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Magnesium alanate—a material for reversible hydrogen storage?

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Abstract

Magnesium alanate was synthesized in a metathesis reaction of magnesium chloride and sodium alanate followed by purification. The material obtained was sufficiently pure and it was investigated by X-ray diffraction (XRD) and by thermogravimetry (TG) and mass spectrometry (MS) of the evolved gas, respectively. Thermal analysis showed a decomposition with a release of hydrogen proceeding in two major steps. Measured in vacuum, the peak decomposition temperature of the first step was found to be 163 °C and the residue at 200 °C consisted of MgH_2 and Al which continues to release hydrogen and transforms into an Al_3Mg_2/Al mixture at higher temperatures. In the first decomposition step 6.6 wt.% of hydrogen was released. To enhance the kinetics of the decomposition, magnesium alanate was doped with a titanium based promoter and ball milled for up to 100 min, resulting in a significantly reduced peak decomposition temperature. First results on determining thermodynamic properties indicate equilibrium desorption pressures in the range of AB_5 compounds. In total, the promising properties determined so far have inspired further investigations on the thermodynamics, kinetics and reabsorption properties of the compound.

Keywords: Metal hydrides; Hydrogen absorbing materials; Earth alkali aluminium hydrides; X-ray diffraction; Thermal analysis

1. Introduction

Mobile applications in combination with hydrogen fuel cell systems require sustainable storage materials which contain large amounts of hydrogen. Furthermore, low decomposition temperatures and fast kinetics for absorption and desorption of hydrogen are required. Stimulated by the work of Bogdanovic et al. [1], researchers investigated the reversible properties of sodium and lithium alanates (e.g. [2–6]). While the hydrogen content of these compounds is high and desorption kinetics seems to be promising, the absorption kinetics still has to be improved. Consequently, the search continues for new materials with a high hydrogen content and sufficiently fast reaction kinetics of absorption and desorption at moderate temperatures.

In this contribution we present some of our results on the synthesis, structure, and thermal properties of magnesium alanate, $Mg(AlH_4)_2$, which contains 9.3 wt.% of hydrogen. The compound has promising desorption properties and could meet at least some of the requirements listed above.

2. Experimental

The solids were handled in an argon-filled glove box equipped with a recirculation system to keep the water and oxygen concentrations below 1 ppm during operation. The synthesis was carried out on the bench under a vacuum or in inert gas (N_2) using Schlenk tube techniques.

The solvents were distilled over sodium before use. Sodium alanate (purum, Sigma-Aldrich) was used in a 1 M THF solution as received. Solvent-free $NaAlH_4$ was obtained by drawing the THF off under a vacuum and heating the dry white solid to 50 °C until a residual pressure of 2×10^{-3} mbar was reached. Magnesium chloride (98%, Sigma-Aldrich) was used as received. Additionally promoted samples were prepared by doping $Mg(AlH_4)_2$ with 2 mol% $TiCl_3$ (99.999%, Sigma-Aldrich) and milled in a SPEX® 8000 ball mill with a ball to powder weight ratio of about 10:1.

The powder X-ray diffraction measurements were per-

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formed with a PHILIPS X'PERT diffractometer (Cu Kα radiation, 2 kW, with X'Celerator RTMS detector, automatic divergence slit). The powder was wetted with mineral oil, and the slurry was spread and measured on a Si single crystal. For data acquisition and evaluation, the X'PERT 1.3e and ProFit 1.0c software were used.

Thermal decomposition of magnesium alanate at ambient pressure was performed in a N_2 (5.0) stream in a JUWE IR 05 combustion/reduction furnace equipped with a radiant heating system.

Thermogravimetric analysis was conducted under a vacuum between room temperature and 400 °C at a heating rate of 2 K/min using a NETZSCH STA 409C analyser equipped with a BALZERS quadrupole mass spectrometer for analysis of the evolved gas. During the measurement, the m/z intensities between 1 and 80 were recorded as a function of time. Typical sample quantities were 5–10 mg.

