

Experimental and numerical study of ammonia oxidation and pyrolysis in a Jet Stirred Flow Reactor

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Abstract

The aim of this work is to present an experimental and numerical study of ammonia oxidation and pyrolysis in a Jet Stirred Flow Reactor. Tests were performed for mixtures with different equivalence ratios and bath gases, changing the mixture inlet temperature. In order to evaluate the potential impact of heterogeneous effects, further tests were performed adding water vapor to the mixtures to passivate the reactor surface. Experimental results were compared with numerical simulations using different kinetics mechanisms available in literature. Experimental results for the ammonia oxidation suggested that it is possible to identify three different kinetics regimes: low, intermediate and high temperatures. NO_x and H₂ concentration profiles are very similar for low and intermediate temperatures but exhibit a strong dependence on the equivalence ratio for high temperatures. Surface effects are restricted to the NO_x profiles in the intermediate temperature regime and do not affect the O₂ and H₂ concentrations. Pyrolysis tests shown that ammonia decomposes at inlet temperature higher than 1100 K. In pyrolytic conditions, the heterogeneous reactions affect the ammonia reactivity, by enhancing its decomposition. None of the used kinetic models could accurately reproduce the experimental data in the considered operating conditions. The main differences among mechanisms is the description of the low-intermediate temperatures reaction pathways.

Introduction

The contemporary energetic scenario is currently faced with necessity to develop new systems for energy production due to the recent several constrains. Global warming acceleration and the request of renewable energy systems have induced to focus attention on non- conventional fuels (i.e. molecules produced by biochemical or thermal treatments of biomass). Energy carriers represent a wide category of molecules, including both conventional and bio-derived fuels as well as molecules used to store both conventional and renewable source energy (de Joannon [1]). Among these molecules, hydrogen and ammonia stand out for their potentiality to be oxidized without CO₂ emission. Currently, the fulfillment of a hydrogen-based economy is a hard challenge due to safety problems in hydrogen supply and distribution. On the other hand, an efficient ammonia transport network is already available. For these reasons, the interest in ammonia consists in both the

opportunity to employ this molecule as hydrogen carrier or as fuel itself. New fuel-flexible combustion technologies and a deep understanding of ammonia chemistry are necessary for these purposes, because the physicochemical properties of ammonia (ignition temperature, calorific value, flame velocity) do not enable its oxidation in traditional combustion systems. Furthermore, its toxicity and the NO_x formation in oxidizing conditions require to identify the best operative conditions to minimize NH₃ slip and pollutant emissions. The development and validation of a kinetic mechanism for the decomposition and oxidation of ammonia need a considerable database of experimental data in model reactors. However, the interpretation of these data must be careful because ammonia is known to interact with surfaces (for example quartz, alumina, steel) by both physical and chemical adsorption [2, 3]. The decrease of the surface-volume ratio (S/V) and the surface passivation by means of water could be useful to reduce the impact of heterogeneous effects [2].

This work presents an experimental and numerical study of ammonia oxidation and pyrolysis in a model reactors. The experimental tests were performed in a quartz Jet Stirred Flow Reactor (JSFR) as a function of inlet temperature, for different mixtures with different equivalence ratios and diluent species. The impact of surface effects was analyzed by means of water surface passivation, according to the literature suggestions. The capability of available kinetic mechanisms to reproduce the experimental data was evaluated by means of numerical simulations.

Experimental and numerical methods

The oxidation and pyrolysis of ammonia were analyzed in a quartz JSFR. The experimental devices consist of a feeding system, a reactor, an air-cooling system at the outlet of the reactor and flue gases analyzers. The JSFR is a spherical reactor with a volume of 113 cm³ which approaches the behavior of a Perfectly Stirred Reactor (PSR). The detailed description of the experimental facility and of the reactor is reported elsewhere [4]. The oxidation experiments were studied as a function of the inlet temperature for different equivalence ratios and bath gases (N₂ and Ar), at fixed pressure, residence time and dilution level. Experiments with a small amount of water vapor as diluent were realized to passivate the reactor surface. The pyrolysis experiments were performed at same conditions, by replacing the oxygen with the same amount of diluent. The details are summarized in table 1.

