Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in
Green and Sustainable Chemistry

Plasma catalysis in ammonia production and decomposition: Use it, or lose it?

Yury Gorbanev, Igor Fedirchyk and Annemie Bogaerts

Abstract

The combination of plasma with catalysis for the synthesis and decomposition of NH_3 is an attractive route to the production of carbon-neutral fertiliser and energy carriers and its conversion into H_2. Recent years have seen fast developments in the field of plasma-catalytic NH_3 life cycle. This work summarises the most recent advances in plasma-catalytic and related NH_3-focussed processes, identifies some of the most important discoveries, and addresses plausible strategies for future developments in plasma-based NH_3 technology.

Addresses

Research Group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium

Corresponding author: Gorbanev, Yury (yury.gorbanev@uantwerpen.be)

Current Opinion in Green and Sustainable Chemistry 2024, **47:**100916

This review comes from a themed issue on **Ammonia-Based Energy Storage and Conversion (2024)**

Edited by **Kevin Rouwenhorst** and **Joshua Makepeace**

https://doi.org/10.1016/j.cogsc.2024.100916

Keywords

Plasma, Nitrogen fixation, Ammonia, Plasma catalysis, Production and decomposition.

Introduction

In recent years, the global annual production of ammonia reached nearly 200 Mt, making it the second most-produced chemical in the world [1]. The uses of NH_3 span from textile and plastics production to pharmaceuticals and the automotive industry, with its main use as a fertiliser. Moreover, the usage of ammonia as a hydrogen carrier, and hence as a carbon-free fuel, is actively investigated [2].

The industry-dominating Haber–Bosch process of producing NH_3 via nitrogen fixation with H_2 is environmentally unbenign, very energy-intensive, and in practice relies on fossil fuels (CH_4). While CO_2 emissions can be reduced by partially electrifying the Haber–Bosch process, it is feasible exclusively on a large scale as a centralised production, which implies distribution and associated energy costs. The European strategy of decarbonisation, together with the current fossil fuel crisis, demands that an alternative be found that would enable an auxiliary (decentralised) NH_3 synthesis based on renewable energy [2,3].

Thermocatalytic NH_3 decomposition, industrially used to generate H_2 for metallurgy, resembles Haber–Bosch in its practical reliance on fossil energy sources (at least up until now) and negative environmental impact. The emergence of NH_3 as a carbon-free hydrogen carrier creates the need for technologies to reduce energy and carbon footprints [4].

One of the most promising ways to do this is with plasma technology. Plasma is a partially ionised gas that comprises electrons, ions, radicals, excited species, and photons. Unlike most industrial processes, plasma can be operated at atmospheric pressure and intermittently, making it compatible with renewable electricity [5]. Furthermore, the effectiveness of plasma-based gas conversion can be increased by combining it with catalysis, with the potential to yield performance unattainable by plasma or thermal catalysis individually [6,7]. However, the question on whether future technologies should “use” plasma catalysis in NH_3 synthesis and/or decomposition, or perhaps it is better to “lose” it, remains open.

Numerous literature reviews describe pathways of NH_3 synthesis by plasma-based nitrogen fixation, including several from the past two years [1,2,8–12], whereas the fairly newer field of plasma-based NH_3 decomposition afforded only one review [4]. These works give a thorough overview of plasma(-catalytic) NH_3 processes. In contrast, the aim of the present paper is not solely to discuss the most recent works on these topics (2022–2023) but also to indicate some of the topics that may lie outside the traditional plasma catalysis scope (Figure 1), but in our opinion, require attention.

Plasma catalysis to produce NH_3

Two general combinations of plasma and catalysis are distinguished: in-plasma catalysis (IPC) and post-plasma catalysis (PPC) [8]. Although hypothetically also pre-plasma catalysis (PREPC) can be envisioned with plasma-generated heat transferred with a heat exchanger, to our knowledge, there are no such reports to date.

In IPC, the catalyst is in direct contact with plasma, i.e. subjected to both the plasma-generated species and the heat. The thermal degradation of most catalysts used for

Abbreviations

DBD	dielectric barrier discharge
IPC	in-plasma catalysis
MW	microwave
(P)CLAS	(plasma) chemical looping ammonia synthesis
PPC	post-plasma catalysis
PREPC	pre-plasma catalysis.

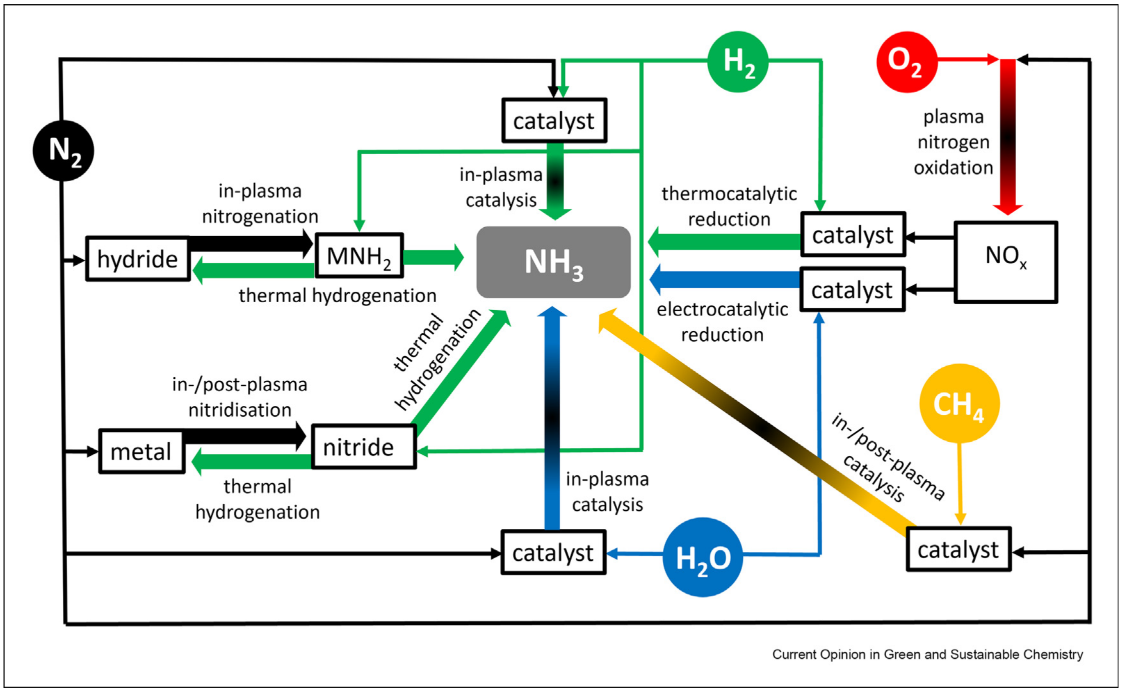
NH_3 synthesis and NH_3 itself limits IPC only to dielectric barrier discharge (DBD) plasma, which has much lower temperatures than other atmospheric pressure plasma types. In PPC, a catalyst is positioned downstream from the plasma and, hence, can be used with multiple plasma types. It must be noted that PREPC and many instances of PPC are thermocatalytic, in which the heat, which would otherwise be dissipated downstream from the plasma, is used to perform thermal catalysis, thus reducing the total energy losses. Various plasma types for PC NH_3 production/decomposition are shown in Table 1.

