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$LiAlD_4$ with VCl_3 additives: Influence of ball-milling energies

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Abstract

The reduction reaction of VCl_3 mixed with $LiAlD_4$ is studied for different ball-mill energies. From low to high ball-milling energies VCl_3 is reduced by the formation of Li–V–Cl metastables phases, LiCl and free Al and V or Al–V phases. It is also shown that the enhancement of the kinetics reaches a limit with increased ball-mill energy. From measurements of the released hydrogen with a Sieverts apparatus and X-ray and neutron diffraction, it is shown that even under mild conditions, at or close to room temperature, the two first steps of the decomposition of VCl_3-enhanced $LiAlD_4$ occurs during the first weeks after milling at temperatures in the range 20–50 °C.

Keywords: Hydrogen-storage materials; Alanates; Metal hydrides; Ball-milling

1. Introduction

Since the work by Bogdanovic and Schwickardi [1] showing the improved kinetics and reversibility of Ti-enhanced $NaAlH_4$ at moderate conditions, alanates mixed with transition metal additives have been widely studied for their possible utilization in onboard hydrogen-storage systems. Initially, wet chemistry methods were used to mix the alanate and the additives (e.g. in [1]) with the disadvantages of contamination and loss of weight capacities because of the use of solvent. Subsequently, dry ball-milling was used to add the transition metals [2], and this is now the preferential method. However, it is difficult to control the process because of the difficulties to accurately define the energy and the physical parameters during the milling.

The dehydrogenation of $LiAlH_4$ upon heating is a three steps reaction [3]:

$$3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2 \quad (1)$$

$$Li_3AlH_6 \rightarrow 3LiH + Al + \tfrac{3}{2}H_2 \quad (2)$$

$$3LiH + 3Al \rightarrow 3LiAl + \tfrac{3}{2}H_2 \quad (3)$$

The desorption temperatures, T_1 and T_2 from Eqs. (1) and (2), can be significantly decreased by ball-milling the alanate with additives like VCl_3 [4,5]. The decomposition of $LiAlH_4$ at room temperature is slow [6] but has been shown to be significantly improved by adding TiF_3 [7].

The aim of the present work is to study the effect of the ball-milling conditions on the reaction between $LiAlD_4$ and VCl_3 and how this influences the decomposition kinetics of the alanate.

2. Experimental

The compounds, $LiAlD_4$ (≥95% purity, containing ~0.2 mol% LiCl) and VCl_3 (99.99%) were purchased from Sigma–Aldrich Corp. $LiAlD_4$ was used in this study instead of $LiAlH_4$ because it is commercially available with a higher purity. The samples were handled and stored in a glove box with a dry argon atmosphere to prevent any contact with oxygen or moisture.

Two different planetary Fritsch ball-mills (BM) were used. The Pulverisette 7 (P7) was equipped with hardened steel vials of 12 cm^3 sealed under argon with three (Ø 12 mm, 7 g) or five steel balls (Ø 10 mm, 4 g). Typically 1 g samples were used, the ball to powder ratio (BPR) was ~20:1. Two different gyration rates were used, 510 and 720 rpm, respectively. The Pulverisette 6 (P6), with a 270 cm^3 hardened steel vial equipped with a Gas pressure and Temperature Measuring system (GTM), allows recording pressure and temperature changes in the vial during the milling. For P6 50 steel balls (Ø 10 mm, 4 g) were used, and for a 1 g sample the BPR is 200:1. The gyration rate was 400 rpm and the temperature inside the vial increased by less than 10 °C during the milling time. The temperature measured in the P6 vials is the average temperature of the whole system including the vial, the balls, the powder and the gas. The increase in temperature during the milling results from the heat produced by the impact of the balls and does not reflect the temperature at the impact point of the balls. This latter cannot easily be detected and is obviously higher than the measured

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temperatures. Nevertheless, no thermal decomposition of $LiAlD_4$ into Li_3AlD_6 and Al was measured after the ball-milling processes (see below).

Based on the expressions developed in [8] the estimated comparisons between the energies transferred to the powder with the BM P6 and P7 are $E_{P6} \approx 20E_{P7}$ for $\omega_{P7} = 720$ rpm and $\omega_{P6} = 400$ rpm, respectively, and $E_{p6} \approx 50E_{p7}$ for $\omega_{P7} = 510$ rpm and $\omega_{P6} = 400$ rpm. Thus, $E_{P6} \gg 50E_{P7}$, and the terminology low and high-energy BM will be used hereafter for milling with P7 and P6, respectively.

Constant temperature decomposition measurements (CTD) were carried out with a Sieverts apparatus. The sample holder with a pressure sensor from Presens AS (relative accuracy 1%) was placed inside a heating chamber with a temperature stability of ±0.02 °C. The total volume of the setup was 10.995 cm^3. 0.6 g samples were used with a typical pressure increase of maximum 30 bar.

Thermal Desorption Spectroscopy experiments (TDS) were carried out in dynamic vacuum at a constant heating rate of 2 °C/min. The vacuum level with empty sample holder was approximately 2×10^{-6} mbar. A Pt thermocouple placed inside the powder continuously recorded the temperature of the sample.

Powder X-ray diffraction data (PXD) were collected with a Bragg Brentano geometry INEL MPD diffractometer with Cu $K\alpha_1$ radiation and a curved 120° position sensitive detector. The powder was uniformly spread as a thin layer in the sample holder, and covered by a thin polyethylene film (PE) to prevent contact with oxygen or moisture during the measurements. A small diffuse scattering halo due to the PE film is visible at around 24° in 2θ in the diffractions patterns.

