
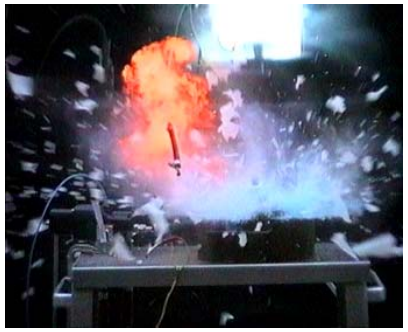


ON THE KINETICS OF ALH3 DECOMPOSITION AND THE SUBSEQUENT AL OXIDATION

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Hydrogen storage:

⇒ High pressure tanks 350 – 700 bar or higher in composites, mechanical stability

⇒ Liquid hydrogen tanks: boil-off, cooling/isolation, safety

⇒ Solid hydrides

⇒Heavy metals: low gravimetric storage

⇒Light metals: adsorption in nano structures

⇒Light metals: chem.bonded hydrides

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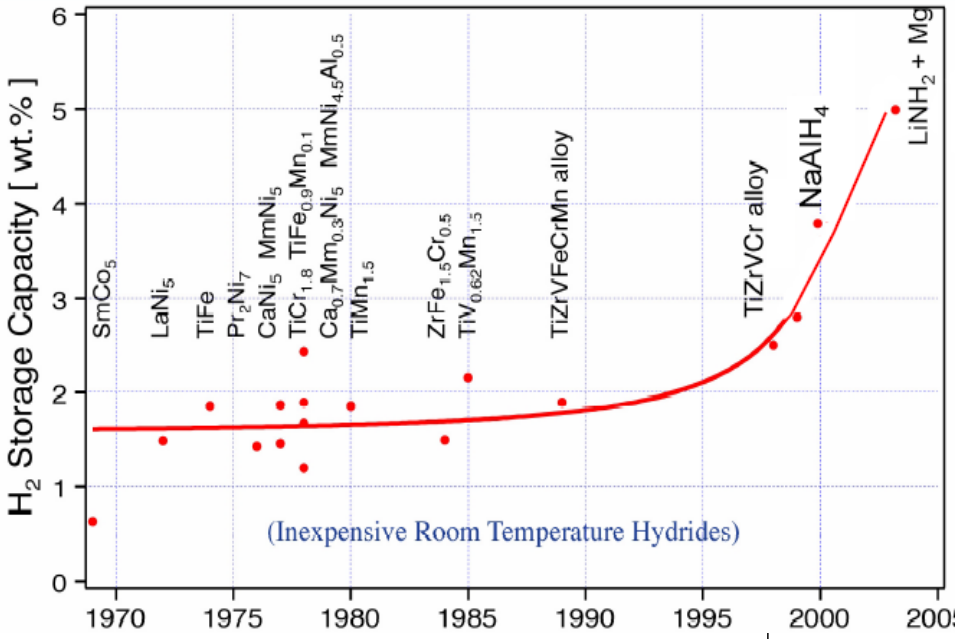
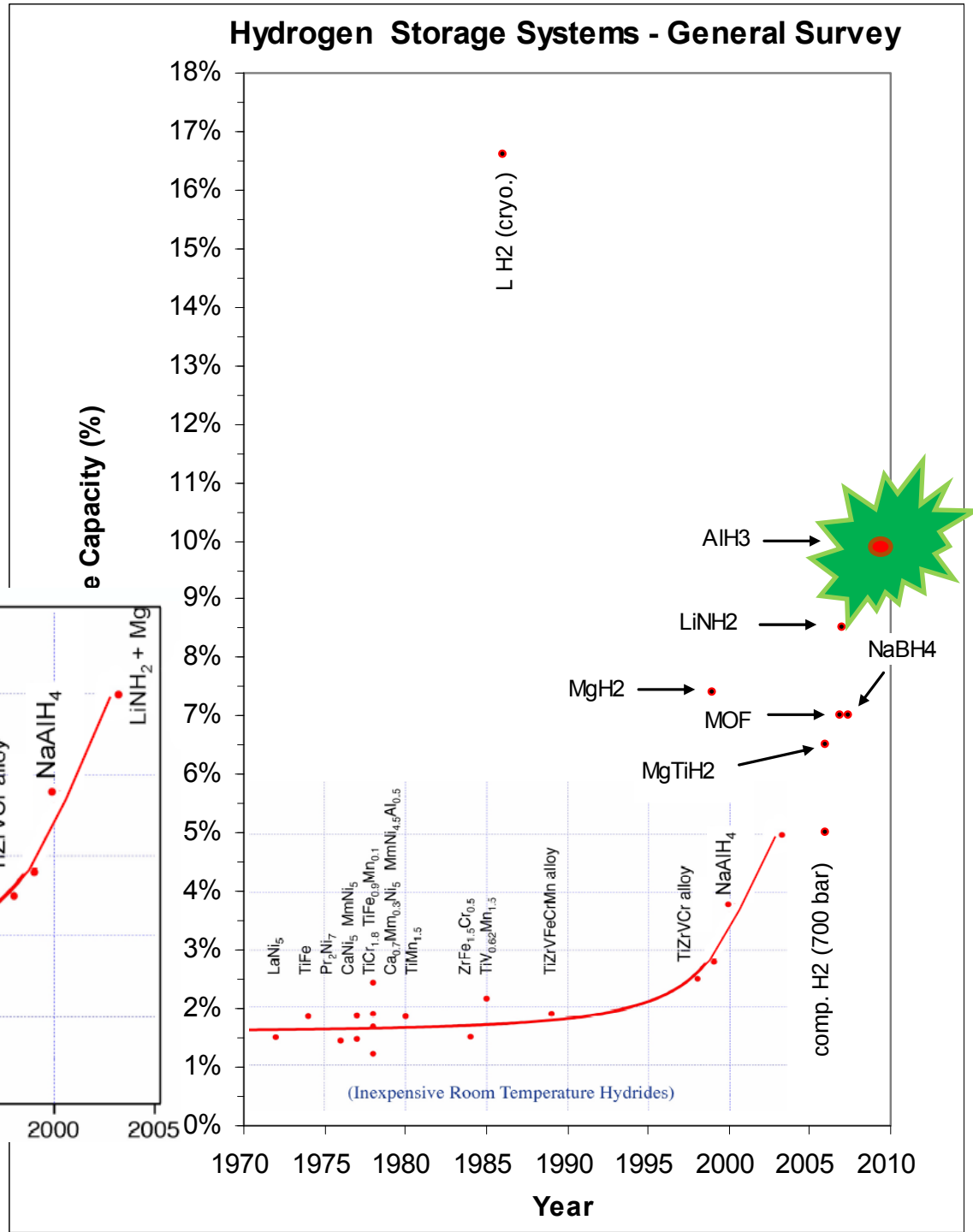
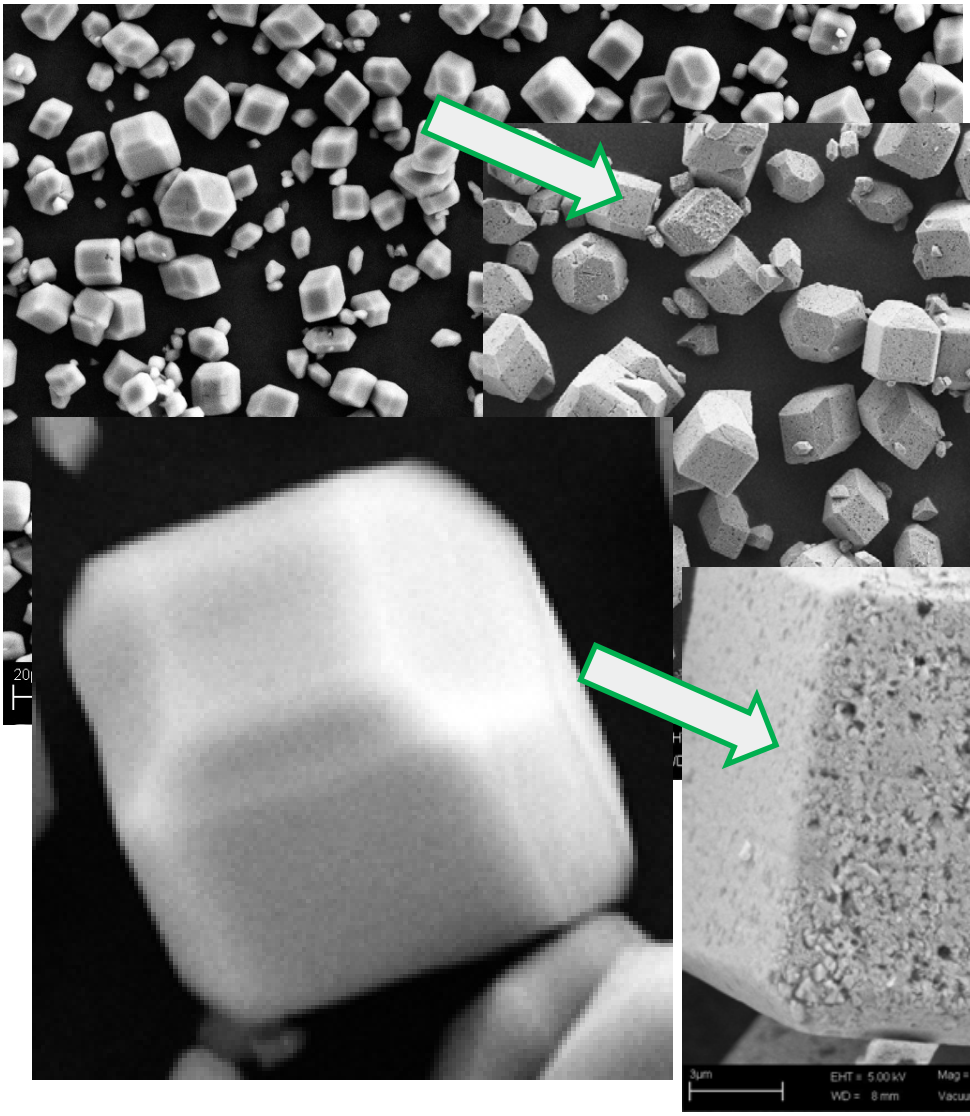
AlH3 as model substance for storage of hydrogene hydride

