ALANATES FOR HYDROGEN STORAGE: TIME-RESOLVED AND HIGH RESOLUTION POWDER DIFFRACTION EXPERIMENTS.

B. C. Hauback[1], H. W. Brinks[1], D. Blanchard[1], P. Norby[2]
[1] Department of physics, Institute for Energy Technology, P. O. Box 40, NO-2027 Kjeller, Norway
[2] Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway.

The project focuses on studies of metal hydrides based on light-weight elements. During the last few years different so-called alanates e.g. $LiAlH_4$, $NaAlH_4$ 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 defective. For possible applications, doping/catalysts are needed, but the effect of the catalyst/dopants on the absorption / desorption process is not 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:

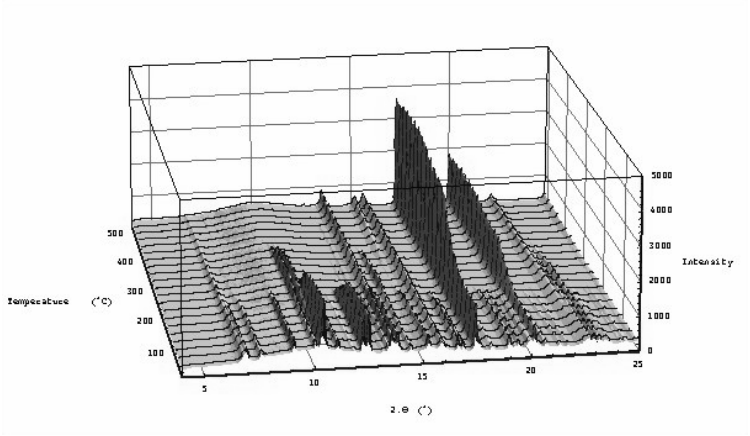
(a) *$LiAlD_4$* both pure and 4 samples with different VCl_3 and $(Ti,Al)Cl_3$ doping.
(b) *$NaAlD_4$* pure and doped with $TiCl_4$.
(c) *$KAlD_4$*.

All samples were mounted in 0.7 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) $LiAlD_4$

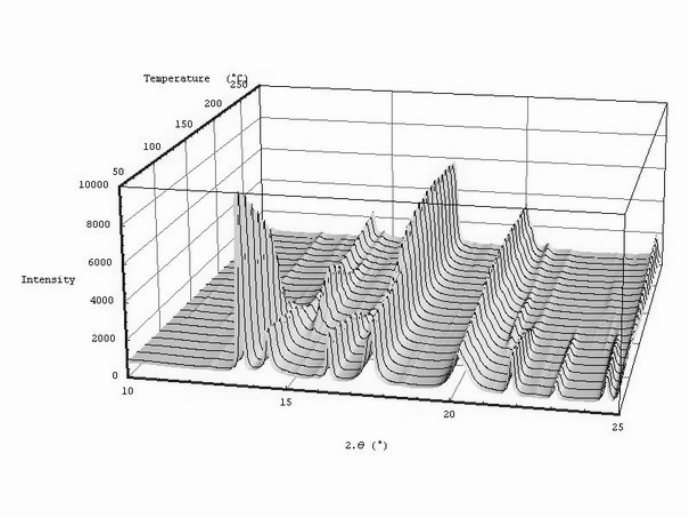
Heating rates 0.5, 1 and 2 °C/min were used for studies of the 5 different samples (pure $LiAlD_4$ and 4 doped). In addition isothermal measurement at temperatures 128, 132, 136 and 140°C were carried out for the pure $LiAlD_4$. Both series of measurements showed the two-step decomposition of $LiAlD_4$ into (i) Li_3AlD_6, Al and LiD at the first stage and (ii) decomposition of Li_3AlD_6 into Al and LiD at the second stage. The temperatures for the evolution of the different phases were extracted from the data for the different dopants, different heating rates and as a function of time for the isothermal measurements.

The figure shows the diffraction diagrams for $LiAlD_4$ + 2% VCl_3. The temperature for decomposition of $LiAlD_4$ to Li_3AlD_6 is reduced from 185 to 125 °C going from pure to 5 mol% VCl_3. The analyses of the isothermal decomposition are in progress.



(b) $NaAlD_4$.

Experiments were carried out with pure $NaAlD_4$ and 2,6 and 10 mol% $TiCl_4$ doped $NaAlD_4$. The final analyses of the data are in progress. The figure shows diffraction diagrams for 2 mol% $TiCl_4$ doped $NaAlD_4$ heated from 50 to 290°C.



(c) $KAlD_4$.

$KAlD_4$, has been shown to be reversible with respect to hydrogen storage (Hiroyuki et al., 2003), and it is therefore of great interest to determine the structures of the constituent phases of the decomposition (including $KAlD_4$ that we recently have found based on experiment 01-01-613 and K_3AlD_6 that is not known) and to follow the decomposition in details. Decomposition into K_3AlD_6 is 100% finished at 290 °C at a heating rate of 0.5 °C/min. A diagram with the K_3AlD_6 and Al phases is shown below. Structural studies of this phase will be based on this diagram in addition to forthcoming powder X-ray (including experiments at SNBL) and neutron diffraction work.