Catalyst role in in-plasma catalysis

The most common pathway of plasma-catalytic NH_3 production is direct N_2 fixation with H_2 (Figure 1, top). Since the first evidence of NH_3 production enhancement by adding a catalyst to plasma [2,8], most plasma catalysis research has focused on catalyst screening and design, varying both the metal and the support, from monometallic catalysts on inert oxides to various dopants and photocatalytically active supports [8,13–15]. Although clear improvements in the energy cost of NH_3 synthesis are seen with catalysts compared to plasma alone (due to the increased NH_3 production rate at the same plasma power), the actual role of the catalyst remains an open question. Sometimes IPC is reported to resemble thermal catalysis, where the properties (e.g. adsorption capacity/binding energy) of the metal sites and the supports govern the process [13,14].

Contrastingly, several studies demonstrate that changing the catalyst chemical composition leads to changes in plasma discharge characteristics. In a comparison of different oxides as DBD packing materials, BeO (possessing the highest dielectric constant and thermal conductivity) afforded the highest production of NH_3 under the same energy input, which was attributed to higher electron energy in the plasma and improved heat transfer from the packing to the gas [16]. In a study with Co-based Al_2O_3-supported catalysts with different transition metals added, their presence in the DBD (as in IPC) changed the number of microdischarges in plasma. Conductive Ce- and La-doped Co catalysts supported on otherwise dielectric Al_2O_3 transitioned the DBD from a purely filamentary to a diffuse regime, reducing the decomposition of the formed NH_3 by the energy-dense microdischarges and thus increasing the net NH_3 production and reducing the energy cost.

Figure 1



Current Opinion in Green and Sustainable Chemistry

Various plasma-based pathways of nitrogen fixation into NH_3 include direct plasma catalysis, plasma with subsequent catalysis, and chemical looping.

Table 1

Qualitative description of various combinations of plasma and catalysis in NH_3 production and decomposition.

Plasma type	Compatible with	Pathways of NH_3		Key parameters	
		Production	Decomposition	Energy cost	Throughput
Nonequilibrium (dielectric barrier discharge)	IPC, PPC	Direct, via NO_x	Direct	High	Low
Quasi-equilibrium – “warm” (microwave, gliding arc)	PPC, PREPC	via NO_x	Direct	Low	High

IPC, in-plasma catalysis; PPC, post-plasma catalysis; PREPC, pre-plasma catalysis.

Under conditions with constant discharge properties, all supported catalysts produced more NH_3 compared to blank supports but performed virtually identically regardless of the chemical nature of the metal [17]. Conversely, the addition of metal sites to a ferroelectric support coated with dielectric Al_2O_3 decreased the NH_3 generation; they were proposed to cause the formation of high-energy microdischarges rather than reducing them [18].

Adding Ag to SBA-15 support gave discrepant results at two different plasma power values, ascribed to the differences between two DBD regimes: lower power made Ag sites beneficial, and vice versa [19]. Thus, catalysts affects the performance of plasma, and plasma affect the catalyst role: lower plasma power decreases the role of gas phase reactions and increases the role of the catalyst surface [17,19].

Mechanisms of in-plasma catalysis for NH_3 production

DBD is commonly low-temperature, but microdischarges onto the metal sites may give a locally increased temperature, making discrimination between plasma-catalytic and thermocatalytic effects in IPC difficult [7]. Moreover, even in nonthermal plasma catalysis, the exact mechanism of NH_3 formation is still a debated subject. While the Eley—Rideal mechanism plays an important role in plasma-catalytic NH_3 synthesis (unlike in thermal catalysis) [20,21], the relative contributions of Eley—Rideal and the Langmuir—Hinshelwood mechanisms may depend on the metal. A kinetic study showed that on MgO-supported transition metals Co, Ru, Pt, Pd, and Cu, the PC NH_3 reaction in DBD proceeded via Eley—Rideal, while on Ag Langmuir—Hinshelwood, it was the dominant mechanism [22].

The energy cost is one of the main factors defining the feasibility of a plasma process (albeit not the only one; e.g. single-pass yield is also an important criterion). The energy cost of IPC NH_3 synthesis is most commonly in the range of 10—100 MJ/mol [17], which is dramatically higher than the suggested target value of 1.5 MJ/mol for plasma-based nitrogen fixation to be fully competitive with the industrial standard [23]. Despite the suggestion that deliberately populating plasma with vibrationally excited $N_2(v)$ molecules (i.e. creating strong nonequilibrium plasma conditions) may reduce the energy cost of NH_3 generation, recent experimental and computational research showed that atomic N is the kinetics-controlling species in plasma-catalytic NH_3 production [21,24—26]. While this means that nonequilibrium DBDs are not strictly needed for PC NH_3 synthesis, other plasmas are too hot for direct NH_3 production.

