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Hydrogen storage properties of γ -Mg(BH₄)₂ modified by MoO₃ and TiO₂

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ABSTRACT

The reversible hydrogen desorption–absorption of γ -Mg(BH₄)₂ ball milled with MoO₃ and TiO₂ has been investigated. No mechanochemical interaction between γ -Mg(BH₄)₂ and TiO₂ was observed while for the 1:1 M ratio with MoO₃, MoB₂ was formed. There was little difference in the properties of γ -Mg(BH₄)₂ and γ -Mg(BH₄)₂ ball-milled with 0.02 mol percent TiO₂ and MoO₃. However, mixing in the same ratio γ -Mg(BH₄)₂ with TiO₂ and MoO₃ that had previously been subjected to high energy milling provided significant effects. For these materials, the DSC peaks appeared broader and were shifted to slightly lower temperatures, while the TPD peaks were decreased by ca. 20 °C, as compared to the pure γ -Mg(BH₄)₂. Faster hydrogen desorption kinetics was observed for the γ -Mg(BH₄)₂-MoO₃ mixture. The reversible hydrogen storage capacity of γ -Mg(BH₄)₂-TiO₂ at 271 °C was found to be 2.4 wt% H₂ in the first cycle.

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Introduction

Magnesium borohydride is one of the most promising hydrogen storage materials though its kinetics and reversibility are still important challenges for the material's use in practical applications [1,2]. The decomposition of Mg(BH₄)₂ occurs via several stages [3–7], and different magnesium polyboranes appear depending on the process conditions. The most stable intermediate observed is magnesium

dodecaborane (MgB₁₂H₁₂), which eventually transforms into MgB₂. The geometrical similarity of the boron icosahedral framework in MgB₁₂H₁₂ and that of bulk boron can be a reason for the kinetic stability of MgB₁₂H₁₂ [8] which may hamper the rehydrogenation to Mg(BH₄)₂. The synthesis of Mg(BH₄)₂ from lower polyboranes might be possible at reasonable hydrogen pressure and temperature [9].

An additive that prevents the dodecaborane formation may be one route to improve the reversibility of Mg(BH₄)₂ dehydrogenation. Therefore development of effective

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materials for the improved decomposition/formation of $\text{Mg}(\text{BH}_4)_2$ is one of the most important problems to solve before its practical application. High valence transition metal carbides, nitrides, oxides or halides have the ability to form bonds with hydrogen in varying stoichiometries. This encourages the fast dissociation into atomic hydrogen or its recombination to hydrogen molecules [10]. Thus the influence of transition metal oxides (TMOs) for the promotion of a reversible hydrogen reaction is important to study. MoO_3 has been suggested as a potential anti-microbial agent, e.g. in polymers, and in contact with water it forms H^+ ions [11]. TiO_2 has potential for use in energy production as a photocatalyst [12]. Recently, the sorption properties of a LiH-MgB_2 composite were considerably improved by adding TiO_2 [13]. Moreover its reversible hydrogen storage capacity during five sorption cycles was found to be reasonably stable (~ 8 wt% of H_2). In NaBH_4 , the addition of Ti-based compounds significantly decreased the onset decomposition temperature of the borohydride through the formation of Na-Ti-based intermediate phases [14]. In recent reports [15,16] $\gamma\text{-Mg}(\text{BH}_4)_2$ was milled with a variety of Ni- and Co- based additives. The results suggest that re-absorption leads to the formation of $\beta\text{-Mg}(\text{BH}_4)_2$ with reversible hydrogen storage capacity of ca. 2 wt% of H_2 in the first cycle. With further cycling the reversible hydrogen capacity decreases with an increase in the amount of nano-crystalline MgO and unidentified boron-hydrogen compounds. In the present paper, MoO_3 and TiO_2 are studied as possible candidates to improve the reversible hydrogen sorption in $\gamma\text{-Mg}(\text{BH}_4)_2$.

Experimental methods

Commercial $\gamma\text{-Mg}(\text{BH}_4)_2$ ($\geq 95\%$, Sigma Aldrich), MoO_3 (99.5%, Sigma Aldrich) and TiO_2 (99.9%, Sigma Aldrich) were used to prepare $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TMO}$ (TMO = $\text{MoO}_3, \text{TiO}_2$) mixtures in molar ratios of 1:0.02, 1:0.1 and 1:1. High energy milling was performed using a Spex 8000 D Mixer Mill. As-received $\gamma\text{-Mg}(\text{BH}_4)_2$ and mixtures of $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TMO}$ were high-energy milled for 5 h. MoO_3 and TiO_2 were pre-milled for 25 h. In addition, the as-received $\gamma\text{-Mg}(\text{BH}_4)_2$ was mixed with high-energy milled MoO_3 and TiO_2 powders in the ratio of 1:0.02 followed by 1 h of ball milling with a planetary micro mill (Fritsch Pulverisette 7) at a speed of ~ 300 rpm. Stainless steel balls with 10 mm diameter, with a ball-to-powder ratio of 40:1, were used. All handling and preparation of the samples took place in a MBRAUN Unilab glove box with continuously purified argon atmosphere where oxygen and moisture values were always kept below 1 ppm.

