ELSEVIER



Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

Plasma-catalytic ammonia synthesis: Packed catalysts act as plasma modifiers

Callie Ndayirinde^{a,*}, Yury Gorbanev^a, Radu-George Ciocarlan^b, Robin De Meyer^{a,c,1}, Alessandro Smets^{a,b}, Evgenii Vlasov^c, Sara Bals^c, Pegie Cool^b, Annemie Bogaerts^a

^a Research group PLASMANT, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Antwerp, Belgium

^b Research group LADCA, Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Antwerp, Belgium

^c Research group EMAT, Department of Physics, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

ARTICLE INFO	A B S T R A C T
Keywords: Plasma catalysis N ₂ fixation Ammonia production Non-thermal plasma Cobalt-based catalysts	We studied the plasma-catalytic production of NH ₃ from H ₂ and N ₂ in a dielectric barrier discharge plasma reactor using five different Co-based catalysts supported on Al ₂ O ₃ , namely Co/Al ₂ O ₃ , CoCe/Al ₂ O ₃ , CoLa/Al ₂ O ₃ , CoCe/Al ₂ O ₃ , CoLa/Al ₂ O ₃ , CoCe/Al ₂ O ₃ and CoCeMg/Al ₂ O ₃ . The catalysts were characterized via several techniques, including SEM-EDX, and their performance was compared. The best performing catalyst was found to be CoLa/Al ₂ O ₃ , but the differences in NH ₃ concentration, energy consumption and production rate between the different catalysts were limited under the same conditions (i.e. feed gas, flow rate and ratio, and applied power). At the same time, the plasma properties, such as the plasma power and current profile, varied significantly depending on the catalyst. Taken together, these findings suggest that in the production of NH ₃ by plasma catalysis, our catalysts act as plasma modifiers, i.e., they change the discharge properties and hence the gas plase plasma chemistry.

chemistry on the catalyst surface.

1. Introduction

The steep increase in the world population results in a growing global demand for a variety of necessities, especially food. [1] To accommodate this growing food demand, fertilizers are widely used to increase the global food production. [2] Ammonia (NH₃) based fertilizers are among the most commonly used fertilizers in the agricultural sector. Besides agricultural purposes, NH₃ is also gaining attention as a hydrogen carrier and energy storage chemical. [3–5].

At present, NH₃ is mainly synthesized via the Haber Bosch (HB) process, which produces over 150 million tons of NH₃ annually. [6–8] However, the production of NH₃ via the HB process is a highly energy-intensive method: it consumes up to 2% of the global energy supply, and requires extremely high pressures (100–450 bar) and high temperatures (400–500 °C) to obtain a significant yield and to make the process cost-effective. [6] To enable these conditions, the HB process

uses fossil fuel (natural gas, oil and coal) as feedstock, and as a result, ca. 1.9 tons of CO_2 is generated per ton of NH_3 produced. [6,8,9].

Importantly, this effect dominates over the direct catalytic effect (as e.g. in thermal catalysis) defined by the

Consequently, alternative strategies [10] for a green NH_3 production are widely investigated. [9,11] Among other techniques, non-thermal plasma (NTP) catalytic NH_3 synthesis has recently gained a lot of attention as a potential sustainable, green alternative for the HB process.

NTPs are characterized by high-energy electrons $(10^4 - 10^5 \text{ K})$ that can cause non-thermal activation of molecules, while the gas temperature remains between 300 K and 1000 K. [12,13] As a result, reactions can take place at lower pressures and temperatures compared to thermal catalysis. However, NTPs contain a wide range of highly reactive species, making it difficult to obtain a single product at a high yield and with a high selectivity. [14] Yet, combining NTPs with catalysts can lead to a synergistic effect with the efficiency of the combined system surpassing that of the individual parts. [14–16] Further, NTPs allow for quick on/off operation making the technology compatible with the

https://doi.org/10.1016/j.cattod.2023.114156

Received 9 November 2022; Received in revised form 23 January 2023; Accepted 8 April 2023 Available online 10 April 2023 0920-5861/© 2023 Published by Elsevier B.V.

Abbreviations: HB, Haber-Bosch; NTP, non-thermal plasma; DBD, dielectric barrier discharge; XRPD, X-ray powder diffraction; SEM, scanning electron microscopy; EDX, energy dispersive X-ray spectroscopy; BET, Brunauer-Emmett-Teller; EC, energy consumption; PR, production rate; SEI, specific energy input; TPD, temperature programmed desorption; PSU, power supply unit.

^{*} Corresponding author.

E-mail address: callie.ndayirinde@uantwerpen.be (C. Ndayirinde).

¹ https://orcid.org/0000-0002-2390-7233

fluctuating renewable energy sources such as wind energy and solar power, enabling a novel green way to synthesize NH₃. [17].

Dielectric barrier discharge (DBD) plasma reactors are often chosen for the plasma-catalytic synthesis of NH3 because they provide good contact between the plasma and the catalysts, and the plasma operates at ambient conditions. [16] In 2018, Mehta et al. [18] designed a density functional theory based microkinetic model, suggesting that vibrationally excited N₂ enhances the N₂ dissociation rate and therefore the NH₃ synthesis rate. Consequently, the top of the classic "volcano" plot, or in other words - the optimal metal catalyst, shifts from Fe and Ru in thermal catalysis, towards weaker binding metals, such as Co and Ni, in plasma catalysis. [18] Various studies have been reported in which the plasma-catalytic synthesis of NH3 has been investigated over different transition metal catalysts, such as Ni, Fe, Cu, Ru and Co. [18-21] Several transition metal catalysts employed in these studies are supported on Al₂O₃ [22], but MgO, SiO₂ and activated carbon are also often used. [22-27] From the aforementioned studies, different catalysts were deemed to be optimal for the plasma-catalytic NH₃ synthesis. One of the reasons for these discrepancies in results is that not only the catalyst changes from one study to another, but also the plasma and reaction conditions are different, rendering the direct comparison difficult.

Furthermore, our recent experimental [21] and computational [28] works showed that the nature of the metal in monometallic catalysts, while having some impact on the catalytic efficiency, does not produce differences large enough to yield a "volcano" plot. The same behaviour was also experimentally observed by other authors.[3,18,29] A brief summary of the reported advances in the state-of-the-art on plasma-catalytic NH₃ synthesis in the past two decades is given in Table S1 in Supporting Information (SI).

Even though quite some advances have been made in the field of plasma-catalytic synthesis of NH₃, many fundamental questions remain open. For example, there is no clear understanding on how (and whether) the knowledge from thermal catalysis, specifically monometallic catalysts, translates into plasma catalysis. The aforementioned shift in the "volcano" plot is a good example of inapplicability of a direct translation. Furthermore, the effect of the active metals on the NH₃ production rate and the interaction or synergy between the catalysts and the plasma remain unclear.

Previous research in plasma catalysis showed the higher efficiency of Co compared to other catalysts. [18,20,21] At the same time, bi- and tri-metallic Co-based catalysts with added Ce and Ba, were shown to be efficient for NH_3 synthesis, in thermal catalysis, under milder conditions than the industry-dominating HB process. [30] To the best of our knowledge, to date the studies on bi- or tri-metallic Co catalysts for plasma-catalytic NH_3 synthesis are scarce. [31] Therefore, to elucidate whether a similar effect is present in plasma catalysis, in this work, we investigated the effect of combining Co with other metals in plasma catalysis. For this, Ce with and without other metals was added to Co-based alumina-supported catalysts.

Specifically, we studied the effect of five different catalysts, namely 20 wt% Co/Al_2O_3 , $CoCe/Al_2O_3$, $CoCeMg/Al_2O_3$, $CoCeLa/Al_2O_3$ and cerium-free $CoLa/Al_2O_3$, on the formation of NH₃ from N₂ and H₂ in a DBD plasma reactor. In our previous investigation [21], we showed that 10 wt% Al_2O_3 -supported catalysts contained metal nanoparticles on the porous alumina, as anticipated. The coverage of the support surface, however, ranged between 7% and 15% of the total catalyst surface area. [21] In continuous flow plasma reactors, the interaction of the gas phase species with the catalytic surface could be a limiting factor. Therefore, in the present work we increased the metal loading so that a larger fraction of the catalyst bead surface is covered with active metals.

The effect of the metal composition of the catalysts on their plasmacatalytic performance for NH_3 synthesis was assessed by evaluating the production rate and the NH_3 concentration in the plasma reactor exhaust, as well as the energy consumption of the process. Moreover, the performance of the bi- and tri-metallic catalysts was compared for this reaction with Co/Al₂O₃, pure Al₂O₃ and plasma alone. Additionally, in order to find the optimal operational conditions, the plasma-catalytic experiments were carried out for three different $H_2:N_2$ ratios (stoichiometric 3:1, 1:1 and 1:3) at three different total feed gas flow rates (100 mLn/min, 200 mLn/min and 400 mLn/min – normal millilitres per minute, referred to as "mL/min" in the rest of the paper for simplicity). [32] In addition, multiple characterization techniques were applied to determine the differences in the physico-chemical properties of the catalysts. Importantly, we also monitored the properties of the discharge to evaluate the effect of the catalyst on plasma – a phenomenon that is often overlooked in plasma-catalytic research.