Preventing NH_3 destruction during synthesis

The decomposition of NH_3 by microdischarges in IPC DBD reduces its net yield, thus increasing the energy cost [20]. In-situ adsorption can reduce this detrimental effect [27]. NH_3 adsorbed in the pores of zeolite 4A and remained protected from plasma, decreasing the energy cost twice compared to plasma alone [3]. It is possible that the results of other recent works with zeolite catalysts supports giving the best performance [14,28] were also influenced by this positive effect, albeit without explicitly evaluating it. Zeolites with phosphate moieties in IPC also improved the NH_3 yield, additionally via the diffusion of excited N_2 into the pores (larger than its kinetic radius of 3.6 Å) [29].

Thus, highly porous materials have several advantages when used as supports for plasma-catalytic NH_3 synthesis. Other materials with high NH_3 sorption affinity can also be used, but the zeolites have the advantage of not undergoing surface deactivation via nitridisation [3].

Chemical looping

Deliberate nitridisation as a part of plasma chemical looping ammonia synthesis (PCLAS) is an attractive strategy. One way of treating PCLAS is by exposing supported metals to N_2 plasma and subsequent hydrogenation of the formed nitrides to release NH_3 and regenerate the “clean” metal surface [30], as shown for a microwave (MW) plasma effluent in contact with Fe, Mn, and CoMo (similar to PPC), followed by thermal H_2 treatment [31]. MW nitrification was quicker than conventional methods, and the resulting metal nitrides gave higher NH_3 production rates. Alternatively, PCLAS can be accomplished by exposing metal hydrides to DBD N_2 plasma (similar to IPC), yielding $-NH_2$ surface moieties, which are released as NH_3 upon subsequent thermal hydrogenation, which also regenerates the metal hydride, albeit the energy cost of NH_3

production is very high (1–2 orders of magnitude higher than for IPC NH_3 production) [32]. Thus, PCLAS can be considered a quasi-catalytic process because the looping implies regeneration of the active surface, but it still remains in its infancy and is currently mostly used for fundamental kinetics studies.

Alternative H-sources for NH_3 production

The methods of plasma-catalytic NH_3 synthesis described above employ H_2 as feedstock for NH_3. Other routes involve different sources of hydrogen, e.g. plasma-enabled nitrogen fixation into NH_3 while simultaneously converting CH_4 (the H source) into value-added hydrocarbons [7], but the main drawback is low selectivity towards NH_3. IPC (DBD with Cu/SiO_2) and PPC (MW with $AgPd/CeO_2$) afforded 7 and 9% NH_3 selectivity, respectively [33,34]. Besides, the process still involves CH_4, which compromises decarbonisation.

H_2O vapour can also be used for IPC-NH_3 synthesis. However, although such a process does not require molecular hydrogen and uses H_2O directly, the net energy cost is higher due to the energy required for H_2O dissociation (with a higher bond energy than H_2) and the formation of by-products (H_2O_2 or NO_x). DBD plasma with Co/SiO_2 produced NH_3 from N_2 and H_2O, albeit with a high energy cost (11 MJ/mol) [35]. DBD air plasma and γ-Al_2O_3 as a catalyst afforded NH_3 with an extreme energy cost of >12 GJ/mol, despite using humid air directly with no costs for N_2 extraction [36]. Both processes suffer from nonselective NH_3 production (due to reductive and oxidative nitrogen fixation by H_2O [35,36] and/or O_2^{36}), high energy costs, and kinetics are limited by the available humidity content (2.1 vol% at 20 °C).

Plasma with subsequent catalysis

Another route to NH_3 is plasma-based nitrogen fixation into NO_x, followed by catalytic reduction into NH_3. This can be viewed as an extreme scenario of PPC, with the nitrogen fixation and the reduction steps separated. A hybrid system with air plasma enabled the induction of NO_2^- and NO_3^- in water and their subsequent electrocatalytic reduction into NH_3 [37]. A controlled process of selective NO_2^- generation (which electrocatalytically reduces to NH_3 more easily) can be done in an aqueous solution of KOH [38]. In brief, this resembles a reversed industrial process of NH_3 and HNO_3 production (where NH_3 produced via Haber–Bosch is catalytically oxidised into HNO_3). It should be noted that currently, the combined industrial process of Haber–Bosch + Ostwald focusses mostly on fertilisers in the form of NH_4NO_3 (where part of the NH_3 from Haber–Bosch is oxidised into HNO_3, and then combined with pristine NH_3). This product can be obtained in a reverse process, by plasma coupled with, e.g. electrocatalytic reduction. First, NO_x is produced and turned into NO_3^- in an aqueous solution, and then partially reduced to NH_4^+ so that the resulting solution contains the fertiliser – NH_4NO_3. Such a process can be done in one pot, and in fewer steps than the Haber–Bosch–Ostwald process.

Thermocatalytic hydrogenation of the plasma-generated NO into NH_3 over a lean NO_x trap catalyst gave the lowest reported energy cost for plasma-based NH_3 of 2.1 MJ/mol, demonstrating the potential competitiveness of plasma-catalytic NH_3 synthesis [39]. Electrolysis-produced H_2 makes it compatible with electrification strategies. Advantageously, the plasma type is not limited to DBD, typically associated with low production rates, “warm” plasmas perform better in generating NO_x (see Table 1). They generally have higher single-pass yields than DBD plasmas and can be catalysis-assisted to increase NO_x production and further reduce the energy cost of this first step [40]. Such a shift towards more thermal (i.e. more equilibrium) plasmas for nitrogen fixation can bridge the gap between plasma-catalytic nitrogen fixation and an industrially viable process of NH_3 generation, albeit an indirect one [3,23].