Elemental analysis of carbon and hydrogen was performed by using a CE Instruments Flash EA 1112 Series analyser with helium as purge gas. The sample quantity typically was 4–6 mg. Benzoic acid and a standardized $LiAlH_4$ were used as standards for calibration.

3. Results

3.1. Synthesis of $Mg(AlH_4)_2$

The synthesis of magnesium alanate was performed via a metathesis reaction between sodium alanate and magnesium chloride as proposed earlier in the literature by Wiberg and Bauer [7]:

$$2NaAlH_4 + MgCl_2 \rightarrow Mg(AlH_4)_2 \cdot Et_2O + 2NaCl/\text{in}\ Et_2O \quad (1)$$

$$Mg(AlH_4)_2 \cdot Et_2O \xrightarrow{\Delta} Mg(AlH_4)_2 + Et_2O\uparrow \quad (2)$$

During the process, the solvent adduct precipitates first. It must be separated from the coprecipitated NaCl by an extraction procedure and dried in order for the pure substance to be obtained. The synthesis and structures of two solvent adducts as well as the solvent-free magnesium alanate are described in detail elsewhere [8]. The yield of the end product was 81%. According to the elemental analysis, it contained 9.02±0.08 wt.% H and 2.3±0.2 wt.% C (theoretical: 9.34 wt.% H). The residual content of NaCl, determined by the Mohr method, was 1.7 wt.%. Taking into account the impurities of sodium chloride and the residual ether, the content of $Mg(AlH_4)_2$ in the final product turned out to be 95%.

4. Structure

The end product of the reaction described in Section 3.1 was investigated by X-ray powder diffractometry. The signal pattern of magnesium alanate in Fig. 1 exhibits a structure of relatively high symmetry which is produced from the less symmetric ether adduct [8]. We simulated a congruent XRD pattern by utilizing calculated spatial positions of the atoms. The positions were obtained from an ab initio DFT calculation of the structure in the solid state. According to the calculations, which were also supported by FTIR measurements, magnesium alanate crystallizes in a trigonal structure, space group $P\bar{3}m1$, consisting of corner sharing MgH_6 octahedrons and AlH_4 tetrahedrons. A detailed description of the method and the structure of the magnesium alanate is in preparation [9].

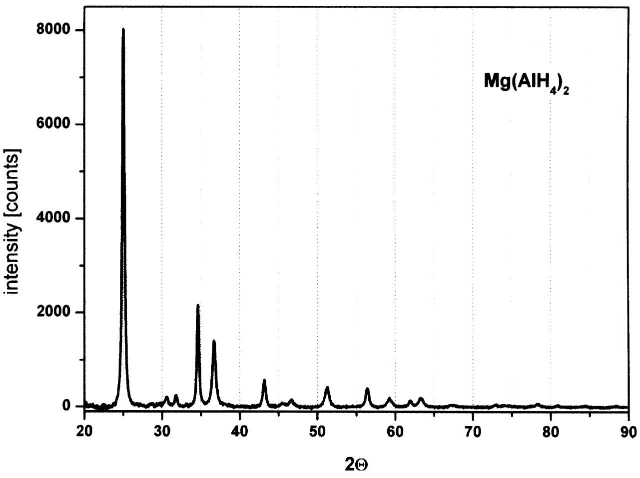

Fig. 1. X-ray powder diffractogram of $Mg(AlH_4)_2$.

A peak shape analysis of the X-ray reflections of the final product indicated that the magnesium alanate produced in this way is a nanocrystalline material with a volume-weighted mean grain size of 30 nm. The structure probably breaks during the drying procedure, as it is likely that high internal stresses are induced into the structure during the thermal release of the diethylether formerly bound.

