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Synthesis of amorphous manganese borohydride in the (NaBH₄–MnCl₂) system, its hydrogen generation properties and crystalline transformation during solvent extraction

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ABSTRACT

The mixture of (2NaBH₄ + MnCl₂) was ball milled in a magneto-mill. No gas release was detected. The XRD patterns of the ball milled mixture exhibit only the Bragg diffraction peaks of the NaCl-type salt which on the basis of the present X-ray diffraction results and the literature is likely to be a solid solution Na(Cl)_x(BH₄)_(1-x), possessing a cubic NaCl-type crystalline structure. No presence of any crystalline hydride was detected by powder X-ray diffraction which clearly shows that NaBH₄ in the initial mixture must have reacted with MnCl₂ forming a NaCl-type by-product and another hydride that does not exhibit X-ray Bragg diffraction peaks. Mass spectrometry (MS) of gas released from the ball milled mixture during combined MS/thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) experiments, confirms mainly hydrogen (H₂) with a small quantity of diborane gas, B₂H₆. The Fourier transform infra-red (FT-IR) spectrum of the ball milled (2NaBH₄ + MnCl₂) is quite similar to the FT-IR spectrum of crystalline manganese borohydride, c-Mn(BH₄)₂, synthesized by ball milling, which strongly suggests that the amorphous hydride mechano-chemically synthesized during ball milling could be an amorphous manganese borohydride. Remarkably, the process of solvent filtration and extraction at 42 °C, resulted in the transformation of mechano-chemically synthesized amorphous manganese borohydride to a nanostructured, crystalline, c-Mn(BH₄)₂ hydride.

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1. Introduction

Hydrogen (H₂) is perceived as a potential future energy carrier which would eventually lead to the implementation of the world-wide Hydrogen Economy [1–3] for which a hydrogen generation/storage system is an important consideration. For the automotive sector, solid state H₂ storage in hydrides has serious constraints one of which is a full H₂ reversibility which demands “on board” rehydrogenation capability [3]. So far, those very serious constraints preclude a full implementation of solid state H₂ storage in the automotive sector [4].

However, there are a number of other potential market applications for H₂ generation systems, rather than reversible storage, at ambient and slightly elevated temperatures, for which “on board” rehydrogenation is not critical. For example, those solid state H₂ systems can utilize disposable H₂ cartridges of various sizes

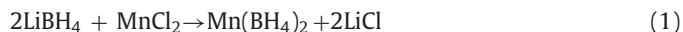
which could be regenerated “off board” after usage. As pointed out in our recent review [4], those novel solid state hydrogen generation systems could be utilized in various capacities in applications such as, stationary auxiliary power systems, off-road vehicles (forklifts, street sweepers etc.), locomotives, submarines, coastal and international shipping, auxiliary devices in air transportation, lawn mowers, disposable cartridges low power military devices (e.g. WFC20 soldier power system: <http://www.ardica.com>), portable electronic devices like smartphones, bulk hydrogen storage and many others.

Our research program is now focused on studying irreversible hydride systems for relatively fast hydrogen generation “on demand” either under mechanical or thermal energy input which could be synthesized in solid state by mechano-chemical activation synthesis (MCAS). For example, we recently reported a rapid release of hydrogen from a (2LiBH₄+FeCl₂) mixture under mechanical energy input through the possible formation/decomposition of amorphous/disordered Fe(BH₄)₂ [5]. In turn, a similar (2LiBH₄ + MnCl₂) system generates H₂ under thermal energy input (ther-

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molysis) at reasonably low temperatures through the formation and subsequent thermolysis of crystalline $\text{Mn}(\text{BH}_4)_2$ [6–12]. So far, crystalline $\text{Mn}(\text{BH}_4)_2$ has been synthesized by MCAS during ball milling as a result of a solid state metathesis reaction between 2LiBH_4 and MnCl_2 [6–9] according to



Mass spectrometry of gas desorbed during thermolysis of crystalline $\text{Mn}(\text{BH}_4)_2$ in reaction (1), combined with thermogravimetric analysis, showed the presence of varying quantities of diborane gas (B_2H_6) mixed with hydrogen gas [10,11].

