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MUTUAL SENSITIZATION OF THE OXIDATION NO AND AMMONIA: EXPERIMENTAL AND KINETIC MODELING

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Abstract

The selective non-catalytic reduction of NO by ammonia (SNCR) has been extensively studied. Recent experiments performed in a jet-stirred reactor (JSR) at atmospheric pressure for various equivalence ratios (0.1–2) and initial concentrations of NH₃ (500 to 1000 ppm) and NO (0 to 1000 ppm) revealed kinetic interactions similar to mutual oxidation sensitization of hydrocarbons and NO. The experiments were performed at fixed residence times of 100 and 200 ms, and variable temperature ranging from 1100 to 1450 K. Kinetic reaction mechanisms were used to simulate these experiments. According to the most reliable model, the mutual sensitization of the oxidation of ammonia and nitric oxide proceeds through several reaction pathways leading to OH production, mainly responsible for ammonia oxidation in the current conditions: $\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}$, $\text{NNH} \rightarrow \text{N}_2 + \text{H}$, $\text{NNH} + \text{O}_2 \rightarrow \text{N}_2 + \text{HO}_2$, $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$, and $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$.

Introduction

Thermal de-NO, also called selective non-catalytic reduction of NO by ammonia (SNCR), is a common NO reduction technique which is efficient in a small temperature range centered around 1200–1250 K. Many experimental and modeling studies concern SNCR [1-5]. However, existing kinetic models show weaknesses and sometimes fail to represent the kinetics of ammonia oxidation [6] whereas interest for this fuel is growing. Nowadays, ammonia is viewed as an alternative zero-carbon fuel which presents potential for future power stations [6]. In this context, ammonia combustion in a gas turbine was recently demonstrated in Japan [7]. However, its combustion needs further studies [6] and kinetic interpretation needs further investigations. Therefore, experiments were performed in a JSR at atmospheric pressure for various equivalence ratios (0.1–2), for several initial concentrations of NH₃ and NO, at fixed residence times and variable temperature. Kinetic modeling was used to interpret the results and delineate reaction pathways.

Experimental

The experiments were performed in a fused-silica JSR presented earlier [8, 9]. A 40 mm o.d. spherical sphere (27.5 cm³ internal volume) equipped with 4 injectors having nozzles of 1 mm i.d., for the admission of the gases achieving the stirring, constitutes the JSR. It is located inside a temperature controlled oven of c.a.1.5 kW, surrounded by insulating material; it operates at atmospheric pressure. Ammonia, NO, N₂, and O₂ flow rates were measured and regulated by thermal mass-flow controllers. The reactor operated under macro-mixing conditions, allowing the use of a perfectly-stirred reactor model. The mixing time was ca. 70 times shorter than the residence time in the reactor. A good thermal homogeneity along the whole vertical axis of the reactor was obtained in the experiments. The temperature was measured using a Pt/Pt-Rh10% thermocouple of 0.1 mm diameter located inside a thin-wall fused-silica tube (<0.5mm), which prevents catalytic reactions on the metal wires. The high degree of dilution used in these experiments yielded a small temperature rise in the JSR (<20 K). Typical temperature variations of < 8 K along the vertical axis of the JSR were measured. Low pressure samples of the reacting mixture (30–40 Torr) were taken using a sonic quartz

probe, for immediate multi-dimensional gas chromatography (GC) analyses. In order to improve the GC detection, these samples were pressurized at 1 bar before injection into the GC column, using a home-made piston. Thermal conductivity detectors were used for permanent gases and on-line Fourier transform infrared (FTIR) was used for measuring H₂O, NO, NO₂, N₂O, and NH₃. The uncertainties on mole fractions were $\pm 10\%$. For NO₂ formed at trace concentration, the uncertainty was ± 2 ppm.

Modeling

The computations were performed using the PSR computer code [10], which computes species concentrations from the balance between the net rate of production of each species by chemical reactions, and the difference between the input and output flow rates of species.

Several kinetic reaction mechanisms were used. We used our previously published SNCR-SO_x mechanism, our HCN-NO_x mechanism (DAG mechanism [11]), Konnov mechanism [12] and the ammonia mechanism proposed by Song et al. recently [13]. The rate constants for the reverse reactions were computed from the forward rate constants and the equilibrium constants, using the appropriate thermochemical data.

