

Plasma-Catalytic Ammonia Synthesis in a DBD Plasma: Role of Microdischarges and Their Afterglows

K. van 't Veer,* Y. Engelmann, F. Reniers, and A. Bogaerts*

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ABSTRACT: Plasma-catalytic ammonia synthesis is receiving ever increasing attention, especially in packed bed dielectric barrier discharge (DBD) reactors. The latter typically operate in the filamentary regime when used for gas conversion applications. While DBDs are in principle well understood and already applied in the industry, the incorporation of packing materials and catalytic surfaces considerably adds to the complexity of the plasma physics and chemistry governing the ammonia formation. We employ a plasma kinetics model to gain insights into the ammonia formation mechanisms, paying special attention to the role of filamentary microdischarges and their afterglows. During the microdischarges, the synthesized ammonia is actually decomposed, but the radicals created upon electron impact dissociation of N₂



and H_2 and the subsequent catalytic reactions cause a net ammonia gain in the afterglows of the microdischarges. Under our plasma conditions, electron impact dissociation of N_2 in the gas phase followed by the adsorption of N atoms is identified as a rate-limiting step, instead of dissociative adsorption of N_2 on the catalyst surface. Both elementary Eley–Rideal and Langmuir–Hinshelwood reaction steps can be found important in plasma-catalytic NH₃ synthesis.

1. INTRODUCTION

The potential applications of decentralized ammonia (NH_3) synthesis on small scale, that is, fertilizer production or energy storage,¹ have caused increasing interest in plasma-catalytic NH₃ synthesis.² Starting late 1960, the synthesis of NH₃ in plasma systems has been attributed to "wall effects," that is, the reactor walls and/or electrodes appear to have a (catalytic-like) contribution to NH₃ formation.² Especially dielectric barrier discharges (DBDs) have received major attention over the past few decades.²⁻⁷ DBDs are already commonly used in the industry, for example, ozone generation,⁸ and are quite well understood. However, for plasma-catalytic synthesis, typically a packing material is introduced into the reactor, yielding a socalled packed bed DBD (PB DBD), greatly increasing the complexity. The packing support material and the catalytic material applied on the support influence the discharge characteristics⁹ and reaction kinetics. In addition, the discharge characteristics and reaction kinetics, especially in the plasma itself, are closely tied to each other. The radicals or excited molecules created in the plasma can, in turn, either influence the physical properties of the catalytic surface¹⁰ or steer the surface reaction kinetics.^{11,12} This causes a complexity that is difficult to resolve with experimental studies only. Hence, modelling studies are helpful, allowing to disentangle the different effects. At the same time, the sheer amount of choice for catalytic and support materials and their intrinsic properties, in combination with the lack of data in the literature on the catalytic reaction rates, make it difficult to capture in detail the full complexity of plasma catalysis in a single model. Therefore, the combination of individual modelling and experimental studies with properly set boundaries can increase our understanding of plasma-catalytic mechanisms. Particularly, NH_3 synthesis from N_2/H_2 feed gas is an important case study because of the simplicity of the reaction (*i.e.*, only NH_x as reaction products).

Mehta et al. proposed that vibrational excitation of N2 can increase the NH₃ synthesis rate by decreasing the dissociative adsorption energy barrier.¹¹ Rouwenhorst et al. confirmed by additional experiments that indeed vibrational excitation in the plasma helps to overcome this barrier and that further hydrogenation toward NH₃ happens on the catalytic surface.¹² However, the specific energy input (SEI) of the DBD plasma was relatively low when compared to typical DBD values, as reported in ref 3. Many researchers observed an increasing NH₃ synthesis rate with increasing plasma power (or SEI).^{13–17} Aihara et al. proposed that NH₃ synthesis occurred through the adsorption of electronically excited N2 with further hydrogenation on the surface based on a direct correlation between the NH₃ synthesis rate and electronically activated N₂.¹³ Zhu et al. also hypothesized that electronically excited metastable N₂ aids in the adsorption processes.¹⁸ Bai *et al.* assumed ionization

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Supporting Information

and H_2 and the subsequent catalytic reactions cause a net ammonia gain in the afterglows of the microdischarges. Under our plasma conditions, electron impact dissociation of N_2 in the gas phase followed by the adsorption of N atoms is identified as a rate-limiting step, instead of dissociative adsorption of N_2 on the catalyst surface. Both elementary Eley–Rideal and Langmuir–Hinshelwood reaction steps can be found important in plasma-catalytic NH₃ synthesis.

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Mehta et al. proposed that vibrational excitation of N2 can increase the NH₃ synthesis rate by decreasing the dissociative adsorption energy barrier.¹¹ Rouwenhorst et al. confirmed by additional experiments that indeed vibrational excitation in the plasma helps to overcome this barrier and that further hydrogenation toward NH₃ happens on the catalytic surface.¹² However, the specific energy input (SEI) of the DBD plasma was relatively low when compared to typical DBD values, as reported in ref 3. Many researchers observed an increasing NH₃ synthesis rate with increasing plasma power (or SEI).^{13–17} Aihara et al. proposed that NH₃ synthesis occurred through the adsorption of electronically excited N2 with further hydrogenation on the surface based on a direct correlation between the NH₃ synthesis rate and electronically activated N₂.¹³ Zhu et al. also hypothesized that electronically excited metastable N₂ aids in the adsorption processes.¹⁸ Bai *et al.* assumed ionization

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to be detrimental for NH₃ formation.¹⁴ Akay and Zhang argued that NH plasma radicals are most likely created between N and H₂ and that NH₃ can be formed by further hydrogenation reactions in the gas phase. At the same time, they also reported NH₃ formation due to hydrogenation on the surface, starting with N₂ and H₂ adsorption, but the gas phase and surface reaction pathways were not linked to each other.¹⁵ Peng et al. reported the stepwise hydrogenation on the surface as the faster pathway.¹⁶ Hong *et al.* performed a detailed kinetic analysis with and without a catalytic surface. They found that the surfaceadsorbed N atoms [*i.e.*, N(s)] were formed mainly by dissociative adsorption of ground-state N2 molecules, followed by the first vibrational level and direct adsorption of N atoms. H(s) was also mainly formed by dissociative adsorption from ground-state H₂ molecules, but followed by direct adsorption of H atoms and only then by dissociative adsorption from the first vibrational level. The rate of H(s) formation was 4 orders of magnitude higher than that of N(s). The authors considered not only stepwise hydrogenation on the surface but also reactions between gas-phase radicals and surface-adsorbed species [socalled Eley-Rideal (ER) reactions], and they actually found that the reaction of gas-phase NH_2 with H(s) was more important in the formation of NH₃.¹⁹

It is clear that the existing studies claim different processes to be important, so there is a clear need for a more detailed understanding. The mentioned studies were all specific to DBDs, but to our knowledge, the strong filamentary microdischarges and what happens in between them are typically not considered separately in the assessment of the reaction mechanisms.

