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## Green ammonia synthesis from stationary NO<sub>x</sub> emission sources on a catalytic lean NO<sub>x</sub> trap†

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**A process for producing ammonia out of NO<sub>x</sub> from hydrogen engine flue gases is proposed. NO<sub>x</sub> is captured on a lean NO<sub>x</sub> 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<sub>3</sub> production.**

Ammonia (NH<sub>3</sub>) 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<sub>3</sub> market is expected to continue growing in the next decennium.<sup>1–6</sup> NH<sub>3</sub> is mainly produced from nitrogen gas (N<sub>2</sub>) and hydrogen gas (H<sub>2</sub>) with Haber–Bosch (HB) processes, at a production volume of 185 M tonnes in 2020.<sup>3,7</sup> Fossil hydrocarbon-based HB is responsible for nearly 2% of the global anthropogenic CO<sub>2</sub> emission.<sup>2,3,8</sup> Green ammonia synthesis avoiding the use of fossil carbon is one of the big challenges preoccupying the scientific community.<sup>9</sup>

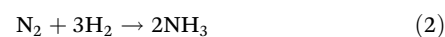
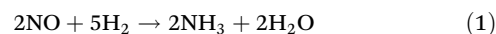
The natural gas-based HB process in which N<sub>2</sub> from air is reduced with H<sub>2</sub> from steam methane reforming (SMR) is very energy-efficient, with an energy cost as low as 0.48 MJ mol<sub>NH<sub>3</sub></sub><sup>-1</sup>.<sup>2,5,6</sup> The use of natural gas as an energy and H-atom source entails a CO<sub>2</sub> emission of *ca.* 1.6 tonne per tonne of NH<sub>3</sub> produced.<sup>5,6</sup> An obvious way of rendering NH<sub>3</sub> 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<sub>NH<sub>3</sub></sub><sup>-1</sup>.<sup>2,10</sup>

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<sup>3,11,12</sup> which does not align well with variable renewable electricity supply.<sup>2,6</sup> Furthermore, the application on land of N-fertiliser of ammonia and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) derived from it is highly decentralised.<sup>13</sup> 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.<sup>1,3,14</sup> Local production complementing centralised production could solve supply chain problems and price volatility, especially for remote farming areas.<sup>15</sup>

Several concepts for the synthesis of ammonia from atmospheric N<sub>2</sub> using renewable energy sources have been proposed, like (i) direct electrocatalytic reduction,<sup>16,17</sup> (ii) plasma-enabled synthesis,<sup>18</sup> and (iii) chemical looping,<sup>19,20</sup> as documented in reviews.<sup>4,6,21</sup> Electrocatalytic N<sub>2</sub> reduction suffers from very low yield.<sup>22</sup> Plasma processes have an energy cost many times higher than those of HB processes.<sup>23</sup> Chemical looping is facing some challenges related to mass transfer, cyclability, material volumes and cost.<sup>21,24</sup> 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.<sup>25–27</sup>

The N<sub>2</sub> molecule is very difficult to activate for chemical reaction. Oxidation of N<sub>2</sub> molecules to nitrogen oxides (NO<sub>x</sub>) or nitrates (NO<sub>3</sub><sup>-</sup>) leads to more reactive N-species. The dissociation energy of the N–O bond in the NO molecule of 204 kJ mol<sup>-1</sup> (ref. 28) is much lower than the energy needed for cleaving the triple N≡N bond in the N<sub>2</sub> molecule (942 kJ mol<sup>-1</sup> (ref. 29)).<sup>30</sup> In an approach proposed earlier<sup>30,31</sup> atmospheric N<sub>2</sub> is oxidised using a plasma process.<sup>27,30</sup> 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.<sup>11,25,30,31</sup>

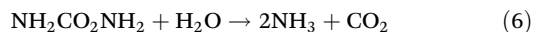
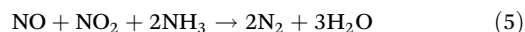
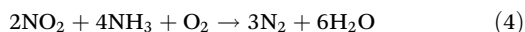
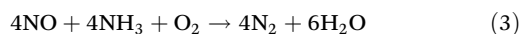


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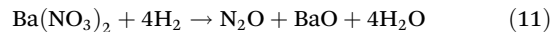
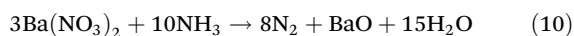
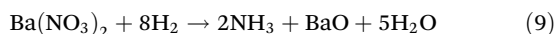
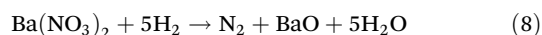
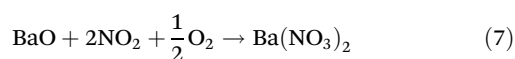