Results and Discussion

Experiments were performed at atmospheric pressure for various equivalence ratios (0.1, 0.5, 1, and 2; $\phi = (\text{NH}_3\% / \text{O}_2\%) / (\text{NH}_3\% / \text{O}_2\%)_{\text{at } \phi=1}$), for two initial concentrations of NH₃ (500 and 1000 ppm) and several initial concentrations of NO (0, 500, and 1000 ppm).

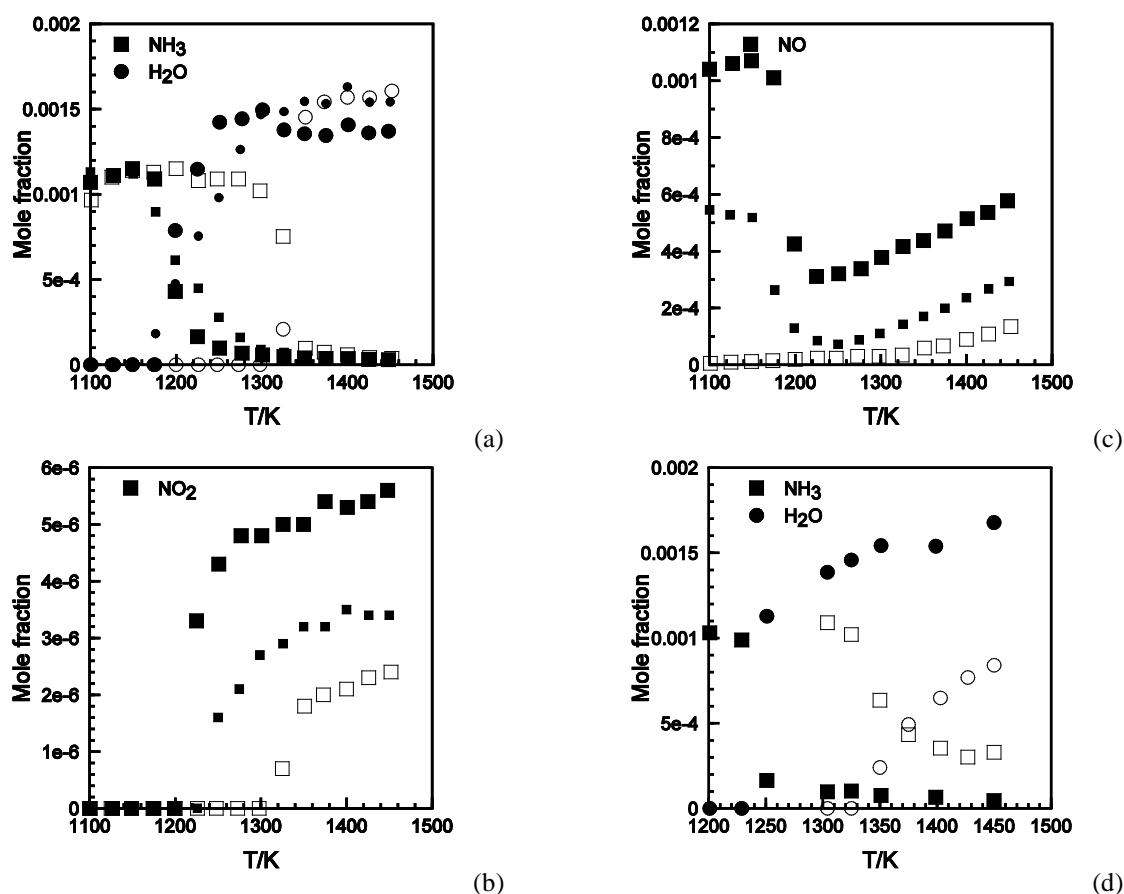


Figure 1. Impact of the initial concentration of NO on NH₃ conversion. Experimental results obtained in a JSR at 1 bar. (a–c): 1000 ppm NH₃, $\tau=100$ ms; $\phi=0.1$; 0 (open symbols), 500 (small black symbols), 1000 (large black symbols) ppm NO; (d): 1000 ppm NH₃, 200ms; $\phi=2$; 0 (open symbols), 1000 (large black symbols) ppm NO.

