

Solar Ammonia Production via Novel Two-step Thermochemical Looping of a $\text{Co}_3\text{Mo}_3\text{N}/\text{Co}_6\text{Mo}_6\text{N}$ pair

Xiang Gao¹, Ivan Ermanoski^{1,2}, Alberto de la Calle¹, Andrea Ambrosini³, and Ellen B. Stechel^{1,4,a)}

¹ ASU LightWorks®, Arizona State University, PO Box 875402, Tempe, AZ 85287-5402, USA

² School of Sustainability, Arizona State University, PO Box 875402, Tempe, AZ 85287-5402, USA

³ Sandia National Laboratories, PO Box 5800, MS 0734, Albuquerque, NM 87185, US

⁴ School of Molecular Sciences, Arizona State University, PO Box 875402, Tempe, AZ 85287-5402, USA

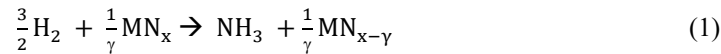
a) Corresponding author: ellen.stechel@asu.edu, 480-965-1657

1. Introduction

Ammonia (NH_3) is one of the most produced industrial chemicals worldwide. Fertilizer for agriculture accounts for about 80% of NH_3 production. Many industrial and household applications such as refrigerant gas, water purification, and plastics manufacture use NH_3 . Furthermore, NH_3 is in consideration as a hydrogen carrier or as an energy vector in a deeply decarbonized energy system. Currently, NH_3 is produced via the Haber-Bosch (H-B) process, which is based on the gas phase exothermic reaction of H_2 and N_2 at 15-25 MPa and temperatures between 350-500 °C. This process also includes obtaining the essential feedstock (H_2 and N_2) from highly carbon-intensive approaches: the source of H_2 is from steam reforming of CH_4 , and the source of N_2 is air after removing the oxygen via combustion with CH_4 . Additionally, methane combustion provides the energy necessary for process heat and for pressurization. In the Solar-Thermal Ammonia Production (STAP) project, we propose a sustainable pathway for NH_3 production using concentrating solar irradiation for process heat and pursuing relatively mild-pressure operating conditions. A renewable NH_3 synthesis pathway will significantly help mitigate greenhouse gas emission and provide price stability avoiding high volatile markets like fossil fuels. There would also be advantages in alternative NH_3 synthesis technologies that can operate flexibly and at a smaller scale than H-B.

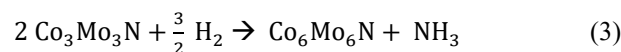
2. Ammonia Production via thermochemical looping of the $\text{Co}_3\text{Mo}_3\text{N}/\text{Co}_6\text{Mo}_6\text{N}$ pair

Recent advances in concentrating solar power technologies have enabled renewable synthesis of N_2 and H_2 via carbon-free processes. Specifically, solar thermochemical cycles can produce high purity N_2 by removing oxygen from air with redox-active metal oxides, and advanced water splitting can produce renewable H_2 via several processes, such as a two-step thermochemical metal oxide cycle, PV-electrolysis, or photo-electrochemical pathways. In this context, renewable N_2 and H_2 can serve as feedstocks to a novel mild-pressure NH_3 production process, characterized by the following chemical looping reactions:



In a mildly endothermic step (1), a stable metal nitride reacts with H_2 to produce NH_3 and a nitrogen deficient metal nitride. In step (2), the nitrogen-deficient nitride reacts with N_2 to regenerate the initial nitride. Preliminary thermodynamic calculations suggest this chemical looping strategy to synthesize NH_3 could reduce the pressure demand considerably, likely by an order of magnitude compared to the H-B process. This significantly liberates the design constraints in a dedicated reactor, as most of the common materials such as 316 stainless steel can easily operate in this pressure range without further protective strengthening.

