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# Understanding Plasma-Assisted Ammonia Synthesis *via* Crossing Discipline Borders of Literature: A Critical Review

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## **Abstract**

Plasma-assisted ammonia ( $\text{NH}_3$ ) synthesis is receiving significant attention.  $\text{NH}_3$  is globally important to fertilizer production and as a fuel. However, plasma research is, intrinsically, significantly cross-disciplinary and encompasses chemistry, physics, materials science and electrical engineering. A consequence is that it is uncommon or perhaps not feasible for plasma researchers to be fully aware of the entirety of plasma-related research beyond a particular discipline. Here for the first time we critically review this cross-disciplinary literature to address this problem using as a case study plasma-enabled  $\text{NH}_3$  synthesis, an important example in process chemistry. A justification is that an improved understanding will be helpful to deal with the complexity of plasma processes which typically involve a set of chemical reactions with an ensemble of many short-lived excited, or reactive, species that vary amongst different plasmas. As an eminent showcase for plasma applications in process chemistry, mechanisms for plasma-driven  $\text{NH}_3$  synthesis are assessed. Modern analytical techniques are critical in deciphering these fundamentals and in this review optical emission spectroscopy (OES) is featured. We conclude that cross-disciplinary methodology is necessary to 1) achieving control over formation of excited and reactive species including, vibrationally- and electronically-excited molecules, ions and radicals and 2) widening the scope for suitable plasma modes and monitoring techniques for robust chemical process control. Findings will be of immediate interest and benefit to a wide range of researchers and manufactures for plasma applications.

**Keywords:** Ammonia synthesis; Catalyst; Microplasmas; Optical emission spectroscopy; Mechanisms

## 1 Introduction

Ammonia ( $\text{NH}_3$ ) is a globally important chemical for energy storage and use in essential products (Chisalita, Petrescu, and Cormos 2020). Some 85 % of global  $\text{NH}_3$  production is used in fertilizers. In addition,  $\text{NH}_3$  is used to remove fly ash and acid gas, and is a significant fuel and energy carrier because of high energy density and ready transport and storage. Significantly, energy density is  $4.32 \text{ kW L}^{-1}$ , a value approximately double that for liquid  $\text{H}_2$  (Ghavam et al. 2021). The liquefaction of  $\text{NH}_3$  is much more readily achieved than for  $\text{H}_2$  given that  $\text{NH}_3$  and  $\text{H}_2$  liquefy at, respectively,  $-33.4$  and  $-253$  °C.

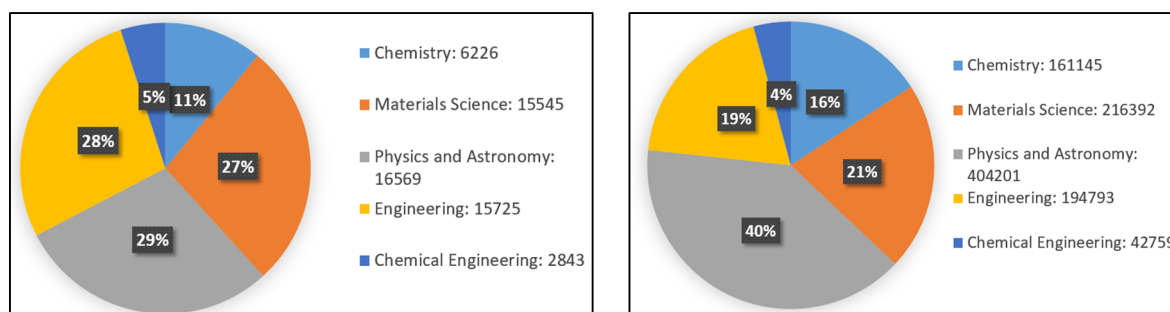
The present widely-used Haber-Bosch process (HB) provides  $> 130$  million tons of  $\text{NH}_3$  annually. However drawbacks include it, uses some 2 % of global energy (Patil et al. 2016; Peng et al. 2018), requires temperatures up to  $500$  °C and pressures to  $300$  bar for reaction on iron-based catalyst (Giddey, Badwal, and Kulkarni 2013), has high-capital cost, and; emits significant greenhouse gas. There is therefore significant research for a viable alternative.

Plasma-assisted  $\text{NH}_3$  synthesis is receiving increasing research attention as an alternative. Generally, low-temperature plasmas are categorized into two (2) types, 1) thermal (equilibrium) plasma (TP), and 2) non-thermal (non-equilibrium) plasma (NTP). TP is not ideal for  $\text{NH}_3$  synthesis because of high operating temperature. In contrast, because of the presence of reactive plasma species in NTP it affords productive catalysis at relatively low room temperature (RT) and atmospheric pressure. This gives greater energy efficiency, lower capital cost and a greater catalyst life-time (Hong, Praver, and Murphy 2018). Additionally, renewable energy can be used as an energy input to NTP synthesis for  $\text{NH}_3$ , and the low NTP operating pressure eliminates a compression step.

Using the  $\text{NH}_3$  synthesis as showcase, this review wants to give a perspective, which is to point on the value of cross-field literature for a multi-disciplinary topic such as plasma processing. Researchers can be ‘trapped’ in their discipline and community, referring to that

discipline. This is quite understandable and in a way productive by maintaining focus, and this focus starts with academic promotion, i.e. managing their career and creating their scientific profile, and ends with acceptance of papers in high-impact journals and presentations at conferences. That is a strong momentum, yet finally compromising cross-disciplinarity. On the other side, there is strong evidence that future innovations are mainly made at the borders of the disciplines.

To support our arguments, we have analyzed the contribution of discipline literature and non-discipline literature with regard to using “plasma processing” (Figure 1a) and “plasma” (Figure 1b) as keywords, via the Scopus web-search tool. With keyword ‘plasma processing’, it is evident that non-chemical engineering contributions dominate by far the information, as given by the numbers of publications. A similar outcome is revealed for ‘plasma’, yet the trend is even stronger. In addition, Figure 1 shows that many more papers exist for ‘plasma’ than for ‘plasma processing’.



**Figure 1** *The contribution of discipline literature and non-discipline literature to Scopus-derived publications, when using the keywords a) plasma processing (left) and b) plasma (right). On the right, the share of chemical engineering publications was not directly supplied by Scopus, so that it was recalculated from the known engineering contributions by taking an equal share in b) than given for a).*

Coming back to NH<sub>3</sub> synthesis, the energy efficiency requires improvement to compare well with, together with an improved yield. One avenue to achieving both is to leverage all

excited and ionized species for chemical reaction i.e. to bring them before rapid decomposition to the catalyst.

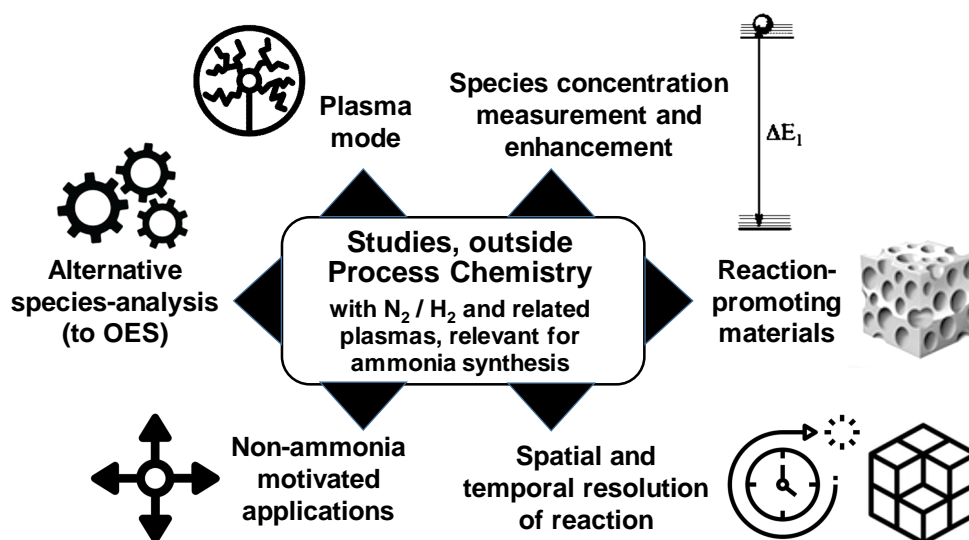
Optical emission spectroscopy (OES) is widely used for identifying and characterizing excited and ionized species including, rotationally-, vibrationally- and electronically-excited molecules, ions and radicals in discharge plasma (Sharma and Saikia 2008). Information from OES diagnostics is determined without damaging the plasma (Sharma and Saikia 2008). Emission lines in the spectrum correspond to electron transitions of neutral N<sub>2</sub> molecules, ionized N<sub>2</sub> molecules, ionized N atoms and radicals (Gómez-Ramírez et al. 2017; Gómez-Ramírez et al. 2015; Patil et al. 2021). Quantitative OES data for rotationally-, vibrationally- and electronically-excited molecules, ions and radicals in discharge plasma, together with intensity, permits identifying the important species, reaction mechanism and operating conditions to maximize number and importance of species. This knowledge of a reaction mechanism is used to improve reaction outcomes *via* optimal operating conditions and guided selection of ‘best’ catalyst is. OES data have evidenced that the rotational temperature ( $T_r$ ) of the nitrogen molecular ion at nitriding conditions is in equilibrium with the cathode temperature (Sharma and Saikia 2008). OES has also been used to analyze chemical effects of laser-induced dielectric breakdown (LIDB) in nitrogen gas (Camacho et al. 2007).