NO<sub>x</sub> is a major air pollutant due to its adverse effect on human health and its role in the chemistry of tropospheric ozone formation and acid rain.<sup>32</sup> NO<sub>x</sub> emissions typically originate from high temperature processes, such as fuel combustion.<sup>33–35</sup> Ever more stringent emission standards have motivated the development of efficient NO<sub>x</sub> elimination technologies.<sup>36</sup> The most common NO<sub>x</sub> emission abatement techniques for stationary industrial processes are selective catalytic reduction (NH<sub>3</sub>-SCR)<sup>37</sup> and selective non-catalytic reduction (NH<sub>3</sub>-SNCR),<sup>38</sup> both of which use NH<sub>3</sub> as a reductant to convert NO<sub>x</sub> into harmless N<sub>2</sub> (eqn (3)–(5)).<sup>39,40</sup> NH<sub>3</sub>-SCR is mainly used in high-emission industries, such as steel and petrochemical plants,<sup>37</sup> while NH<sub>3</sub>-SNCR is generally applicable in low-emission industries, e.g., gas boilers.<sup>38</sup> Ammonia is mostly injected in the form of an aqueous urea solution, which is hydrolysed *in situ* to form NH<sub>3</sub> (eqn (6)).



One of the commercial NO<sub>x</sub> abatement technologies for lean-burn automobile combustion engines is the lean NO<sub>x</sub> trap (LNT) also known as the NO<sub>x</sub> storage and reduction (NSR) system or NO<sub>x</sub> adsorber.<sup>41</sup> The washcoat of an LNT monolith typically consists of platinum and barium oxide supported on alumina (Pt–Ba/Al<sub>2</sub>O<sub>3</sub>).<sup>42,43</sup> An internal combustion engine equipped with LNT is alternately run on lean and rich fuel mixtures. During the lean phase, NO<sub>x</sub> is trapped on the LNT and converted to barium nitrate (Ba(NO<sub>3</sub>)<sub>2</sub>) (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)).<sup>42</sup> Among H<sub>2</sub>, CO and hydrocarbon reductants in the exhaust from rich fuel mixtures, at low temperatures H<sub>2</sub> is most reactive.<sup>44</sup>

In the pollution abatement application, N<sub>2</sub> is the desired reaction product (eqn (8)). NH<sub>3</sub> is a reaction intermediate in the two-step formation of N<sub>2</sub> (eqn (9) and (10)), while N<sub>2</sub>O is an unwanted by-product (eqn (11)).<sup>43,45–48</sup> The reaction of eqn (10) is slow and rate determining for the formation of N<sub>2</sub> at temperatures below 150 °C.<sup>48</sup> Limiting the conversion of Ba(NO<sub>3</sub>)<sub>2</sub> to the first step (eqn (9)) is a way to produce ammonia. High NH<sub>3</sub>-selectivity of nitrate reduction on LNT catalysts in the range of 75–90% has been reported.<sup>47–52</sup> Provided green hydrogen is available, the ammonia produced in this way on an LNT can be qualified as “green”.



Flue gases of stationary emission sources are considered as a NO<sub>x</sub> source for a NO<sub>x</sub> capture and catalytic reduction to ammonia process, NOCCRA. The use of NO<sub>x</sub> emission sources for ammonia synthesis has three major advantages: (i) the use of an inexpensive source of NO<sub>x</sub> which otherwise would entail a cost of elimination, (ii) resolving the NO<sub>x</sub> emission issue of flue gases, and (iii) in contrast to state-of-the-art NO<sub>x</sub> abatement technologies, NH<sub>3</sub> is now produced instead of consumed for reducing NO<sub>x</sub> to N<sub>2</sub>.

