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Green ammonia synthesis from stationary NO_x emission sources on a catalytic lean NO_x trap†

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A process for producing ammonia out of NO_x from hydrogen engine flue gases is proposed. NO_x is captured on a lean NO_x trap (LNT) and catalytically reduced with hydrogen to ammonia (NOCCRA). The energy requirement is similar to that of Haber–Bosch processes. NOCCRA is attractive for decentralised green NH_3 production.

Ammonia (NH_3) is the base chemical for producing N-fertilisers, explosives, and nitrogen-containing organic chemicals, and its use as an energy vector is emerging. The global NH_3 market is expected to continue growing in the next decennium.[1–6] NH_3 is mainly produced from nitrogen gas (N_2) and hydrogen gas (H_2) with Haber–Bosch (HB) processes, at a production volume of 185 M tonnes in 2020.[3,7] Fossil hydrocarbon-based HB is responsible for nearly 2% of the global anthropogenic CO_2 emission.[2,3,8] Green ammonia synthesis avoiding the use of fossil carbon is one of the big challenges preoccupying the scientific community.[9]

The natural gas-based HB process in which N_2 from air is reduced with H_2 from steam methane reforming (SMR) is very energy-efficient, with an energy cost as low as 0.48 MJ $mol_{NH_3}^{-1}$.[2,5,6] The use of natural gas as an energy and H-atom source entails a CO_2 emission of *ca.* 1.6 tonne per tonne of NH_3 produced.[5,6] An obvious way of rendering NH_3 synthesis more sustainable is by using green instead of grey hydrogen. An HB plant, running with hydrogen from water electrolysis using renewable electricity, has an estimated energy cost of *ca.* 0.65–0.70 MJ $mol_{NH_3}^{-1}$.[2,10]

Powering the HB process with renewable energy is challenging because of the large scale at which the process is cost-effective. The economy of scale of HB results from the need for a reaction pressure of 10–40 MPa at 400–650 °C. Such reaction conditions impose a requirement of continuous operation[3,11,12] which does not align well with variable renewable electricity supply.[2,6] Furthermore, the application on land of N-fertiliser of ammonia and ammonium nitrate (NH_4NO_3) derived from it is highly decentralised.[13] This makes small-scale ammonia production under mild reaction conditions with flexible production schemes, despite a slightly higher energy cost, a viable alternative to the centralised HB process.[1,3,14] Local production complementing centralised production could solve supply chain problems and price volatility, especially for remote farming areas.[15]

Several concepts for the synthesis of ammonia from atmospheric N_2 using renewable energy sources have been proposed, like (i) direct electrocatalytic reduction,[16,17] (ii) plasma-enabled synthesis,[18] and (iii) chemical looping,[19,20] as documented in reviews.[4,6,21] Electrocatalytic N_2 reduction suffers from very low yield.[22] Plasma processes have an energy cost many times higher than those of HB processes.[23] Chemical looping is facing some challenges related to mass transfer, cyclability, material volumes and cost.[21,24] An additional option for producing ammonia is to extract and convert N-sources contained in side products and waste streams from the agro-industry, contributing in this way to N-circularity.[25–27]

The N_2 molecule is very difficult to activate for chemical reaction. Oxidation of N_2 molecules to nitrogen oxides (NO_x) or nitrates (NO_3^-) leads to more reactive N-species. The dissociation energy of the N–O bond in the NO molecule of 204 kJ mol^{-1} (ref. 28) is much lower than the energy needed for cleaving the triple N≡N bond in the N_2 molecule (942 kJ mol^{-1} (ref. 29)).[30] In an approach proposed earlier[30,31] atmospheric N_2 is oxidised using a plasma process.[27,30] The downside of oxidising first and performing the reduction to ammonia in a second step is the need for more hydrogen molecules per ammonia molecule (eqn (1) compared to 2). Nevertheless, producing ammonia according to the reaction of eqn (1) could be attractive because of the less severe reaction conditions.[11,25,30,31]

