Supplementary information

Reversed plasma catalysis process design for efficient ammonia decomposition.

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Section 1: Experimental work on thermocatalytic cracking

Catalyst preparation and characterization

The decomposition catalyst is composed of $K/Ru/Al_2O_3$ with a nominal weight ratio of 10/5/100. γ-Al_2O_3 pellets (Alfa Aesar) were crushed and sieved. The particle fraction of 125-250 µm was calcined for 5 h in air at 550°C. Ru was first loaded on the alumina powder by incipient wetness impregnation with an aqueous solution of $RuCl_3.xH_2O$ (Strem Chemicals Inc, > 99,9%). This powder sample was then dried at room temperature overnight and at 120°C for 5 h, and calcinated in air at 550°C for 5 h (with a heating rate of 1°C.min^{-1}). This powder was defined as $5Ru/Al_2O_3$ sample. After cooling, potassium nitrate (KNO_3) (Merck, 99%) was next loaded by incipient wetness impregnation on the $5Ru/Al_2O_3$ sample, followed by the same drying and calcination steps. Finally, the sample was again sieved and the 125-250 µm particle fraction was used as catalyst powder to guarantee optimal plug flow through the catalyst bed.

Catalytic decomposition tests

Catalytic NH_3 decomposition tests were performed in a fixed-bed microreactor. A schematic overview of the reactor set-up is given in Figure S1. There were two separate gas flow lines: one for NH_3 and one for H_2, N_2 and He, which came together before entering the reactor. The gasses were supplied by Air Liquide (0-150 mL.min^{-1}). The outlet concentration of all gasses was continuously monitored with a Quadrupole Mass Spectrometer (MS HPR-20 QIC, Hidden Analytical). The outlet flow was sent through an acid trap preventing the uncracked NH_3 to be released in the atmosphere.
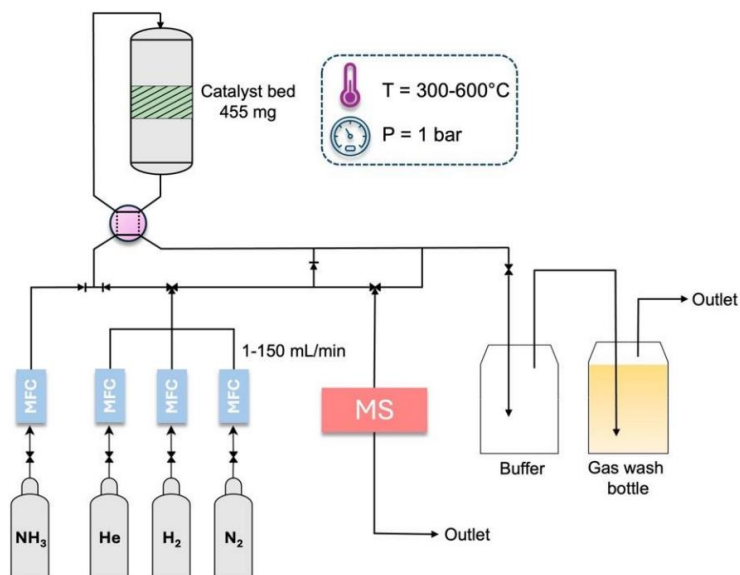

Figure S1: Schematic overview of the ammonia cracking microreactor set-up.

The catalyst pellets (mass = 455 mg, size = 125-250 µm) were fixed in the reactor. A thermocouple was placed inside the catalyst bed. Prior to a cracking experiment, the catalyst was activated in a flowing gas mixture composed of 20 vol% H_2 in N_2 carrier gas at 615°C for 1 h. NH_3 cracking tests were performed at atmospheric pressure at selected temperatures in the range from 615°C to 315°C. The feed gas was pure NH_3 or a mixture produced by the plasma cracking of NH_3 upstream from the catalytic reactor. The weight hour space velocity (WHSV) (h^{-1}) can be calculated with equation S1.

$$WHSV\ (h^{-1}) = \frac{F_{NH3}^{in}\left(\frac{L}{min}\right)*60\left(\frac{min}{h}\right)*MW_{NH3}\left(\frac{g}{mol}\right)}{mass_{cat}(g)*V_m\left(\frac{L}{mol}\right)} \tag{S1}$$

