Ammonia production in a low- to mid-pressure microwave discharge

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Ammonia (NH_3) is an important chemical, widely used for fertilizer production and in the chemical industry, also showing potential as a storage for energy from renewable sources and for hydrogen [1]. Recently, plasma-catalytic synthesis of NH_3 has attracted great interest as plasma reactors allow for intermittent operation and an efficient scale down as compared to the thermal-catalytic Haber-Bosch process, allowing for an easier use of electricity generated by renewable energy sources [2]. By providing ions, photons, radicals and metastable states, the plasma yields additional activation of the precursor molecules hydrogen and nitrogen, thereby lowering the activation energy needed for the generation of ammonia [3].

In order to link plasma parameters to the ammonia output, the experimental setup shown in Fig. 1 is used. A H_2 - N_2 mixture is introduced into a quartz glass tube with the length of $1\,\mathrm{m}$ and an inner diameter of $17\,\mathrm{mm}$. The setup is pumped by a rotary vane pump on the other side, leading to a directional gas flow at pressures between 10 - $1000\,\mathrm{Pa}$. Using a waveguide-based launcher (surfaguide) [4], a plasma column is generated in the quartz tube by a $2.45\,\mathrm{GHz}$ microwave generator with a power of $600\,\mathrm{W}$. Downstream of the plasma, a movable package made of stainless steel mesh containing a commercial Ruthenium catalyst ($2\,\mathrm{wt}\%$ Ru on γ-Al_2O_3 pellets) is located. Before measurements, the catalyst is pre-treated by in-situ heating to $620\,\mathrm{K}$ for two hours in a $20\,\mathrm{sccm}$ Ar gas stream in order to allow for sufficient desorption of adsorbates (water etc.) from the surface.
For detecting the composition of the output gas mixture, a residual gas analyzer (RGA) is located on the downstream side of the experiment. The system is calibrated using different calibration gases allowing to determine the concentrations of H_2, N_2, NH_3 and H_2O in the gas mixture. To further enhance accuracy for the determination of the NH_3 concentration ($m/z = 17$), the influence of the dissociative ionisation of H_2O molecules (cracking pattern, leading to a signal by OH^+ at $m/z = 17$) is also accounted for.
Optical emission spectroscopy (OES) is used to correlate the ammonia output and plasma parameters. For detecting the emission of the plasma in near UV to NIR range, a spectrometer with a FWHM $\Delta\lambda = 0.018\,\mathrm{nm}$ at a wavelength of $650\,\mathrm{nm}$ is used. By fitting the $\Delta\nu = -2$ sequence of the electronic $C^3\Pi_u \rightarrow B^3\Pi_g$ transition of molecular nitrogen at $360\,\mathrm{nm}$ - $380\,\mathrm{nm}$ using MassiveOES [5], the rotational and vibrational temperatures of the C state $T_{\mathrm{rot,C}}$ & $T_{\mathrm{vib,C}}$ can be determined. The Franck-Condon principle is utilized to translate the vibrational temperature to the ground state, $T_{\mathrm{vib,X}}$. The rotational temperature in the ground state ($T_{\mathrm{rot,X}}$) is obtained by considering the rotational constants of the ground and excited states [6].

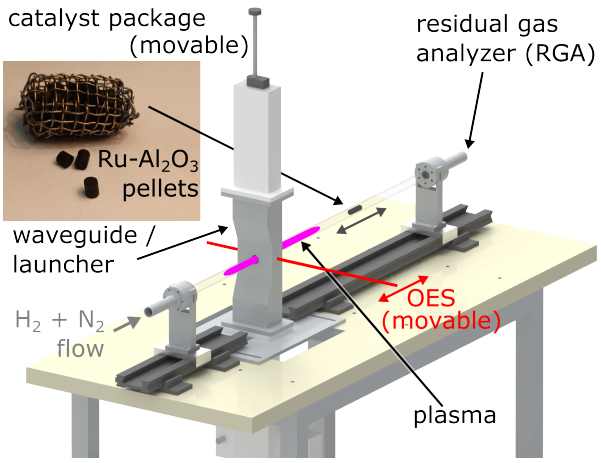

Fig. 1: Setup of the Surfaguide Gas Conversion Experiment (SurGE) with an image of the catalyst pellets used. Optical emission spectroscopy (OES) is available at a movable line of sight perpendicular to the quartz tube. A residual gas analyzer (RGA) is used to measure the gas composition.