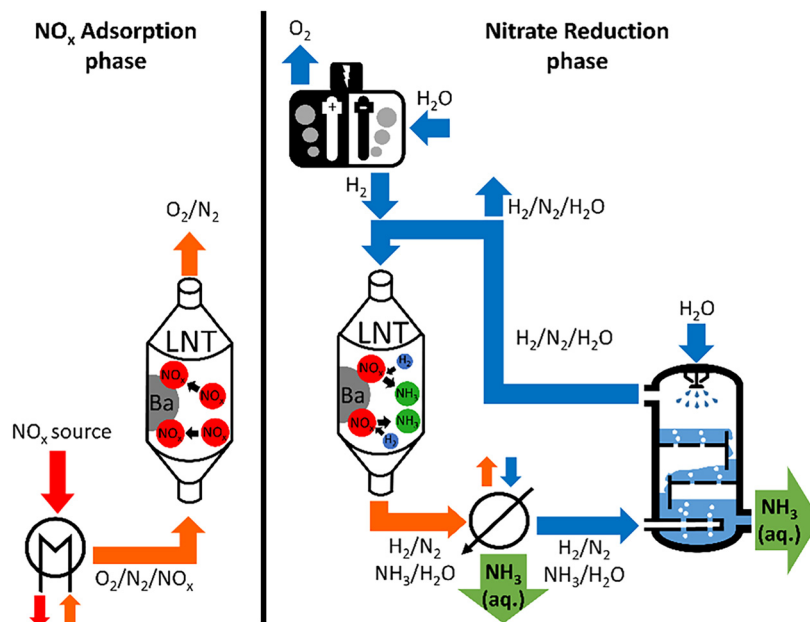
NO<sub>x</sub>-containing flue gas is the feed of the NOCCRA process (Fig. 1). It is sent over an LNT to selectively chemisorb the NO<sub>x</sub>. During the subsequent reduction phase, nitrate molecules stored on the LNT are reduced with green H<sub>2</sub> from an electrolyser to ammonia which desorbs spontaneously. NH<sub>3</sub> is separated from the outlet gas stream by phase transfer to an aqueous solution in a washing column. In this way, residual H<sub>2</sub> remaining in the gas phase can be recovered and reused. The LNT alternates between phases of NO<sub>x</sub> trapping and chemical reduction. For achieving continuous ammonia production with NOCCRA at least two LNT units, alternating between NO<sub>x</sub> adsorption and NH<sub>3</sub> formation, are needed.

Experimental details of the laboratory setup are provided in the ESI (sections 1 and 2†). Pt/Ba/Al<sub>2</sub>O<sub>3</sub> catalyst pellets were prepared as described earlier.<sup>31</sup> The Pt/Ba/Al<sub>2</sub>O<sub>3</sub> weight ratios were 1/20/100. The performance of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> pellets in a NOCCRA cycle was investigated in a tubular flow reactor described earlier.<sup>31</sup> 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<sub>2</sub> and 1.5% H<sub>2</sub>O in N<sub>2</sub> carrier gas was fed to the reactor at a gas flow rate of 0.1 mL h<sup>−1</sup> g<sup>−1</sup> for 250 s. Chemical reduction of adsorbed NO<sub>x</sub> was performed using a gas mixture of 5% H<sub>2</sub> with 1.5% H<sub>2</sub>O in N<sub>2</sub> 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.

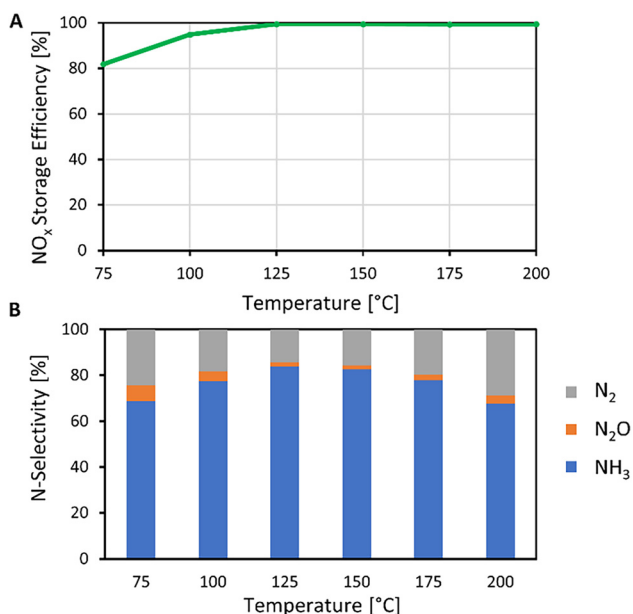
At temperatures above 100 °C all NO<sub>x</sub> in the feed was captured on the Pt/Ba/Al<sub>2</sub>O<sub>3</sub> LNT material (Fig. 2A). The NH<sub>3</sub>-selectivity showed a maximum of 84% at 125 °C (Fig. 2B). The N<sub>2</sub>O-selectivity showed a minimum of 1.7% at 150 °C. Over the investigated reaction temperature range, the N<sub>2</sub>O-concentration in the product attained an average of ca. 0.4 ppm, which is four orders of magnitudes lower than the typical N<sub>2</sub>O concentration in the flue gas of nitric acid plants.<sup>54,55</sup> These results confirm the feasibility of producing ammonia from flue gas on an LNT.

