

The impact of H₂ and CO on the NH₃ / NO / O₂ chemistry - a step towards a predictive tool for NH₃ oxidation

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Abstract

Due to the poor ignition and oxidation properties of NH₃, its use as a carbon-free fuel typically requires presence of a co-fuel. Downstream of the ignition region in an ammonia-fueled engine or gas turbine, combustibles formed by partial oxidation of the co-fuel are present together with unburned ammonia and trace amounts of nitric oxide, formed in the initial stage. The oxidation of NH₃ under these conditions determines the heat release rate as well as the emission levels for NH₃, NO and N₂O. It is important to develop predictive models for this chemistry for use in design. In the present work, a wide range of experimental studies from the literature on the effect of H₂ and/or CO on the NH₃ oxidation in the presence of NO is re-interpreted in terms of a detailed chemical kinetic model. The key reactions are identified and the ability of the kinetic models to describe this chemistry is discussed. With increasing levels of H₂ or CO, the generation of chain carriers gradually shifts from being controlled by the NH₂ + NO reaction to being dominated by the oxidation chemistry of the combustible. The temperature range where amines serve to reduce NO becomes narrower and shifts to lower temperatures. At the elevated temperatures typical of the relevant applications, the combustibles thus cause a change in selectivity from N₂ to NO. This may have implications for the design of the dual-fuel injection systems.

1 Introduction

Climate change, security of energy supply, and fossil fuels depletion provide an incentive for a transition to a low-carbon economy. Ammonia is a carbon-free fuel and can be a suitable alternative for stationary power, transportation, and energy storage applications. Challenges of using ammonia in engines and gas turbines are investigated extensively [1–4]. There has been a number of studies on the use of NH₃ as an engine fuel, but its poor combustion characteristics for conventional engine combustion techniques have been difficult to overcome. Hence, additional fuels such as hydrogen or carbon-based fuels such as alcohols or diesel fuel have been suggested as combustion promoters.

To facilitate use of ammonia as an energy carrier, it is important to have access to reliable and versatile chemical kinetic models for ignition and oxidation of NH₃. Downstream of the ignition region in engines and gas turbines, ammonia will be oxidized in an environment, which contains other combustibles, e.g., hydrogen or carbon monoxide, as well as oxygen and nitrogen oxides. The reaction of NH₃ with NO in the presence of O₂ has been studied extensively due to its importance in selective non-catalytic reduction of NO (SNCR) with ammonia [5, 6]. Even though the SNCR mechanism is now well understood and the main features of the process can be predicted satisfactorily, quantitative modeling predictions over a wider range of conditions are still elusive [6].

In an engine or gas turbine setting, combustibles deriving from the use of a co-fuel is expected to be present in the post-ignition region, together with unburned ammonia and nitric oxide formed in the initial stage. The impact of addition of combustibles on SNCR with NH₃ has been studied widely, and results are available for a wide range of hydrocarbons and alcohols. Considering that the co-fuel must be more reactive than NH₃ to promote ignition, it can be assumed that it is largely converted to CO and H₂, prior to oxidation of the major part of the ammonia. Reported work on SNCR include investigation of addition of H₂ [7–13] and CO [8, 12–21], as well as mixtures of the two [12].

It is of interest to investigate the impact of both CO and H₂ on NH₃ oxidation in the presence of NO, since these combustibles affect the radical pool in different ways [12]. In the present work, the oxidation chemistry of NH₃ with CO and/or H₂, and trace amounts of NO is investigated. Available experimental data in the literature are reviewed. The most well-defined and reliable results are chosen for further analysis. Data for which the reaction temperature is uncertain (lack of measured temperature profiles in the reactor or significant heat release due to high reactant concentrations) are not considered further. The selected flow reactor data are analyzed in terms of a detailed chemical kinetic model. The starting mechanism is drawn from the review by Glarborg et al. [6], but modifications are made according to more recent work.

2 Results and Discussion

Figures 1 and 2 show selected comparisons between experimental results and modeling predictions, with H₂ and CO, respectively, as the combustible additive. During its oxidation, ammonia is converted to the amino radical (NH₂) by reaction with the radical pool. The fate of the NH₂ radical controls the ignition delay and the oxidation rate. The combustion properties of ammonia can be explained in terms of the low reactivity of the amino radical towards O₂. At high temperatures, NH₂ reacts mainly with the O/H radical pool, either through the sequence $\text{NH}_2 \xrightarrow{+\text{OH}, \text{H}} \text{NH} \xrightarrow{+\text{OH}, \text{H}} \text{N}$, or the NH_i radicals may react with O, OH, or O₂, forming eventually NO.