Therefore, in this study, we present a reaction kinetics analysis based on a zero-dimensional (0D) plasma kinetics model, in which we explicitly capture the filamentary behavior of an experimental PB DBD. In the assessment of the reaction mechanisms, we pay special attention to the separate notion of the filamentary microdischarges and their afterglows. We consider both elementary ER and Langmuir–Hinshelwood (LH) reaction steps. The LH reactions correspond to the classical (thermal) hydrogenations on the surface, while the ER reactions describe the interaction of plasma radicals with the surface-adsorbed species. We will discuss the evolution of the species densities and reaction rates as well as the overall NH₃ formation mechanisms.

2. COMPUTATIONAL DETAILS

We used a time-dependent 0D plasma kinetics model, called ZDPlasKin, 20,21 to investigate the plasma-catalytic synthesis of NH₃ from a N₂/H₂ 1:3 stoichiometric gas mixture in a PB DBD at 400 K and atmospheric pressure. This plasma kinetics model uses rate coefficients from the literature to describe the density evolution of various species, that is, the precursor gases, various plasma radicals, electrons, various ions, electronically and vibrationally excited molecules, as well as surface-adsorbed atoms and molecules. The rate coefficients and the concentrations of these species provide the actual reaction rates, which in turn govern the time evolution of all these species, described by the continuity equation

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = S_i = \sum_r c_{i,r} R_r = \sum_r c_{i,r} \left(k_r \prod_c n_c \right) \tag{1}$$

where n is the concentration or density of species i, S is the source term, c is the stoichiometric number of the species in

reaction r, R is the reaction rate, k is the rate coefficient, and the subscript c represents the colliding species in the reaction.

The considered gas phase and surface kinetics were reported in our recent paper²² and are also listed in the Supporting Information (Section S1.1). The surface kinetics use reaction rates based on sticking coefficients corresponding to a metal surface, which could be related to iron,^{19,23–27} and they describe the catalytic reactions leading to N, H, and NH_x adsorption or hydrogenation and the eventual desorption of NH₃. Both elementary ER and LH reaction steps are included.

We assume a surface site density of 10^{15} cm⁻², which is generally representative of metal surfaces.²⁴ This value, together with the volume-to-surface area ratio of the reactor, is used to convert the rate coefficients of the catalytic reactions from s⁻¹ to cm³ s⁻¹ or cm⁶ s⁻¹ in the case of dissociative adsorption. A volume-to-surface area ratio of 0.007 cm was used.²³ Any change in these parameters would cause an equal change in the rate coefficients of all surface reactions, that is, the relative surface reaction rates remain the same.

The surface kinetics are subject to many assumptions and thus also to uncertainties. That includes the exact surface described, that is, step or surface sites. We describe the surface as being representative of iron, merely for reference and context. A detailed description of the surface kinetics would require microkinetics models.^{11,28,29} The latter type of model uses surface reaction rates more closely derived from density functional theory calculations and generally solves a system under steady-state conditions while not including a full gasphase chemistry. To our knowledge, such models have not yet been combined with a full time-dependent plasma kinetics model, as developed in the present study. The present study focusses mainly on the plasma chemistry and the temporal discharge behavior (i.e., the role of microdischarges and their afterglows). We believe it provides important insights that will allow to better focus on future studies, considering that such a combined model would yield an increased number of degrees of freedom (such as the surface, described by the surface binding energy).

We chose to only describe one surface in our model and neglect the wall effect² due to the electrodes or dielectric barrier, which represents different gas–surface interfaces. Indeed, those surfaces would require different kinetic parameters which are subject to the same uncertainties.²⁵ Furthermore, recent experimental insights show us that the NH₃ formation in an empty reactor is very low compared to a reactor packed with supports (Al₂O₃) and that both cases are significantly lower than when a (metal) catalyst is loaded onto the supports.

The principles to capture the properties of a PB DBD in a 0D model, that is, how the applied plasma power is distributed over the microdischarges and their afterglows, are also described in our previous work.²² In the present work, we derive the plasma conditions from experimentally measured current and voltage characteristics of a PB DBD (see Figures S2 and S3 in the Supporting Information). The average plasma power was 68 W, and a discharge frequency of 23.5 kHz was applied. The reactor volume was 20 mL. The flow rate was 100 mL/min. The reactor was packed with 1.9-2.0 mm diameter Al₂O₃ beads. The measured electrical characteristics determine the plasma parameters during the calculations. Generally, we see no large difference in these characteristics between the Al₂O₃ supports alone and when a metallic coating (5-10 wt %) is on the beads. A detailed translation of the experimental conditions is given in the Supporting Information (Section S1.2).

To summarize, we mimic the microdischarges by applying the experimentally measured plasma power over 50 triangular pulses with a pulse duration of 200 ns (100 ns at full width at halfmaximum) equally spaced over the residence time of 3.84 s. In practice, there will be millions of microdischarges in the reactor during this typical residence time, but individual gas molecules are never exposed to all microdischarges. Therefore, we consider that individual gas molecules see, on average, 50 microdischarges over their full gas residence time. This number is based on the average number of microdischarges that we counted during a single discharge cycle. Each microdischarge is followed by weaker plasma conditions with 76.8 ms duration, which we refer to as the afterglow of a microdischarge. In addition, the first microdischarge in the model starts at 38.4 ms to account for the gas that is already present in the plasma reactor before being exposed to an actual microdischarge.

The adopted maximum and minimum instantaneous plasma power (*i.e.*, during the microdischarges and their afterglows) correspond to 332 and 33 W, respectively, based on the typical experimentally measured instantaneous plasma power. These values are converted to a maximum and minimum power density of 3.4×10^6 and 12 W/cm^3 for the microdischarges and their afterglows, respectively. The discharge volumes used in these conversions are based on the microdischarge and reactor volume, respectively, as described in detail in the Supporting Information (Section S1.2). This power is used to heat the electrons, allowing us to also self-consistently calculate the reduced electric field in our model.²²

3. RESULTS AND DISCUSSION

We studied the production and destruction mechanisms of NH_3 and its precursors during a single microdischarge and its afterglow. We evaluated the mechanisms in all successive microdischarge and afterglow pairs and found that the most important reactions are always the same. Therefore, in the following sections, we focus on the reaction kinetics in the first microdischarge and afterglow pair, as well as the overall NH_3 evolution during the full residence time.

3.1. Surface Coverages and Plasma Species Densities in the Microdischarges and Their Afterglows. Our model predicts that the electrons, plasma radicals, and surfaceadsorbed species [indicated with (s)] govern the most important reactions taking place, leading to NH_3 production. Some of these species are mainly important in the microdischarges, while others mainly in the afterglows. Figure 1a depicts the surface coverage from the start of the plasma until the end of the first afterglow, while in Figure 1b, the concentrations of the gas-phase species are plotted.