2. Material and methods

2.1. Catalyst preparation

The metal catalysts were prepared via wet impregnation of γ -Al₂O₃ beads (1.8 mm diameter), obtained from Sasol. γ -Al₂O₃ was chosen because it is a common choice of support in plasma-catalysis. [5,22,31, 33] This facilitates comparison with other works. The following metal nitrate hydrates were used as precursors (all purchased from Sigma-Aldrich): Ce(NO₃)₃·6H₂O (99%), Mg(NO₃)₂·6H₂O (99%), Co (NO₃)₂·6H₂O (98%) and La(NO₃)₃·6H₂O (p.a.). The quantities of the precursor solutions were calculated so that the amount of the adsorbed metal nitrates would correspond to a 20 wt% loading of the respective reduced metals.

An aqueous solution containing one, two or three metal precursors, i. e., Ce(NO₃)₃·6H₂O (99%), Mg(NO₃)₂·6H₂O (99%), Co(NO₃)₂·6H₂O (98%) and La(NO₃)₃·6H₂O (p.a.), was prepared for the wet impregnation of the γ -Al₂O₃ beads for the synthesis of the mono-, bi- and trimetallic catalysts, respectively. The volume of solution (0.69 mL per 1 g of beads) was found empirically as the maximal volume which can be absorbed by the beads. The solution was added to the beads and stirred manually until the beads were homogeneously coloured. The coloured beads were dried overnight at room temperature (RT) in air. Next, the beads were dried in an oven at 120 °C for 24 h. At this point, a metal loading of 10 wt% on the γ -Al₂O₃ beads was obtained. Afterwards, the wet impregnation process was repeated with the dried spheres to reach a total loading of 20 wt%. The impregnated Al₂O₃ beads were again dried overnight at RT in air. Finally, the beads were dried in an oven at 120 $^\circ C$ for 24 h, followed by a calcination at 600 °C under atmospheric air for 6 h, at a ramp of 2 °C/min. Prior to plasma experiments, the catalysts were reduced in an H₂ plasma for 8 h.

2.2. Reactor setup

The DBD reactor consists of an inner ground electrode (stainless steel, 8.0 mm diameter) which is placed in the centre of a hollow ceramic cylinder, illustrated in Fig. 1. Mass flow controllers (Bronkhorst F-201CV), that are connected to an H₂ gas cylinder (99.999%, Air Liquide) and an N2 gas cylinder (99.999%, Praxair) introduce the feed gasses H₂ and N₂ into the DBD reactor. The ceramic cylinder functions as a dielectric barrier and has an inner diameter of 17.4 mm and a thickness of 2.4 mm. As a result, a gap of ca. 4.7 mm exists between the ceramic and the inner electrode. A stainless steel mesh electrode (165.0 mm length, ca. 1 mm thickness) is wrapped around the ceramic cylinder, held in place with Kapton tape, and is powered by high voltage. The catalytic materials (Al₂O₃ beads impregnated with catalytically active metals) are introduced inside this gap until the volume inside the ceramic tube corresponding to the outer electrode length is filled with them. When measured with a volumetric cylinder, the total occupied volume of beads was ca. 30 mL and ca. 16 g in each experiment. The beads are held in place on both sides by glass wool.

The discharge is sustained by a power supply unit (PSU) (AFS GmbH, G10S-V2x), connected to a transformer. The PSU is used at a set power of 100 W (total PSU power) and a frequency of 23.5 kHz for all experiments. The power adsorbed by the plasma, often referred to as plasma



Fig. 1. Schematic representation of the DBD reactor used for plasma-catalytic NH₃ synthesis.

power or deposited power, is estimated from the charge-voltage (Q-U) Lissajous figures by calculating the area enclosed under the curves. [34] In this work we focus on using a set PSU power, due to the specifics of the power supply, which does not allow for direct adjustments of the current, nor the plasma-deposited power. The percentage of the total PSU-supplied power deposited into plasma is not constant and depends on multiple parameters, that could not be easily controlled in our experiments. The plasma power is often lower than the set PSU power but maximising the power consumed by the plasma is out of the scope of our work. [35].

In addition, the electrical properties of the plasma discharge setup are monitored with an oscilloscope (Pico Technology, PicoScope 6402D) by means of a high voltage probe (Tektronix P6015A) and a current monitor (Pearson Electronics, Model 4100).

The NH₃ concentration in the gas outlet from the DBD reactor was measured by non-dispersive infrared (NDIR) (Emerson, RosemountTM X-stream Enhanced XEGP Continuous Gas Analyzer). Prior to the measurements, the NDIR was calibrated with 4.89 vol% NH₃ in He, purchased from Praxair. The calibration curve is shown in SI section S1.

2.3. Catalyst characterization

The structural properties of the catalysts were investigated using Raman spectroscopy and X-Ray powder diffraction (XRPD). The XRPD measurements were executed with a Bruker D8 ADVANCE Eco X-ray diffractometer equipped with an X-ray source of CuK α radiation $\lambda = 0.15406$ nm. The analysis was carried out over a 2 θ range of 10–80 degrees in steps of 0.04° and 4 s per step. All catalyst beads were crushed into a homogeneous powder with a mortar and pestle prior to the analysis.

The Raman spectra were recorded on a Horiba XploRA Plus Raman spectrometer equipped with a diode-pumped solid-state laser of 532 nm and a power of 25 mW. The samples were measured with an acquisition time of 10 s, 10 accumulations and in a spectral range of $100-2000 \text{ cm}^{-1}$. The spectra were acquired in two different spots on two different beads, in order to verify the homogeneity of the catalysts.

The metal loading and distribution throughout the bead were investigated using scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). The analysis was performed using the FEI Quanta FEG 250 ESEM, operated at 20 kV and under high vacuum. Before analysis, all the catalyst beads were embedded in a two-component epoxy resin (EPO-TEK 353ND-T4), which was hardened

and cross-sectioned via polishing. After polishing, the samples were coated with 10 nm carbon to prevent charging during further analysis. The analysis was performed on two different beads, in order to verify the homogeneity of the catalysts. SEM-EDX maps were acquired using an X-Max (Oxford Instruments) silicon drift detector. Data acquisition and quantification were performed using INCA software. The maps were acquired from a rectangular area covering the center of the bead to the edge, as illustrated in SI in Fig. S4(F). During the post-processing stage, a MATLAB script was used to retrieve the radial distribution of the metal content over the acquired map after detection of the center of the beads and their edges.

The pore volume and specific surface area were investigated using N_2 physisorption. The N_2 sorption analysis was carried out on a Quantachrome Quadrasorb SI automated gas sorption system. First the samples were degassed under vacuum for 16 h at a temperature of 200 $^\circ C$. The actual measurements were executed at the temperature of liquid N_2 (–196 $^\circ C)$ and N_2 was used as an adsorbate.

Lastly, the acidity of the catalysts was assessed by temperatureprogrammed desorption of ammonia (NH₃-TPD) on an Anton Paar QuantaChrome Chemstar TPx+ with TCD detector. The sample (80 mg) was pretreated at 400 °C under He flow at 40 mL/min for 1 h and then cooled down to 100 °C. Next, the adsorption was performed using 30 pulses of 10% NH₃ in He at 40 mL/min in order to fully saturate the sample with ammonia, and the sample was purged with a He flow at 40 mL/min for 1 h at 100 °C to flush away the physisorbed NH₃. The NH₃-TPD profiles were obtained in a broad temperature range of 100–650 °C and the evolution of the outlet gasses was monitored by mass spectrometry. Lastly, a pulse calibration was performed using 10 pulses at 40 mL/min.

3. Calculation of key performance indicators and electrical characteristics

The energy consumption (EC) in MJ per mol NH_3 produced, production rate (PR) of NH_3 in mg/h and the specific energy input (SEI) were calculated with formulae F1-F4.

In this study the EC was calculated in the following manner, to account for the contraction of gas due to the stoichiometry of $\rm NH_3$ formation:

$$EC(MJ/mol) = \frac{P(W)}{\frac{F_{NH_3}(\frac{m}{mh})}{V_m(\frac{1}{m})\cdot 10^{5/(\frac{m}{m})\cdot 60(\frac{m}{mh})}}} \cdot 10^{-6} \left(\frac{MJ}{J}\right)$$
(F1)

and
$$F_{NH_3}(mL/min) \frac{\left[\left(F_{H_2}\left(\frac{mL}{min} \right) + F_{N_2}\left(\frac{mL}{min} \right) \right) \cdot \frac{C_{NH_3(vol5)}}{100} \right]}{\left[1 + \frac{C_{NH_3(vol5)}}{100} \right]}$$
 (F2)

With P = power deposited into plasma,

 $V_m{=}$ molar volume of an ideal gas at normal conditions (i.e. 22.4 L/ mol at 1 atm and 273 Kelvin). $\cite{[32]}$

 $F_x = gas$ flow rate of compound x.

