



# Metal chloride-doped ammonia borane thermolysis: Positive effect on induction period as well as hydrogen and borazine release

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## ABSTRACT

In this work we studied the effect of metal chlorides ( $\text{CoCl}_2$ ,  $\text{FeCl}_3$  and  $\text{AlCl}_3$ ) on thermal decomposition of ammonia borane  $\text{NH}_3\text{BH}_3$  (AB). The chlorides were chosen because they are simple and cost-effective. They showed promising performances as the onset temperature of AB decomposition decreased. Temperatures of 52, 65 and 85 °C were determined for  $\text{CoCl}_2$ -,  $\text{FeCl}_3$ - and  $\text{AlCl}_3$ -doped AB whereas it was 99 °C for AB. The induction period of AB dehydrogenation has been reduced. The relative mass losses were found as being 11.9, 12.3 and 10.4 wt% at about 110 °C but at 85 °C they were 4.5, 4.5 and 1.6 wt%, respectively. The gaseous side-products were analyzed and traces of borazine  $\text{B}_3\text{N}_3\text{H}_6$  were detected. It was found that the  $\text{CoCl}_2$  presence has a positive effect on the  $\text{B}_3\text{N}_3\text{H}_6$  evolution. The solid by-products were characterized by XRD and IR:  $[\text{NH}_2\text{BH}_2]_x$  forms after the first decomposition of AB and  $[\text{BNH}_x]_z$  forms after the second decomposition. The IR-print of  $[\text{BNH}_x]_z$  resembles that of BN, what suggests high dehydrogenation extent. These results are analyzed and discussed in the present paper.

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## 1. Introduction

Molecular hydrogen ( $\text{H}_2$ ) is often announced as being the energy carrier of our near future. The prospect of developing a hydrogen economy is very attractive but there are still many challenges to be addressed, one of them being hydrogen storage. Hydrogen storage is currently much investigated and science is on the look-out for finding storage solutions. In this context, ammonia borane ( $\text{NH}_3\text{BH}_3$ , AB) has showed its high potential owing to a gravimetric hydrogen density of 19.5 wt% [1]. The stored hydrogen can be released by thermal decomposition [2]. Nevertheless, AB has to release 11 wt% of pure  $\text{H}_2$  at temperatures up to 85 °C as this value is the revised 2015 target set by the U.S. Department of Energy (US DOE) for on-board hydrogen storage systems [3]. Unfortunately, only one third of the total hydrogen content (i.e., 6.5 wt%) is recoverable in the temperature range 70–120 °C [4]. Actually, there are four main issues that hinder the effective implementing of AB: that is, a high  $\text{H}_2$  release temperature, low content of hydrogen released up to 85 °C, too low  $\text{H}_2$  generation rate, and storage irreversibility [5].

Promoting the  $\text{H}_2$  release has therefore attracted much attention. In this regard, transition metal-promoted thermal decomposition [6,7] has been examined with AB. Jaska et al. [8] demonstrated the catalytic efficiency of a rhodium complex,

i.e.,  $[\text{Rh}(1,5\text{-cod})(\mu\text{-Cl})_2]$ , which nature is not exactly known. Denney et al. [9] have reported the rapid thermal decomposition of AB catalyzed by a homogeneous iridium pincer complex (i.e.,  $(\text{POCOP})\text{Ir}(\text{H})_2$  and  $\text{POCOP} = [\eta^3\text{-}1,3\text{-(OP}^t\text{Bu)}_2\text{C}_6\text{H}_3]$ ); for a 0.5 mol% catalyst loading in a tetrahydrofuran solution of AB it was observed that 1 equiv.  $\text{H}_2$  released within 14 min at room temperature. De Benedetto et al. [10] successfully used a platinum salt, i.e.,  $\text{H}_2\text{PtCl}_6$ ,  $\text{H}_2$  release starting at temperatures lower than 73 °C. Keaton et al. [11], Yang and Hall [12] and Zimmerman et al. [13] focused on active nickel N-heterocyclic carbene complexes; for example, an important  $\text{H}_2$  release (>2.5 equiv.  $\text{H}_2$ ) for a 25 wt% AB solution in diglyme was observed at 60 °C [11]. Each of the promoters given heretofore permitted to decrease the temperature of  $\text{H}_2$  release. It is noteworthy that most of them are metal-based complexes which preparation needs more or less complicated processes and various chemicals.

