A combined experimental and modelling study for the development of a plasmachemical kinetic reaction mechanism for NH₃ cracking

S. Bang¹, R. Snoeckx¹ and M.S. Cha¹

¹CCRC, Physical Science and Engineering (PSE) Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

Abstract: Plasma-assisted decomposition of NH_3 could offer a cost-effective and energyefficient method for cracking NH_3 into H_2 . Here, we present further investigations into the role of both electron-induced and thermally induced reactions on the decomposition of NH_3 through a temperature-dependent plasma-chemical kinetic study. We believe that the findings of this research will generate significant interest in addressing current limitations and will contribute to the advancement of plasma-assisted NH_3 cracking technology.

Keywords: NH₃ cracking, N₂, H₂, chemical kinetics, non-thermal plasma.

1. Introduction

As the global community strives for sustainability through electrification, the use of carbon-free fuels and efuels can play a crucial role in decarbonizing industrial sectors where direct electrification is not yet feasible. [1] For this purpose, ammonia (NH₃) has attracted attention as the H₂ carrier with the highest percentage of hydrogen atoms at 17.7 % and energy density of 3,000 Wh/kg. Importantly, it is the only carrier that is completely carbon-free.

Utilization of NH_3 also offers the potential to leverage existing infrastructure and knowledge for long-distance transportation, additionally it eliminates the need for cryogenic temperatures and CO_2 emissions during the conversion process. If NH_3 cracking to H_2 can be made efficient, the entire process of NH_3 utilization could be more energy-efficient and cost-effective compared to transporting pure hydrogen.

The traditional method of converting NH_3 into H_2 , such as thermal reforming or pyrolysis, typically requires high temperatures of around 1300 K [2], while the use of catalysts can lower the temperature to around 700 K [3], it remains high and limits its applications. An alternative method is to use electrical discharges or non-thermal plasmas, which allow initiating chemical reactions at room temperature. [1]

In this context, we recently performed a combined experimental and computational study to develop a comprehensive plasma-chemical kinetic reaction mechanism for NH₃ cracking. Using a N₂-diluted NH₃ mixture, we highlighted the challenges to develop a comprehensive plasma-chemical kinetics mechanism [4]: (i) missing electron collisional cross-section data for NH_x species and products; (ii) overestimated reaction rate constants for some of the major pyrolysis reactions (i.e. NH₂ + H + M \leftrightarrow NH₃ + M), at low temperatures; (iii) limited understanding and insight in N_xH_y-related reactions; (iv) strong effect of dissociative quenching of N₂ metastable states by NH₃.

Here, we further explored the decomposition of NH₃ highly diluted in H₂. For the experiment, we investigated the conversion of NH₃ as a function of the discharge power (P_{dis}) and the gas temperature (T_{g}). For the modelling, we employed the same plasma-chemical kinetic reaction

mechanism as for the NH_3 highly diluted in N_2 to study the underlying reaction pathways. Throughout this study, we aim to improve the previous plasma-chemical kinetic reaction mechanism and further validate it for the plasma-assisted cracking of pure NH_3 .

2. Method

2.1 Plasma-chemical kinetic modelling (KAUSTKin)

In order to simultaneously consider both electron-driven and thermally-driven chemistry, we employed KAUSTKin [5], which is a zero-dimensional plasma-chemical kinetic model that combines the capabilities of ZDPlaskin [6] and CHEMKIN. [7] This model calculates the time-evolution of species number densities through balance equations. The rate coefficients for electron-driven reactions are determined using BOLSIG+ [8] (Boltzmann equation solver) within ZDPlaskin, while coefficients for thermallydriven chemistry are obtained through CHEMKIN. As the model is zero-dimensional, transport of chemical species is not taken into account. However, the model can account for the nature of a Dielectric Barrier Discharge (DBD) reactor by applying electrical pulses throughout the simulation, which imitates the electrical discharges experienced by molecules as they pass through the discharge zone. Further information on the model can be found in our previous work. [4,5]

The model conditions such as initial gas concentration, gas temperature (T_g) , residence time (t_{res}) , and reduced electric field (E/N) were equivalent to the conditions from the experiments (Table 1). For the plasma-chemical kinetic reaction mechanism, PCMech-1 was selected from our recent work, because it qualitatively captured the conversion trend of NH₃ as shown in Fig 2. The mechanism contains 41 species and 231 reactions. [4]

Table 1. Reduced electric fields from experiments at P_{dis} = 20 W; a fixed flow rate of 1 SLPM.