The experiments were performed at fixed residence times $\tau=100$ and $\tau=200$ ms, and the temperature was varied stepwise over the range 1100–1450 K. The mole fractions of O_2 , NH_3 , NO , NO_2 , N_2O , and H_2O were measured. The experimental results revealed a strong influence of NO on ammonia conversion which had not been reported previously. As can be seen from Figure 1, the presence of 500–1000 ppm of NO shifts ammonia ignition by ca. -120 K in fuel-lean and fuel-rich conditions. This kinetic interaction between NO and NH_3 looks similar to mutual oxidation sensitization of hydrocarbons and NO where NO boosts the oxidation of the fuel which in turn favors the NO to NO_2 conversion[14-23]. The data also show that the reduction of NO by ammonia is maximized around 1250K, as already shown in the literature.

In our previous modeling of the kinetics of SNCR in a JSR [1], it was noted that although the kinetic model used could predict NO -reduction, the conversion of ammonia vs. temperature was too fast. Therefore, other more recent kinetic models available from the literature were tested against our JSR data (Figure 2).

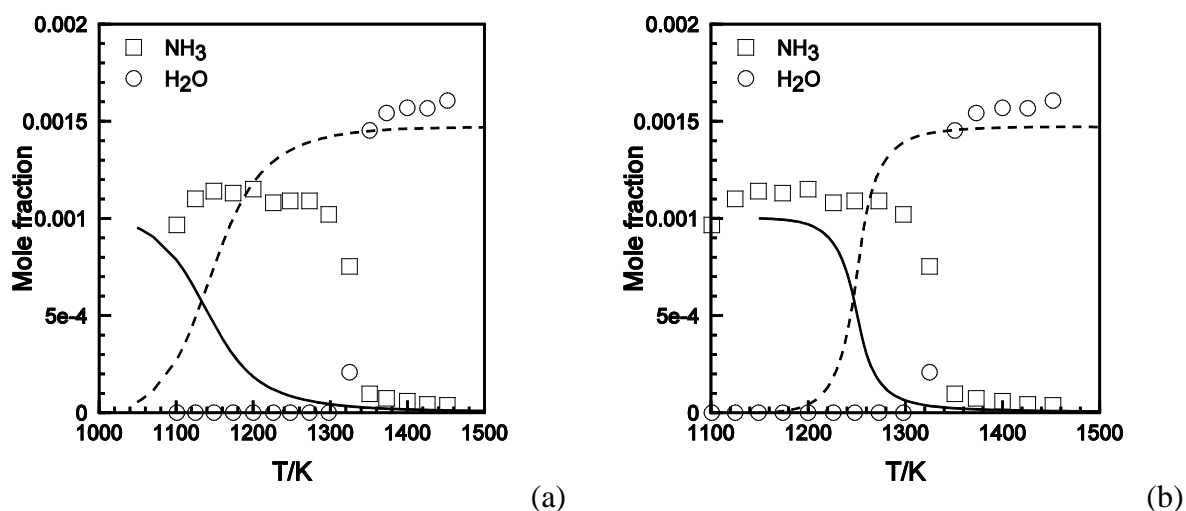


Figure 2. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH_3 in a JSR: 1000 ppm of NH_3 , $\tau=100$ ms; $\phi=0.1$. Literature models: (a) Konnov [12], (b) Song et al.[24].

As can be seen from Figure 2, the fastest oxidation of ammonia was predicted by the model of Konnov, which is consistent with recent modeling efforts [6, 25]. The most recent model of Song et al. also predicts ammonia oxidation too fast. Therefore, the previously proposed DAG model [11] was tested since it was demonstrated to predict well ammonia ignition and burning velocities [6]. Figures 3–6 present comparisons between the experimental results obtained for the oxidation of neat ammonia from fuel-lean to fuel-rich conditions. They show that the DAG mechanism predicts well the oxidation of the fuel whereas, for minor products, the agreement between the modeling and the experiments could be improved.