4.1. Thermal decomposition

For evaluation of the thermogravimetric measurements, the sample mass at $T = 100$ °C was taken as the 100% starting value. As can be seen from the TG/MS data in Fig. 2, decomposition started approximately at 110 °C as indicated by a rise in the signal at $m/z = 2$ (H_2^+). However, detailed analysis of the H_2^+ intensity revealed an exponential rise of its slope with an increase in intensity by a factor of 10 between 50 °C and 120 °C. It was also observed that the alanate lost 0.5 wt.% hydrogen when it was kept in the glove box at room temperature for 4 months.

Fig. 2 indicates that there were two contributions to the signal at 132 °C and 163 °C in the first major decomposition step. Repeated measurements with different samples obtained by different preparation methods showed that the relative amounts of the two components of the signal

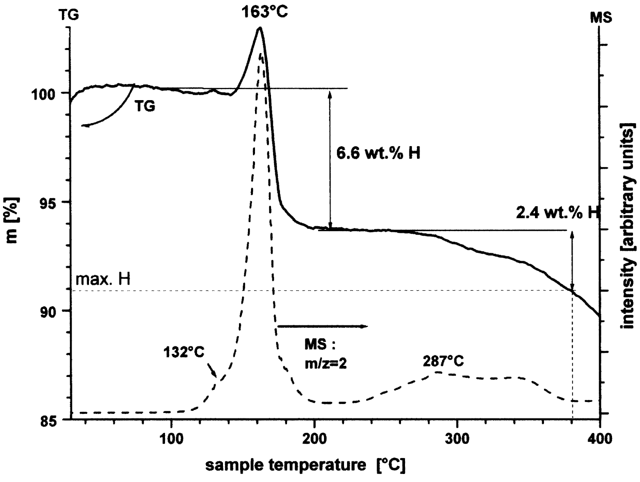

Fig. 2. TG/MS data of the thermal decomposition of $Mg(AlH_4)_2$.

varied while their positions remained stable within a few degrees centigrade. The apparent rise in the TG curve at around 160 °C was caused by the repulsion of the sample holder, which is induced by the high hydrogen production rate at these temperatures. Hence, the highest intensity of the MS signal was found together with the maximum repulsion at the same temperature. The first event at 132 °C appeared as a small bump in the TG curve. After peaking at 163 °C, the TG curve declined to a value of 93.4 mass %, which was reached at approximately 200 °C. This completed the first major decomposition step. A third component of the mass signal at 180 °C was not always reproducible. In the first step, the sample lost 6.6 wt.%, which was attributable almost exclusively to hydrogen. As the sample contained 9.0 wt.% hydrogen before the measurement, 73.3%, i.e., about three quarters of the total stored hydrogen within the experimental error, was released.

An X-ray powder diffractogram of magnesium alanate treated for 30 min in an inert N_2 stream at 200 °C is shown in Fig. 3. The signals in the pattern could be assigned to MgH_2 and Al, the products of the first decomposition step. The small peak at $2\theta = 31.6°$ was attributed to the most intense reflection of NaCl, which was present as an impurity.

Further heating lead to the decomposition of MgH_2 and the production of hydrogen gas in two steps at 287 °C and 345 °C. At 400 °C, the hydrogen was released completely and the sample decomposed. According to the TG curve, the loss of mass between 200 °C and 400 °C was 2.4 wt.%, which is about one quarter of the total amount of the stored hydrogen.

Fig. 4 shows an X-ray diffraction pattern of a sample which has been heated at a temperature of 400 °C for 30 min. The signals in the pattern can be attributed to a mixture of Al and Al_3Mg_2 (and NaCl). A diffractogram of another sample, which has been treated in N_2 at 300 °C, includes additional MgH_2 signals.

