in the conditions of interest (i.e. diluted fuel and/or low temperature) in ideal reactors. Figure 1 shows the predictions of ignition delay times in different conditions. Trends are predicted remarkably well in diluted conditions: the model well reproduces the ignition behavior of the mixture by varying both pressure and equivalence ratio. The model does not predict the curvature observed by the ignition delay time at lower temperatures (Figure 1b), when ammonia/air mixtures are investigated. This can be attributed to the non-ideal behavior of the experimental device (gas-phase dynamic effects), which are more important for longer ignition times (i.e. lower temperatures). Finally, the model overpredicts ignition delay time at lower temperatures (T = 1000 K) by a factor ~2, although correctly predicting the apparent activation energy. Anyway, this is in agreement with the predictions of most kinetic models, as it can be observed in the reference work [10].
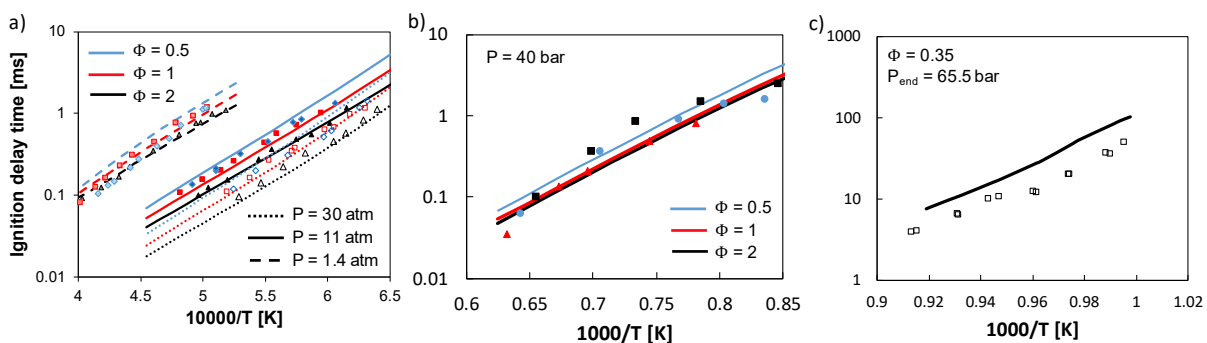

Figure 1. Ignition delay times of NH_3/O_2 mixtures: a) Shock tube at high temperatures, with with 99% Ar dilution [11]; b) Shock tube at intermediate temperatures (NH_3/air) [12]. C) $NH_3/O_2/N_2/O_2$ mixture in a rapid compression machine [10].

Results

For the purposes of this study, the experimental campaigns were carried out with three different compositions, listed in Table 1.

Exp.	X_{NH3} [-]	X_{O2} [-]	Φ [-]
1	0.0005	0.00	∞
2	0.0005	0.02	0.0188
3	0.0005	0.04	0.0093

Table 1. Experimental conditions. Ar is used as balance gas.

A first, experimental campaign in pyrolysis conditions was carried out to verify the presence of surface effects on the quartz walls. Previous works [13] have reviewed different cases where

ammonia decomposed on quartz surfaces, forming mainly H_2 and N_2. On the same surface, radical recombination effects were observed, too. Interestingly, ammonia decomposition is observed in pyrolysis conditions as early as at 700 K, following a linear decrease until obtaining a ~10% conversion at 1200 K. Considering the thermal stability of NH_3, such temperatures are too low to justify any homogeneous reactivity.
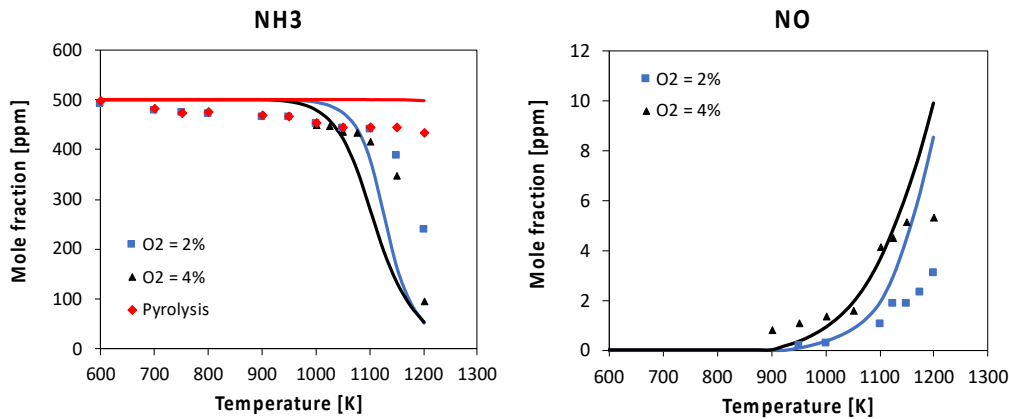