NO<sub>x</sub> adsorption and its reduction to NH<sub>3</sub> using hydrogen are exothermic processes.<sup>42</sup> 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<sub>x</sub>. The NOCCRA energy consumption essentially depends on the energy efficiency of the electrolyser and the NH<sub>3</sub>-selectivity of nitrate reduction reached on the LNT. As excess, unconverted H<sub>2</sub> is separated from the produced NH<sub>3</sub> in the washing column and





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



**Fig. 2** (A)  $\text{NO}_x$  storage efficiency [%] and (B) reduction selectivity [%] of LNT catalyst (Pt/Ba/ $\text{Al}_2\text{O}_3$  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  $\text{NO}$ , 5%  $\text{O}_2$  and 1.5%  $\text{H}_2\text{O}$  in  $\text{N}_2$  carrier gas fed at a gas feed rate of  $0.1 \text{ mL h}^{-1} \text{ g}^{-1}$ . Reduction conditions: 5%  $\text{H}_2$  with 1.5%  $\text{H}_2\text{O}$  in  $\text{N}_2$  carrier gas at the same gas feed rate and temperature.

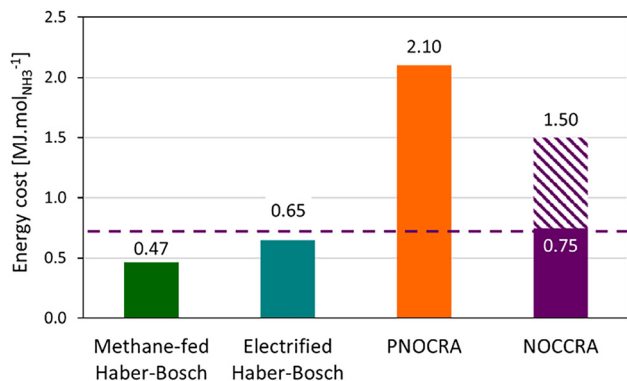
recirculated in the NOCCRA process, near-complete utilization of  $\text{H}_2$  can be achieved. Stoichiometrically 4 moles of  $\text{H}_2$  are needed for producing 1 mol of  $\text{NH}_3$  (eqn (8)). Hence, assuming

100%  $\text{NH}_3$ -selectivity of the barium nitrate reduction reaction, the hydrogen production in an electrolyser with an efficiency of 70%<sup>56</sup> would need 1.37 MJ per mol  $\text{NH}_3$  (estimations detailed in the ESI, section 3†). At an  $\text{NH}_3$ -selectivity of 84% reached experimentally at 125 °C (Fig. 2B), the energy consumption amounts to  $1.50 \text{ MJ mol}_{\text{NH}_3}^{-1}$ . In earlier work, a related process called PNOCCRA (“plasma nitrogen oxidation coupled with catalytic reduction to ammonia”) was proposed, in which the feed consists of  $\text{NO}_x$  generated from air by a plasma reactor.<sup>30,31</sup> The plasma process producing  $\text{NO}_x$  requires energy, lifting the total energy cost of ammonia production with PNOCCRA to  $2.10 \text{ MJ mol}_{\text{NH}_3}^{-1}$ .<sup>31</sup>

Natural gas-based HB processes are run at an energy cost of  $0.47\text{--}0.71 \text{ MJ mol}_{\text{NH}_3}^{-1}$ .<sup>2,5</sup> Green HB processes in which  $\text{H}_2$  is generated by  $\text{H}_2\text{O}$  electrolysis have energy costs of  $0.65\text{--}0.70 \text{ MJ mol}_{\text{NH}_3}^{-1}$ .<sup>2,10</sup> While NOCCRA is more energy demanding, its benefits are rather indirect. Besides producing ammonia, NOCCRA can be considered to be a depollution technique for  $\text{NO}_x$  emissions. State-of-the-art  $\text{NO}_x$  emission abatement techniques, such as  $\text{NH}_3$ -SCR and SNCR, consume  $\text{NH}_3$ , while NOCCRA produces it.  $\text{NH}_3$ -SCR and SNCR require 1 mol of  $\text{NH}_3$  to eliminate 1 mol of  $\text{NO}_x$ .<sup>37,38</sup> In this way, the NOCCRA process saves 1 mol of  $\text{NH}_3$  and generates 1 mol of  $\text{NH}_3$ . Taking this benefit into consideration, the energy requirement of NOCCRA is reduced to  $0.75 \text{ MJ mol}_{\text{NH}_3}^{-1}$ , 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<sub>NH<sub>3</sub></sub><sup>-1</sup>] of the ammonia synthesis processes: natural gas-based Haber–Bosch,<sup>2</sup> electrified Haber–Bosch,<sup>2</sup> PNOCCRA<sup>31</sup> and NOCCRA with and without accounting for the savings of NH<sub>3</sub> by avoiding the need for an S(N)CR process for NO<sub>x</sub> abatement.