Table 1. Experimental conditions for the JSRF tests.

Conditions	Oxidation	Pyrolysis
Inlet temperature (T_{in})	900-1350 K	1000-1350 K
Equivalence ratio (Φ)	0.8, 1.0, 1.2	1
Residence time (τ)	0.25 s	0.25 s
Pressure	1.2 atm	1.2 atm

Diluent (d)	86% N ₂ , Ar 84.3% N ₂ , Ar - 1.7% H ₂ O	92% Ar 90.3% Ar - 1.7% H ₂ O
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The experimental results were simulated using the PSR code of the Chemkin PRO [5] package. Four different detailed gas-phase chemical kinetic models were used: Konnov [6], Glarborg et al. [2], Song et al. [7], Nakamura et al. [8].

Experimental results

Fig.1 shows the main species profiles for the oxidation of NH₃/O₂/N₂ mixtures at different ϕ as a function of T_{in} .

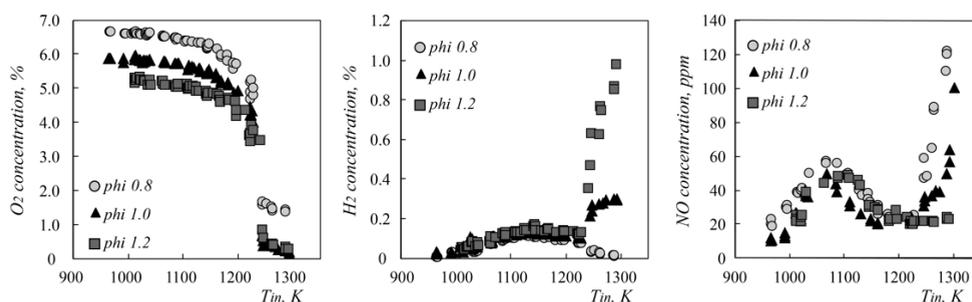


Figure 1. O₂, H₂ and NO concentrations as a function of T_{in} for different ϕ .

The mixtures reactivity is independent of ϕ according to the O₂ profiles: the ignition temperature is at around 1225 K for all the considered compositions. The H₂ profiles are overlapped for $T_{in} < 1225$ K and exhibit a non-monotonous trends with a relative maximum value at $T_{in} = 1100$ K. Significant differences can be observed for $T_{in} > 1225$ K, in particular the higher amount of H₂ is produced at $\phi = 1.2$. NO profiles exhibit similar trends, since NO concentration is slightly dependent on ϕ at $T_{in} < 1225$ K and present a non-monotonous trends with a relative maximum value $T_{in} = 1100$ K. At higher temperatures the maximum NO values can be observed at $\phi = 0.8$. H₂ and NO profiles suggest that it is possible to identify three different kinetic regimes in ammonia oxidation: low ($T_{in} < 1100$ K), intermediate ($1100 < T_{in} < 1225$ K) and high ($T_{in} > 1225$ K) temperatures. The potential effect of heterogeneous reactions was evaluated by means of experimental tests for the stoichiometric NH₃/O₂/N₂ and NH₃/O₂/Ar mixtures by adding 1.7% of H₂O in order to passivate the reactor surface. The comparison among the main species profiles for the mixtures with and without water is shown in fig.2.