The first afterglow ends after approximately 115 ms. At this time scale, the 200 ns microdischarge pulse is not resolved in Figure 1. For the sake of completeness, we plot the time evolutions of the various species during the microdischarge alone in the Supporting Information (Section S2 and Figure S5). Typical densities of all species in Figure 1 are also summarized in Table S8.

Figure 1 shows that all adsorbed and gas-phase species rise (either quickly or more gradually) during the first (few) ms and reach a plateau after approximately 15 ms, that is, well before the first microdischarge takes place, while the fraction of empty sites decreases over 3 orders of magnitude. H(s) is the main adsorbate, and both H(s) and N(s) reach their plateau within 0.3 ms. The coverages or concentrations of NH(s), $NH_2(s)$, H, N, electrons, NH, and NH_2 clearly increase due to the



Figure 1. Surface coverages and fraction of empty surface sites (a) and number densities of the neutral gas-phase species and electrons (b) as a function of time in the plasma, from the start of the plasma to the end of the first microdischarge and afterglow pair. The microdischarge with 200 ns duration takes place at 38.4 ms. The feed gas was N_2/H_2 1:3, and the N_2 and H_2 densities were approximately 4.6×10^{18} and 1.4×10^{19} cm⁻³, respectively.

microdischarge (up to 6 orders of magnitude), after which they drop back smoothly to almost their original values over approximately 20 ms, but both NH and NH₂ rise slightly again in the late afterglow. The N(s) coverage stays almost constant during the microdischarge, but rises in the early afterglow, while H(s) is the main adsorbate throughout. The latter is initially due to the dissociative adsorption, which has an initial high reaction rate, and then due to radical adsorption (which is discussed later and in Supporting Information Section S4 and Figure S12). The NH₃ concentration decreases during the microdischarges (but only slightly in the first microdischarge where the NH₃ concentration is still low, see Figure S5b) but rises in the early afterglow.

Figure 1b shows that radicals are already present in the gas phase before the first microdischarge. This is due to the non-zero power density outside of the microdischarges. Thus, the electrons are already slightly heated by a small amount of power deposition, allowing for electron impact reactions that create the various plasma radicals. However, the reaction rates are of course small compared to the microdischarge itself.

It is also clear from Figure 1b that besides the H_2 and N_2 gas molecules (with concentrations of approximately 75 and 25% or 1.4×10^{19} and 4.6×10^{18} cm⁻³, respectively; not plotted in Figure 1), the H atoms have the highest density in the plasma $(1.2 \times 10^{17} \text{ and } 1.0 \times 10^{14} \text{ cm}^{-3} \text{ in the microdischarge and afterglow, respectively, corresponding to an H₂ dissociation$



Figure 2. Number densities of the N_2 (solid lines) and H_2 (dashed lines) molecules in the ground state and the sum of the electronically and vibrationally excited states as a function of time in the plasma, from the start of the plasma to the end of the first microdischarge and afterglow pair. The microdischarge with 200 ns duration takes place at 38.4 ms.

degree of 0.4 and 0.0004%, respectively), followed by NH₃ (up to 38 ppm or 6.9×10^{14} cm⁻³ after the first microdischarge and afterglow pair). The N atom density is 2 orders of magnitude lower than that of H, corresponding to a maximum concentration of 8.4×10^{14} cm⁻³ in the microdischarge and an N₂ dissociation degree of 0.01%, attributed to the much higher bond strength of N₂ (9.8 eV) *vs* H₂ (4.5 eV).³⁰ The NH radical density (1.5×10^{11} cm⁻³) is the same order of magnitude as the N atom density in the afterglow, while the NH₂ density is 1 order of magnitude higher (1.9×10^{12} cm⁻³).

Of course, this figure applies to the first pair of microdischarge and afterglow. The picture is a bit different after a periodic steady state is reached, at least for the NH_3 concentration, because NH_3 will accumulate during successive microdischarge and afterglow pairs, while the other plasma species already reach a periodic steady state after the first pair (see discussions in the next section).

Under the present DBD plasma conditions, the electron impact collisions with N_2 and H_2 typically involve not only the ground state but also both the electronically and vibrationally excited molecules. In Figure 2 we show the time-evolution of the number densities of N_2 and H_2 in the ground state as well as in the vibrationally and electronically excited states, while in Figure 3 we plot the N_2 vibrational distribution function (VDF) in the microdischarges at various moments in time. The timeevolution of the number densities in the microdischarge is depicted in the Supporting Information (Section S2 and Figure S6) as well as the H_2 VDF for completeness (Figure S7).

Clearly, in the afterglows, the vibrationally excited N_2 and H_2 molecules are higher in density than the electronically excited molecules, and this is most apparent for N_2 . The vibrational temperature is approximately 700 K in the afterglows (*cf.* Figure S8a). Also, during the microdischarges, the vibrationally excited N_2 molecules have a higher density than the electronically excited states, and the vibrational temperature reaches 2100 K. On the other hand, the electronically excited H_2 molecules have a higher density excited states during the microdischarges (*cf.* Figure S6). The N_2 VDF shows a clear overpopulation compared to a Boltzmann distribution at the gas temperature, both at the start and especially during the microdischarges. Note that the start of a microdischarge corresponds to the end of the previous afterglow. An



Figure 3. N_2 VDF at various moments in the microdischarge as well as the Boltzmann distribution at the gas temperature (400 K).

overpopulation is also observed in the afterglows because of the non-zero power deposition between the microdischarges, which allows for continuous electron impact vibrational excitation, in turn causing a nonequilibrium compared to the gas temperature of 400 K.

3.2. Production and Destruction of Plasma Radicals, Adsorbed Species, and NH₃ in the Microdischarges and Their Afterglows. To illustrate more clearly whether species are being produced or destroyed during the microdischarges and the afterglows, we present in Figure 4 their time-averaged source terms for a single microdischarge and its afterglow separately. As noted before, NH₂(s), NH(s), NH₂, N(s), and especially NH, H, N, and the electrons are net produced during the microdischarges. For all these neutral species, the source term in the afterglows is destructive but small (compare red bar to the gray background and keeping in mind the log-scale), except for H, which is largely destroyed, and N(s), which is also produced in the afterglow, but again the net production is relatively small (cf. gray background). In other words, the actual production and destruction in the afterglows (gray bars) are nearly equal for all these species, which means that upon formation, the species are quickly converted into other species. For the electrons, the destruction far exceeds the production in the afterglows. This is attributed to the lack of electron impact ionization processes in the afterglows, where the plasma is significantly weaker compared to the microdischarges.

In contrast to the above species, NH₃ is largely destroyed during the microdischarges and produced in the afterglows. Likewise, the N₂ and H₂ ground-state molecules also exhibit high loss rates during the microdischarges because they are converted into reactive species by the electron impact reactions, but their population slightly increases again in the afterglows because of recombination of these reactive species. This is also illustrated in Figure 5, showing the time-averaged source terms of the ground states and electronically and vibrationally excited molecules of both H₂ and N₂. During the microdischarges, the ground-state H₂ and N₂ molecules get destroyed, while the electronically and vibrationally excited molecules are produced, and the opposite is true for the afterglows. The production of the N₂ vibrational levels in the microdischarges and the subsequent depopulation in the afterglows are most pronounced, corresponding to their highest number density (cf. Figure 2).