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \qquad (1)$$

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (2)$$

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NO_x is a major air pollutant due to its adverse effect on human health and its role in the chemistry of tropospheric ozone formation and acid rain.[32] NO_x emissions typically originate from high temperature processes, such as fuel combustion.[33–35] Ever more stringent emission standards have motivated the development of efficient NO_x elimination technologies.[36] The most common NO_x emission abatement techniques for stationary industrial processes are selective catalytic reduction (NH_3-SCR)[37] and selective non-catalytic reduction (NH_3-SNCR),[38] both of which use NH_3 as a reductant to convert NO_x into harmless N_2 (eqn (3)–(5)).[39,40] NH_3-SCR is mainly used in high-emission industries, such as steel and petrochemical plants,[37] while NH_3-SNCR is generally applicable in low-emission industries, *e.g.*, gas boilers.[38] Ammonia is mostly injected in the form of an aqueous urea solution, which is hydrolysed *in situ* to form NH_3 (eqn (6)).

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \tag{3}$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \tag{4}$$

$$NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O \tag{5}$$

$$NH_2CO_2NH_2 + H_2O \rightarrow 2NH_3 + CO_2 \tag{6}$$

One of the commercial NO_x abatement technologies for lean-burn automobile combustion engines is the lean NO_x trap (LNT) also known as the NO_x storage and reduction (NSR) system or NO_x adsorber.[41] The washcoat of an LNT monolith typically consists of platinum and barium oxide supported on alumina (Pt–Ba/Al_2O_3).[42,43] An internal combustion engine equipped with LNT is alternatingly run on lean and rich fuel mixtures. During the lean phase, NO_x is trapped on the LNT and converted to barium nitrate ($Ba(NO_3)_2$) (eqn (7)). During the rich phase, the LNT is regenerated by chemical reduction of the trapped nitrates with reductants produced in the engine (eqn (8)).[42] Among H_2, CO and hydrocarbon reductants in the exhaust from rich fuel mixtures, at low temperatures H_2 is most reactive.[44]

In the pollution abatement application, N_2 is the desired reaction product (eqn (8)). NH_3 is a reaction intermediate in the two-step formation of N_2 (eqn (9) and (10)), while N_2O is an unwanted by-product (eqn (11)).[43,45–48] The reaction of eqn (10) is slow and rate determining for the formation of N_2 at temperatures below 150 °C.[48] Limiting the conversion of $Ba(NO_3)_2$ to the first step (eqn (9)) is a way to produce ammonia. High NH_3-selectivity of nitrate reduction on LNT catalysts in the range of 75–90% has been reported.[47–52] Provided green hydrogen is available, the ammonia produced in this way on an LNT can be qualified as "green".

$$BaO + 2NO_2 + \frac{1}{2}O_2 \rightarrow Ba(NO_3)_2 \tag{7}$$

$$Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O \tag{8}$$

$$Ba(NO_3)_2 + 8H_2 \rightarrow 2NH_3 + BaO + 5H_2O \tag{9}$$

$$3Ba(NO_3)_2 + 10NH_3 \rightarrow 8N_2 + BaO + 15H_2O \tag{10}$$

$$Ba(NO_3)_2 + 4H_2 \rightarrow N_2O + BaO + 4H_2O \tag{11}$$

Flue gases of stationary emission sources are considered as a NO_x source for a NO_x capture and catalytic reduction to ammonia process, NOCCRA. The use of NO_x emission sources for ammonia synthesis has three major advantages: (i) the use of an inexpensive source of NO_x which otherwise would entail a cost of elimination, (ii) resolving the NO_x emission issue of flue gases, and (iii) in contrast to state-of-the-art NO_x abatement technologies, NH_3 is now produced instead of consumed for reducing NO_x to N_2.

