### **TOPICAL REVIEW**

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# **Topical Review**

# On the mechanism for the plasma-activated N<sub>2</sub> dissociation on Ru surfaces

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### Abstract

Plasma-activation of  $N_2$  via vibrational excitations or electronic excitations enhances the dissociative sticking probability on Ru-surfaces with respect to ground-state  $N_2$ . We propose that this is primarily due to a weaker nitrogen–nitrogen bond, facilitating direct adsorption of both nitrogen atoms on the metallic surface, a pathway with a high barrier for ground-state  $N_2$  due to the short bond distance of 110 pm. Furthermore, we show that the increased sticking probability is not only a heating artefact, as the activation barrier for  $N_2$  dissociation decreases upon plasma-activation. Recent modelling studies show that the binding strengths of surface adsorbates, as well as the barrier for dissociation may change as a result of high electric fields, as well as high degrees of charging metal particles. We show that the effect of plasma-induced electric fields is negligible in dielectric barrier discharge reactors, and other non-thermal plasma reactors. The effect of alkali promoters on the local electric fields is orders of magnitude larger than the electric field of the plasma. The role of plasma-induced metal surface charging during  $N_2$  dissociation is currently not known for metal clusters on a support.

Keywords: ammonia, plasma catalysis, ruthenium, N2 dissociation

(Some figures may appear in colour only in the online journal)

### 1. Background

Plasma-catalysis is an emerging field for activating strong chemical bonds in molecules such as  $CO_2$ ,  $CH_4$  and  $N_2$  [1–3]. Rather than fully dissociating the molecules in the plasma, mild activation in the plasma via vibrational or electronic excitation, followed by dissociation on a catalyst may allow for a lower activation barrier on the catalyst [4]. For  $CH_4$  it is established that the 1st vibrational level lowers the total activation barrier for dissociation [5], thereby increasing the dissociative sticking probability on Ni(100) surfaces [6].

However, the molecular mechanisms for plasma-catalytic  $\mathrm{CO}_2$  and  $\mathrm{N}_2$  dissociation are less understood.

Plasmas can be divided in the categories thermal plasmas and non-thermal plasmas [7–10]. In a thermal plasma, the electrons and the heavier plasma species (molecules, radicals, and ions) are in thermal equilibrium, resulting in temperatures in the order of  $10^4$  K [10]. In a non-thermal plasma, the electrons are not in equilibrium with the heavier plasma species, resulting in a substantially lower gas temperature as compared to the electron temperature [10]. Non-thermal plasmas can be classified as cold plasmas with a gas temperature typically near room temperature, and warm plasmas with gas temperatures of several  $10^3$  K [1, 10]. The dominating activation channels in cold non-thermal plasmas, e.g. in a dielectric barrier discharge

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(DBD) reactor [11], are primarily electronic excitations with a minor role for vibrational excitations [1, 2]. Warm plasmas combine characteristics of a thermal and non-thermal plasma, with a much higher electron temperature than the gas temperature, while the gas temperature is still typically several  $10^3$  K [1, 10]. The primary activation channel of molecules in such warm plasmas is vibrational excitation [1, 2].

Thermal plasmas and warm plasmas typically have such high temperatures, e.g. in the order  $10^4$  K and  $10^3$  K [1, 10], such that no catalysts exist with sufficient thermal stability. However, various studies have attempted to couple plasma and catalyst in warm plasma reactors [12, 13]. Alternatively, the catalyst can be placed after the plasma zone, where temperatures are lower [14, 15]. At the other hand, the overall temperature in a cold non-thermal plasma is sufficiently low for plasma-catalyst combination inside the plasma zone [3, 14, 15].

N<sub>2</sub> is an extremely stable molecule, and breaking the triple N $\equiv$ N bond is difficult, even in the presence of a catalyst. Typical barriers for thermal-catalytic N<sub>2</sub> dissociation are as high as 60–115 kJ mol<sup>-1</sup> for Fe and Ru catalysts [16–18]. Therefore, N<sub>2</sub> dissociation is usually the rate-determining step for thermal-catalytic NH<sub>3</sub> synthesis [17], and temperatures of 400 °C–500 °C are typically required for NH<sub>3</sub> synthesis under industrial conditions [19–21].

