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Instability of the $CuCl_2$–NH_3BH_3 mixture followed by TGA and DSC

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ABSTRACT

In the field of 'hydrogen storage and generation', ammonia borane NH_3BH_3 (AB) destabilization can be achieved by adding a metal halide, here copper chloride ($CuCl_2$). Improved dehydrogenation properties can be achieved with a fresh mixture of $CuCl_2$–NH_3BH_3. Using a systematic approach, we followed the stability of the mixture using thermogravimetric analysis, differential scanning calorimetry and (micro) gas chromatography while it was stored under argon at room temperature over 6 months. The aged samples showed improved dehydrogenation properties compared to pristine AB. However, the performance deteriorated in comparison to the fresh mixture indicating that $CuCl_2$–NH_3BH_3 evolves over time, decomposing with slow kinetics. This is detrimental in terms of stability during storage, making long-term storage of $CuCl_2$ inconceivable for safety and performance reasons. This is discussed herein.

1. Introduction

In chemical hydrogen storage, ammonia borane (NH_3BH_3, AB) has been shown to be one of the most promising thermolytic hydrides. The compound is hydrogen-rich, constituted of 19.5 wt% H. Half of the hydrogen atoms are in the form of $H^{\delta+}$ and the other half as $H^{\delta-}$. This is a significant attribute being very convenient for generating hydrogen through intra- and/or inter-molecular interactions [1].

Thermolytic dehydrogenation of AB is a three-step process, which is preceded by melting [2–4]:

$$n\mathrm{NH_3BH_3(s)} \rightarrow n\mathrm{NH_3BH_3(l)} \quad (1)$$

$$n\mathrm{NH_3BH_3(l)} \rightarrow [\sim\mathrm{NH_2BH_2}\sim]_n\mathrm{(s)} + n\mathrm{H_2(g)} \quad (2)$$

$$[\sim\mathrm{NH_2BH_2}\sim]_n\mathrm{(s)} \rightarrow [\sim\mathrm{NHBH}\sim]_n\mathrm{(s)} + n\mathrm{H_2(g)} \quad (3)$$

$$[\sim\mathrm{NHBH}\sim]_n\mathrm{(s)} \rightarrow [\sim\mathrm{NB}\sim]_n\mathrm{(s)} + n\mathrm{H_2(g)} \quad (4)$$

Pristine AB is able to release the first 2 equiv. H_2 (13 wt% H) over the range 100–200 °C. Release of the third equiv. H_2 occurs at a high temperature (>500 °C) and is generally not taken into account in thermolytic dehydrogenation. Efforts have therefore focused on decreasing the temperature for reactions (2) and (3) [1]. This was our first objective.

On heating, AB decomposes and releases unwanted gaseous by-products, with the most abundant being borazine $B_3N_3H_6$. Its formation mainly occurs during reaction (5):

$$[\sim\mathrm{NH_2BH_2}\sim]_3\mathrm{(s)} \rightarrow \mathrm{B_3N_3H_6(g)} + 3\mathrm{H_2(g)} \quad (5)$$

$$[\sim\mathrm{NH_2BH_2}\sim]_n\mathrm{(s)} \rightarrow [\sim\mathrm{NHBH}\sim]_{n-3m}\mathrm{(s)} + m\mathrm{B_3N_3H_6(g)} + n\mathrm{H_2(g)} \quad (6)$$

The formation of monomeric aminoborane NH_2BH_2, diborane B_2H_6 and ammonia NH_3 were also reported [5,6]. Hence, we also focused on suppressing the formation of unwanted gaseous by-products and this was our second objective.

From a mechanistic point of view, reaction (1) is rather complex. It can be decomposed into three stages: first, induction where the hydrogen network of the AB molecules, which exists through intermolecular $H^{\delta+}\cdots H^{\delta-}$ interactions, is disrupted and an amorphous phase of AB forms. After that, the intermediate diammoniate of diborane $[(NH_3)_2BH_2]^+BH_4^-$ forms by isomerization of 2 AB molecules. This is the nucleation step. Diammoniate of diborane is a very reactive intermediate and is at the origin of the initiation of AB dehydrogenation. Finally, there is the growth step consisting in head-to-tail dehydrocoupling of AB molecules through activation of B—H and N—H bonds [7,8].

