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Towards Green Ammonia Synthesis through Reduction of NO_x from the Combustion Process

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ABSTRACT

Ammonia is a commonly used industrial chemical that is of great importance in the chemical and fertilizer production industries. It also attracts increasing attention as a green energy carrier. Haber-Bosch process is the predominant process to synthesis ammonia. However, as an energy intensive process, it can only have a low level of energy consumption when it is running on a large scale. Therefore, in this work, we present the ODSCRA process (a flue gas purification unit, a deaerator unit, a selective catalytic reduction reactor), and the NO_x generated from the plasma technology can act as the alternative NO_x source. ODSCAR can also decentralize the manufacture of ammonium nitrate fertilizers, making it particularly appealing for small- and medium-scale decentralized ammonia synthesis.

Keywords: Ammonia synthesis, Nitric oxides, NOx emissions, SCR

NONMENCLATURE

Abbreviations	
ODSCAR	Oxynitride Directly Selective Catalytic Rection to Ammonia

1. INTRODUCTION

Nitrogen fixation, the processes of converting inert N_2 into biologically available nitrogen (reactive nitrogen compounds), is the very initial step for both natural and industrial utilization of nitrogen element [1]. Ammonia, the most important artificial nitrogen fixation product, is a crucial chemical manufactured and used all over the world. It is the main source of artificial fertilizer. Moreover, chemical and pharmaceutical industries rely heavily on the production of ammonia. In recent years, it acts as an alternative carbonless renewable fuel, and therefore garners a great deal of attention. The Haber-Bosch process, as one of the critical achievements in the 20th century, is the commercial and mature ammonia production process. There are about 150 million tons of ammonia produced via the Haber-Bosch process annually. However, the Haber-Bosch process requires high temperatures (300-500 °C) and high pressure (150-300 atm), as well as pure N_2 and H_2. Thus, the synthesis ammonia process is a high energy-consumption and high carbon emissions process [2]. It was estimated that the Haber-Bosch process operated with nature gas results in ca. 1.5 kg CO_2 production per 1 kg of NH_3. Therefore, there is an urgent need to develop a small-scale, decentralized, on-demand, renewable energy powered technology for ammonia manufacturing that is environmentally friendly.

The review of emitters of NO_x in China reveals that the emission of nitrogen oxides in the national exhaust gas was 10.197 million tons in 2020, of which the emission of nitrogen oxides in the exhaust gas of industrial sources was 4.175 million tons (accounted for about 40.94%) [3]. In addition to this, the majority of NO_x was converted into N_2 by the SCR system. Take a 300 MW coal fired power plant for example, it will generate 8.8 million m^3 of flue gas and 2640 tons of NO_x on the assumption that the SCR inlet concentration of NO_x is 300

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mg/Nm^3. Therefore, if the NO_x generated in power plants was used to synthesize ammonia, it will save a lot of ammonia consumption in NH_3-SCR system, meanwhile a considerable sum of extra NH_3 will be recovered.

Recently, the production of NH_3 through the electrocatalytic nitrogen oxide reaction (eNRR) has gained increasing attention. The eNRR process has many benefits over the conventional Haber-Bosch process. Jing et al. [4] proposed a hybrid plasma and electrocatalytic process for sustainable ammonia production. The NO_x made from a plasma unit was converted to ammonia at a rate of 23.2 mg/h. Many scholars had similar ideas, such as Zhou et al. [5], Ren e. al. [6], Wu et al. [7]. They all produced NOx from air by using plasma technology and then electrocatalytic reduction them into ammonia. Some other scholars studied the electrolytic activities of different nitrogen sources, such as NO_x, nitrogen, nitrates and nitrites by experimental and calculations method [8–14]. But the commercial prospects of the eNRR process remain uncertain because of low ammonia production rates currently.

In this work, we propose a novel ODSCRA (Oxynitride Directly Selective Catalytic Rection to Ammonia) process, in which NO_x emissions from combustion process can be directly used to synthesis ammonia after purifying the SO_2, H_2O and particulate matters. The operation of ODSCRA is proposed based on our work that is still going on.