However, only a handful of studies have used another alkaline metal borohydride, such as NaBH_4 , in the mechano-chemical synthesis of $\text{Mn}(\text{BH}_4)_2$ [13–17]. In general, NaBH_4 is a much cheaper chemical compound than its counterpart, LiBH_4 , which is an important economical factor. Severa et al. [13] claimed that regardless of the LiBH_4 or NaBH_4 precursor used, all the Mn borohydride complexes synthesized by both mechano-chemical activation synthesis (MCAS) and solvent synthesis were amorphous and could not be detected by X-ray diffraction. Their conclusion is in apparent disagreement with the results reported in Refs. [6–12] which all support a formation of crystalline $\text{Mn}(\text{BH}_4)_2$ when the LiBH_4 precursor was used. Severa et al. [13] also claimed that mechano-chemical synthesis of LiBH_4 with MnCl_2 produced amorphous $\text{Mn}(\text{BH}_4)_2$ whereas the usage of the NaBH_4 precursor supposedly produced a different species, mainly, amorphous $\text{Na}_2\text{Mn}(\text{BH}_4)_4$ or $\text{NaMn}_2(\text{BH}_4)_5$. Llamas-Jansa et al. [14] reported a formation of $\text{Na}(\text{BH}_4)_{1-x}\text{Cl}_x$ solid solutions possessing a cubic NaCl-type structure when a mixture of ($3\text{NaBH}_4 + \text{MnCl}_2$) was ball milled in a Fritsch Pulverisette planetary mono-mill.

Nakamori et al. [15,16] reported that when NaBH_4 was used in reaction (1) then only the NaCl peaks were present. This peculiar observation was interpreted by Nakamori et al. as evidence of the “disordering” (or alternatively amorphization) of the crystal structure of $\text{Mn}(\text{BH}_4)_2$ in which there is no long-range order of the Mn^{2+} and $(\text{BH}_4)^-$ units forming a proper crystalline structure but a short-range order still exists. Nakamori et al. [15,16] concluded that reaction (1) with LiBH_4 occurred easier producing crystalline $\text{Mn}(\text{BH}_4)_2$ than the same reaction with NaBH_4 , owing to the similar ionic radii of Li^+ (0.076 nm) and Mn^{2+} (0.067 nm) in solid–solid cation exchange reaction (1) as compared to a larger ionic radius of Na^+ (0.102 nm). Very recently, Guda et al. [17] used NaBH_4 with MnCl_2 to synthesize $\text{Mn}(\text{BH}_4)_2$ by ball milling. They reported that the final product contained crystalline $\text{Mn}(\text{BH}_4)_2$ and about 5 wt% of NaBH_4 . This result is rather surprising since they did not report the presence of NaCl which is a commonly observed by-product of the metathesis reaction between NaBH_4 and MnCl_2 (reaction (1) with NaBH_4).

It is clear that there is still a great controversy about the nature of species produced by MCAS when the NaBH_4 precursor/reactant is used in the mixture with MnCl_2 in reaction (1). Therefore, the scientific objective of the present study is to investigate the microstructure of the ($2\text{NaBH}_4 + \text{MnCl}_2$) mixture processed by ball milling and its hydrogen generation behavior. Furthermore, for the first time the results of the solvent extraction/filtration of $\text{Mn}(\text{BH}_4)_2$ from a mixture with a NaCl-type salt will be presented and discussed. One of the most remarkable results in this work, is the crystallization of likely amorphous $\text{Mn}(\text{BH}_4)_2$ produced after MCAS, during the subsequent filtration/extraction process which has never been reported before.