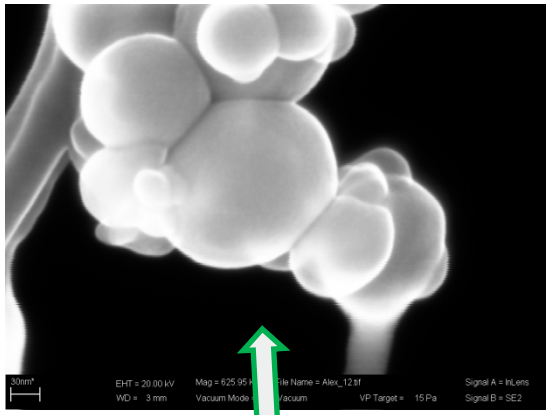
Amorphous light metal powders are about 5%





α-AlH_3 polyhedra as cubes, cubic octahedron and hexagonal prisms





For comparison:
Alex: electro-exploded Al surface **12.28 m²/g**

Resulting Al is not passivated !!!

On dehydrogenation => nano-porous Al structures emerge with surface **15 to 20 m²/g** from AlH3 of 0.69 m²/g surface area

Risks arising from dehydrogenated hydrides*:

- The solids are highly porous or nano-structured to expose high surface areas to easy hydrogen access but also to easy air access on accidents.
- The metals => pure state, highly sensitive to oxidation if contact to air.
- The temperatures are elevated on operation in relation to oxidation reactions of metals, even they are considered moderate.
- In addition gaseous hydrogen is present

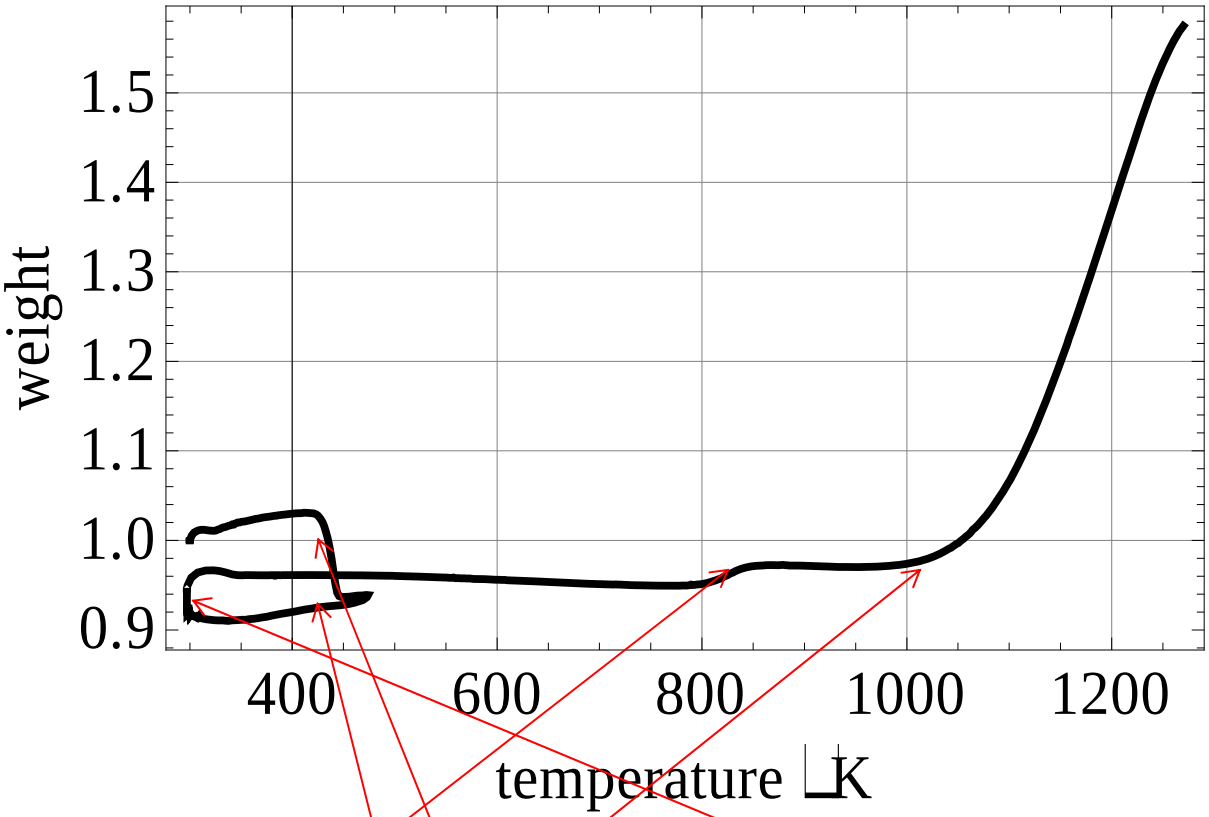
- Passivation reactions: thin protecting oxide layers (for Al ~ 2 – 4 nm)

