

Decomposition of NH_3BH_3 studied by coupling Calorimetry, Sievert's method and Mass Spectrometry

INTRODUCTION

Of the many different hydrogen storage materials being developed today chemical hydrides have been attracting a considerable amount of interest because of their extremely high hydrogen storage capacities. Ammonia borane is an exciting example of such a chemical hydride because its hydrogen storage capacity approaches a very high 20 percent hydrogen by weight.

The chief drawback of ammonia borane, however, has been the lack of energy-efficient methods to reintroduce hydrogen back into the spent fuel once it has been released. The irreversibility under typical hydriding conditions also poses issues in accurately measuring the equilibrium energy of hydrogen release. By coupling a CALVET calorimeter together with a GASPRO gas sorption analyser and at the same time an FLEXI HP MS high-pressure mass spectrometer, we can simultaneously study during the decomposition, the desorbed amount of hydrogen, the heat of the different reactions and the nature of the evolved gas.

Reactions	Density*, wt.% H_2	Desorption temperature, °C
$\text{NH}_4\text{BH}_4 \rightarrow \text{NH}_3\text{BH}_3 + \text{H}_2$	6.1	< 25
$\text{NH}_3\text{BH}_3 \rightarrow \text{NH}_2\text{BH}_2 + \text{H}_2$	6.5	< 120
$\text{NH}_2\text{BH}_2 \rightarrow \text{NHBH} + \text{H}_2$	6.9	> 120
$\text{NHBH} \rightarrow \text{BN} + \text{H}_2$	7.3	> 500

ammonia borane desorbs hydrogen in four consecutive reactions. The first and the fourth reaction are of little practical application due to the low and high temperatures (respectively) required. The most interesting reactions for hydrogen storage are the two intermediate steps which occur with only moderate heating. The objective of the current study was to decouple the two steps, and simultaneously observe the occurrence of any side reactions. An additional interest was the influence of the pressure on the reaction.

EXPERIMENT

Two reactions steps were performed using the GASPRO to control the sample environment:

- The first experiment started with an overpressure of 0.5 bar of Ar.
- The second experiment started with an overpressure of 20 bar of H_2 .
- Approximately 80 mg of ammonia borane was loaded into the GASPRO sample cell. The temperature program was identical for both runs and it can be seen in the figures 1 and 2. It consist of a mix between isothermal and temperature ramping profiles as controlled by the CALVET.

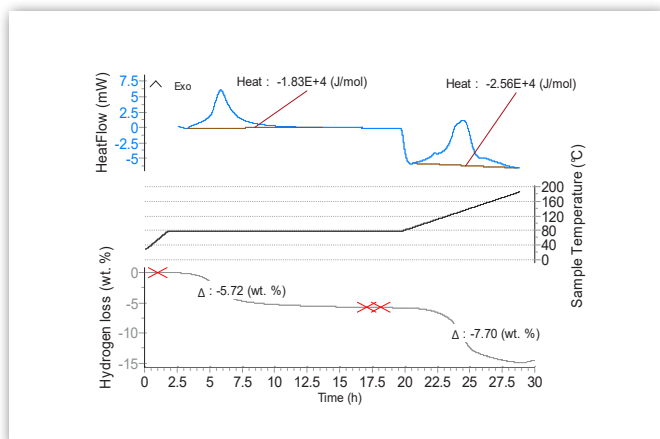


Fig 1. Heat flow (blue), temperature (black) and hydrogen uptake (gray) of the 1st experiment started with 0.5 bar of Ar.

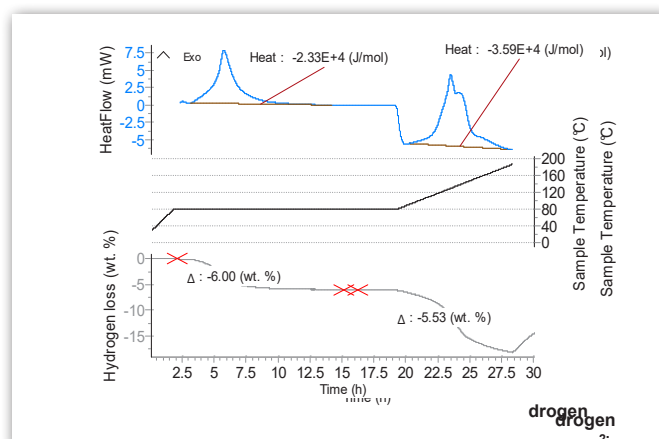


Fig 2. Heat flow (blue), temperature (black) and hydrogen uptake (grey) of the 1st experiment started with 20 bar of H_2 .

RESULTS AND CONCLUSION

- The first observation is that the reaction was not complete in the first experiment.
- The reaction enthalpies are more significant with applied hydrogen pressure (fig. 1 and 2.)
- Experiment without an initial hydrogen pressure, gave a total hydrogen uptake exactly matching the theoretical reaction equations (table below)
- On the contrary with an initial hydrogen over-pressure the reaction did not go to completion (fig. 2 and table)
- The in-situ mass spectrometry demonstrates that only hydrogen is evolved during all decomposition steps (fig. 3). No significant trace of others decomposition products such as ammonia, borane, diborane,... were observed.
- Comparison of the exothermic peaks give some indication that the reactions exhibit different paths depending on the applied over-pressure.

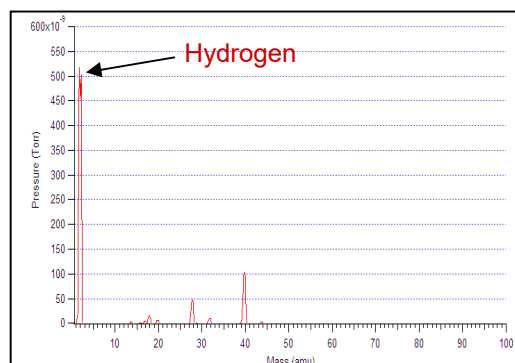


Fig 3. Mass spectra taken in dosing mode.

Summary table

	1 st experiment started with 0.5 bar of Ar		2 nd experiment started with 20 bar of H ₂	
	1 st reaction	2 nd reaction	1 st reaction	2 nd reaction
Quantity of desorbed hydrogen	4.731 mmol	7.26 mmol	4.663 mmol	4.794 mmol
	5.72 wt. %	7.70 wt. %	6.00 wt. %	5.53 wt. %
Heat of reaction	-44.64 J	-62.60 J	-51.30 J	-78.88 J
Enthalpy per NH ₃ BH ₃ mol basis	18.3 kJ/mol	25.6 kJ/mol	23.3 kJ/mol	35.9 kJ/mol

This example demonstrates the capability and importance of measuring quantitative hydrogen uptake and release combined with calorimetry and mass spectrometry to obtain the true enthalpies of reaction. This is particularly crucial for unstable chemical hydrides where the H₂ sorption is not reversible under normal conditions preventing enthalpy determination from equilibrium pressure measurements.

INSTRUMENT

GASPRO

-260°C to 500°C



VARIETY OF MODES OF OPERATION

ability to combine PCT, kinetics and cycle life modes to 200bar to determine the quantity and rate of sample gas interaction and its aging characteristics all in one instrument and operation

PRECISION MEASUREMENT OF SMALL SAMPLES

using the patented microdoser option to inject small doses of gas on the sample

HIGH ACCURACY VERSION

to reduce cumulative error across multiple measurements points

EXTERNAL CALORIMETER COUPLING CAPABILITY

to increase your research options