The PR was calculated in the following manner:

$$Production \ rate(mg/h) = \frac{F_{\rm NH_3}\left(\frac{mL}{\min}\right)}{V_{\rm m}\left(\frac{L}{\max}\right)} \cdot 10^{-3} \left(\frac{L}{mL}\right) \cdot 60 \ \left(\frac{\min}{h}\right) \cdot M_{\rm NH_3}\left(\frac{g}{mol}\right) \cdot 10^{3} \left(\frac{mg}{g}\right)$$

oxides. The XRPD patterns of the catalysts (Fig. 2) exhibit diffraction maxima at $2\theta = 19^{\circ}$, 31° , 37° , 39° , 45° , 57° , 60° , 65° , 74° and 77° , which can be assigned to (111), (220), (311), (222), (400), (422), (511), (440), (620) and (533) crystallographic planes of cubic Co₃O₄ and cubic CoAl₂O₄ since these compounds have similar spinel cubic crystallographic structure (Fd-3 m). [36–38] Furthermore, these crystallographic planes can also be assigned to MgAl₂O₄, which is characterized by the Fd-3 m crystallographic structure, in the case of CoCeMg/Al₂O₃.[39] In addition, all samples show diffraction maxima at $2\theta = 19^{\circ}$, 30° , 37° , 46° and 67° , which correspond to the reflections of the (111), (220), (311), (400) and (440) planes of cubic γ -Al₂O₃, the support of the catalysts. [40,41] Besides, CoCe/Al₂O₃, CoCeMg/Al₂O₃ and CoCeLa/Al₂O₃ present diffraction maxima at $2\theta = 29^{\circ}$, 33° , 48° , 57° , 70° , 77° and 79° ,

(F3)

The SEI is calculated in the following manner:

$$SEI\left(\frac{J}{L}\right) = \frac{P(W) * 60\left(\frac{s}{\min}\right)}{F_{gas}\left(\frac{L}{\min}\right)}$$
(F4)

Lastly, in order to evaluate the effect of the catalysts on the plasma behavior, we also calculated the cell capacitance and effective capacitance, as the latter gives an indication of the plasma behavior: "diffuse" vs filamentary character of the plasma. The cell capacitance (C_{cell}) is obtained by taking the minimum observed slope of the "discharge off" phase of the Lissajous figure, while the effective capacitance (C_{eff}) is calculated by taking the maximum observed slope of the "plasma on" phase of the Lissajous figure. [34] More explanation on C_{eff} and C_{cell} is given in section S2 in SI.

4. Results and discussion

4.1. Catalyst characterization

4.1.1. XRPD

XRPD and Raman spectroscopic analyses showed that the freshly prepared unreduced catalysts were comprised of the respective metal



Fig. 2. The XRPD patterns of fresh and spent Co/Al₂O₃, CoCe/Al₂O₃, CoCeMg/Al₂O₃, CoCeLa/Al₂O₃ and CoLa/Al₂O₃ catalysts.

which can be attributed to (111), (200), (220), (311), (400), (331) and (420) planes of cubic fluorite CeO₂. [42,43].

In addition, the spent catalysts show additional diffraction maxima at $2\theta = 37^{\circ}$, 42° , 62° and 78° , which correspond to (111), (200), (220) and (222) planes of face centered cubic (fcc) CoO. [44–46] The presence of CoO in the X-ray diffractograms proves that the H₂ plasma indeed reduces the catalysts. Yet, no metallic Co, Ce, Mg or La was observed because reduction by an H₂ plasma mainly reduces the outer surface of the beads and prior to the XRD analysis, the beads were crushed. As a result, the reduced outer surface of the beads only makes up a fraction of the entire sample and possibly the metallic phases are not reflected in the measurements. However, this reduction method is sufficient for NTP experiments that employ mesoporous catalysts since the plasma does not ignite inside the pores [47] and the gas temperature (<120 °C) [21] is too low for thermal-catalytic conversion to occur inside the pores. [48]

No phase containing lanthanum is detected for the lanthanumcontaining samples, indicating that lanthanum oxide is amorphous or highly dispersed, which could result in crystallites with sizes below the detection limit, or form spinel-like structures with the characteristic features overlapping the other spinel structures. However, the presence of these metals can be confirmed by SEM-EDX. The results of the Raman spectroscopic analyses are shown in SI section S3.

4.1.2. SEM-EDX

During the synthesis, a total metal loading of 20 wt% was anticipated for all catalysts, with a 3:1 (Co:M1) molar ratio for the bimetallic catalysts, a 2:1:1 (Co:Ce:La) molar ratio for CoCeLa/Al₂O₃ and a 3:1:3 (Co: Ce:Mg) molar ratio for CoCeMg/Al₂O₃. The EDX maps of the crosssection samples were acquired with the SEM at an acceleration

able 1	
he metal loading and molar ratio of the spent Al ₂ O ₂ -supported ca	alvsts.

	U			-	* 11	Į.
Catalyst	Co (wt%)	Ce (wt%)	La (wt %)	Mg (wt %)	Total metal loading (wt%)	Molar ratio (Co:M1:M2)
Co/Al ₂ O ₃	16.9 + 1.6	-	-	-	16.9 ± 1.6	-
CoCe/ Al ₂ O ₃	14.2 ± 0.4	$\begin{array}{c} 12.7 \\ \pm \ 2.2 \end{array}$	-	-	26.9 ± 2.6	2.7:1.0
CoCeMg/ Al ₂ O ₃	$\begin{array}{c} 10.0 \\ \pm \ 0.5 \end{array}$	$\begin{array}{c} 7.2 \\ \pm 1.2 \end{array}$	-	$\begin{array}{c} 3.4 \\ \pm \ 0.1 \end{array}$	$\textbf{20.7} \pm \textbf{0.8}$	2.8:1.0:2.7
CoLa/	10.3	-	9.9	-	$\textbf{20.3} \pm \textbf{1.6}$	2.5:1.0
Al_2O_3	\pm 1.1		± 0.6			
CoCeLa/	7.2	8.35	7.9	-	$\textbf{23.5} \pm \textbf{0.8}$	2.0:1.0:1.0
Al_2O_3	± 0.6	± 0.05	± 0.1			

T T voltage of 20 kV. The obtained metal content and molar ratio of the spent catalysts is shown in Table 1. Generally, the metal loading and molar ratios are in good agreement with the values calculated in preparation. The minor discrepancies between expected and measured metal loading and molar ratio of metals are likely due to SEM-EDX being an inherently local analysis, and a not perfectly uniform distribution of metal over the total number of catalyst beads. The SEM images, the radial distribution of metal content over catalytic beads and the EDX maps are shown in SI in section S4.

The goal was to produce catalysts with high coverage of the outer surface of the bead by the active metal. Zhang et al. demonstrated that a plasma streamer only occurs in pores with a diameter larger than the Debye length [47] and that a metallic coating makes it more difficult for a plasma streamer to propagate in a catalyst pore due to the lack of surface charging. [49] Under our experimental conditions, the Debye length of the plasma is an order of magnitude larger than the pores of our mesoporous catalysts. Hence, there are no plasma discharges inside the pores of our catalysts. The internal surface could still function as a thermal catalyst by aiding surface and molecular collisions. However, at these temperatures the activity will be close to zero. [50] Therefore, the experiments were designed with a goal of maximizing the metal content on the outer surface of the bead, as being beneficial for the plasma-catalytic synthesis of NH₃.

Our analysis shows that for every sample, the total metal content shows a sharp increase at the edge of the bead, as is also illustrated in the SEM images in Fig. 3. When reduced, this metallic layer at the outer region of the beads can strongly affect the conductivity of the packing material. This, in turn, drastically changes the plasma properties, as is shown in the Lissajous figures and the voltage-current graphs (see below). To monitor the oxidation state of the catalyst metals during plasma operation, in-situ experiments would be required, as they could elucidate small differences between different metal combinations.

4.1.3. N 2 physisorption

The Brunauer-Emmett-Teller (BET) surface area and the pore volume values are listed in Table 2. Coating the Al₂O₃ beads with metaloxides leads to a decrease in surface area and pore volume, due to the coverage of the surface or pore-blocking of the Al₂O₃ support by the metal oxides, as expected. The strongest decrease in surface area compared to pristine Al_2O_3 (207 m²/g) is in the case of CoCeMg/Al₂O₃ (118 m²/g). Although in our DBD reactor used for plasma-catalytic NH3 synthesis, the temperature of the gas does not exceed 120 °C [21], the microscale temperature of a site on the catalyst bead may reach much higher temperatures due to the interaction with the microdischarges, which could aid in the decomposition of NH3 since at atmospheric pressures NH₃ is only thermodynamically favoured at low temperatures.[51] Moreover, a local high temperature may cause sintering, which could change the catalyst properties. However, the surface area and pore volume of Co/Al2O3, CoCe/Al2O3, CoLa/Al2O3 and CoCeLa/Al2O3 before and after exposure to plasma remain virtually unchanged, indicating the stability of these catalysts in the plasma discharge. The



Fig. 3. SEM image of CoCe (A) and CoLa (B). The brighter areas at the edge indicate the presence of a higher amount of catalyst elements at the surface of the beads. The images were acquired in backscattered electron mode which is sensitive to local variations in the composition (average atomic number).

Table 2

The surface area and pore volume of fresh and/or spent Co/Al₂O₃, CoCe/Al₂O₃, CoLa/Al₂O₃, CoCeLa/Al₂O₃ and CoCeMg/Al₂O₃.

Catalyst	Surface area (m ² /g)		Pore volu	Pore volume (cm ³ /g)	
	Fresh	Spent	Fresh	Spent	
Al ₂ O ₃	207	-	0.54	-	
Co/Al ₂ O ₃	144	141	0.39	0.36	
CoCe/Al ₂ O ₃	131	132	0.31	0.31	
CoLa/Al ₂ O ₃	152	150	0.37	0.36	
CoCeMg/Al ₂ O ₃ ^a	-	118	-	0.30	
CoCeLa/Al ₂ O ₃	143	147	0.33	0.33	

^a During the calcination and the reduction processes, a large number of the CoCeMg/Al₂O₃ beads lost structural integrity. To ensure a sufficient amount of this catalyst for the catalyst bed to be filled, we did not perform the analysis of the fresh CoCeMg/Al₂O₃ beads (which potentially could reduce the number of the usable beads even further).

physisorption isotherms of the fresh and spent catalysts are shown in SI in section S5.