2. Experimental

Sodium borohydride (NaBH_4) and manganese chloride (MnCl_2) purchased from Alfa Aesar Canada having purity of 98% and 99.99%, respectively, were mixed in the 2:1 molar ratio. Ball

milling of the mixture was carried out for 0.5, 1 and 5 h in ultra-high purity hydrogen gas atmosphere (purity 99.999%; $\text{O}_2 < 2$ ppm, $\text{H}_2\text{O} < 3$ ppm, $\text{CO}_2 < 1$ ppm, $\text{N}_2 < 6$ ppm, $\text{CO} < 1$ ppm, $\text{THC} < 1$ ppm) at ~ 450 kPa pressure in the magneto-mill, Uni-Ball-Mill 5 [3,18–20] purchased from A.O.C. Scientific Engineering Pty Ltd., Australia. The strong impact mode (IMP68) with two magnets positioned at 6 and 8 o'clock, at the distance from the vial of ~ 10 and ~ 2 mm, respectively was used in the milling process. The powder mixture was loaded into an air-tight milling vial with an O-ring and equipped with a pressure valve mounted on the lid. Four hardened steel balls were placed in the vial with the ball-to-powder weight ratio (R) of 132 and the rotational speed of milling vial of ~ 200 rpm. The vial was continuously cooled by an air fan during milling process. The possible release of hydrogen during ball milling was continuously monitored by the pressure increase in the milling vial measured by a pressure gage (the accuracy ± 0.1 wt% H_2).

In order to avoid reactions between the powder samples and moisture or oxygen from air, all processes during preparation of the samples were handled in a glove box containing moisture-absorbing Drierite granulated compound. Before handling, the glove box was purged a few times with high purity argon gas (99.999% purity) in order to minimize any possible contamination by moisture or oxygen from air.

Fig. 1 shows a schematic of a very simple solvent filtration/extraction method performed in this work. The ball milled ($2\text{NaBH}_4 + \text{MnCl}_2$) powder was mixed with diethyl ether (Et_2O) with the mass ratio of 1:4 and subsequently stirred for 2 h at room temperature (RT) with a rotational speed of 225 rpm in order to dissolve the newly formed $\text{Mn}(\text{BH}_4)_2$ in the Et_2O solvent and separate it from NaCl. The suspension after stirring was injected into a 60 mL syringe and filtered with a $0.2 \mu\text{m}$ syringe filter. The filtering was done to collect NaCl at the filter and allow suspended $\text{Mn}(\text{BH}_4)_2$ to pass through the filter. In order to extract $\text{Mn}(\text{BH}_4)_2$ from the suspension in Et_2O , an evaporation process of the suspension after filtering was carried out on a hot plate at a temperature of 42°C for 20 min, accompanied by a simultaneous vigorous stirring at 1000 rpm to agitate the solution. Unfortunately, the average yield of the process in Fig. 1 was only about 4.4% and was further modified. This will be described in a separate paper.

A sample of the powder after evaporation was characterized by XRD and other techniques. The solvent extraction procedure was carried out entirely in the glove box that was purged and subsequently filled up with high purity argon gas (99.999% purity).

The thermal gas desorption was evaluated by means of a second generation volumetric Sieverts-type apparatus [3,21] custom-built by A.O.C. Scientific Engineering Pty Ltd., Australia. This apparatus, built entirely of 316 austenitic stainless steel, allows loading a powder sample into a stainless steel reactor in a glove box under high purity argon and its subsequent transfer to the main unit in a sealed reactor without any exposure to the environment. Samples with nearly constant masses of 30–40 mg were used in a desorption test. Before starting the desorption test, the inner tubing of the apparatus was evacuated and purged four times with ultra-high purity hydrogen. The furnace of the apparatus was heated separately to the desired test temperature and subsequently inserted onto a tightly sealed powder sample reactor inside which an atmospheric pressure of 1 bar H_2 was kept. The powder sample in the reactor usually reaches the furnace temperature within ~ 400 s in the temperature range of 100 – 200°C which is negligible compared to desorption completion time. Hence, the test can be considered as isothermal. Desorption curves were corrected for the hydrogen gas expansion due to increase in temperature. The amount of desorbed hydrogen was calculated from the ideal gas law as described in detail in [3] and expressed in wt% with respect to the total weight of powder sample. The calibrated

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