Where $F_{NH_3}^{in}$ is the volumetric flow rate of NH_3 in the feed, MW_{NH3} is the molar weight of NH_3, which is equal to 17 g.mol^{-1}, $mass_{cat}$ is the mass of the catalyst loaded in the reactor, V_m is the molar volume of the feed gas, for which we use 22.4 nL.mol^{-1}. The conversion was calculated from the NH_3 outlet mol fraction (y_{NH3}) (equation S2).

$$NH_3\ conversion = \frac{(1-y_{NH3})}{1+y_{NH3}} \tag{S2}$$

Section 2: Experimental work on plasma cracking

The experimental plasma cracking of NH_3 was conducted using the set-up illustrated in Figure S2. The experimental set-up comprised a gas supply, a plasma reactor connected to a power supply, and an analytics part.
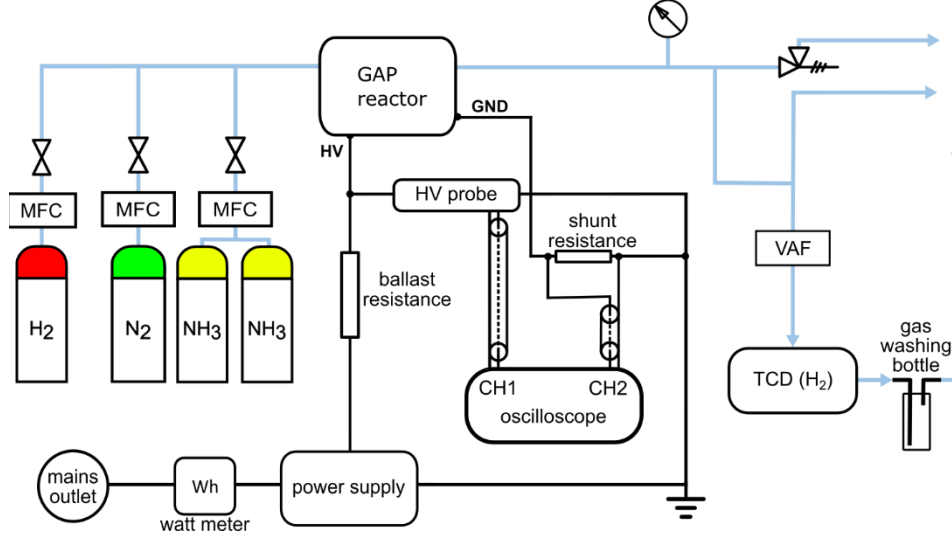

Figure S2: Schematic overview of the plasma reactor set-up for ammonia cracking.

The plasma reactor was based on the Gliding Arc Plasmatron (GAP) design, in which an electric arc is ignited in a vortex flow of gas between two electrodes. It was powered by a current-controlled direct current (DC) linear power supply (Topower Tn-XX02). The power consumed by the plasma reactor (P_{plasma}) was determined from measuring power input into the electric arc using oscillograms of its current and voltage. NH_3 (≈99.96%, Air Liquide), H_2 (≈99.995%, Air Liquide), and N_2 (≈99.999%, Air Liquide) were supplied into the plasma reactor from gas cylinders using Brooks SLA5850 mass flow controllers (MFC). The reactor feed consisted of mixtures of NH_3, H_2 and N_2 corresponding to either pure NH_3 feed or a feed produced by the thermal catalytic cracking of NH_3 upstream from the plasma reactor. The performance of NH_3 cracking via the plasma reactor was evaluated using the following parameters: specific energy input (SEI) per mole of NH_3 in the gas feed, NH_3 conversion (X_{NH_3}), and energy consumption (EC) of decomposing one mole of NH_3. The SEI is calculated using equation S3.

$$SEI\left(\frac{kJ}{mol}\right) = \frac{P_{plasma}\,(W)\cdot 60\left(\frac{s}{min}\right)}{1000\left(\frac{W}{kW}\right)\cdot Q_{NH_3}^{in}\left(\frac{Ln}{min}\right)} \cdot V_m\left(\frac{Ln}{mol}\right) \tag{S3}$$

where $Q_{NH_3}^{in}$ is the mass flow rate of NH_3 in the feed, and V_m is the molar volume of the feed gas, for which we use 22.4 nL.mol^{-1}. X_{NH_3} was calculated from the H_2 concentration in the decomposition products based on the assumption that NH_3 decomposes to a 3:1 mixture of H_2 and N_2 with a statistically insignificant quantity of other byproducts. We must account for gas expansion during NH_3 decomposition because 2 moles of NH_3 decompose into 3 moles of H_2 and 1 mole of N_2. Therefore, X_{NH_3} is equal to (S4):

