Low temperature synthesis of ammonia by a chemical looping process based on metal imides as nitrogen carrier

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Introduction

While global warming becomes more and more tangible, joint efforts to decarbonize all human activities are intensifying. Among the sector that would benefit from carbon mitigation, the chemical industry holds a significant position. Beyond the fact it was responsible for 4.2% of the global CO_2 emissions in 2019, 1.2% are attributable to the production of ammonia alone, making it one of the largest CO_2 emitters of the chemical industry [1, 2]. The main reason behind this considerable contribution is the fossil-based Steam Methane Reforming process (SMR) used to produce hydrogen, which is then fed to the Haber-Bosch (HB) process for NH_3 synthesis. Furthermore, it is worth noting that half of the world's food production currently relies on fertilizers produced with synthetic ammonia through this method, making it a critical challenge to tackle [3]. Several alternative technologies have already been proposed and are currently being studied [4]. Among them is the electrification of the H_2 production, replacing SMR with electrolysis, which will have several implications on the process and will inevitably lead to new challenges [5]. However, such a solution revolves only around the replacement of the SMR. Transitioning to a lower operating conditions process such as alkaline water electrolysis (60-90°C & 1-30 bar) can lead to the entire process being rethought, including the well-established Haber-Bosch technique (350-500°C & 150-300 bar). In this work, a novel technique is investigated to fully replace the HB process with a low temperature and pressure chemical looping process.
Introduced in the early 20th century for hydrocarbon fuel conversion, the principle of chemical looping is based on the decoupling of a catalytic reaction in sub-reactions supported on a catalyst that passes through an intermediate state and is then regenerated in a loop. Nowadays, chemical looping emerges as a promising technology for various applications, including low-temperature and pressure ammonia synthesis [6, 7]. Among the recent studies on the subject, one demonstrated unparalleled NH_3 production rates at mild conditions using Ni-BaH_2/BaNH as a catalyst via reaction (1) and (2) [8].

$$4BaH_{2(s)} + 2N_{2(g)} = 4BaNH_{(s)} + 2H_{2(g)} \tag{1}$$
$$2BaNH_{(s)} + 4H_{2(g)} = 2BaH_{2(s)} + 2NH_{3(g)} \tag{2}$$

Ammonia started forming at ambient pressure and temperatures as low as 100°C, with the synthesis rate reaching 3125 µmol g^{-1} h^{-1} at 300°C. Within the context of electrifying ammonia production, such low conditions would better match with alkaline water electrolysis.

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The present work provides an in-depth analysis of the behavior of Ni-BaH_2 during nitridation (reaction (1)) under isothermal conditions. Parallel experiments were conducted on both N_2 Temperature-Programmed Reaction (N2-TPR) and time-resolved in situ X-Ray Diffraction (XRD) to observe reaction (1) at 5 distinct temperatures ranging from 180°C to 300°C.

Methodology

Material synthesis

Ni-BaH_2 was prepared with a loading of 50% Ni nanopowder (Merck, <100 nm, 99%) and 50% BaH_2 (Strem) grinded by hand with an agate mortar and pestle inside an Ar-filled Jacomex P(BOX) glove box. The sample studied in this work was prepared by grinding 850mg of each powder for 1h, in 4 periods of 15minutes. 1mL of acetone was added each time after 15, 30 and 45min to improve homogeneity and prevent adherence to the edges of the mortar.

Experimental methods

N2-TPR measurements were carried out on a Micromeritics Autochem II 2920 setup connected to a Thermal Conductivity Detector (TCD) and the outlet gas composition was analyzed with a Mass Spectrometer (MS) detector. 200mg of Ni-BaH_2 was loaded in a quartz reactor and heated at 90°C/min in a He flow at atmospheric pressure (30 ml min^{-1}) to the target temperature, monitored by a thermocouple directly placed in the sample. After reaching the isothermal regime, the gas flow was switched manually to a N_2 flow at atmospheric pressure (30 ml min^{-1}). After 15min, the reactor was cooled down to room temperature. The sample was then retrieved from the reactor in an Ar-filled glove box.

