

The use of complex metal hydrides as hydrogen storage materials: Synthesis and XRD-studies of $\text{Ca}(\text{AlH}_4)_2$ and $\text{Mg}(\text{AlH}_4)_2$

M. Schwarz^a, A. Haiduc^a, H. Stil^{a,*}, P. Paulus^b, H. Geerlings^a

^a Shell Global Solutions International B.V., P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

^b Shell International Chemicals B.V., 1030 BN Amsterdam, The Netherlands

Received 2 June 2004; received in revised form 14 December 2004; accepted 20 December 2004

Available online 18 July 2005

Abstract

Different methods of synthesis and purification for the tetrahydrofuran (THF) adduct of calcium aluminum hydride – $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ (x = various amounts/not quantified) – are presented. The highly exothermic reaction of AlCl_3 and CaH_2 in THF and subsequent purification based on filtration leads to the formation of the THF-adduct of $\text{Ca}(\text{AlH}_4)_2$. The compound synthesized by the stabilization of AlH_3 THF using CaH_2 showed a different morphology from the former as proved by XRD. Decomposition of the material due to the release of coordinated THF and hydrogen produces CaH_2 and Al as verified by XRD. Likewise, the Et_2O -adduct of $\text{Mg}(\text{AlH}_4)_2$ showed, depending on the synthesis method, a similar morphological behavior as demonstrated by XRD. The amount of stabilizing ether molecules incorporated in the materials determines the structure and therefore the stability against decomposition.

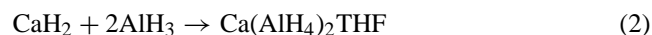
© 2005 Elsevier B.V. All rights reserved.

Keywords: Hydrogen storage materials; X-ray diffraction; Alanates; Amorphous materials

1. Introduction

A challenge for the scientific community is to design alternative lightweight hydrogen storage materials enabling sustainable solutions for mass mobility. Complex metal hydrides as $\text{M}^{\text{I}}\text{AlH}_4$ or $\text{M}^{\text{II}}(\text{AlH}_4)_2$ ($\text{M}^{\text{I}} = \text{Li, Na, or K}$ and $\text{M}^{\text{II}} = \text{Mg or Ca}$) partly meet these requirements [1]. Bogdanovi et al. [2] made the main breakthrough in the field of alanates for use as hydrogen storage materials. Upon doping with titanium-catalysts, NaAlH_4 (7.5 wt.% theoretical hydrogen content for complete desorption to Na) becomes reversibly chargeable ($\text{NaAlH}_4 \leftrightarrow \text{Na}_3\text{AlH}_6 \leftrightarrow \text{NaH}$). In order to transfer this existing knowledge to other complex metal hydrides with higher storage capacities, e.g. $\text{Mg}(\text{AlH}_4)_2$ (9.3 wt.% theoretical hydrogen content for complete desorption to Mg) or $\text{Ca}(\text{AlH}_4)_2$ (7.7 wt.% theoretical hydrogen content for complete desorption to Ca), the materials have to be accessible in gram amounts. In this contribution we present some of our results on the synthesis and analysis of these compounds. Finholt et al. described in a patent [3] the preparation of calcium

aluminum hydride using aluminum chloride and calcium hydride in THF. Schwab and Wintersberger, further investigated the reaction mechanism [4]. They have reported that AlH_3 is formed in the first step (1). This was stabilized by adding an excess of CaH_2 leading to the desired product, $\text{Ca}(\text{AlH}_4)_2$, as a stable solvent adduct (2):



In addition, it is reported in the literature [5] that it is possible to prepare AlH_3 using LiAlH_4 or NaAlH_4 . Dymova et al. and Bulychev et al. [6] published a synthetic approach using solid phase transformation techniques for $\text{Ca}(\text{AlH}_4)_2$ and $\text{Mg}(\text{AlH}_4)_2$. More recently Fichtner et al. [7] published the synthesis and structure of $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$.

2. Experimental part

All operations were performed under argon using standard Schlenk techniques. Solids were handled in an argon-filled glove box equipped with a recirculation system to

* Corresponding author. Tel.: +31 20 630 2214; fax: +31 20 630 3964.