$$X_{NH_3} = \frac{y_{NH_3}^{in}-y_{NH_3}^{out}}{y_{NH_3}^{in}+y_{NH_3}^{out}} \tag{S4}$$

where $y_{NH_3}^{in}$ is the fraction of NH_3 in the feed (for the feed containing only NH_3, $y_{NH_3}^{in}=1$), and $y_{NH_3}^{out}$ is the fraction of NH_3 in the decomposition products. The EC of NH_3 decomposition is calculated using SEI and X_{NH_3} (S5)

$$EC\left(\frac{kJ}{mol}\right) = \frac{SEI\left(\frac{kJ}{mol}\right)}{X_{NH_3}} \tag{S5}$$

Section 3: Aspen plus input data

A chemical process model of the *reversed plasma catalysis* process was designed in Aspen Plus V14, as well as of the *plasma catalysis* and *thermocatalysis* process. NRTL was selected as property method. The components NH_3, N_2 and H_2 were inserted. The input of the simulation of the *reversed plasma catalysis* process is given in Table S1. Experimental data were implemented in the simulation. The process schemes of the three processes can be found in Figure S3-S5.

Table S1: Input parameters of the input stream and blocks of the Aspen plus model

|	Input parameter	Value
Input feed		
	Temperature	-33°C
	Pressure	1 bar
	Flow rate	0.001 kmol.h⁻¹
	Mol fraction (NH_3)	1
Heat exchanger (feed – hot product gas)		
	Exchanger specification	Cold stream outlet temperature
	Outlet gas temperature	410°C
	Minimum temperature approach	10°C
Stoichiometric reactor (catalytic)		
	Temperature	410°C
	Pressure drop	0 bar
	Fractional conversion	92.3%
Heater (plasma)		
	Pressure drop	0 bar
	Duty	0.0292 kW
Stoichiometric reactor (plasma)		
	Pressure drop	0 bar
	Duty	0 cal.s⁻¹
	Fractional conversion	77.2%
Heater (between hot plasma gas & catalytic reactor)		
	Pressure drop	0 bar
	Duty	-0.0124 kW
Heater (cooling of hot product gas)		
	Temperature	50°C
	Pressure drop	0 bar
Mcomp (compression of product gas)		
	Number of stages	4
	Compressor model	Isentropic using ASME method
	Fix discharge pressure from last stage	50 bar
	Efficiencies: Isentropic	75%[1]
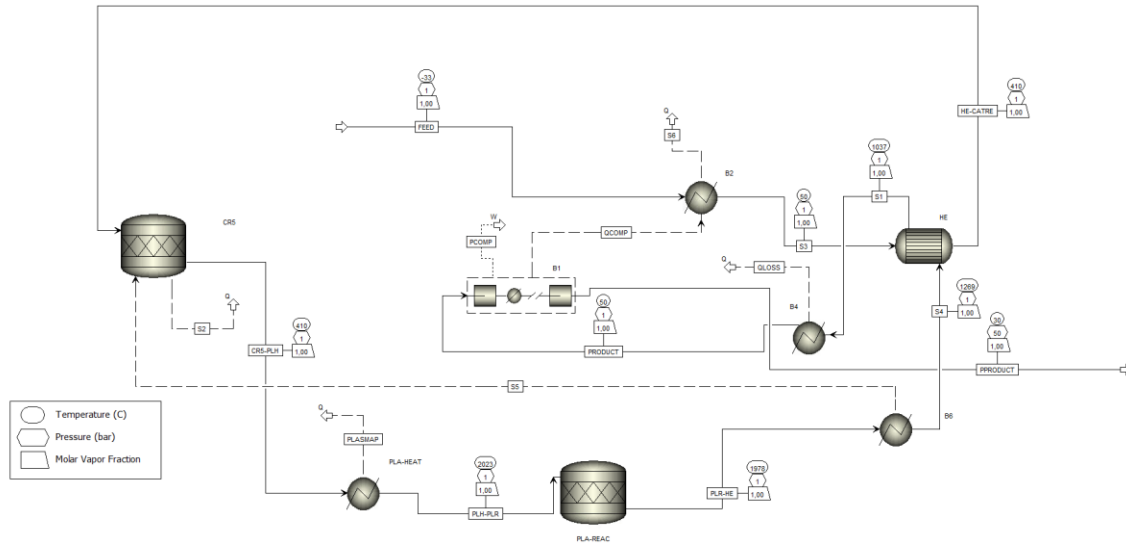
Figure S3: Process scheme of reversed plasma catalysis process with temperature, pressure and molar vapor fraction of all streams, designed in Aspen Plus V14 software.
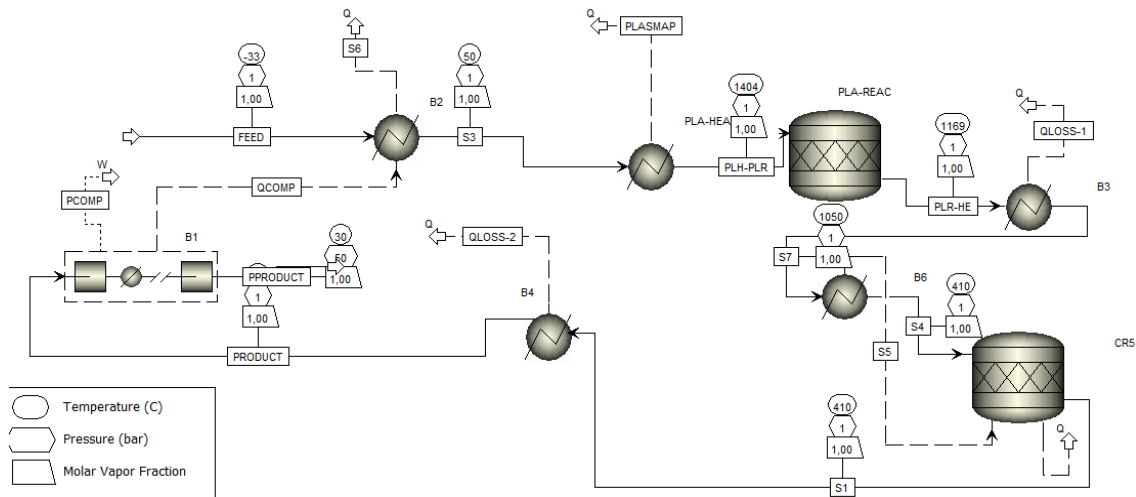