=> 10-30% of metals might be oxidised at high reaction rates:

  - Thermal explosion of container and the subsequent distribution
  - Explosion of released metal of nano-size in air
  - Even a Deflagration Detonation Transfer might be possible if well distributed nano-particles in air ignite.

Investigation of this effect in more detail!!!

Al from dehydrogenated AlH_3 behaves like Al nano or ultra-fine particles



TG-curve heated (2 K/min) in an inert Ar-atmosphere till 480K initiating dehydrogenation, then cooled down to 50 K with air entrainment causing passivation and subsequent heating to 1300 K (5 K/min) with two steps of oxidation at 850 K and 1100 K

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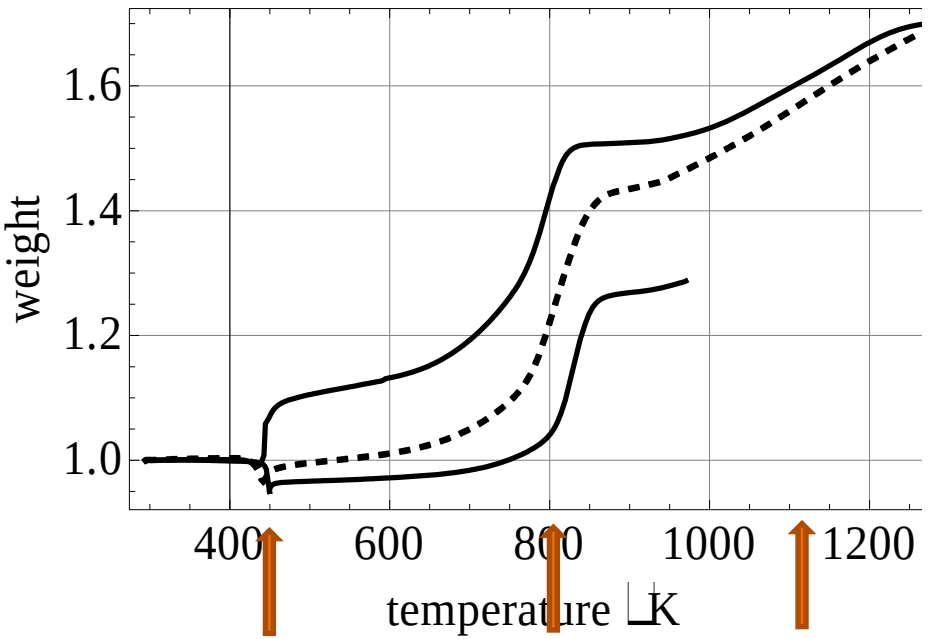
Modelling the reactions => kinetics for simulation of thermal explosions

