STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE – desorption experiments – 01-02-631.

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The project focuses on studies of metal hydrides based on light-weight elements. During the last few years different so-called alanates e.g. $LiAlH_4$, $NaAlH_4$ and $Mg(AlH_4)_2$ containing up to 10 wt% hydrogen have been intensely studied. Even though these materials have been known for a long time, details about structure of the starting material and desorption products are limited. For possible applications, doping/catalysts are needed, but the effect of the catalyst/dopants on the absorption / desorption process is not well understood.

The time-resolved in situ diffraction experiments aim on detailed studies of the desorption process of undoped and doped alanate samples. The following materials were investigated during the experiment carried out in November 2003:

(a) *$LiAlD_4$* both pure and 2 samples with different VCl_3 and $(Ti,Al)Cl_3$ doping.
(b) *$KAlD_4$*.
(c) *$Mg(AlH_4)_2$*

All samples were mounted in 0.5 mm quartz-glass capillaries mounted in a Swagelok fitting connected to a vacuum pump. A hot air blower was used to heat the sample to maximum 400°C. Data were collected with the MAR345 image plate system. The wavelength was 0.7100 Å. Expose time was 30 sec. for every experiment (and about 1 ½ min. is needed to read out the detectors, meaning an experiment every 2. minute). Both experiments at different heating rates and at isothermal conditions were carried out.

(a)Doped and undoped $LiAlD_4$

The isothermal decomposition of (i) pure $LiAlD_4$, (ii) $LiAlD_4$ added with 2 mol% VCl_3, and (iii) $LiAlD_4$ added with 2 mol% $3TiCl_3.AlCl_3$ were studied. For all samples diffraction diagrams were collected at five temperatures, for the undoped sample: 136, 138, 140, 144, 148°C and for the two doped samples: 122, 126, 130, 134 and 138°C. Because of the temperature range, only the first decomposition step was expected to occur:

$$3LiAlD_4 \rightarrow Li_3AlD_6 + 2Al + D_2 \quad (1)$$

Figure 1 shows the diffraction patterns for $LiAlD_4$ + 2 mol% VCl_3 at 138 ^oC. The decomposition starts immediately reaching the temperature set point and is completed after 50 min. All performed measurements gave similar patterns.

Based on Rietveld refinement of all diffraction patterns, the changes in molar percentage of each of the crystalline phases, their cell parameters and apparently their particle sizes can be followed at each temperature.

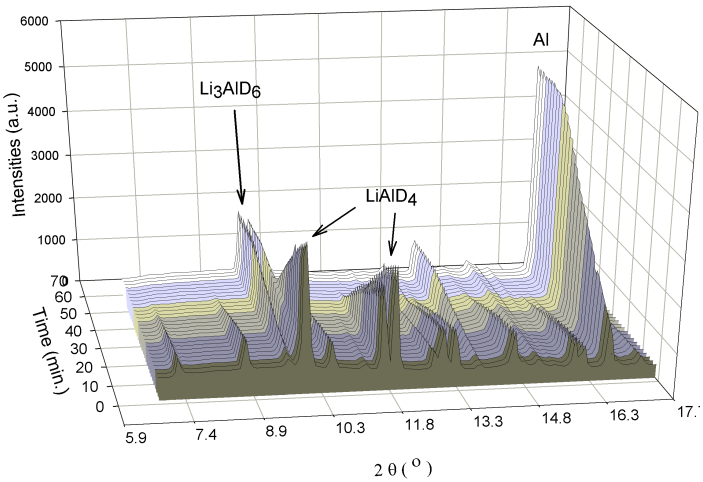
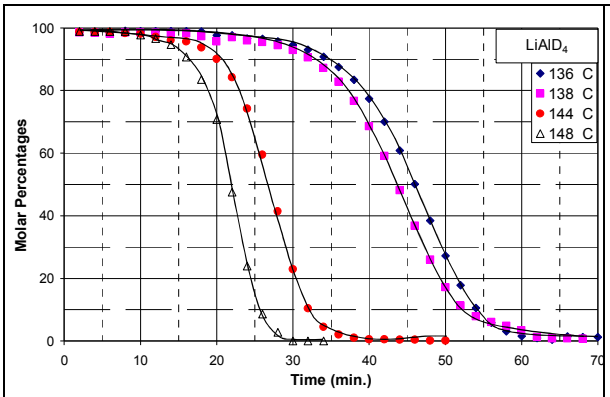
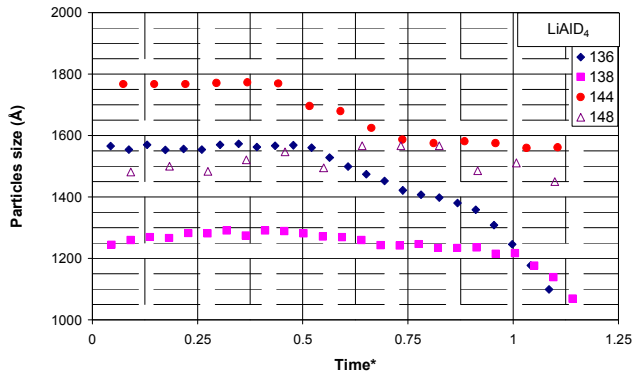