Figure S4: Process scheme of plasma catalysis process with temperature, pressure and molar vapor fraction of all streams, designed in Aspen Plus V14 software.
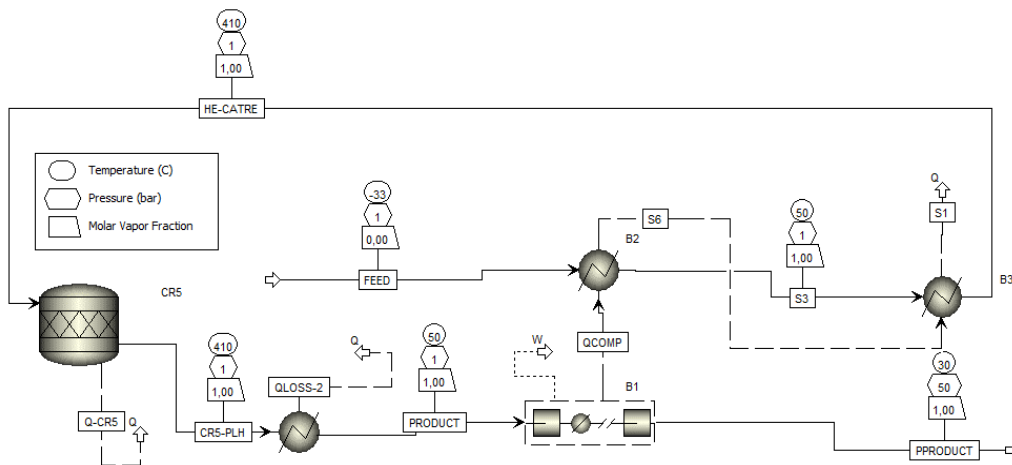

Figure S5: Process scheme of thermocatalysis process with temperature, pressure and molar vapor fraction of all streams, designed in Aspen Plus V14 software.

Section 4: Exergy analysis

A concise exergy analysis was executed to make a correct process comparison between the three experimentally tested and Aspen simulated processes: *thermocatalysis*, *plasma catalysis* and *reversed plasma catalysis*. Exergy can be defined as the available work from an energy source. It takes the quality of the energy into account.