NO_x-containing flue gas is the feed of the NOCCRA process (Fig. 1). It is sent over an LNT to selectively chemisorb the NO_x. During the subsequent reduction phase, nitrate molecules stored on the LNT are reduced with green H_2 from an electrolyser to ammonia which desorbs spontaneously. NH_3 is separated from the outlet gas stream by phase transfer to an aqueous solution in a washing column. In this way, residual H_2 remaining in the gas phase can be recovered and reused. The LNT alternates between phases of NO_x trapping and chemical reduction. For achieving continuous ammonia production with NOCCRA at least two LNT units, alternating between NO_x adsorption and NH_3 formation, are needed.

Experimental details of the laboratory setup are provided in the ESI (sections 1 and 2†). Pt/Ba/Al_2O_3 catalyst pellets were prepared as described earlier.[31] The Pt/Ba/Al_2O_3 weight ratios were 1/20/100. The performance of Pt/Ba/Al_2O_3 pellets in a NOCCRA cycle was investigated in a tubular flow reactor described earlier.[31] More information about the automated reactor set-up can be found in ref. 53. A flue gas mimic composed of 200 ppm NO, 5% O_2 and 1.5% H_2O in N_2 carrier gas was fed to the reactor at a gas flow rate of 0.1 mL h^{-1} g^{-1} for 250 s. Chemical reduction of adsorbed NO_x was performed using a gas mixture of 5% H_2 with 1.5% H_2O in N_2 carrier gas at the same gas feed rate and temperature during 1800 s. The temperature was varied in the range of 75–200 °C. The operating pressure was always atmospheric.

At temperatures above 100 °C all NO_x in the feed was captured on the Pt/Ba/Al_2O_3 LNT material (Fig. 2A). The NH_3-selectivity showed a maximum of 84% at 125 °C (Fig. 2B). The N_2O-selectivity showed a minimum of 1.7% at 150 °C. Over the investigated reaction temperature range, the N_2O-concentration in the product attained an average of *ca.* 0.4 ppm, which is four orders of magnitudes lower than the typical N_2O concentration in the flue gas of nitric acid plants.[54,55] These results confirm the feasibility of producing ammonia from flue gas on an LNT.

NO_x adsorption and its reduction to NH_3 using hydrogen are exothermic processes.[42] It is envisioned to use hot flue gas as a feed such that NOCCRA will be self-sufficient in terms of heating. Energy is consumed in the production of hydrogen gas, needed for reducing the adsorbed NO_x. The NOCCRA energy consumption essentially depends on the energy efficiency of the electrolyser and the NH_3-selectivity of nitrate reduction reached on the LNT. As excess, unconverted H_2 is separated from the produced NH_3 in the washing column and