TG in Air 2, 5, 10K/min

Methods of Thermal Analysis: DSC, TG, X-Ray

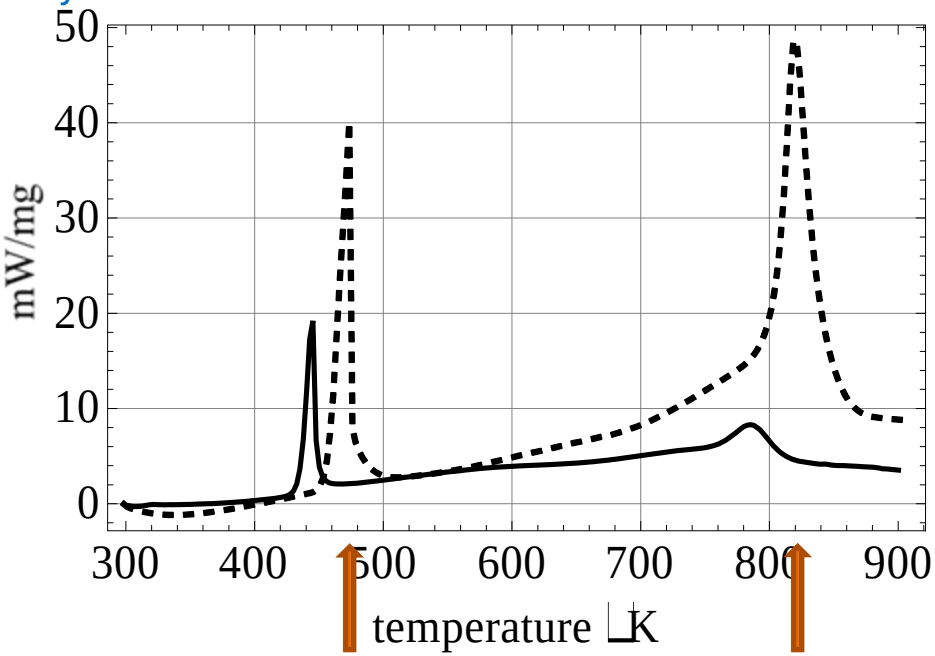
DSC in Air 2, 10 K/min



Dehydrogenation and formation of Al_2O_3 2-4nm passivation layer

chemical controlled 10 nm thick particle oxidation

diffusion controlled particle oxidation



Dehydrogenation and formation of Al_2O_3 2-4 nm passivation layer

Chemical Controlled 10 nm thick particle oxidation

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Reaction at 440 K: AlH_3 => Al => Al-crystallites + O_2 => Al-crystallites with Alumina-layer (higher T, further oxidation)

$$\frac{d[AlH_3]}{dT} = -n\frac{k_1(Z,E,T)}{A}[AlH_3](-\ln[AlH_3])^{\frac{n-1}{n}}$$

Alane dehydration = Avrami-Erofeev-Mechanism

$$\frac{d[Al]}{dT} = \frac{d[AlH_3]}{dt} - \frac{k_{2,cryst}(Z,E,T)}{A} f_{cryst}([Al]) - \frac{k_{3,oxid}(Z,E,T)}{A} f([Al])$$

$$\frac{d[Al_2O_3]}{dT} = \frac{k_{3,oxid}(Z,E,T)}{A} f([Al])$$

Al passivation = 1st order oxidation-Mechanism

Solution:

$$[Al] = ne^{-\frac{Z_2}{A}S_2(E_2T)} \int_0^T k_1(u)\left(\frac{Z_1}{A}S_1(E_1,u)\right)^{n-1} e^{\frac{Z_2}{A}S\ (E_2,u)-(\frac{Z_1}{A}S_1(E_1u))^n} du$$

$$[Al]_{cryst} = \int_0^T k_2(u)[Al](u)du$$

$$[AlH_3] = e^{-(\frac{Z}{A}S(E,T))^n}$$

$$[Al_2O_3] = \int_0^T k_4(u)[Al](u)du$$

$$k(Z,E,T) = Ze^{-\frac{E}{RT}}; S(E,T) = \int e^{-\frac{E}{RT}}dT = Te^{-\frac{E}{RT}}\sum_{n=1}^{N} n!(-1)^{n-1}\left(\frac{RT}{E}\right)^n$$

Kinetic model related to TG and DSC – curves

TG + DSC curves are constructed from the set of equations solving the reaction scheme by:

$TG(T) = W_{alane} - W_{hyd} + p\, W_{oxy}$;
$W_{alane} \sim [AlH_3]$, $W_{oxy} \sim [Al_2O_3]$, $W_{hyd} \sim [Al]$

and the DSC curve by:
$DSC(T) = Q_1\, d[AlH_3]/dT + p\, Q_2\, d[Al_2O_3]/dT$

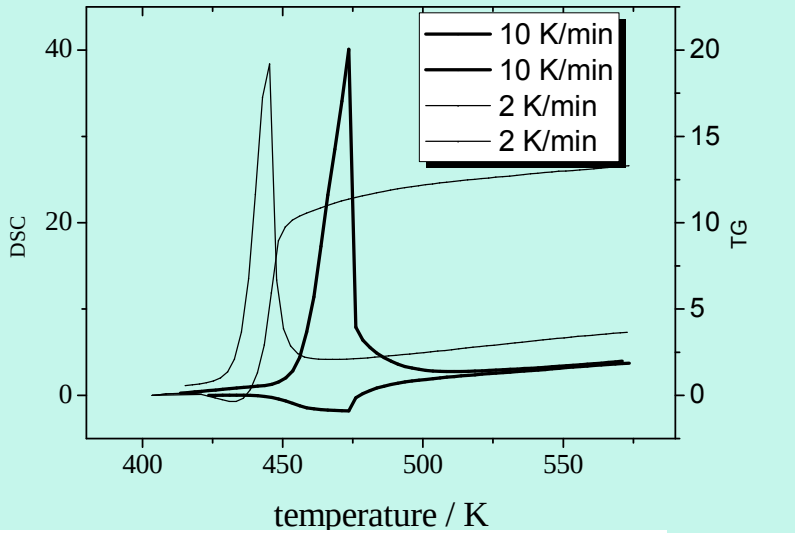
Least squares fit of TG(T) and DSC(T) to achieve E and Z the different reaction

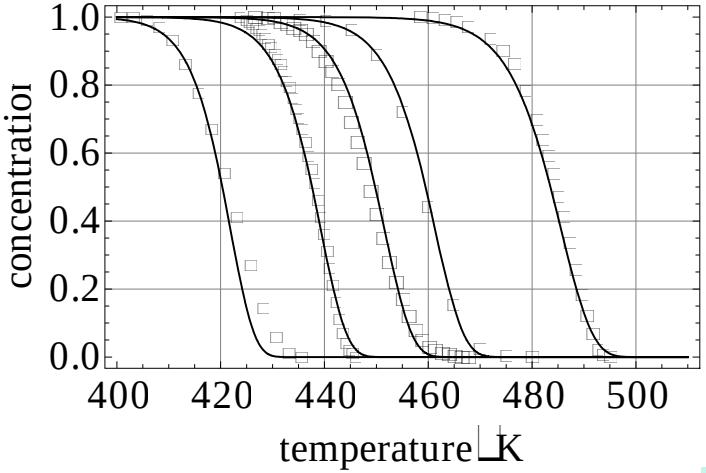
Achieve kinetic parameters of alane dehydrogenation in a separate experiment with total exclusion of air

TG(T) = W = weight of TG curve
DSC(T) = DSC-curve
Q1 and Q2 = heat of reactions, p partial oxidation of Al in passivation reaction

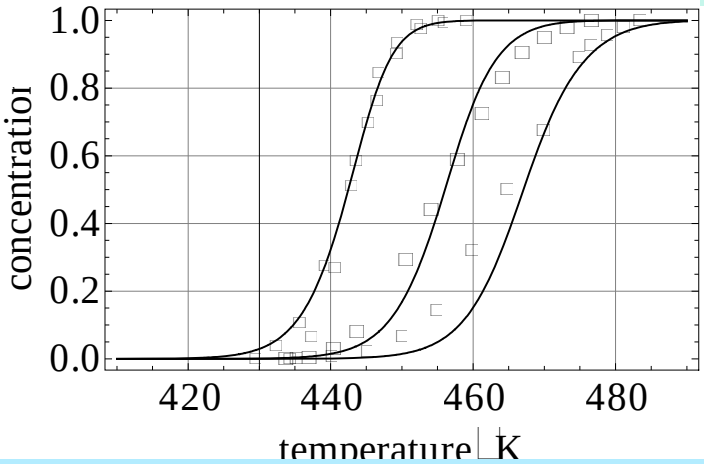
Modelling of Alane dehydrogenation and passivation (at 450 K) – fit of TG / DSC curves at heating rates 0.5 -10 K/min