Plasma catalysis to decompose NH_3 into N_2 and H_2

Catalysts during IPC NH_3 decomposition impose similar limitations on the process as during NH_3 synthesis, equally restricting IPC to low-temperature plasma (DBD). While IPC (and the associated low-temperature DBD) are reasonable for exothermic NH_3 synthesis, endothermic NH_3 decomposition is severely limited in this scenario. Conversely, in PPC NH_3 decomposition, the plasma-produced heat is used by a downstream catalyst for further decomposition [41].

In-plasma catalysis for NH_3 decomposition

IPC NH_3 decomposition (“cracking”) resembles IPC-NH_3 production in many ways. The main focus is to develop catalysts by screening for efficient support, metal, and their morphology [42,43]. Unlike thermocatalytic cracking, IPC showed an increase in conversion in the presence of only support material, and the electrical properties of the supports had a more significant impact on conversion than surface area or pore volume: $MgAl_2O_4$ and γ-Al_2O_3 (with high dielectric constants of 10–30) were the most synergistic with plasma [44]. Deposited metals exhibited both a negative [45] and positive [44] impact on the catalyst performance, although the latter, even optimised (IPC DBD with Ru/Al_2O_3), still gave a high energy cost of 400 kJ/mol, ca. 4.5 times higher than thermocatalytic NH_3 cracking with Ru catalysts [44]. Reducing the particle size of the Mo_2N catalyst shifted the DBD mode from filamentary to surface discharges, improving the decomposition and lowering the energy cost. Surface discharges were proposed to facilitate the delivery of plasma-generated reactive species to the catalyst surface, thus enhancing surface reactions [45]. Mo_2N catalysts produced via nitrification at different temperatures performed differently, although the underlying nature (different catalytic activity or changes to discharge properties by catalysts) remained unclear [46].

Kinetic studies showed that IPC NH_3 decomposition is initiated mainly in the gas phase by electron impact dissociation [47,48]. A decrease in the threshold temperature for NH_3 decomposition by 100–120 °C was reported for a variety of catalysts in a DBD plasma where the reactors were supplied with external heat sources that operated at lower temperatures than those required for thermal catalysis, leading to the conclusion that the plasma contribution is not limited to thermal conversion [44,45,49,50]. We note, however, that the temperature of DBD microdischarge filaments is higher than the bulk gas temperature, and thus thermal decomposition as the driving force cannot be completely ruled out.

Mechanistically, the Eley–Rideal mechanism is reported to be important in IPC NH_3 decomposition: it enhances the decomposition by reactive plasma species (NH_3*, NH_2, NH), which facilitate the removal of N from the catalyst surface [48,50] (although the high temperature in the microdischarge filaments may also enhance this), and inhibits it by NH_3 formation via reaction between adsorbed H and NH_2 [48]. The synergistic effect between plasma and catalyst is generally assumed to arise from the catalyst providing reaction pathways unavailable in plasma and plasma promoting NH_3 decomposition and inhibiting the formation of nitrides on the catalyst surface [44,49] (which is generally detrimental besides the aforementioned Mo_2N).

A drastically different process involved igniting plasma in-liquid in a 25 wt% aqueous NH_4OH solution using Ni–Bi titanates [51] and zeolites [52] as photocatalysts. Catalysts were suspended in liquid and agitated to ensure their contact with the localised in-liquid plasma. Insufficient intensity of UV radiation or heat reaching the catalysts resulted in a very high energy cost of NH_3 decomposition (0.9 GJ/mol), with a relative increase in H_2 production rate of only 20% when using catalysts compared to in-liquid plasma alone, and most of H_2 originated from H_2O instead of NH_3.

Post-plasma catalysis for NH_3 decomposition

The only approach to PPC NH_3 cracking was described in a slightly older work from 2021 and involved an arc plasma torch with a NiO/Al_2O_3 catalyst placed downstream from the plasma, enabling the second, thermocatalytic step of NH_3 cracking in addition to the initial plasma cracking [41]. This afforded an energy cost reduction from 200 (only plasma) to 160 (PPC) kJ/mol, nearly approaching the value of purely thermocatalytic cracking (90 kJ/mol [4]). Both plasma and catalysis steps were governed by thermal effects, with the PPC step utilising the plasma-produced heat (which would otherwise be lost), thus decreasing the energy cost. Despite the promising results, to our knowledge, no further PPC studies were reported.

Conclusions and outlook

In this work, we attempted to answer the question on whether plasma catalysis in the NH_3 lifecycle is promising (“we should use it”) or not (“we should lose it”). Despite vigorous investigations into plasma-catalytic NH_3 formation/decomposition, the question of its feasibility on an industrial scale remains open.

Regarding IPC NH_3 formation/decomposition (“direct” plasma catalysis, realistically only available in DBD plasma), many attempts in different directions aim to improve the process performance. IPC NH_3 processing, although providing better formation/decomposition metrics at ambient temperatures than thermocatalytic processes, can become fully viable only if two critical issues are addressed: the high EC and low throughput of DBD plasma reactors, most common for direct plasma catalysis.

In contrast, the initial generation of NO_x by warm plasma, and their subsequent thermo- or electrocatalytic reduction into NH_3 offer more attractive options. Of all the literature reports to date, the least energy costly process of NH_3 production is via plasma(-catalytic) nitrogen fixation into NO_x and further catalytic reduction into NH_3. The first step can be done by warm plasmas, which exhibit much lower energy costs and higher throughput than DBDs.