Plasma-catalytic NH<sub>3</sub> synthesis has been studied widely in recent years [22–24], with emphasis on Ru catalysts in DBD reactors [25–31]. It was reported that plasma-activation of N<sub>2</sub> lowers the N<sub>2</sub> dissociation barrier on Ru catalysts, potentially allowing for operation at lower temperatures [27, 32, 33]. The barrier for N<sub>2</sub> dissociation decreases from 60 to 115 kJ mol<sup>-1</sup> for thermal-catalytic NH<sub>3</sub> synthesis on Ru to 20–40 kJ mol<sup>-1</sup> for plasma-catalytic NH<sub>3</sub> synthesis on Ru when operating at 0.1–0.4 kJ l<sup>-1</sup> specific energy input (SEI) [27]. At higher SEI, N<sub>2</sub> is increasingly dissociated in the plasma, and adsorption of N radicals will dominate plasma-catalytic NH<sub>3</sub> synthesis [13, 28, 34].

The goal of this topical review is to provide an overview of current understanding of plasma-catalytic ammonia synthesis, based on available literature from various disciplines. Therefore, we first discuss the current understanding of thermalcatalytic  $N_2$  dissociation on Ru catalysts [35–39]. We postulate that weakening of the N≡N triple bond by vibrational excitation and electronic excitation in a non-thermal plasma at low SEI leads to an increase in the distance between the nitrogen atoms, thereby facilitating a lower barrier pathway for N<sub>2</sub> dissociation as compared to ground-state N<sub>2</sub>. We also discuss the role of surface heating, and we show that electric fields in non-thermal plasma are insufficient for enhancing dissociation of N2 on Ru catalysts. However, the role of plasmainduced charging of metal particles is not well understood at this moment, and this remains an open question in the field of plasma-catalysis.

### 2. Thermal-catalytic N<sub>2</sub> dissociation on Ru catalysts

In the past few decades, theoretical physical chemistry has been used to better understand fundamentals of catalytic reactions [40]. Amongst others, understanding of  $N_2$  dissociation on Ru catalysts is better understood using Ru(0001) as a model system [35, 36]. A fundamental understanding of  $N_2$ dissociation may aid in the development of more active catalysts for NH<sub>3</sub> synthesis.

Thermal-catalytic  $N_2$  dissociation is an activated process on most transition metals. In accordance with the Polanyi principle [41, 42], metals with a relatively weaker N binding energy have a higher activation barrier for  $N_2$  dissociation [43, 44].

From molecular beam experiments it was found that the dissociative sticking probability of N<sub>2</sub> on Ru(0001) increases with incident energy in N<sub>2</sub> [37-39], and more specifically vibrational excitation [38]. Various molecular beam experiments for N<sub>2</sub> dissociation on Ru(0001) surfaces are shown in figure 1. In the ground state, the dissociative sticking probability of N<sub>2</sub> is in the order  $10^{-6}$  [38], while the dissociation barrier on Ru(0001) surface is in the order of 100 kJ mol<sup>-1</sup>. Mild activation of N<sub>2</sub> via vibrational excitation or electronic excitation is expected to increase the sticking probability substantially, as decreasing the nitrogen-nitrogen bond strength or excitation of the N2 molecule may result in a lower dissociation barrier to be overcome for dissociation on the metal surface [32]. However, even at translational energies as high as 400 kJ mol<sup>-1</sup> (far above the barrier for N<sub>2</sub> dissociation on Ru(0001)), the dissociative sticking probability is still limited to  $10^{-2}$  and does not approach 1 [37, 38]. Apparently, the energy partially dissipates to the surface via another pathway than N2 dissociation. This limited dissociative sticking is most recently ascribed to translational and rotational motion of N2 along the surface [35, 36].

A high surface coverage affects the  $N_2$  dissociation rate as the number of empty sites decreases, thereby limiting additional adsorption. Furthermore, an increased surface coverage of atoms such as N or S increases the barrier of  $N_2$  dissociation, due to a change in d band density of states (DOS) [45–47].