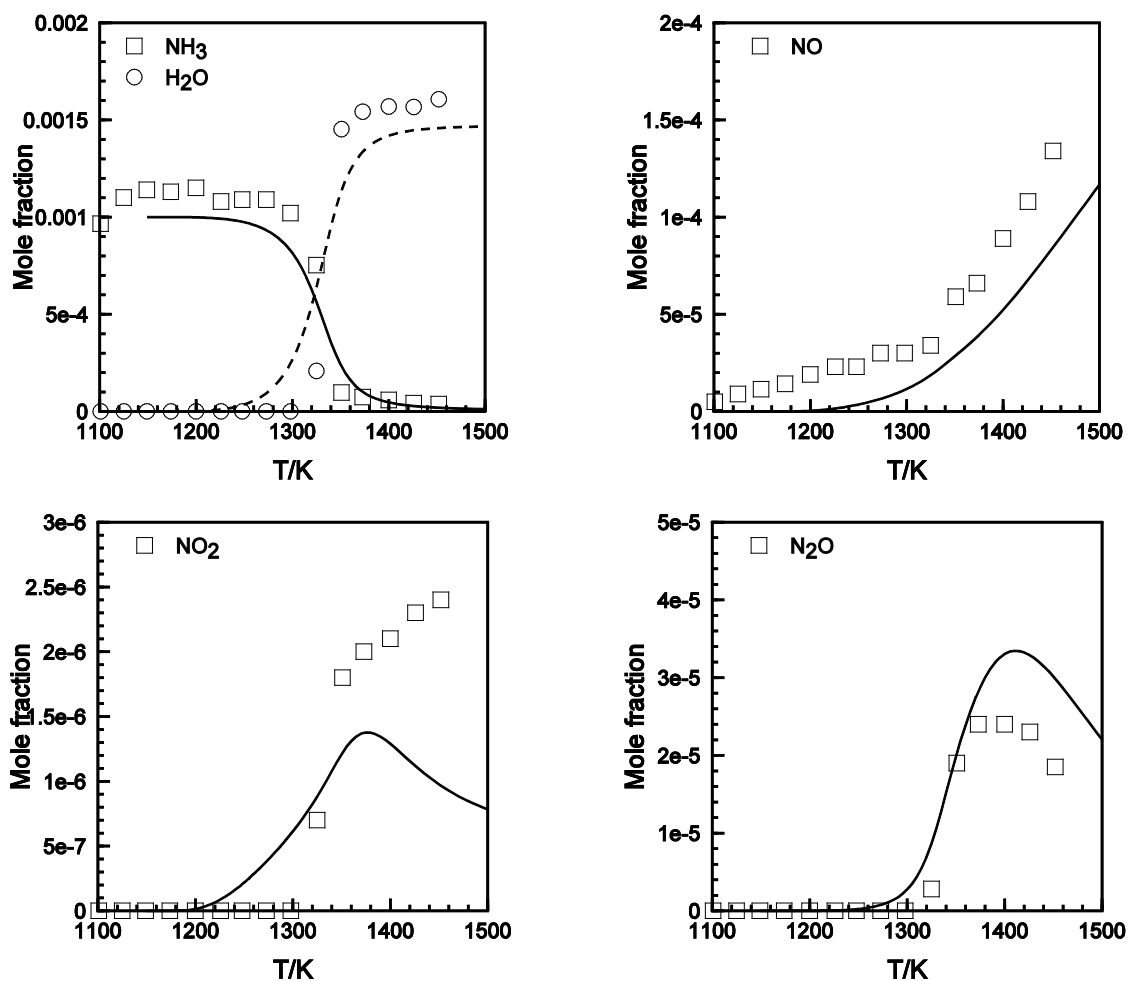


Figure 3. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH₃ in a JSR: 1000 ppm of NH₃, τ=100ms; φ=0.1.