As for decomposition, the examples of using “warm” plasmas for NH_3 decomposition (i.e. without catalysts) show that plasma-initiated thermal conversion has several advantages, not only over the IPC NH_3 decomposition, but also over the thermocatalytic process: the instantaneous start and intermittent operation allowing the use of renewable electricity, and reaching a high temperature (required for plasma-based thermal NH_3 decomposition) faster than with conventional gas heating. The major challenge is reducing the energy cost of such a process. Plasma with an additional catalytic step (PPC and/or PREPC) presents a promising direction for future developments of plasma technology in NH_3 decomposition.

This ultimately means we should not aim to “lose” plasma catalysis in the NH_3 lifecycle altogether; instead, we should “use” the most technologically feasible version of it. At this stage of development, the most attractive plasmas are “warm” plasmas, with catalysis not directly integrated into the plasma (i.e. not IPC). Nonetheless, we find it possible that future scientific developments can shift the appeal towards IPC NH_3 synthesis/decomposition and other near-catalytic approaches, such as, e.g. PCLAS.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data were used for the research described in the article.

Acknowledgements

The work was supported by the Fund for Scientific Research (FWO) Flanders Bioeconomy project (grant G0G2322N) funded by the European Union-NextGenerationEU, the HyPACT project funded by the Belgian Energy Transition Fund, and the MSCA4Ukraine project 1233629 funded by the European Union.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Huang Z, Xiao A, Liu D, Lu X, Ostrikov K: **Plasma-water-based nitrogen fixation: status, mechanisms, and opportunities**. *Plasma Process Polym* 2022, **19**, 2100198. https://doi.org/10.1002/ppap.202100198.

2. Zhang J, Li X, Zheng J, Du M, Wu X, Song J, Cheng C, Li T, Yang W: **Non-thermal plasma-assisted ammonia production: a review**. *Energy Convers Manag* 2023, **293**, 117482. https://doi.org/10.1016/j.enconman.2023.117482.

3. * Rouwenhorst KHR, Mani S, Lefferts L: **Improving the energy yield of plasma-based ammonia synthesis with in situ adsorption**. *ACS Sustain Chem Eng* 2022, **10**:1994–2000. https://doi.org/10.1021/acssuschemeng.1c08467.

Highly porous zeolite materials were used in plasma-catalytic NH_3 synthesis in a DBD from N_2 and H_2. Adsorption of the formed NH_3 inside the pores of the materials helped prevent the destruction of NH_3 by high-energy DBD plasma filaments and thus increased the net production of NH_3. Under the experimental conditions used, this led to a decrease in the energy cost from ca. 57 MJ/mol to 27 MJ/mol NH_3, demonstrating the advantage of using adsorbents as supports.

4. Moszczyńska J, Liu X, Wiśniewski M: **Green hydrogen production through ammonia decomposition using non-thermal plasma**. *Int J Mol Sci* 2023, **24**, 14397.

5. Adamovich I, Agarwal S, Ahedo E, Alves LL, Baalrud S, Babaeva N, Bogaerts A, Bourdon A, Bruggeman PJ, Canal C, Choi EH, Coulombe S, Donkó Z, Graves DB, Hamaguchi S, Hegemann D, Hori M, Kim HH, Kroesen GMW, Kushner MJ, Laricchiuta A, Li X, Magin TE, Mededovic Thagard S, Miller V, Murphy AB, Oehrlein GS, Puac N, Sankaran RM, Samukawa S, Shiratani M, Šimek M, Tarasenko N, Terashima K, Thomas Jr E, Trieschmann J, Tsikata S, Turner MM, van der Walt IJ, van de Sanden MCM, von Woedtke T: **The 2022 Plasma Roadmap: low temperature plasma science and technology**. *J Phys D Appl Phys* 2022, **55**, 373001. https://doi.org/10.1088/1361-6463/ac5e1c.

6. Yan C, Waitt C, Akintola I, Lee G, Easa J, Clarke R, Geng F, Poirier D, Otor HO, Rivera-Castro G, Go DB, O'Brien CP, Hicks JC, Schneider WF, Ma H: **Recent advances in plasma catalysis**. *Ind Eng Chem Res* 2022, **61**:7675–7678. https://doi.org/10.1021/acs.iecr.2c01594.

7. Bogaerts A, Centi G, Hessel V, Rebrov E: **Challenges in unconventional catalysis**. *Catal Today* 2023, **420**, 114180. https://doi.org/10.1016/j.cattod.2023.114180.

8. Hosseini H: **Dielectric barrier discharge plasma catalysis as an alternative approach for the synthesis of ammonia: a review**. *RSC Adv* 2023, **13**:28211–28223. https://doi.org/10.1039/D3RA05580A.

9. Nguyen M, H, Omidkar A, Song H: **Technical challenges and prospects in sustainable plasma catalytic ammonia production from methane and nitrogen**. *ChemPlusChem* 2023, **88**, e202300129. https://doi.org/10.1002/cplu.202300129.

10. Zhao X, Tian Y: **Sustainable nitrogen fixation by plasma-liquid interactions**. *Cell Rep Phys Sci* 2023, **4**, 101618. https://doi.org/10.1016/j.xcrp.2023.101618.

11. Qu Z, Zhou R, Sun J, Gao Y, Li Z, Zhang T, Zhou R, Liu D, Tu X, Cullen P, Ostrikov K: **Plasma-assisted sustainable nitrogen-to-ammonia fixation: mixed-phase, synergistic processes and mechanisms**. *ChemSusChem* 2024, e202300783. https://doi.org/10.1002/cssc.202300783.

12. Van Duc Long N, Al-Bared M, Lin L, Davey K, Tran NN, Pourali N, Ken Ostrikov K, Rebrov E, Hessel V: **Understanding plasma-assisted ammonia synthesis via crossing discipline borders of literature: a critical review**. *Chem Eng Sci* 2022, **263**, 118097. https://doi.org/10.1016/j.ces.2022.118097.

13. van Raak TABJ, Li S, Gallucci F: **Prevailing surface reactions in the plasma-catalytic ammonia synthesis with Ru/CeO_2 and $Ru/Ti\text{-}CeO_2$**. *Chem Eng J* 2023, **455**, 140691. https://doi.org/10.1016/j.cej.2022.140691.