E-mail address: hans.stil@shell.com (H. Stil).

keep the water and oxygen concentrations below 1 ppm. THF and Et₂O were dried over and distilled from sodium/benzophenone before use and stored under an inert atmosphere. Starting materials were either purchased from Aldrich Chemical Co. or prepared according to literature procedures and used without further purification. CaH₂ was milled in a SPEX[®]8000 ball mill before use in order to obtain an activated finely powdered material. X-ray diffraction patterns of the products were recorded on two different systems, both using Cu K α radiation, and Bragg–Brentano geometry, namely a Philips PW 1800 diffractometer equipped with a curved graphite monochromator and a Panalytical X'Pert Pro system (without monochromator). Sample transfer was done using special airtight sample holders. The data were collected in the range $2\theta = 5\text{--}80^\circ$ with a step size of 0.033° . Qualitative analysis of the measured patterns was done by comparison with entries from the ICDD PDF2 2000 database.

2.1. Synthesis of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$

THF (50 mL) was added in a three-neck flask equipped with a reflux cooler, a dropping funnel and a gas inlet to a mixture of CaH₂ (2.66 g, 0.06 mol) and AlCl₃ (1.68 g, 0.013 mol). After the exothermic reaction the white mixture was stirred at 25 °C for 10 h. After filtration THF was removed under reduced pressure. The white solid obtained was subsequently analyzed by XRD.

2.2. Synthesis of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ via the AlH_3THF route starting from LiAlH_4

THF (50 mL) was added to a three-neck flask – equipped with a reflux cooler, a dropping funnel and a gas inlet – to AlCl₃ (2.69 g, 0.02 mol). While stirring at 25 °C LiAlH₄ (2.44 g, 0.06 mol) was added. There was an immediate reaction resulting in the formation of LiCl. After filtration under exclusion of air, a white powder later identified as AlH₃THF (0.6 g, 0.0058 mol) was obtained. The product was not perfectly dried in order to prevent spontaneous decomposition. AlH₃THF (0.6 g, 0.0058 mol) was dissolved in THF (100 mL) using a three-neck flask equipped with a reflux cooler, a dropping funnel and a gas inlet. CaH₂ (0.84 g, 0.02 mol) was added to the solution. After stirring for 10 h the mixture was filtered and THF was removed under reduced pressure. The white powdered material obtained with moderate yield was subsequently characterized by XRD.

2.3. Synthesis of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ via the AlH_3THF route starting from NaAlH_4

THF (70 mL) was added to a three-neck flask – equipped with a reflux cooler, a dropping funnel and a gas inlet – to AlCl₃ (0.82 g, 0.006 mol). At 25 °C NaAlH₄ (1 g, 0.02 mol) was added. Without any further purification CaH₂ (2.2 g, 0.05 mol) was added to the solution. After stirring overnight the mixture was filtered, the liquid phase was removed with

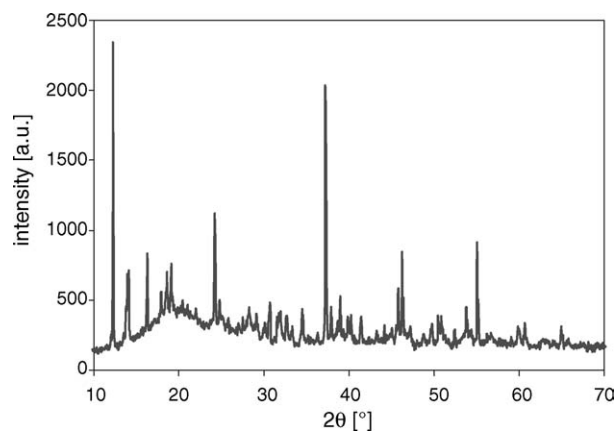


Fig. 1. X-ray powder pattern of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ produced according to reaction 2.1.

a double-ended needle and THF was removed under reduced pressure, a white powder-like material was obtained with moderate yield and characterized by XRD.

3. Results and discussion

3.1. XRD results

3.1.1. XRD results for $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$

The product of the reaction described in Section 2.1 was investigated by XRD. The signal pattern of the THF-adduct of $\text{Ca}(\text{AlH}_4)_2$ is shown in Fig. 1.

