1	Plasma-Catalytic Ammonia Synthesis in a Dielectric Barrier Dis-									
2	charge Reactor: A Combined Experimental Study and Kinetic									
3	Modeling									
4	Supporting Information									
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## 20 1 Model inputs

21 The model uses several input parameters, as described in the computational method section (section 3) 22 in the main article. Table S1 shows the parameters determined from the examined  $N_2$ :H<sub>2</sub> feed ratios. Many 23 of these parameters were determined from the experimental findings, such as gas temperature  $(T_g)$ , gas 24 residence time ( $\tau_g$ ), and pressure. The number of micro-discharges per half cycle ( $N_{MD}$ ) and the lifetime 25 of a micro-discharge ( $au_{MD}$ ) are determined from the current measurements (see Figure S1). By plotting a Q-U Lissajous diagram (charge and voltage measurements), the charge transfer ( $Q_0$ ), the burning voltage 26 27  $(\Delta U)$ , the capacitance of the cell ( $C_{cell}$ ), the effective capacitance ( $\zeta_{diel}$ ), and the dielectric capacitance  $(C_{diel})$  can be determined as described in [1]. The average plasma power ( $\overline{P}$ , Equation S1) can be calculated 28 29 from these parameters. In these calculations, the partial discharging scenario was taking into account as 30 described by Peeters and van de Sanden [2]. The partial discharging scenario defines a non-discharging 31 fraction ( $\alpha$ ) of the volume (plasma volume not fully ignited), described by Equation S2, and a discharging 32 fraction ( $\beta$ ) described by  $\beta = 1 - \alpha$ , when operating with non-noble gases.

$$\bar{P} = 2U_b \Delta Q_D f_D = 2\left(1 + \frac{\alpha}{\beta} \frac{C_{cell}}{C_{diel}}\right) \Delta U \frac{Q_0}{1 - \frac{C_{cell}}{C_{diel}}} f_D \qquad \text{Eq S1}$$

$$\alpha = \frac{C_{diel} - \zeta_{diel}}{C_{diel} - C_{cell}}$$
 Eq. S2

In the experiments, a constant frequency  $(f_D)$  of 3.0 kHz was used, and therefore applied in the kinetic modeling. An average maximum and minimum instantaneous power can be calculated from the average plasma power, which is used to determine equivalent maximum and minimum power densities. From the power densities, the periodic power density function (p(t)) can be calculated, as described in [3]. The electric field (E) (Equation S3) can then be evaluated from p(t) and the electron conductivity ( $\sigma$ , Equation S4).

$$E = \sqrt{\frac{p(t)}{\sigma}}$$
 Eq S3

$$\sigma = e n_e \mu_e$$
 Eq. S4

39 In Equation S4, *e* is the elementary charge,  $n_e$  is the electron number density, and  $\mu_e$  is the electron

40 mobility, calculated by BOLSIG+.

	N2:H2	Tg [°C]	<i>Q</i> <sub>0</sub> [nC]	$\Delta U$ [V]	C <sub>cell</sub> [pF]	$\zeta_{diel}$ [pF]	N <sub>MD</sub>	$ au_{MD}$ [ns]	$\tau_g[s]$
No packing	3:1	100	749.1	4515	7.353	66.87	10	100	6.06
No packing	2:1	100	733.1	4630	7.168	69.03	11	100	6.09
No packing	1:1	100	734.9	4715	7.265	69.06	10	100	6.09
No packing	1:2	100	721.6	4675	7.308	72.68	12	100	6.09
No packing	1:3	100	693.0	4690	7.340	73.87	12	100	6.04
Packed	3:1	100	491.9	5400	10.37	72.19	36	100	2.10
Packed	2:1	100	522.5	5175	10.43	72.75	37	100	2.10
Packed	1:1	100	547.0	5115	10.50	73.21	42	100	2.09
Packed	1:2	100	563.4	4960	10.48	72.33	49	100	2.08
Packed	1:3	100	561.9	4900	10.49	73.21	44	100	2.08

41 Table S1. Case-specific parameters used as input to the plasma kinetic model.

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Figure S1 shows the measured current and voltage as function of time for the plasma alone, MgAl<sub>2</sub>O<sub>4</sub>, Ru/MgAl<sub>2</sub>O<sub>4</sub>, and Co/MgAl<sub>2</sub>O<sub>4</sub> at a plasma power of 20 W and a feed flow rate of 80 Nml/min with a feed ratio of N<sub>2</sub>:H<sub>2</sub>=1:1. It is clearly seen that the introduction of these materials alters the I-V characteristic, as the intensity in current spikes are lowered and almost disappear for the Co/MgAl<sub>2</sub>O<sub>4</sub>. This is likely do to enhanced surface discharges in the presence of metal particles. However, the number of micro-discharges per half cycle is increased drastically for packed compared to no packing (also see Table S1).



51 Figure S1. Experimental measurement of current and voltage for (a) plasma alone, (b) MgAl<sub>2</sub>O<sub>4</sub>, (c) Ru/MgAl<sub>2</sub>O<sub>4</sub>, and 52 (d) Co/MgAl<sub>2</sub>O<sub>4</sub> packing at 20 W, feed flow rate of 80 Nml/min and  $N_2$ :H<sub>2</sub>=1:1.

