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Ammonia suppression during decomposition of sodium amide by the addition of metal hydride

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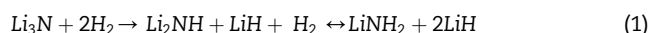
ABSTRACT

The decomposition of NaNH₂ has been reported, mainly decomposing into NaH, N₂ and H₂. Ammonia is also produced in addition to N₂ and H₂. To the best of our knowledge, very few scattered reports on the effect of alkali hydrides on NaNH₂ exist in literature. Thus, we choose NaNH₂–MH (M = Li, Na, K, Mg, Ca) system to be investigated in detail. Since NaNH₂–NaH is the simplest combination due to same cation, it was tested for the establishment of reaction mechanism using transmission electron microscopy (TEM). It is observed that the entire process follows NH₃ mediated reaction similar to LiNH₂–LiH system. Sodium amide first decompose into Na metal and NH₃, then generated NH₃ reacted with added NaH to form NaNH₂ and release H₂. This process continues until the consumption of NaH, thus suppresses NH₃ evolution to a great extent. The investigation has been extended further to the other metal hydrides and it is found that the addition of other metal hydride i.e. LiH, KH, MgH₂, and CaH₂ have also effectively suppressed the NH₃ evolution. The detailed reaction mechanism has been elucidated for all the amide hydride systems. It is observed that the decomposition takes place through an intermediate step of double-cation amide formation.

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Introduction

Metal amides are well known as a hydrogen storage material since their invention by Chen et al., in 2002 [1]. Lithium amide was proposed as a first candidate of this family which can store 10.4 wt% of hydrogen according to the following conversion reactions:



The addition of hydride to this amide follow NH₃ mediated reaction i.e. amide first decomposes into imide phase and NH₃. The generated NH₃ then reacts with added hydride exothermically [2]. After the proposal of this mechanism, several combinations of amides and hydrides have been proposed by several researchers worldwide. Specially LiNH₂ and

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Mg(NH₂)₂ based amide systems have attracted the attention of H₂ community due to their favorable pressure temperature (P–T) window of sorption properties. However, sodium amide (NaNH₂) based system has not been investigated till now due to its high reactivity, low melting point, high enthalpy and above all the complexity involved with this system. Sodium amide decomposition was first reported by Titherley in 1894 as follows [3]:



The presence of sodium hydride or sodium metal as final product depends on the back pressure inside the system [4]. Excess gaseous pressure than the dissociation pressure of NaH allows first reaction to proceed while the lower pressure allows the decomposition of NaH. In both cases, ammonia is also produced in addition to N₂ and H₂. Although the above reactions were proposed long back, there are no other reports with the solid experimental evidence on the above system except very recent reports by our group [5,6] and Jepsen et al. [7]. Jain et al. [5] and Jepsen et al. [7] have reported that NaNH₂ decompose directly into Na metal and NH₃ as major products with small amount of N₂ and H₂. However, more recently Yamaguchi et al. [6] found an imide-like intermediate during decomposition under vacuum. The authors have suggested that the partial pressure of gaseous species strongly affect the decomposition pathway of sodium amide. There are few scattered reports available in literature on NaNH₂–MgH₂ [8–10], NaNH₂–CaH₂ [11,12], NaNH₂–LiAlH₄ [13] etc. However, to the best of our knowledge, no report except above mentioned articles [5–7] contains the thermal desorption data of sodium amide decomposition with proper characterization of resultant products. Herein, we report the decomposition pathway of sodium amide first time using Mass spectroscopy as well as Transmission Electron Microscopy (TEM). Since the main issue associated with the practical use of sodium amide for hydrogen storage is NH₃ emission similar to other amides, we also present our findings on NH₃ suppression using different metal hydrides as additives.

