Supplementary information

Green Ammonia Synthesis from Stationary NO_x Emission Sources on Catalytic Lean NO_x Trap

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Section 1: Experimental work on Lean NO_x Trap

Catalyst preparation and characterization

The LNT catalyst is composed of Pt/Ba/Al_2O_3 with a nominal weight ratio of 1/20/100. 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 500°C. Pt was loaded on the alumina powder by incipient wetness impregnation with an aqueous solution of $H_2PtCl_6.6H_2O$ (Merck, 99.95%). This powder sample was then dried at room temperature for 1h and at 60°C for 1h, and calcinated in air at 550°C for 5 h. After cooling, barium acetate (Merck, 99%) was next loaded by incipient wetness impregnation, followed by the same drying and calcination steps. Finally, the sample was again sieved and the 125-250 µm particle fraction was used as LNT catalyst to guarantee optimal plug flow through the catalyst bed.

Catalytic tests

NO_x adsorption-reduction experiments were performed in an automated continuous fixed-bed microreactor with online reaction product analysis. 60 mg of the catalyst sample was loaded into a quartz tube (inner diameter: 4 mm, length: 15 cm) and placed in the microreactor set-up in vertical position. The catalyst bed was supported by a plug of quartz wool. Air liquid supplies following gasses: N_2 (≥99.999%), O_2 (≥99.5%), NO (5% in He, ≥99.99%), H_2 (≥99.999%). Concentrations of NO, NO_2 and NH_3 in the gas outlet stream were analysed by an ABB AO2020-Limas11HW UV photometer and N_2O by an ABB AO2020-URAS26 NDIR photometer. A data point is collected each second, providing real-time data. The collected data are processed with *MATLAB* software. A schematic reactor setup is given by **Figure S1**.

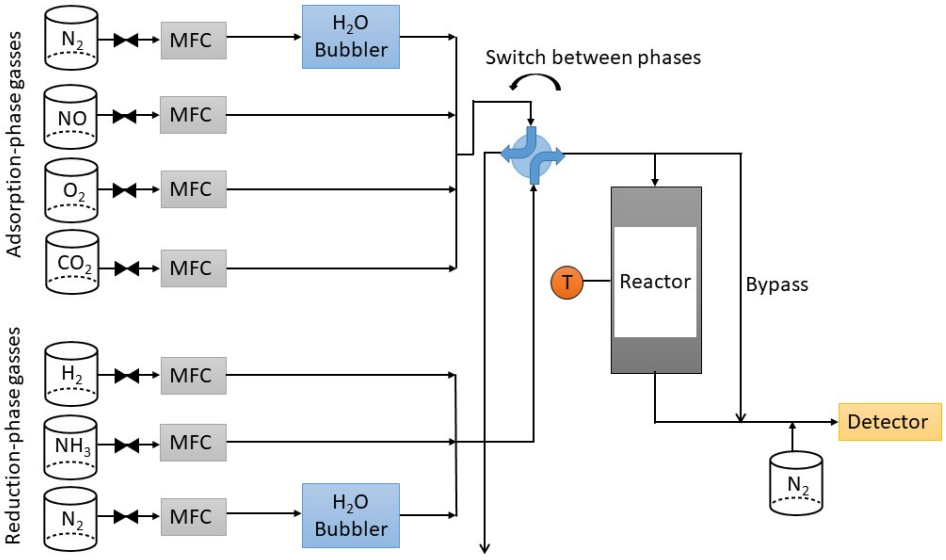

Figure S1: *Schematic illustration of the microreactor set-up.*

One adsorption-reduction cycle is composed of an adsorption and reduction phase. First, a gas mixture of 200 ppm NO, 5% O_2 and 1.5% H_2O in N_2 carrier gas was sent over the LNT for 250 s (NO_x adsorption phase). Second, the reduction of trapped NO_x was performed by 5% H_2 and the same amount of H_2O in N_2 carrier gas for 1,800 s (reduction phase). The total gas flow rate was set at 6 $L.h^{-1}$, corresponding to a gas hour space velocity (GHSV) of around 60,000 h^{-1}. The test temperature and amount of H_2O in the gas mixture are indicated in the caption of each figure. Prior to each experimental run, an activation experiment was executed of three adsorption-reduction cycles at 350°C with 1000 ppm NO concentration during adsorption phase.