On the other hand, the presence of alkali promoters increases the N<sub>2</sub> dissociation rate on Ru catalysts, as the NH<sub>3</sub> synthesis rate increases upon introducing alkali promoters on Ru catalysts [17, 47]. The introduction of alkali promoters has little to no effect on the d band DOS [45, 46]. Instead, the barrier for N<sub>2</sub> dissociation is decreased by strong electric fields of 0.5–1.0 V Å<sup>-1</sup> caused by alkali ions via polarization of the nitrogen molecule [45–47].

The proposed pathway for thermal-catalytic  $N_2$  dissociation on Ru(0001) is shown in figure 2. Initially,  $N_2$  is physisorbed perpendicularly to the Ru surface (*I*). Then,  $N_2$ is chemisorbed in a metastable state (*M*), increasing the nitrogen–nitrogen bond distance from 110 to 121 pm [48]. Finally, the nitrogen–nitrogen bond is further weakened in the transition-state (TS), after which complete rupture occurs (*F*).

### 3. Plasma-activated N<sub>2</sub> dissociation on Ru

The molecular beam experiments in figure 1 indicate that the dissociative sticking probability may be increased for  $N_2$  molecules with vibrational excitation and translational



**Figure 1.** Effect of the N<sub>2</sub> kinetic energy on the dissociative sticking probability from molecular beam experiments. The figure is constructed based on the figure 1 in [37]. Original data from Romm *et al* with a nozzle temperature <700 K (crosses), and with a nozzle temperature of 1750 K, probably with more vibrational activation in N<sub>2</sub> (triangles) [38], Egeberg *et al* (diamonds) [39], Diekhöner *et al* (squares) [37]. The circle represents the sticking probability of N radicals (e.g. fully dissociated N<sub>2</sub>).



**Figure 2.** Proposed mechanism for  $N_2$  dissociation on Ru(0001). The bond length *b* is the bond length between the two nitrogen atoms. The (*I*) state refers to the physisorbed state in which  $N_2$  is physisorbed perpendicularly to the Ru surface. The (*M*) state refers to the metastable chemisorbed state, in which the molecular nitrogen–nitrogen bond distance is increased from 110 to 121 pm [48]. The (TS) state refers to the transition-state, in which the nitrogen–nitrogen bond is further weakened. The (*F*) state refers to the total rupture of the N<sub>2</sub> molecule to two N atoms. Reprinted from [45], Copyright (1998), with permission from Elsevier. Reprinted from [48], Copyright (1997), with permission from Elsevier.



**Figure 3.** Left: postulated effect of plasma-induced N<sub>2</sub> activation on the catalytic activity at 400 K (thermal catalysis, plasma-activated N<sub>2</sub> with Treanor distribution, and vibrational distribution function (VDF) uniform plasma). For VDF uniform plasma, see [3]. Courtesy Yannick Engelmann. Right: apparent activation barriers for plasma-catalytic ammonia synthesis on Ru-catalysts at 200 °C-300 °C and 1 bar. Reprinted with permission from [27]. Copyright (2019) American Chemical Society.

excitation in a non-thermal plasma. The question arises whether the increased dissociative sticking probability of  $N_2$ upon plasma-activation is just due to a heating artefact [37], or to a decrease in the barrier for  $N_2$  dissociation [27, 32]. Heating effects in non-thermal plasma depend on the type of plasma and may occur very locally caused by plasma-catalyst interaction, possibly enhancing the dissociative adsorption rate of  $N_2$ [10, 49].

