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# An alternative process for nitric oxide and hydrogen production using metal oxides

Sonal K. Thengane<sup>a,b,c</sup>, Santanu Bandyopadhyay<sup>b</sup>, Sagar Mitra<sup>b</sup>,  
Sankar Bhattacharya<sup>c</sup>, Andrew Hoadley<sup>c,\*</sup>

<sup>a</sup> IITB Monash Research Academy, Indian Institute of Technology Bombay, Mumbai 400076, India

<sup>b</sup> Department of Energy Science and Engineering, Indian Institute of Technology Bombay, Mumbai 400076, India

<sup>c</sup> Department of Chemical Engineering, Monash University, Clayton 3168, Victoria, Australia

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## ABSTRACT

A new process employing metal oxide is proposed for the production of nitric oxide and hydrogen which are precursors to the production of nitric acid. There have only been a few studies reporting the oxidation of ammonia by metal oxides, but the ammonia–metal oxide reactions for the simultaneous production of NO and H<sub>2</sub> have not yet been reported. The reaction of ammonia with different metal oxides is investigated in detail, including thermodynamic feasibility calculations. The salient feature of the proposed reaction is the production of H<sub>2</sub> in addition to NO. Experiments are performed for the most feasible metal oxides in a semi batch reactor. These experiments confirm the feasibility of the ammonia–metal oxide reaction for cupric oxide (CuO), ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) and cobalt oxide (Co<sub>3</sub>O<sub>4</sub>) at 825 °C, 830 °C and 530 °C, respectively. The maximum yields of NO are around 90% for each metal oxide. The effect of varying the different parameters such as temperature, ammonia concentration, and particle size on the yield of nitric oxide is reported for the case of CuO and a reaction mechanism is proposed to explain these results. These results are used to develop two different chemical looping based processes for NO and H<sub>2</sub> production depending on the mode of regeneration of metal oxides.

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## 1. Introduction

The annual world production of nitric acid is about 60 million tonnes, 85% of which is used in the fertiliser industry as ammonium nitrate (“The Essential Chemical Industry,” 2015). As shown in Fig. 1, the conventional process for the production of nitric acid starts with steam methane reforming (SMR) of natural gas to produce hydrogen, which is reacted to produce ammonia followed by catalytic oxidation of ammonia to produce nitric oxide (NO). This is further oxidised to nitrogen dioxide (NO<sub>2</sub>), which in turn is hydrolysed to produce nitric acid (Thiemann et al., 2012). This process relies on fossil fuel (natural gas) and is efficient, but has significant atmospheric

emissions in each stage of the process. The presence of excess air (normally 10% ammonia and 90% air) and Pt/Rh catalyst at a high temperature of 900 °C, 10 bar pressure results in almost complete conversion of ammonia to oxides of nitrogen (Scientific American Supplement, 1913; Thiemann et al., 2012). There have been several improvements to the original century-old Ostwald Process (1902), but no significant changes in the process reactions except for the modification of catalysts. The requirement of H<sub>2</sub> as a precursor for NH<sub>3</sub> and hence NO emphasises the need of developing a process that could produce NO and H<sub>2</sub> simultaneously. In the 1950s a new method was proposed to prepare NO from heating a dry powdered mixture of potassium nitrite, potassium nitrate, chromic oxide

\* Corresponding author. Present address: Room 208, Building 69, Clayton Campus, 3168 Melbourne, Australia. Tel.: +61 3 990 53421.

E-mail addresses: [thenganesonal@gmail.com](mailto:thenganesonal@gmail.com) (S.K. Thengane), [santanub@iitb.ac.in](mailto:santanub@iitb.ac.in) (S. Bandyopadhyay), [sagar.mitra@iitb.ac.in](mailto:sagar.mitra@iitb.ac.in) (S. Mitra), [sankar.bhattacharya@monash.edu](mailto:sankar.bhattacharya@monash.edu) (S. Bhattacharya), [andrew.hoadley@monash.edu](mailto:andrew.hoadley@monash.edu) (A. Hoadley).  
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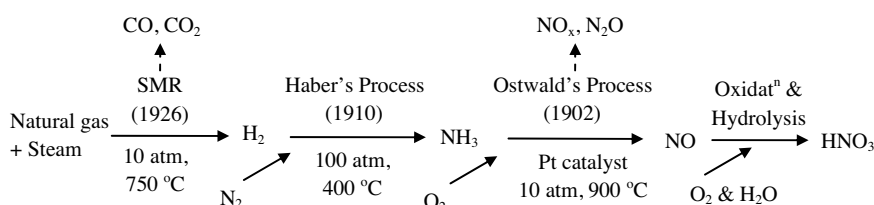


Fig. 1 – Conventional process scheme for nitric acid production.

and ferric oxide above 300 °C (Ray and Ogg, 1956). Though the process produced 99.78% pure nitric oxide, it was not explored further due to its overall complexity. Other proposed processes are focused on obtaining a high NO concentration or reducing impurities such as nitrous oxide (N<sub>2</sub>O) in particular, either by adding intermediate cooling and separation stages (Echegaray et al., 2000; Jockers et al., 1970), or by modifying the catalyst (Hunt, 1958; Theodore, 1995).