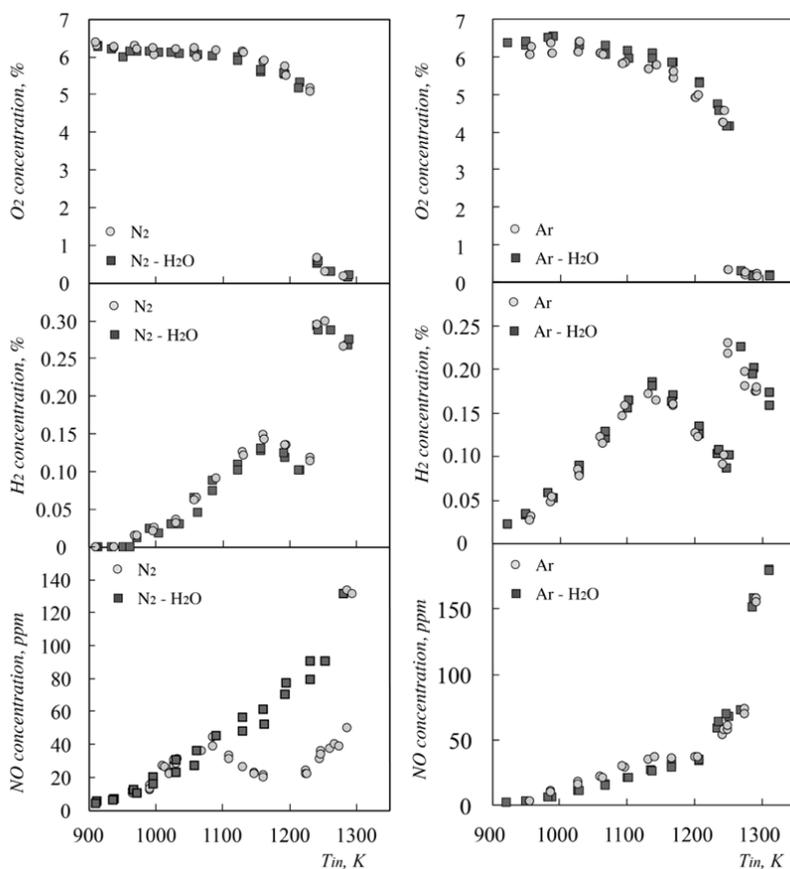


Figure 2. O_2 , H_2 and NO concentrations as a function of T_{in} for mixture with and without H_2O , with N_2 (on the left) and Ar (on the right) as diluent.

The same considerations can be referred to both $NH_3/O_2/N_2$ and $NH_3/O_2/Ar$ mixtures. The O_2 and H_2 profiles are overlapped for the mixtures with and without water, thus suggesting that the heterogeneous reactions do not affect NH_3 reactivity and H_2 production/consumption. Instead the NO concentrations exhibit different trends in the intermediate temperature regime. These results show that the impact of heterogeneous effects is restricted to NO concentration in the intermediate temperature regime and does not affect the existence of the different kinetic regimes.

The interaction of ammonia with quartz surface is stronger in pyrolytic conditions. The decomposition starts at $T_{in} > 1100$ K independently of the presence of water. However, the comparison between H_2 and N_2 profiles for the mixtures NH_3/Ar and $NH_3/Ar/H_2O$ (fig.3) suggests that the heterogeneous reactions enhance significantly the ammonia decomposition, probably due to the slow homogeneous reaction rates that characterize the pyrolytic processes.

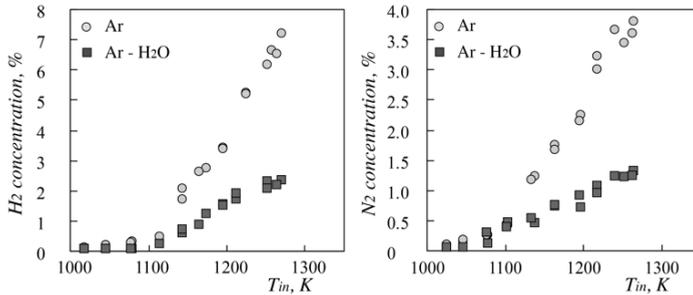


Figure 3. H₂ and N₂ concentrations as a function of T_{in} for NH₃ pyrolysis.

Numerical results

Experimental results were compared with numerical simulations performed by four different kinetic mechanisms. For the sake of brevity, only the results obtained for the oxidation of the stoichiometric NH₃/O₂/Ar/H₂O mixture and the pyrolysis of NH₃/Ar/H₂O mixture are reported here (fig. 4-5).