Recent research has provided support for the hypothesis that the barrier for dissociative adsorption of N2 on Ru surfaces is decreased for plasma-activated N2 as compared to groundstate N<sub>2</sub> [27, 32]. Mehta et al [32] postulated that the barrier for N<sub>2</sub> dissociation can be decreased by vibrational excitation, while the subsequent hydrogenation steps of Nads to ammonia were proposed to not change (see figure 3). Rouwenhorst et al [27] provided experimental supporting evidence for the claim that the barrier for N<sub>2</sub> dissociation is decreased by plasmaactivation, based on a kinetic analysis of ammonia synthesis on Ru catalysts in a DBD reactor. In case of thermal catalysis (i.e. without a plasma), the apparent activation barrier of ammonia synthesis is about 60–115 kJ mol $^{-1}$ , which can be attributed to the dissociation of N<sub>2</sub> [16, 50]. Upon plasma activation, the authors found that the apparent activation barrier for ammonia synthesis decreased to about  $20-40 \text{ kJ mol}^{-1}$ , which was attributed to a lower barrier for  $N_2$  dissociation [27]. This mechanism was found to be relevant for catalysts with, at least some, thermal-catalytic activity combined with relatively low plasma powers (0.1–0.4 kJ l<sup>-1</sup>). Furthermore, the influence of cations on activity of Ru catalysts has also been described based on the electronegativity of the support and of the alkali promoter for both thermal catalysis and plasma-catalysis in a DBD plasma. In both cases, the activity for N<sub>2</sub> dissociation increases with decreasing electronegativity of the support and the alkali promoter, as is inferred from the higher activity for ammonia synthesis [27].

Various authors suggested that the adsorption of N radicals present in the plasma can also be a kinetically relevant pathway for ammonia synthesis in the presence of a plasma and a catalyst [13, 28, 34]. This mechanism is dominant in case of relatively high plasma power, when the density of N radicals is substantial, and for catalysts that cannot dissociate  $N_2$ , even in case of vibrationally or electronically excited molecular  $N_2$  [23, 34, 51].

The ratio  $\frac{S_{\rm N}\rho_{\rm N}}{S_{\rm N_2(ex)}\rho_{\rm N_2(ex)}}$  expresses which of the two pathways is dominant for the adsorption of atomic nitrogen on the surface, activated  $N_2$  or N radicals, where  $S_N$  is the sticking probability of N radicals and S<sub>N2(ex)</sub> is the dissociative sticking probability of plasma-activated N<sub>2</sub>, whereas  $\rho_N$  and  $\rho_{N2(ex)}$ are the densities of N radicals and plasma-activated N2 in the plasma near the catalyst surface. The term plasma-excited N<sub>2</sub> is used for the combined vibrationally-excited N<sub>2</sub> molecules and electronically-excited N2 molecules. From figure 1 it follows that the values of  $S_N$  and  $S_{N2(ex)}$  on Ru(0001) are about 1 and in the order  $10^{-2}$ , respectively. As N radicals do not have a barrier for adsorption on Ru, the dissociative sticking probability is about 1. Plasma-activated N<sub>2</sub> is assumed to be in the order  $10^{-2}$ , as this is the sticking probability for translationally-activated N<sub>2</sub> with an energy of 400 kJ mol<sup>-1</sup> [38], as shown in figure 1. Dominant electronic excitations in  $N_2$  in a DBD reactor have an energy of 600 or 713 kJ mol<sup>-1</sup> [52], respectively, so this may be a conservative estimate.

This means the density of plasma-activated  $N_2$  must be more than two orders of magnitude higher than that of N radicals for plasma-activated  $N_2$  to be the dominant nitrogen species for plasma-catalytic ammonia synthesis. The densities of activated  $N_2$  and N radicals depend on the plasma characteristics and the power applied [1, 2]. Plasma modelling studies provide an estimation of the densities of activated  $N_2$ and N radicals [53, 54]. Typical densities for N radicals during the micro discharges in a DBD plasma are in the order  $10^{-5}$  kg m<sup>-3</sup> [54]. With increasing plasma power, the density of N radicals increases.

Recent modelling work of van 't Veer *et al* [54] shows that densities of above  $10^{-3}$  kg m<sup>-3</sup> are possible for

electronically-excited N<sub>2</sub> molecules during micro-discharges in DBD reactors. In that case, the ratio  $\frac{S_N\rho_N}{S_{N_2(ex)}\rho_{N_2(ex)}}$  becomes  $\frac{1 \times 10^{-5}}{10^{-2} \times 10^{-3}} = 1$ . Alternatively, vibrationally-excited N<sub>2</sub> may dissociate on the Ru surface. For example, the first five vibrational levels for vibrationally-excited N<sub>2</sub> molecules with an excitation level up to about 140 kJ mol<sup>-1</sup> show densities above  $10^{-2}$  kg m<sup>-3</sup> during micro-discharges according to van 't Veer *et al* [54]. As shown in figure 1, this results in a dissociative sticking probability in the order 2 × 10<sup>-5</sup>. In that case, the ratio  $\frac{S_N\rho_N}{S_{N_2(ex)}\rho_{N_2(ex)}}$  becomes  $\frac{1 \times 10^{-5}}{2 \times 10^{-5} \times 10^{-2}} = 50$ , e.g. favouring reactions with N radicals.