Fig. 1: Diffraction patterns measured during the isothermal decomposition of $LiAlD_4$ + 2 mol% VCl_3 at 138 °C

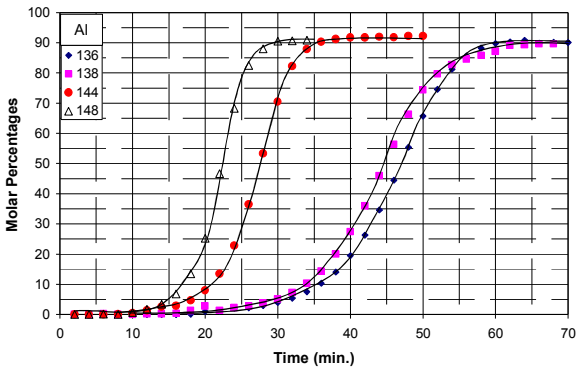
Figure 2 shows some of the data derived for the pure $LiAlD_4$. Still some further corrections are needed, but the plots give the approximate behaviour of the molar percentage of $LiAlD_4$, Al and Li_3AlD_6 and their estimated particles sizes as a function of time for the different temperatures. From equation (1) the aluminium phase seems to be over represented in comparison with the Li_3AlD_6 phase. From Figure 2 (e) it appears that even if the temperature is rather low, also Li_3AlD_6 start slowly to decompose. The Al content slowly increases after the completion of the first step of the decomposition. This slow decomposition will be examined at the next experiments at SNBL.



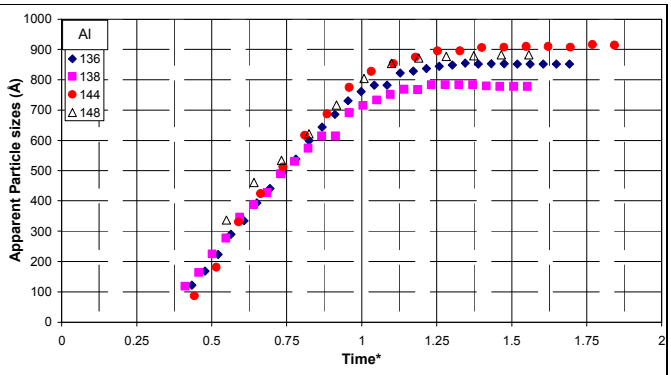
a) Evolution of the molar percentage of $LiAlD_4$ during the decomposition



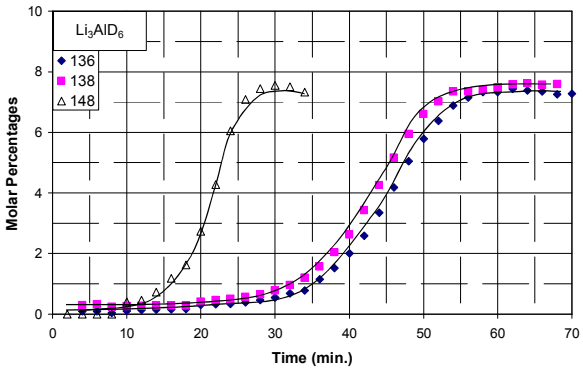
b) Evolution of the apparent particle sizes of $LiAlD_4$ during the decomposition



