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A $NaAlH_4$-$Ca(BH_4)_2$ composite system for hydrogen storage

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Mechanochemical treatment (ball-milling) of $NaAlH_4$-$Ca(BH_4)_2$ mixtures leads to partial formation of $NaBH_4$ and $Ca(AlH_4)_2$ by a metathesis reaction. The reaction proceeds to different extents depending on the applied ball-milling times, which is confirmed by powder X-ray diffraction and infrared spectroscopy. Additionally, an *in-situ* synchrotron radiation powder X-ray diffraction study reveals that the metathesis reaction continues due to thermal treatment while the data also supports a two-step decomposition of the formed $Ca(AlH_4)_2$. Finally, the reactive hydride composite system was investigated by mass spectrometry and Sieverts' measurement, which reveal release of ~6 wt% H_2 at $T < 400$ °C.

1. Introduction

An efficient energy storage system, where large amounts of renewable energy can be stored, is generally pursued *e.g.* concentrating solar thermal power plants or as hydrogen [1,2]. An energy storage system can level out the intermittent supply of renewable energy to match our oscillating energy demand and also be used for mobile applications [3–5]. Thus, hydrogen as an energy carrier has been considered for decades now owing to its unique properties *e.g.* the high gravimetric energy density of ~120 kJ/g (lower heating value) [1,3]. The discovery of the reversible $NaAlH_4$-$TiCl_3$ hydrogen storage system led to significantly increased interest in complex metal hydrides [6]. Among them, $Ca(BH_4)_2$, with a gravimetric hydrogen density of $\rho_m = 11.6$ wt%, has been thoroughly studied [7–10]. On the other hand, calcium alanate, $Ca(AlH_4)_2$, $\rho_m = 7.9$ wt%, is a less studied metal alanate [11,12].

A combination of the two well studied compounds, $NaAlH_4$ and $Ca(BH_4)_2$, is the focus of the present investigation. The reactive hydride composite, $NaAlH_4$-$Ca(BH_4)_2$, contains 9.77 wt% of hydrogen and is thus worth attention. Previously, similar composite systems of $NaAlH_4$-$LiBH_4$ and $NaAlH_4$-$Mg(BH_4)_2$ have been investigated with the formation of $NaBH_4$ and $LiAlH_4$ or $Mg(AlH_4)_2$, respectively, as a result [13–15]. Additionally, mechanochemical and solvent mediated synthesis of $Ca(AlH_4)_2$ has been performed from CaH_2 and AlH_3 or $NaAlH_4$ and $CaCl_2$ [11,12,16,17]. However, the formation of salts *e.g.* NaCl decreases the hydrogen capacity of the reactive hydride composite.

In this work, the reactive hydride composite $NaAlH_4$-$Ca(BH_4)_2$ has been studied with the outcome of formation of $Ca(AlH_4)_2$ and $NaBH_4$. The composite has been studied in detail by *in-situ* synchrotron radiation powder X-ray diffraction, Fourier transform infrared spectroscopy and mass spectrometry. The reaction between $NaAlH_4$ and $Ca(BH_4)_2$ is not only mechanically induced but continues during thermal treatment.

2. Experimental

2.1. Sample preparation

$Ca(BH_4)_2$ was synthesized from commercially available CaH_2 (Sigma Aldrich, reagent grade, 95%) and a borane dimethyl sulphide complex (DMS-BH_3, Sigma-Aldrich) which was stirred together for ~2 days at $T = 40$ °C using a similar approach as to synthesize $Sr(BH_4)_2$ [18]. Finally, the solution was dried under vacuum at room temperature (*RT*) on a Schlenk line. The final product was confirmed by powder X-ray diffraction to be α-$Ca(BH_4)_2$.

$NaAlH_4$ (Sigma-Aldrich, Tech. grade) and the as-synthesized

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$Ca(BH_4)_2$ in a 1:1 ratio were treated mechanochemically in the Fritsch Pulverisette 6 in WC vials (80 mL) with WC balls ($d = 8$ mm) under an argon atmosphere with a ball-to-powder mass ratio of 40. The powder was ball-milled for 5 min at 350 rpm followed by a break of 3 min, to prevent sample overheating and possible decomposition of products. The milling program was repeated 12, 36 or 72 times to establish an effective ball-milling time of 1, 3 or 6 h, respectively.

2.2. Powder X-ray diffraction (PXD)

PXD data of as-prepared samples were measured on a Rigaku Smart Lab diffractometer using a Cu source and a convergent beam mirror (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.540593$ Å). Data were collected in the 2θ-range 10°–80° at 2.5°/min using a Rigaku D/tex detector. All samples were mounted in an argon-filled glovebox in 0.5 mm glass capillaries sealed with glue.

2.3. Fourier transform infrared spectroscopy (FT-IR)

All as-milled samples were characterized by infrared absorption spectroscopy using a NICOLET 380 FT-IR spectrometer from Thermo Electron Corporation. Data were measured in the range 4000–400 cm^{-1} and 32 scans with a spectral resolution of 4 cm^{-1} were collected per sample and averaged. The samples were exposed to air for approximately 15 s when transferring the powder from the sample vial to the instrument.

