

PRODUCTION OF AMMONIA IN A PACKED-BED DIELECTRIC BARRIER DISCHARGE

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ABSTRACT

We investigate the production of ammonia from nitrogen and hydrogen in a dielectric barrier discharge packed with glass spheres and magnesium oxide pellets close to atmospheric pressure. In particular, the influence of the discharge power and the gas composition is studied. The maximum ammonia production yields obtained is 4.9% conversion efficiency of H₂ to NH₃ and the maximum energy efficiency is 0.47 g/kWh. Ammonia synthesis from gas phase reactions only (without a catalyst) was also tested. We find that catalytic surface reactions dominate, allowing relatively high concentrations of ammonia to be produced despite the low electron energies present in a low-temperature non-equilibrium plasma.

1. INTRODUCTION

The standard Haber–Bosch process for ammonia production requires high pressures and temperatures (typically 200 bar and 500°C), as well as a catalyst, for acceptable production rates and yields, usually around a 15% conversion of hydrogen to ammonia. By combining an atmospheric-pressure plasma with a catalyst, it is, however, possible to produce ammonia from nitrogen and hydrogen at atmospheric pressure and room temperature [1].

In order to increase ammonia production, a wide range of catalysts and different plasma–catalyst configurations has been tested [2-5]. The catalyst can be in the form of a surface, a wire or beads; Pd, Pt, Fe, MgO, and Al₂O₃ have been most frequently-used catalytic materials. The catalyst can be placed within or downstream from the discharge. Ruan et al. [6] reported the highest

ammonia concentration, 12% by volume, using a dielectric-barrier discharge packed with beads of MgO supporting Cs-Ru, with the residence time of 120 min.

We use a dielectric-barrier-discharge reactor, similar to that of Ruan et al., packed with glass and MgO beads with the residence time of 23 to 102 s. We investigate the influence of the input gas composition (including the addition of argon to the nitrogen–hydrogen mixture) and applied voltage on the production of ammonia. We use electrical measurements and emission spectroscopy to obtain the power, the electron density, the electron energy distribution function (EEDF) and rotational and vibrational temperatures, and use these data to understand the influence of applied voltage and gas composition. For comparison, we also present results obtained for the reactor without any glass or MgO beads present.

2. EXPERIMENT

A cylindrical dielectric-barrier discharge reactor was used in this work and the reactor has a stainless-steel central high-voltage electrode, a 4-mm-thick borosilicate glass tube as a dielectric barrier and a 200-mm-long and 56-mm-diameter bronze-mesh cylinder as the outer ground electrode. The 5-mm gap between the high-voltage electrode and the dielectric barrier was filled with soda-lime glass spheres (3 mm diameter) and MgO pellets (approximately 2 mm long and 1 mm diameter). For comparison, the reactor was also operated without glass spheres and MgO pellets.

A Trek 20/20C high-voltage amplifier, fed by a 1 kHz sine wave, was used as the power source. The ammonia concentration in the exit gas was

measured using a mass spectrometer (Stanford Research Systems SRS-300) or a Fourier-transform infrared (FT-IR) spectrometer (Perkin-Elmer Frontier), calibrated against measurements made using a Thermo Fisher Scientific Orion ammonia ion-selective electrode.

Measured I–V characteristics were used to determine the absorbed power, estimate the electron density, and to obtain, using BOLSIG+ [7], the electron energy distribution function (EEDF). Emission spectra were obtained using a Princeton Instruments Acton SP2500 spectrometer. The rotational and vibrational temperatures and the relative population densities of the different vibrational excited states were estimated from the measured N_2^+ spectra between 385 and 395 nm using the LIFBASE 2.1 software [8].

3. RESULTS AND DISCUSSION

3.1 Influence of applied voltage and argon

The influence of applied voltage and the addition of argon on the NH_3 production yield (conversion of H_2 to NH_3) is investigated using FT-IR. The pressure was 1 atm. The measurement results are shown in Fig. 1. The yield increases from 1.6 to 4.9%, corresponding to NH_3 production rate of 12.8 and 37.6 $\mu\text{mol}/\text{min}$ respectively, when the voltage is increased and argon added. At the same time, the absorbed power increases from 35 to 90 W and the rotational temperature from 300 ± 50 K to 450 ± 50 K.

The EEDF for different conditions is shown in Fig. 2. Since the dissociation energy of N_2 is 9.8 eV, the likelihood of direct dissociation by electron impact is low, particularly for the lower applied voltage. Increasing the applied voltage increases the reduced electric field strength E/N , where E is the electric field strength across the gas gap and N denotes the gas number density, and shifts the EEDF to higher energies. The addition of Ar slightly reduces the calculated E/N , and resulted in a small decrease in the number of high energy electrons. The molecular N_2 and N_2^+ emission intensities are observed to be enhanced by the addition of Ar, as well as by the increased voltage, as shown in Fig. 3. Increased vibrational excitation of N_2 may increase the likelihood of dissociative adsorption on the catalyst surface,

which is claimed to be the main method of N_2 dissociation [1]. The addition of Ar may also increase gas-phase dissociation. The electron density is increased $15 \pm 3\%$ with Ar addition at the same voltage, suggesting that a significant density of Ar^+ ions is produced. The charge transfer reaction with Ar^+ will lead to increased dissociation of N_2 [9] and supports the higher emission intensity of N_2^+ and enhanced NH_3 production yield.

