Green NH_3 production from NO_x stationary emissions

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Significance and Relevance

In this work we demonstrate the possibility to abate NO_x from stationary combustion processes while producing (*green*) NH_3 with high selectivity from renewable H_2 using a cyclic process of capture and conversion at atmospheric pressure. With the right catalyst formulation and the right experimental conditions – compatible with those of combustion flue gases – it is possible to obtain good NH_3 yields while efficiently abating NO_x.

Preferred Topic: Automotive and Stationary Emission Control
Preferred presentation: Oral preferred

Introduction and Motivations

Green ammonia is expected to play a crucial role in the energy transition as it serves as a sustainable base chemical and a versatile energy carrier. With its potential to store and transport hydrogen, it will facilitate the integration of renewable energy sources into various sectors, thus accelerating the shift towards a cleaner and more resilient energy infrastructure[1]. Nowadays, ammonia production is energy intensive, as the energy required to sever the N-N bond is significant. NO_x is a waste toxic compound present in combustion flue gases, which is nowadays abated using NH_3 as a reactant according to the well-established SCR process to comply with environmental regulations. In this scenario, the production of green ammonia using NO_x as N source is very appealing[2], as it could turn emission abatement from a cost to a potential resource, allowing for a decentralized production of green NH_3. Noble metal-based catalysts are established materials in NO_x capture and reduction, and could be well suited to this application. Indeed, typical Lean NOx Traps (LNT) catalysts such as $Pt/Ba/Al_2O_3$ can adsorb NO_x from flue gases and converting it to N_2. Both the adsorption and the reduction of NOx are activated processes: catalytic oxidation of NO is needed to adsorb NO as nitrate/nitrite and catalytic reduction of stored species. The reduction follows a two-step mechanism[3], where stored NO_x is reduced first to NH_3, which then reduces downstream NOx to N_2. Hence, in this work we prepare and test different catalysts and experimental conditions to verify the possibility to efficiently capture NO_x while selectively producing NH_3 upon H_2 exposure.

Materials and Methods

1% Pt, 0.5% Rh or 0.5% Ru are impregnated in equimolar amounts on γ-Al_2O_3 (Sasol Puralox) and calcined at 500 °C; the obtained catalyst is then impregnated with Ba acetate to obtain a nominal Ba loading of 16% and calcined again at 500 °C. The obtained catalysts are then characterized by N_2 physisorption, XRD, SEM-EDS and H_2 chemisorption, and with NO-TPA (Temperature Programmed Adsorption) followed by TPD or H_2-TPSR. Testing is performed in transient conditions cycling an oxidizing adsorption atmosphere (500 ppm NO + 3% O_2, 5 min) with a reducing H_2 pulse (4% H_2, 5 min), spaced out by an inert purge. The system is cycled isothermally in the range 250-350°C. The same experimental conditions are repeated also in the presence of 1% CO_2 and/or H_2O during the adsorption step. Dedicated experiments were replicated using an *operando* FT-IR setup.

Results and Discussion

Cyclic experiments at different temperatures with only NO and O_2 during the adsorption step (**Fig 1A-C**) show the highest NH_3 productivity per cycle on Rh-based catalyst, because of its high NH_3 selectivity and relatively high NO_x uptake. Pt- and Ru-based catalysts lead to lower NH_3 yields, due to low NH_3 selectivity and low NO_x uptake, respectively. These data point out that a trade-off between NO_x storage capacity (favored at higher temperatures) and NH_3 selectivity (favored at lower T) has to be chosen to maximize NH_3 production.

When CO_2 is also present in the adsorption atmosphere, it competes with NO_x for the same adsorption sites and hinders NO_x uptake below 350°C for Rh and Ru-based catalyst, while no significant effects are seen on Pt (**Fig 2A**), suggesting a kinetic inhibition in the case of Rh and Ru in the presence of CO_2. In terms of NH_3 selectivity, in the presence of CO_2 Rh and Ru show minor enhancements while Pt almost doubles its NH_3 selectivity at low temperatures. Accordingly, in terms of NH_3 production (**Fig. 2C**), a substantial decrease is observed for the Rh-based catalyst, no significant changes are visible for the Ru-based catalyst whereas a significant increase in the NH_3 production per cycle at low temperatures is observed for Pt-based catalyst.

