# NH<sub>3</sub> synthesis in a catalytic atmospheric RF discharge

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**Abstract:** This contribution will present experimental results on the NH<sub>3</sub> synthesis in an atmospheric catalytic homogenous RF discharge in a  $N_2+H_2+He$  gas mixture. Initial results on the plasma synthesis indicate that the NH<sub>3</sub> formation is reduced with increasing  $N_2$  admixture, which can be attributed to a reduced plasma density or an increasing contribution of NH<sub>3</sub> losses by collisions with  $N_2^*$  with increasing  $N_2$  admixture.

Keywords: NH<sub>3</sub> synthesis, atmospheric plasma, RF discharge, plasma-catalytic synergism

## **1.Introduction**

Since the beginning of the last century, a growing fraction of humankind depends on the availability of artificial fertilisers. Ammonia is one of the main ingredients of nitrogen-based fertilisers. At the moment, this substance is synthesised with the Haber-Bosch process, which uses a significant amount of the global energy consumption. A potential alternative would be plasma catalysis, since such a reactor can be easily switched on/off depending on an on-site demand and the supplied renewable energy.

In this contribution, the NH<sub>3</sub> synthesis in an N<sub>2</sub>+H<sub>2</sub>+He atmospheric catalytic RF plasma is studied. The goal is to observe and characterise plasma-catalytic synergism. This is done with a reactor that is optimised for studying potential plasma-catalytic synergism by maximising the surface to volume ratio. The NH<sub>3</sub> concentrations are obtained with Fourier Transform Infrared (FTIR) absorption spectroscopy. Additionally, optical emission spectroscopy (OES) is used to characterise the excitation of N<sub>2</sub> by observing the second positive (SPS) and first negative (FNS) systems. These emission spectra depict a highly non-equilibrium environment in the plasma that is beneficial for N<sub>2</sub> dissociation processes, e.g. dissociative adsorption on a catalytic surface.



Figure 1: A side view of the atmospheric RF discharge reactor, where the copper electrodes (I) are shielded from the plasma (III) using glass plates (II). The red dashed circle indicates the section of the plasma observed during the OES measurements.

### 2. Experimental setup

For this contribution, the NH<sub>3</sub> synthesis is studied in a helium dominated atmospheric RF discharge, where up to 1% of the gas mixture is  $N_2+H_2$ . The reactor is discussed in detail by Stewig *et al* [1], so merely a brief overview is given here. The rectangular configuration of the reactor consists of two parallel copper electrodes that are protected from the plasma by glass plates, see figure 1. The plasma side of the glass plates will be modified, when investigating the influence of different (catalytic) surfaces. Additionally, the temperature of the reactor can be regulated with an ecocooling thermostat (Eco RF 145S, Lauda Gmbh).

The exhaust of the reactor is directed towards a multipass cell, which is installed in the sample compartment of a FTIR (Vertex 70v, Bruker). The absorption path length – of the IR light – is set up to 7.2 meters, which results in a lower detection limit of 0.05 ppm NH<sub>3</sub>. Also, the temperature of the cell is controlled up to 200 °C by an accompanying temperature PID-system.

Furthermore, the OES measurements are performed with a 0.5 meter long Spectrograph (SpectraPro-500i, Acton Research Corporation). The light is collected by a multicore optical fiber (LG-455-020-3) that is placed in front of the reactor and directly couples the light into the spectrograph. The red dashed line of figure 1 depicts the section of light originating from the plasma that is captured by the fiber, which is roughly 50% of the viewing field. Finally, the spectra of N<sub>2</sub> are fitted to obtain the rotational and vibrational temperatures of the individual N<sub>2</sub> systems and the ratio of the intensity between these systems.



Figure 2: FTIR spectrum for the symmetric bending mode of  $NH_3$  between 800 and 1200 cm<sup>-1</sup>, where the concentration of the best fit is  $14\pm1$  ppm and  $T_{cell}=80^{\circ}C$ .

### 3.NH<sub>3</sub> concentration measurement

The  $NH_3$  concentrations that will be presented in this contribution are obtained with IR absorption spectroscopy. A typical spectrum is depicted in figure 2. Here, the spectra (blue) is shown together with the baseline correction (black, dashed) and best fit (orange). The baseline correction is required due to minor intensity fluctuations during the acquisition time. Also, in the lower panel, the

residual between the data and the fit is shown. The spectrum is assumed to be in thermal equilibrium, because it is measured *ex situ*. Therefore, the spectrum is only characterised by a single temperature and a concentration, as opposed to the non-equilibrium spectra obtained with *in situ* measurements. The equilibrium temperature is set by regulating the temperature of the multipass cell. Finally, the concentration is defined with respect to the total number of species at atmospheric pressure.