The effects of pressure in the range of $15\,\mathrm{Pa}$ to $1000\,\mathrm{Pa}$, the hydrogen-nitrogen gas composition from $10\,\%$ to $90\,\%$ N_2, and the presence and position of the Ru-Al_2O_3 catalyst on ammonia production are investigated. Fig. 2 shows the concentration of H_2O and NH_3 obtained with the RGA over time can be seen for a microwave power of $600\,\mathrm{W}$, a pressure of $85\,\mathrm{Pa}$, a feed gas mixture of $\sim$50 % N_2 and $\sim$50 % H_2, and a fresh catalyst sample (after pre-treatment). Before the plasma is

switched on the catalyst package is far from the envisaged plasma region at the end of the quartz tube, and water, desorbed from the experiment walls and catalyst pellets, is dominant with a contribution of less than 0.5 ‰. As soon as the plasma is switched on at $t = 8\,\mathrm{min}$, NH_3 becomes dominant. After circa one minute plasma on time, the ammonia concentration reaches 7.5 ‰ due to ammonia generation in the bulk plasma and on the surface of the quartz tube. At the same time, water concentration reaches 1.8 ‰ due to desorption from surfaces heated by the plasma. At $t \approx 10\,\mathrm{min}$ (dashed line in the graph), the catalyst is moved to a position 3 cm behind the end of the plasma column. This leads to a sudden increase in the detected ammonia signal with the ammonia concentration reaching 15.0 ‰ at $t = 15\,\mathrm{min}$. As the catalyst is now heated by the plasma, also more water is desorbed. After reaching a maximum of 3.1 ‰ at 11 min, the H_2O amount slowly decreases again to 0.4 ‰ while the NH_3 concentration increases to a stable plateau of 17.5 ‰. This shows the importance of the presence of a catalyst, which in this case doubles the NH_3 concentration as obtained with the RGA. Apart from that, a time scale for an initial stabilization of the system of 15 to 20 min can be observed.

From measurements along the axis of the plasma column using OES and a thermocouple it could be derived that the gas temperature at the position of the catalyst package is in the range of $\sim$ 550 K. When moving the package into contact with the end of the plasma column, the temperature rises to $\sim$ 780 K and the ammonia yield decreases to 16.8 ‰. If the catalyst package is moved 3 cm further into the plasma, this leads to a shortening of the plasma column, whereas the catalyst is in range of even higher temperatures of $\sim$ 1100 K and the detected ammonia decreases to 10.0 ‰. This suggests a detrimental effect of high gas temperatures for ammonia generation, as is expected from literature [7].

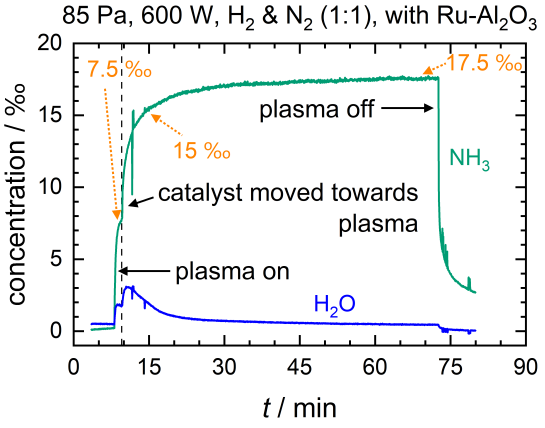

Fig. 2: NH_3 and H_2O concentration as determined with the RGA over time.

With a constant catalyst-plasma distance of 3 cm during an increase in pressure over two orders of magnitude, the ammonia concentration decreases by one order of magnitude. Simultaneously, $T_{\mathrm{vib,X}}$ and $T_{\mathrm{rot,X}}$ as determined by OES near the edge of the plasma column show a gradual equilibration, with $T_{\mathrm{rot,X}}$ increasing from $\sim$ 600 K to $\sim$ 1300 K and $T_{\mathrm{vib,X}}$ decreasing from 7000 K to 2500 K. A T_{vib} decrease goes along with decreased population of highly vibrationally excited N_2 molecules and hence, indicates less available activated precursor molecules and thus less NH_3 production. On the other hand a T_{rot} increase again indicates a possible contribution of increased NH_3 destruction. The next steps include further investigations with reference to plasma parameters like atomic densities (N & H), electron temperature and density, and the correlation between NH emission and NH_3 output as a measure of a precursor molecule.

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