Figs. 2 and 3 show the X-ray diffraction pattern of materials prepared according to the reaction of AlH₃ with CaH₂—the reaction of a low temperature with a high temperature hydride to form a medium temperature complex metal hydride. The diffraction patterns of the materials are completely different reflecting a different degree of crystallinity and/or a different amount of THF incorporated in the lattice. Both patterns differ also significantly from the XRD experimental data published by Panwen et al. [8]. We conclude that the formation of a $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ compound with a defined

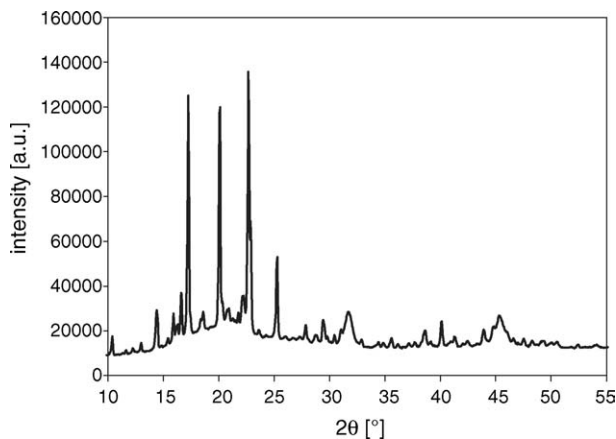


Fig. 2. X-ray powder pattern of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ produced according to reaction 2.2.

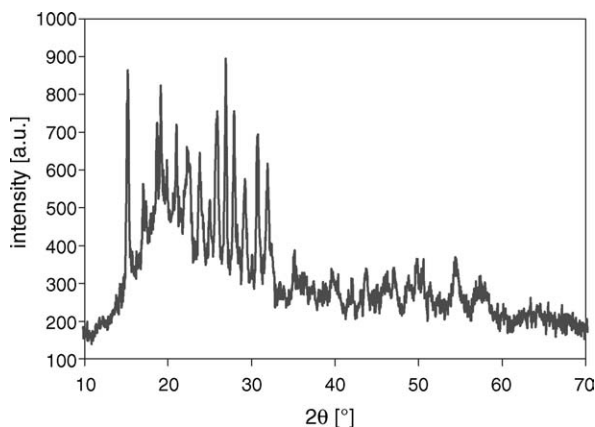


Fig. 3. X-ray powder pattern of $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ produced according to reaction 2.3.

stoichiometry is not reproducible and the amount of coordinated ether can have a broad range leading to materials with different morphology, composition and hydrogen storage capacities. So far it was not possible by optimizing the reaction conditions to prepare a defined perfectly crystalline and stable material or to remove selectively the coordinated solvent. Decomposition of the material due to the spontaneous release of coordinated THF and hydrogen produces CaH_2 and Al as verified by XRD (pattern not shown). Attempts to prepare sufficiently stable and clean single crystals for X-ray analysis are currently undertaken.

3.1.2. XRD results for $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$

Likewise, the investigations of $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$ prepared according to the procedure of Fichtner et al. [7] showed that the effect of incorporating different amounts of solvent molecules is clearly visible, as illustrated in Figs. 4 and 5. The material analyzed in Fig. 4 is highly crystalline and stable.

When pouring the compound (Fig. 4) into water neither evolution of hydrogen nor a violent reaction was observed. The material stays completely unreacted without dissolving because of the perfect ordering and incorporation of ether molecules, which protect the material. By contrast, the amor-

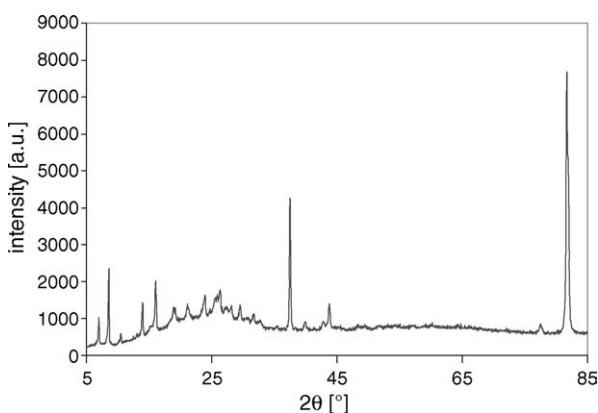


Fig. 4. X-ray powder pattern of $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$ (crystalline material).