4.1.4. NH3-TPD

The NH₃-TPD profiles of the different catalysts show great similarity. This is in line with our results for the catalytic performance, where the different catalysts also show only minor variations. The NH₃-TPD results are discussed in detail in SI, section S6.

4.2. Plasma-catalytic performance

The molar ratio and gas flow rate were varied to find the most optimal conditions for the production of NH₃. Our previous study showed that the 1:1 H₂:N₂ ratio was the ideal feed gas ratio. [21] However, different studies have reported different optimal H₂:N₂ feed gas ratios ranging from 3:1–1:2, which suggests that this parameter strongly depends on the plasma characteristics. [21,23,25,52] In our study we varied the feed gas ratio to be 3:1, 1:1, and 1:3. As seen in Fig. 4, the stoichiometric 3:1 H₂:N₂ ratio yields the highest NH₃ concentration and the lowest EC in two scenarios: the empty reactor and Al₂O₃-packed reactor. Contrary, for the Co-based catalysts, the optimal feed gas ratio shifts towards the 1:1 H₂:N₂ ratio. These findings are in good agreement with reports by Zhu et al. and Gorky et al. [12,22,24].

As the packing of the reactor results in a reduction of the effective gas volume inside the reactor, the residence time of the gas inside the packed bed compartment of the reactor would be different compared to an empty reactor, at the same mass flow rate. [21] Based on the work by Uytdenhouwen et al. [53] and given the similar dimensions of our reactor and packing material, we can assume a similar packing efficiency of approximately 50%. Therefore, in terms of residence time, the empty reactor experiments at a gas flow rate of 200 mL/min are comparable to packed reactor experiments at 100 mL/min. At the same time, in terms of mass flow rate, the empty reactor experiments at a gas flow rate of 100 mL/min are comparable to the packed reactor experiments at 100 mL/min.

It must be noted that when the flow rate increases, the residence time of the gas inside the plasma decreases. This could potentially yield lower amount of produced NH₃ (due to reduced residence time within the plasma region/packed bed), but also to a higher net NH₃ production (due to reduced possible destruction of the formed NH₃ in the plasma). [54].

Our experiments showed that a higher flow rate of the feed gas mixture yielded a minor decrease in both the concentration and EC of NH_3 production, while the PR increased slightly (Fig. S14 in SI). At constant power, the specific energy input (SEI) and gas flow rate are reversely proportional (see formula F4) and therefore the decrease in NH_3 concentration can be linked to the lower SEI at higher flow rates, due to the shorter residence time. However, the decrease is minor, and this is due to the competing effect of NH_3 decomposition during the



Fig. 4. (A) NH₃ concentration and plasma power, and (B) EC and PR, for an empty DBD reactor, and a DBD reactor packed with Al_2O_3 , Co/Al_2O_3 , Co

microdischarges, as mentioned above. Indeed, at constant plasma power, a lower SEI, due to a rise in flow rate, may lead to a smaller number of microdischarges felt by the molecules during their residence time in the plasma reactor, which in turn gives less effective collisions that can destroy the produced NH₃. As far as the EC is concerned, the story is more complicated: it depends on how fast the NH₃ concentration reduces with the decrease in SEI (due to the higher flow rate): if it reduces faster, the EC will rise; if it reduces more slowly, the EC will decrease (see formula F1). In our case, the NH₃ concentration reduces only slightly with a decrease in SEI, explaining why the EC indeed decreases as well. Lastly, the PR is proportional to the gas flow rate (Formula F3), thus it rises with increasing gas flow rate. The effect of the gas flow rate on the PR is shown in Fig. S14 in SI.

However, it was shown that for an efficient process of plasma-driven NH₃ production with an industrial potential, higher concentrations (at least around 1 vol%, or 10000 ppm) of NH3 in the reactor exhaust are required. [55,56] Therefore, despite the higher PR values at higher flow rates, we focus here on the results obtained with a feed gas flow rate of 100 mL/min, which provided the highest NH₃ concentration (Fig. 4). The same results, but at a flow rate of 200 mL/min, are presented in Fig. S15 in SI. Fig. S16 shows the general progression of the concentration as a function of time for the reaction using CoLa/Al₂O₃ as packed catalysts. A steady-like state of $\rm NH_3$ production was reached after ca. 1 h in each case, seen as a plateau in Fig. S16. For each experimental condition, the reported concentration was a time-average of the steady state concentrations (which fluctuated within a few hundred ppm). A total of three experiments was conducted per condition, and the average of these triplicates is shown in Fig. 4 and Fig. S15. The error bars represent the standard deviation between the triplicates.

Evidently, even without any packing, some NH₃ is formed due to the plasma performance alone. For the empty DBD reactor with the same apparent residence time, a maximum NH₃ concentration of 2300 ppm and a minimum EC of 192 MJ/mol are obtained, while for the empty DBD reactor with the same gas flow rate, a maximum NH₃ concentration and a minimum EC of 3300 ppm and 248 MJ/mol are obtained, respectively, both at the 3:1 H₂:N₂ ratio. The PR under these conditions did not exceed 15 mg/h. In an empty reactor, gas phase reactions are dominant. Electron-impact reactions with H₂ and N₂ molecules in the

gas phase yield reactive species, ultimately producing NH_3 in the gas phase.

When the packed catalysts are added to the DBD reactor, gas phase reactions occur alongside surface reactions, via Langmuir-Hinschelwood and/or Eley-Rideal reactions, as shown previously. [28] Furthermore, adding a dielectric packing material to the DBD reactor results in an enhancement of the local electric field. [57] This causes higher electron energies, resulting in more effective inelastic collisions, a higher NH₃ concentration and a lower EC. Indeed, adding pure γ -Al₂O₃ as a packing material to the empty reactor, already results in an increase in NH₃ concentration (4300 ppm) and PR (19 mg/h) and a decrease in EC (205 MJ/mol) at the 3:1 H₂:N₂ ratio.

Impregnating the Al_2O_3 support with metals even further improves the NH_3 concentration (8400 ppm), PR (38 mg/h) and EC (111 MJ/mol) for the Co/Al_2O_3 catalyst. This confirms that the addition of metal active sites to alumina has a beneficial effect for plasma catalysis, where in the first approximation the metal sites can facilitate the dissociation of N_2 molecules. [3].

Including additional metals to Co, like Ce, La, CeLa and CeMg, leads to slight variations in PR, NH₃ concentration and EC. Overall, the best results are obtained using CoLa/Al₂O₃ with a maximal NH₃ concentration of 9000 ppm, a PR of 41 mg/h and an EC of 77 MJ/mol at a 1:1 $\rm H_2:$ $N_2\, ratio$ and 100 mL/min – despite the fact that the plasma power in the case of CoLa, as well as CoCe, was lower, for the same applied (PSU) power as seen in Fig. 4(A) (this phenomenon is discussed in the following section). La was reported to improve the dispersion of Co and to function as a structural promoter. [58] Additionally, introduction of La in Co-based catalysts significantly reduces sintering of the catalyst particles due to thermal effects like during calcination. [59] This is confirmed by our XRPD data that did not show any segregated phases of lanthanum (oxides). Hence, small, uniformly distributed La oxide nanoparticles could be formed after calcination, which are below the detection limit of XRPD. The latter is beneficial for the dispersion of other metals. Moreover, the N2 physisorption analysis showed that adding lanthanum as a co-catalyst slightly increases the specific surface area compared to Co/Al_2O_3 (144 m²/g), i.e. the highest specific surface area was observed for CoLa/Al₂O₃ (152 m^2/g), in agreement with Zybert et al. [60] For the other bi- and tri-metallic catalysts, the NH₃

concentration, EC and PR values range between 7000 and 8700 ppm, 83–125 MJ/mol, and 32–39 mg/h, respectively.

To evaluate the stability of the catalysts during plasma operation, each catalyst was subjected to a total of 18 cycles of plasma experiments, of which every cycle lasted ca. 2–3 h. As was shown by the N₂ physisorption analysis, the catalysts remained virtually unchanged after 18 cycles, indicating the stability of the catalysts. On the other hand, CoCeMg/Al₂O₃ was only exposed to 6 cycles of plasma experiments before the beads broke, lost integrity and showed discoloration. This could be due to the formation of MgAl₂O₄ from MgO and Al₂O₃, which is accompanied by a volume expansion of approximately 5%. [61,62] As a result, the formation of MgAl₂O₄ that occurs on the outer surface, as well as inside the pores, causes the beads to break. [63] The XRD patterns show that MgAl₂O₄ is already present after calcination and indeed after calcination, a small fraction of beads was already broken. It must be noted that only beads that remained intact were used for the plasma experiments.

In short, the reactor with packed catalysts performs significantly better than the empty reactor and the Al₂O₃-packed reactor, but the differences in performance between the different catalysts are not dramatic. Even when the concentrations are normalized over the surface area, as is shown in Fig. S17, it is clear that changing the metal composition does not lead to notable improvements in performance. This result is similar to the work by Zhang et al., who used bimetallic RuCo/MgTiO₃ catalyst for plasma-catalytic NH₃ synthesis, and only observed a minor improvement in NH3 synthesis rate compared to monometallic Ru/MgTiO₃ and Co/MgTiO₃. [64] At the same time, Rarog-Pilecka et al. reported an increase in thermocatalytic performance of CoCe catalyst with an added metal by ca. 10 times compared to the bimetallic CoCe catalyst. [30] In our work, we used La, however, we did not observe any comparable improvement in the catalyst performance, which underlines that the effects of thermal catalysis cannot be directly adapted into plasma catalysis. In addition, our results confirm earlier model predictions by our group about the importance of radicals (rather than vibrationally excited molecules) and Eley-Rideal reactions in plasma-catalytic NH3 production, as these give rise to only small variations in NH3 concentrations for different metallic catalysts, in line with our results. [28].