The release of potential plasma-excited species toward reaction is termed ‘plasma catalysis’. Its practical development is a major driver at present, however, with few reported findings. This is because of a lack of, 1) understanding in creating excited species, 2) ability to bring them to place of reaction, and 3) getting them to react in a way intended. Achieving this involves, among other things, control over hydrodynamics with impact on matter transport and, over complex mechanisms underlying the plasma–catalyst interactions.

In this timely Review we therefore, for the first time, critically assess reported information in a novel manner to link data from related fields including, matter physics, material surfaces,

electrical engineering, and chemical processing. A justification is that a ‘meta-analysis’ of these data, non-chemical with  $N_2$ - $H_2$  and related plasma data, might be better used to practically develop process solutions for plasma-based  $NH_3$  synthesis.

We address the need to identify the fundamental role and mechanism of diverse reactive species in plasma-driven  $NH_3$  synthesis from  $N_2$  and  $H_2$ , and to better understand plasma physics involving electron, vibrational and rotational temperature, density and electric field. We develop analyses of relevant literature data for the species- and mechanism-focused plasma studies, for process-chemical and non-process-chemical, relevant to plasma  $NH_3$  synthesis. This entails a focus on cross-disciplinary fields and reported sources outside chemical engineering (i.e. the authors’ field). Non-chemical studies data have practical potential to build on a chemical engineering perspective (Figure 2). This review wants to create awareness about potential to improve plasma-chemical processes.



**Figure 2** Value description of non-chemical studies with  $N_2 / H_2$  and related plasmas, yet relevant for a plasma-based ammonia synthesis.

The review aims to combine relevant reaction engineering and process development knowledge with knowledge outside the field. The plasma-based synthesis of ammonia was chosen as example, as this considers one of the most produced industrial chemical on this

planet, and valuing its function to energy and food as key to global survival; rather than being lost in the multiplicity of information around all kinds of plasma processes. Mechanistic information, deciphered by optical emission spectroscopy (OES), is considered to be key the plasma-ammonia synthesis and plasma-chemical syntheses in general. We consider both catalysed and non-catalysed routes in Section 3, comprising the information known and accessible to chemical engineers. More importantly, Section 4 points at information likely not known to the chemical engineers, and crossing discipline borders to material science, matter physics, electric engineering and more.

This review aims to link both scientific documentations in order to motivate and create benefit at the example of the plasma-based synthesis of ammonia. To widen the context, plasma-based nitrogen fixation (N fixation) is considered, i.e. the conversion of  $N_2$  into nitrogen species such as ammonium ( $NH_4^+$ ), surface-attached amino groups ( $NH_2$ ), and so on.

## **2 Plasma Techniques for $NH_3$ Synthesis and $N_2$ Fixation**

The two (2) types of plasma, TP and NTP, have significantly different temperature of plasma species. Major drawbacks with TP include a, low excitation selectivity and significantly high gas temperature, highly significant quenching requirements and electrode problems. This results in limited energy efficiency and applicability of thermal plasma sources (Kustova 2022). Therefore NTP including low-pressure glow and radio frequency (RF), microwave discharges, dielectric barrier discharges and laser-produced plasmas have been used due to their high selectivity in plasma chemical reactions, operating effectively at low temperatures and without quenching.

With TP, electron, ions and background-gas are at the same temperature of  $\sim 10^4$  K. Arc plasma and plasma torches work with TP. With NTP, electrons are at highly significant temperatures of  $\sim 10^5$  K because of smaller mass, and ions and background-gas are at RT (Patil



et al. 2015). Therefore the electric field selectively heats the electrons, and the heavy particles, including neutral species, or ions, remain ‘cold’ (Fridman et al., 2008; Neyts et al., 2012). TP is not ideal for  $\text{NH}_3$  synthesis because of the high operating temperature. Because of this, research has focused on NTP for  $\text{NH}_3$ .

Miniaturization of plasma reactors has practical potential for low power operation. In general, electric field strength in the gap between two electrodes increases proportionately to inverse of gap width, therefore it is possible to overcome the first ionization potential of the gas with a low voltage (Lozano-Parada and Zimmerman 2010). As is given in Paschen’s law, the breakdown-voltage of a discharge for a gas is determined by its pressure and the gap distance between two electrodes (Lin et al. 2019). Several reports demonstrate that the confinement of the discharge space leads to ‘new’ physical behaviour (Lin et al. 2021). It is possible to ignite and maintain small-scale plasma at high pressure, including atmospheric pressure or greater, by applying a relatively low voltage.

As a special category in NTP, microplasmas refer to discharges that are confined to sub-millimetre scale in at least one dimension (Lin and Wang 2015). Electric field distributions change because of the large surface-to-volume ratios and decreased electrode distances. As a result, the plasma physical structure, together with the energy distribution of the plasma species e.g. electrons, ions, excited molecules, radicals and atomic species, are significantly impacted. Compared with bulk plasmas, microplasmas possess unique properties that make them preferable for selected applications including, nanofabrication, 3D printing, optical metamaterials, medical devices and advanced light sources. Because of these unique characteristics, many microplasma systems/configurations have been proposed including, dielectric barrier discharge (DBD) microplasma, microplasma jets, microplasma array, hollow-cathode microplasma, and micro-cavity discharges (Lin and Wang 2015). jets, microplasma array, hollow-cathode microplasma, and micro-cavity discharges (Lin and Wang 2015).

### 3 Reaction Mechanisms in Plasma Synthesis of NH<sub>3</sub> - Chemical Engineering Literature

A necessary analysis of plasma-catalytic reaction mechanisms, including which species in N<sub>2</sub>-H<sub>2</sub> plasmas are relevant, and function, in chemical formation of NH<sub>3</sub> follows:

#### 3.1 OES-derived species and reaction mechanisms

##### 3.1.1 Optical Emission Spectroscopy (OES)

OES is the more widely used analytical technique for mechanistic plasma analyses. OES is an optical-device that captures, separates and measures light. It uses high-resolution grating to separate incoming light into element-specific wavelengths. A corresponding detector is used to measure intensity for each wavelength that is unique to each element. The spectra are interpreted *via* comparison with a reference. However, not all species are detectable using OES, including N\*.

OES is a non-intrusive plasma diagnosis that permits identification of reactive species e.g. excited ions and molecules, in discharges. A combination of spatial confinement and relatively greater density of the reactive species in microplasma makes it suitable tool for *in-situ* characterization. Parameters including, excitation and electron temperature, and electron density (based on Stark broadening of atomic emission lines) can be determined. Additionally, OES provides an estimate of vibrational temperature of species, and background-gas temperature, based on rotational branch of spectral lines.

Patil *et al.* (Patil et al. 2021) reported methodological and analytical considerations needed to ensure good quality-OES diagnoses. Highest intensity OES-related emission is observed when there is no catalyst in the reactor. The presence of packed material absorbs and shields OES emissions. This was confirmed by Wang *et al.* who evidenced that OES signal intensity was significantly lower in the presence of Fe-based catalyst compared with without catalyst (Wang et al. 2017).

### 3.1.2 Species and reaction mechanisms

Typically, OES spectra for N<sub>2</sub>-H<sub>2</sub> plasmas show numerous signals for multiple species, also for admixed gas species including, Ar (to facilitate plasma formation). Therefore more numerous OES signals overlay in one spectrum.

The resolution of typical OES signals is sufficiently high to permit detection of all species of overall interest. Consequently, a number of researchers are able to report on the nature of species, and excited species created in a range of N<sub>2</sub>-H<sub>2</sub> plasma systems (Gómez-Ramírez et al., 2015; Nakajima & Sekiguchi, 2008). The species in N<sub>2</sub>-H<sub>2</sub> plasma reactions detected *via* OES under different operating conditions of a plasma reactor, including electronic transition, band and wavelength, are presented in Table 1.

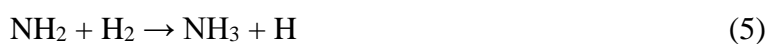
**Table 1** Species in N<sub>2</sub>-H<sub>2</sub> plasma reaction detected *via* OES under different operating conditions of a plasma reactor.