The best fit is obtained with a python script [2] by calculating the spectrum using the constants from the HITRAN-database [3] and assuming that the instrumental broadening of the FTIR can be approximated by a Gaussian line shape and a half-width-at-half-maximum of  $0.194\pm0.002$  cm<sup>-1</sup>. Table 1 shows the parameters used to characterise the measured spectra.

Table 1: List of fit parameters with the corresponding settings.

Parameter:	Vary	Init. guess:	Range
Pressure	No	1 atm	-
Path length	No	7.2 m	-
Wavenumber offset	Yes	0 cm <sup>-1</sup>	-1, 1 cm <sup>-1</sup>
Gaussian instr.	Yes	0.1 cm <sup>-1</sup>	0, 1.0 cm <sup>-1</sup>
Fraction NH <sub>3</sub>	Yes	5 ppm	0, 10%
Equil. Temperature	No	$T_{cell}$	-

Unfortunately, the best fit has a notable difference for 4 rotational lines in the R-branch of the symmetric bending mode transition  $|0^{s}\rangle \rightarrow |1^{a}\rangle$ , which are observed between 1047 and 1123 cm<sup>-1</sup>. Future calibration measurements with a known NH<sub>3</sub> gas mixture should elucidate the origin of this discrepancy.



Figure 3: The measured (blue)  $NH_3$  concentration for 1%  $N_2+H_2$ , 5.7W and 1:3  $N_2:H_2$ . Theoretical build-up of nonabsorbing species (dashed black) and best fit (orange) temporal evolution of  $NH_3$  in the multipass cell of the multilayer adsorption model.

The measured  $NH_3$  concentration in the multipass cell increases on a time scale longer than expected from the simple residence time of the multipass cell of 6.2 minutes, as illustrated in figure 3. The much longer time constant of the measured  $NH_3$  concentration can be attributed to multilayer adsorption of  $NH_3$  on the inside walls of the multipass cell. This time constant is reduced by increasing the temperature of the multipass cell to enhance desorption from the inner walls. Moreover, a calibration with a known concentration of  $NH_3$  will be used to validate this model and to determine relevant constants.

### 4. Plasma synthesis of NH<sub>3</sub>

The plasma synthesis of  $NH_3$  is studied to serve as a benchmark when introducing different (catalytic) surfaces to the reactor. The  $NH_3$  formation is quantified for different plasma conditions. This is connected to the excitation of  $N_2$ , which is determined from SPS and FNS of  $N_2$ . Also, the excitation of  $N_2$  is of importance as the dissociation – of this stable molecule – is a bottle neck in  $NH_3$  formation.

In figure 4, the NH<sub>3</sub> concentration is plotted as function of the relative N<sub>2</sub> admixture, which is defined as the N<sub>2</sub>/(N<sub>2</sub>+H<sub>2</sub>+He) flow ratio. Here, the plotted concentrations are estimated from the extrapolation of the time dependent build-up of the NH<sub>3</sub> concentration in the multipass cell, similar to figure 3. The corresponding error bars are an estimate of the confidence interval for this extrapolation.



Figure 4: The NH<sub>3</sub> concentration as function of the N<sub>2</sub> admixture for 1% N<sub>2</sub>+H<sub>2</sub> admixture, a power of  $5\pm1W$ , and a controlled reactor temperature of 20°C.

Preliminary results show that the maximum  $NH_3$  formation occurs at  $N_2$  deficient gas mixtures. This could be attributed to either a reduced plasma density with increasing  $N_2$  admixture to the He-discharge or to the increasing contribution of back-reactions, where  $NH_3$  is destroyed in collisions with excited nitrogen species.