Powder diffraction and time-resolved in situ XRD experiments were both conducted on a Bruker-AXS D8 Discover apparatus (Cu Kα radiation of 0.154 nm). 50mg of the sample was disposed on a silicon wafer, placed on a heating plate and enclosed in a home-built reaction chamber. Vacuum was progressively applied until a pressure of $5*10^{-2}$ mbar was reached. The chamber was then filled with He until atmospheric pressure. In situ XRD collects series of measurements at regular time intervals (10 seconds) in restricted angular ranges ($2\theta = 19° - 38°$) and allows the analysis of samples in reaction conditions. In this case, it was set to follow the same temperature and gas protocol as the N2-TPR. The sample was heated to the target temperature at 90°C/min under He at atmospheric pressure (1000 ml min^{-1}). As the preset temperature provided to the program corresponds to that of the heating plate, a deliberate adjustment of +10°C was applied to account for heat losses. Upon reaching the target temperature, gas flow was then manually switched to a N_2 flow at atmospheric pressure (1000 ml min^{-1}). The sample was cooled down to room temperature after 15min.

Discussion

N2-TPR

The nitridation of Ni-BaH_2 as detailed in reaction (1) was tested by N2-TPR on 5 temperatures (180°C, 210°C, 240°C, 270°C and 300°C). The resulting signals are displayed on Figure 1. As expected from reaction (1), H_2 is produced during N2-TPR, as can be seen on Figure 1a & 1b (green section). Despite it being expressed in arbitrary units, the signal appears to be increasing with temperature, which confirms the increasing yield demonstrated in previous studies [8, 9]. However, the signal is decreasing again at 300°C.

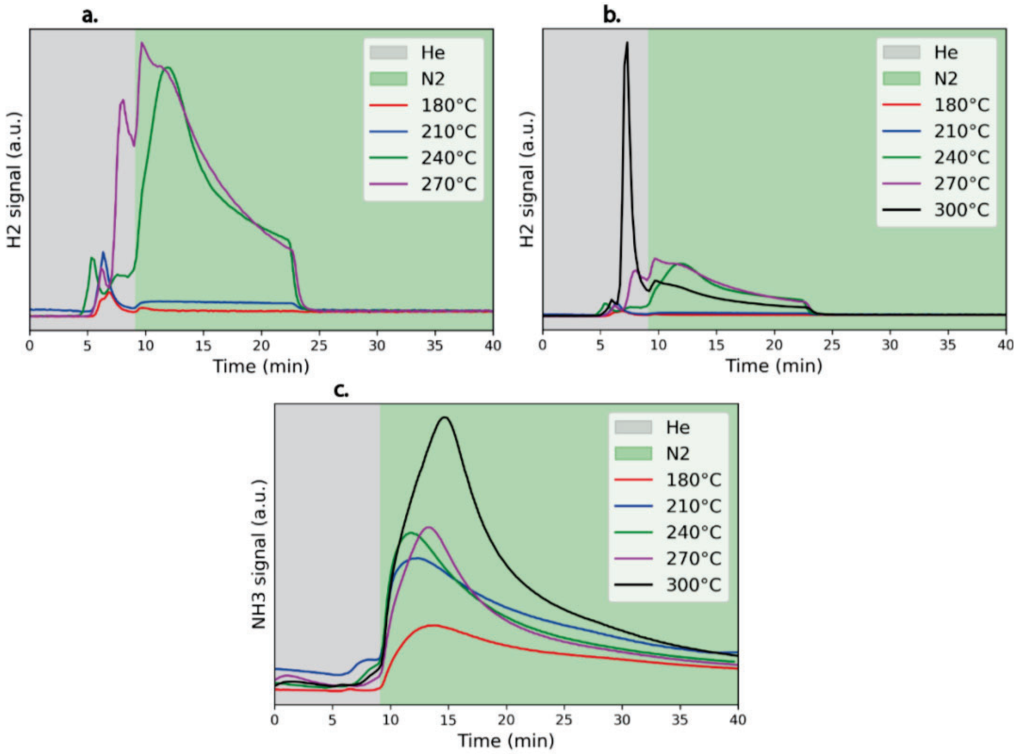

Figure 1: N2-TPR profiles of Ni-BaH_2. **a & b** H_2 signal through time for 180°C, 210°C, 240°C, 270°C (**a**) and 300°C (**b**) isothermals. **c.** NH_3 signal through time for the 5 isothermal experiments. (a.u.) = arbitrary units.