The net exergy consumption is given by the total exergy input minus the useful exergy output.

For the *plasma catalysis* and *reversed plasma catalysis* processes, the total exergy input is the sum of the electrical power of the plasma reactor and of the compressor, together with the chemical exergy of the NH_3 feed. For electricity, the exergy is equal to the applied electrical energy, found in Table S2. For the *thermocatalysis* process, the total exergy input is composed of heating the feed and thermocatalytic reactor, together with the chemical exergy of the NH_3 feed. Heating is assumed to be electrically.

The standard chemical exergy of NH_3 at room temperature (T^0 = 298 K) and atmospheric pressure (P^0 = 1 bar) is 331.5 kJ. mol_{NH3}^{-1} [2]. The chemical exergy of NH_3 at -33°C and atmospheric pressure can be calculated via following formula (S6):

$$Ex_{ch,NH3,-33°C} = Ex_{ch,NH3}^0 - T * \Delta S = Ex_{ch,NH3}^0 - T * \ln\left(\frac{T}{T°}\right) = 333.3 \; kJ.mol_{NH3}^{-1} \tag{S6}$$

The useful exergy output is the sum of the excess heat generated by the process and the chemical exergy of the product at 5 MPa. This latter can be calculated as a mixture of 75 vol% hydrogen (Ex_{H2}^0 = 236.1 kJ.mol_{H2}^{-1} [2]) and 25 vol% nitrogen (Ex_{N2}^0 = 0.72 kJ.mol_{N2}^{-1} [2]) (S7):

$$Ex_{ch,mixture} = y_{H2} * (Ex_{ch,H2}^0 + R * T * \ln(y_{H2})) + y_{N2} * (Ex_{ch,N2}^0 + R * T * \ln(y_{N2})) = 175.7 \; kJ.mol^{-1} \tag{S7}$$

This chemical exergy of the product gas still has to be corrected for the increased pressure (S8):

$$Ex_{ch,product,50bar} = Ex_{ch,mixture} + R * T * \ln\left(\frac{P}{P°}\right) = 185.4 \; kJ.mol_{product}^{-1} \tag{S8}$$

Secondly, the chemical exergy has to be converted to kJ.mol_{NH3}^{-1} (S9):

$$Ex_{ch,product,50bar} = 185.4 \; kJ.mol_{product}^{-1} * 2 \frac{mol_{product}}{mol_{NH3}} * 0.982 = 364.0 \; kJ.mol_{NH3}^{-1} \tag{S9}$$

The excess heat (Q) is converted in exergy via following formula (S10) [3,4]:

$$Ex_{heat} = Q * \left(1 - \frac{T_h}{T°}\right) \tag{S10}$$

Table S2: The exergy input, exergy output and results (net exergy output and exergy efficiency) for both tested configurations: plasma catalysis and reversed plasma catalysis

Process configuration	Plasma catalysis	Reversed plasma catalysis	Thermocatalysis
EXERGY INPUT			
Plasma power (kJ.mol_{NH3}^{-1})	97.6	105.1	
Compressor power (kJ.mol_{NH3}^{-1})	30.9	30.8	29.9
Heating feed & reactor (kJ.mol_{NH3}^{-1})			58.9
Chemical exergy of feed (kJ.mol_{NH3}^{-1})	333.3	333.3	333.3
Total exergy input (kJ.mol_{NH3}^{-1})	461.7	469.2	422.1
USEFUL EXERGY OUTPUT			
Excess heat after plasma reactor (kJ.mol_{NH3}^{-1})	25.4	36.3	11.7
(T_h)	(1508°C)	(1978°C)	(410°C)
Excess heat after heat exchange (kJ.mol_{NH3}^{-1})	11.8	5.5	
(T_h)	(410°C)	(263°C)	
Chemical exergy of product (kJ.mol_{NH3}^{-1})	364.0	364.0	364.0
RESULTS			
NET EXERGY CONSUMPTION (kJ.mol_{NH3}^{-1})	60.4	60.5	46.3
EXERGY EFFICIENCY (%)	86.9	87.1	89.0

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1 Air Supply UK, A guide to air compressor efficiency: how to calculate and maximise efficiency, https://www.airsupply.co.uk/blogs/a-guide-to-air-compressor-efficiency-how-to-calculate-and-maximise-efficiency/, (accessed 15 November 2024).

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