hints at its potential for practical application. NOCCRA, being an integration of green ammonia production and NO<sub>x</sub> 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<sub>x</sub> 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<sub>2</sub>SO<sub>4</sub>) or nitric acid (HNO<sub>3</sub>) to produce ammonium sulphate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) or ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), respectively.<sup>3</sup> The product is directly applicable as fertiliser. Concentration of the ammonia is not needed for that application, implying no additional energy cost.<sup>57</sup> 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<sub>3</sub> in large-scale, highly centralised production facilities,<sup>58</sup> which require a steady supply of vast amounts of green electricity. However, when green electricity is intermittently available, and when NO<sub>x</sub> emissions are present, NOCCRA becomes attractive for the distributed small- and medium-scale production of NH<sub>3</sub>-based fertilisers.<sup>16,17</sup> Intermittent green hydrogen production and storage are easy to accommodate in small plants running a NOCCRA process. Given that locally produced NH<sub>3</sub> 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.<sup>11,59</sup> The commercial use of LNT technology in the automotive industry provides evidence for scalability.<sup>60</sup>

One limitation of NOCCRA is the need for a local NO<sub>x</sub> 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<sub>x</sub> source to provide a market for the ammonia fertiliser product.

The exhaust from fossil fuel-based combustion processes contains sulphur oxides (SO<sub>x</sub>) which are poisons of LNT catalysts so that they require periodic regeneration.<sup>61,62</sup> The transition towards green energy carriers, such as hydrogen gas, offers a futureproof perspective overcoming this sulphur problem. Combustion of hydrogen causes thermal NO<sub>x</sub> formation, but the absence of CO<sub>2</sub> and SO<sub>x</sub> in the exhaust gas makes it an ideal inlet gas feed for the NOCCRA process.<sup>63,64</sup>

The potential of NOCCRA for distributed production of ammonia is illustrated by the following case of a hydrogen-fuelled combustion engine for electricity generation.<sup>65</sup> 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<sup>3</sup> h<sup>-1</sup>.<sup>66</sup> Flue gases of such hydrogen engines typically contain NO<sub>x</sub> at an average concentration of 500 ppm.<sup>65</sup> Such a NO<sub>x</sub> source represents a potential NH<sub>3</sub> production capacity of 62.5 tonnes per year, assuming an NH<sub>3</sub>-selectivity of 84% (Fig. 2B). This local NH<sub>3</sub> production by one industrial NOCCRA plant would meet the yearly fertiliser demand of *ca.* 730 ha of cropland,<sup>13</sup> assuming an average nitrogen fertiliser demand of 86 kg<sub>N</sub> ha<sup>-1</sup> in the European Union<sup>67</sup> (estimation provided in the ESI, section 4†).

## Conclusion & future perspectives

A novel green ammonia production process, called NOCCRA (NO<sub>x</sub> capture & catalytic reduction to ammonia) based on stationary NO<sub>x</sub> emissions, water and renewable electricity is proposed. The NOCCRA process works with alternating phases of NO<sub>x</sub> storage and catalytic reduction of temporarily stored NO<sub>x</sub> with green hydrogen to NH<sub>3</sub> on a lean NO<sub>x</sub> trap such as those employed for exhaust gas purification in automotive applications. Experimentally, a NO<sub>x</sub> storage efficiency of almost 100% and an NH<sub>3</sub>-selectivity of 84% were achieved with an LNT catalyst composed of Pt/Ba/Al<sub>2</sub>O<sub>3</sub> at atmospheric pressure and a temperature of 125 °C.

The energy cost of ammonia production with NOCCRA is estimated at 1.50 MJ mol<sub>NH<sub>3</sub></sub><sup>-1</sup>. Considering that NOCCRA avoids NH<sub>3</sub> consumption for abating NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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<sub>3</sub>-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.<sup>68</sup>

## 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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