Specie	Electronic transition	Band	Wavelength (nm)	Experimental conditions	References
N <sub>2</sub> (SPS)	[C <sup>3</sup> Π → B <sup>3</sup> Π]	0 - 0	357.9	DBD	(Gómez-Ramírez et al., 2015; Petitjean & Ricard, 1984)
N <sub>2</sub> (SPS)	[C <sup>3</sup> Π → B <sup>3</sup> Π]		300 to 450	Microwave discharge at atmospheric pressure	(Nakajima and Sekiguchi 2008)
N <sub>2</sub>	C <sup>3</sup> Π <sub>v</sub> → B <sup>3</sup> Π <sub>g</sub>	0 - 0	337.1	Glow discharge	(Petitjean and Ricard 1984)
N <sub>2</sub>	C <sup>3</sup> Π <sub>v</sub> → B <sup>3</sup> Π <sub>g</sub>	0 - 2	380.4	Glow discharge	(Petitjean and Ricard 1984)
N <sub>2</sub>	B <sup>3</sup> Π <sub>g</sub> → A <sup>3</sup> Σ <sub>u</sub> <sup>-</sup>	6 - 3	662.3	Glow discharge	(Petitjean and Ricard 1984)
N <sub>2</sub> <sup>+</sup> (FNS)	[B <sup>2</sup> Σ <sub>u</sub> <sup>+</sup> → X <sup>2</sup> Σ <sub>g</sub> <sup>+</sup> ]		391.4	DBD	(Gómez-Ramírez et al. 2015)
N <sub>2</sub> <sup>+</sup>			< 250	DBD	(Patil et al. 2021)
NH*	[A <sup>3</sup> Π → X <sup>3</sup> Σ]	0 - 0	336	DBD	(Gómez-Ramírez et al., 2015) (Bhaskar S. Patil et al., 2021)
NH*	[A <sup>3</sup> Π → X <sup>3</sup> Σ]	0 - 0	336	Microwave discharge at atmospheric pressure	(Nakajima and Sekiguchi 2008)

$N_2^*$	0 - 0	337	DBD	(Gómez-Ramírez et al. 2015)
$N_2^*$	0 - 0	337.1	Microwave discharge at atmospheric pressure	(Nakajima and Sekiguchi 2008)
$N^{2+}$		< 250	DBD	(Patil et al. 2021)
$H_\alpha$		656.3	DBD	(Wang et al. 2019)

### 3.2 OES-derived reaction mechanisms without catalyst

Without catalyst, the main reactions in the plasma-assisted process include, dissociation, ionisation, excitation leading to the formation of NH, NH<sub>2</sub> and, NH<sub>3</sub> species. Initially, H<sub>2</sub> and N<sub>2</sub> dissociation occurs to produce radicals. Ionization and excitation of N<sub>2</sub> and H<sub>2</sub> molecules partially take place under strong electric field. These reactions are followed by NH radicals formation (Li et al. 2018), and NH<sub>3</sub> production, namely:



The maximum energy yield for NH<sub>3</sub> formation from plasma chemistry of 54.4 g-NH<sub>3</sub> kW h<sup>-1</sup> is significantly greater than is tolerable for practical application, and there is the need to use a catalyst for a plasma-assisted NH<sub>3</sub> synthesis (Rouwenhorst et al. 2020).

### 3.3 OES-derived reaction mechanisms with catalyst

Adding catalyst to plasma-assisted NH<sub>3</sub> synthesis generates active radicals and ions. Combinations of plasma and catalyst, create a chemically reactive environment without the supply of high thermal energy (Carrasco et al. 2011). Plasma catalysis means that the plasma reactions and the catalytic surface reactions are closely interconnected. These interactions

occur chemically *via* creating and reacting space, and involve changes to the electrical and material properties of the plasma system (Hong et al. 2018).

### 3.3.1 Plasma excited species in the presence of catalyst

OES is used to detect plasma species of  $\text{NH}^*$ ,  $\text{N}_2^+$  and  $\text{N}_2^*$  that form  $\text{NH}_3$  in a DBD reactor catalyzed by ferroelectric material ( $\text{BaTiO}_3$  *versus* PZT) (Gómez-Ramírez et al. 2015). The transitions  $[\text{C}^3\Pi \rightarrow \text{B}^3\Pi]$ ,  $[\text{B}^2\Sigma_u^+ \rightarrow \text{X}^2\Sigma_g^+]$  and  $[\text{A}^3\Pi \rightarrow \text{X}^3\Sigma]$  corresponding to the, second positive system (SPS) for nitrogen (357.9 nm), first negative system (FNS) for  $\text{N}_2^+$ , (391.4 nm) and excited  $\text{NH}^*$  species (336 nm), were exhibited in OES spectra. Additionally,  $\text{N}_2^*$  is recorded at 337 nm, a value close to the emission for  $\text{NH}^*$ .  $\text{N}_2^+$  was confirmed as an essential species, and a thermochemically feasible mechanism tentatively hypothesized.

Recently,  $\text{N}_2^+$  and  $\text{NH}^*$  were identified as two (2) signature species for which intensity varies as a function of voltage (Gómez-Ramírez et al. 2017).  $\text{N}_2^+$ , which is formed *via*  $\text{N}_2 + \text{e}^- \rightarrow \text{N}_2^+ + 2\text{e}^-$  or  $\text{N}_2^* + \text{N}_2^* \rightarrow \text{N}_2^+ + \text{N}_2 + \text{e}^-$ , is the intermediate species involved in  $\text{NH}_3$  formation, whilst  $\text{NH}^*$  is important for both  $\text{NH}_3$  formation and decomposition, respectively,  $\text{N}_2^+ + \text{H}_2 \rightarrow \text{NH}^*$  and  $\text{NH}_3 + \text{e}^- \rightarrow \text{NH}^* + 2\text{H}^* + \text{e}^-$ . More recently, an optical fibre connected to a spectrometer was used to obtain emission spectra for plasma in the presence of, and without, catalyst in the reactor (Patil et al. 2021). Based on OES spectra, the lines  $< 250$  nm correspond to ionized nitrogen atoms and molecules, whilst excited nitrogen molecules exhibit at lines between 300 and 380 nm. FNS for  $\text{N}_2^+$ ,  $[\text{B}^2\Sigma_u^+ \rightarrow \text{X}^2\Sigma_g^+]$  was found at 391.4 nm in the work reported by Gómez-Ramírez *et al.* (Gómez-Ramírez et al. 2015), whilst ionized nitrogen molecule  $\text{N}_2^+$  exhibited at lines  $< 250$  nm. Emission from the  $\text{H}_2$  species was not observed (Gómez-Ramírez et al. 2017; Gómez-Ramírez et al. 2015; Patil et al. 2021).

Through the use of microwave discharge for  $\text{NH}_3$  synthesis at atmospheric pressure, it was found that the production of active nitrogen species, atomic nitrogen, nitrogen molecular ions and excited metastable nitrogen molecules, are important (Nakajima and Sekiguchi 2008).

Research on the generation of radicals in nitrogen plasma using plasma jet confirmed that excited nitrogen molecules in a metastable state of  $N_2(A_3\Sigma_u^+)$  was the dominant species (Uhm 2015).

$NH_x$  radicals and H atoms have been suggested as critical species in  $NH_3$  synthesis (Mizushima et al., 2007; Uyama & Matsumoto, 1989). The  $NH_3$  produced was altered through varying NH radicals, hydrogen atoms and hydrogen molecules. Hong *et al.* evidenced that NH is an important species for initiation of synthesis (Hong et al. 2017).

### 3.3.2 Catalyst surface reactions

Detailed kinetic modelling to elicit the underlying mechanism(s) of plasma chemistry in  $N_2-H_2$  discharges has focused on low-pressure plasma conditions, with relatively high-energy electron and ion kinetics (Carrasco et al. 2011; Colonna, Capitelli, and Giordano 2001; Garscadden and Nagpal 1995; Gordiets et al. 1998a, 1998b). However in many applications, including  $NH_3$  synthesis, operation at greater pressures gives greater yield and energy efficiency.

Hong *et al.* (Hong et al. 2017) is the first attempt at detailed kinetic modelling of non-equilibrium  $N_2-H_2$  atmospheric-pressure discharges for catalytic  $NH_3$  synthesis. The model considered both electron and vibrational kinetics, including excited  $N_2(X, v)$  and  $H_2(X, v)$  species, and surface reactions including those occurring by the Eley–Rideal (E-R) and Langmuir–Hinshelwood (L-H) mechanisms and dissociative adsorption of molecules. Significantly, adsorbed  $NH_x(s)$  species are generated through E-R reaction, whilst the L-H reaction includes interaction between surface-adsorbed nitrogen atoms N(s) and hydrogen atoms H(s) (Hong et al. 2017).