In general, the average production and destruction rates and thus the species source terms are much larger in the



Figure 4. Time-averaged species source terms in the first microdischarge and its afterglow of the surface-adsorbed and neutral gas-phase species and the electrons. The source term is either positive or negative, representing net production (top *y*-axis) and net destruction (bottom *y*-axis), respectively. The logarithm of the (absolute) source terms S_i is plotted. The gray bars indicate the total production and destruction source terms of the species *i*, $S_{i,p}$ and $S_{i,d}$, respectively. The net production or destruction $S_i = S_{i,p} - |S_{i,d}|$. Note: the units of *S* are in cm⁻³ s⁻¹. Comparing the blue or red bars with the gray background reveals whether production is much larger than destruction (or *vice versa*) (*i.e.*, when the blue or red bar is as large as the gray background) or whether they are nearly equal to each other (*i.e.*, when the blue or red bar is smaller than the gray background). In other words, the colored bars correspond to the source terms S_i (*cf.* eq 1 and *y* axis labels) which can either be positive (production, upper panel) or negative (destruction, lower panel), and the gray background specifically corresponds to $S_{i,p}$ and $S_{i,d}$ in the microdischarge and its afterglow.



Figure 5. Time-averaged species source terms in the first microdischarge and its afterglow of the ground state (X), electronically excited (E), and vibrationally excited (V) H_2 and N_2 molecules. *cf.* caption of Figure 4 for more information.

microdischarges than in the afterglows (*i.e.*, typically 10^{16} to 10^{23} cm⁻³ s⁻¹ vs 10^{14} to 10^{18} cm⁻³ s⁻¹), attributed to the stronger plasma environment (*cf.* the difference in power density, mentioned in Section 3) and the associated high radical and electron densities. However, the microdischarge lifetime is significantly shorter than the afterglow duration (*i.e.*, 200 ns vs 76.8 ms).

Hence, to determine whether the various species accumulate or drop in consecutive microdischarge and afterglow pairs, we also need to account for the duration of the microdischarge and afterglow. We calculate the average production-to-destruction ratio across one pair with

$$\frac{P}{D} = \left| \frac{S_{\text{afterglow}} \times \tau_{\text{afterglow}}}{S_{\text{micro-discharge}} \times \tau_{\text{micro-discharge}}} \right|^{\alpha}$$
(2)

where *S* is the average source term (*i.e.*, production minus destruction; red and blue bars in Figures 4 and 5) of a species in the afterglow or microdischarge, τ is the duration of the afterglow or microdischarge, and α is given by

$$\alpha = \begin{cases} 1, & S_{\text{afterglow}} > 0 \text{ and } S_{\text{micro-discharge}} < 0 \\ -1, & S_{\text{afterglow}} < 0 \text{ and } S_{\text{micro-discharge}} > 0 \end{cases}$$
(3)

For all gas-phase and surface-adsorbed species, including electronically and vibrationally excited molecules, eq 2 yields a value of approximately 1, except for NH_3 . This means that the surface coverages and gas-phase concentrations of all species very quickly reach a periodic steady state, while NH_3 is able to accumulate by the consecutive microdischarges and afterglows, as shown in Figure 6.



Figure 6. Production-to-destruction ratio of NH_3 based on the net production in the afterglows and net destruction in the microdischarges (eq 2, left *y*-axis) and NH_3 concentration (right *y*-axis) as a function of time (bottom *x*-axis) and microdischarge pulse number (top *x*-axis).

In this figure, the vertical lines in the NH_3 concentration correspond to the destruction of NH_3 in each microdischarge, followed by the strong rise in the beginning of each subsequent afterglow. Considering that the electron concentration immediately reaches a periodic steady state, it is logical that the drop in each microdischarge increases with rising NH_3 concentration as the electron impact dissociation rate is proportional to the NH_3 concentration. We identified this process as the main loss mechanism of NH_3 in the microdischarges. The NH_3 production in the afterglows has to overcome this dissociation

in the microdischarges in order to increase the overall NH_3 concentration. Note that electron impact dissociation still occurs in the afterglows as well, despite a very low electron density. Hence, even in the afterglows, electron impact dissociation determines the eventual steady-state NH_3 concentration.

The presented results are for a stoichiometric feed gas ratio (i.e., N_2/H_2 of 1:3), but our model predicts the NH₃ concentration to reach values up to 2000 ppm at higher N₂ contents (not shown). Indeed, for plasma-catalytic NH₃ synthesis, the optimal ratio does not necessary correspond to the stoichiometric gas ratio, among others, because N₂ dissociation requires more energy than H_2 dissociation.³⁰ Furthermore, while we believe that the adopted plasma conditions in our model are representative for a PB DBD, the exact conditions, however, are subject to uncertainties. Therefore, higher NH₃ yields may be reached by using other input values, such as the maximum and minimum instantaneous power, the microdischarge volumes, and the number of microdischarges. However, we have generally observed no drastic differences in reaction mechanisms as a function of these model parameters (see also the species density evolution in our previous work under different conditions²²). Therefore, while the exact species concentrations in Figures 1 and 6 must be considered with caution, as they depend on the conditions assumed in the model, the qualitative reaction mechanisms and the related discussions presented in the next sections should still contribute to a better insight.

3.3. NH₃ Formation: Reaction Rates and Determination of the Rate-Limiting Step. In reaction kinetics, the complete system can reach a steady state, meaning that the plasma parameters and the various species concentrations remain unchanged as a function of time, but reactions can still take place, with the total production and destruction rates of species being equal to each other. When in a chain of consecutive reactions, the reaction rate of the final reaction is equal to those of the preceding steps, the rate-limiting step can be determined. A DBD is a periodic discharge, and thus such steady state is not evident. Instead, a periodic steady state might be reached, that is, each discharge period becomes identical.