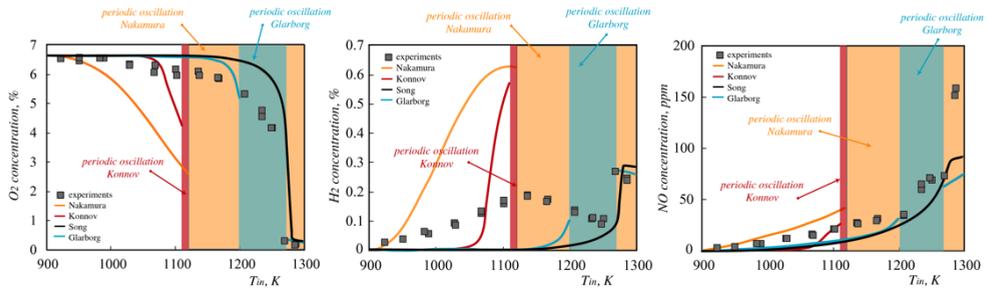


Figure 4. Comparison among experimental data and numerical profiles for NH₃ oxidation.

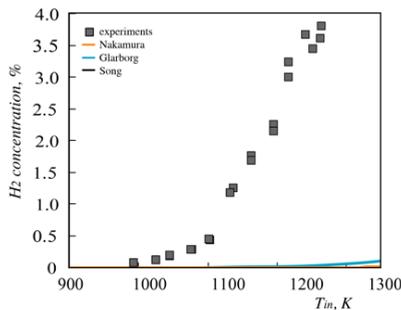


Figure 5. Comparison among experimental data and numerical profiles for NH₃ pyrolysis.

The considered models are not able to accurately predict the experimental data in the considered conditions. “Konnov” and “Nakamura” models predict a higher reactivity at low temperatures with respect to the experimental data while the other two mechanisms predict no reactivity at low temperatures. Three models (“Konnov”, “Nakamura” and “Glarborg”) suggest the occurrence of dynamic behaviors. “Nakamura” scheme reproduces the experimental H₂ and NO trends at low temperature but values are too overestimated, while “Song” and “Glarborg” mechanisms reproduce H₂ profile at higher temperatures. Same considerations can be referred to NO profile. The agreement among experimental and numerical data is worse for the pyrolytic conditions (fig. 5) since all the models cannot predict the ammonia decomposition in the considered temperature range. Reaction rate and sensitivity analyses (not reported here) highlight that the models describe similar reaction pathways for the ammonia oxidation at high temperatures, but predict different routes at low-intermediate ones, which involve intermediate species like N₂H₂ and N₂H₄ (produced by NH₂ recombination reactions) or H₂NO and HNO (formed by NH₂ oxidation). The same analyses for the pyrolytic conditions suggest that NH₂ recombination reactions are important also for the ammonia decomposition.

Conclusions

The present work characterized the oxidation and the pyrolysis of ammonia mixtures in a JSFR, for different bath gases and equivalence ratios, as a function of the inlet temperature. The results obtained for NH₃/O₂/N₂ mixtures suggested that the reactivity is independent of ϕ and the ignition temperature is 1225 K. The main species profiles (H₂ and NO) exhibited the same non-monotonous trends at $T_{in} < 1225$ K with a maximum value at around 1100 K, independently of ϕ . At $T_{in} > 1225$ K they were mostly affected by ϕ . H₂ and NO profiles suggest that it is possible to identify three different kinetic regimes in ammonia oxidation: low ($T_{in} < 1100$ K), intermediate ($1100 < T_{in} < 1225$ K) and high ($T_{in} > 1225$ K) temperatures. The potential effect of heterogeneous reactions was evaluated by means of further experimental tests for the stoichiometric NH₃/O₂/N₂ and NH₃/O₂/Ar mixtures by adding 1.7% of H₂O in order to passivate the reactor surface. The comparison among the main species profiles for the mixtures with and without water shown that the surface effects were restricted to NO profiles in the intermediate temperature regime and does not affect the ammonia reactivity and the existence of the different kinetic regimes. In pyrolytic conditions, ammonia decomposed at $T_{in} > 1100$ K. In this case, the presence of water strongly affected the process by inhibiting the ammonia decompositions. Experimental data were compared with numerical results obtained using different kinetic mechanisms. In general, models are not able to predict the experimental data for the investigated conditions, in particular, the prediction of the experimental data completely fails for the pyrolytic conditions. These results highlighted that the models are not

adequately updated to describe ammonia pyrolysis and, perhaps, this aspect could affect also the prediction of the species profiles for the ammonia oxidation.

References

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