Once NO is formed, the production of chain carriers is typically controlled by the fast NH₂ + NO reaction, with NH₂ + O₂ being too slow to play a role. The NH₂ + NO reaction has two product channels,



Reaction R1a is chain branching while reaction R1b is chain terminating. The radical pool is thus very sensitive to the branching fraction for the reaction, defined as $\alpha = k_{1a}/(k_{1a} + k_{1b})$. Our knowledge of the interaction of ammonia oxidation with nitrogen oxides comes from work on selective, non-catalytic reduction of NO using NH₃. Characteristic of the process is that nitric oxide removal is possible only in a narrow temperature range centered at 1250 K and only in the presence of oxygen [5, 6]. At temperatures above 1400 K, reactions of NH₂ with the radical pool becomes dominating and NH₃ is oxidized to NO rather than to N₂.

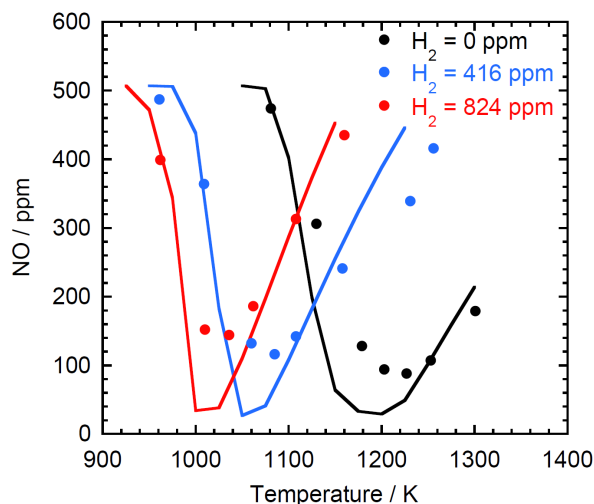


Figure 1: Comparison of predictions of the present model with the experimental results of Duo et al. [108] for NO as a function of temperature and hydrogen concentration in the Thermal DeNO_x process. Inlet mole fractions: NH₃ = 832 ppm, NO = 507 ppm, H₂ = 0/416/824 ppm, O₂ = 4.0%, H₂O = trace, balance N₂. Residence time (s) = 92.7/T (K).

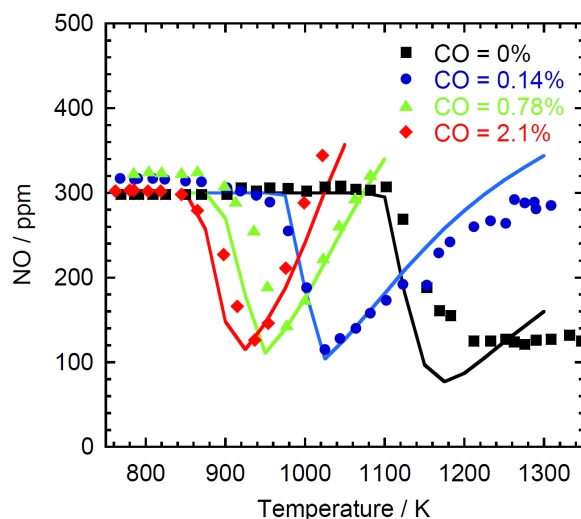


Figure 2: Comparison of experimental data [14] and modeling predictions for reduction of NO by NH₃ in a quartz flow reactor: effect of CO concentration. Symbols denote experimental data, while solid lines denote modeling predictions. Inlet concentrations: 300 ppm NH₃, 300 ppm NO, 4.0% O₂, 4.5% H₂O; balance N₂. Pressure is 1.1 atm. Residence time at 1200 K (constant molar rate) is about 150 ms. The reactor surface/volume ratio was 4.4 cm⁻¹.

Presence of combustibles such as H₂ or CO shifts the window for NO removal towards lower temperatures by replenishing the radical pool. Furthermore, it leads to a narrowing of the process window, because the enhanced radical levels cause oxidation of NH₃ to NO to compete more efficiently with the NO removal reactions. These effects are seen for both H₂ and CO as additives. The shift in onset temperature as well as the narrowing of the temperature window are captured quite well by the model.

The key reactions in the reaction mechanism are identified and the ability of the kinetic model to describe the impact of H₂ and CO on the NH₃ / NO / O₂ chemistry is discussed. Furthermore, the implications of the presence of combustibles for emissions when using ammonia as a fuel in engines and gas turbines

are investigated.

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