Thus, the mechanism with plasma-excited N<sub>2</sub> is plausible in case the plasma power is relatively low, typically below  $10^2$  J  $1^{-1}$  for DBD reactors [27]. For higher plasma powers, typically in the order  $10^3-10^4$  J  $1^{-1}$  for DBD reactors, the reduced electric field increases, which implies a higher fraction of the activated N<sub>2</sub> will be dissociated [1]. It should be noted that the plasma characteristics in a DBD reactor are stochastic (e.g. varying in time and space), and the densities of plasma species vary during the streamer discharges and the afterglow [54, 55]. As the catalyst material determines the sticking probability of  $S_{N2(ex)}$ , this analysis is valid for Ru exclusively.

It should be noted that the ratio  $\frac{S_N \rho_N}{S_{N_2(ex)} \rho_{N_2(ex)}}$  is a first approximation to estimate the dominant pathway. The gas temperature, and subsequently the translational energy, the molar weight and the kinetic diameters of the gas species, among other factors, also influence the collision frequency in the plasma and with the surface. However, the differences in these properties between activated N<sub>2</sub> molecules and N radicals are only minor. Therefore, the ratio  $\frac{S_N \rho_N}{S_{N_2(ex)} \rho_{N_2(ex)}}$  allows for a reasonable estimate for the dominant pathway.

We propose that the enhancing effect of plasma activation in N2 dissociation can be understood based on the dissociation mechanism as described in figure 2 [45, 48]. Plasma-activation by electronic excitation weakens the nitrogen-nitrogen bond, which increases the distance between the nitrogen atoms. In DBD plasmas, plasma-activation via electronic excitations in  $N_2$  is dominant, with an energy of 713 kJ mol<sup>-1</sup> (7.39 eV, the  $B^3\Pi_g$  state) resulting in an interatomic distance of 121 pm [52, 56]. For reference, the bond interatomic distance for  $N_2$  in the ground-state  $(B^2\Sigma_u^+)$  is 110 pm. Alternatively, vibrational excitations in N2 may result in a similar nitrogen-nitrogen bond weakening [38], potentially with a higher energy efficiency [57]. In case of vibrational excitation, the nitrogennitrogen bond varies around an average bond length due to harmonic and anharmonic vibrations. With increasing vibrational excitation, the amplitude increases and the vibration become increasingly anharmonic, resulting in a higher average bond length between the nitrogen atoms.

As discussed in section 2, the bond-distance varies between the different adsorbed states of  $N_2$  on Ru(0001). Groundstate  $N_2$  first physisorbs perpendicular to the Ru surface (see figure 2), as the interatomic distance for  $N_2$  in the ground state is too small (110 pm) for direct parallel adsorption with both nitrogen atoms interacting with the metal surface, which

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would be optimal with a nitrogen–nitrogen bond distance of 121 pm [48]. For reference, the nitrogen–nitrogen distance in the physisorbed state perpendicular to the Ru surface is about 112 pm (see figure 2). We propose that increased nitrogen–nitrogen bond distance in N<sub>2</sub> due to plasma-activation may open an alternative adsorption pathway. Rather than initial physisorption perpendicular to the Ru surface, we propose that plasma-activated N<sub>2</sub> with a bond distance of 121 pm can directly chemisorb on Ru surface sites with both nitrogen atoms in contact with the surface, similar to the *M* state in thermal catalysis (see figure 4). This allows for a lower total barrier for N<sub>2</sub> dissociation for plasma-activated N<sub>2</sub> as compared to dissociation of N<sub>2</sub> from the ground-state.