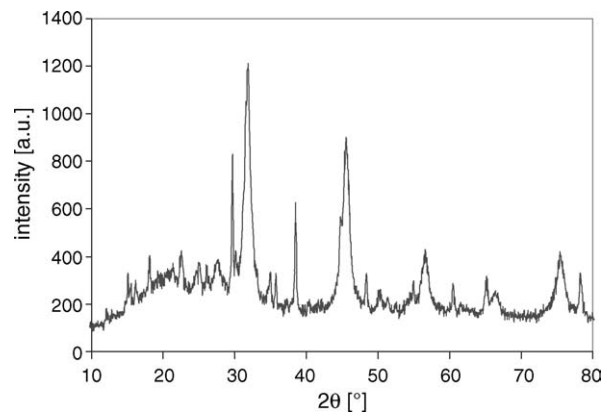


Fig. 5. X-ray powder pattern of $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$ (amorphous material).

phous $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$ that gave the pattern shown in Fig. 5 reacted violently with water. The synthesis is not reproducible with respect to morphology and stability of the material obtained.

4. Conclusions

Realizing the compatibility of H_2 storage with the requirements of a fuel cell for mobile applications is a key issue for the scientific community working on innovative materials. Further knowledge is necessary in order to produce materials with higher hydrogen storage capacities, e.g. alanates, which are not yet commercially available. Attempts to change this situation, synthetic routes to such compounds were presented in this contribution and the materials were characterized by XRD. Thus we have successfully synthesized the complex metal hydride $\text{Ca}(\text{AlH}_4)_2\text{THF}_x$ and $\text{Mg}(\text{AlH}_4)_2\text{Et}_2\text{O}$ in gram amounts. The various synthetic routes used, resulted in materials with different structures, as presented by XRD. The difference was possible due to the different amount of solvent that was incorporated in the alanate. The characterization of these compounds proved to be extremely difficult due to their inherent instability. Thus, attempts to remove the coordinated solvent resulted in decomposition of the materials. The compounds with more ordering show a higher degree of stability as proven by the hydrolysis reaction.

Acknowledgements

This work was supported by the Marie Curie Foundation and the HYDROCHEM-RTN Project number HPRN-CT-2002-00176 on New Chemistry and Catalysis with Hydride Compounds.

References

- [1] L. Schlapbach, A. Züttel, *Nature* 414 (2001) 353–358.
- [2] B. Bogdanovi, M. Schwickardi, *J. Alloys Compd.* 253 (1997) 1–9.
- [3] (a) A.E. Finholt, H.I. Schlesinger, *A. Patent* 2-567-972 (1951);
(b) A.E. Finholt, *A. Patent* 2-550-985 (1951);

- (c) A.E. Finholt, G.D. Barbaras, G.K. Barbaras, G. Urry, T. Wartik, H.I. Schlesinger, *J. Inorg. Nucl. Chem.* 1 (1955) 317–325.
- [4] (a) W. Schwab, K. Wintersberger, *Z. Naturforsch.* 8b (1953) 690–691;
(b) E.C. Ashby, *J. Organomet. Chem.* 200 (1980) 1–10;
(c) J.A. Dilts, E.C. Ashby, *Inorg. Chem.* 11 (1972) 1230–1236.
- [5] A.E. Finholt, A. Patent 760774 (1954).
- [6] (a) T.N. Dymova, V.N. Konoplev, A.S. Sizareva, D.P. Aleksandrov, *Russian J. Inorg. Chem.* 25 (1999) 312–316;
(b) B.M. Bulychev, A.V. Golubeva, P.A. Storozhenko, *Russian J. Inorg. Chem.* 43 (1998) 1637–1642.
- [7] (a) M. Fichtner, O. Fuhr, *J. Alloys Compd.* 345 (2002) 286–296;
(b) M. Fichtner, J. Engels, O. Fuhr, O. Kircher, O. Rubner, *Mater. Sci. Eng. B* 108 (2004) 42–47;
(c) M. Fichtner, O. Fuhr, O. Kircher, *J. Alloys Compd.* 356/357 (2003) 418–422;
(d) M. Fichtner, J. Engel, O. Fuhr, A. Glöss, O. Rubner, R. Ahlrichs, *Inorg. Chem.* 42 (2003) 7060–7066.
- [8] S. Panwen, Z. Yungshi, C. Shengchang, F. Xianbao, L. Tong, *Huaxue Tongbao* 9 (1986) 31–32.