A zero-dimensional plasma kinetics model, including both surface and gas phase kinetics, was presented to determine the role of vibrationally excited states in plasma-catalytic  $NH_3$  synthesis (Van 't Veer, Reniers, and Bogaerts 2020). Surface kinetics included direct

adsorption, dissociative adsorption, recombination desorption, elementary E-R and L-H reaction steps, and surface relaxation of excited states. The observed mechanisms evidence rapid surface coverage by H(s).

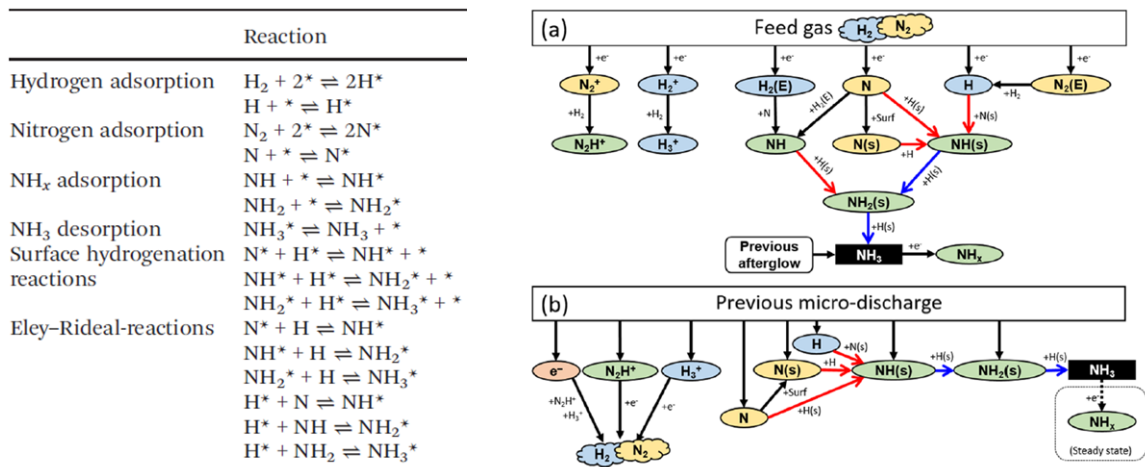
Plasma–surface interactions can be readily divided into, a) adsorption, b) surface diffusion, c) Eley–Rideal (E–R) interactions, d) Langmuir–Hinshelwood (L–H) interactions, and e) desorption (Hong et al. 2017). NH<sub>3</sub> can be produced through gas-phase reactions, although most is from surface reactions (Hong et al. 2017).

The E-R mechanism is dominant in low-temperature plasma catalysis (Hong et al. 2018) and therefore involves interaction with the plasma gas phase. E–R reactions of molecular species are boosted by vibrational excitation (Quan et al. 2019). As system temperature increases, L-H mechanism becomes more important and leads to a significant increase in NH<sub>3</sub> produced (Ertl, 1980; Hong et al., 2018).

Rouwenhorst *et al.* defined the conversion of plasma-generated radicals to NH<sub>3</sub> over a catalyst as surface-enhanced plasma-driven synthesis (SEPDAS), whilst conversion of plasma-activated molecular N<sub>2</sub> to NH<sub>3</sub> over a catalyst as plasma-enhanced catalytic NH<sub>3</sub> synthesis (PECAS) (Rouwenhorst et al. 2020). Figure 3 (left) shows possible surface reactions for SEPDAS and PECAS. Recent research attention has focused on mechanisms in follow-up microdischarges and afterglows shown in Figure 3 (right) (Van't Veer et al. 2020). During microdischarges, following generation by electron impact excitation, electronically excited levels H<sub>2</sub>(E) yield NH radicals *via* collision with N atoms, whilst N<sub>2</sub>(E) molecules contribute to H<sub>2</sub> dissociation. Two (2) types of ER reactions [N(s) + H and H(s) + N] form NH(s). Both NH and NH(s) form NH<sub>2</sub>(s) on reaction with H(s), that is, in ER and LH reactions, prior to forming NH<sub>3</sub>.

In the afterglows, 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

NH<sub>2</sub>(s) (LH), reacting again with H(s) to NH<sub>3</sub> (LH). Both ER and LH mechanisms are critical in plasma-catalytic NH<sub>3</sub> synthesis.



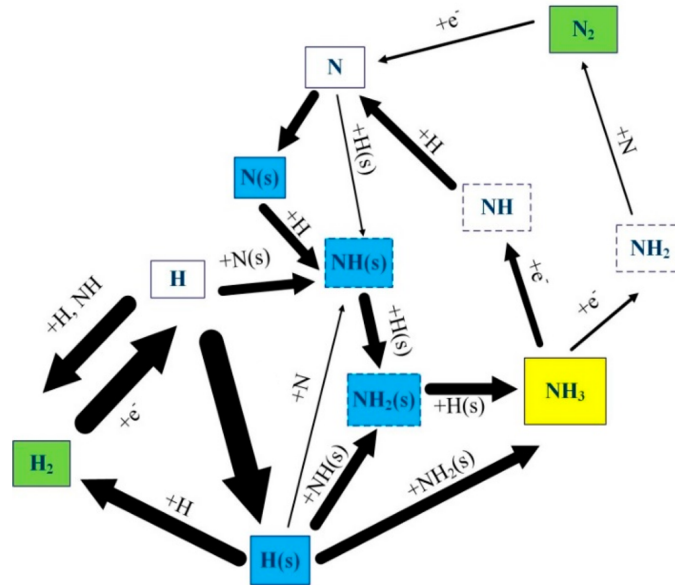
**Figure 3** Possible surface reactions for SEPDAS and PECAS (Rouwenhorst et al. 2020) and types of DBD plasma activation for NH<sub>3</sub> synthesis in (a) microdischarge and (b) afterglow (Van't Veer et al. 2020).

\* denotes an adsorption site on catalyst. Although high-energy electrons are important in producing NH<sub>3</sub> they are responsible for the major loss of NH<sub>3</sub> (Hong et al. 2018).

### 3.3.3 Reaction mechanisms

Findings from NH<sub>3</sub> synthesis using radio frequency plasma catalysis confirmed that NH<sub>2</sub>(s) is a critical precursor to NH<sub>3</sub> formation (Shah et al. 2018). The E–R interaction is also important with a relative contribution of 38 % for synthesis of NH<sub>2</sub>(s) without catalyst. Additionally, it was found that L-H reactions are important in low pressure discharge plasmas. A scheme was proposed of the dominant reaction pathways as is shown in Figure 4.





**Figure 4** Schematic for reaction pathways for plasma-catalytic (Fe) NH<sub>3</sub> synthesis. Thickness of arrows is degree of relevance (Shah et al. 2018).

Hong *et al.* (Hong, Prawer, and Murphy 2014) investigated the impact of addition of Ar to a DBD reactor. The discharge power, uniformity and gas temperature were all improved to give greater production. This was accompanied by an increase in N<sup>+</sup>, as was confirmed *via* OES.

N<sub>2</sub>-fixation in water was investigated using NTP nitrogen plasma jet (Lamichhane et al. 2020) in which nitrogen gas was excited to rapidly yield ammonia, nitrite, nitrate and hydrogen ions. The OES spectrum confirmed that UV radiation UVC originated from NO $\gamma$  (280 to 200 nm), UVB from OH radicals (309 to 306 nm) and UVA from nitrogen SPS (380 to 311 nm) and FNS (410 to 390 nm).

Additionally, OES has been used to study electronically excited state NH<sub>3</sub><sup>\*</sup> in NH<sub>3</sub> decomposition (Wang et al. 2017). Amongst species, NH<sub>3</sub><sup>\*</sup> was determined to be the major species. This was because of intensity under different input powers and being closely linked with decomposition of NH<sub>3</sub>. The increase in NH<sub>3</sub><sup>\*</sup> species intensity and NH<sub>3</sub><sup>\*</sup> correspondingly increased with input power. The decomposition of NH<sub>3</sub> and the generation of the main products

were measured varying the power and substrate temperature (Kang and Donnelly 2007). The OES spectrum evidenced the N<sub>2</sub> second positive (C<sup>3</sup>Π<sub>u</sub>→B<sup>3</sup>Π<sub>g</sub>) system and NH (A<sup>3</sup>Π<sub>i</sub>→X<sup>3</sup>Σ<sup>-</sup>) 0–0 band. The authors stated that NH<sub>3</sub><sup>\*</sup> was the important species.

#### 3.3.4 Microplasmas and excited species

Confining plasma to microscale is used to achieve low temperature and high pressure operation of discharges. In microplasma medium high-energy electrons receive inelastic collisions to generate additional excited species through collisions with background-gas, leading to a concentration of reactive species. Because of nonequilibrium and miniaturised geometry, the density and internal energy of plasma excited species e.g. electrons, ions, excited molecules, radicals and atomic species, are greater in comparison with the bulk plasma. Therefore, microplasmas are a powerful means to create charged and electrically excited atoms and molecules (Chiang et al. 2019).