Initial gas concentration [mol%]		Reduced electric field (E/N) [Td]	
NH ₃	H ₂	79, 99, 119, 145, 270, 243, 223 ($T_{\rm g} = 300{-}900~{\rm K},~\Delta T_{\rm g} = 100$)	
1.0	99.0		
NH ₃	N_2	90, 123, 143, 164, 241, 188, 159 ($T_{\rm g}$ = 300–900 K, $\Delta T_{\rm g}$ = 100)	
1.0	99.0		

2.2 Experiment (temperature-controlled DBD reactor)



Fig. 1. The schematic diagram of experimental setup

The experimental setup consisted of a temperaturecontrolled dielectric barrier discharge (DBD) reactor, a reactant-supply system, a power supply system, and an analytical system (Fig. 1). The temperature-controlled DBD reactor consisted of an electric furnace and a flow reactor. The reactor has two quartz barriers to avoid catalytic decomposition of NH3 due to direct contact between NH₃ and metallic electrodes. [9] The gas mixture reaches the designated $T_{\rm g}$ within a pre-heating zone before entering the DBD section. The gas gap between the quartz tubes at the DBD section was 2 mm. A stainless-steel sheet inserted in the inner quartz tube served as a high voltage (HV) electrode, while a stainless-steel mesh surrounding the outer quartz tube served as ground electrode. The mass flow rates of NH₃ and H₂ were controlled by two mass flow controllers (Brooks, SLA5850) with a total mass flow rate of 1.0 SLPM. The DBD reactor was powered by a high voltage amplifier (Trek, 30/20 A) and a function generator (Tektronix, AFG 3021B). Pdis was measured by voltage probes (Tektronix, P6015A and TPP1000) and a digital oscilloscope (DPO 4140B, Tektronix). An inline Fourier Transform InfraRed spectroscope (FTIR, Thermo Fischer Scientific, Nicolet iS10) measured the conversion of NH₃. More details about the experimental setup can be found in [5]. The investigated experimental conditions are summarized in Table 2.

Table 2. Experimental conditions at atmospheric pressure; a fixed total flow rate of 1.0 SLPM.

Initial gas concentration [mol%]		Discharge power	Gas temperature
NH ₃	H_2	$(P_{\rm dis})$ [W]	(1g) [K]
1.0	99.0	20	300-900 ($\Delta T_{\rm g} = 100$)

3. Results & Discussions

In Fig. 2, we present the results of the combined experimental (symbols) and numerical (lines) study on the conversion of NH₃ at $P_{\text{dis}} = 20$ W. T_{g} was varied from 300 to 900 K. The experimental data showed that for the NH₃

mixture diluted in 99-mol% H₂, the conversion of NH₃ is zero (red circles), while the conversion of NH₃ diluted in 99-mol% N₂ showed conversions of 7 % at $T_g = 300$ K, and a maximum of 17 % at $T_g = 600$ K (black diamonds).

The lack of conversion of NH_3 when diluted in H_2 is not surprising. Most of the electron energy is transferred to H_2 due to its dominant concentration, which results in the abundant production of H radicals via electron-impact dissociation, next these H radicals will react with the dissociation products of NH_3 , i.e. NH_2 and NH, which in turn mitigates the NH_3 decomposition.

However, our previous reaction mechanism did not predict zero conversion for this mixture and instead showed conversion of NH₃ for T_g above 700 K. The model predicted a conversion of 3.8 % and 18.8 % at 800 and 900 K, respectively (red line). This discrepancy between the experimental and simulation results highlighted the need for further research to develop a suitable temperaturedependent plasma-chemical kinetic reaction mechanism for the cracking of NH₃.



Fig. 2. NH₃ conversion in terms of $T_g = 300-900$ K at a fixed $P_{dis} = 20$ W; 1-mol% NH₃ in 99-mol% H₂ (red) and N₂ (black); *E/N* from Table 1.

To understand the reactions responsible for the predicted conversion of NH₃ in H₂ mixtures, we conducted a chemical analysis by studying the rates of the various reactions at different $T_g = 300, 500, 700, 900$ K; a fixed $P_{\text{dis}} = 20$ W and a fixed E/N = 150 Td.

The results of the analysis are presented in Fig. 3, which displays the 9 major reactions whose rate was higher than 3×10^{15} cm⁻³ s⁻¹. This visualization provides insight into the key reactions responsible for the predicted conversion of NH₃ in H₂ mixtures.