In the present work, we studied the effect of metal chlorides (cobalt chloride, iron chloride and, for the first time, aluminum chloride) on thermal decomposition of AB. The reaction was considered in homogeneous solid–solid phases. Our objective was to search for simple, cost-effective, efficient metal-based activators both to reduce the induction period of AB dehydrogenation and increase  $\text{H}_2$  release at temperatures up to 85 °C. The study was mostly based on thermogravimetric and calorimetric techniques, which can besides be coupled to gas chromatography–mass spectrometry in order to analyze the gas stream (especially the side-products). Herein, it is showed that in the presence of some of the metal chlorides we regarded the onset temperature of AB

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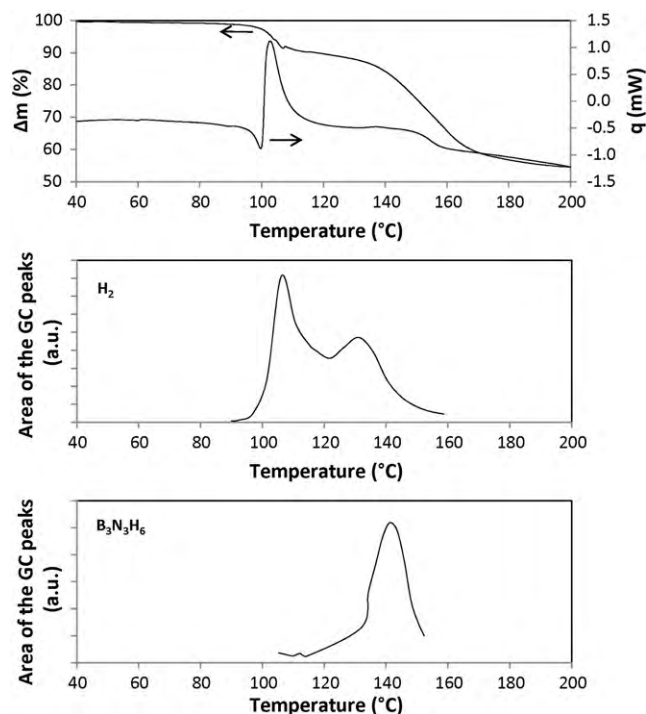
decomposition is decreased, H<sub>2</sub> starting to release at temperatures much lower than 100 °C. As a matter of fact, the halides presence has a positive effect on reducing the induction period of AB decomposition as well as on decreasing the amount of unwanted gaseous side-products.

## 2. Experimental

AB (Sigma Aldrich, 97%), CoCl<sub>2</sub> (Acros Organics), FeCl<sub>3</sub> (Fluka) and AlCl<sub>3</sub> (Fluka) were used as received and were handled in an argon-filled glove box. Safety information: AlCl<sub>3</sub> is particularly unstable in the presence of moisture, reacting violently with generation of fumes and heat. Promoted AB samples were prepared as follows. AB and 10 wt% of metal chloride were mixed together and ground in a mortar. Reproducible results in terms of thermal and calorimetric characterizations have been obtained.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed with TGA/SDTA 851<sup>e</sup> and DSC1 (Mettler Toledo) under the following conditions: sample mass 2–3 mg, aluminum crucible of 100 μl with a pin-hole, heating rate of 1, 3 or 5 °C min<sup>-1</sup>, and atmosphere of N<sub>2</sub> (50 ml min<sup>-1</sup>). Sample mass loss and associated thermal effects were obtained by TGA/SDTA. In order to integrate the different mass loss steps the TGA first derivation (mass loss rate) was used because even at the rate of 1 °C min<sup>-1</sup> the resolution (i.e., mass loss steps well defined) was not ideal. The thermal study of the decomposition process was also investigated by DSC. Both instruments were calibrated in the studied range of temperature, i.e., 25–200 °C min<sup>-1</sup>. The melting points and melting enthalpies of four standards (gallium, naphthalene, indium and tin) were used for the calibration of the DSC in terms of heat flow, temperature and tau lag. The calibration gave a straight line with a regression coefficient of 0.9997. Concerning the TGA, the melting points of five compounds (phenyl salicylate, naphthalene, benzoic acid, indium and tin) obtained from the DTA signals were used for the sample temperature calibration. The calibration gave a straight line with a regression coefficient of 1. Calcium oxalate monohydrate was used for the sample mass calibration and in doing so the experiment showed a difference in the 1st mass loss of 3.5% in relation to the theoretical value (experimental conditions: 2–3 mg of sample, heating rate of 1 °C min<sup>-1</sup>, temperature range 25–200 °C). As reported by Wendlandt and co-authors [2], the AB samples undergo a voluminous swelling, which may cause an artifact on the TGA profile or a contact with the internal walls of the TGA furnace. Hence, the mass was limited to 2–3 mg (±0.01 mg). Each TGA or DSC experiment was performed three times to ensure the reproducibility of the results.