4.3. Effect of metal composition on plasma discharge

By monitoring the discharge properties (voltage, current and Lissajous figures), we found that the plasma power varied depending on the packed catalyst. In all experiments, we maintained the power applied by the PSU constant at 100 W. However, the power deposited into plasma (plasma power) was different for some catalysts. For most systems, the plasma power is ca. 65 W, regardless of the flow rate (see Fig. 4(A) and Fig. S15(A) in SI). Nonetheless, when CoCe/Al₂O₃ and CoLa/Al₂O₃ are introduced, the plasma power decreases to ca. 45–50 W. A higher plasma power could result in a higher NH₃ yield; however, this cannot be tuned at the set PSU power. Yet, for small-scale NH₃ production, an NH₃ yield of 1% might be sufficient [55,56], and higher yields (potentially obtained at higher power) would come at the cost of a higher EC. In fact, the energy required to separate ca. 1 vol% NH₃ from a gas mixture is in the range of the EC of the HB process (ca. 0.5 MJ/mol). [55, 65] Further research should focus on lowering the EC, and the right choice of catalyst can contribute to that.

To illustrate the changes in the discharge characteristics, Fig. 5 presents the Lissajous figures, and Fig. 6 shows the current and voltage profiles, for the different conditions, i.e., only plasma, plasma using blank Al_2O_3 and Al_2O_3 -supported catalysts. We specifically note that the observed differences in the Lissajous figures did not arise from differences in packing between different catalysts. All our experiments were repeated thrice as mentioned above, and for each repetition the catalyst were removed from the reactor and then re-packed. The plasma properties (and hence the Lissajous figures) did not change between the three repeats when the catalyst was the same.

The plasma power is defined as the area enclosed by the Lissajous figures. [23] As seen in Fig. 5, the shape of the Lissajous figure varies, depending on the metal composition of the catalyst. Generally, every presented Lissajous figure is almond-shaped, which is typical for discharges with non-uniform gap widths, such as our packed DBD reactor. This type of system will cause the plasma to ignite over a broad range of gap voltages and as a result, the plasma gradually expands during the discharge across the available dielectric area. [34] The differences lie in the slopes of the discharge phase of the Lissajous figures, which vary most significantly as a function of the packed catalyst. The slopes of the Lissajous figures give an indication of the effective capacitance of the system. [66] Specifically, the slopes exhibit the highest increase in the case of CoCe/Al₂O₃, and CoLa/Al₂O₃ compared to pure Al₂O₃ (Fig. 5). Indeed, the effective capacitance and the capacitance of the cell when CoCe/Al₂O₃ and CoLa/Al₂O₃ are introduced, are higher than for the other systems, as shown in Table 3. A higher effective capacitance indicates that a more diffuse plasma is generated throughout the entire reaction volume. [66,67].

Interestingly, this rise in effective capacitance is not observed for the trimetallic CoCeLa/Al₂O₃ catalyst. From the SEM image and the radial distribution of metal content over a CoCeLa/Al₂O₃ bead, shown in Fig. S4(D) and Fig. S5(D), it is clear that the metal content at the edge of the bead is lower for CoCeLa/Al₂O₃ than for CoLa/Al₂O₃ and CoCe/Al₂O₃, even though, all catalysts were synthesized via the same method, i.e., wet impregnation. As a result, the plasma discharge will not be influenced to the same extent as for the two bimetallic catalysts, hence, a lower effective capacitance is observed for CoCeLa/Al₂O₃. It is



Fig. 5. Lissajous plots of the plasma using (A) the empty reactor, pristine Al₂O₃ and Co/Al₂O₃, and (B) CoLa/Al₂O₃, CoCeLa/Al₂O₃, CoCeMg/Al₂O₃ and CoCe/Al₂O₃,



Fig. 6. Current and voltage profiles observed in the empty DBD reactor and the DBD reactor packed with pristine Al₂O₃ and the different Al₂O₃-supported catalysts.

important to note that the applied voltage varies for the different packed catalysts, as different packed catalysts require different voltages to sustain the plasma. This makes direct comparison of the Lissajous figures more difficult. However, a change in applied voltage, as a function of the packed catalysts, not only reveals information about the total conductivity of the system, but also allows for the comparison of different plasma discharges at the same applied power.

In summary, the Lissajous figures demonstrate that the CoCe/Al₂O₃

and CoLa/Al $_2O_3$ catalysts give rise to a more diffuse plasma, while the other catalysts lead to a more filamentary plasma.

The aforementioned shift in plasma behaviour can also be observed from the current waveform profiles, as plotted in Fig. 6. The peaks in the current profile (sharp "spikes" at the extrema of the current sine) correspond to the microdischarges. The empty reactor displays typical filamentary discharges. When introducing Al_2O_3 into the reactor, the number and the intensity of these spikes increases compared to the

Table 3

Capacitance of the cell and the effective capacitance of a plasma experiment using an empty DBD reactor, and a DBD reactor packed with Al₂O₃, Co/Al₂O₃, Co/Ce/Al₂O₃, Co/Ce/Al₂O₃, Co/Ce/Al₂O₃, Co/Ce/Al₂O₃, Co/Ce/Al₂O₃, and CoLa/Al₂O₃ catalysts, as deduced from the Lissajous plots in Fig. 5.

Catalyst	C _{Cell} (pF)	C _{Eff} (pF)
Empty reactor Al ₂ O ₃ Co/Al ₂ O ₃ CoCe/Al ₂ O ₃ CoCeMg/Al ₂ O ₃ CoCeLa/Al ₂ O ₃	$ \begin{array}{c} 14 \pm 2 \\ 19 \pm 1 \\ 46 \pm 1 \\ 67 \pm 1 \\ 47 \pm 10 \\ 26 \pm 3 \\ 72 \pm 6 \end{array} $	$\begin{array}{c} 83 \pm 3 \\ 105 \pm 22 \\ 168 \pm 3 \\ 211 \pm 4 \\ 163 \pm 7 \\ 145 \pm 31 \\ \end{array}$
CoLa/Al ₂ O ₃	72 ± 9	218 ± 21

empty reactor. A larger number of microdischarges results in the generation of more high-energy electrons and reactive nitrogen and hydrogen species, hence a higher NH_3 formation. On the other hand, the higher electron density can also result in more NH_3 decomposition by electron impact reactions. [54,68–71].

When Co-based catalysts are introduced, both the intensity and the number of the microdischarges decrease compared to Al_2O_3 packing and the empty reactor (Fig. 6), although the NH₃ concentration and PR are higher (and hence the EC is lower) (Fig. 4 and Fig. S15 in SI). Therefore, we imply that these improvements in NH₃ concentration, EC and PR are the result of (i) a change in reaction mechanism, due to the presence of the metal sites on the Co-based catalysts, as well as (ii) a change in plasma discharge properties.

Furthermore, depending on the exact metal composition of the catalyst, the current profile also varies strongly. The most significant difference is once more observed for $CoCe/Al_2O_3$ and $CoLa/Al_2O_3$. Unlike the current profiles in the presence of the other catalysts, Al_2O_3 and plasma only, there are clearly fewer microdischarges, indicating a more diffuse plasma instead of a filamentary discharge, when these two catalysts are introduced [66,67], hence, in line with the above Lissajous plots. A similar change in the discharge profiles was observed by Patil et al., however they only discussed the lower number of microdischarges and not the change of the overall discharge mode. [5] A decrease in the number of microdischarges results in less NH₃ decomposition and explains why even at lower plasma power, CoCe/Al₂O₃, and CoLa/Al₂O₃ show the highest performance. [71]

Additionally, once the Al_2O_3 beads are impregnated with a metal oxide which is further reduced to the respective metal, the conductivity of the beads increases. We hypothesize that CoCe/Al₂O₃ and CoLa/Al₂O₃ show higher electrical conductivity after reduction, compared to the other catalysts. Conductive materials can promote charge transfer in the plasma discharge by improving the charge carrier mobility. [72] As a result, the charge is more spread over the surface of the beads, causing a change in the discharge properties. [73] A similar change in plasma behaviour was also observed by Pribyl et al. after introducing 20 wt% MgAl₂O₄ supported on Al₂O₃, in their DBD reactor. [74].

On the contrary, in a study conducted by Herrera et al., various 5 wt % transition metal catalysts supported on Al_2O_3 were synthesized, and they did not observe any statistical difference in plasma properties, specifically in terms of capacitance and filamentary current behaviour. [75] Yet, the difference with our study lies in the total metal loading of the catalysts, which is 20 wt% in our case. As mentioned earlier, this metal loading was chosen to increase the fraction of metals on the support surface. Indeed, our SEM-EDX analysis showed that there is a sharp increase in metal content at the edge of the beads, which affected the plasma behaviour. Moreover, in the study by Herrera et al., only 17% of the discharge interacted with the catalysts, so it is possible that any effects the catalyst may have on the plasma, only occurred in such a small fraction of the overall plasma volume, that they were not reflected in their measurements. On the other hand, in our study, the entire plasma volume was packed with catalysts so their effect on the plasma

behaviour clearly has a larger influence on our measurements.