The rates of electron impact reactions are constant for all examined T_g because E/N was fixed at 150 Td. This means that the fraction of electron energy loss to different electron impact reactions was consistent across all T_g .

In contrast to the electron impact reactions, the neutralneutral species reactions vary with respect to $T_{\rm g}$. The results showed that the H-abstraction reaction of NH₃ (as well as its corresponding backward reaction, as shown in Fig. 3) led to the overprediction of the model for $T_{\rm g} > 700$ K.

The reaction $NH_3 + H \leftrightarrow NH_2 + H_2$ (R1) was found to be the most sensitive to temperature changes, with a negligible reaction rate at 300 and 500 K, but an increase of two orders of magnitude at 900 K. Additionally, the reaction $NH_2 + H + M \leftrightarrow NH_3 + M$ (R2) also plays an important role in H₂ mixtures.

To address the overpredicted conversions in the model, we adjusted the reaction rate coefficients of reactions R1 and R2. Furthermore, the backward reaction of R1 was defined separately, as the reaction rate of the backward reaction estimated from CHEMKIN can deviate by a factor three depending on the thermodynamic data implemented. [10]



Fig. 3. Reaction rates of major reactions for the NH₃/H₂ mixtures for different $T_g = 300$, 500, 700, 900 K at $P_{dis} = 20$ W; E/N = 150 Td.

Fig. 4 illustrates the modelling results of the adjusted mechanisms: (1) R1 (red line); (2) R1 + R2 (blue line); and (3) R1 + R2 + the separately defined backward reaction of R1 (green line).

For the NH₃/H₂ mixture (shown in Fig. 4a), it was observed that the first adjustment, a decrease in the rate of reaction R1 (red line), had a direct effect on the conversion of NH₃. At $T_g = 800$ and 900 K, the conversions were 1 % and 10 %, respectively, which were about four and two times lower than the conversions of 3.8 % and 18.8 % obtained from the original mechanism (black line). With adjustment (2), the conversion further decreased and reached zero at $T_g = 800$ K, while the conversion at $T_g = 900$ K still remained at 1.3 % (blue line). When we separately defined the reaction rate of the backward reaction of R1 to avoid errors from the thermodynamic data, the conversion became almost zero for all tested T_g (green line).

In our previous research on the NH₃/N₂ mixture [5], we recommended using the reaction rate obtained by Altinay and Macdonald [11], as it was found that the well-known rate of Davidson et al. [12] was greatly overestimated for lower temperature ranges. This was due to it being validated for thermal pyrolysis of NH₃ at $T_g > 2200$ K. However, the results of this study seem to indicate that the previous correction for the N₂ mixture leads to an overprediction of the NH₃ conversion in the H₂ mixture for $T_g > 700$ K.



Fig. 4. Conversion of NH₃ with different variations in the mechanism (1) adjusting (R1) NH₃ + H \leftrightarrow NH₂ + H₂; (2) adjusting (R2) NH₂ + H + M \leftrightarrow NH₃ + M; (3) defining the backward reaction of R1. (a) H₂-diluted NH₃ and (b) N₂-

diluted NH₃ at $P_{\text{dis}} = 20$ W; $T_{\text{g}} = 300-900$ K; E/N from Table 1.

We also investigated the influence of the changes in the reaction rate coefficients on the model predictions for the NH_3/N_2 mixture (Fig. 4b). Interestingly, the decreasing rate of R1 increased the conversion of NH_3 in the N_2 mixture (red line), while this decreased the conversion in the H_2 mixture. However, this increase is not sustained when the main pyrolysis reaction R2 was adjusted (blue line). Splitting the backward reaction of R1 had no significant effect on the NH_3/N_2 mixture, thus the conversion of NH_3 is almost equal for adjustments (2) and (3).

To gain a deeper understanding of the plasma-assisted cracking of NH₃, we are in the progress of conducting further experiments using different mixtures and pure NH₃. These experimental results will provide valuable insights and allow us to validate the temperature-dependent plasma-chemical kinetic reaction mechanism for NH₃ cracking for the entire range of mixture variations. By studying the mixture of NH3 with H2 and N2, we investigated the influence of the H₂ and N₂-related reactions, which helped us to improve the accuracy of our reaction mechanism and expand the potential applications and utilization of NH₃ as a sustainable and renewable energy carrier. It is especially important to consider the effects of H₂ and N₂, as they are the products produced from the cracking of NH₃, and therefore their impact will grow during the cracking process.

