Experimental report

30/10/2015

Proposal: **5-24-544** **Council:** 4/2014

Title: A PND Study on Phase Evolution During Dehydrogenation of Stoichiometric Lithium Hydride - Melamine System

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Duncan GREGORY**

Experimental team: Tina Yu-Ting SU

Local contacts: Thomas HANSEN
Clemens RITTER

Samples: LiD, C3D6N6

Instrument	Requested days	Allocated days	From	To
D20	1	1	07/10/2014	08/10/2014
D2B	2	1	09/10/2014	10/10/2014

Abstract:

The 6:1 LiH-C3N6H6 system contains 6.97 wt % of H2 and consists of commercially available materials in LiH and C3N6H6. Such relatively cheap materials are of interest since H2 production must meet the 2017 cost target of $400/kg H2, set by the US Department of Energy. The full theoretical capacity of hydrogen is released through a multi-step-process on heating the milled materials to 400 °C. Using differential thermalanalysis data, we have isolated several intermediate solid-state products at different temperature points and conducted ex-situ powder X-ray diffraction and FT Infrared Spectroscopy. Although we identify Li2NCN as the only solid-state product after all hydrogen is released, the dehydrogenation pathway is still unclear. Quantitative phase information vs. temperature will be determined from in-situ powder neutron diffraction data. The accurate structure of Li2NCN and possible nonstoichiometric intermediate compounds will be elucidated via Rietveld refinement against ex-situ PND data. Moreover, PND will help define the dehydrogenation pathway as the melamine ring is cleaved and allow us to extract kinetic information for the multistep reaction.

Proposal 5-24-544: A PND Study on Phase Evolution during Dehydrogenation of Stoichiometric Lithium Hydride – Melamine System

T. Y. Su, T. K. A. Hoang, D. H. Gregory

Introduction

One day of beam time each on D20 and D2B were allocated to study the phase evolution during dehydrogenation of the stoichiometric 6LiH : $C_3N_6H_6$ hydrogen storage system by *in situ* and *ex situ* neutron diffraction. The system releases its theoretical limit of 6.98 wt.% H_2 by *ca*. 320 °C *via* a multi-step decomposition as observed in TG-DTA experiments. The sole solid reaction product is Li_2NCN (I4/mmm) (from PXD and FTIR data). Neutron diffraction was employed to identify light element (Li, C, N, D) containing phases and to elucidate the structure of intermediates and products during the dehydrogenation process. The pivotal region is between 285-400 °C where the 1,3,5-triazine skeleton of melamine was observed by FTIR to break in association with the release of *ca*. 4.5 wt% H_2. The main purpose of our investigation was therefore to examine whether the breakdown of the triazine ring is a spontaneous or stepwise process synergic with the hydrogen release.

Sample preparation

To enhance scattering contrast on the hydrogen position LiD was purchased from Sigma (98 at.%) while deuterated melamine was synthesized in the laboratory using CaNCN, D_2O and D_2SO_4[1]. In an argon glove box, the phase-pure reactants were weighed into an airtight 50 ml stainless steel jar with ten 10 mm stainless steel balls which was then revolved in the Retsch PM100 planetary mill. The milling conditions used were: 450 RPM for 6 h with a 35:1 ball to powder weight ratio and a milling frequency of 5 min with 30 s rest periods.

Experimental set up

In situ measurements were conducted on the D20 beamline with two batches of as-milled 6LiD : melamine$_d$ samples, which were loaded into quartz tubes in an argon glove box. The measurements were performed with flowing argon and heated from RT to 400 °C. These two batches were measured at $\lambda = 1.36$ and 1.87 Å for approximately 10 h each. The $\lambda = 1.87$ Å experiment was conducted over a step-wise heating programme first from RT to 150 °C, and then measured over 10 min scans at each 5 °C increment. For the $\lambda = 1.36$ Å experiment, data were collected at RT, 150 °C and then in a continuous manner over 3 °C increments with 10 min count times.

Ex situ measurements were conducted on the D2B beamline scanning 4 samples: (1) as-milled materials and (2-4) samples heated to 180, 285 and 400 °C respectively. Each sample was loaded into a vanadium can with indium seal in an argon glove box. Data were collected for 2 h at $\lambda = 1.59$ Å in each case.