Microplasma behaviour in NH<sub>3</sub> synthesis has is reported by several researchers (Bai et al., 2003, 2008). Those experimental results prove that nonequilibrium plasma produced inside the reactor by the microgap dielectric barrier discharge at ambient pressure can ionize and dissociate N and H molecules to form a large number of the activated species. In particular, after inelastic collisions, the gas molecules N and H are ionized and dissociated into N<sup>\*</sup>, N<sup>+</sup>, H<sup>\*</sup>, and H<sup>+</sup> to form NH<sup>+</sup>, NH<sub>2</sub><sup>+</sup>, NH<sub>3</sub><sup>+</sup>, NH<sub>4</sub><sup>+</sup>, and so on and NH gas is synthesized. Understanding can be inferred however from research findings from alternative N<sub>2</sub>-fixation in converting N<sub>2</sub> to molecules other than NH<sub>3</sub>.

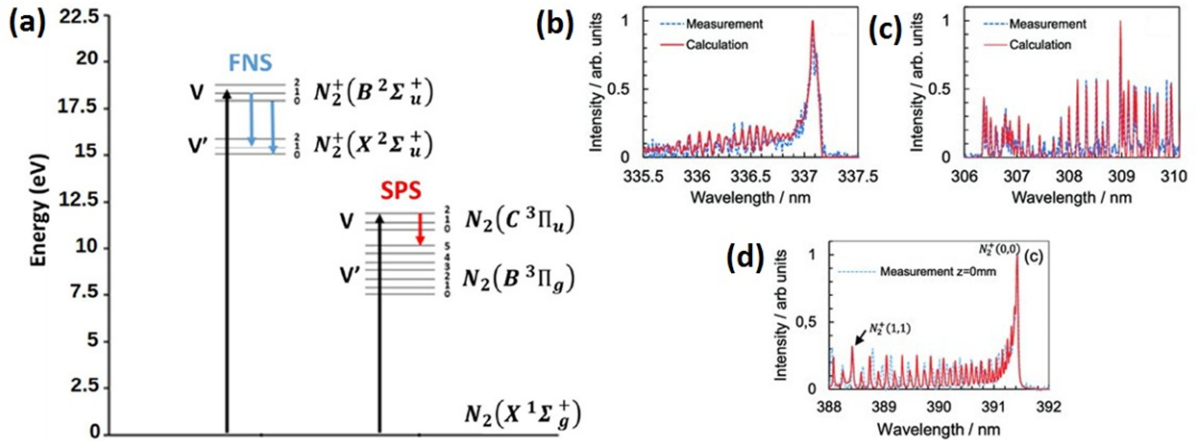
For example, in the work of Lin *et al.*, a hollow-cathode microplasma was applied for continuous synthesis of TiN nanoparticles from TiCl<sub>4</sub> and N<sub>2</sub>, where an optical emission spectrometer was used for *in-situ* analyses of synthesis (Liangliang Lin et al. 2017). Based on OES spectra recorded in plasma with differing TiCl<sub>4</sub> and H<sub>2</sub> concentrations, the strongest peaks in the range 690 to 850 nm were attributable to Ar atomic transitions (Ar I). Emission bands

for N<sub>2</sub> (C→B transitions) were observed at 310 to 410 nm, that were suppressed following introduction of H<sub>2</sub>. However, atomic hydrogen lines (H<sub>β</sub> 489.6 nm, H<sub>α</sub> 657.2 nm) appeared, and were more intense with increasing H<sub>2</sub> concentration. Because the bond energy for H<sub>2</sub> of 4.52 eV is less than for N<sub>2</sub> of 9.79 eV, it is more readily dissociated compared with N<sub>2</sub>. Inline mixing of TiCl<sub>4</sub> vapours into the plasma also leads to emission lines for Ti radicals, evidencing that they were dissociated in the microplasma.

### 3.3.5 Microplasmas and electrical plasma characteristics

In addition to identifying reactive species, OES can be used to determine electron density and temperature, and gas temperature of the microplasma when combined with collisional-radiative models. The relation between the intensities in the molecular emission bands of OES permits in contactless mode, determination of gas temperature. For example, the gas temperature can be derived by data-fitting the spectrum of distinct vibrational bands with simulated ones i.e. SPECAIR model, because the rotational temperature of the microplasma can be considered being nearly that of the gas temperature (Laux et al. 2003; L. Lin et al. 2017; Xu et al. 2019).

In the report of Zerrouki *et al.*, a micro-air corona discharge was characterized by OES for its characteristics including, temperature and density of electrons, rotational temperatures of excited species, gas temperature and density of molecular nitrogen. In N<sub>2</sub> microplasma, the N<sub>2</sub> molecular transition generates N<sub>2</sub> SPS and N<sub>2</sub><sup>+</sup> FNS emissions that permit determination of electron temperature directly from the spectra intensity, as is seen in Figure 5(a).



**Figure 5** (a) Schematic for generation of  $N_2$  SPS and  $N_2$  FNS system, (b-d) Experimental data together with simulated spectra for (b)  $N_2$  SPS, (c) OH and (d)  $N_2^+$ , state.

SPECAIR and LIFbase models were used to simulate  $N_2$  SPS, OH and  $N_2^+$  emissions. The rotational temperature was computed to be 700 K for the  $N_2$  SPS state, 2350 K for OH and 2000 K for  $N_2^+$ , confirming characteristics of non-equilibrium.

### 3.3.6 Water-droplet multiphase microplasmas and plasma characteristics

Sankaran *et al.* developed a plasma-water droplet reactor for  $N_2$ -fixation under atmospheric pressure (Toth et al. 2020). Liquid water was carried *via* gas flow to generate small, aerosol droplets using a nebulizer, before transport to a DBD reactor.

$N_2$ -fixation was controlled under two (2) atmospheres, 1) water droplets and  $N_2$ , and 2) water droplets and Ar/ $N_2$  (90/10). OES was used to estimate the gas temperature in the DBD reactor *via* the emission bands for the  $N_2$  second positive system. Findings confirmed the gas temperature was  $\sim 650 \pm 70$  °C for the water droplets with  $N_2$  plasma, and increased to  $\sim 760 \pm 80$  °C for the water droplets with Ar/ $N_2$  plasma. Addition of Ar significantly impacted the plasma properties including, the electron density, molecular and atomic states of Ar and  $N_2$ , and as a net effect, chemical reactivity at the interface to the water, that lead to decreased  $N_2$ -fixation efficiency.

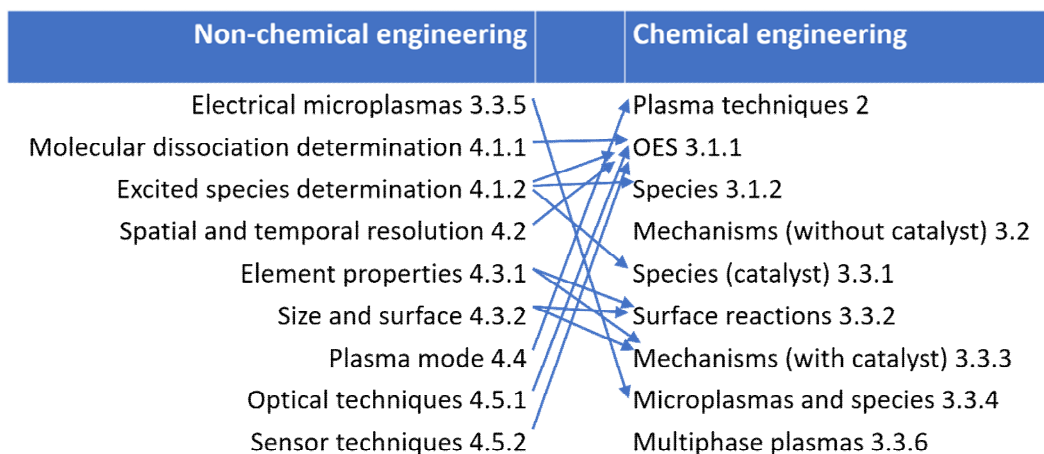
#### **4 N<sub>2</sub>- H<sub>2</sub> and Plasmas not for NH<sub>3</sub> Process Development – ‘Non Chemical Engineering’ Literature**

The plasma-literature contains a number of non-ammonia syntheses related studies that have information relevant to plasma-based NH<sub>3</sub> synthesis.

These are directed more to electrical engineering, energy storage and matter physics or material science. These therefore involve, amongst other things, determination of NH<sub>3</sub> decomposition as a means to energy conversion through CO-free H<sub>2</sub> from a storage of NH<sub>3</sub> and the use of NH<sub>3</sub> or N<sub>2</sub>-H<sub>2</sub> plasmas for surface coating of industrial materials including, nitridation of steel.

This mirrors the heterogeneous plasma science field and combines research from significantly different disciplines. Plasma process chemical studies are not as established as those for conventional chemical engineering. This is due in part to an insufficient application of analytical techniques and mechanistic understanding to design for chemical reactions and process. Whilst the likely explanation is in the complexity of plasma chemical reactions, it is for this reason that plasma chemical process engineers need to ‘cross-borders’ and become familiar with relevant literature from these other disciplines.