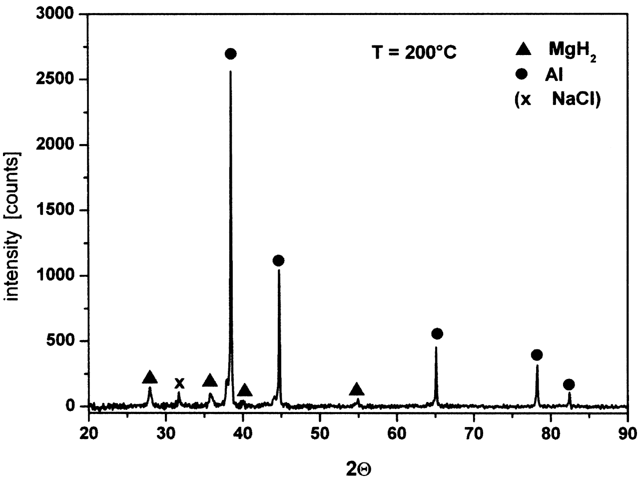

Fig. 3. X-ray powder diffractogram of $Mg(AlH_4)_2$ treated in N_2 at 200 °C for 30 min.

These observations support a decomposition mechanism similar to the one observed for alkali alanates, which is in agreement with the observations made by Claudy et al. [10]. Accordingly, the following transition occurs in the first step of the decomposition (110–200 °C):

$$Mg(AlH_4)_2 \rightarrow MgH_2 + 2Al + 3H_2 \tag{3}$$

The second step (240–380 °C, decomposition of magnesium hydride) proceeds as follows:

$$MgH_2 \rightarrow Mg + H_2 \tag{4}$$

At temperatures around 400 °C an intermetallic compound is formed consisting of the precipitated aluminum from step 1 and the magnesium from step 2:

$$2Al + Mg \rightarrow \tfrac{1}{2}Al_3Mg_2 + \tfrac{1}{2}Al \tag{5}$$

Although there are apparent similarities in the decomposi-

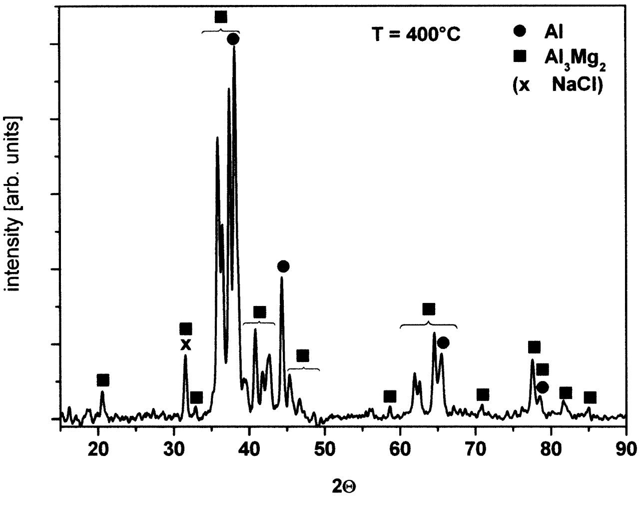

Fig. 4. X-ray powder diffractogram of $Mg(AlH_4)_2$ treated in N_2 at 400 °C for 30 min.

tion behaviour of magnesium alanate and the alkali alanates, there are differences as well. According to the well reproduced data obtained so far by TG, DSC, XRD and volumetric measurements, the first decomposition step (3) seems to be a transition from the alanate directly to the metal hydride MgH_2. This is different compared to the decomposition mechanism of $LiAlH_4$ and $NaAlH_4$ [11,12], where the analogous transition is known to be a two-step procedure: The alkali alanates decompose first to M_3AlH_6 (M = Li, Na), a relatively stable intermediate with a cryolithe structure, and then to the alkali hydride and aluminum. Nevertheless, it might be that there are one or more intermediates in the transition of $Mg(AlH_4)_2 \rightarrow MgH_2$ which were not resolved by our methods. It is therefore intended to make more detailed investigations in the region of decomposition, e.g. by temperature programmed diffraction measurements.

Another difference in the decomposition mechanisms is the formation of a stable intermetallic compound (Al_3Mg_2) in the last step (5) which obviously does not occur with the alkali alanates because of the positive formation enthalpies of the respective compound.