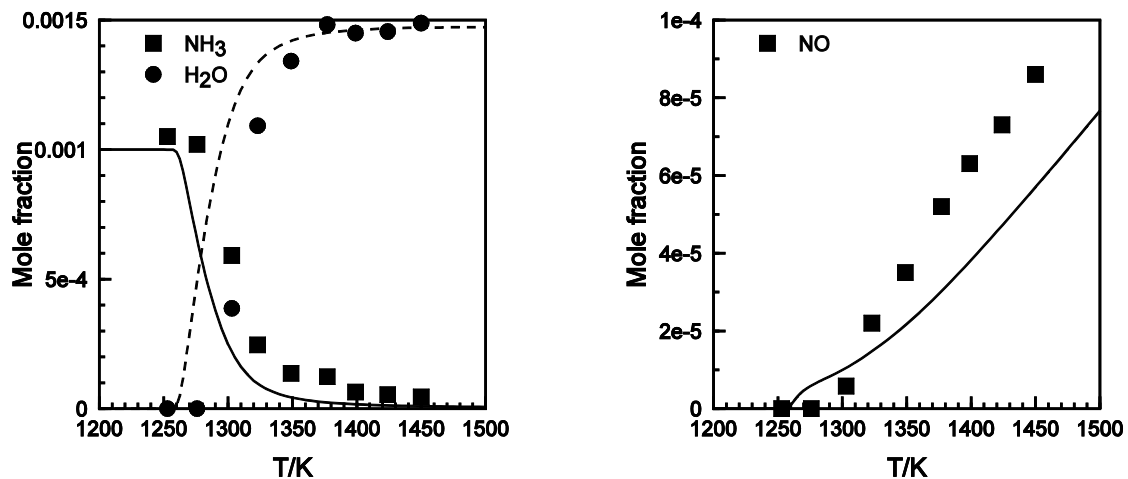


Figure 4. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH₃ in a JSR: 1000 ppm of NH₃, τ=200ms; φ=0.5.

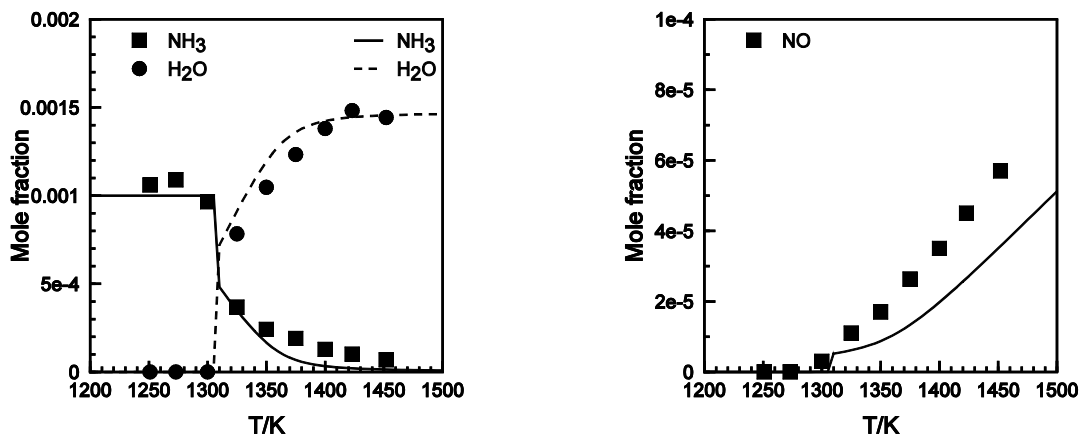


Figure 5. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH_3 in a JSR: 1000 ppm of NH_3 , $\tau=200\text{ms}$; $\phi=1$

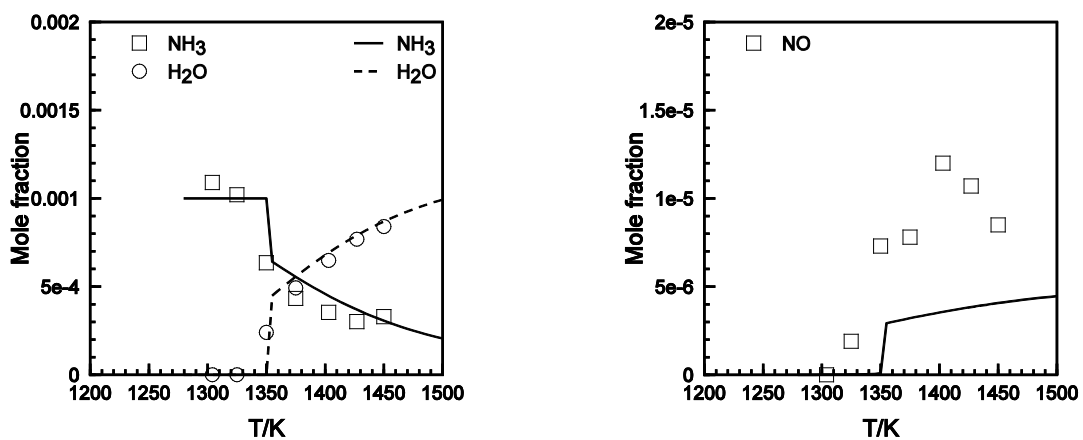


Figure 6. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH_3 in a JSR: 1000 ppm of NH_3 , $\tau=200\text{ms}$; $\phi=2$.

The model was also tested for the NO-seeded experiments from fuel-lean to fuel rich conditions. The results are presented in Figures 7–9 where the good predictions of the DAG model are demonstrated.