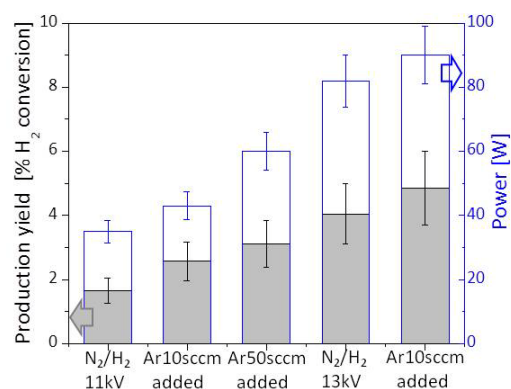


Fig. 1 NH_3 production yield and power consumption for different applied voltages and different argon flows. The N_2 flow is 30 sccm and the H_2 flow is 30 sccm. The voltage is 11 kV for the 3 cases on the left, and 13 kV for the 2 cases on the right.

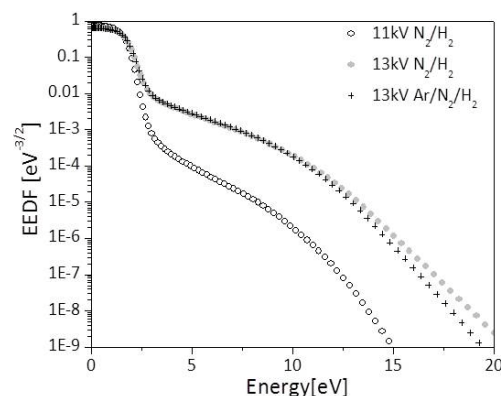


Fig. 2 Influence of applied voltage and argon addition on EEDF. The N_2 , H_2 and Ar flows are respectively 30, 30 and 10 sccm.

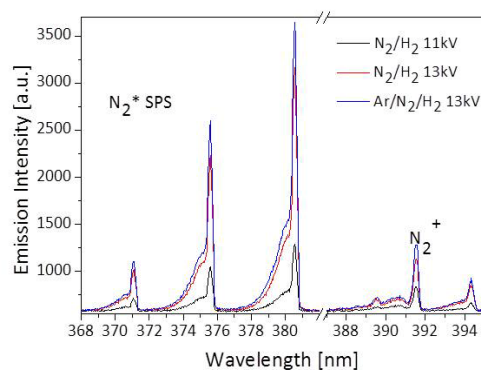


Fig. 3 N_2 2nd positive system $N_2(C^3\Pi_u) \rightarrow N_2(B^3\Pi_g)$ and N_2^+ emission intensities, for the same conditions used for Fig. 2

3.2 Influence of H₂ input flow

To understand the influence of H₂ on NH₃ generation, we performed a series of measurements for different H₂ input flow rates. In these experiments, NH₃ production was measured with the mass spectrometer. Unlike the experiments reported in Sec. 3.1, the pressure at the gas outlet of the reactor was sub-atmospheric, 310 ± 50 torr. Although the pressure in the reactor is expected to be higher, the pressure at the gas exit was used in calculation of the production yield to give a conservative estimate.

As shown in Fig. 4, the NH₃ production rate increases monotonically with H₂ input flow rate, but the conversion efficiency of H₂ to NH₃ is largest at the lowest H₂ flow rate of 10 sccm.

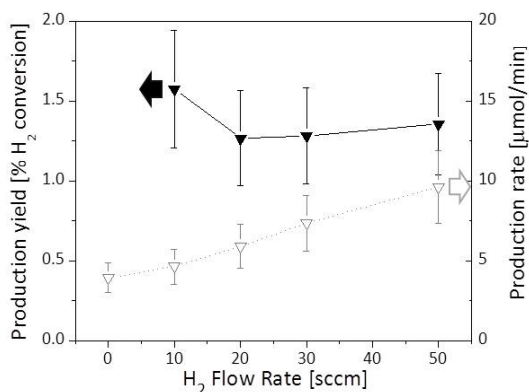


Fig.4. Dependence on H₂ input flow rate of the NH₃ production yield and production rate. The N₂ input flow rate is 30 sccm, and the applied voltage is 12 kV.

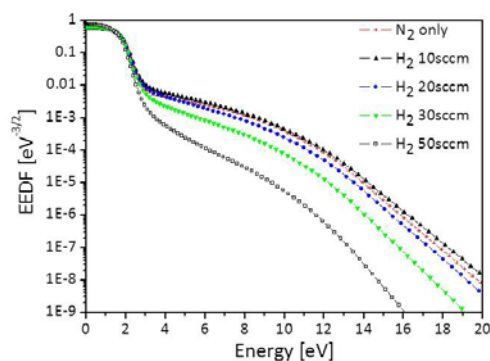


Fig.5. EEDF for different H₂ input flow rates

Addition of H₂ shifts the EEDF to lower electron energies, as shown in Fig. 5, except for a small increase for 10 sccm H₂. Note that the EEDFs were calculated for a pressure of 1 atm; using a lower pressure shifts the EEDFs to higher energies, but the trends observed for increasing H₂ flows are the same.