Our calculations reveal that electron impact dissociation of N₂ in the plasma, followed by N adsorption on the catalyst surface, is the rate-limiting step for NH₃ synthesis at our conditions and not dissociative adsorption of N₂. This can be explained by the observation that shortly after a microdischarge, when NH₃ increases (cf. Figure 1b), multiple surface catalytic reaction rates are almost equal to each other. This is true for the formation of NH₃ as well as the NH₃ precursors. Hence, all intermediate surface species, that is, N(s), NH(s), and $NH_2(s)$, created during the afterglows are immediately converted toward NH₃ according to our model. In addition, electron impact dissociation of the feed gas becomes negligible during this period. The NH₃ formation rate was found to be equal to the various adsorption rates of N atoms, that is, both direct adsorption and the ER reaction between N and H(s). As mentioned, in the early afterglow, the N atom source (electron impact dissociation of N_2) is not present, and thus, the N atoms are consumed by adsorption, reducing the N density and thus also the N adsorption rate. Consequently, the rates of the further processes (*i.e.*, hydrogenation steps) that exhibit the same rate as the N atom adsorption also drop and thus also the densities of the NH₃ precursors [*i.e.*, NH(s) and NH₂(s), *cf.* figure 1a]. We summarize this observation in Figure 7, while in Figure 8 we



Figure 7. Graphical summary of the detailed analysis presented in the Supporting Information (Section S4) showing surface reaction rates that are identical shortly after the microdischarge (indicated with the arrow) and the N₂ electron impact dissociation rate in the plasma as a function of time, from the start of the plasma to the end of the first microdischarge and afterglow pair. The microdischarge with a 200 ns duration takes place at 38.4 ms. The electron impact N₂ dissociation rate, and thus the N atom source, become negligible after the microdischarge. The first group of overlapping reaction rates (1) consists of N + H(s) \rightarrow NH(s), NH(s) + H(s) \rightarrow NH₂(s), and NH₂(s) + H(s) \rightarrow NH₃. The second group of overlapping reaction rates (2) consists of N + surface \rightarrow N(s) and H + N(s) \rightarrow NH(s). The reactions are also depicted in Figure 8.



Figure 8. Schematic diagram of the various surface reactions, starting with N atoms, which form NH_3 shortly after a microdischarge. The blue and red arrows correspond to the reactions in group (1) and (2) in Figure 7, respectively.

schematically depict the involved surface reaction mechanisms. A more detailed analysis is presented in the Supporting Information (Section S4). We note that the mechanisms in Figure 8 are in principle subject to the actual catalytic surface and the temperature at which the process takes place.

As part of our detailed analysis (cf. Supporting Information, Section S4), we saw a relatively large increase in NH₃ concentration when increasing the N atomic adsorption rates [*i.e.*, N + surface \rightarrow N(s), N + H(s) \rightarrow NH(s), and N + N(s) \rightarrow N_2] and an even larger increase when increasing the N_2 electron impact dissociation rate (cf. Figure S14). We conclude that, among the surface reactions, the adsorption of N atoms is the rate-limiting step, both through the ER reaction between N and H(s) and direct adsorption of N, which leads to the other ER reaction, H + N(s) (see Figure 8: blue and red arrows, respectively). This is attributed to both the relatively low N atom gas-phase density and the large H(s) surface coverage. Note that the latter reaction is less significant to the formation of NH(s)[cf. Figure 7, group (2) compared to group (1)] under the conditions investigated. It is clear that the rate of these reactions can be increased by increasing the N atom density, that is, by a

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Figure 9. N_2 electron impact dissociation rates from the ground state (X) and electronically (E) and vibrationally (V) excited states in the plasma as a function of time, from the start of the plasma to the end of the first microdischarge and afterglow pair (a) and as a function of time in the first microdischarge (b). In (a), the microdischarge with a 200 ns duration takes place at 38.4 ms.

higher N_2 gas-phase dissociation. Thus, we conclude that electron impact N_2 dissociation in the plasma, followed by N adsorption on the surface, is the rate-limiting step determining the NH₃ yield in our DBD. In other words, we do not find that the dissociative N_2 adsorption, from the ground state or vibrational levels, due to the surface itself is rate limiting.

3.4. N₂ Dissociation Rates in the Plasma. The dissociation of N2 in the plasma occurs exclusively by electron impact collisions. In Figure 9, we show the various electron impact N₂ dissociation rates as a function of time. The dissociation is only significant in the microdischarges, and consequently, the N atoms are consumed directly after the microdischarges. In our previous work, we showed that even in a filamentary DBD, vibrational excitation and thus dissociation from vibrational levels can be important.²² In experiments, high N₂ vibrational temperatures were also reported for PB DBDs.^{11,31} Colonna et al. showed the significance of the VDF and electron energy distribution function in strong nanosecond pulsed N_2 and H_2 discharges.^{32,33} As discussed before, our model predicts a maximum N₂ vibrational temperature slightly above 2100 K during the microdischarges at the conditions under study, and it relaxes back to slightly above the gas temperature (700 K compared to 400 K) in the afterglows over approximately 1 ms (cf. Supporting Information Section S3 and Figure S8a). Thus, vibrational excitation is quite prominent during the microdischarges. The reduced electric field (E/N)and electron temperature are also plotted as a function of time in the Supporting Information (Section S3 and Figure S8b). The maximum E/N was calculated to be 105 Td in each microdischarge, and the maximum electron temperature (T_e) was 5.9 eV. In the afterglows, they reach constant values, around E/N = 6 Td and $T_e = 0.7$ eV.

When comparing the N_2 dissociation rates from the ground state, vibrational levels, and electronically excited states in Figure 9, it is clear that ground-state dissociation is always the highest, followed by dissociation from the vibrational levels in the afterglows and from the electronically excited levels during the microdischarges. However, dissociation from the vibrational levels during the microdischarges is still high and contributes 8% to the total electron impact N_2 dissociation, while the contribution of the ground state and the electronically excited states is 73 and 19%, respectively. Compared to the microdischarges, the dissociation in the afterglows is much lower and mainly due to the ground state (98.4%), but dissociation from the vibrational levels (1.6%) is higher than from electronically excited levels (only 0.0001%). Even if we account for the duration of the microdischarges (200 ns) and afterglows (76.8 ms), similar to before (*cf.* eq 2), we find that 99% of all N_2 electron impact dissociation occurs during the microdischarges.

Many authors reported an increase in NH₃ yield upon increasing plasma power or applied voltage.^{13–17} A higher plasma power or applied voltage leads to a stronger plasma and thus higher electron densities and/or energies and faster electron impact processes, including N₂ dissociation. Hence, these experimental observations from the literature qualitatively support our model prediction that electron impact N₂ dissociation in the plasma directly affects the NH₃ formation rate, or in other words, that it can be considered the rate-limiting step for NH₃ formation in DBD plasma.

3.5. NH₃ Formation Reaction Scheme for the Microdischarges and Their Afterglows. Based on the preceding sections, we can summarize the NH₃ formation mechanisms as follows, as revealed by our model. First, dissociative adsorption of H₂ covers the surface with H(s) before the first microdischarge occurs because of the large amount of free surface sites (*cf.* Figure 1a and Supporting Information, Section S2).

$$H_2 + surface \rightarrow H(s) + H(s)$$
 (4)

Subsequently, during the microdischarges (indicated with md), first electron impact dissociation of the feed gases takes place from the ground state and also from the electronically and vibrationally excited states (*cf.* Figure 9)

$$(md) e^{-} + N_2(X, V, E) \rightarrow e^{-} + N + N$$
 (5)

$$(md) e^{-} + H_2(X, V, E) \rightarrow e^{-} + H + H$$
 (6)

The dissociation is enhanced by the high electron density and high electron energy in the microdischarges (*cf.* Figures 1b and S8b). The high electron density is a result of ionization of the feed gases.