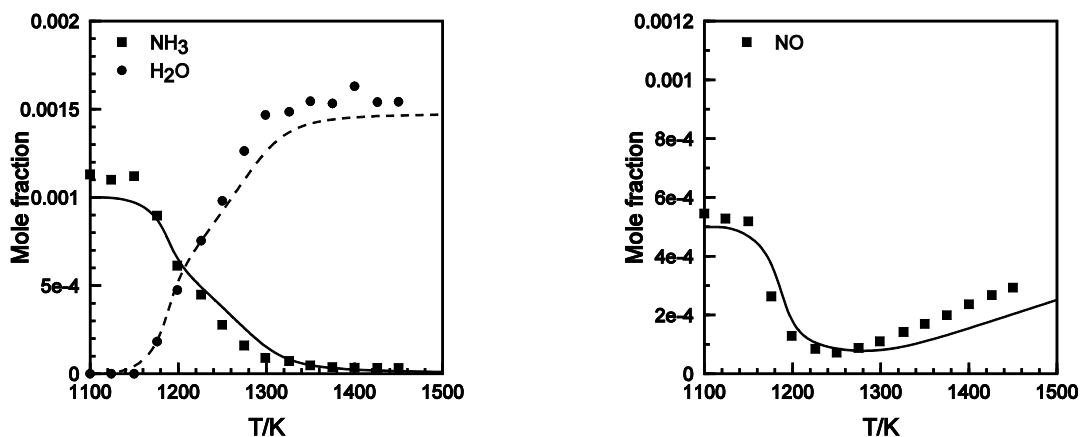


Figure 7. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH_3 in a JSR: 1000 ppm of NH_3 and 500 ppm of NO , $\tau=100\text{ms}$; $\phi=0.1$.

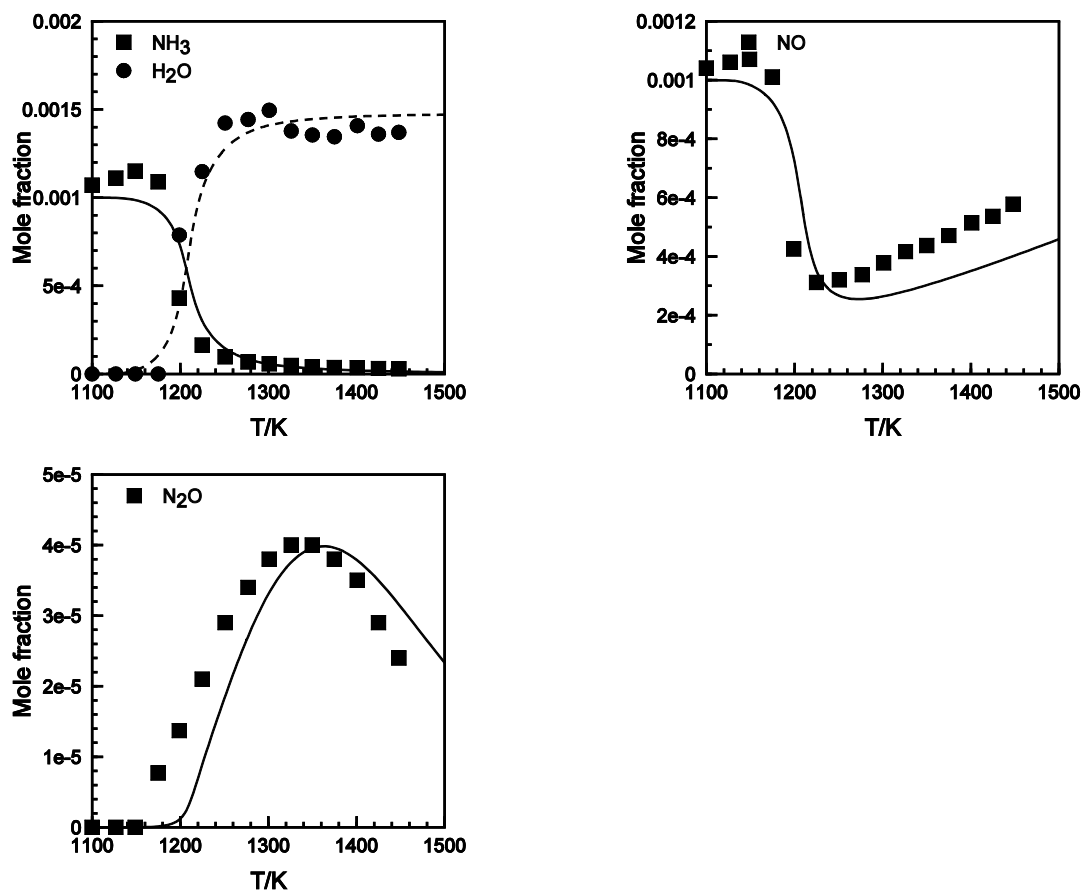


Figure 8. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH₃ in a JSR: 1000 ppm of NH₃ and 1000 ppm of NO, $\tau=100\text{ms}$; $\phi=0.1$.