Figure 6 shows how the viewpoint of non-disciplinary literature can inform investigations run by disciplinary literature, along the lines of the sub-chapters given in this review. It is evident that almost each chemical engineering-motivated investigations could have profited from non-chemical engineering literature.



**Figure 6** *The correlation between the disciplinary and non-disciplinary literature.*

The review ends with non-ammonia motivated applications, using  $N_2 / H_2$  plasmas for surface treatments, thin layer deposition, and other applications.

#### 4.1 Species concentration measurement

The quantitative determination of the excited plasma species is significantly important to understanding reaction engineering of plasma processes and kinetics. Whilst the plasma chemical process literature reports a number of kinetic modelling studies, direct confirmation *via* experiment of kinetics is rare. Findings are often only indirectly evidenced from trends in global-reaction outcomes, including reactant conversion i.e. dependency on a reactant concentration or temperature.

In consequence, experimental plasma chemical processes often are qualitative rather than quantitative. However, the non-chemical plasma literature reports a number of techniques to measure concentration of excited species in  $H_2$ -  $N_2$  plasmas. For example, the two studies deal with a quantitative determination of the degree of molecular dissociation of  $NH_3$ ,  $N_2$  or  $H_2$ , as target quantity, meaning the reverse-reaction to  $NH_3$  synthesis.

##### 4.1.1 Quantitative determination of molecular dissociation

This section aims to supply relevant information for part 3.1.1. because quantitative determination of molecular dissociation applications is a central mechanistic detail deciphered by OES.

The dissociation of  $\text{NH}_3$  in  $\text{NH}_3/\text{Ar}/\text{He}$  plasmas was diagnosed by a combination of ultraviolet optical absorption spectroscopy, and OES (Kang and Donnelly 2007). This physics-motivated diagnosis provided understanding from a methodological perspective. A ‘self-actinometry’ method was used to measure the absolute number density of  $\text{N}_2$ , generated through the dissociation of  $\text{NH}_3$  and secondary reactions. Another methodological step using an accurate calibration-factor was determined to convert relative  $\text{N}_2$  emission intensities into absolute number densities. This permitted, for example, measurement of the absolute  $\text{NH}_3$  number density decline as a function of plasma power and temperature, and gave 90 % dissociation at 400 W and 900 K.  $\text{N}_2$  density increased with power and temperature. This study also reported the semi-quantitative H-atom density.  $\text{H}_2$  was shown to be the major hydrogen species, and at greater power H-atoms were detected.

A quantitative OES-based determination of the molecular dissociation was made in a surface wave-driven discharge  $\text{N}_2\text{--H}_2$  plasma under pressure (Tatarova et al. 2002). The dissociation of nitrogen molecules  $[\text{N}(4\text{S})]/[\text{N}_2]$  increases with the hydrogen content up to 50 %, with increasing electron temperature at a constant electron density and pressure. The number of hydrogen atoms remained quasi-constant when the  $\text{H}_2$  content is increased between 10 and 50 %. Along the length of the plasma column, the degree of dissociation decreases to reflect assorted decrease in electron density.

#### 4.1.2 Quantitative determination of excited species and plasma characteristics

Quantitative determination of excited species and plasma characteristics in this section is useful to compare and widen the view of the same analysis by OES mentioned in section 3.1.1.

In addition, this section supports describing the description of species detected *via* OES in the section 3.1.2.

The density for NH and NH<sub>2</sub> radicals in N<sub>2</sub>-H<sub>2</sub> plasmas and in N<sub>2</sub> plasmas to which H<sub>2</sub> was added were determined (Van Helden et al. 2007). Cavity ring-down spectroscopy confirmed a NH radical density of  $5 \times 10^{18} \text{ m}^{-3}$  for both plasmas and for NH<sub>2</sub> a radical density of  $7 \times 10^{18} \text{ m}^{-3}$  when both N<sub>2</sub> and H<sub>2</sub> are fed through the plasma. This evidences how to ‘elegantly’ trigger species formation *via* a plasma mixture. Additionally, reaction mechanistic information was interpreted. For example, NH radicals are produced mainly *via* reaction of N atoms with H<sub>2</sub> molecules, and less by reaction of N<sup>+</sup> with H<sub>2</sub>. It was determined also that NH<sub>x</sub> radicals act as precursors for N and H atoms, and therefore are necessary to generation of N<sub>2</sub>, H<sub>2</sub> and NH<sub>2</sub>. Detailed qualitative data were obtained on the excited species. For example, the NH radical exhibited transitions in the (0,0), (1,1) and (2,2) vibrational bands of the A<sup>3</sup>Π<sub>r</sub> X<sup>3</sup>Σ<sup>-</sup> electronic transition. The NH<sub>2</sub> radical was excited to the (0,9,0) r (0,0,0) band of the A<sup>~</sup>2 A<sub>1</sub> r X<sup>~</sup>2 B<sub>1</sub>.

OES findings confirmed the relative intensity of the species N<sub>2</sub><sup>+</sup>, N<sub>2</sub> and H<sub>a</sub> in an N<sub>2</sub>-Ar-H<sub>2</sub> plasma as a function of reactant flow (Braz, Filho, and Jr 2010) ratio of these species was non-linear with variation.

The measurable impact when mixing minute amounts of H<sub>2</sub> of up to 5 % into N<sub>2</sub>, was investigated for a capacitively-coupled plasma produced in a radio-frequency mode (Ahmed Mahjoub, A. Gouveia, Nathalie Carrasco, C. D. Pintassilgo, L. Marques 2011). The electrical discharge and the plasma were monitored to the RF nitrogen plasma. The bands for the nitrogen second positive system (SPS) of N<sub>2</sub>, the nitrogen ionic first negative system (FNS) of N<sub>2</sub><sup>+</sup> and the hydrogen line H<sub>β</sub> were recorded as a function of H<sub>2</sub> concentration at different pressures.

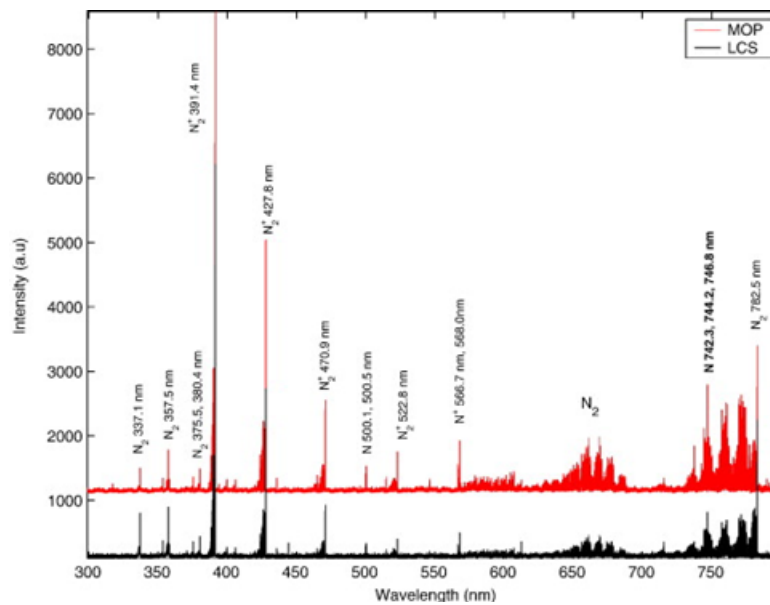
## 4.2 Spatial and temporal resolution of reaction

This section provides information about the spatial and temporal resolution of a reaction which is not easily accessible by OES measurements as mentioned in the section 3.1.1.



Spatial and temporal reaction data are important to chemical processes, particularly when operated in instationary mode. Plasma processes commonly exhibit temporal variability when operated in pulsed mode. Spatial variability is determined from local concentration profiles, e.g. due to the short-life of excited species from position created.

It was found from a study with locally resolved OES of plasma species concentration near an electrode (Suraj et al. 2007) that hydrogen boosted the sticking/adsorption of N on the cathode surface. Figure 7 presents the spectra for the pure nitrogen discharge which was collected from the light collecting system (LCS) and moving optical probe (MOP). These data evidenced the MOP spectra and that local effects are minor.



**Figure 7** Matching of light collecting system (LCS) and moving optical probe (MOP) spectra for nitrogen plasma (Suraj et al. 2007).

Time-resolved measurements for Ar, N<sub>2</sub>, N<sup>+</sup><sub>2</sub>, N and H emission lines were derived via OES for pulsed microwave discharges in Ar-N<sub>2</sub> and Ar-N<sub>2</sub>-H<sub>2</sub> plasmas (Britun, Godfroid, and Snyders 2012) in which the gas temperature, and N<sub>2</sub> rotational and vibrational temperatures were analysed. Process was optimized based on several important parameters. Mechanistic

understanding was gained, for example, that  $N_2$  dissociation depends mainly on presence of nitrogen ions, together with the fact that a minute,  $\sim 0.2\%$ , addition of  $H_2$  highly significantly changes impacted  $N_2$  dissociation mechanism.