### 4. Effects of the plasma on the catalyst

Upon plasma illumination, there is a mutual influence of the plasma on the catalyst and vice versa [3, 49, 58–60]. Numerous effects have been described to be of potential importance, such as surface heating effects, plasma-induced electric fields, plasma-induced surface polarization, as well as an enhanced adsorption rate of plasma-activated molecules. Hereafter, we aim to estimate the potential contributions of these phenomena for plasma-catalytic ammonia synthesis.

### 4.1. The role of surface heating

Plasma-induced heating can be very significant, especially when operating at near-ambient conditions and with high plasma powers [14, 58]. Various authors showed that plasmainduced heating increases with increasing plasma power or SEI [14, 61, 62]. For catalytic NH<sub>3</sub> synthesis, the effects are twofold: (a) the intrinsic activity for N<sub>2</sub> dissociation and hydrogenation on the catalyst increases with increasing temperature, and (b) product desorption is enhanced with increasing temperature, resulting in more free sites available for adsorption of reactants. In principle, the energy of plasmaactivated N<sub>2</sub> that is not used for decreasing the barrier for N<sub>2</sub> dissociation is dissipated as heat. Furthermore, electrons and radical species such as N, H, and NH<sub>X</sub> may adsorb on the surface, further increasing surface heating, as adsorption is exothermic [49]. Radical species such as N, H, and  $NH_X$  can also react in the plasma phase itself, resulting in significant heat formation [10].

However, heating effects cannot account for the observed decrease in activation barrier from 60–115 kJ mol<sup>-1</sup> for thermal-catalytic NH<sub>3</sub> synthesis on Ru to 20–40 kJ mol<sup>-1</sup> for plasma-catalytic NH<sub>3</sub> synthesis on Ru at 200 °C–330 °C and at SEIs of 0.1–0.4 kJ l<sup>-1</sup> [27]. Heating effects may only become significant at substantially higher SEIs [10].

### 4.2. The role of electric fields

Electric fields are present in all types of plasmas including non-thermal plasmas, such as DBDs. The potential role of electric fields has recently gained attention for plasma catalysis in various research groups [63–66]. Hereafter, we



**Figure 4.** Proposed mechanism for plasma-activated  $N_2$  dissociation on Ru catalysts. The (*I*) state refers to the physisorbed state in which  $N_2$  is physisorbed perpendicularly to the Ru surface. The (*M*) state refers to the metastable chemisorbed state, in which the molecular nitrogen–nitrogen bond distance is increased from 110 to 121 pm [48]. The (TS) state refers to the transition-state, in which the nitrogen–nitrogen bond is further weakened. The (*F*) state refers to the total rupture of the  $N_2$  molecule to two N atoms.

discuss whether plasma-induced electric fields are sufficiently strong to influence catalytic reactions.

As discussed in section 2, the barrier for  $N_2$  dissociation on Ru catalysts is decreased by alkali promoters, which is attributed to electric fields of 0.5–1.0 V Å<sup>-1</sup> [45, 46]. Shetty et al [67] recently demonstrated with density functional theory (DFT) calculations that electric fields of  $\pm 1.0$  V Å<sup>-1</sup> also lead to a minor increase of 0.1 eV in the binding strength of  $N_2^*$ . The adsorption of other molecules on surfaces under electric fields has been reported as well. For instance, Susarrey-Arce et al [68] reported that an electric field as low as  $10^{-3}$  V Å<sup>-1</sup> changes the mode of adsorption of CO on Pt, i.e. linear adsorption versus bridge bonded CO, without changing the reactivity of CO. Shetty et al [67] reported an increased CO bond strength on Pt surfaces under electric fields with DFT calculations, albeit the increase was found to be as small as 0.025 eV under an electric field of 1 V Å<sup>-1</sup>. Neyts et al [63-66] performed theoretical studies on the effect of electric fields on the binding strength of CO<sub>2</sub> on various metal surfaces. For strong electric fields of 1.0–1.5 V Å<sup>-1</sup>, the authors reported an increase in CO<sub>2</sub> binding strength on Cu surfaces.