To fulfill the aforementioned objectives, four approaches have been considered so far: (i) dispersing AB in an organic solvent (with the presence of a homogeneous metal-based catalyst) [9] or in an ionic liquid [10]; (ii) mixing AB with a chemical additive (promoter) [11,12]; (iii) nanoconfining AB into a porous host matrix [13]; and (iv) chemically modifying AB to obtain a derivative [14].

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Each of these approaches has a positive effect on reducing the induction period, so reducing the dehydrogenation temperatures and decreasing the emission of unwanted gaseous by-products. Recently, we chose the second approach; metal(II)chlorides were used as a chemical additive [15]. It was clear that $CuCl_2$ is the most efficient additive with 0.8 equiv. H_2 released at ~85 °C (heating rate 1 °C min^{-1}).

In our previous work [15], we handled and tested the $CuCl_2$–NH_3BH_3 mixture in a fresh state. In other words, the decomposition of $CuCl_2$–NH_3BH_3 was analyzed immediately after its preparation. We observed that, on heating, the metal salt activated the decomposition of AB through Lewis acid-based interactions. The occurrence of such interactions questions the stability of $CuCl_2$–NH_3BH_3 over time. The work presented hereafter aimed at understanding this question.

2. Experimental

Ammonia borane NH_3BH_3 (Sigma–Aldrich, 97%) and copper chloride $CuCl_2$ (Sigma–Aldrich, 97%) were used as received and handled in an argon-filled glove box (JACOMEX BS522). The $CuCl_2$–NH_3BH_3 mixture was prepared as follows. In the glove box, 20 wt% of $CuCl_2$ were added to NH_3BH_3, ground and mixed together in a mortar. The content of $CuCl_2$ was fixed at 20 wt% to have enough material for the characterizations. By elemental analysis (ICP-AES performed at "Service Central d'Analyses du CNRS", in Solaize, France), the loading was found to be consistent with the target 20 wt%. The as-prepared mixture $CuCl_2$–NH_3BH_3 was then stored in the argon-filled glove box at room temperature.

For technical and safety reasons, the samples were stored in the aforementioned conditions. In fact, it was important to have a neutral atmosphere with controlled purity, which is only possible in an argon-filled glove box. The storage conditions were at room conditions, *i.e.* temperatures ranged between 19 and 22 °C (air-conditioning). In fact, it was not possible to put a cooler or a heater inside the glove box to have a fixed temperature because these devices use fluids that must be avoided in the argon-filled glove box. The choice of the glove box was also motivated for safety reasons. Our concern was to avoid any risk of explosion that could be due to the uncontrolled generation of H_2 from the aging samples. Hence, storage of the argon-filled vials under air was excluded.

Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851^e (Mettler Toledo). We considered the following experimental conditions: sample mass of 2–3 mg, aluminum crucible of 100 μl with a pinhole (∅ = 670 μm), heating rate of 1 °C min^{-1}, temperature range of 25–200 °C, and a N_2 atmosphere (50 mL min^{-1}). To integrate the different mass loss steps, we used the TGA first derivation (mass loss rate). It is worth noting that the apparatus was calibrated over the range 25–200 °C min^{-1}. The melting points of five compounds (phenyl salicylate, naphthalene, benzoic acid, indium and tin) obtained from the differential thermal analysis (DTA) signals were used for the sample temperature calibration. Calcium oxalate monohydrate was used for the sample mass calibration. Differential scanning calorimetry (DSC; DSC1 Mettler Toledo) was also employed to study the AB decomposition process. The experimental conditions were identical to those used in TGA. The DSC device was also calibrated over the range 25–200 °C, and the melting points and enthalpies of standards were used for the calibration in terms of heat flow (indium and zinc), temperature and tau lag (indium and tin). The samples were analyzed by TGA and DSC three times to ensure result reproducibility.