In summary, these data suggest that the catalysts act as plasma modifiers, i.e., they change the discharge properties and thus the gas phase plasma chemistry. At the same time, we showed that when the discharge properties are similar, the metal composition of the catalyst does not have a strong effect on the reaction performance, as seen in Fig. 4 and Fig. S15 in SI, as well as in our previous work. [21] Taken together, our results suggest that our catalysts used in plasma-catalytic NH₃ synthesis act more as plasma modifiers, and this effect seems to dominate over the direct catalytic effect governed by the chemistry on the catalyst surface. However, it is important to note that while our data reveal the importance of the physical effect of the catalysts, the role of the chemical effect is not negligible and further research is necessary to fully understand the entire picture. For instance, a change in plasma behaviour, as induced by the catalyst, will affect the electron energy distribution function (EEDF), hence the production of reactive plasma species, and as a result the plasma chemistry will be affected.[13] In addition, as mentioned above, the catalyst may determine whether the discharge is more filamentary or more homogeneous. When the discharge is more filamentary, the plasma power in the filaments is higher, generating more N atoms due to electron impact dissociation, while in the case of a more homogeneous discharge (typically characterized by lower power), such as when CoLa/Al2O3 and CoCe/Al2O3 are introduced, the N2 vibrationally excited molecules will play a relatively more important role. [50,76] Indeed, at lower powers, the plasma will vibrationally (and/or electronically) excite the molecules, which lowers the dissociation energy barrier at the catalyst surface, thus making the role of the catalyst more important. Hence, this could be the case for CoLa/Al₂O₃ and CoCe/Al₂O₃ catalysts, which result in a more homogeneous discharge. However, at the conditions used in our work, changing the catalysts did not generate major improvements in performance, as shown in Fig. 4 above. This suggests that the chemistry is plasma-driven, and more specifically - a plasma-phase NH3 synthesis seems to take place. In other words, in our case, most dissociation occurs in the plasma phase, reducing the role of the catalysts, which is typical for DBD plasmas at high power, as described by Rouwenhorst et al. [14, 77] On the other hand, in a recent study by van Raak et al., the influence of TiO₂ addition on surface reactions in the plasma-catalytic NH₃ synthesis was studied. [78] They observed greater improvements in NH3 concentration and energy consumption in the presence of Ru/Ti-CeO₂ over Ru/CeO₂ in the plasma-catalytic NH₃ synthesis. They propose three different reaction mechanisms that could result in the overall NH₃ production. [78] This underlines that depending on the experimental conditions, the "classical" chemical effect of introducing the catalysts can still play an important role.

We believe that further research should focus on employing lowpower DBDs for the plasma-catalytic synthesis of NH_3 . Indeed, at higher powers, N_2 (and H_2) will be dissociated in the plasma phase, reducing the role of the catalysts, while at lower power, the plasma could promote the vibrational and/or electronic excitation of N_2 and H_2 , and thus facilitate the further dissociation of these excited N_2 and H_2 molecules on the catalytic surface, generating a synergy between both systems. [14] The latter could be accompanied by great improvements in energy efficiency, which is one of the biggest challenges in the field of plasma catalysis today.

5. Conclusion

We studied plasma-catalytic NH₃ synthesis over various catalysts (20 wt% Co/Al₂O₃, CoCe/Al₂O₃, CoLa/Al₂O₃, CoCeLa/Al₂O₃ and CoCeMg/Al₂O₃) in a DBD plasma reactor. The catalysts were synthesized via wet impregnation, and the structural and physicochemical properties of the catalysts were determined via XRPD, Raman spectroscopy, SEM-EDX and N₂ physisorption.

Introducing the transition metal catalysts into the reactor yielded an enhancement of more than 4 times in NH_3 concentration and in PR and a

reduction of ca. 5 times in EC, as obtained with the CoLa/Al₂O₃ catalyst, compared to the empty reactor at the same 1:1 H_2 :N₂ ratio and the same flow rate of 100 mL/min. Yet, the difference in plasma-catalytic performance between the various Co-based catalysts was limited, in line with previous model predictions and experimental observations by our group and others. [3,18,21,28,29].

Instead, we observed significant differences in deposited plasma power and electrical current profile as a function of the metal composition of the catalyst. Depending on the catalyst, these plasma characteristics change drastically, unambiguously indicating that the catalysts act as plasma modifiers. While the chemical composition of the catalysts under the same plasma properties did not change the reaction performance significantly, the changes in plasma properties resulted in a considerable improvement by reducing the EC. Hence, the "plasma modifier" effect of the catalysts dominates over the direct catalytic effect defined by the chemistry on the catalyst surface.

Our findings suggest that the performance of the plasma-catalytic NH_3 synthesis can be tuned by employing catalysts which change the plasma properties to the desired mode, e.g. fewer microdischarges and a shift towards the diffuse discharge mode, as demonstrated in our work. Moreover, the right choice of catalyst could result in a lower deposited power and as a result, a lower energy consumption. Assigning the specific effects is the subject of future investigations.

We are aware that the metals used in this study, namely Co, Mg, La and Ce, are Critical Raw Materials and are thus subject to a supply risk. [79] However, our study is of a more fundamental nature, focused on understanding the underlying reasons responsible for the effect of the catalysts. Moreover, our findings in this work are in agreement with our previous study, in which we showed that the chemical nature of metal supported on alumina beads does not have a dramatic effect in terms of "classical" catalytic effects. [21] In other words, the absence of the pronounced Sabatier effect (volcano plot), studied both experimentally [21] and computationally [28] suggests that the traditional chemical catalysis effect may not be the main effect of introducing catalysts into the DBD plasma, at least for the conditions under study in our work.

As a result, different metals could be used as catalysts for the plasmacatalytic synthesis of $\rm NH_3$ – as long as the plasma discharge properties remain optimal for the reaction.

Our study reveals an important phenomenon for further developments of plasma technology, and emphasizes the inapplicability of direct translation of chemical knowledge from thermal catalysis into plasma-catalytic systems.

CRediT authorship contribution statement

Callie Ndayirinde: Conceptualization, Methodology, Investigation, Writing-Original Draft, Visualization Yury Gorbanev: Conceptualization, Methodology, Writing - Review & Editing, Supervision Radu-George Ciocarlan: Conceptualization, Methodology, Writing - Review & Editing, Supervision Robin De Meyer: Investigation, Software, Visualization, Writing - Review & Editing Alessandro Smets: Investigation Evgenii Vlasov: Investigation, Writing - Review & Editing Sara Bals: Writing - Review & Editing, Funding acquisition. Pegie Cool: Writing - Review & Editing, Funding acquisition. Annemie Bogaerts: Writing - Review & Editing, Funding acquisition.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Callie Ndayirinde reports financial support was provided by European Research Council. Annemie Bogaerts reports financial support was provided by European Research Council.

Data availability

Data will be made available on request.

Acknowledgement

This research was supported by the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 810182 – SCOPE ERC Synergy project) and the Methusalem project of the University of Antwerp. We also gratefully acknowledge the NH₃-TPD analysis performed by Sander Bossier.

Associated content

Supporting information: additional characterization details and experimental data.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.cattod.2023.114156.

References

- United Nations, World population prospects: The 2019 Revison, United Nations-, New York, 2019.
- [2] O. Calicioglu, A. Flammini, S. Bracco, L. Bellù, R. Sims, The future challenges of food and agriculture: an integrated analysis of trends and solutions, Sustainability 11 (2019) 222.
- [3] Y. Wang, M. Craven, X. Yu, J. Ding, P. Bryant, J. Huang, X. Tu, Plasma-Enhanced Catalytic Synthesis of Ammonia over a Ni/Al2O3 Catalyst at Near-Room Temperature: Insights into the Importance of the Catalyst Surface on the Reaction Mechanism, ACS Catal. 9 (2019) 10780–10793.
- [4] K.H.R. Rouwenhorst, H.G.B. Burbach, D.W. Vogel, J. Núñez Paulí, B. Geerdink, L. Lefferts, Plasma-catalytic ammonia synthesis beyond thermal equilibrium on Rubased catalysts in non-thermal plasma, Catal. Sci. Technol. 11 (2021) 2834–2843.
- [5] B.S. Patil, N. Cherkasov, N.V. Srinath, J. Lang, A.O. Ibhadon, Q. Wang, V. Hessel, The role of heterogeneous catalysts in the plasma-catalytic ammonia synthesis, Catal. Today 362 (2021) 2–10.
- [6] J.H. Montoya, C. Tsai, A. Vojvodic, J.K. Nørskov, The challenge of electrochemical ammonia synthesis: a new perspective on the role of nitrogen scaling relations, ChemSusChem 8 (2015) 2180–2186.
- [7] V. Kyriakou, I. Garagounis, A. Vourros, E. Vasileiou, M. Stoukides, An electrochemical haber-bosch, Process, Joule 4 (2020) 142–158.
- [8] Y. Wang, T.J. Meyer, A. Route, to Renewable Energy Triggered by the Haber-Bosch, Process, Chem. 5 (2019) 496–497.
- [9] R. Lan, J.T. Irvine, S. Tao, Synthesis of ammonia directly from air and water at ambient temperature and pressure, Sci. Rep. 3 (2013) 1–7.
- [10] S. Ghavam, M. Vahdati, I. Wilson, P. Styring, Sustainable ammonia production processes, Front. Energy Res. 9 (2021) 34.
- [11] Z.J. Schiffer, K. Manthiram, Electrification and decarbonization of the chemical industry, Joule 1 (2017) 10–14.
- [12] F. Gorky, A. Best, J. Jasinski, B.J. Allen, A.C. Alba-Rubio, M.L. Carreon, Plasma catalytic ammonia synthesis on Ni nanoparticles: The size effect, J. Catal. 393 (2021) 369–380.
- [13] A. Bogaerts, X. Tu, J.C. Whitehead, G. Centi, L. Lefferts, O. Guaitella, F. Azzolina-Jury, H.-H. Kim, A.B. Murphy, W.F. Schneider, T. Nozaki, J.C. Hicks, A. Rousseau, F. Thevenet, A. Khacef, M. Carreon, The 2020 plasma catalysis roadmap, J Phys D: Appl Phys., 53 (2020) 443001.
- [14] K.H.R. Rouwenhorst, Y. Engelmann, K. van 't Veer, R.S. Postma, A. Bogaerts, L. Lefferts, Plasma-driven catalysis: green ammonia synthesis with intermittent electricity, Green. Chem. 22 (2020) 6258–6287.
- [15] B.S. Patil, Q. Wang, V. Hessel, J. Lang, Plasma N2-fixation: 1900–2014, Catal. Today 256 (2015) 49–66.
- [16] A. Bogaerts, E.C. Neyts, O. Guaitella, A.B. Murphy, Foundations of plasma catalysis for environmental applications, Plasma Sources Sci. Technol. 31 (2022).
- [17] Y. Wang, W. Yang, S. Xu, S. Zhao, G. Chen, A. Weidenkaff, C. Hardacre, X. Fan, J. Huang, X. Tu, Shielding Protection by Mesoporous Catalysts for Improving Plasma-Catalytic Ambient Ammonia Synthesis, J. Am. Chem. Soc. 144 (2022) 12020–12031.
- [18] P. Mehta, P. Barboun, F.A. Herrera, J. Kim, P. Rumbach, D.B. Go, J.C. Hicks, W. F. Schneider, Overcoming ammonia synthesis scaling relations with plasmaenabled catalysis, Nat. Catal. 1 (2018) 269–275.
- [19] Y. Liu, C.W. Wang, X.F. Xu, B.W. Liu, G.M. Zhang, Z.W. Liu, Q. Chen, H.B. Zhang, Synergistic Effect of Co–Ni Bimetal on Plasma Catalytic Ammonia Synthesis, Plasma Chem. 42 (2022) 267–282.