Figure 2. Comparison between experimental species profiles (symbols) and modeling predictions (lines) in the combustion of 500 ppm NH_3 in a Jet Stirred Reactor (He as balance gas).

Even in the presence of oxygen (either 2 or 4%), the same linear decrease is observed until the inception of oxidation, at ~1050 K. On the other side, the model anticipates the start of consumption by ~50 K, although correctly predicting the slope of decrease and the higher reactivity of the leaner mixture. Reasonable predictions are also observed for NO formation, with slight over-predictions at T > 1100 K. Sensitivity analysis was carried out on both NH_3 and NO to identify the governing reaction pathways. Results are shown in Figure 3 for both of them: fuel consumption is mostly determined by the branching ratio of the two product channels of the reaction of NO with NH_2, but also by the oxidation of nitroxide (H_2NO), which was identified as particularly critical in low-temperature ignition, too (Figure 1c). Such step is crucial in the formation of NO: in addition to the aforementioned branching ratio, the formation of NO is enhanced by all those reaction steps concurring to the increase of the oxidation rate of H_2NO, e.g. reactions of NH_2 radical with HO_2 and NO_2, respectively.
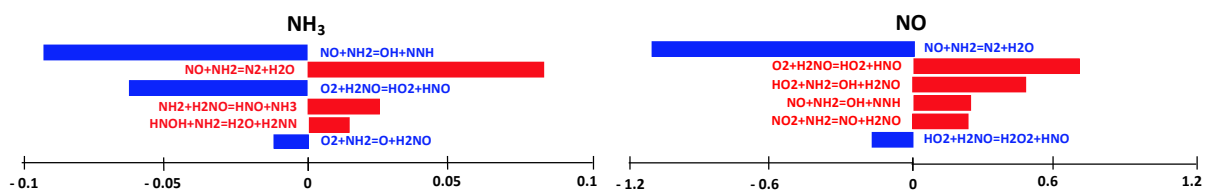

Figure 3. Sensitivity Analysis to the formation of NH_3 (left) and NO for O_2 = 2%. T = 1050 K.

Conclusions

In this work, the oxidation of ammonia in trace amounts has been investigated in a Jet Stirred Reactor in a temperature range 500 – 1200 K, with a residence time of 1.5 s. The development of a comprehensive kinetic model for ammonia oxidation has allowed to analyze the obtained results. Such coupling has allowed to identify two main critical points. First of all, the use of a quartz reactor cannot disregard surface effects of ammonia: the experimental campaign in pyrolysis conditions has identified a small consumption of ammonia, increasing with temperature up to an overall 10% conversion. Therefore, although the kinetic model has been successfully validated in a variety of configurations, due to his homogeneous nature it is not able alone to fully characterize these trends, and further investigation is required on heterogeneous reactivity. In spite of it, the kinetic model has been able to characterize the key reaction steps involved in

homogeneous oxidation: the major role of NO and NO_2 as "reactivity catalysts" has been framed, which demands a high accuracy in the branching ratios of their reactions with NH_2. Moreover, the importance of H_2NO as a reaction intermediate has been confirmed; this suggests further theoretical and experimental work on the related kinetics, in particular its direct oxidation.

Acknowledgements

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