In this work, we demonstrate this two-step thermochemical looping concept for NH_3 production with a $\text{Co}_3\text{Mo}_3\text{N}$ (331)/ $\text{Co}_6\text{Mo}_6\text{N}$ (661) nitride pair, via the reactions below:



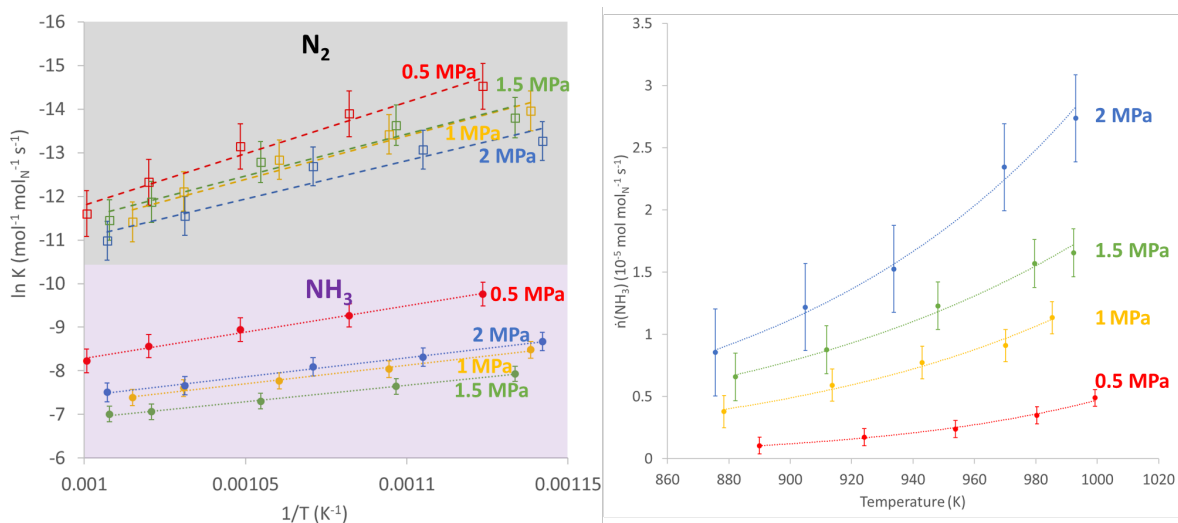
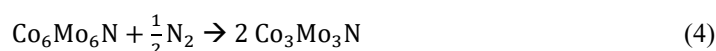


Figure 1: Kinetic results of NH_3 production via the two-step thermochemical looping mechanism. (a) Determination of the activation energies for NH_3 and N_2 production from reducing 331 in 100% H_2 stream, as a function of H_2 pressure. (b) NH_3 production rates as a function of temperature and H_2 pressure.



We have demonstrated the feasibility of NH_3 production with this thermochemical cycle in a mild-pressure custom-designed Ammonia Synthesis Reactor (ASR) operating at an isothermal temperature of 650°C and a constant pressure of 2 MPa. To demonstrate the cyclability of the process, numerous cycles were carried out alternating the partial pressures between H_2 and N_2 . We tested several temperatures and pressures to find the best operating conditions (Figure 1). With this experimental campaign, we observed nearly 100% of the theoretical reversible lattice nitrogen resulted from the 331 to 661 reduction (Eq. 3) without conversion loss over multiple cycles, and we achieved consistently more than 50% of selectivity from the lattice nitrogen towards NH_3 (vs. N_2) as the product. The overall NH_3 yield in this process, more than 50%, is 3-4 times higher than the established catalyzed H-B process, without sacrificing the ability to operate at kinetically favored high temperatures, and with an order of magnitude less of pressure requirement.

Our preliminary kinetics analysis of the NH_3 synthesis (Eq. 3) reveals an activation energy for NH_3 comparable to that of the H-B forward reaction, indicating great potential for kinetic optimization via high-temperature catalysis on the 331/661 pair. Further study on engineering the nitride pair via ionic substitution to optimize the equilibrium at $> 600^\circ\text{C}$ temperatures and < 3 MPa pressures and further improve selectivity towards NH_3 is also warranted. This alternative strategy for NH_3 production opens up more opportunities for energy-efficient, cost-effective and flexible nitrogen fixation technologies via renewable pathways.

Acknowledgment

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