2. RESULTS AND DISCUSSION

2.1 NO_x capture and storage

Currently, the NH_3-SCR process using ammonia as the reducing agent has been commercially applied in stationary source combustion units that require a higher removal efficiency of NO_x than SNCR (Selective noncatalytic reduction) or combustion controls. In China, more than 90% of power industry, cement industry, coking industry and iron and steel industry used NH_3-SCR technology to abate NO_x from the flue gas. In the United States, more than 1000 SCR systems have been implemented to reduce NO_x from industrial boilers, process heaters, steel mills, chemical plants etc. Therefore, the capture and storage of nitrogen oxides is not the most important means of eliminating nitrogen oxides today.

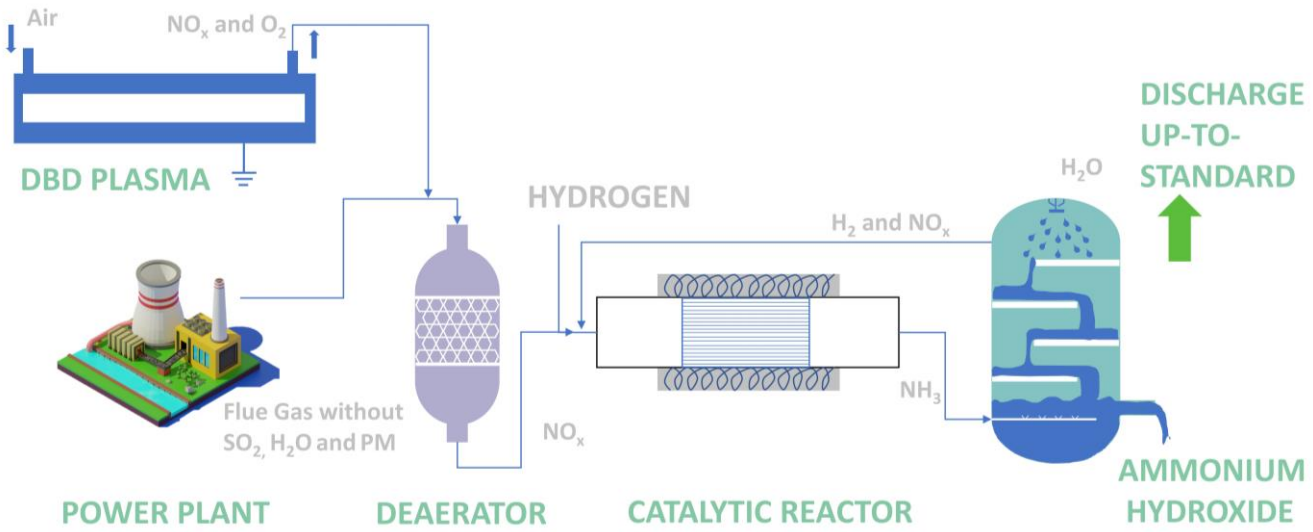

Fig. 1. Schematics illustrating the proposed novel plasma catalyst-integrated system for amonia synthesis

Although there are few related studies, there are still some researchers working on the capture and storage of nitrogen oxides. BaO is a good adsorbent that can store NO_x [15]. Erik et al. prepared Al_2O_3 supported Pt/BaO catalyst, and studied the NO_x storage capacity at temperature range of 100 to 300 °C [16]. However, the capture and storage of nitrogen oxides using an adsorption process requires multi-parallel connection of gas flow reactors, pulse switching between adsorption and desorption, which is not only time-consuming but also expensive. Therefore, direct reduction of NO_x process is particularly important.

2.2 Directly reduction of NO_x

In industry, nitrogen oxides are most used to prepare nitric acid through the Ostwald process [17]. And the global market of nitric acid is also expanding due to the requirement in fertilizers production industry. However, the Ostwald process is also an energy-intensive and high

cost process, it consumes about 1.7 times the energy to produce ammonia [18]. Therefore, low concentrations of NOx are hardly used to synthesis the nitric acid by Ostwald process due to the high cost.