TG/DSC of dehydr. AlH_3 and Al passivation

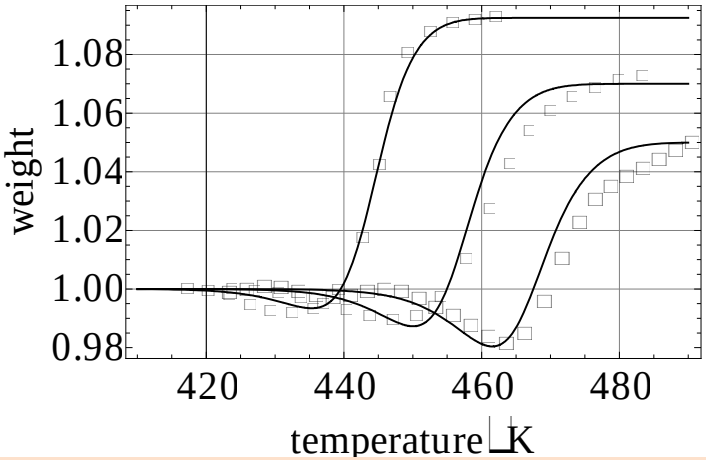




TG of dehydrogenation AlH_3



Recovered TG/conc. of dehydr. AlH_3



Fit of TG: dehydr. AlH_3 and Al passivation

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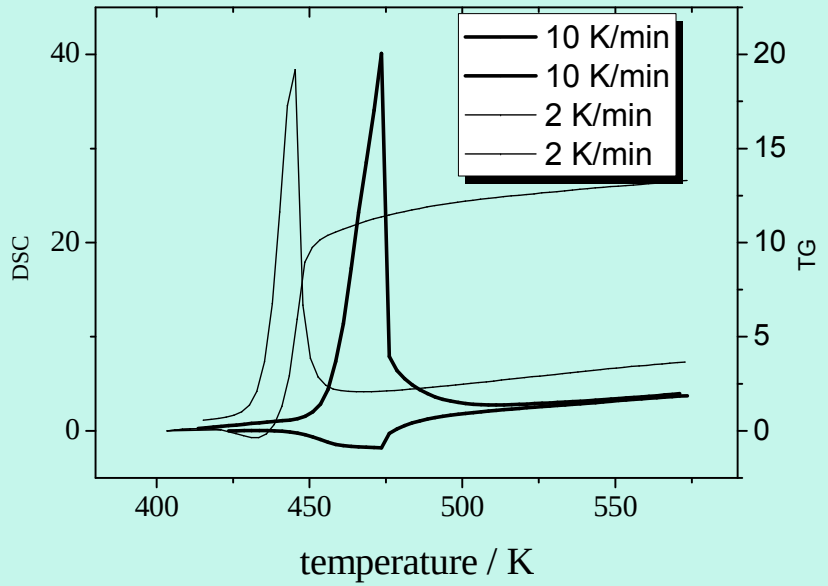
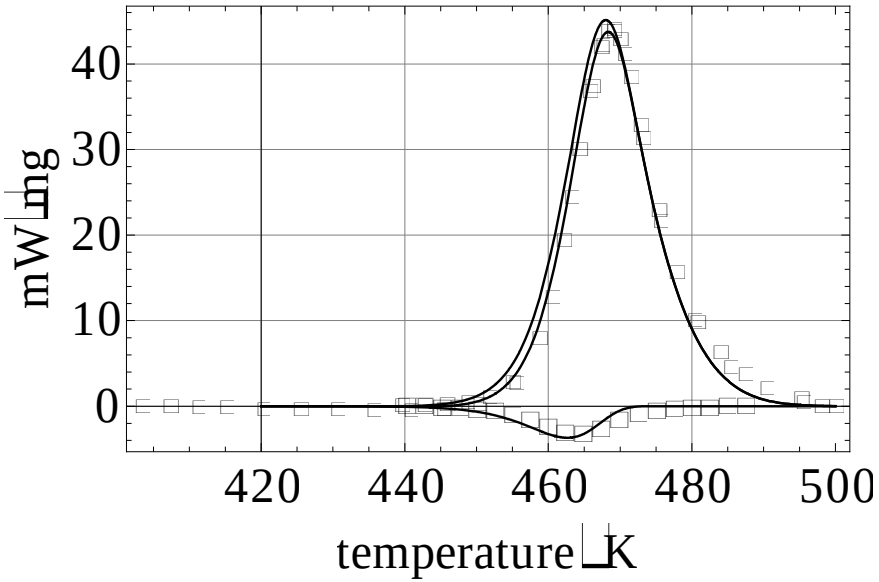
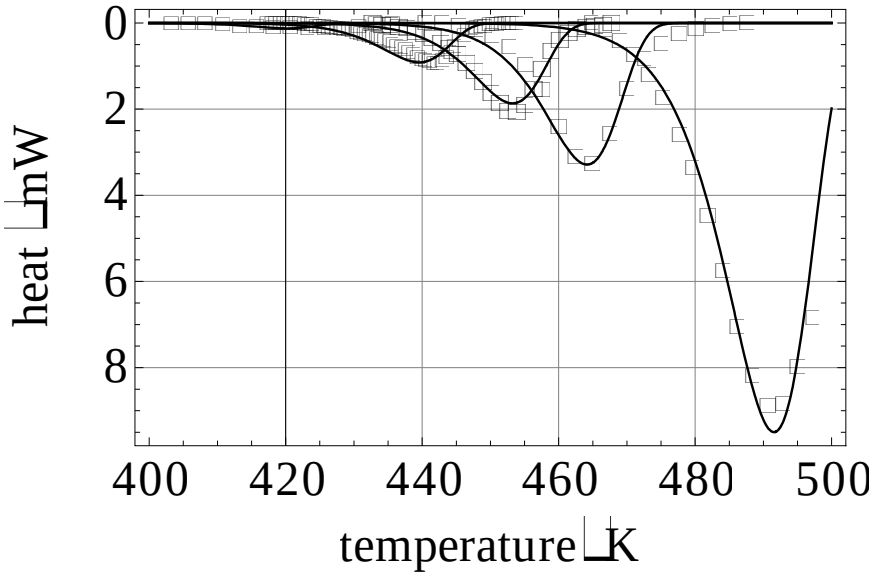