C. Ndayirinde et al.

- [20] P. Barboun, P. Mehta, F.A. Herrera, D.B. Go, W.F. Schneider, J.C. Hicks, Distinguishing Plasma Contributions to Catalyst Performance in Plasma-Assisted Ammonia Synthesis, ACS Sustain, Chem. Eng. 7 (2019) 8621–8630.
- [21] Y. Gorbanev, Y. Engelmann, K. van't Veer, E. Vlasov, C. Ndayirinde, Y. Yi, S. Bals, A. Bogaerts, Al2O3-Supported Transition Metals for Plasma-Catalytic NH3 Synthesis in a DBD Plasma: Metal Activity and Insights into Mechanisms, Catalysts 11 (2021) 1230.
- [22] X. Zhu, X. Hu, X. Wu, Y. Cai, H. Zhang, X. Tu, Ammonia synthesis over γ-Al2O3 pellets in a packed-bed dielectric barrier discharge reactor, J. Phys. D: Appl. Phys. 53 (2020), 164002.
- [23] Q. Xie, S. Zhuge, X. Song, M. Lu, F. Yu, R. Ruan, Y. Nie, Non-thermal atmospheric plasma synthesis of ammonia in a DBD reactor packed with various catalysts, J. Phys. D: Appl. Phys. 53 (2019), 064002.
- [24] X. Zhu, J. Liu, X. Hu, Z. Zhou, X. Li, W. Wang, R. Wu, X. Tu, Plasma-catalytic synthesis of ammonia over Ru-based catalysts: Insights into the support effect, J. Energy Inst. 102 (2022) 240–246.
- [25] X. Hu, X. Zhu, X. Wu, Y. Cai, X. Tu, Plasma-enhanced NH3 synthesis over activated carbon-based catalysts: Effect of active metal phase, Plasma Process Polym. 17 (2020) 2000072.
- [26] G. Akay, K. Zhang, Process intensification in ammonia synthesis using novel coassembled supported microporous catalysts promoted by nonthermal plasma, Ind. Eng. Chem. Res. 56 (2017) 457–468.
- [27] K.H. Rouwenhorst, H.G. Burbach, D.W. Vogel, J.N. Paulí, B. Geerdink, L. Lefferts, Plasma-catalytic ammonia synthesis beyond thermal equilibrium on Ru-based catalysts in non-thermal plasma, Catal. Sci. Technol. 11 (2021) 2834–2843.
- [28] Y. Engelmann, K. van 't, Y. Veer, E.C. Gorbanev, W.F. Neyts, A. Schneider, Bogaerts, Plasma catalysis for ammonia synthesis: a microkinetic modeling study on the contributions of eley-rideal reactions, ACS Sustain, Chem. Eng. 9 (2021) 13151–13163.
- [29] J. Shah, F. Gorky, P. Psarras, B. Seong, D.A. Gómez-Gualdrón, M.L. Carreon, Enhancement of the Yield of Ammonia by Hydrogen-Sink Effect during Plasma Catalysis, ChemCatChem 12 (2019) 1200–1211.
- [30] W. Raróg-Pilecka, M. Karolewska, E. Truszkiewicz, E. Iwanek, B. Mierzwa, Cobalt catalyst doped with cerium and barium obtained by co-precipitation method for ammonia synthesis process, Catal. Lett. 141 (2011) 678–684.
- [31] Y. Liu, C.-W. Wang, X.-F. Xu, B.-W. Liu, G.-M. Zhang, Z.-W. Liu, Q. Chen, H.-B. Zhang, Synergistic Effect of Co-Ni Bimetal on Plasma Catalytic Ammonia Synthesis, Plasma Chem. Plasma Process (2022) 1–16.
- [32] C. King, Do you know why Mass Flow reference conditions matter?, Bronkhorst, Ruurlo, 2019.
- [33] Y. Gorbanev, Y. Engelmann, K. van't Veer, E. Vlasov, C. Ndayirinde, Y. Yi, S. Bals, A. Bogaerts, Al2O3-Supported Transition Metals for Plasma-Catalytic NH3 Synthesis in a DBD Plasma: Metal Activity and Insights into Mechanisms, Catalysts 11 (2021).
- [34] F. Peeters, T. Butterworth, Electrical diagnostics of dielectric barrier discharges, in: Z.C. Anton Nikiforov (Ed.) Atmospheric Pressure Plasma: from Diagnostics to Applications, BoD – Books on Demand2019, pp. 144.
- [35] E. Vervloessem, Y. Gorbanev, A. Nikiforov, N. De Geyter, A. Bogaerts, Sustainable NOx production from air in pulsed plasma: elucidating the chemistry behind the low energy consumption, Green. Chem. 24 (2022) 916–929.
- [36] L. Zhang, X. Zhao, W. Ma, M. Wu, N. Qian, W. Lu, Novel three-dimensional Co 3 O 4 dendritic superstructures: hydrothermal synthesis, formation mechanism and magnetic properties, CrystEngComm 15 (2013) 1389–1396.
- [37] X. Duan, M. Pan, F. Yu, D. Yuan, Synthesis, structure and optical properties of CoAl2O4, Spine nanocrystals, J. Alloy. Compd. 509 (2011) 1079–1083.
- [38] N. Srisawad, W. Chaitree, O. Mekasuwandumrong, P. Praserthdam, J. Panpranot, Formation of CoAl2O4 Nanoparticles via Low-Temperature Solid-State Reaction of Fine Gibbsite and Cobalt Precursor, J. Nanomater. 2012 (2012), 108369.
- [39] S. Dash, R.K. Sahoo, A. Das, S. Bajpai, D. Debasish, S.K. Singh, Synthesis of MgAl2O4, Spine Therm. Plasma its Synerg. Struct. Study, J. Alloy. Compd. 726 (2017) 1186–1194.
- [40] F. Kanwal, A. Batool, M. Adnan, S. Naseem, The effect of molecular structure, band gap energy and morphology on the dc electrical conductivity of polyaniline/ aluminium oxide composites, Mater. Res. Innov. 19 (2015). S8-354-S358-358.
- [41] V.R.B. Gurram, S.S. Enumula, S. Mutyala, R. Pochamoni, P.S.S. Prasad, D.R. Burri, S.R.R. Kamaraju, The advantage of ceria loading over V2O5/Al2O3 catalyst for vapor phase oxidative dehydrogenation of ethylbenzene to styrene using CO₂ as a soft oxidant, Appl. Petrochem. Res. 6 (2016) 427–437.
- [42] J. Wang, Z. Li, S. Zhang, S. Yan, B. Cao, Z. Wang, Y. Fu, Enhanced NH3 gas-sensing performance of silica modified CeO2 nanostructure based sensors, Sensors and Actuators B: Chemical 255 (2018) 862–870.
- [43] S.-F. Xue, W.-Y. Wu, X. Bian, Z.-F. Wang, Y.-F. Wu, Facile preparation of CeO2 microspheres with high surface area by ultrasonic spray pyrolysis, Green. Process. Synth. 7 (2018) 241–247.
- [44] X. Zhao, D. Ceresoli, D. Vanderbilt, Structural, electronic, and dielectric properties of amorphousZrO2fromab initiomolecular dynamics, Phys. Rev. B 71 (2005).
- [45] K. Deori, S. Deka, Morphology oriented surfactant dependent CoO and reaction time dependent Co 3 O 4 nanocrystals from single synthesis method and their optical and magnetic properties, CrystEngComm 15 (2013) 8465–8474.
- [46] Y.C. Sui, Y. Zhao, J. Zhang, S. Jaswal, X.Z. Li, D.J. Sellmyer, Ferromagnetic multipods fabricated by solution phase synthesis and hydrogen reduction, IEEE Trans. Magn. 43 (2007) 3115–3117.
- [47] Q.-Z. Zhang, A. Bogaerts, Propagation of a plasma streamer in catalyst pores, Plasma Sources Sci. Technol. 27 (2018), 035009.
- [48] J.S.J. Hargreaves, Y.-M. Chung, W.-S. Ahn, T. Hisatomi, K. Domen, M.C. Kung, H. H. Kung, Minimizing energy demand and environmental impact for sustainable

NH3 and H2O2 production—A perspective on contributions from thermal, electro-, and photo-catalysis, Appl. Catal. 594 (2020), 117419.