### 2 Effect of plasma power and feed flow rate on the NH<sub>3</sub> concentration and en-53

#### ergy balance 54

The effect of the plasma power on the NH<sub>3</sub> concentration is shown in Figure S2, for the plasma alone, 55 56 MgAl<sub>2</sub>O<sub>4</sub>, Ru/MgAl<sub>2</sub>O<sub>4</sub>, and Co/MgAl<sub>2</sub>O<sub>4</sub> packing. For the plasma alone, a plateau in the NH<sub>3</sub> concentration 57 is reached at 20 W for the N<sub>2</sub>-rich feed, while the concentration is slightly increasing for the equimolar feed ratio and the H<sub>2</sub>-rich feed. The MgAl<sub>2</sub>O<sub>4</sub> packing shows a clear optimal feed ratio (N<sub>2</sub>:H<sub>2</sub>=1:1), and 58

59 utilizing a feed ratio with either higher N<sub>2</sub> or H<sub>2</sub> content results in a similar effect. A shift to a better per-60 formance with a N<sub>2</sub>-rich feed compared to a H<sub>2</sub>-rich feed is observed for both Ru/MgAl<sub>2</sub>O<sub>4</sub> and 61 Co/MgAl<sub>2</sub>O<sub>4</sub>, with a feed ratio of N<sub>2</sub>:H<sub>2</sub>=1:1 and 2:1 yielding similar NH<sub>3</sub> synthesis rates.



Figure S2. NH<sub>3</sub> concentration as function of plasma power and feed ratio for (a) plasma alone, (b) MgAl<sub>2</sub>O<sub>4</sub>, (c)
Ru/MgAl<sub>2</sub>O<sub>4</sub>, and (d) Co/MgAl<sub>2</sub>O<sub>4</sub> packing, at a flow rate of 80 Nml/min.

The NH<sub>3</sub> concentration is found to decrease as the feed flow rate is increased for the plasma alone and the tested packing materials (Figure S3), as mentioned in the main article. A decrease of ca. 40 % in the NH<sub>3</sub> concentration is observed for the plasma alone when increasing the flow rate from 40 to 100 Nml/min, while the packing materials show a decrease of ca. 50 %.





Figure S3. NH<sub>3</sub> concentration as function of feed flow rate, at a plasma power of 20 W and a feed ratio of N<sub>2</sub>:H<sub>2</sub>=1:1.

The energy efficiency (g/kWh) is calculated as shown in Equation S5, where  $\dot{m}_{NH_3}$  is the mass flow rate of ammonia in g/h and P is the plasma power in kW.

$$\eta \left[ g/kWh \right] = \frac{\dot{m}_{NH_3}}{P}$$
 Eq. S5

Figure S4 shows the energy efficiency as function of plasma power for the investigated feed ratios (N<sub>2</sub>:H<sub>2</sub> =3:1-3:1) with no packing material (plasma alone) and with MgAl<sub>2</sub>O<sub>4</sub>, Ru/MgAl<sub>2</sub>O<sub>4</sub>, and Co/MgAl<sub>2</sub>O<sub>4</sub> in the plasma zone. Generally, the energy efficiency decreases as the plasma power increase, except for the Co/MgAl<sub>2</sub>O<sub>4</sub> at a feed ratio of N<sub>2</sub>:H<sub>2</sub> = 1:1 and with a higher N<sub>2</sub> content. For these cases the energy efficiency increases going from 15 to 25 W.



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83 The energy efficiency is found to increase with increasing feed flow rate (40 to 100 Nml/min) as shown in 84 Figure S5. Furthermore, the energy efficiency is observed to increase for all conditions when increasing 85 the temperature from 100 to 200 °C. The highest achieved energy efficiency of 1.19 g/kWh was obtained 86 with Co/MgAl<sub>2</sub>O<sub>4</sub> at a feed ratio of N<sub>2</sub>:H<sub>2</sub> = 1:1 and 210°C, which is significantly lower than the energy 87 efficiency of 150–200 g/kWh reported for small-scale traditional NH<sub>3</sub> synthesis technologies [4]. This low efficiency is likely a result of the high energy input needed to dissociate N<sub>2</sub> in the gas phase, where a 88 89 significant recombination also occur, which is in contrast to thermal catalysis where the presence of the 90 catalyst lowers the energy barrier needed for N<sub>2</sub> dissociation on the surface. To achieve a higher energy 91 efficiency it could be beneficial to only excite N<sub>2</sub>, either vibrationally (V) or electrically (X), such that the



92 dissociation occurs when  $N_2(V,X)$  adsorb on the catalyst surface [5].

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94 Figure S5. Energy efficiency as function of feed flow rate at (a) 100 °C and (b) 200 °C, at a plasma power of 20 W.