DSC-curve of dehydrogenation in Argon subtracted from DSC-curve in air



Fit of DSC: dehydrogenation of AlH_3 and Al passivation at 10K/min



DSC fit of dehydrogenation AlH_3 at 4 heating rates

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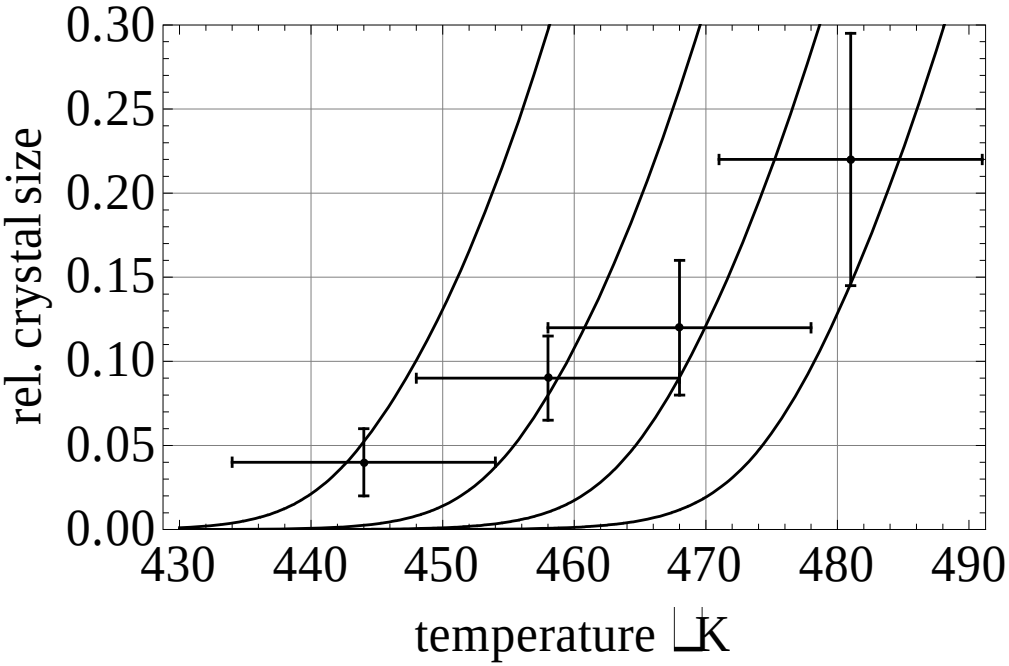

Crystal growths estimated from weight increase on passivation depending on the heating rate 2, 5, 10 and 20 K/min

At higher temperatures of dehydrogenation, less surface area is available for passivation and therefore for the oxidation reaction, which might lead to hazardous thermal explosion

Results of kinetic parameters / *discussion of kinetic compensations effect in the paper*

Method: evaluated simultaneously	Dehydrogenation TG-DSC	Dehydrogenation TG-DSC (fitted n)	Oxidation TG- DSC
Activation energy [J]	115031	117770	83077
Pre-expon. Log Z	11.04	11.37	7.62
Avrami-Erofeev order n	3	2.58	3

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