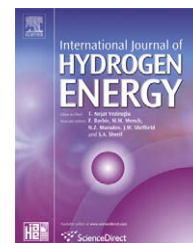


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A search for new Mg- and K-containing alanates for hydrogen storage

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ARTICLE INFO

Article history:

Received 13 March 2008

Received in revised form

18 April 2008

Accepted 31 October 2008

Available online 13 December 2008

Keywords:

Hydrogen storage materials

Reactive milling

Alanates

ABSTRACT

In this work Mg- and K-containing alanates have been investigated as possible hydrogen storage materials. Ball milling was carried out under argon or at moderate/high hydrogen pressure in order to obtain an improved driving force for the formation of potential new alanate phases. Powder X-ray diffraction and volumetric measurements were used in order to identify reaction mechanisms and phases forming in these systems. New unidentified peaks were detected for the mixtures $2\text{MgH}_2 + 3\text{Al} + \text{KH}$ and $2\text{CaH}_2 + \text{Al} + 2\text{KH}$. However, they do not seem to belong to reversible hydride phases.

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1. Introduction

Since the work by Bogdanovic in 1997, showing the reversible hydrogenation of Ti-enhanced NaAlH_4 [1], aluminium-based complex hydrides, “alanates”, have been regarded as highly promising group of materials in order to develop lightweight and high reversible capacity hydrogen storage units for mobile applications. Alanates with high H-content exist, e.g. LiAlH_4 (10.6 wt%) and $\text{Mg}(\text{AlH}_4)_2$ (9.3 wt%), but these compounds are not reversible at moderate conditions [2–4]. A modelling study from Løvvik and Swang [5] predicted that mixed alanates (alanates with more than one alkali or alkaline earth atom) such as $\text{Na}_2\text{LiAlH}_6$, K_2LiAlH_6 and K_2NaAlH_6 are stable compounds, and in fact they have been synthesised [6–8]. These compounds resulted reversible, but with too high enthalpies of reaction (>50 kJ/mol H_2). Mixed Mg-alanates with (partial) substitution by Ca, and Ca-alanates with (partial) substitution by Li or Na, were investigated as possible

hydrogen storage materials [9]. However, the new phases formed in these systems upon milling under hydrogen pressures (up to 100 bar) did not seem to be reversible. Moreover, the study found that a higher milling speed favours the formation of the new phases.

In this paper we have investigated the feasibility to (partially) substitute Mg by Na or K, in Mg-alanates and to (partially) substitute Ca by K in Ca-alanates in order to evaluate thermodynamic stability and reversibility of possible new mixed hydride phases.

2. Experimental

All chemicals were purchased from commercial sources. CaH_2 (95% purity; Sigma–Aldrich), MgH_2 (95% purity; M.C.P. Technologies S.A. and Goldschmidt), KH (35 wt% dispersion in mineral oil; Sigma–Aldrich), Al (99.97% purity; Alfa Aesar), and

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NaH (95% purity; Sigma–Aldrich) were obtained as powders. KH was filtered and washed and then recrystallised. All handling of samples was carried out in an Ar atmosphere in a glove box and transferred to sealed milling vials to prevent reaction with moisture and O₂. Ball milling was carried out with Fritsch Pulverisette 6 (P6), with Fritsch Pulverisette 7 (P7) and with a Spex 8000. Reactive milling was performed with in-house built high-pressure vials.

Three systems were studied: alanates based on Mg–Al–Na–H, Mg–Al–K–H and Ca–Al–K–H, respectively.

In the Mg–Al–Na–H system 2MgH₂ + 3Al + NaH were milled under Ar using a Spex 8000 and hydrided/dehydrided in order to determine which stable phases are formed. In a second approach, reactive milling under high hydrogen pressure (160 bar) was carried out in order to obtain high driving forces and investigate possible formation of less stable phases or phases whose formation is kinetically impeded. For this purpose the starting powders were pre-milled using a Spex 8000, under Ar, in order to obtain fine microstructures. One part of the resulting material was used for reactive milling (4 g), while the other part was preserved as a reference for comparison (2 g). Reactive milling was carried out in a Fritsch planetary ball mill. Moderate milling conditions (150 rpm, ball-to-powder ratio (BPR): 10:1) were applied in order to avoid any critical increase of temperature during milling. A long milling time of 1 week was chosen, because the formation of new alanate phases at room temperature without added catalysts is expected to be rather slow.

In the Mg–Al–K–H system the mixture 2MgH₂ + 3Al + KH was milled under Ar at the same conditions as for the Mg–Al–Na–H system.