It is possible that converting NO_x selectively to ammonia with a hydrogenation catalyst. The cyclic "lean NO_x trap" has been well studied. Pt/BaO based materials were the core catalyst that was used to capture and store low concentrations of NOx and then react with hydrogen in a cyclic mode [19]. But the hydrogenation catalyst's selectivity easily reduces NO_x to N_2 instead of NH_3 there. Equations 1–4 show intended reactions.

$$2NO+O_2 \rightarrow NO_2 \quad (1)$$

$$BaO+{}_3NO_2 \rightarrow Ba(NO_3)_2+NO \quad (2)$$

$$Ba(NO_3)_2+8H_2 \rightarrow 2NH_3+BaO+5H_2O \quad (3)$$

$$Ba(NO_3)_2+5H_2 \rightarrow N_2+BaO+5H_2O \quad (4)$$

Therefore, to reduce nitrogen oxides to ammonia, it is necessary to develop a catalyst based on the NH_3 selectivity. Clayton et al. tested three $Pt/Ba/Al_2O_3$ catalysts with varied Pt dispersion. The lowest Pt dispersion yielded 87% NH_3 selectivity. Additional studies found that catalysts with NH_3 selectivity of 75% or greater [18,19].

However, the cyclic mode production of NH_3 cannot run continuously, which will restrict the further application of the synthetic ammonia pathway. Therefore, we have been working on the development of catalysts and processes that can directly reduce nitrogen oxides to ammonia using hydrogen, and it has been successful. We can achieve nearly 100% NO_x conversion efficiency and NH_3 selectivity at 400 °C.

2.3 Design of the ODSCRA process

The direct recovery of NO_x from the combustion process is illustrated in Fig. 1. It coupled a flue gas purification unit, a deaerator unit and a selective catalytic reduction reactor. First of all, the purification of the flue gas. SO_2, H_2O and particular matter should be removed before it is introduced into the deaerator unit. And then removing the oxygen in the flue gas through a tank with molecular sieve adsorbents. At last, the pure gas containing nitrogen oxide is passed into the selective catalytic reduction reactor.

As a supplement, the source of nitrogen oxides can also be obtained by treating the air with a DBD (Dielectric Barrier Discharge) plasma, which has been carried out in our laboratory. Nowadays, plasma-based NOx synthesis technologies have been maturing. They can convert N_2 into NO_x with low energy consumption [18,20].

3. CONCLUSIONS

In the end, we support the ODSCRA process to make a small amount of green ammonia. If ODSCRA uses just air, water, and renewable electricity, it not only leaves no trace of carbon dioxide in the atmosphere but also is a good way to eliminate pollutants from the flue gas. As compared to the energy efficiency of NH_3 synthesis from N_2 and H_2, ODSCRA is a clear winner. The novel approach has novel possibilities for changing the current situation of flue gas treatment for all combustion boilers. Moreover, ODSCAR can also decentralize the manufacture of ammonium nitrate fertilizers, making it particularly appealing for small- and medium-scale decentralized ammonia synthesis.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

[1] Qing G, Ghazfar R, Jackowski ST, Habibzadeh F, Ashtiani MM, Chen CP, et al. Recent Advances and Challenges of Electrocatalytic N_2 Reduction to Ammonia. Chem Rev 2020;120:5437–516.

[2] Hollevoet L, Jardali F, Gorbanev Y, Creel J, Bogaerts A, Martens JA. Towards Green Ammonia Synthesis through Plasma-Driven Nitrogen Oxidation and Catalytic Reduction. Angew Chemie 2020;132:24033–7.

[3] Wang H, Chen H, Wang Y, Lyu YK. Performance and mechanism comparison of manganese oxides at different valence states for catalytic oxidation of NO. Chem Eng J 2019;361:1161–72.