The gas stream (H<sub>2</sub> and side-products) was analyzed with a portable micro-chromatograph μGC M200 from Agilent M Series, which has 2 columns and 1 micro-thermal conductivity detector (μ-TCD). H<sub>2</sub> was separated on a molecular sieve column (12 m × 0.32 mm, 5 Å) and quantified with the TCD detector. Another OV1 column (10 m × 0.15 mm i.d.) separated borazine, its identification being realized by coupling the μGC with a mass selective detector (MSD). The μGC/MSD is commercialized by S.R.A. Instruments. As the M200 chromatograph does not permit any temperature program, preliminary measurements were undertaken to set the optimal temperature. Different column temperatures were tested: i.e., 70, 90 and 110 °C. For the present study, 90 °C was found to be the most appropriate temperature. The μGC sampling time was 20 s and the injection time 250 ms; the head column pressure was fixed at 27.8 psi for the molecular sieve column and 30.8 psi for the OV1 one. Helium and argon were used as carrier gas for the separation of borazine and H<sub>2</sub>, respectively. Accordingly, for our sample, 2 analyses had to be done in order to separate the gases.



**Fig. 1.** TGA and DSC curves of neat AB thermolysis at a heating rate of 1 °C min<sup>-1</sup> (note that the artifact on the TGA curve of neat AB at about 110 °C is due to the sample swelling [Sit-1987]) and, evolution of H<sub>2</sub> and that of B<sub>3</sub>N<sub>3</sub>H<sub>6</sub> (i.e., variation of their peak surface areas as a function of temperature; it is noteworthy that the proportion of H<sub>2</sub> is independent on that of B<sub>3</sub>N<sub>3</sub>H<sub>6</sub>).

The solid by-products were recovered and analyzed by X-ray diffraction (XRD, Bruker D5005 powder diffractometer, CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ )) and diffuse reflectance Fourier transform infrared spectroscopy (IR, FTIR Nicolet 380). They were obtained in large amounts by heating 300 mg of AB (or doped AB) in a furnace at 115 °C or 200 °C (ramp 1 °C min<sup>-1</sup>) under nitrogen flow (100 ml min<sup>-1</sup>). No heating at 200 °C was performed on AlCl<sub>3</sub>-doped AB because of the low melting point of anhydrous AlCl<sub>3</sub> (i.e., 192 °C). AB, doped AB and their by-products were handled under argon.

## 3. Results and discussion

### 3.1. Neat AB

The thermal decomposition of neat AB was first studied in our experimental conditions, which was essential to determine the best TGA/DSC operating conditions. The TGA results are summarized in Table 1. Both onset temperature and mass loss increase while the heating rate goes up. Accordingly, the heating rate of 1 °C min<sup>-1</sup> was set for our experiments. The TGA curve obtained at this rate is given in Fig. 1. The thermal decomposition of AB was besides followed by DSC (1 °C min<sup>-1</sup>) and showed two exothermic processes [14], i.e., two decomposition steps (99 and 132 °C), which confirmed the TGA results. The enthalpy of the first decomposition has been determined as being  $-16.6 \text{ kJ mol}^{-1}$  AB (the enthalpy of the second decomposition is  $-7.4 \text{ kJ mol}^{-1}$  AB). The former value has been underestimated because an endothermic peak starting at 97 °C partially compensated the first exothermic peak. Nevertheless, the apparent value is quite consistent with previously reported enthalpies from  $-15$  to  $-24 \text{ kJ mol}^{-1}$  AB [15,16]. The endothermic process is assigned to AB melting [16] which enthalpy is  $2.2 \text{ kJ mol}^{-1}$  AB.

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