When assuming chemical equilibrium for the plasma gas, both the reduced plasma density and the back-reaction model yield the same relation for the NH<sub>3</sub> formation as function of N<sub>2</sub> admixture. The first one, by using reaction (1) and assuming the forward reaction rate  $k_1$  to be proportional to the plasma density, which is in turn inversely proportional to the N<sub>2</sub> admixture. This would result in two constants that are related to the ratio of the forward and backward reaction rate  $k_1/k_{-1}$  and to the influence N<sub>2</sub> admixture has on the plasma density. For the back-reaction model, reaction (2) is used in addition to (1). This results in a curve with two constants as well. Again, one constant is related to  $k_1/k_{-1}$ . Whilst the other constant is related to fraction of NH<sub>3</sub> lost due to N<sub>2</sub>\* instead of the general losses, i.e. the ratio  $k_2/k_{-1}$ .

$$N_2 + 3H_2 \leftrightarrows NH_3 \tag{1}$$

$$\mathrm{NH}_3 + 2\mathrm{N}_2^* \to 3\mathrm{N}_2 + 3\mathrm{H}_2 \tag{2}$$

The SPS and FNS of  $N_2$  are measured to study the excitation of  $N_2$  by the plasma. The former system is used to deduce the importance of excitation by electron collisions and by Pooling reactions – between excited  $N_2$  species – and its vibrational temperature is used to characterise the level of excitation. Furthermore, according to Benedictis *et al*, the emission of the FNS is the result of Penning excitation by He\* of  $N_2(X)$  [4]. Thus, the ratio of the intensity FNS/SPS gives insight in the importance of  $N_2$  excitation by excited He-species.

In figure 5, the vibrational temperature obtained from the SPS and the intensity ratio FNS/SPS is given as a function of the  $N_2$  admixture for different plasma powers. The observed spectra for 0%  $N_2$  admixture are attributed to impurities from air, since – unlike for figure 4 – the reactor was not operated in a vacuum chamber.



Figure 5: The vibrational temperature of the SPS of  $N_2$  (a) and the intensity of FNS to SPS (b), which is normalised to the value of 4.0 W, 0% N<sub>2</sub>.

The excitation of N<sub>2</sub> is dominated by Penning excitation by He<sup>\*</sup> and excitation by electron collisions. Pooling reactions between excited N<sub>2</sub> species is ruled out on basis of the rotational temperature of the SPS [5]. The rotational temperature of the SPS – which is found to be between 300 and 350 K – conforms to the gas temperature found in a previous study [1], thus the upper electronically excited state of SPS is created through excitation by electron collisions, and not by the Pooling reaction N2(A)+N2(A)  $\rightarrow$ N2(C)+N2(X).

Furthermore, with increasing  $N_2$  admixture, the excitation by electron collisions becomes more dominant than by Penning excitation by He\*. This is deduced from the inversely proportional relation of the intensity ratio FNS/SPS to the increasing  $N_2$  admixture in panel 5(b). In the future, these results – which were obtained with  $N_2$ +He

– will be compared to  $N_2+H_2+He$  mixtures to study the impact of  $H_2$  has on the excitation of  $N_2$ .

The vibrational temperatures, in panel (a), show an inconclusive picture when identifying the origin of a reduced NH<sub>3</sub> concentration at higher N<sub>2</sub> admixtures. On the one hand, the 'high' temperatures will stimulate vibrational excitation of NH<sub>3</sub>, via vibrational energy exchange. Thereby, promoting the destruction of NH<sub>3</sub> by excited nitrogen species. On the other hand, however, the decrease of the vibrational temperature with increasing N<sub>2</sub> admixture is in line with the assumption that a lower NH<sub>3</sub> conversion follows from a reduced plasma density with increasing N<sub>2</sub> admixture.

According to literature, NH<sub>3</sub> is formed by stepwise hydrogenation of N-species, where surface reactions are important [6]. Therefore, for studying the effect different surfaces have on the conversion, the plasma-side of the glass plate will be modified in the future, to increase the surface area and to introduce catalytic materials. Also, the high vibrational temperatures of N<sub>2</sub> – reported in panel 5(a) – should be beneficial for dissociative adsorption, thereby overcoming the bottle neck of dissociating N<sub>2</sub> [7].

#### 5. Conclusion

In this contribution, a fundamental study on the NH<sub>3</sub> synthesis in a plasma catalytic reactor is performed, with the goal of observing and quantifying plasma-catalytic synergism. Initial efforts were focussed on characterising the plasma synthesis of NH<sub>3</sub>. The observed reduced NH<sub>3</sub> conversion with increasing N<sub>2</sub> admixture is either attributed to a reduced plasma density or to an increasing contribution of back-reactions with increasing N<sub>2</sub> admixture.

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