4. Conclusions

This study aimed to further develop the temperaturedependent plasma-chemical kinetic reaction mechanism for the cracking of NH3 by investigating the NH3 conversion in 99-mol% H₂ through a combined experimental and computational study. From the chemical analysis it was shown that the H-abstraction reaction of NH_3 (R1: $NH_3 + H \leftrightarrow NH_2 + H_2$) caused an overprediction of the conversion in our model at $T_{\rm g} > 700$ K. To address this issue, the reaction rate of this reaction, as well as the reaction rate of R2 (NH₂ + H + M \leftrightarrow NH₃ + M), were adjusted. Additionally, the backward reaction of R1 was defined separately to avoid carrying over errors from inaccurate thermodynamic data. The adjustments made to the reaction rates had a significant impact on the conversion of NH₃ in the H₂ mixture, decreasing it from 3.8 and 18.8 % to almost zero for all tested $T_{\rm g}$, similar to the experimental data. Furthermore, the study also investigated the influence of changes in the reaction rates for the NH₃/N₂ mixture, which showed that the decreasing rate of R1 increased the conversion of NH₃ in the N₂ mixture, while it decreased the conversion in the H₂ mixture.

Future work will concentrate on further experiments using different mixtures and pure NH₃ to gain a deeper understanding of the plasma-assisted cracking of NH₃. This will allow us to develop a validated temperature-dependent plasma-chemical kinetic reaction mechanism, which can be used for a wide variety of plasma-assisted processes, such as NH_3 cracking, catalysis and combustion.

5. Acknowledgements

The authors acknowledge financial support from King Abdullah University of Science and Technology (KAUST), under award number BAS/1/1384-01-01.

6.References

- [1] MS Cha, R Snoeckx. Plasma Technology–Preparing for the Electrified Future. Frontiers in Mechanical Engineering 2022;8.
- [2] M Benés, G Pozo, M Abián, Á Millera, R Bilbao, MU Alzueta. Experimental Study of the Pyrolysis of NH₃ under Flow Reactor Conditions. Energy Fuels 2021;35:7193–200.
- [3] F Schüth, R Palkovits, R Schlögl, DS Su. Ammonia as a possible element in an energy infrastructure: catalysts for ammonia decomposition. Energy Environ Sci 2012;5:6278–89.
- [4] S Bang, R Snoeckx, MS Cha. Kinetic Study for Plasma Assisted Cracking of NH₃: Approaches and Challenges. J Phys Chem A 2023.
- [5] R Snoeckx, D Jun, BJ Lee, MS Cha. Kinetic study of plasma assisted oxidation of H₂ for an undiluted lean mixture. Combustion and Flame 2022;242:112205.
- [6] S Pancheshnyi, B Eismann, G Hagelaar, L Pitchford. Computer code ZDPlasKin, www.zdplaskin.laplace.univ-tlse.fr. 2008.
- [7] RJ Kee, FM Rupley, JA Miller. Chemkin-II: A Fortran chemical kinetics package for the analysis of gas-phase chemical kinetics. Sandia National Lab. (SNL-CA), Livermore, CA (United States); 1989.
- [8] GJM Hagelaar, LC Pitchford. Solving the Boltzmann equation to obtain electron transport coefficients and rate coefficients for fluid models. Plasma Sources Science and Technology 2005;14:722–33.
- [9] L Wang, Y Zhao, C Liu, W Gong, H Guo. Plasma driven ammonia decomposition on a Fe-catalyst: eliminating surface nitrogen poisoning. Chem Commun 2013;49:3787.
- [10] G Friedrichs, HG Wagner. Direct Measurements of the Reaction NH₂ + H₂ → NH₃ + H at Temperatures from 1360 to 2130 K 2000;214:1151.
- [11] G Altinay, RG Macdonald. Determination of the Rate Constants for the $NH_2(X^2B^1) + NH_2(X^2B^1)$ and $NH_2(X^2B^1) + H$ Recombination Reactions in N_2 as a Function of Temperature and Pressure. J Phys Chem A 2015;119:7593–610.
- [12] DF Davidson, K Kohse-Höinghaus, AY Chang, RK Hanson. A pyrolysis mechanism for ammonia. International Journal of Chemical Kinetics 1990;22:513–35.