In the Ca–Al–K–H system samples were prepared following two routes. Ball milling was carried out in P7 and P6 under Ar or under hydrogen pressure, respectively. In order to avoid a critical increase of temperature during milling, the mill was stopped for 5 min every 20 min of ball milling with P6. One sample was obtained by milling the starting materials (2CaH₂ + Al + 2KH) for 3 h under Ar with P7 at 750 rpm and a BPR of 15:1. The second sample was obtained by ball milling the same amount of the starting materials (2CaH₂ + Al + 2KH) in a reactive atmosphere (90 bar H₂) and for a much longer time (40 h) with P6 at 600 rpm and a BPR of 12:1.

The resulting powders were characterised in terms of their structural, thermal and kinetics properties.

Powder X-ray diffraction (PXD) data were collected with two instruments. A Siemens D5000 diffractometer using CuK_{α1} radiation ($\lambda = 1.540598 \text{ \AA}$) was used. The measurement was performed in transmission mode in the range $2\theta = 10\text{--}90^\circ$ with a step length of 0.0153° and 1 s/step. An INEL MPD diffractometer with monochromized CuK_{α1} radiation, flat plate geometry and CPS-120 curved, position-sensitive detector that continuously cover the 2θ range from 2° to 120° ($\Delta 2\theta = 0.029^\circ$) was also used. The samples were covered by a thin plastic film or Kapton foil to prevent reaction with air.

Thermal desorption spectroscopy (TDS) experiments were carried out in dynamic vacuum at a temperature rate of $0.2^\circ\text{C}/\text{min}$. The background level (with empty sample holder) was $\sim 10^{-6}$ mbar.

Absorption and desorption of hydrogen were performed in a Sievert's type apparatus (HERA, Quebec, Canada). The

powder samples were filled in a sample holder under purified argon.

3. Results and discussion

3.1. The Mg–Al–Na–H system

The result of the ball milling under argon of 2MgH₂ + 3Al + NaH at moderate conditions was a composite, with the original phases still present (Fig. 1, scan A). After hydrogenation at 160 bar and 80 °C the PXD data show clearly the formation of NaAlH₄, however, no additional new phase could be found (Fig. 1, scan B). It is important to notice that Na₃AlH₆ as the intermediate step for the formation of NaAlH₄ was not formed in this system. Upon dehydrogenation NaMgH₃ was formed (see Fig. 1, scan C). A subsequent hydrogenation at 160 bar and 80 °C only led to stronger reflections from NaMgH₃ (Fig. 1, scan D). The experiments indicate that NaMgH₃ is preferably formed in the system, and the formation of any new alanate from this phase could not be achieved.

To investigate the reactions between the hydride phases further, the mixture of 2MgH₂ + 3Al + NaH was hydrogenated at 160 bar and 80 °C for 12 h (obtaining NaAlH₄, MgH₂ and Al, as in Fig. 1, scan B) and subsequently the release of hydrogen was recorded at increasing temperature with a Sievert's apparatus as shown in Fig. 2. The hydrogen content was normalised to the number of hydrogen atoms per mol of 2MgH₂ + 3Al + NaH. About 6.3 hydrogen atoms are released in

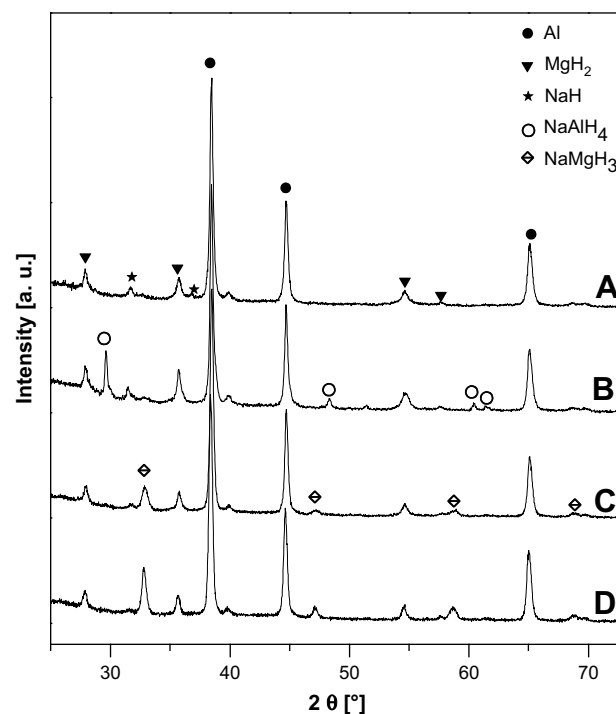


Fig. 1 – PXD diagrams of 2MgH₂ + 3Al + NaH system at different conditions. **A:** after milling; **B:** as A and subsequent absorption (160 bar, 80 °C); **C:** as B and subsequent desorption (100 mbar, 80 °C); and **D:** as C and subsequent absorption (160 bar, 80 °C).

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