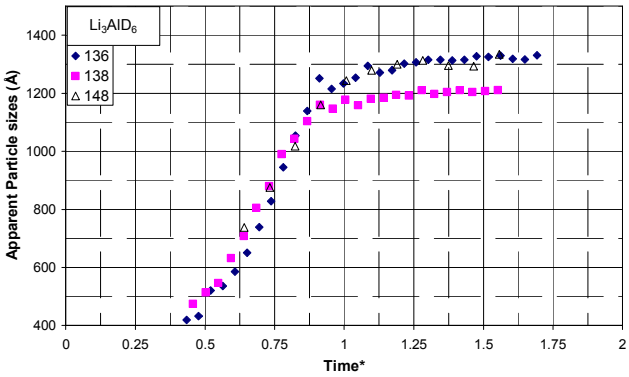
c) Evolution of the molar percentage of Al during the decomposition



d) Evolution of the apparent particle sizes of Al during the decomposition



e) Evolution of the molar percentage of Li_3AlD_6 during the decomposition



f) Evolution of the apparent particle sizes of Li_3AlD_6 during the decomposition

Fig. 2: Evolution of the molar percentage and the apparent particle sizes of $LiAlD_4$, Al and Li_3AlD_6 during isothermal decomposition at several temperatures, of pure $LiAlD_4$. The time, noted **Time*** is the ratio between the present time and when 80% of $LiAlD_4$ has decomposed.

Similar results were obtained for the decomposition of the two doped samples, and with similar conclusions. The comparison of the kinetics between the decomposition of doped and undoped samples is important. Figure 3 shows the evolution of the molar percentage of undoped and doped (with VCl_3) $LiAlD_4$ during decomposed at 138°C. The effect of the dopant is clearly illustrated; the decomposition is finished at least 10 minutes earlier for the doped samples.

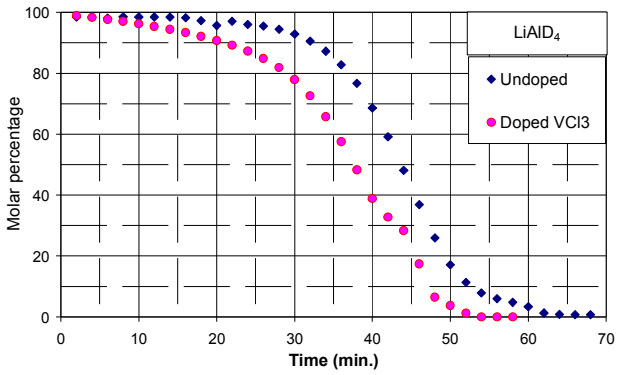


Fig. 3: The molar percentage for undoped and doped (VCl_3) $LiAlD_4$ decomposed at 138°C.

$KAlD_4$

The decomposition of $KAlD_4$ has been studied with a constant heating rate of 2°K/min. The diffraction patterns clearly show a two-step decomposition (Fig. 4). The first decomposition is finished at about 180 while the second step is completed at around 280°C. The decomposition seems to follow the route described by the following set of equations:

$$3\ KAlD_4 \rightarrow K_3AlD_6 + 2Al + 3D_2 \quad (2)$$
$$K_3AlD_6 \rightarrow 3KD + Al + 3/2D_2 \quad (3)$$

The structure of $KAlH_4$ is known, while K_3AlH_6, is still unknown. Both decompositions are rather fast. Furthermore, it is possible that the first one occurs together with melting of $KAlD_4$ that re-crystallize at higher temperature as K_3AlD_6. This will be carefully examined during our next experiments at SNBL.