14. Zhu X, Liu J, Hu X, Zhou Z, Li X, Wang W, Wu R, Tu X: **Plasma-catalytic synthesis of ammonia over Ru-based catalysts: insights into the support effect**. *J Energy Inst* 2022, **102**:240–246. https://doi.org/10.1016/j.joei.2022.02.014.

15. Liu J, Zhu X, Jiang S, Zhang H, Hong Y, Chen G, Tu X: **Plasma-catalytic synthesis of ammonia over Ru/$BaTiO_3$-based bimetallic catalysts: synergistic effect from dual-metal active sites**. *Fuel Process Technol* 2023, **250**, 107851. https://doi.org/10.1016/j.fuproc.2023.107851.

16. Liu J, Zhu X, Hu X, Tu X: **Plasma-assisted ammonia synthesis in a packed-bed dielectric barrier discharge reactor: roles of dielectric constant and thermal conductivity of packing materials**. *Plasma Sci Technol* 2022, **24**, 025503. https://doi.org/10.1088/2058-6272/ac39fb.

17. * Ndayirinde C, Gorbanev Y, Ciocarlan R-G, De Meyer R, Smets A, Vlasov E, Bals S, Cool P, Bogaerts A: **Plasma-catalytic ammonia synthesis: packed catalysts act as plasma modifiers**. *Catal Today* 2023, **419**, 114156. https://doi.org/10.1016/j.cattod.2023.114156.

Different Co-based catalysts supported by γ-Al_2O_3 were studied for NH_3 production in a DBD from various N_2/H_2 mixtures. Different catalysts were found to affect the plasma discharge characteristics in different ways. Bimetallic CoLa and CoCe catalysts exhibited the best performance, affording the highest NH_3 concentrations of ca. 9000 ppm, and the lowest energy cost of 80 MJ/mol NH_3 (several times higher and lower than other catalysts). The improved performance was ascribed to the catalysts' ability to change the discharge type from filamentary to more diffuse, which limited the decomposition of the produced NH_3.

18. Navascués P, Garrido-García J, Cotrino J, González-Elipe AR, Gómez-Ramírez A: **Incorporation of a metal catalyst for the ammonia synthesis in a ferroelectric packed-bed plasma reactor: does it really matter?** *ACS Sustain Chem Eng* 2023, **11**:3621–3632. https://doi.org/10.1021/acssuschemeng.2c05877.

19. ** Gershman S, Fetsch H, Gorky F, Carreon ML: **Identifying regimes during plasma catalytic ammonia synthesis**. *Plasma Chem Plasma Process* 2022, **42**:731–757. https://doi.org/10.1007/s11090-022-10258-y.

SBA-15 zeolite, pristine and with deposited Ag nanoparticles, was used in plasma-catalytic NH_3 synthesis in a DBD from N_2 and H_2. The concentration of the produced NH_3 increased with Ag/SBA-15 at lower plasma power and decreased at higher plasma power (11 and 19 W, respectively). The difference was explained by identifying two different PC regimes: gas phase plasma chemistry dominated (19 W), and catalyst surface dominated (11 W).

20. Andersen JA, Holm MC, van't Veer K, Christensen JM, Østberg M, Bogaerts A, Jensen AD: **Plasma-catalytic ammonia synthesis in a dielectric barrier discharge reactor: a combined experimental study and kinetic modeling**. *Chem*

Eng J 2023, **457**, 141294. https://doi.org/10.1016/j.cej.2023.141294.

21. Liu T-W, Gorky F, Carreon ML, Gómez-Gualdrón DA: **Energetics of reaction pathways enabled by N and H radicals during catalytic, plasma-assisted NH_3 synthesis**. *ACS Sustain Chem Eng* 2022, **10**:2034–2051. https://doi.org/10.1021/acssuschemeng.1c05660.

22. Rouwenhorstm KHR, Lefferts L: **Plasma-catalytic ammonia synthesis via Eley-Rideal reactions: a kinetic analysis**. *ChemCatChem* 2023, **15**, e202300078. https://doi.org/10.1002/cctc.202300078.

23. Rouwenhorst KHR, Jardali F, Bogaerts A, Lefferts L: **Correction: from the Birkeland–Eyde process towards energy-efficient plasma-based NOX synthesis: a techno-economic analysis**. *Energy Environ Sci* 2023, **16**:6170–6173. https://doi.org/10.1039/D3EE90066E.

24. Liu T-W, Gorky F, Carreon ML, Gomez-Gualdron DA: **Plasma radicals as kinetics-controlling species during plasma-assisted catalytic NH_3 formation: support from microkinetic modeling**. *ACS Sustain Chem Eng* 2023, **11**:16749–16763. https://doi.org/10.1021/acssuschemeng.3c03813.

25. * * Bayer BN, Bruggeman PJ, Bhan A: **Species, pathways, and timescales for NH_3 formation by low-temperature atmospheric pressure plasma catalysis**. *ACS Catal* 2023, **13**: 2619–2630. https://doi.org/10.1021/acscatal.2c05492.

Using molecular beam mass spectrometry, the density of various reactive species (including N atoms and N_2(v) vibrationally excited states) was measured in plasma-catalytic NH_3 synthesis in N_2/H_2 mixtures, with the catalyst positioned downstream at varied distances from the radio frequency plasma jet. The correlation of the densities of the measured species showed that NH_3 is produced in the same quantities as N atoms are consumed. It was proposed that the main mechanism leading to NH_3 on the catalyst surface involves atomic N generated by plasma.

26. Bayer BN, Raskar S, Adamovich IV, Bruggeman PJ, Bhan A: **Availability and reactivity of N2(v) for NH_3 synthesis by plasma catalysis**. *Plasma Sources Sci Technol* 2023, **32**, 125005. https://doi.org/10.1088/1361-6595/ad10f0.