Cyclic experiments were replicated in an *operando* FTIR set-up to qualify surface species during adsorption and regeneration cycles. Spectral data indicated that at low temperatures in the presence of CO_2 and NO_x, nitrates/nitrites and carbonates coexist on the catalyst surface, while at high temperatures nitrates dominate by far the pool of adsorbed species. At low temperatures, when the atmosphere is switched to reducing conditions, stored carbonates are reduced to CO: this adsorbs on the noble metal, creating a poisoning effect and reducing the catalytically active sites that are able to convert NH_3 and stored NO_x to N_2, thus increasing the NH_3 selectivity.

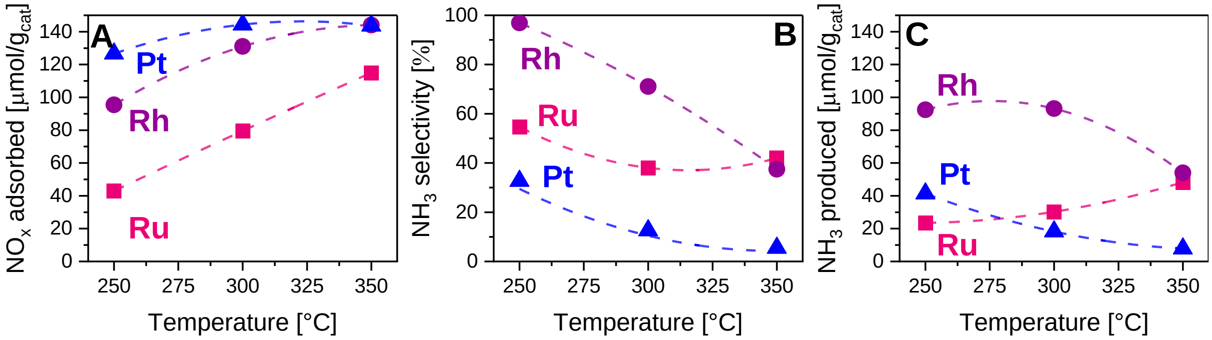

Figure 1. NO_x uptake (A), NH_3 selectivity (B) and NH_3 production (C) per isothermal cycle. Process conditions = Adsorption: 500 ppm NO + 3% O_2/He, 5 min; Reduction: 4% H_2/He, 5 min; constant GHSV = 100 L(STP)/h/g

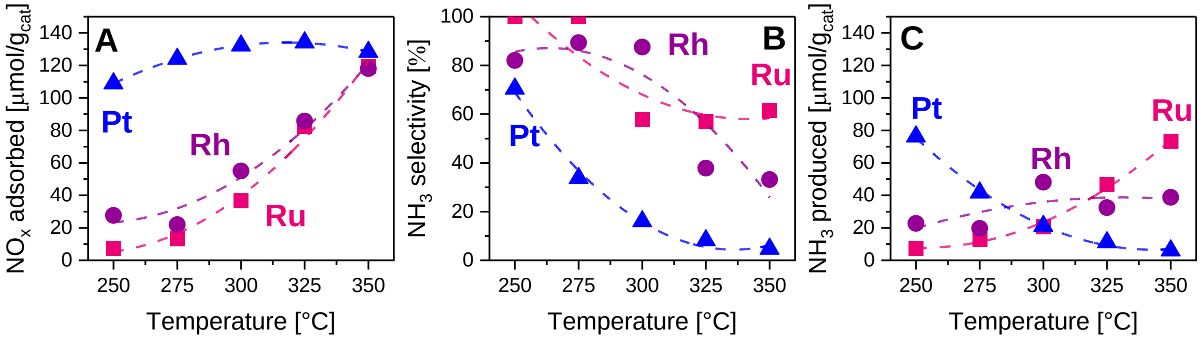

Figure 2. NO_x uptake (A), NH_3 selectivity (B) and NH_3 production (C) per isothermal cycle. Process conditions = Adsorption: 500 ppm NO + 1% CO_2 + 3% O_2/He, 5 min; Reduction: 4% H_2/He, 5 min; constant GHSV = 100 L(STP)/h/g

References

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