Hydrogen seems to be released even before N_2 is fed to the reactor, during the heating-up under He flow, indicating that a dehydrogenation reaction is taking place. This phenomenon was studied by Guan et al. in 2022 [9]. They first noticed a dehydrogenation happening under an Ar flow starting from 300°C, and then demonstrated that a pretreatment under argon at that same temperature would be beneficial for the later N_2 fixation, thanks to H vacancies being formed. Here however, the H_2 signal starts as low as 50°C as shown on Figure 2a, with an apparent maximum reached around 150°C. During the 2 highest isothermal experiments (270°C and 300°C), a second dehydrogenation mechanism seems to take place, starting from 210-230°C. On Figure 2b, one can notice that a second maximum is achieved around 275°C for both these isothermals. It is also noticeable as a second peak showing on Figure 2b. This 2-step dehydrogenation can be regarded as an indicator that 2 different hydrogen sites are at stake. The first (and weakest) dehydrogenation signal may be coming from a second hydride formed in lower quantity as a byproduct during the catalyst synthesis, such as Ni_2H. The second (and highest) dehydrogenation signal most certainly originates from BaH_2, the principal hydride of the sample.

Figure 1c shows that NH_3 is also produced during N2-TPR, which indicates that the second step of the chemical looping process, as detailed in reaction (2), is already taking place during the first nitridation step. This can also explain the decreased H_2 signal highlighted earlier at 300°C, as H_2 would be consumed to produce NH_3.

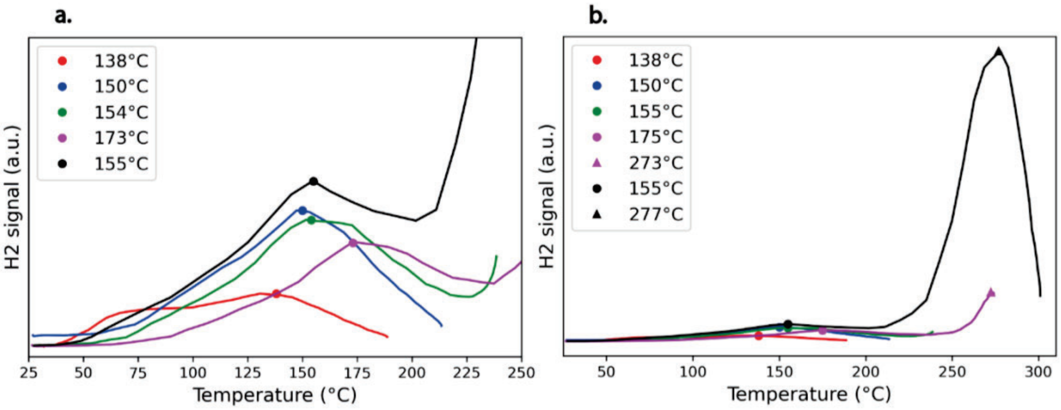

Figure 2: H_2 signal through temperature during heating-up for 180°C, 210°C, 240°C, 270°C (**a**) and 300°C (**b**) isothermals. (a.u.) = arbitrary units.

In-Situ XRD

Parallel to the N2-TPR, the same conditions were reproduced inside an in-situ XRD setup. Figure 3 displays the full diffraction pattern obtained after each isothermal N2-TPR, as well as the as-prepared sample. Some barium oxide ($BaO_{1.3}$) and nickel oxide (NiO) seem to have formed in the sample, as a result of the short exposure to the air when transferring the sample to the reaction chamber. It can be noted that the diffractograms do not vary after the first 3 isothermal experiments. However, changes appear clearly on the 280°C and 300°C isothermals.