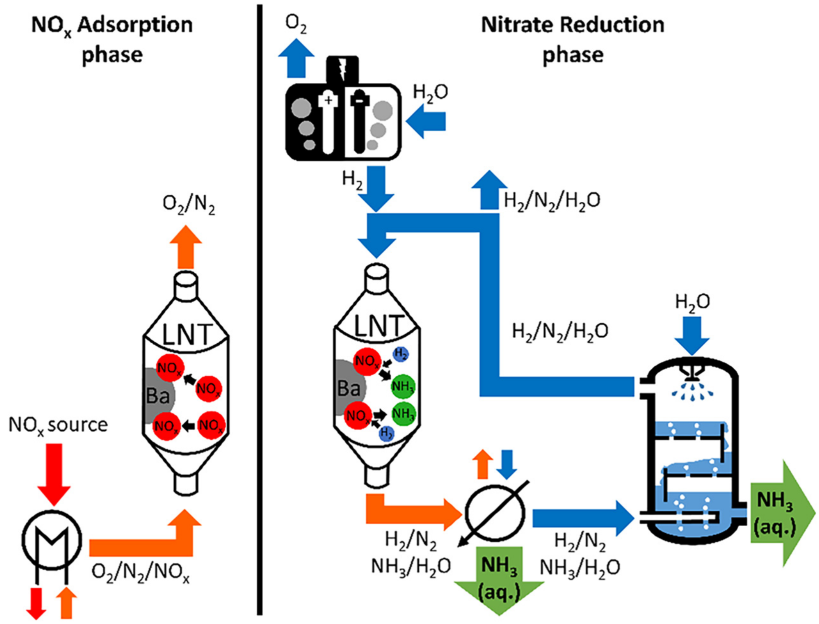

Fig. 1 NOCCRA process. NO$_x$ adsorption phase: NO$_x$-containing exhaust gas is cooled and sent over the LNT, which captures NO$_x$ on the Ba sites; nitrate reduction phase: H$_2$ generated through water electrolysis is sent over the LNT, reducing the captured NO$_x$ to NH$_3$ which is separated from the gas stream in a gas washing column.

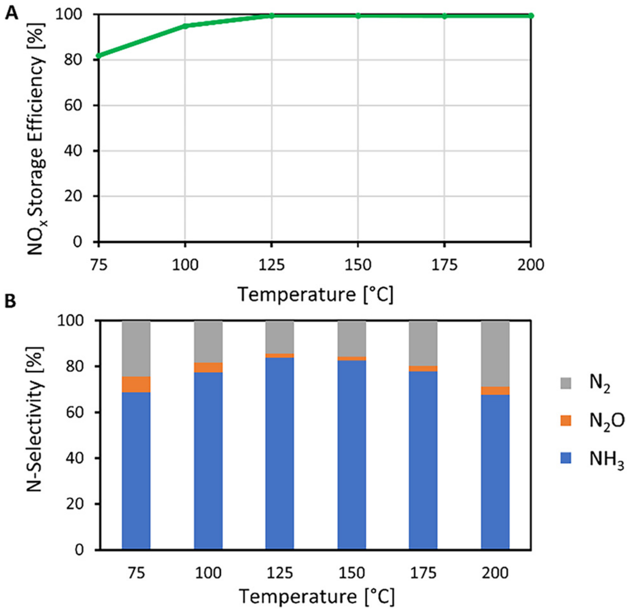

Fig. 2 (A) NO$_x$ storage efficiency [%] and (B) reduction selectivity [%] of LNT catalyst (Pt/Ba/Al$_2$O$_3$ 1/20/100) at different temperatures (75–200 °C), tested for three cycles of adsorption–reduction (250 s/1800 s). Adsorption conditions: gas mixture of 200 ppm NO, 5% O$_2$ and 1.5% H$_2$O in N$_2$ carrier gas fed at a gas feed rate of 0.1 mL h^{-1} g^{-1}. Reduction conditions: 5% H$_2$ with 1.5% H$_2$O in N$_2$ carrier gas at the same gas feed rate and temperature.

recirculated in the NOCCRA process, near-complete utilization of H$_2$ can be achieved. Stoichiometrically 4 moles of H$_2$ are needed for producing 1 mol of NH$_3$ (eqn (8)). Hence, assuming 100% NH$_3$-selectivity of the barium nitrate reduction reaction, the hydrogen production in an electrolyser with an efficiency of 70%[56] would need 1.37 MJ per mol NH$_3$ (estimations detailed in the ESI, section 3†). At an NH$_3$-selectivity of 84% reached experimentally at 125 °C (Fig. 2B), the energy consumption amounts to 1.50 MJ mol$_{NH_3}$$^{-1}$. In earlier work, a related process called PNOCRA ("plasma nitrogen oxidation coupled with catalytic reduction to ammonia") was proposed, in which the feed consists of NO$_x$ generated from air by a plasma reactor.[30,31] The plasma process producing NO$_x$ requires energy, lifting the total energy cost of ammonia production with PNOCRA to 2.10 MJ mol$_{NH_3}$$^{-1}$.[31]