Experimental

The starting material NaNH₂ and MH (M = Li, Na, K, Mg and Ca) were milled under 0.1 MPa Ar at 400 rpm for 2 h using Fritsch P7 ball milling apparatus. The ratio for amide and hydride components was kept 1:1 for alkali metal hydrides, whereas it was kept 2:1 for MgH₂ and CaH₂. The phase changes during the decomposition process were observed using X-ray diffraction (XRD) on Rigaku-RINT 2500 instrument equipped with CuK α radiation. The N–H bonding states in the samples at different stages were tracked using Fourier Transform Infrared (FTIR) spectroscopy at room temperature using diffuse-reflection cell in Perkin Elmer – Spectrum one unit at a resolution of 1 cm⁻¹. In addition to XRD, in-situ Transmission Electron Microscopy (TEM) experiment was performed on pristine sodium amide and sodium hydride added NaNH₂ sample to track the reaction mechanism using 200 kV TEM (JEOL JEM-

2010) in the temperature range RT – 400 °C. The sample was dispersed on a Mo TEM grid, and then transferred into TEM chamber using plastic bag method [14] in order to keep the sample intact from atmospheric conditions. The thermal decomposition was studied using differential scanning calorimetry (DSC, TA Instruments Q10PDSC) up to 400 °C with scan rate 5 °C/min under closed system with initial pressure of 0.1 MPa. The evolved gases during decomposition process were observed using combined Thermogravimetry (Rigaku, TG 8120) and thermal desorption mass spectroscopy (TDMS; Anelva, M-QA 200 TS) system installed inside Ar-filled glove box. The TG-TDMS experiment was performed up to 400 °C with scan rate 5 °C/min under 0.1 MPa Ar flow.

Results & discussion

The decomposition of NaNH₂ and NaNH₂–NaH system was observed using mass spectroscopy. Fig. 1 shows H₂ and NH₃ MS profile for both systems. It is clearly observed that sodium amide start decomposing at around 240 °C evolving NH₃ as major gaseous species with a small amount of H₂ observed only beyond 350 °C. In addition to H₂ and NH₃, two peaks corresponding to N₂ emission is also observed at around 150 °C and 325 °C, however, the corresponding weight loss is very small as discussed in our recent report [5]. The XRD measurement after decomposition, shown elsewhere [5], confirms the final product as sodium metal. Whereas, NH₃ is the main gas evolved during NaNH₂ decomposition, it is greatly suppressed when sodium amide is mixed with sodium hydride, as can be seen from the MS profile shown in the upper panel of Fig. 1. It is observed that the decomposition start at much lower temperature i.e. 150 °C, although it is very slow as observed from a small peak corresponding to H₂ MS profile. The major H₂ evolution occurred in the temperature range of 275–350 °C with peak temperature at 330 °C. A small amount of NH₃ is also evolved as evident from a small broader peak in the temperature range of 300–400 °C. In order to

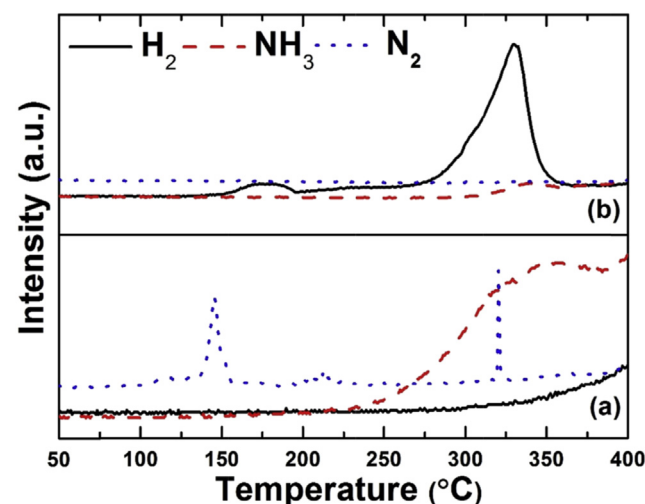


Fig. 1 – H₂, N₂ and NH₃ MS profile for (a) NaNH₂ and (b) NaNH₂–NaH decomposition.

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