### **4.3 Reaction-promoting materials**

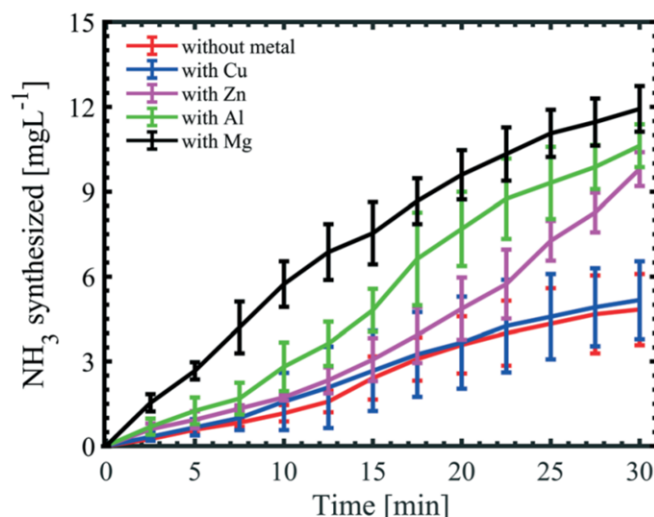
This section adds similar information to the section 3.3.2 because materials of the electrode and catalyst in a plasma reactor impact the reaction outcome.

The materials can function as catalyst for the chemical species, and modify the electrical field. The latter is a function of the type of material and surface shapes (contours) for e.g. needles and plain surfaces of the same material, will likely influence plasma in different manner. Materials in a plasma in this context refer to the electrode and catalyst, accordingly.

#### 4.3.1 Materials – elemental properties

Metals were added as a catalyst to plasma-activated water (PAW), a nitrogen fixing gas-liquid plasma that generates ammonia, nitrite, nitrate and hydrogen ions in water (Lamichhane et al. 2020). Using a nitrogen plasma jet for addition, it was found that Mg, Al, Zn and Cu oxidised the water, and the released electrons reduced hydrogen ions to a hydrogen radical that formed  $NH_3$  by reaction with nitrogen.

The presence of an additional hydrogen donor increased rate of  $NH_3$  formation, Figure 8.



**Figure 8**  $\text{NH}_3$  yield for selected metals added to plasma-activated water (Lamichhane *et al.* 2020).

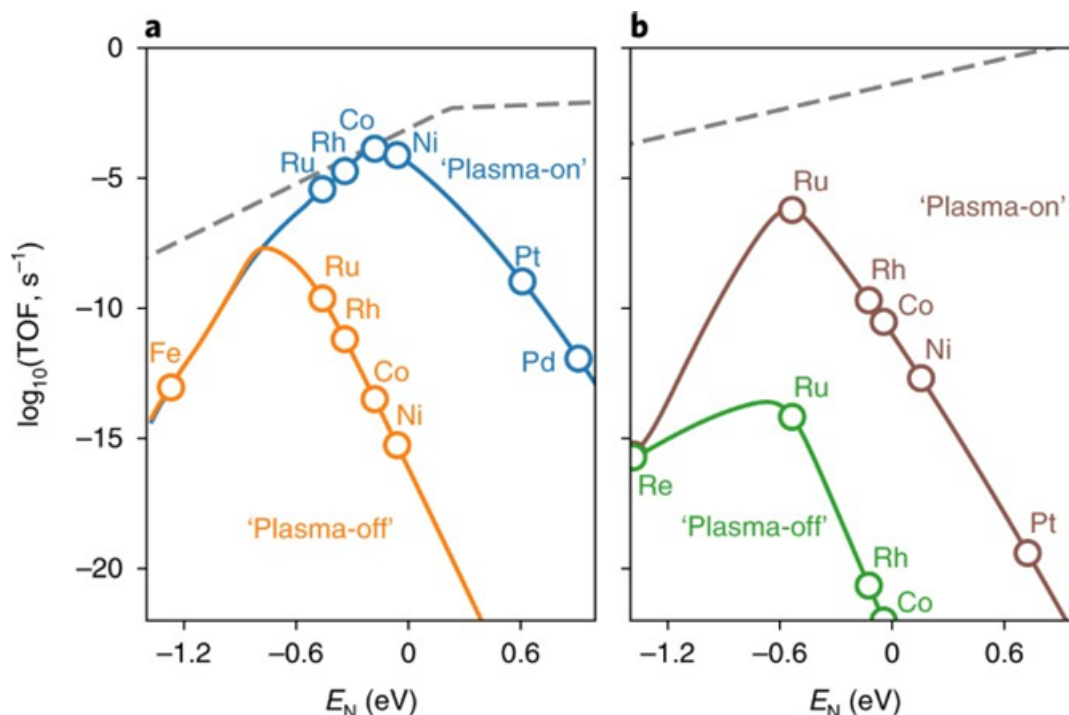
Wang *et al.* investigated plasma-catalytic effects for  $\text{NH}_3$  decomposition using it as an energy storage carrier (Wang *et al.* 2015). The material involved catalysts made of metals, zeolites, silicates, aluminates and titanates.

#### 4.3.2 Materials – size and surface

Catalyst particle size can boost catalytic activity as was demonstrated in an  $\text{NH}_3$  decomposition (Bell *et al.* 2020). Particle size is controlled by formation of the catalyst particles i.e. precipitation. Whilst the latter is expected, an unintuitive finding was made that impurities stemming from catalyst synthesis including, B and Cl<sup>-</sup>, have a significant detrimental impact on plasma activity.

The ability to bind reacting species is important in any catalysis. It is a property of the surface groups and topology of the catalyst (Mehta *et al.* 2018). The high reactivity of plasma excited species evidences that the optimal binding strength might be lowered, as with conventional catalysis. It was reported that for NTP that conversion is high on metals with weak bonding to nitrogen. Additionally, that plasma-induced vibrational excitations for  $\text{N}_2$  lower the energy for dissociation, whilst conserving the reaction scheme and outcome(s). Figure 9 presents the

vibrationally excited (plasma-on) reaction rates as compared with thermal catalytic (plasma-off) rates for selected catalytic materials. As is seen in the figure the introduction of a plasma leads to a shift in the position of the maximum for the Volcano plot.



**Figure 9**  $N_2$  vibrationally excited (plasma-on) versus thermal (plasma-off) rate for  $NH_3$  synthesis in presence of selected catalytic materials. Curves in (a) and (b) are rates observed at, respectively, step and terrace sites (1 atm,  $T_{\text{gas}} = 473$  K,  $T_{\text{vib}} = 3,000$  K, conversion = 1 %). Dashed lines show maximum rate for hydrogenation (Mehta et al. 2018).

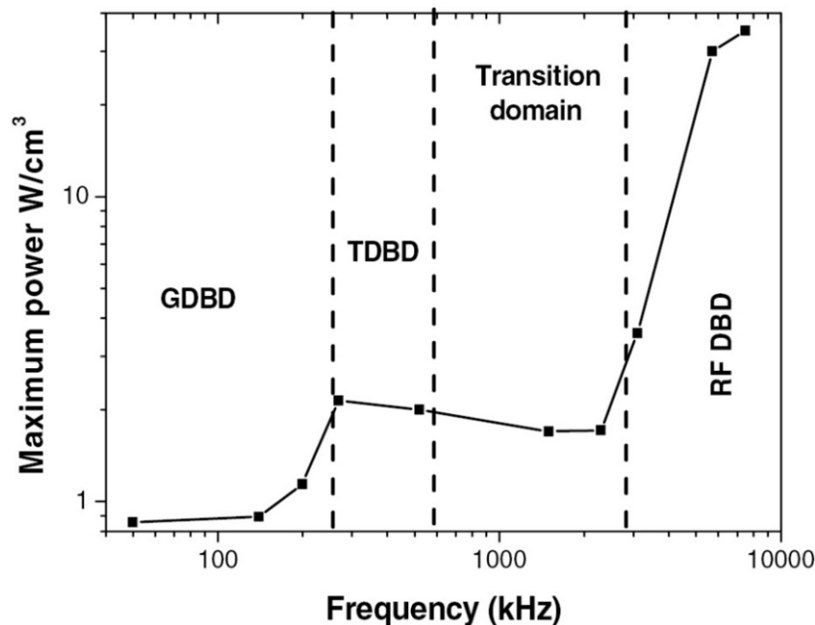
The highest plasma-on reaction rates i.e. the peak in curves are several orders of magnitude greater than the highest for the thermal catalysis. This behaviour is observed for both types of catalytic sites, namely, steps and terraces. This example underscores operational plasma catalysis when rates of thermally catalysed reactions at surfaces are limited.