The catalytic and non-catalytic oxidation of ammonia by different oxygen carriers has been studied extensively. The traditional method of oxidation of NH<sub>3</sub> by air or oxygen is highly exothermic which results in high temperatures, but this process only has partial energy recovery through steam production. Hence, the replacement of air or oxygen by an oxygen carrier such as a metal oxide that would react with NH<sub>3</sub> is a worthwhile option to be explored. In recent years, thermochemical processes have gained wide interest in exploring alternative ways to produce chemicals such as ammonia (Lan et al., 2013), hydrogen (Abanades et al., 2006), etc. These are also termed as chemical looping based processes in which solid metal oxides are employed as the oxygen-carrier for the conversion of fuel to synthesis gas. The application of metal oxides as oxygen carriers can be extended to the formation of feedstock for mineral acids such as nitric acid (HNO<sub>3</sub>) where NH<sub>3</sub> can be oxidised by a metal oxide as one step in the chemical looping process. Fig. 2 shows the schematic of conventional chemical looping process based on two-step metal oxide cycles where the reduced metal oxide is re-oxidised back to original state either by air or water. Cheng et al. (2015) studied the oxidation of NH<sub>3</sub> with and without syngas over ilmenite as an oxygen carrier without oxygen uncoupling

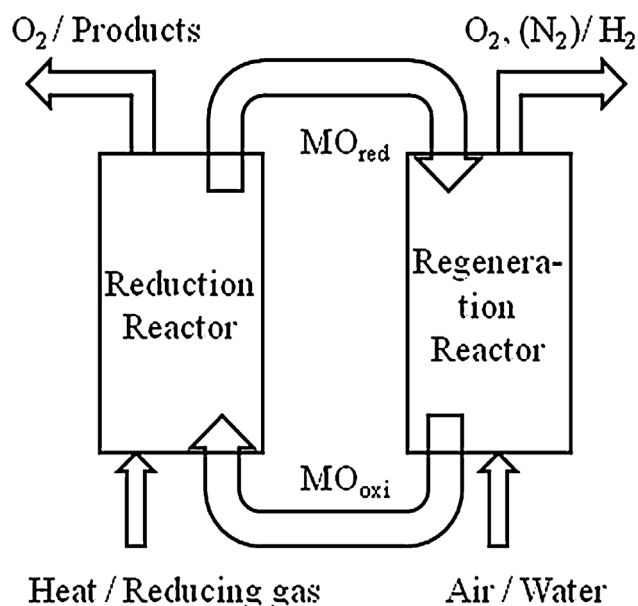
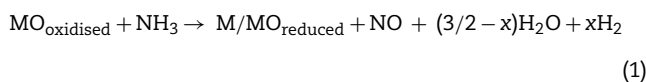


Fig. 2 – Chemical looping process schematic for two-step metal oxide cycles.

capability. More recently, Normann et al. (2016) investigated the oxidation of NH<sub>3</sub> in a mixture with syngas over copper oxide and interpreted the results using additional gas-phase modelling of the combustion and nitrogen chemistry. The fully oxidised oxygen carriers resulted in considerable amounts of NO formation which later decreased as the oxygen carrier becomes more reduced.

The reaction proposed for nitric oxide and hydrogen production in present work is as follows:



As per reaction (1), the metal oxide is reduced by ammonia to the metal or reduced metal oxide producing NO, H<sub>2</sub> and H<sub>2</sub>O. The H<sub>2</sub> to NO ratio ( $x$ ) is one of the important outcomes of this work and is discussed in more detail in later sections. The reduced metal oxide can be re-oxidised to its original state, however, the present study is focused only on ammonia–metal oxide reaction for NO and H<sub>2</sub> production. The proposed reaction can be operated at lower pressures without the need for expensive catalysts. The hydrogen produced can be utilised for total or partial production of the ammonia required for nitric acid production.

This paper reports the process for NO and H<sub>2</sub> production from the reaction of ammonia with metal oxide. First a thermodynamic analysis is conducted to identify the feasible metal oxides followed by an experimental study to confirm the reaction conditions and conversion. A reaction mechanism is proposed based on the experimental results obtained particularly for the case of cupric oxide (CuO). Finally the possibility of developing chemical looping based process for NO and H<sub>2</sub> production with thermodynamic feasibility calculations is also reported.

## 2. Thermodynamic feasibility

Table 1 present the calculations for thermodynamic feasibility for different metal oxide cases using the reaction equations tab of the software package HSC Chemistry Version 7.1 (“HSC Chemistry,” 2015). For the purpose of these calculations, the value of  $x$  (the H<sub>2</sub> to NO ratio) in Eq. (1) is assumed to be 0.5. As will be shown in the experimental section, the value of  $x$  changes over time as the oxygen in the metal oxide is consumed.

The temperature at which a reaction becomes spontaneous is found by applying the Gibbs–Helmholtz equation. The equilibrium temperature ( $T_e$ ) is the temperature at which Gibbs free energy of reaction becomes zero, and the reaction temperature ( $T_r$ ) is the temperature at which the reaction is assumed to occur in the forward direction for a Gibbs free energy of about  $-50$  kJ per mole of NH<sub>3</sub>. A  $\Delta G_r$  value close to  $-50$  kJ/mol is a reasonable criterion for a reaction to go to 100% conversion. A

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