(md) $e^{-} + N_2 \rightarrow e^{-} + e^{-} + N_2^{+}$ (7)

(md)
$$e^- + H_2 \rightarrow e^- + e^- + H_2^+$$
 (8)

In addition, dissociation of H_2 also occurs upon collisions with electronically excited N_2 (contribution of 10%).

$$(md) e^{-} + N_2 \rightarrow e^{-} + N_2(E)$$
 (9)

$$(md) N_2(E) + H_2 \rightarrow N_2 + H + H$$
 (10)

During the microdischarges, the formation of $NH_2(s)$ from NH and H(s) (ER reaction) is also significant, and even more, it

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only happens significantly during the microdischarges (*cf.* Figure S9). The full pathway of this formation mechanism is as follows

$$(md) e^- + H_2 \to e^- + H_2(E)$$
 (11)

$$(md) N + H_2(E) \rightarrow H + NH$$
(12)

$$(md) NH + H(s) \to NH_2(s) \tag{13}$$

This causes some depletion of H(s) on the surface, but the latter is immediately compensated by the supply of fresh H(s) upon H atom adsorption in the afterglows (indicated with ag) (*cf.* Figures S12 and S13).

$$(ag) H + surface \rightarrow H(s) \tag{14}$$

Note that during the microdischarges, H(s) is also consumed via the very large number of H atoms in the plasma (cf. Figure 1b and Supporting Information, Section S2).

$$(md) H + H(s) \to H_2 \tag{15}$$

H atom recombination is also reported by Shah *et al.* to be more significant due to the surface in comparison with gas-phase reactions.³⁴

Looking further to the NH_3 formation, the NH_3 precursors are formed according to the same reactions during both the microdischarges and afterglows, that is, a combination of ER and LH reactions (*cf.* Figures 7 and 8).

$$(md + ag) N + H(s) \rightarrow NH(s)$$
 (16)

$$(md + ag) N + surface \rightarrow N(s)$$
 (17)

$$(md + ag) H + N(s) \rightarrow NH(s)$$
 (18)

$$(md + ag) NH(s) + H(s) \rightarrow NH_2(s)$$
 (19)

Finally, NH_3 is formed by the following LH reaction (*cf.* Figures 7 and 8).

$$(md + ag) NH_2(s) + H(s) \rightarrow NH_3$$
(20)

This process takes place both during the microdischarges and their afterglows, but in the microdischarges, a larger fraction of NH_3 is dissociated (*cf.* Figure 4) because of the high electron density.

$$(md + ag)e^{-} + NH_3 \rightarrow e^{-} + NH_2 + H$$
 (21)

$$(md + ag) e^- + NH_3 \rightarrow e^- + NH + H_2$$
(22)

The same reactions govern the eventual NH₃ yield, that is, in the steady state, in the afterglows (*cf.* Figure 6). In other words, reactions 21 and 22 balance with the NH₃ formation in the late afterglow because of the high NH₃ density, in spite of the low electron density in the afterglows (*cf.* Figure 1b). The most significant NH₃ formation in the late afterglow is actually the ER reaction with NH₂.

$$(ag) NH_2 + H(s) \rightarrow NH_3$$
(23)

It should be noted however that this reaction does not contribute to the actual net NH_3 formation (*cf.* Figures 1 and S9a). NH_3 is mainly formed by reaction 20.

The electrons created in the microdischarges are lost in the afterglows because of the recombination reactions.

$$(ag) e^{-} + H_3^{+} \to H_2 + H$$
 (24)

$$(ag) e^{-} + H_{3}^{+} \rightarrow H + H + H$$
 (25)

$$(ag) e^{-} + N_2 H^{+} \rightarrow N_2 + H$$
 (26)

The formation of these ions occurs in the microdischarges through the quick conversion of N_2^+ and H_2^+ .

$$(md) H_2^+ + H_2 \to H_3^+ + H$$
 (27)

$$(md) N_2^{+} + H_2 \to N_2 H^{+} + H$$
(28)

As mentioned, the electrons govern the NH₃ steady-state yield (through reactions 21 and 22). They are produced upon ionization reactions 7 and 8, which are followed by charge transfer reactions 27 and 28, of which the products eventually recombine again with the electrons (reactions 24–26). Thus, the electron source in the microdischarges is directly linked to the electron losses in the afterglows. This could explain why in the literature, no saturation in NH₃ yield is observed upon increasing the plasma power or applied voltage.^{13–17} Nevertheless, Mizushima *et al.* do speculate that NH₃ decomposition is promoted with increasing applied voltage.³⁵

Note that recombination reaction 26 is often mentioned in the literature to be important for the formation of NH.^{36–38} In our model, this is not the case. The latter is in agreement with Molek *et al.* who reports that only 5% of this recombination leads to NH.³⁹ On the other hand, this NH formation mechanism may become important at different plasma conditions, such as low pressure.^{40–46}

Hong et al. performed a kinetic analysis based on a similar model as ours, but the plasma conditions, albeit derived from a PB DBD as well, were described as constants. Thus, their model did not explicitly capture the microdischarges. They also found that the surface is covered with H(s) under all plasma conditions because of dissociative adsorption (reaction 4), which they attribute to the low dissociation rates in the plasma.¹⁹ This agrees with our model up to the first microdischarge. Once a microdischarge occurs, the dissociation rate in the plasma increases, and our model predicts that direct adsorption of N and H atoms (reactions 14 and 17) is more important. In addition, instead of reaction 12, Hong et al. observed the formation of NH from vibrationally excited H₂.¹⁹ At our plasma conditions, however, the NH formation is only important during the microdischarges, which represent a stronger plasma than in ref 19, and thus it is logical that electronic excitation is more significant, explaining the difference in predicted NH precursors by both models. Furthermore, the subsequent ER reaction that forms $NH_2(s)$ (reaction 13) was reported to be the main $NH_2(s)$ source in ref 19, while in our study, this is again only true during the microdischarges. In the afterglows, the formation is attributed to an LH reaction instead (reaction 19). Finally, Hong et al. did not observe the ions to play an important role in the formation of NH or NH₃,¹⁹ in agreement with our study, and they also found that gas-phase NH₂ arises from the dissociation of NH_3 (reaction 21). However, they claimed that NH_2 is recirculated back to the desired products,¹⁹ which is in contrast to the conclusions of our model.