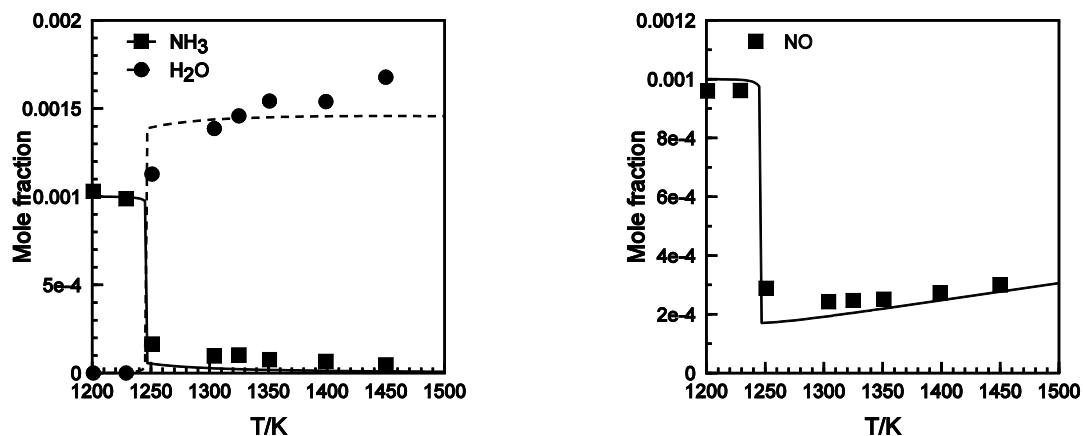


Figure 9. Comparison between experimental (symbols) and computed (lines) results for the oxidation of NH₃ in a JSR: 1000 ppm of NH₃ and 1000 ppm of NO, $\tau=200\text{ms}$; $\phi=2$.

Reaction pathway analyses were performed to delineate the mechanism responsible for the mutual sensitization of ammonia and nitric oxide. In the conditions of Figure 3 (1000 ppm of NH₃, $\tau=100\text{ms}$; $\phi=0.1$) and Figure 7 (1000 ppm of NH₃ and 500 ppm of NO, $\tau=100\text{ms}$; $\phi=0.1$). Schematic presentations are given in Figure 10a and b, respectively. The analyses were performed at 1197 K at which ammonia starts to react.

The neat oxidation of ammonia mainly proceeds through oxidation by OH (78%) and O (21%), yielding the NH₂ radical. This radical oxidizes by reaction with HO₂ (45%) and O₂

(12%), yielding H_2NO . H_2NO oxidizes by reaction with O_2 (48%) yielding HO_2 and HNO , and by reaction with NH_2 also yielding HNO . HNO oxidizes by reaction with O_2 yielding HO_2 and NO which in turn is reduced by reaction with NH_2 . The decomposition of NNH , formed by the reaction of NO and NH_2 , yields H atoms which provide branching through reaction with O_2 : $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$.