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# 96 **3 Effect of temperature on the Q-U figure**

A digital Picotech oscilloscope (Picoscope 6402C) recorded the electrical parameters of the NH<sub>3</sub> synthesis, as described in the main article. The measured applied voltage (U) and generated charges (Q) for the Co/MgAl<sub>2</sub>O<sub>4</sub> catalyst with and without insulation material are shown in Figure S6. Note that the insulation gives rise to a temperature of 200-210°C, as compared to 100 °C without insulation. Only a minor effect on the maximum and minimum value of the generated charges is observed from the addition of insulation (i.e., increased temperature), thereby changing the effective capacitance marginally [2].



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Figure S6. Q-U plot for the Co/MgAl<sub>2</sub>O<sub>4</sub> catalyst obtained with and without insulation material (Plasma power 20 W at 3.0 kHz and feed flow rate of 80 Nml/min with a feed ratio N<sub>2</sub>:H<sub>2</sub>=1:1).

## 106 **4 Additional model results and uncertainties**

107 The effect of increasing the number of surface sites and the temperature in the plasma kinetic model is 108 shown in Figure S7. Increasing the number of surface sites also yields an insight to having a lower specific 109 volume-to-surface area, essentially meaning that a larger surface area is utilized, which could be some of 110 the pore surface. In Figure S7, the NH<sub>3</sub> concentration is found to increase by a factor of 6 when increasing the number of surface sites from  $6 \times 10^{15}$  to  $6 \times 10^{16}$  and by a factor of 4 when increasing the number of 111 112 surface sites from 6 x  $10^{16}$  to 6 x  $10^{17}$ . The surface coverage of the individual species was found to be 113 different for the different number of surface sites applied (see Figure S8), which also affects the final NH<sub>3</sub> 114 concentration. Increasing the gas temperature from 100 to 200 °C raised the NH<sub>3</sub> concentration from 306 115 to 368 ppm, and shows the importance of accurate temperature measurements. In this work, the tem-116 perature was measured on the outside of the reactor wall, just after the plasma was turned off, which 117 therefore inflicts some uncertainty in the actual gas temperatures. In the model, the gas temperature and 118 the surface temperature are assumed to be the same. However, with the electric field present, a metal,

- such as cobalt (ferromagnetic), on the support material could be heated through electromagnetic induc-
- tion, causing the metal particles to become "hot spots" with thermal insulation from the support material.
- 121 The surface reaction temperature is therefore likely higher than the gas temperature.

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Figure S7. Effect of number of surface sites and temperature on the NH<sub>3</sub> concentration (flow rate of 80 Nml/min at
 N<sub>2</sub>:H<sub>2</sub>=1:1, plasma power of 20W at 3.0 kHz, and a particle size of 0.85-1.18 mm).

Figure S8 illustrates the surface coverage during the initial milliseconds and the first couple of micro-discharges for two different number of surface sites ( $n_{surf0} = 6 \times 10^{16}$  and  $6 \times 10^{17}$ ). The order of the species regarding high to low coverage is the same for the two cases, but the actual coverage values are different. Especially, NH(s) and NH<sub>2</sub>(s) show a lower peak and minimum coverage at the higher number of surface sites. Vice versa, the N(s) coverage is observed to be relatively stable with a coverage of ca.  $6.4 \times 10^{-4}$  for  $n_{surf0} = 6 \times 10^{17}$ . H(s) remains the main adsorbent and shows an almost constant coverage, with relative small drops (not noticeable in Figure S8) during the micro-discharges.



Figure S8. Fraction of empty sites and surface species as function of residence time for a)  $n_{surf0} = 6 \times 10^{16}$  and b) n<sub>surf0</sub> =  $6 \times 10^{17}$ .

In the previous work by van 't Veer et al. [3,5], it was stated that some of the rate coefficients utilized in the plasma kinetic model were taken from earlier models for NH<sub>3</sub> synthesis, which obtained the coefficients from a number of sources with diverse operating conditions. The rate coefficients are therefore subject to significant uncertainties. van 't Veer et al. [5] specifically point out that this may be a problem for the Eley-Rideal sticking coefficients, due to the lack of reliable kinetic data.

140 Interestingly, we observed in the main text (Figure 4) that the relative difference between the 141 unpacked and the packed setup was somewhat captured by the model, but the actual synthesis rates are 142 15-20 times lower than the experimental values. We believe that there could be several reasons for this 143 variance such as:

- 144
- Accuracy of electrical measurements
- Interpretation of the experimental electrical data and application in the model
- Too low rate coefficient of N<sub>2</sub> dissociation or too high rate coefficient of N<sub>2</sub> recombination and NH<sub>3</sub>
   dissociation (in the gas phase)
- Uncertainty in the surface reaction kinetic data [6–8] (the adopted rate coefficient model and the
   number of assumed available surface sites)

An important factor in the model is the power density distribution factor ( $\gamma$ ), which determines the minimum power density of the afterglow based on the maximum power density in a micro-discharge. This factor is determined based on the appearance of the experimentally obtained plasma power. However, agreement for both maximum and minimum power between the experimental and model values was not obtainable.  $\gamma$  was therefore determined to match the minimum power. Indeed, this could also be part of the reason for the lower NH<sub>3</sub> synthesis rate determined by the model, as changes in the  $\gamma$  previously has been shown to alter the NH<sub>3</sub> concentration [3].

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