The vibrational temperature decreases from 2200 K to 1250 K, and the electron temperature from 15 900 K to 12 300 K, as the H₂ flow rate increases, as shown in Fig. 6. As a result, the relative population density of the first excited vibrational energy state of N₂⁺(B) relative to the ground state, $n[\text{N}_2^+(\text{B},v=1)] / n[\text{N}_2^+(\text{B},v=0)]$, is reduced from 0.212 to 0.065. The light emission intensity from the N₂ 2nd positive system is observed to be significantly weakened, even for 10 sccm H₂ input flow. This means the population densities of the electronically-excited states N₂(C³Π_u) and N₂(B³Π_g) are expected to be decreased as well as the vibrationally-excited states of N₂⁺(B). There is, however, a remarkable increase in the electron number density, also shown in Fig. 6. Since the addition of H₂ decreases the electron energy distribution function at higher energies, and reduces the population densities of the excited states of N₂ and N₂⁺, the increased electron density is likely to be due to the ionization of hydrogen. The results indicate that high-energy electrons are being lost due their interactions with H₂, leading to vibrational excitation and ionization. The increased production rate, and approximately constant yield, which occur in spite of decreased vibrational excitation of N₂, suggests that vibrationally-excited and ionized H₂ molecules play an important role in NH₃ production.

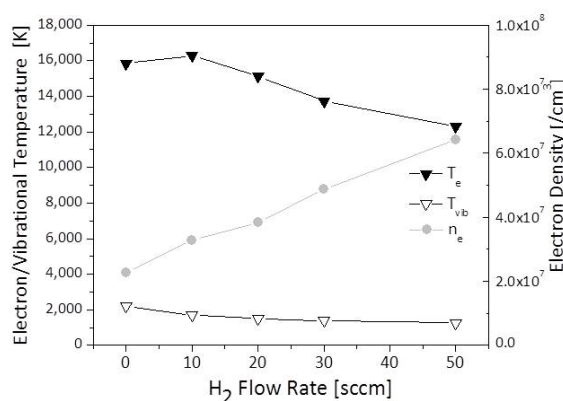


Fig.6. Dependence of electron and vibrational temperatures and electron density on H₂ input flow rate. Other parameters are as for Fig. 4.

3.3 Comparison with gas-phase reaction

In order to investigate the importance of the surface reactions, the reactor was run without MgO beads and glass spheres. Because of the large 5 mm gap, 50 sccm of Ar was added to assist breakdown. The pressure in the reactor was 120 ± 20 torr. The coupled power and the energy

efficiency of NH_3 production are compared to the packed-bed reactor case in Fig. 7.

Removing the MgO and glass spheres increased both the coupled power and the gas temperature; despite this the production yield is decreased by a factor of 4.4 for an H_2 input flow rate of 50 sccm. The energy efficiency is decreased by a factor of 5.6 times at the same flow rate.

The results suggest that surface reactions play an important role in the production of NH_3 . It is likely that surface reactions on the stainless-steel inner electrode and the glass tube contribute to the production of NH_3 , so the contribution of gas-phase reactions is probably even smaller than the approximately 20% immediately suggested by the results.

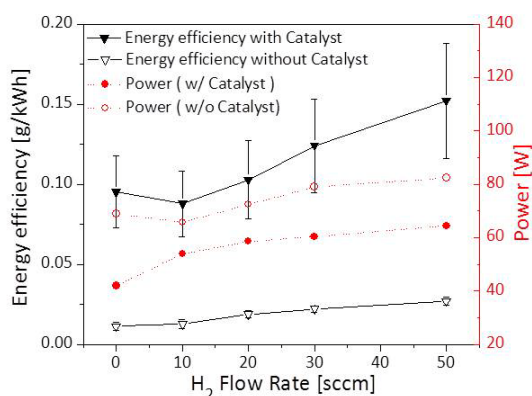


Fig.7. Comparison of energy efficiency of NH_3 production and coupled power for the reactor with and without MgO beads and glass spheres. The N_2 and Ar flow rates were 30 sccm and 50 sccm respectively, and the applied voltage was 12 kV.

4. CONCLUSIONS

The heterogeneous production of NH_3 from N_2 and H_2 has been investigated with a packed-bed dielectric-barrier discharge reactor. Appreciable yields of NH_3 have been obtained, especially with addition of Ar. Experiments performed without the presence of catalyst suggest that gas-phase reactions are responsible for only a small portion of the NH_3 synthesis.

We have derived EEDFs, electron densities and electron and vibrational temperatures, in an effort to understand the important reactions that lead to the production of NH_3 . It is clear that the presence of Ar and H_2 ions leads to increased NH_3 production, possibly through charge-transfer reactions.

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