Natural gas-based HB processes are run at an energy cost of 0.47–0.71 MJ mol$_{NH_3}$$^{-1}$.[2,5] Green HB processes in which H$_2$ is generated by H$_2$O electrolysis have energy costs of 0.65–0.70 MJ mol$_{NH_3}$$^{-1}$.[2,10] While NOCCRA is more energy demanding, its benefits are rather indirect. Besides producing ammonia, NOCCRA can be considered to be a depollution technique for NO$_x$ emissions. State-of-the-art NO$_x$ emission abatement techniques, such as NH$_3$-SCR and SNCR, consume NH$_3$, while NOCCRA produces it. NH$_3$-SCR and SNCR require 1 mol of NH$_3$ to eliminate 1 mol of NO$_x$.[37,38] In this way, the NOCCRA process saves 1 mol of NH$_3$ and generates 1 mol of NH$_3$. Taking this benefit into consideration, the energy requirement of NOCCRA is reduced to 0.75 MJ mol$_{NH_3}$$^{-1}$, making it more competitive with HB processes (Fig. 3).

Besides the operating cost of which energy is the largest share, the installation cost of NOCCRA determines the economic viability. In this early stage of research and development, a detailed techno-economic analysis would be inaccurate. Qualitative comparison of NOCCRA with competing processes

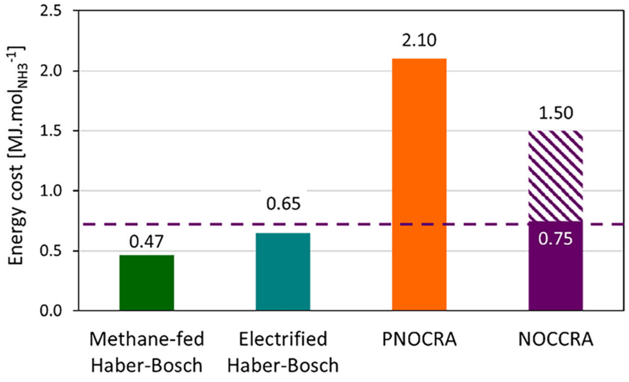

Fig. 3 Energy requirement [MJ $mol_{NH_3}^{-1}$] of the ammonia synthesis processes: natural gas-based Haber–Bosch,[2] electrified Haber–Bosch,[2] PNOCRA[31] and NOCCRA with and without accounting for the savings of NH_3 by avoiding the need for an S(N)CR process for NO_x abatement.

hints at its potential for practical application. NOCCRA, being an integration of green ammonia production and NO_x abatement, intrinsically has the potential to lower the equipment cost. Compared to the HB process for ammonia synthesis, NOCCRA operates at much lower pressures and temperatures. Long lifetimes are predicted for the lean NO_x trap of NOCCRA based on experience in the automotive industry, but the downside of this benefit is the use of a noble metal-based catalyst (Pt).

In the NOCCRA process, ammonia is recovered at the outlet of the LNT using a gas scrubber (Fig. 1). The scrubber can be run using water, sulphuric acid (H_2SO_4) or nitric acid (HNO_3) to produce ammonium sulphate ($(NH_4)_2SO_4$) or ammonium nitrate (NH_4NO_3), respectively.[3] The product is directly applicable as fertiliser. Concentration of the ammonia is not needed for that application, implying no additional energy cost.[57] In this manner, NOCCRA also avoids corrosive substances like anhydrous ammonia, which enables the use of low-cost materials for reactors and conducts.