Powder X-ray diffraction (PXRD) patterns were collected in transmission mode using Cu K_α radiation (1.5418 Å) in a Bruker AXS D8 Advance diffractometer equipped with a Göbel mirror and LynxEye™ 1D strip detector. The samples were encapsulated in glass capillaries (o.d. = 0.8 mm) sealed with water-free glue in the glove box. Data acquisition was performed with a step size of 0.02° and 2s/step measurement time in the 2θ range of $5\text{--}65^\circ$. The Bruker-AXS software EVA [17] coupled with the PDF-4 structure database was used for phase identification.

Scanning Electron Microscopy (SEM) experiments were performed with a Hitachi S-4800 electron microscope operated at 6.0 kV. Commercial TiO_2 powder was deposited on a sticky carbon tape while high-energy milled TiO_2 powder was introduced in a copper grid. All samples were carbon-coated to reduce charging. SEM micrographs were taken using the backscattered electron detector.

Temperature-programmed desorption (TPD) coupled with a residual gas analyzer (RGA, MKS Microvision-IP) was used to study the gas release from the samples during thermal decomposition. The samples were introduced inside a stainless steel sample holder, and the gas desorption was analyzed under vacuum ($\sim 10^{-4}$ mbar) during a programmed heating rate of $2^\circ\text{C}/\text{min}$ from room temperature (RT) to 500°C .

Simultaneous TG/DSC experiments were conducted under flowing Argon gas (flow: 50 ml/min) in a Netzsch STA 449 F3 Jupiter instrument between RT and 500°C with a heating rate of $2^\circ\text{C}/\text{min}$. Samples were contained in Al crucibles fitted with pierced lids. The data were baseline corrected using two empty Al pans in the reference and sample position which were heated under identical conditions.

Hydrogen absorption and desorption measurements were carried out for selected samples in an in-house built Sieverts type apparatus. Hydrogen desorption of the $\gamma\text{-Mg}(\text{BH}_4)_2\text{-MoO}_3$ with pre-milled MoO_3 in the molar ratio of 1:0.02 and pure $\gamma\text{-Mg}(\text{BH}_4)_2$ was carried out under vacuum ($\sim 10^{-5}$ mbar) at 267°C . The $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TiO}_2$ mixture with pre-milled TiO_2 in the molar ratio of 1:0.02 was dehydrogenated under vacuum ($\sim 10^{-5}$ mbar) and then hydrogenated under 140 bar of hydrogen pressure at 271°C in a stainless steel sample holder.

^{11}B solid state NMR experiments were performed at 11.7 T on a Bruker Avance III spectrometer using a 4.0 mm double resonance MAS probe head at room temperature. The MAS rate was 14.5 kHz and the spectra were obtained using 256 scans, with 1 s recycle delay, and 1 μs long pulses. The ^{11}B chemical shifts were referred to $\text{F}_3\text{B}\cdot\text{O}(\text{CH}_2\text{CH}_3)_2$ (0 ppm) via the substitution method [18].

Results and discussions

Synthesis and characterization of the $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TMO}$ mixtures

Some thermodynamic and structural properties of MoO_3 and TiO_2 [19] are summarized in Table 1. The melting temperatures and standard enthalpies of formation indicate that TiO_2 is more stable than MoO_3 . This could be attributed to the 3D network structure of TiO_2 compared to the layered structure of MoO_3 .

Fig. 1 shows the PXRD data of the 5 h high-energy milled $\gamma\text{-Mg}(\text{BH}_4)_2$ and $\gamma\text{-Mg}(\text{BH}_4)_2\text{-TMO}$ mixtures in different molar ratios as well as the commercial oxides. The as-received $\gamma\text{-Mg}(\text{BH}_4)_2$ was crystalline, and its PXRD pattern is in good agreement with previously reported structural data [20,21]. The PXRD data show that during the high energy milling $\gamma\text{-Mg}(\text{BH}_4)_2$ becomes amorphous (in agreement with [22]), and only diffraction peaks of the added oxides are visible. However, these latter peaks are much broader compared to the

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