According to our reaction analysis, NH₂ only occurs as a product of reaction 21, that is, NH₃ electron impact dissociation, and it does not actively contribute toward NH₃ formation despite NH₂ + H(s) \rightarrow NH₃ (reaction 23) having the highest NH₃ formation rate in the late afterglow (*cf.* Figure S9a). Indeed, collisions with neutral species convert NH₂ into NH and back to the feed gas. These collisions account for 71% of the NH₂ destruction in the afterglow, while reaction 23 accounts for 10% (*cf.* Section S6 and Table S11). Furthermore, our model reveals



Figure 10. Reaction mechanisms governing the formation of NH_3 in a DBD during the microdischarges (a) and their afterglows (b). Elementary ER and LH reaction steps are drawn with red and blue arrows, respectively. In (a), the creation of reactive species during the microdischarges from electron impact collisions with the feed gas is shown next to the further reactions of these species into NH_3 formation as well as NH_3 destruction. In (b), the further reactions of these species leading to a net production of NH_3 in the afterglows are shown, starting with the radicals produced in the previous microdischarge.

that $N_2(E)$, $H_2(E)$, and NH radicals do not contribute toward NH_3 formation in the afterglows. Indeed, these three species are produced by electron impact collisions, which have a much lower rate in the afterglows than in the microdischarges (see *e.g.*, Figure 6), and they are quenched back to the feed gas.

As mentioned above, at the DBD conditions under study, our calculations reveal that dissociative adsorption of N2 does not play a significant role in the NH₃ synthesis. Furthermore, the surface is most significantly covered by H(s). Mehta et al. proposed that vibrational excitation of N2 increases the NH3 synthesis rate by an enhanced dissociative adsorption rate.¹¹ If we consider all N(s) sources, that is, both direct adsorption of N atoms and dissociative adsorption from N2 ground state and excited molecules, we find that only at the very beginning, dissociative adsorption of N2 molecules in the ground state or from vibrational levels causes the initial coverage with N(s) (96 and 4% contribution for ground state and vibrational levels, respectively). The same applies to the initial H(s) adsorption, that is, due to the empty surface sites and the lack of other radicals. However, quickly thereafter and already before the first microdischarge, the contribution from direct adsorption of N atoms is already 98%, while dissociative adsorption accounts for the remainder of N(s) (*i.e.*, 1.6% from the ground state and 0.1% from the vibrational levels). During the microdischarges, the contribution of dissociative adsorption does not rise because the N atom density largely increases (cf. Figure 1b). After the microdischarges, the contribution of dissociative adsorption reduces further to only 0.28 and 0.02% for the ground state and vibrationally excited levels, respectively. Still the contribution of the vibrational levels in the afterglow is generally higher than that of the electronically excited molecules in dissociative adsorption; see also Figure S16.

The above reaction mechanisms are summarized in Figure 10, in which we also distinguish between the microdischarges and their afterglows. During the microdischarges, electron impact excitation creates electronically excited levels $[H_2(E)]$ and

 $N_2(E)]$ and vibrationally excited levels, while electron impact dissociation of H_2 and N_2 ground state and electronic and vibrationally excited molecules create H and N atoms, and electron impact ionization creates H_2^+ and N_2^+ ions. The latter are converted into H_3^+ and N_2H^+ ions, which recombine with the electrons in the afterglows. These ions do not contribute to the NH₃ formation. The $N_2(E)$ molecules also contribute to H_2 dissociation. The collision between $H_2(E)$ molecules and N atoms yields NH radicals. In addition, the N atoms adsorb on the surface. Two types of ER reactions [N(s) + H and H(s) + N] form NH(s). Both NH and NH(s) form NH₂(s) upon reaction with H(s), that is, in ER and LH reactions, respectively. Finally, NH₂(s) forms NH₃, but the latter gets destroyed in the microdischarges upon electron impact dissociation.

In the afterglows, roughly the same processes occur as during the microdischarges, that is, the two ER reactions [N(s) + H and H(s) + N] form NH(s), which reacts further with H(s) to form NH₂(s) (LH). Note that the ER reaction $[NH + H(s) \rightarrow$ NH₂(s)] does not occur in the afterglows because there are virtually no NH radicals present in the afterglows. The same is true for NH₂ radicals, which are actually quenched back to the feed gas (not shown). Finally, NH₂(s) reacts again with H(s) into NH₃ (LH), but in contrast to the microdischarges, NH₃ is virtually not consumed through electron impact dissociation (except by some residual electrons), so there is net NH₃ formation in the afterglows, until a periodic steady state is reached (when NH₃ formation is balanced by dissociation due to the residual electrons and the high NH₃ density).

The data used in the assessment of the reaction mechanisms (reactions 4 through 28 and Figure 10) is presented in detail in the Supporting Information (Section S6), where we comment on the sensitivity of the assessed mechanisms to possible uncertainties in the underlying reaction rate coefficients. The effect of the uncertainties in rate coefficients has been studied in the past by our group for plasma-based CO₂ conversion and dry reforming of methane.^{47,48} While the absolute values of model

outputs, for example, conversion, were greatly affected by the uncertainties in reaction rate coefficients, the general plasma behavior and reaction pathways remained the same. Hence, we have to keep in mind that the present study aims at qualitatively clarifying the reaction mechanisms rather than providing quantitative predictions.

Within the reaction mechanisms of Figure 10, we can thus identify four elementary ER reaction steps taking place during the microdischarges [*i.e.*, N + H(s) \rightarrow NH(s); H + N(s) \rightarrow NH(s); NH + H(s) \rightarrow NH₂(s); and H + H(s) \rightarrow H₂; reactions 13, 16, 18, and 15 above]. Two of these reactions (reactions 16 and 18) also play an important role in the afterglows. In addition, both in the microdischarges and afterglows, two elementary LH reaction steps occur [*i.e.*, NH(s) + H(s) \rightarrow NH₂(s) and NH₂(s) + H(s) \rightarrow NH₃; reactions 19 and 20 above], but the ER reactions are mainly responsible for the formation of the precursor, NH(s) (reactions 16 and 18), indicating the overall importance of ER reactions in a DBD plasma.

If we would only consider the gas-phase reactions, the most significant NH₃ formation (in the afterglow) is due to H + NH₂ + M and NH + H₂ + M, both with reaction rates in the order of 10^{14} to 10^{15} cm⁻³ s⁻¹. These reactions account for less than 10% of the overall NH₃ formation rate. A calculation with only the gas-phase reactions taken into account results in only 20 ppm of NH₃ formed, compared to 220 ppm with the catalytic reactions (*cf.* Figure 6).