27. Rouwenhorst, K. H. R.; Lefferts, L. Plasma-based conversions with in situ product removal. *Plasma Process Polym* n/a (n/a), e2200244. doi: https://doi.org/10.1002/ppap.202200244.

28. Meloni E, Cafiero L, Martino M, Palma V: **Structured catalysts for non-thermal plasma-assisted ammonia synthesis**. *Energies* 2023, **16**:3218.

29. Gorky F, Nambo A, Carreon MA, Carreon ML: **Plasma catalytic conversion of nitrogen and hydrogen to ammonia over silico alumino phosphate (SAPO) zeolites**. *Plasma Chem Plasma Process* 2023. https://doi.org/10.1007/s11090-023-10397-w.

30. Barboun PM, Otor HO, Ma H, Goswami A, Schneider WF, Hicks JC: **Plasma-catalyst reactivity control of surface nitrogen species through plasma-temperature-programmed hydrogenation to ammonia**. *ACS Sustain Chem Eng* 2022, **10**: 15741–15748. https://doi.org/10.1021/acssuschemeng.2c04217.

31. Brown S, Ahmat Ibrahim S, Robinson BR, Caiola A, Tiwari S, Wang Y, Bhattacharyya D, Che F, Hu J: **Ambient carbon-neutral ammonia generation via a cyclic microwave plasma process**. *ACS Appl Mater Interfaces* 2023, **15**:23255–23264. https://doi.org/10.1021/acsami.3c02508.

32. * Wu H, Yang L, Wen J, Xu Y, Cai Y, Gao W, Wang Q, Guan Y, Feng S, Cao H, He T, Liu L, Zhang S, Guo J, Chen P: **Plasma-Driven nitrogen fixation on sodium hydride**. *Adv Energy Mater* 2023, **13**, 2300722. https://doi.org/10.1002/aenm.202300722.

A chemical looping process for plasma-based NH_3 synthesis was proposed, involving the nitrogenation of NaH or KH into $NaNH_2$ or KNH_2, followed by thermal hydrogenation, which caused the release of NH_3 from the surface and regeneration of the initial NaH. When exposing 20 wt% NaH/MgO to a DBD N_2 plasma, the NH_3 production rate was ca. 2100 μmol NH_3/(g·h), while the use of thermal CLAS even at elevated temperatures (>300 °C) did not yield any NH_3, thus demonstrating the applicability of PCLAS at milder conditions than thermal CLAS. The very high energy cost (>400 MJ/mol NH_3) was proposed to be improved by using different plasma discharge types.

33. Nguyen HM, Omidkar A, Li W, Meng S, Li Z, Song H: **Non-thermal plasma assisted catalytic nitrogen fixation with methane at ambient conditions**. *Chem Eng J* 2023, **471**, 144748. https://doi.org/10.1016/j.cej.2023.144748.

34. Tiwari S, Ibrahim SA, Robinson B, Brown S, Wang Q, Che F, Hu J: **Post-plasma catalysis: charge effect on product selectivity in conversion of methane and nitrogen plasma to ethylene and ammonia**. *Catal Sci Technol* 2023, **13**:2966–2981. https://doi.org/10.1039/D2CY02077G.

35. Nguyen HM, Gorky F, Guthrie S, Carreon ML: **Sustainable ammonia synthesis from nitrogen wet with sea water by single-step plasma catalysis**. *Catal Today* 2023, **418**, 114141. https://doi.org/10.1016/j.cattod.2023.114141.

36. * Feng J, Ning P, Li K, Sun X, Wang C, Jia L, Fan M: **One-step synthesis of ammonia directly from wet air/N_2 by plasma combined with a γ-Al_2O_3 catalyst**. *ACS Sustain Chem Eng* 2023, **11**:804–814. https://doi.org/10.1021/acssuschemeng.2c06706.

Air containing H_2O vapour was used for nitrogen fixation in a DBD with $A_{l2}O_3$ as catalysts. The process demonstrates the possibility of producing NH_3 directly from O_2-containing N_2 mixtures, with H_2O vapour as a source of hydrogen. Under ambient conditions (i.e. without using the heated water bath), the NH_3 production rate and energy cost from humid air were ca. 3 μmol/(g·h) and 12200 MJ/mol.

37. Sun J, Zhou R, Hong J, Gao Y, Qu Z, Liu Z, Liu D, Zhang T, Zhou R, Ostrikov K, Cullen P, Lovell EC, Amal R, Jalili AR: **Sustainable ammonia production via nanosecond-pulsed plasma oxidation and electrocatalytic reduction**. *Appl Catal B Environ* 2024, **342**, 123426. https://doi.org/10.1016/j.apcatb.2023.123426.

38. Luo Y, Jiang H, Ding L-X, Chen S, Zou Y, Chen G-F, Wang H: **Selective synthesis of either nitric acid or ammonia from air by electrolyte regulation in a plasma electrolytic system**. *ACS Sustain Chem Eng* 2023, **11**:11737–11744. https://doi.org/10.1021/acssuschemeng.2c06506.

39. * * Hollevoet L, Vervloessem E, Gorbanev Y, Nikiforov A, De Geyter N, Bogaerts A, Martens JA: **Energy-efficient small-scale ammonia synthesis process with plasma-enabled nitrogen oxidation and catalytic reduction of adsorbed NOx**. *ChemSusChem* 2022, **15**, e202102526. https://doi.org/10.1002/cssc.202102526.

A hybrid process consisting of NO_x generation by a pulsed spark plasma from air and their subsequent thermocatalytic over-reduction by H_2 over a lean NO_x trap catalyst ($Pt/BaO/Al_2O_3$), enabled NH_3 production with the lowest energy cost reported to date for a plasma-based NH_3 production process – 2.1 MJ/mol NH_3. Such a low energy cost was achievable partly due to the energy-efficient nitrogen oxidation by plasma, and partly due to the absence of an extra separation step of NO_x from air after plasma: the catalyst acts as NO_x adsorber itself.