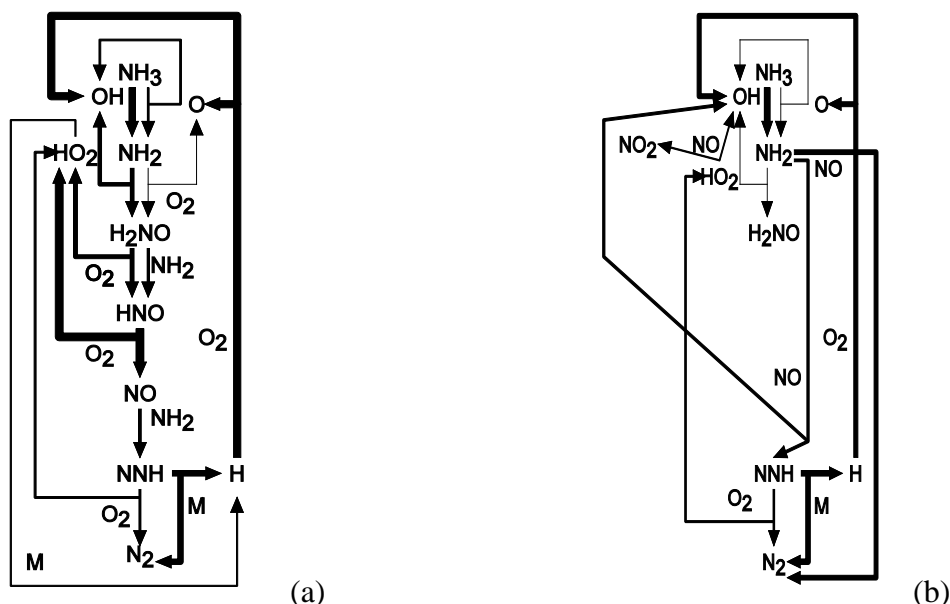


Figure 10. Computed reaction pathways for the oxidation of NH_3 in a JSR. (a): 1000 ppm of NH_3 , $\tau=100\text{ms}$; $\phi=0.1$; (b): 1000 ppm of NH_3 and 500 ppm of NO , $\tau=100\text{ms}$; $\phi=0.1$.

When 500 ppm of NO are introduced, ammonia is still mainly oxidized by OH (87%) and O (12%), yielding the NH_2 radical. This radical still oxidizes by reaction with HO_2 , but to a much less extent (<2%). The NH_2 radical mostly reacts with NO to form N_2 (57%) and NNH (34%). The decomposition of NNH , yields H atoms (67%), which provide branching through reaction with O_2 : $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, and HO_2 by reaction with O_2 (26%). NO reaction with HO_2 (13%) also contributes to OH production (16%).

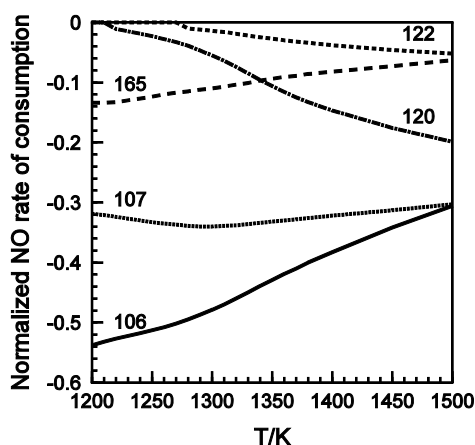


Figure 11. Computed reaction pathways for the conversion of NO in a JSR (1000 ppm of NH_3 and 500 ppm of NO , $\tau=100\text{ms}$; $\phi=0.1$). Important reactions are 106: $\text{NH}_2 + \text{NO} \rightleftharpoons \text{N}_2 + \text{H}_2\text{O}$; 107: $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$; 120: $\text{NH} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H}$; 122: $\text{NH} + \text{NO} \rightleftharpoons \text{N}_2 + \text{OH}$; 165: $\text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH}$.

Figure 11 shows the evolution of the importance of the main reactions consuming NO. One can see that the importance of reaction 165, responsible for NO₂ formation, is decreasing with increasing temperature. At low temperature, it is the third most important reaction pathway while at 1500 K it becomes one of the less important.

Conclusion

Experiments performed in a jet-stirred reactor (JSR) at atmospheric pressure for various equivalence ratios (0.1–2) and initial concentrations of NH₃ (500 to 1000 ppm) and NO (0 to 1000 ppm) revealed kinetic interactions similar to mutual oxidation sensitization of hydrocarbons and NO. The experiments were performed at fixed residence times of 100 and 200 ms, and variable temperature, ranging from 1100 to 1450 K. A kinetic reaction mechanism was used to simulate these experiments. According to the model, the mutual sensitization of the oxidation of ammonia and nitric oxide proceeds through several reaction pathways leading to OH production, mainly responsible for ammonia oxidation. In the present conditions HO₂ is mainly produced via: $\text{NNH} + \text{O}_2 \rightarrow \text{N}_2 + \text{HO}_2$ and $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$. The production of OH results from a sequence of reaction including $\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}$, $\text{NNH} \rightarrow \text{N}_2 + \text{H}$, $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, and $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$.

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