Typical reduced electric fields in DBD reactors operated at atmospheric pressure are in the range of 100–1000 Td [1], which translates to electric field strengths between  $3 \times 10^{-4}$ and  $3 \times 10^{-3}$  V Å<sup>-1</sup>. On the other hand, typical reduced electrical field strengths in low pressure plasma reactors such as radiofrequency and microwave reactors are less than 100 Td and gas densities are much lower at lower pressures, resulting in even lower electric field strengths than in DBD reactors. Modelling studies of DBD reactors confirm electric fields strengths of maximum  $10^{-3}$  V Å<sup>-1</sup> near contact points in packed beds [69–71]. Recent imaging studies of the electric field strength near a plasma-surface with iCCD cameras reveal a maximum field strength of about  $0.5 \times 10^{-4}$  V Å<sup>-1</sup> [72]. Thus, plasma-induced electric fields in DBD reactors are much smaller than electric fields that are required to influence the catalytic activity, e.g. by alkali promoters in ammonia synthesis as discussed above [45, 46]. For reference, a reduced electric field of 37 200 Td would be required to attain an electric field strength of 1.0 V Å<sup>-1</sup>, which is not realistic for any type of non-thermal plasma.

Another argument for the negligible role of plasma-induced electric fields is based on experimental results. If electric fields were a dominant factor for plasma-catalytic  $N_2$  dissociation, the role of the alkali promoters would be limited for plasma-catalysis. However, Rouwenhorst *et al* [27, 28] found that the role of alkali promoters is equally significant for  $N_2$  dissociation in case of thermal catalysis and plasma catalysis with plasma-activated molecular  $N_2$ . In both cases, the activity for ammonia synthesis is about an order of magnitude higher for the alkali promoted catalyst, as compared to the unpromoted catalysts [27]. Concluding, plasma-induced electric fields are too weak to play a significant role in  $N_2$  activation.

### 4.3. The role of charging of metal particles

Hereafter we evaluate the potential role of charging of metal particles in a non-thermal plasma, such as a DBD plasma. Charging of metal particles by excess electrons from the plasma, thereby changing the Fermi level, can influence the N binding energy and consequently the barrier for  $N_2$  dissociation.

Various authors have reported on the role of charging on metal particles in plasmas, especially for CO<sub>2</sub> adsorption. Bal et al [65] reported in a theoretical study that the binding strength of CO<sub>2</sub>, CO, O, and OH increases for single atom catalysts (Ti/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> and Cu/Al<sub>2</sub>O<sub>3</sub>) in the presence of an excess electron. Furthermore, Bal et al [66] reported that the binding strength of CO<sub>2</sub> increases on boron nitride (BN) nanosheets in the presence of surface charging. Jafarzadeh et al [64] reported on nanoclusters of five Ni or Cu atoms on  $TiO_2$ . The authors found that the adsorption strength of CO2 on Ni5/TiO2 and Cu5/TiO2 increases upon adding negative charge to the surface. Jafarzadeh et al [63] also reported on the role of excess electrons combined with an electric field for various Cu surfaces. The adsorption energy of CO<sub>2</sub> was found to increase assuming a strong electric field of 1.0-1.5 V Å<sup>-1</sup> [63], which is however not realistic for any type of non-thermal plasma as discussed above. The combination of a strong electric field of 1.0–1.5 V Å<sup>-1</sup> and an excess electron further increases the adsorption energy of CO<sub>2</sub> based on theoretical calculations, while an excess electron in absence of an electric field had no significant influence on the binding strength of CO<sub>2</sub> to the Cu facets. Concluding, the effect of charging metal surfaces has been studied by several authors. Effects on adsorption strength have been reported for CO<sub>2</sub> and CO, however, no information is available on any influence on reactivity. Furthermore, no information is available for N<sub>2</sub> adsorption and dissociation. Additional research would be required to assess whether charging of metal particles has any significant effect on N<sub>2</sub> dissociation.