Results

Data from *in situ* experiments on D20 with λ = 1.87 and 1.36 Å are compiled in Figure 1. Figure 2 shows the room temperature (blue) and final (red) diffraction patterns for the two experiments. Both room temperature measurements showed no clear trace of the expected starting materials, LiD and melamine$_d$, but rather broad reflections of the product Li_2NCN. Two peaks were identified matching no known Li-N-C-H phases between the Li_2NCN (101) and (110) reflections. By *ca*. 450 K (λ = 1.87 Å) and 430 K (λ = 1.36 Å) the broad reflections observed in the room temperature data sets had narrowed and intensified and the expected weaker reflections from $Li_2(NCN)$ were evident. The data indicated the progressive sintering/crystallisation of $Li_2(NCN)$ over the experimental temperature range.

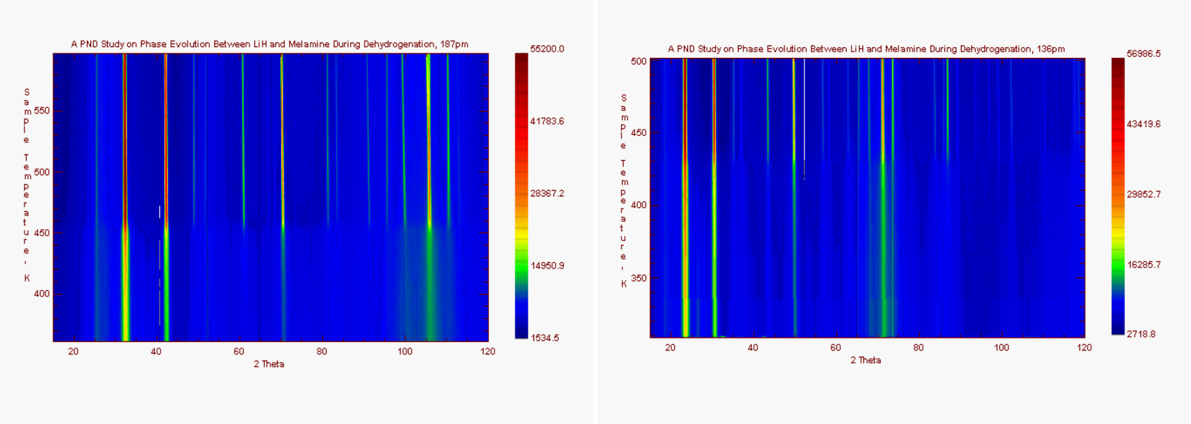

Figure 1. *In situ* neutron diffraction experiments (left λ = 1.87 Å, right λ = 1.36 Å) between 6LiD:melamine$_d$ against sample temperature. Diffraction intensities are colour coded according to the respective colour contour bars legend on the right of each plot.

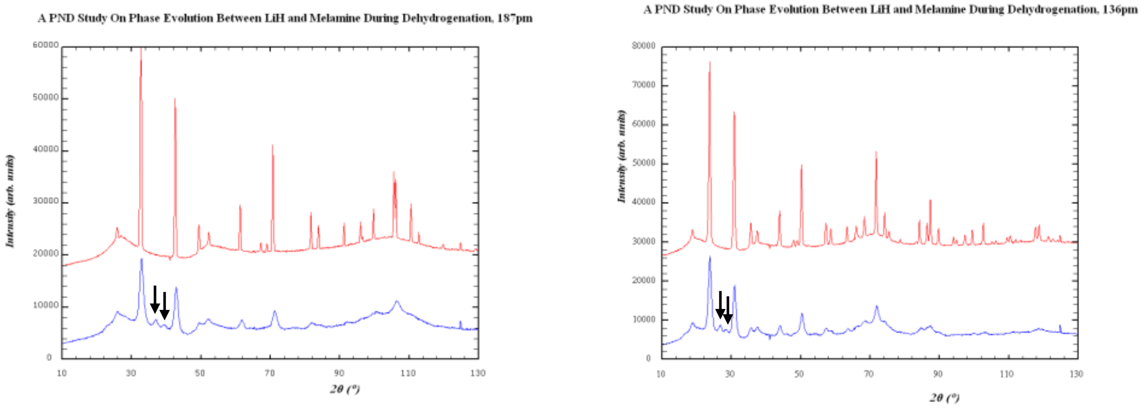

Figure 2. Room temperature and final neutron diffraction patterns (left λ = 1.87 Å, right λ = 1.36 Å) between 6LiD and melamine$_d$. The black arrows point to two unidentified peaks while the remainder originate from Li_2NCN.