- [49] Q.-Z. Zhang, W.-Z. Wang, A. Bogaerts, Importance of surface charging during plasma streamer propagation in catalyst pores, Plasma Sources Sci. Technol. 27 (2018), 065009.
- [50] J.A. Andersen, M.C. Holm, K. van 't, J.M. Veer, M. Christensen, A. Østberg, A. D. Bogaerts, Jensen, Plasma-catalytic ammonia synthesis in a dielectric barrier discharge reactor: A combined experimental study and kinetic modeling, Chem. Eng. J. 457 (2023).
- [51] L.R. Winter, B. Ashford, J. Hong, A.B. Murphy, J.G. Chen, Identifying surface reaction intermediates in plasma catalytic ammonia synthesis, ACS Catal. 10 (2020) 14763–14774.
- [52] S. Li, T. Van Raak, F. Gallucci, Investigating the operation parameters for ammonia synthesis in dielectric barrier discharge reactors, J. Phys. D: Appl. Phys. 53 (2019), 014008.
- [53] Y. Uytdenhouwen, K.M. Bal, I. Michielsen, E.C. Neyts, V. Meynen, P. Cool, A. Bogaerts, How process parameters and packing materials tune chemical equilibrium and kinetics in plasma-based CO₂ conversion, Chem. Eng. J. 372 (2019) 1253–1264.
- [54] K. van 't Veer, Y. Engelmann, F. Reniers, A. Bogaerts, Plasma-catalytic ammonia synthesis in a DBD plasma: role of microdischarges and their afterglows, J. Phys. Chem. C. 124 (2020) 22871–22883.
- [55] L. Hollevoet, F. Jardali, Y. Gorbanev, J. Creel, A. Bogaerts, J.A. Martens, Towards green ammonia synthesis through plasma-driven nitrogen oxidation and catalytic reduction, Angew. Chem. Int. Ed. 59 (2020) 23825–23829.
- [56] L. Hollevoet, E. Vervloessem, Y. Gorbanev, A. Nikiforov, N. De Geyter, A. Bogaerts, J.A. Martens, Energy-efficient small-scale ammonia synthesis process with plasmaenabled nitrogen oxidation and catalytic reduction of adsorbed NOx, ChemSusChem 15 (2022), e202102526.
- [57] K. Van Laer, A. Bogaerts, Influence of gap size and dielectric constant of the packing material on the plasma behaviour in a packed bed DBD reactor: a fluid modelling study, Plasma Process Polym. 14 (2017) 1600129.
- [58] M. Zybert, M. Karasińska, E. Truszkiewicz, B. Mierzwa, W. Raróg-Pilecka, Properties and activity of the cobalt catalysts for NH3 synthesis obtained by coprecipitation – the effect of lanthanum addition, Pol. J. Chem. Technol. 17 (2015) 138–143.
- [59] Y. Xun, X. He, H. Yan, Z. Gao, Z. Jin, C. Jia, Fe- and Co-doped, lanthanum oxides Catal. Ammon. Decompos.: Struct. Catal. Perform., J. Rare Earths 35 (2017) 15–23.
- [60] M. Zybert, A. Tarka, B. Mierzwa, L. Kępiński, W. Raróg-Pilecka, Promotion effect of lanthanum on the Co/La/Ba ammonia synthesis catalysts—the influence of lanthanum content, Appl. Catal. 515 (2016) 16–24.
- [61] A. Mazzoni, M. Sainz, A. Caballero, E. Aglietti, Formation and sintering of spinels (MgAl2O4) in reducing atmospheres, Mater. Chem. Phys. 78 (2003) 30–37.
- [62] L.R. Ping, A.-M. Azad, T.W. Dung, Magnesium aluminate (MgAl2O4) spinel produced via self-heat-sustained (SHS) technique, Mater. Res. Bull. 36 (2001) 1417–1430.
- [63] P. Zhang, A. Chen, D. Ding, S. Gao, X. Liu, G. Ye, G. Liao, Trace nanoscale Al2O3 in Al2O3-MgAl2O4 castable for improved thermal shock performance, Ceram. Int. 45 (2019) 23029–23036.
- [64] Y. Zhang, S. Li, Z. Yuan, H. Chen, X. Fan, Mechanochemical Synthesis of RuCo/ MgTiO3 Catalysts for Nonthermal Plasma-Assisted Ammonia Synthesis, Ind. Eng. Chem. Res. 61 (2022) 14199–14210.
- [65] N. Cherkasov, A. Ibhadon, P. Fitzpatrick, A review of the existing and alternative methods for greener nitrogen fixation, Chem. Eng. Process. 90 (2015) 24–33.
- [66] M. Ramakers, I. Michielsen, R. Aerts, V. Meynen, A. Bogaerts, Effect of Argon or Helium on the CO2Conversion in a Dielectric Barrier Discharge, Plasma Process Polym. 12 (2015) 755–763.
- [67] Y. Uytdenhouwen, S. Van Alphen, I. Michielsen, V. Meynen, P. Cool, A. Bogaerts, A packed-bed DBD micro plasma reactor for CO₂ dissociation: does size matter? Chem. Eng. J. 348 (2018) 557–568.
- [68] F. Gorky, J.M. Lucero, J.M. Crawford, B.A. Blake, S.R. Guthrie, M.A. Carreon, M. L. Carreon, Insights on cold plasma ammonia synthesis and decomposition using alkaline earth metal-based perovskites, Catal. Sci. Technol. 11 (2021) 5109–5118.
- [69] P. Navascués, J.M. Obrero-Pérez, J. Cotrino, A.R. González-Elipe, A. Gómez-Ramírez, Unraveling discharge and surface mechanisms in plasma-assisted ammonia reactions, ACS Sustain. Chem. Eng. 8 (2020) 14855–14866.
- [70] K. van't Veer, S. Van Alphen, A. Remy, Y. Gorbanev, N. De Geyter, R. Snyders, F. Reniers, A. Bogaerts, Spatially and temporally non-uniform plasmas: microdischarges from the perspective of molecules in a packed bed plasma reactor, J. Phys. D: Appl. Phys. 54 (2021), 174002.
- [71] J.A. Andersen, J.M. Christensen, M. Østberg, A. Bogaerts, A.D. Jensen, Plasmacatalytic ammonia decomposition using a packed-bed dielectric barrier discharge reactor, Int. J. Hydrog, Energy 47 (2022) 32081–32091.
- [72] X. Tu, H.J. Gallon, M.V. Twigg, P.A. Gorry, J.C. Whitehead, Dry reforming of methane over a Ni/Al2O3 catalyst in a coaxial dielectric barrier discharge reactor, J. Phys. D: Appl. Phys. 44 (2011), 274007.
- [73] N. Naude, F. Massines, Influence of the surface conductivity on the stability of a glow dielectric-barrier discharge, IEEE Trans. Plasma Sci. 36 (2008) 1322–1323.
- [74] R. Pribyl, P. Stastny, M. Pazderka, J. Kelar, Z.K. Tucekova, M. Zemanek, M. Trunec, M. Cernak, Properties of MgAl2O4 doped alumina barrier layers for dielectric barrier discharge, J. Phys. D: Appl. Phys. 53 (2020), 505202.
- [75] F.A. Herrera, G.H. Brown, P. Barboun, N. Turan, P. Mehta, W.F. Schneider, J. C. Hicks, D.B. Go, The impact of transition metal catalysts on macroscopic dielectric barrier discharge (DBD) characteristics in an ammonia synthesis plasma catalysis reactor, J. Phys. D: Appl. Phys. 52 (2019), 224002.

C. Ndayirinde et al.

Catalysis Today 419 (2023) 114156

- [76] K. van 't Veer, F. Reniers, A. Bogaerts, Zero-dimensional modeling of unpacked and packed bed dielectric barrier discharges: the role of vibrational kinetics in ammonia synthesis, Plasma, Sources Sci. Technol. 29 (2020).
- [77] K.H.R. Rouwenhorst, H.-H. Kim, L. Lefferts, Vibrationally excited activation of N2 in plasma-enhanced catalytic ammonia synthesis: a kinetic analysis, ACS Sustain, Chem. Eng. 7 (2019) 17515–17522.
- [78] T.A.B.J. van Raak, S. Li, F. Gallucci, Prevailing surface reactions in the plasmacatalytic ammonia synthesis with Ru/CeO2 and Ru/Ti-CeO2, Chem. Eng. J. 455 (2023).
- [79] M. Hofmann, H. Hofmann, C. Hagelüken, A. Hool, Critical raw materials: a perspective from the materials science community, SM&T 17 (2018), e00074.