It is currently an open question in the field of plasmacatalysis to what degree metal nanoparticles will be charged by excess electrons. The plasma is locally highly transient, and the density of electrons varies over time. During the micro discharges, electron density is the highest (typically  $10^{21}$  m<sup>-3</sup> s<sup>-1</sup> [10, 54]), while the electron density decreases during the afterglow (down to  $10^{15}$  m<sup>-3</sup> s<sup>-1</sup> [10, 51, 73]). The degree of charging of metal nanoparticles depends on the rate of metal surface charging during the micro discharges, and the rate of metal surface discharging during the afterglow. Thus, the degree of metal charging of metal particles varies over time. If there is any significant effect of charging of metal particles, it is expected to occur during the micro discharges. Additional research is required to assess the role of charging metal particles over time.

Concluding, the significance of metal surface charging in plasma-catalysis in general is currently not well understood. Thus, the role and significance of metal surface charging is a known unknown in plasma-catalysis [58, 59]. Furthermore, it is unknown whether metal surface charging is sufficient to influence the rate of  $N_2$  dissociation.

### 4.4. Maximizing plasma-catalyst interaction

Upon coupling a plasma and a catalyst, the plasma is typically exclusively formed with the external surface of the catalyst.

Plasmas cannot penetrate pores with a diameter smaller than the (sub-)micron range for atmospheric pressure DBD plasmas [73]. Typical pore diameters of catalysts are smaller than 50 nm [4, 23], implying a plasma is not formed inside the pores of the catalyst. Very high onset potentials would be required to generate and sustain plasmas inside such small pores, in accordance with Paschen's law [10].

However, plasma species may still penetrate into the catalyst pores, if the lifetime and diffusion rate is sufficient to reach the metal nanoparticles inside the catalyst pores [14]. The typical diffusion coefficient  $(D_i)$  of N<sub>2</sub> molecules is 0.2 cm<sup>2</sup> s<sup>-1</sup>, while vibrationally activated N<sub>2</sub> species have a lifetime  $(\tau)$  of about 60 ns [74]. This results in a potential penetration length  $(L_D)$  into the pores of about 1.5  $\mu$ m, as estimated according to  $L_D = \sqrt{2D_i\tau}$ . Thus, plasma species may penetrate pores to some extent, even though plasma cannot be generated inside pores with a diameter smaller than typically 1  $\mu$ m.

Therefore, it is desirable to use thin layers of catalyst material in order to maximize the external surface area in structured reactors, such as coated wall reactors [75, 76]. In general, macro-porous support materials would be preferred for plasma catalysis, be it that consequently the number of active sites per unit of volume would be small. Furthermore, Paschen's law dictates that the voltage required for breakdown is minimum at about 10  $\mu$ m, implying a microchannel plasma reactor with a thin catalyst layer would probably be the best way to maximize the plasma-catalyst interaction [10, 14], while minimizing the voltage required for breakdown.

### 5. Conclusion

Plasma-activation of  $N_2$  via vibrational excitations or electronic excitations enhances the dissociative sticking probability on Ru-surfaces. This is not an artefact caused by heating, as it is reported that the activation barrier for  $N_2$  dissociation decreases upon plasma-activation.

Plasma-activation of N<sub>2</sub> decreases the nitrogen–nitrogen bond strength, thereby increasing the bond length from 110 pm in the ground-state ( $B^2\Sigma_u^+$ ) to 121 pm by for instance electronic excitation (7.39 eV, the  $B^3\Pi_g$  state). We propose that the increased bond distance allows for the direct adsorption of both nitrogen atoms in the N<sub>2</sub> molecule on the metallic surface, a pathway prohibited for ground-state N<sub>2</sub> due to the too short bond length of 110 pm.

Recent modelling studies show that for high electric fields or high degrees of charging metal particles, the binding strengths of surface adsorbates may change. We show that the role of plasma-induced electric fields is too weak to cause any change in reaction rates in DBD reactors, and other nonthermal plasma reactors. The effect of alkali promoters on the local electric fields is orders of magnitude larger than the electrical field in a DBD reactor. It is not known whether plasmainduced metal surface charging has any effect on  $N_2$  dissociation. Main uncertainties are the extent of surface charging in DBD plasma considering heterogeneity in the plasma and its dynamic behaviour. Additional research would be required to address this.

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### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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