2.4. In-situ synchrotron radiation powder X-ray diffraction (SR-PXD)

In-situ time-resolved SR-PXD data was collected at beamline I11 at Diamond Light Source, Oxford, UK, utilizing a wide-angle position sensitive detector (PSD) based on Mythen-2 Si strip modules, $\lambda = 0.8258$ Å. The powdered sample was packed in a 0.5 mm quartz capillary in an argon-filled glovebox (O_2, $H_2O < 1$ ppm) and rotated during measurement. Additionally, the sample was heated from *RT* to 400 °C ($\Delta T/\Delta t = 10$ °C/min) using a heat blower available at I11 and the temperature of the sample was calibrated using NaCl as a standard [19,20].

2.5. Mass spectrometry

Mass spectrometry (MS) analysis of the evolved gas was performed using a Hiden Analytical HPR-20 QMS sampling system. Approx. 8 mg of sample was loaded in an argon glovebox into a Al_2O_3 crucible and sealed with a Al_2O_3 lid. The samples were heated from 30 to 450 °C ($\Delta T/\Delta t = 5$ °C/min) in an argon flow of 40 mL/min and the evolved gas was analyzed for hydrogen.

2.6. Sieverts' measurement

The samples were desorbed in a stainless steel high-temperature autoclave attached to a custom made Sieverts apparatus [21]. The desorptions were carried out by heating the sample from *RT* to 450 °C ($\Delta T/\Delta t = 3$ °C/min, $p(H_2) = 1$ bar) and keeping it isothermal at 450 °C for 30 min. Subsequently, the sample was naturally cooled to *RT*.

3. Results and discussion

3.1. Powder X-ray diffraction

Fig. 1 shows the PXD patterns of the as-milled $NaAlH_4$-$Ca(BH_4)_2$ samples. In the diffraction pattern of the 1 h ball-milled sample, predominantly both starting reactants are present. However, as the ball-milling time is increased to 3 h, Bragg reflections belonging to $NaBH_4$ appear and they become more significant after 6 h of milling. Meanwhile, the intensity of Bragg reflections from $NaAlH_4$ and, to some extent, $Ca(BH_4)_2$, decreases.

This tendency points towards the following metathesis reaction during mechanochemical treatment:

$$2NaAlH_4\,(s) + Ca(BH_4)_2\,(s) \rightarrow 2NaBH_4\,(s) + Ca(AlH_4)_2\,(s) \quad (1)$$

which is further supported by the absence of Bragg reflections from NaH, CaH_2, CaB_6, and Al in the diffraction patterns. Thus, the complex hydrides, $NaAlH_4$, $NaBH_4$, $Ca(BH_4)_2$ and $Ca(AlH_4)_2$ appear not to decompose during mechanochemical treatment.

Finally, the $Ca(AlH_4)_2$ formed seems to be unstable over time as PXD after 10 months shows the presence of Al, as seen in Fig. S1. Possibly, CaH_2 is present too, however, the most intense Bragg reflections from CaH_2 overlap with the Bragg reflections of $NaAlH_4$ and $NaBH_4$ and it is thus uncertain.

3.2. Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy data is presented in Fig. 2. The data reveals two B···H stretches at 2300 and 2255 cm^{-1} originating from both $Ca(BH_4)_2$ and $NaBH_4$, as the stretching modes overlap, and two Al···H stretches at 1783 and 1674 cm^{-1} assigned to $Ca(AlH_4)_2$ and $NaAlH_4$, respectively [11,22].

Furthermore, B···H bending modes are observed between 1195 and 1075 cm^{-1} while Al···H stretches are present at around 650 cm^{-1}. Interestingly, the ratio between the signal of $Ca(AlH_4)_2$ and $NaAlH_4$ changes in favour of $Ca(AlH_4)_2$ as the ball-milling time is increased. Meanwhile, the intensity of the stretching mode at 2300 cm^{-1} and the bending mode at 1118 cm^{-1}, which are the most intense modes of $NaBH_4$ [22], increases. These observations are in agreement with the evolution of more $NaBH_4$ formed as milling-time is increased as observed in PXD. Hence, reaction **1** occurs to a larger extend as milling time is increased.

3.3. In-situ synchrotron radiation powder X-ray diffraction study

The *in-situ* SR-PXD data of $NaAlH_4$-$Ca(BH_4)_2$ (1 h BM) is

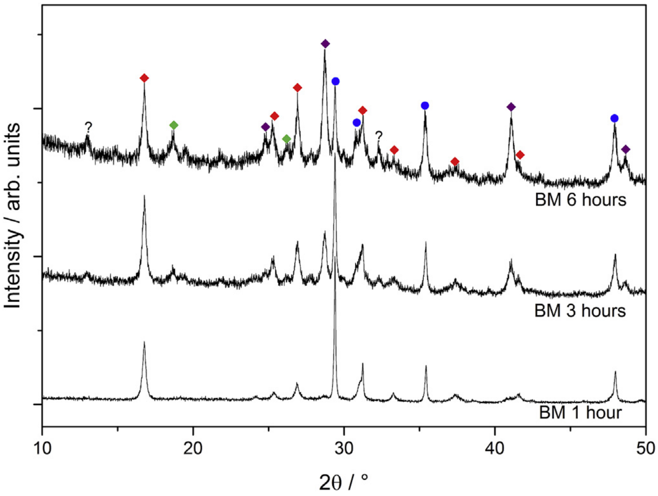

Fig. 1. Powder X-ray diffraction data of the $NaAlH_4$–$Ca(BH_4)_2$ samples after different degrees of mechanochemical treatment ($\lambda = 1.5406$ Å). Markers: Red diamonds: α-$Ca(BH_4)_2$, green diamonds: β-$Ca(BH_4)_2$, purple diamonds: $NaBH_4$, blue spheres: $NaAlH_4$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)