#### 4.4 Plasma mode

The information in this section can support the operational expertise addressed in section 2, which concerns plasma techniques for ammonia synthesis and nitrogen fixation.

Traditional chemical engineering can make use of continuous stirred tank reactors (CSTR) and plug-flow reactors (PFR). However, plasma-chemical reactors have a multiplicity of designs and operation principles. These include, microwave, barrier discharge and, jet or gliding arc plasmas. These can differ including in, shape, jet, and gliding arc, and type of excited species. Plasma researchers rely continuously on one plasma mode and do not change, this is in part because it requires high cost investment in equipment to change. This action contrasts to microfluidics as a process intensification technology where researchers maintain different flow equipment, and may compare these in the one study.

As an exemption to what is said above, Bazinette *et al.* reported a plasma study on three (3) homogeneous DBD modes in an Ar-NH<sub>3</sub> Penning plasma, i.e. the ionisation of an atom by the transfer of the excitation energy from a metastable atom (Bazinette, Paillol, and Massines 2015). As is seen in Figure 10, the DBD peak power was plotted against frequency to show the three plasma regimes, namely, glow (GDBD), Townsend-like (TDBD) and radiofrequency (RF DBD) plasma.



**Figure 10** Maximum power of three (3) DBD plasma regimes as function of frequency; glow (GDBD), Townsend-like (TDBD) and radiofrequency (RF DBD) (Bazinette *et al.* 2015).

A transition was found of the plasma from GDBD to TDBD to RF DBD in the range 50 kHz to 9.6 MHz. This transition significantly increased density of the less energetic electrons, and was accompanied by an increase in NH radicals.

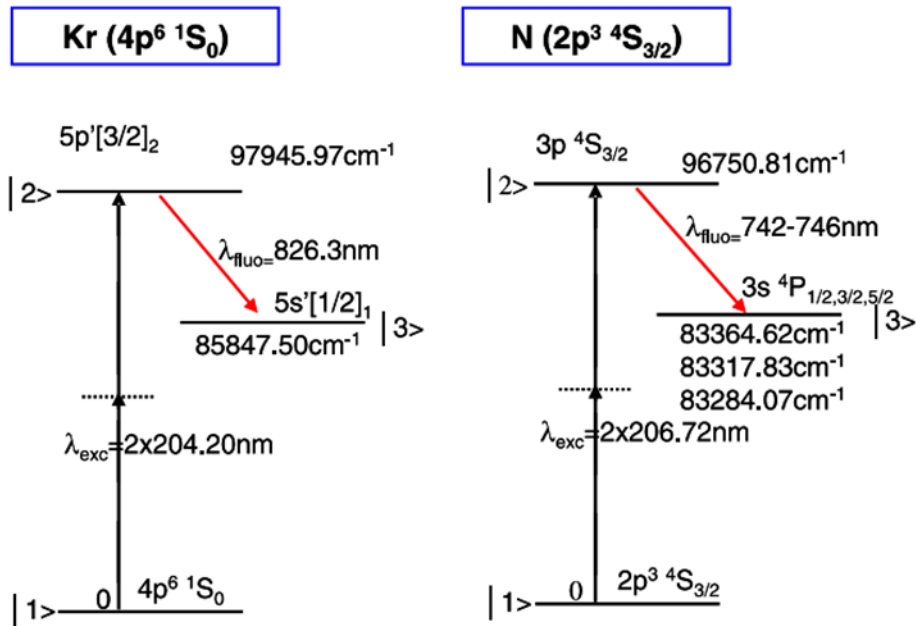
#### **4.5 Alternative species-analyses to OES**

It is important to utilize alternative analytical techniques to OES, which dominates the information given in the section 3.1.1. Especially, plasma physics literature provides a diversity in analytical techniques which allow to gather information not accessible by OES.

##### 4.5.1 Optical techniques

Infrared (IR) emission spectroscopy permits findings of atomic and molecular transitions in N<sub>2</sub> and N<sub>2</sub>-H<sub>2</sub> microwave discharge plasma, together with estimation of plasma temperature in N<sub>2</sub> and N<sub>2</sub>-H<sub>2</sub> plasmas (Mavadat et al. 2011). IR is a however rarely applied to, plasma species and diagnosis. In contrast it is more common in standard chemical engineering analytical use.

Two-photon absorption laser-induced fluorescence (TALIF) spectroscopy is used to diagnose plasma post-discharge absolute ground-state nitrogen atomic densities, ‘near’, ‘pink’ and late GDBD, with regard to its absolute ground-state nitrogen atomic densities (Es-Sebbar et al. 2009). With TALIF an important finding was that the microwave plasma post-discharge provides N (4S) atoms in late GDBD. Figure 11 is a summary energy level diagram from TALIF for atomic nitrogen and Kr (as reference). It was found that TALIF can be used determine gas temperature. A drawback however is that TALIF is specialist technology, and not readily accessible.



**Figure 11** Energy level for the two-photon excitation laser-induced fluorescence (TALIF) for atomic N and Kr (Es-Sebbar et al. 2009).

A Langmuir probe and OES diagnosis were used concurrently for pulsed N<sub>2</sub>-H<sub>2</sub> plasma with an admixture of CH<sub>4</sub> at low pressure (Hannemann et al. 2013). The temporal change in the electron density and temperature was investigated, together with plasma excited species. It was observed that the ratio of H<sub>2</sub> to N<sub>2</sub> in the feed significantly impacted the intensity ratio of N<sub>2</sub><sup>+</sup>-(0-0)- band to N<sub>2</sub>-(0-2)-band. The presence of CH<sub>4</sub> significantly impacted the electron parameters. This development was for active screen plasma nitriding.

It is concluded therefore that advanced optical TALIF and Langmuir probes should be considered for use in plasma research, and to advance practically in collaboration with specialists.

#### 4.5.2 Sensor techniques

Quartz sensor analysis can be used to diagnose production of NH<sub>3</sub> in N<sub>2</sub>-H<sub>2</sub> plasmas, in combination with gas analysis with quadrupole mass spectrometer (Suzuki and Asahina 2012). This was applied to plasma nitriding.

It is clear that modern sensor techniques are underused in plasma-chemical process analyses. Therefore access to sensors, needs to be improved.

## 5 Conclusions

This review shows that cross-disciplinary knowledge needs to understand fundamentals in a different way. There is an important, fundamental difference between conventional reactor engineering and plasma reactor engineering. Conventional chemical reactor engineering design is widely established and is readily available from a range of texts and specialised journals from the community of chemical engineers and chemists. This is not the case for design with plasma-chemical engineering. The difference underscores the need for a continuing cross-disciplinary methodology.

It is concluded that the need for cross-disciplinary knowledge is at the fundamental level and this review informs about the reason and how cross-boundary view can bridge this gap. This gap in fact stops many process and catalyst chemists from involving in plasma-chemistry research, while possibly being genuinely interested to do so. Such a situation is not uncommon for enabling technologies, it is actually one of the obstacles which commonly needs to be overcome. For example, a similar situation arose one decade ago when flow chemistry emerged, and it was solved first by raising awareness on interdisciplinary knowledge, and secondly by field-specific process development and reactor design advice as well as multiple training programs. This is the key point of this paper - the plasma chemistry will be successful by learning from those information- and trust-building measures.

Because conventional chemistry is enabled *via* catalytic processes with generally understood kinetics and intermediates, given the same process parameters, the same product is reliably formed for a range of different chemical reactor-types, but with varying quality on the engineering outcomes such as the selectivity, conversion, or space-time yield. With plasma



chemistry however, the plasma reactor determines product. Reactive plasmas comprise a mix of excited species determined by transition and non-equilibrium states, where species commonly have significantly short lifetimes that add to practical engineering design. This is in contrast to intermediates with conventional chemistry.

It is concluded therefore that cross-disciplinary methodology is necessary to 1) achieving control over formation of excited and reactive species including, vibrationally- and electronically- excited molecules, ions and radicals, and 2) widening choice of plasma modes and monitoring techniques for good chemical process control.

Optical emission spectroscopy (OES) is critical to deciphering fundamentals and reactive plasma-generated species and in determining plasma parameters including, electron density and temperature, and gas temperature when combined with collisional-radiative models. Findings add to information about species and to boosting of species concentration. Additionally, quantitative data is determined on spatially- and temporally- resolved characteristics of species defining  $\text{NH}_3$  synthesis

Cross-disciplinary literature, properly interpreted, can be practically applied to 1) guide use of reaction-promoting catalysts to accelerate and control chemical reactions, and 2) increase awareness of suitable plasma modes and alternatives to OES for process monitoring. OES however might not be suitable for a process-analytical technology (PAT) because of relative complexity.

Findings will be of interest and benefit to a range of researchers and manufactures in design and application of plasma for  $\text{NH}_3$  synthesis.

## **6 Acknowledgements**

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