The purity of H_2 was analyzed with a portable microchromatograph, μGC M200 from Agilent M Series, which has 2 columns and 1 micro-thermal conductivity detector (μ-TCD). Hydrogen was separated on a molecular sieve column (12 m × 0.32 mm; 5 Å; Ar carrier gas; 70 °C; head column pressure fixed at 27.6 psi) and quantified with the μ-TCD detector. Another OV1 column (10 m × 0.15 mm i.d.; He carrier gas; 90 °C; head column pressure fixed at 30.8 psi) separated borazine (and other possible gases like ammonia and diborane, which were not detected here). The identification of borazine was done by coupling the μGC with a mass selective detector (MSD). The μGC/MSD is commercialized by S.R.A. Instruments. The μGC runtime was 60 and 120 s for hydrogen and borazine, respectively. The injection time was fixed at 200 ms. In order to quantify the amounts of H_2, the μGC/MSD was calibrated with a gas sample of known concentration, *i.e.* 2000 ppm of H_2 in a N_2 balance.

The solids, consisting of B- and N-based compounds and metal-based particles, were analyzed by attenuated total reflectance Fourier transform infrared spectroscopy (IR, FTIR Nicolet 380), X-ray diffraction (XRD, PANalytical X'pert pro MPD powder diffractometer, CuKα radiation (λ = 1.5406 Å)), and X-ray photoelectron spectroscopy (XPS, performed at "Science et Surface", in Ecully, France, on a PHI Quantera SXM spectrometer equipped with an Al Kα; *i.e.* $h\nu$ = 280 eV, and 47.7 W; the spectrometer binding energy (E_b) scale was calibrated using the position of C 1s (284.8 eV) core level.

3. Results and discussion

3.1. The issue

Ammonia borane as a pristine solid is not appropriate for a chemical hydrogen storage application. Its implementation is strongly dependent on several key factors, with one of them being its destabilization and thus its dehydrogenation at low temperatures. In this way, one of the convenient approaches has been to add a chemical promoter to the AB matrix. Metal halides are attractive candidates because they are commercially-available, easily handled, and able to reduce into a catalytic form *in situ* [11]. In our experimental conditions, $CuCl_2$ was shown to be the most efficient promoter and a fresh mixture of $CuCl_2$–NH_3BH_3 was used as is and tested [15]. However, for an application, the sample should be stored in a closed vessel for a certain time in room conditions and we would then expect no evolution and/or modification. This is crucial for two reasons: safety (emission of H_2 or other gases) and performance.

In the present work, it was decided to investigate the stability of $CuCl_2$–NH_3BH_3 over six months. A batch of the mixture consisting of $CuCl_2$ and NH_3BH_3 was prepared. It was split into seven samples. The first, *i.e.* the fresh one, was immediately analyzed. The results were similar to those reported elsewhere [15]. The sample is denoted M0. The other samples were transferred into six different vials, sealed and stored in the argon-filled glove box at room conditions. After 1, 2, 3, 4, 5 and 6 months, the aged samples were analyzed one after the other. They are denoted M1, M2, M3, M4, M5 and M6, respectively.

3.2. Thermogravimetric and calorimetric characterizations

The thermal decomposition of M1–M6 was followed by TGA (Fig. 1). The calorimetry of the process was analyzed by DSC (Fig. 2). The TGA and DSC curves are typical of those encountered with metal halide: NH_3BH_3 mixtures [15,16]. The onset temperature is lower than that of pristine AB. The additive $CuCl_2$, even after storage of 1–6 months, has a positive effect in reducing the induction period and making the decomposition of AB begin in milder conditions. The TGA and DSC curves show mainly 3 main decomposition stages over the temperature ranges 25–85, 85–120 and 120–200 °C. The first stage confirms the improved decomposition properties of AB.