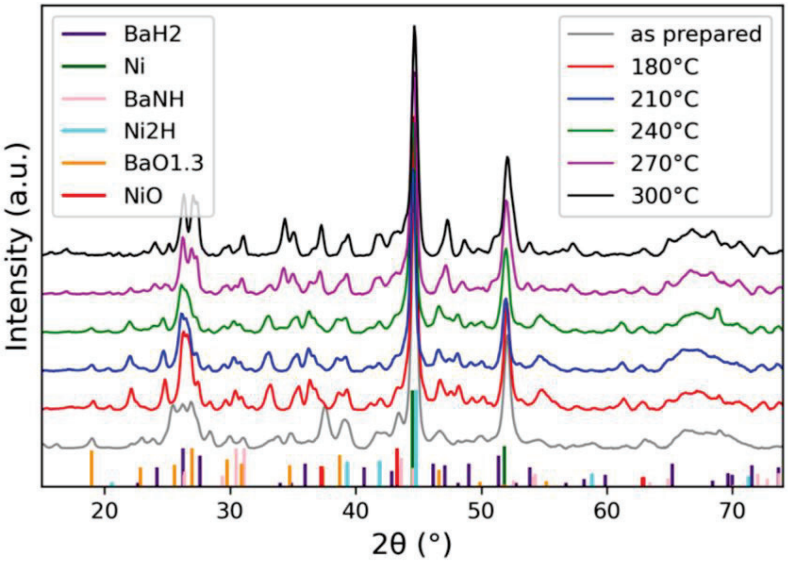

Figure 3: XRD patterns of the as-prepared sample and the sample after each isothermal experiments. (a.u.) = arbitrary units.

This is where in-situ XRD brings more detail to the measurements, as the sample was periodically scanned for the whole duration of the heating up and N_2 exposure. Figure 4 shows 3 diffraction patterns extracted from those measurements. The patterns are shown on a restricted angular range from 19° to 38° where the most prominent peaks for both BaH_2 and BaNH are located. On Figure 4.a, the initial state of the as-prepared sample can be seen. Figure

4.b and 4.c show the post-transition states at the corresponding temperatures where the transitions took place: 153°C and 275°C. Both these temperatures are very close to the ones observed earlier in the dehydrogenation steps during N2-TPR, and both happened during the heating-up under He. The 2-step dehydrogenation could then explain both transitions observed in the diffraction pattern. Furthermore, the idea that a secondary hydride Ni_2H is implied in one of the dehydrogenation mechanisms is supported by the presence of its peaks in the diffraction pattern on Figure 3. Finally, the last scan taken directly after the second transition (Figure 4.c) does not show a peak at 26.3° anymore. That specific diffraction peak is notably the strongest of BaH_2 and is associated to the (120) plane. This may be regarded as a shift in the diffraction plane following the appearance of H vacancies, especially given that they appear preferably on the (120) surface [9].