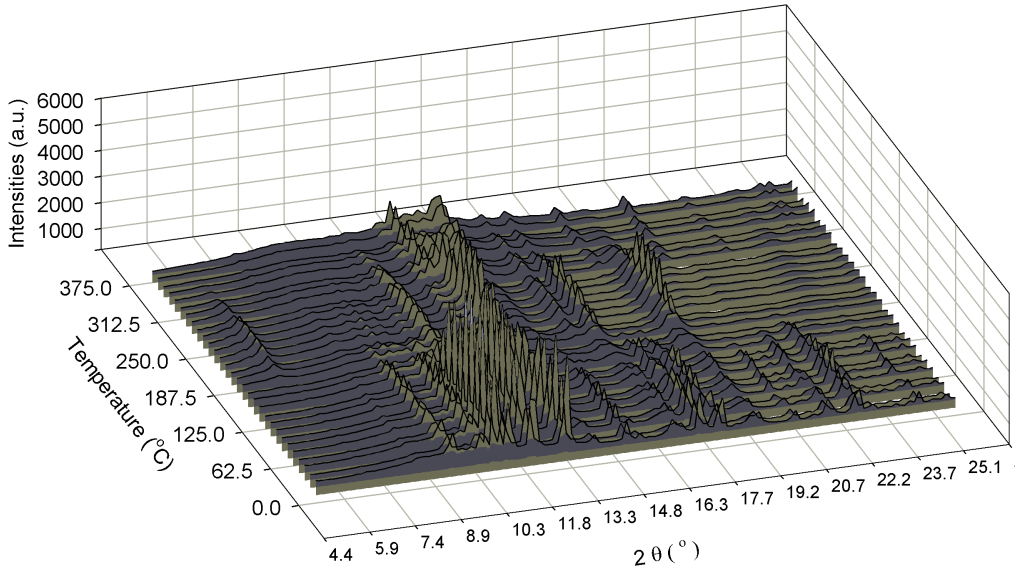


Figure 4: Diffraction patterns during decomposition of $KAlD_4$. Heating rate 2°K/min.

$Mg(AlH_4)_2$:

The decomposition of $Mg(AlH_4)_2$ was studied during heating with constant heating rates of 2, 5 and 10°C/min. The 5°C/min experiment was performed twice in order to study the reproducibility of the decomposition reactions. All four measurement series showed a two-step decomposition of $Mg(AlH_4)_2$ to (1) MgH_2 and Al in the first step and (2) two to three $Al_{1-x}Mg_x$ solid solutions in the second step, which is heavily governed by metastability.

Figure 5 shows the diffraction patterns for one of the experiments with a heating rate of 5°C/min. The starting temperature of decomposition of $Mg(AlH_4)_2$ to MgH_2 increases from 160°C to 190°C upon increasing the heating rate from 2 °C/min to 10 °C/min, whereas completion of the first decomposition step is seen at 190 and 275°C, respectively. Onset of the second reaction step, decomposition of MgH_2, is found in the temperature range 250-350°C. The reaction of MgH_2 and Al to $Al_{1-x}Mg_x$ is completed at 340-415°C.

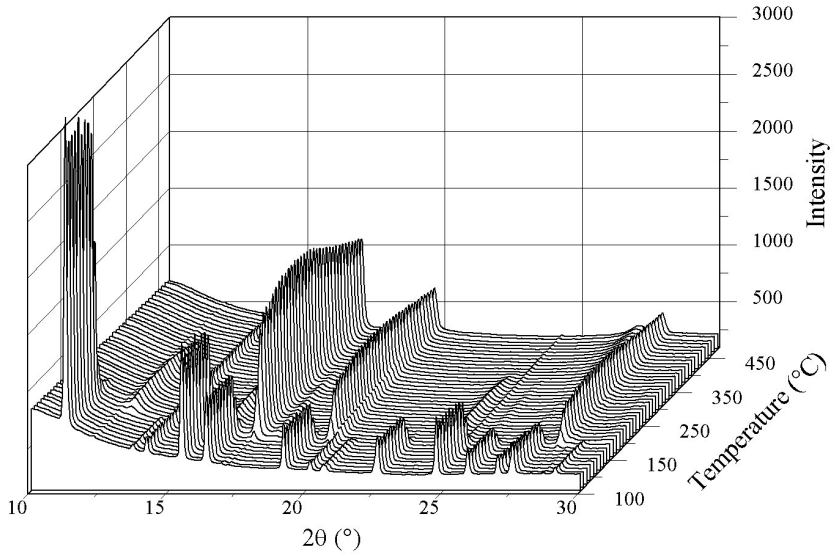


Fig. 5: Diffraction patterns during decomposition of $Mg(AlH_4)_2$. Heating rate of 5°C/min.