Further potential advantages of NOCCRA are related to the intermittent character of renewable energy supply. An electrified HB process will produce green NH_3 in large-scale, highly centralised production facilities,[58] which require a steady supply of vast amounts of green electricity. However, when green electricity is intermittently available, and when NO_x emissions are present, NOCCRA becomes attractive for the distributed small- and medium-scale production of NH_3-based fertilisers.[16,17] Intermittent green hydrogen production and storage are easy to accommodate in small plants running a NOCCRA process. Given that locally produced NH_3 with NOCCRA is not intended to be stored over long periods nor transported over long distances, it can be applied directly to fields *via* fertigation, or irrigation with fertiliser solutions.[11,59] The commercial use of LNT technology in the automotive industry provides evidence for scalability.[60]

One limitation of NOCCRA is the need for a local NO_x source. Stationary sources are qualified, while mobile applications such as automobiles would be impractical due to the need for on-board ammonia storage. Another limitation is that agricultural activities need to be present within the vicinity of the NO_x source to provide a market for the ammonia fertiliser product.

The exhaust from fossil fuel-based combustion processes contains sulphur oxides (SO_x) which are poisons of LNT catalysts so that they require periodic regeneration.[61,62] The transition towards green energy carriers, such as hydrogen gas, offers a futureproof perspective overcoming this sulphur problem. Combustion of hydrogen causes thermal NO_x formation, but the absence of CO_2 and SO_x in the exhaust gas makes it an ideal inlet gas feed for the NOCCRA process.[63,64]

The potential of NOCCRA for distributed production of ammonia is illustrated by the following case of a hydrogen-fuelled combustion engine for electricity generation.[65] Small-scale internal engines, such as gas turbines or combined heat and power systems, with a capacity of 100 kW and powered by hydrogen gas at 100%, have a flue gas flow rate of 22 400 m^3 h^{-1}.[66] Flue gases of such hydrogen engines typically contain NO_x at an average concentration of 500 ppm.[65] Such a NO_x source represents a potential NH_3 production capacity of 62.5 tonnes per year, assuming an NH_3-selectivity of 84% (Fig. 2B). This local NH_3 production by one industrial NOCCRA plant would meet the yearly fertiliser demand of *ca.* 730 ha of cropland,[13] assuming an average nitrogen fertiliser demand of 86 kg_N ha^{-1} in the European Union[67] (estimation provided in the ESI, section 4†).

Conclusion & future perspectives

A novel green ammonia production process, called NOCCRA (NO_x capture & catalytic reduction to ammonia) based on stationary NO_x emissions, water and renewable electricity is proposed. The NOCCRA process works with alternating phases of NO_x storage and catalytic reduction of temporarily stored NO_x with green hydrogen to NH_3 on a lean NO_x trap such as those employed for exhaust gas purification in automotive applications. Experimentally, a NO_x storage efficiency of almost 100% and an NH_3-selectivity of 84% were achieved with an LNT catalyst composed of $Pt/Ba/Al_2O_3$ at atmospheric pressure and a temperature of 125 °C.

The energy cost of ammonia production with NOCCRA is estimated at 1.50 MJ $mol_{NH_3}^{-1}$. Considering that NOCCRA avoids NH_3 consumption for abating NO_x emissions the net energy cost becomes competitive with electrified HB processes. The NOCCRA process serves as both a green ammonia production method and a NO_x abatement technique, consolidating two distinct processes into a single one, thereby offering potential advantages in terms of reduced installation cost.

NOCCRA enables the small-scale decentralised production of green ammonium nitrate fertiliser in remote farming areas. NOCCRA uses intermittently available renewable energy sources. A convincing example of a hydrogen engine from which the NO_x emission is used to produce green ammonium nitrate is presented.

Some scientific challenges remain to make NOCCRA fully competitive, including better matching of the two phases of the NOCCRA cycle and catalyst development to enhance the NH_3-selectivity and productivity of the precious metal catalyst. Platinum is a high-cost precious metal, and therefore, replacing it with Earth abundant metals would reduce the cost of the NOCCRA process.[68]

Author contributions

Van Steenweghen Frea: investigation, data curation, visualization, writing – original draft. Hollevoet Lander: conceptualization, formal analysis, writing – review & editing. Martens Johan: supervision, writing – review & editing.

Conflicts of interest

There are no conflicts to declare.

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