Section 2: Results and data processing of testing LNT catalysts

NO and NH_3 concentration in function of time

In **Figure S2**, the detected NH_3 and NO concentration are plotted in function of time for three cycles of adsorption and reduction. The NH_3 peak occurs at the beginning of the reduction phase and is around 900 ppm high. In each cycle the peak is comparable, meaning that the test is reproducible. Almost no NO is detected at the outlet, which means that all NO is trapped and converted on the LNT.

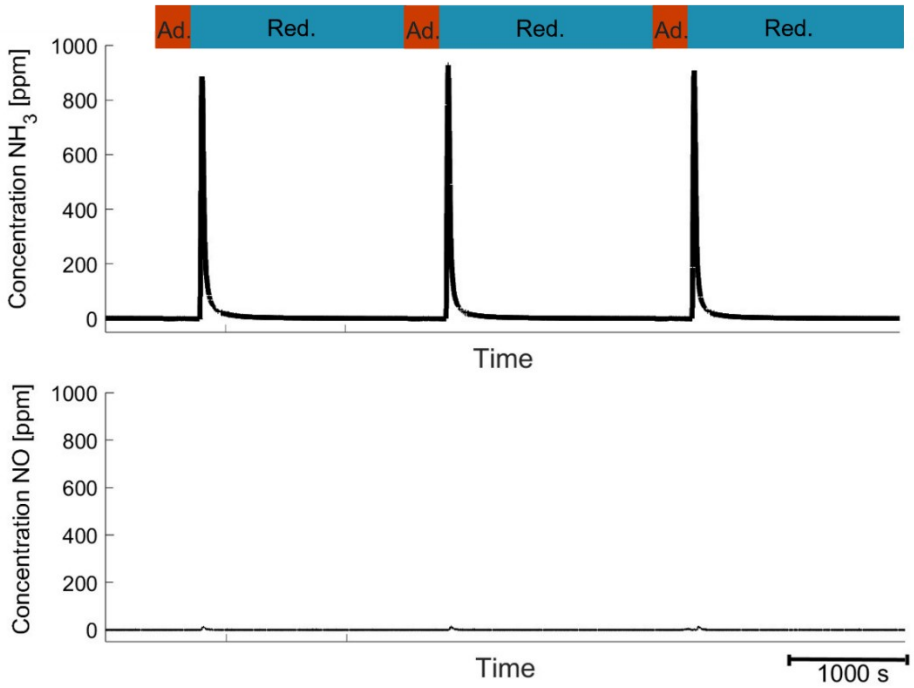

Figure S2: *NH_3 and NO concentration [ppm] in function of time for three adsorption-reduction cycles (250 s/1800 s) with 4.2% H_2O at 125°C with an LNT catalyst ($Pt/Ba/Al_2O_3$, 1/20/100).*

Storage efficiency and N-selectivity in function of temperature

The NO_x storage efficiency is calculated by following formula:

$$\eta_{storage} = \frac{\int_0^{t_{ads}} \left(\dot{n_{NO,in}} - \dot{n_{NO,out}} - \dot{n_{NO2,out}}\right) * dt}{\int_0^{t_{ads}} \left(\dot{n_{NO,in}}\right) * dt}$$

With

$$\dot{n_i} = y_i * \frac{\dot{v_{tot}}}{V_m}$$

With $\eta_{storage}$ the NO_x storage efficiency, $\dot{n_i}$ the molar flow rate of species i [mol.s^{-1}], y_i the gas fraction of species i, $\dot{v_{tot}}$ total gas flow rate [L.s^{-1}], V_m molar volume of an ideal gas at standard temperature (273.15 K) and pressure (1 atm), which is equal to 22.4 L.mol^{-1}.

The selectivity to NH_3 (S_{NH3}), N_2O (S_{N2O}) and N_2 (S_{N2}) can be calculated as follows. Since N_2 is not detectable, the selectivity can be found from the N-balance, assuming that NH_3, N_2O and N_2 are the only products.

$$S_{NH3} = \frac{\int_{t_{0,red}}^{t_{end,red}} (\dot{n_{NH3,out}}) * dt}{n_{NOadsorbed}}$$

$$S_{N2O} = \frac{\int_{t_{0,red}}^{t_{end,red}} (\dot{n_{N2O,out}}) * dt}{n_{NOadsorbed}}$$

$$S_{N2} = 1 - S_{NH3} - S_{N2O}$$

Section 3: Calculation of the energy cost of NOCCRA with different scenarios

Based on the N-selectivity, the amount of each N-product is calculated for producing 1 mol of NH_3. Together with the stoichiometrically mols of H_2 needed per product, the consumed amount of H_2 for producing one mol of NH_3 is estimated.