To enhance the kinetics of the dehydrogenation of $Mg(AlH_4)_2$ we doped the sample with 2 mol% of $TiCl_3$ and reduced the grain size of the compound by high energy ball milling for up to 100 min. Fig. 5 shows the peak temperature of the MS signal and the mass loss of the first decomposition step in magnesium alanate for the unmilled, pure sample and for three different milling times of 10, 30 and 100 min, respectively. While the starting point of hydrogen release could be clearly shifted to lower temperatures by milling the doped magnesium alanate samples, the completion of the first decomposition step still was observed to be at around 200 °C, i.e., not all of the hydrogen was released at lower temperatures, which, however, may not necessarily be a mechanistic effect. Moreover, it is also conceivable that the broad signal was due to inhomogeneities in the sample, caused by the short milling times.

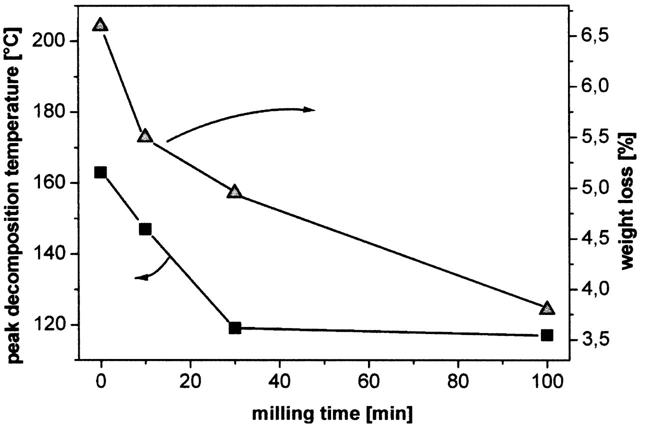

Fig. 5. Peak decomposition temperature and mass loss by H_2 of the first decomposition step of unmilled $Mg(AlH_4)_2$ and $Mg(AlH_4)_2$ doped with 2 mol% $TiCl_3$ for 3 different milling times.

The reduced hydrogen release with increasing milling times is based on the fact that $TiCl_3$ may be reduced by the alanate under consumption of hydrogen and that ball milling provides sufficient mechanical and thermal energy to release a significant part of the stored hydrogen during the milling process.

5. Conclusion and outlook

The results show that $Mg(AlH_4)_2$ exhibits some promising features as a hydrogen storage material. Due to its high hydrogen content of 9.3 wt.%, a maximum reversible content of 7 wt.% may be expected if reaction (3) can be made reversible. Another interesting aspect is the nanocrystallinity of the material when it is synthesized as described above. This seems to be a good starting point, as it has already been observed that the kinetic barriers in nanocrystalline hydrides should be low compared to coarse-grained materials [2]. The peak decomposition temperature of the unmilled magnesium alanate in vacuum is 163 °C, which is in the range of the values for alkali alanates. By adding a $TiCl_3$ promoter and ball milling the samples the peak temperature could be reduced by up to 45 °C, however accompanied by a reduced hydrogen release. Finally, it may be of interest that the substance has a sustainable composition of elements, which is an important issue only for mass applications.

Although the properties investigated so far are promising for mobile applications, some important issues still have to be explored. These include the thermodynamic properties of the substance as well as the kinetics of hydrogen absorption and release. The formation of stable MgH_2 as an intermediate or Al_3Mg_2 as an end product might negatively influence the reabsorption of hydrogen when starting from the respective dehydrogenated state of the material.

The high desorption pressures in the range of AB_5 compounds make the material on one hand promising as a low temperature hydride. On the other hand, to avoid very high loading pressures, this would require reabsorption at low temperatures which might lead to an unfavorable kinetic behaviour.

One focus of our future work will therefore be the investigation of the reabsorption properties of the material, which can be accomplished when equilibrium desorption pressures for different temperatures have been determined.

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