[4] Sun J, Alam D, Daiyan R, Masood H, Zhang T, Zhou R, et al. A hybrid plasma electrocatalytic process for sustainable ammonia production. Energy Environ Sci 2021;14:865–72.

[5] Yimeng Z, Jiabao L, Yaqi P, Xiaoqing L, Xingjie L, Qiulin Y, et al. Ar-plasma enhanced copper-nickel alloy catalysis for ammonia synthesis. Waste Dispos Sustain Energy 2022;1:1–7.

[6] Ren Y, Yu C, Wang L, Tan X, Wang Z, Wei Q, et al. Microscopic-Level Insights into the Mechanism of Enhanced NH_3 Synthesis in Plasma-Enabled Cascade N_2

Oxidation–Electroreduction System. J Am Chem Soc 2022;17:26.
[7] Wu A, Yang J, Xu B, Wu X-Y, Wang Y, Lv X, et al. Direct ammonia synthesis from the air via gliding arc plasma integrated with single atom electrocatalysis. Appl Catal B Environ 2021;299:120667.
[8] Li Y, Cheng C, Han S, Huang Y, Du X, Zhang B, et al. Electrocatalytic Reduction of Low-Concentration Nitric Oxide into Ammonia over Ru Nanosheets. ACS Energy Lett 2022;7:1187–94.
[9] He C, Sun R, Fu L, Huo J, Zhao C, Li X, et al. Defect engineering for high-selection-performance of NO reduction to NH_3 over CeO_2 (111) surface: A DFT study. Chinese Chem Lett 2022;33:527–32.
[10] Lin Y, Liang J, Li H, Zhang L, Mou T, Li T, et al. Bi nanodendrites for highly efficient electrocatalytic NO reduction to NH_3 at ambient conditions. Mater Today Phys 2022;22:100611.
[11] Liang J, Liu P, Li Q, Li T, Yue L, Luo Y, et al. Amorphous Boron Carbide on Titanium Dioxide Nanobelt Arrays for High-Efficiency Electrocatalytic NO Reduction to NH_3. Angew Chemie Int Ed 2022:e202202087.
[12] Li R, Wang D, Li R, Wang D. Superiority of Dual-Atom Catalysts in Electrocatalysis: One Step Further Than Single-Atom Catalysts. Adv Energy Mater 2022;12:2103564.
[13] Liang J, Zhou Q, Mou T, Chen H, Yue L, Luo Y, et al. FeP nanorod array: A high-efficiency catalyst for electroreduction of NO to NH_3 under ambient conditions. Nano Res 2022 2022:1–6.
[14] Liu P, Liang J, Wang J, Zhang L, Li J, Yue L, et al. High-performance NH_3 production via NO electroreduction over a NiO nanosheet array. Chem Commun 2021;57:13562–5.
[15] Broqvist P, Grönbeck H, Fridell E, Panas I. NOx storage on BaO: theory and experiment. Catal Today 2004;96:71–8.
[16] Burch R, Shestov AA, Sullivan JA. A Transient Kinetic Study of the Mechanism of the NO+H_2 Reaction over Pt/SiO_2 Catalysts. J Catal 1999;186:353–61.
[17] Lim J, Fernández CA, Lee SW, Hatzell MC. Ammonia and Nitric Acid Demands for Fertilizer Use in 2050. ACS Energy Lett 2021;6:3676–85.
[18] Rouwenhorst KHR, Jardali F, Bogaerts A, Lefferts L. From the Birkeland–Eyde process towards energy-efficient plasma-based NO_X synthesis: a techno-economic analysis. Energy Environ Sci 2021;14:2520–34.
[19] Partridge WP, Choi JS. NH_3 formation and utilization in regeneration of Pt/Ba/Al_2O_3 NOx storage-reduction catalyst with H2. Appl Catal B Environ 2009;91:144–51.
[20] Kelly S, Bogaerts A. Nitrogen fixation in an electrode-free microwave plasma. Joule 2021;5:3006–30.