High-resolution synchrotron radiation powder diffraction data (SR-PXD) were measured at the Swiss-Norwegian beam line (SNBL) at station BM01B at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The samples were kept in rotating 0.8 mm glass capillaries. The wavelength 0.49956 Å was obtained from a channel-cut Si (1 1 1) monochromator.

Powder neutron diffraction (PND) in situ data were collected between $2\theta = 10°$ and 130° with the PUS instrument at the JEEP II reactor at Kjeller, Norway [9]. The data were rebinned in steps of $\Delta(2\theta) = 0.05°$. Neutrons with wavelength 1.5554 Å were obtained from a focusing Ge(5 1 1) monochromator. The sample was kept in a quartz tube (Ø 6 mm) connected to a vacuum pump. A water-cooled furnace placed around the sample was used to heat the sample. The sample was kept at 40 and 50 °C for 6 h, and then cooled to 18 °C for the PND measurements.

Rietveld refinements of the diffraction patterns were carried out using Rietica [10] and Fullprof [11] softwares. Structural data for $LiAlD_4$ and Li_3AlD_6 were taken from [12] and [13], respectively. In Rietica, Voigt profile functions were used and the background was modeled by Chebychev II polynoms. Pseudo-Voigt functions and interpolation between manually selected background points were used in Fullprof.

3. Results and discussion

3.1. Reactions during ball-milling

High-energy BM using P6 were carried out for $LiAlD_4$ mixed with 5, 10 and 25 mol% VCl_3, respectively. The pressure and the temperature within the vial were recorded during the milling. Fig. 1 shows the quantity $n_{D_2}/6n_{VCl_3}$ versus the time t for the three samples. This quantity should be equal to one if the reduction of VCl_3 is complete and follows the reaction:

$$3LiAlD_4 + VCl_3 \xrightarrow{BM} V + 3LiCl + 3Al + 6D_2 \quad (4)$$

The pressure in the vial was monitored during the milling process. The milling times were chosen in order to achieve a complete reduction of VCl_3 and to avoid possible thermal decomposition of $LiAlD_4$ that may occur with longer milling times.

n_{D_2}, the number of moles of deuterium formed during the milling, is calculated from the pressure and temperature measurements using the equation of state. n_{VCl_3} is the number

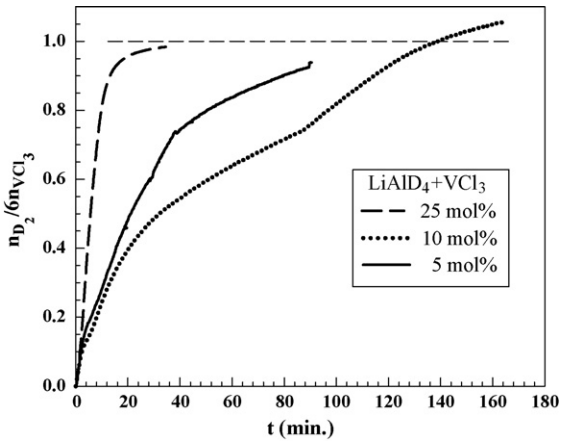

Fig. 1. The evolution of $n_{D_2}/6n_{VCl_3}$ as a function of time for BM $LiAlD_4$ with 5, 10 and 25 mol% VCl_3.

of moles of VCl_3 introduced in the vial. For all experiments $n_{D_2}/6n_{VCl_3}$ approach values close to 1, in agreement with Eq. (4). The final value is slightly higher ~1.035 for the 10 mol% VCl_3 sample. This deviation may result from experimental errors or from the thermal decomposition of a fraction of $LiAlD_4$ into Li_3AlD_6, and Al. However, this decomposition must be very small since Li_3AlD_6 was not found in the PXD pattern (see below).

A stoichiometric mixture of $LiAlD_4$ with 25 mol% VCl_3 gave $n_{D_2}/6n_{VCl_3} > 0.98$ after 32 min of milling. In that case LiCl is the only well-crystallized phase seen by PXD (Fig. 2a). A broad peak, with its maximum at approximately $2\theta = 41°$ and covering 10° in 2θ, is also present in the diffraction pattern. After annealing the powder for 16 h at 400 °C under vacuum, the broad peak is no longer present, and new well-defined peaks from Al_3V are observed in the PXD data (Fig. 2b). The phase composition of the annealed sample was calculated by quantitative phase analysis (QPA) to be 22 mol% Al_3V and 78 mol% LiCl. This is close to the theoretical values of 25 and 75 mol%, respectively. Solid-solution of Al(V) and V(Al) as well as some metastable Al–V phases have been observed in a ball-milled 75% Al–25%

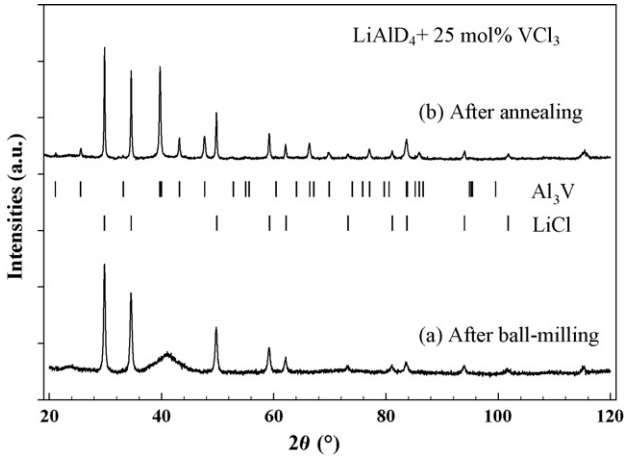

Fig. 2. PXD patterns of $LiAlD_4$ with 25 mol% VCl_3. (a) After BM. The position of the Bragg peaks for LiCl and Al_3V are shown. (b) After BM and annealing at 400 °C for 15 h.