Different scenarios are calculated with each time either different NH_3-selectivity or a different energy efficiency of the electrolyser. The N_2O selectivity is fixed at 1% and assuming that NH_3, N_2O and N_2 are the only products, the N_2 selectivity is calculated from the N-balance. The lower heating value (LHV) of H_2 is 119.9 MJ.kg^{-1} or 0.2398 MJ.mol^{-1}.

Scenario 1 takes the measured N-selectivity's at 125°C, shown in Figure 2, and with an electrolyser efficiency of 70%. Scenario 2 represents the ideal situation of 100% selectivity towards NH_3 and with the same electrolyser efficiency. Scenario 3 represents a 10% increase in NH_3-selectivity compared to Scenario 1, and Scenario 4 a 10% increase in energy efficiency of the electrolyser compared to scenario 1.

Table S1: *Calculation of energy cost of the NOCCRA process for different scenarios, varying the NH_3-selectivity reached in the LNT, or the energy efficiency of the electrolyser*

Scenario nr.	**η** **[%]**	**Sel. NH_3** **[%]**	**molH_2.molNH_3^{-1}**	**Calculated energy cost (MJ.mol$_{NH3}^{-1}$)**
1	70	84	4.369	1.50
2	70	100	4	1.37
3	70	94	4.117	1.41
4	80	84	4.369	1.31

Section 4: Calculation numerical example

To clarify the potential of NOCCRA, a realistic implementation of NOCCRA was worked out. The characteristics of a typical industrial hydrogen combustion plant and the fertilizer demand of a typical farm was obtained from literature. The NH_3 selectivity was determined experimentally (**Table S2**). With these numbers, the amount of NH_3 produced by one industrial plant is estimated, as well as the size of cropland that could be fed with NH_3 by applying NOCCRA to one industrial plant.

Table S2: *Characteristics with the used amounts and associated reference, required for calculation of a realistic implementation of the NOCCRA process*

Characteristic	**Amount**	**Ref.**
Power capacity	100 kW	[1]
H_2 combustion efficiency	45%	[2]
Energy content H_2	120 MJ.kg^{-1}	[3]
Flue gas NO_x conc.	500 ppm	[4]
NH_3-selectivity NOCCRA	84%	/
Mass N fertilizer use/ha	86 kg.ha^{-1}	[5]

$$Inlet\ H2\ flow\ of\ combustion\ engine = \frac{0.100\ MW}{120\frac{MJ}{kg\ H_2} * 45\%} * \frac{1000}{2\frac{g}{mol}} = 92.6\frac{mol\ H_2}{s}$$

$$Flue\ gas\ flow\ rate = 92.6\frac{mol\ H_2}{s} * \frac{6\ mol\ out}{2\ mol\ H_2} * \frac{22.4\frac{L}{mol\ out}}{1000\frac{L}{m^3}} * 3600\frac{s}{hr} = 22{,}400\frac{m^3}{hr}$$

$$NO\ inlet\ flow\ rate = \frac{22{,}400\frac{m^3}{hr} * 1000\frac{L}{m^3} * 24\frac{hr}{day}}{22.4\frac{L}{mol}} * 500\left(\frac{mol\ NO}{10^6\ mol}\right) = 6{,}378.3\ \frac{mol\ NO}{day}$$

$$Production\ rate = 6{,}378.3\frac{mol\ NO}{day} * 0.84 * 17\frac{g}{mol} * \frac{365\frac{day}{year}}{10^6} = 62.55\ \frac{ton\ NH_3}{year}$$

$$\#\ ha\ fed\ by\ one\ industrial\ plant = \frac{62.55\ \frac{ton\ NH_3}{year} * 1000\frac{kg}{ton}}{86\frac{kg}{ha}} = 727.3\frac{ha}{year}$$

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