The D2B high intensity, *ex situ* data for each of the four temperature points (RT 180, 285 and 400 °C) are displayed in Figure 3. The RT plot shows a typical diffraction pattern from ball milled LiD and melamine$_d$, with broad reflections from nanocrystalline melamine as a result of ball milling; only the most intense reflections (011), (210) and (201) can be identified. LiD, however remains crystalline and the reflections remain narrow and intense. Figure 3b shows the diffraction pattern of 6LiD:melamine$_d$ heated to 180 °C. Melamine reflections diminish and Li_2NCN begins to form. By 285 °C the sample is predominately Li_2NCN. There was no obvious difference between the 285 and 400 °C diffraction patterns to suggest the presence of crystalline intermediate products. Structure refinements performed on the patterns using the Rietveld method provided no indication that the individual phases had changed appreciably (i.e. apart from the expected thermal expansion) over the reaction temperature range.

Through the series of *in situ* and *ex situ* experiments we did not observe any crystalline intermediate phases during the dehydrogenation reaction between LiH and melamine. Specifically, no notable changes were observed between 285 and 400 °C, where FTIR data had indicated that the triazine fractures. Hence, we were unable to deduce whether the breakdown of the triazine ring is indeed relevant to the second hydrogen release step. A combination of spectroscopic methods are currently being employed to study the system further.

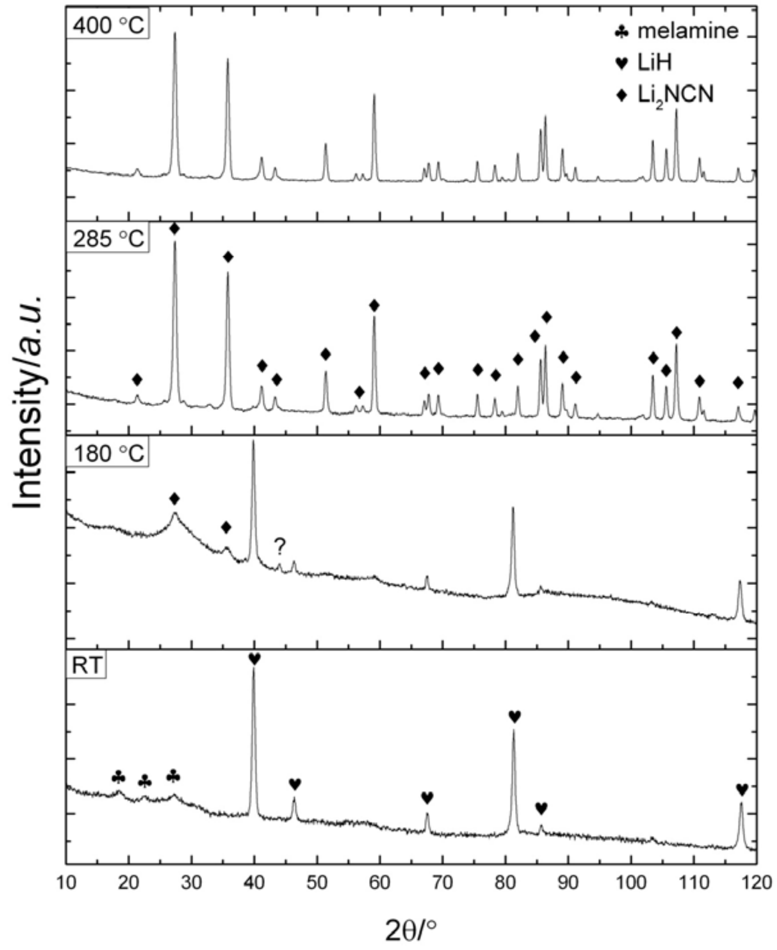

Figure 3. *Ex situ* neutron diffraction experiments for 6LiD:melamine$_d$ heated to 180, 285 and 400 °C.