40. Pei X, Li Y, Luo Y, Man C, Zhang Y, Lu X, Graves DB. Nitrogen fixation as NOx using air plasma coupled with heterogeneous catalysis at atmospheric pressure. *Plasma Process Polym* n/a (n/a), e2300135. doi: https://doi.org/10.1002/ppap.202300135.

41. * * Lin QF, Jiang YM, Liu CZ, Chen LW, Zhang WJ, Ding J, Li JG: **Instantaneous hydrogen production from ammonia by non-thermal arc plasma combining with catalyst**. *Energy Rep* 2021, **7**:4064–4070. https://doi.org/10.1016/j.egyr.2021.06.087.

Warm arc plasma was used for the NH_3 decomposition in a PPC configuration with a NiO/Al_2O_3 catalyst. The heat produced by plasma during the NH_3 decomposition was re-used for thermally activating the catalyst in PPC configuration. The process metrics are the lowest reported to date for direct plasma-based NH_3 decomposition and PPC NH_3 decomposition (200 and 160 kJ/mol, respectively). PPC setups with heat integration are shown to be more efficient than IPC setups and get close to the energy cost of thermocatalytic NH_3 cracking.

42. Andersen JA, Christensen JM, Østberg M, Bogaerts A, Jensen AD: **Plasma-catalytic ammonia decomposition using a packed-bed dielectric barrier discharge reactor**. *Int J Hydrog Energy* 2022, **47**:32081–32091. https://doi.org/10.1016/j.ijhydene.2022.07.102.

43. Chen G, Qu J, Cheah P, Cao D, Zhao Y, Xiang Y: **Size-dependent activity of iron nanoparticles in both thermal and plasma driven catalytic ammonia decomposition**. *Ind Eng Chem Res*

2022, **61**:11436–11443. https://doi.org/10.1021/acs.iecr.2c02092.

44. Wang Z, He G, Zhang H, Liao C, Yang C, Zhao F, Lei G, Zheng G, Mao X, Zhang K: **Plasma-promoted ammonia decomposition over supported ruthenium catalysts for COx-free H_2 production**. *ChemSusChem* 2023, **16**, e202202370. https://doi.org/10.1002/cssc.202202370.

45. * Wang Z, Zhang H, Ye Z, He G, Liao C, Deng J, Lei G, Zheng G, Zhang K, Gou F, Mao X: **H_2 production from ammonia decomposition with Mo_2N catalyst driven by dielectric barrier discharge plasma**. *Int J Hydrog Energy* 2024, **49**:1375–1385. https://doi.org/10.1016/j.ijhydene.2023.06.173.

The use of Mo_2N powder instead of larger particles during IPC led to DBD switching from filamentary discharge to surface discharge and achieving complete NH_3 cracking at one of the lowest reported IPC energy costs for NH_3 decomposition (530 kJ/mol). A difference was also observed with thermal catalysis, but to a much smaller extent. Additionally, the temperature of the catalyst bed was higher during IPC with Mo_2N powder compared to larger Mo_2N particles, leading to a synergy of plasma-catalytic and thermocatalytic effects.

46. Yu X, Hu K, Zhang H, He G, Xia Y, Deng M, Shi Y, Yang C, Mao X, Wang Z: **Plasma-catalytic ammonia decomposition for carbon-free hydrogen production using low pressure-synthesized Mo_2N catalyst**. *Plasma Chem Plasma Process* 2023, **43**:183–197. https://doi.org/10.1007/s11090-022-10282-y.

47. ** Bang S, Snoeckx R, Cha MS: **Kinetic study for plasma assisted cracking of NH_3: approaches and challenges**. *J Phys Chem A* 2023, **127**:1271–1282. https://doi.org/10.1021/acs.jpca.2c06919.

A kinetic study highlights major challenges in the development of models for NH_3 decomposition in both plasma-catalytic and thermocatalytic systems. Three existing thermal mechanisms of NH_3 decomposition were integrated with plasma-catalytic NH_3 decomposition mechanisms and compared against each other and against experimental data. The temperature window of NH_3 decomposition was demonstrated to be lower in plasma catalysis, to the point of conversion occurring even at room temperature.

48. Andersen JA, van't Veer K, Christensen JM, Østberg M, Bogaerts A, Jensen AD: **Ammonia decomposition in a dielectric barrier discharge plasma: insights from experiments and kinetic modeling**. *Chem Eng Sci* 2023, **271**, 118550. https://doi.org/10.1016/j.ces.2023.118550.

49. Gao Y, Hu E, Yi Y, Yin G, Huang Z: **Plasma-assisted low temperature ammonia decomposition on 3d transition metal (Fe, Co and Ni) doped CeO_2 catalysts: synergetic effect of morphology and co-doping**. *Fuel Process Technol* 2023, **244**, 107695. https://doi.org/10.1016/j.fuproc.2023.107695.

50. Meng S, Li S, Sun S, Bogaerts A, Liu Y, Yi Y: **NH_3 decomposition for H_2 production by thermal and plasma catalysis using bimetallic catalysts**. *Chem Eng Sci* 2024, **283**, 119449. https://doi.org/10.1016/j.ces.2023.119449.

51. Chung K-H, Lam SS, Park Y-K, An K-H, Jung S-C: **Preparation of nickel-bismuth titanates enhanced visible-light photosensitivity and their photocatalytic properties for hydrogen generation by plasma cracking**. *Mol Catal* 2023, **545**, 113239. https://doi.org/10.1016/j.mcat.2023.113239.

52. Chung K-H, Park Y-K, Kim S-J, Kim S-C, Jung S-C: **Green hydrogen production from ammonia water by liquid–plasma cracking on solid acid catalysts**. *Renew Energy* 2023, **216**, 119052. https://doi.org/10.1016/j.renene.2023.119052.