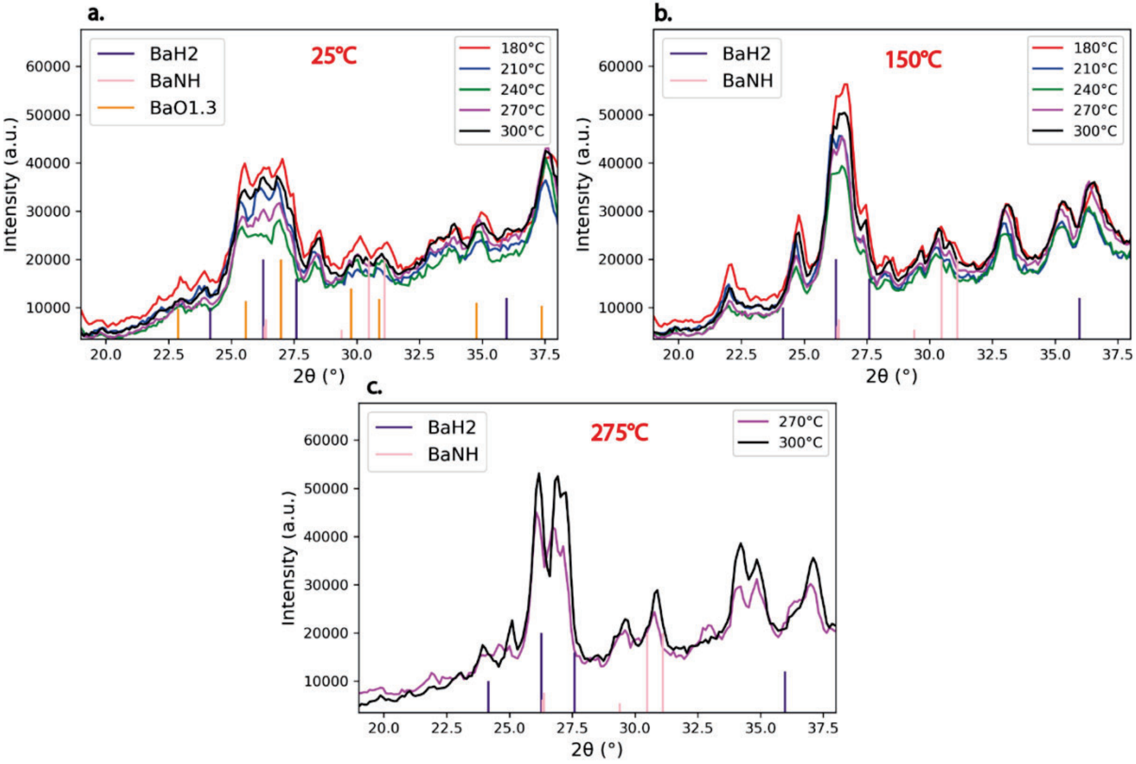

Figure 4: in-situ XRD patterns extracted at ambient temperature (**a**), 150°C (**b**) and 275°C (**c**) for each isothermal experiments. (a.u.) = arbitrary units.

It is important to highlight that no variations took place during the nitridation step when the N_2 was flowed, showing no traces of BaNH whatsoever. The typical peaks around 2θ = 30-31° should have no link with BaNH as they were present before N_2 was flowed. Moreover, two $BaO_{1.3}$ peaks are also located in the same range and could very well be confused with BaNH.

Further work

In this work, the nitridation of Ni-BaH_2 could only be proven from the release of H_2 and NH_3 as observed during N2-TPR. However, no direct traces of BaNH have yet been highlighted. In subsequent research, more tests could be conducted using the same setups but with adapted parameters. For instance, it was shown that the nitridation increased with longer exposure to N_2 (40% of nitridation after 30 minutes of exposure to N_2 at 265°C) [8]. Another possibility currently envisioned is the use of environmental Transmission Electron Microscopy (TEM) to observe the catalyst behavior in-situ on a submicron-scale under reaction conditions.

Conclusions

- Nitridation of Ni-BaH_2 was studied isothermally at five distinct temperatures (180°C, 210°C, 240°C, 270°C and 300°C).
- Hydrogen production during N2-TPR confirmed the nitridation process. Increased H_2 with increased temperature also confirmed literature results on the reaction yield.
- A two-step dehydrogenation was observed under helium flow during heating at 150°C and 275°C respectively.
- Ammonia production indicated the progression of the chemical looping process as the emitted hydrogen provides the reactant for the second reaction.
- Analysis of powder diffraction patterns revealed the formation of barium oxide ($BaO_{1.3}$) and nickel oxide (NiO) in the as-prepared sample, probably after a short exposure to air when transferring it to the in-situ XRD reactor chamber.
- The two-step dehydrogenation observed during N2-TPR experiments aligns with the changes in the diffraction pattern taking place at similar temperatures (153°C and 275°C).
- The presence of Ni_2H may indicate it is the second source of hydrogen acting in the dehydrogenation with BaH_2.

Acknowledgements

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