The exact reaction mechanisms, of course, depend on the reaction and activation energies, and in turn, the latter can depend on the surface. For example, the activation barriers for LH reactions are different across different metals.¹¹ Our present model does not easily capture the properties of different metal surfaces, but we have seen that the reaction mechanisms beyond the formation of NH(s) indeed depend on the activation energies of LH reactions and the overall available reactions in the chemistry description, and this should be subject to future studies. In the Supporting Information (Section S7), we provide a small analysis, which reveals that indeed with faster LH reactions, the results are unchanged and that with slower reactions, other reactions will form NH₃ with the same reaction rate, resulting in the same NH₃ concentrations because of the reactions being limited by the ER formation of NH(s). Based on these test cases, we found that NH₃ can also be formed in a single ER reaction (instead of reactions 19 and 20).

$$H_2 + NH(s) \rightarrow NH_3 \tag{29}$$

We acknowledge that this reaction appears to be a thermalonly process but that it is generally not considered in typical thermal catalytic models of ammonia synthesis. When this reaction was not considered, we found that the stepwise ER hydrogenation reactions can form NH_3 instead.

$$H + NH(s) \rightarrow NH_2(s) \tag{30}$$

$$H + NH_2(s) \to NH_3 \tag{31}$$

In addition, the surface is quickly covered by H(s) because of dissociative adsorption due to the large presence of empty surface sites and the lack of radicals at the start of the plasma. The dissociative adsorption rates in principle also depend on the metal surface. This in combination with various feed gas mixtures, that is, an excess of N₂, could change the (initial) surface coverage toward more N(s). Because of the high gas-phase dissociation rate of H₂, the ER reaction between N(s) and

H to form NH(s) is then expected to gain importance relative to $H(s) + N \rightarrow NH(s)$.

Our model reveals that radicals play an important role in the assessed reaction mechanisms through direct adsorption and elementary ER reaction steps. Although the underlying rate coefficients suffer from large uncertainties, as there are no extensive (density functional theory calculation) reports on these type of reactions available yet, Engelmann *et al.* showed that for typical gas-phase concentrations found in DBDs, the radical–surface interactions are important over a wide range of ER activation barriers (*i.e.*, 0-1.5 eV) for these type of reactions.²⁸

Apart from NH₃, which is created due to the presence of the catalytic reactions, the surface is most likely to influence the gasphase composition through the N and H atoms and NH₂ radicals. The former are the most significant gas-phase precursors and undergo radical adsorption. The latter is a dissociation product of NH₃ and thus dependent on the formation of NH₃, which happens mainly through the surface reactions. A change in the radical adsorption would either deplete the gas-phase N and H atoms quicker or slower. A change in the NH₃ synthesis would result in more or less NH₃ dissociation and consequently NH₂.

The gas-phase concentrations would be more directly influenced by the plasma conditions themselves. These conditions serve as the model input (*i.e.*, the power density) and are derived from experimental current and voltage characteristics of a PB DBD. Next to the catalytic reaction rates, the type of packing and the precise catalytic surface can also influence the current—voltage characteristics, which present another way of packing or catalytic surface to directly influence the gas-phase reaction rates, for example, dissociation. Indeed, the dielectric constant of the support is known to influence the discharge characteristics.⁹ In addition, Patil *et al.* observed an effect of the (metal) catalyst on the discharge characteristics, but no clear explanation has yet been given.⁴⁹

In their recent paper,¹² Rouwenhorst *et al.* proposed four plasma-catalytic NH₃ synthesis regimes: (1) NH₃ synthesis in the plasma phase only, (2) NH₃ formation in the plasma phase and on the catalytic surface through direct adsorption of N and H atoms, which are first formed in the plasma by electron impact dissociation, (3) the same as (2), but H₂ adsorbs dissociatively onto the catalytic surface, and (4) both H₂ and N₂ undergoing dissociative adsorption on the catalytic surface and NH₃ formation occuring on the surface only. In the latter case, the dissociative adsorption of N₂ is promoted by vibrational excitation in the plasma, and this regime was claimed to be energetically most favourable.¹² Our model reveals that the conditions under study mostly give rise to the third proposed mechanism, except that in our case, NH₃ is not significantly formed in the gas phase and the adsorption of N atoms does not occur only onto free surface sites.

4. CONCLUSIONS

We performed a detailed kinetic study of NH_3 synthesis in a PB DBD. Such plasma operates in a filamentary regime, characterized by strong microdischarges followed by weaker afterglows. Hence, we determined the formation mechanisms that take place in the microdischarges and their afterglows, as well as how they are connected. Our findings can be summarized as follows.

• Initial surface coverage with H(s).

- Creation of plasma radicals (*e.g.*, N, H, and NH) by electron impact collisions in the microdischarges.
- Adsorption of these radicals onto the surface and subsequent hydrogenation until desorption of NH₃.

The last step causes a net production of NH_3 in the afterglows, while during the microdischarges, the formed NH_3 is destroyed again by electron impact dissociation.

Specifically, we could identify electron impact dissociation of N2 during the microdischarges and the subsequent adsorption of N atoms on the catalyst surface as a rate-limiting reaction step for NH₃ formation in a DBD, and thus determining the eventual NH₃ yield, and not dissociative adsorption of N₂. Despite the fact that a PB DBD is typically a filamentary plasma, electron impact dissociation from vibrationally excited N2 levels still contributes about 8% to the overall N_2 dissociation rate in the plasma. The larger this contribution, the more energy efficient the overall NH₃ synthesis would be, as the required dissociation energy is reduced by vibrational excitation. While vibrational excitation can also overcome the energy barrier of dissociative adsorption, within our reaction mechanisms, we did not observe this process to play an important role. The N(s) formation is accounted for by the direct adsorption of N atoms for at least 98%.

Overall, our model reveals that both elementary ER and LH reaction steps can play an important role in plasma-catalytic NH_3 synthesis. The ER reactions (involving N, H, and NH) are mainly attributed to the large abundance of plasma radicals in the microdischarges, while in the afterglows, only the H and N atoms contribute to ER reactions, forming NH(s), but the subsequent NH_3 formation occurs by LH steps.

However, the rate coefficients used in the model are subject to significant uncertainties. They are adopted from earlier plasmacatalytic models of NH₃ synthesis, and they are often collected from various sources with different conditions (e.g., pressure) and are sometimes explicitly assumed therein. Hence, the model conclusions are only as reliable as the assumptions used, and the assumptions should be considered with caution. This applies especially to the ER sticking coefficients because there are no reliable kinetics data available. In addition, the results will also be sensitive to the reaction temperature and the choice of the catalyst. For instance, changing the reaction temperature will significantly influence the surface coverage of adsorbed species and the relative rates of the LH vs ER reactions. Therefore, the presented results should also be considered carefully, certainly in terms of absolute values. However, the predicted trends on the importance of certain pathways are expected to be reliable as they were found to be the same even when varying the rate coefficients within their range of uncertainties.

In the future, we plan to combine the presented plasma kinetics model with a more detailed surface kinetics model, in which both the specific catalytic surface and the feed gas ratio will be explored. The present study gives novel insights on the interplay between the microdischarges and their afterglows, which will allow to better focus future studies.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c05110.

Description of the model, plasma kinetic and surface kinetic reactions, translation of experimentally measured current and voltage characteristics to the model conditions, relationship between instantaneous power and power density, choice of discharge volumes, surface coverages and gas-phase concentrations in the microdischarge, calculated plasma parameters, NH_3 formation, detailed analysis of the reaction rates and determination of the rate-limiting step, N_2 dissociative adsorption compared against N atom direct adsorption, data used in the assessment of the reaction mechanisms, and influence of LH reactions and alternative reaction mechanisms (PDF)

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Notes

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