Alantes as potential hydrogen storage materials – state of the art and perspectives

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The Requirements

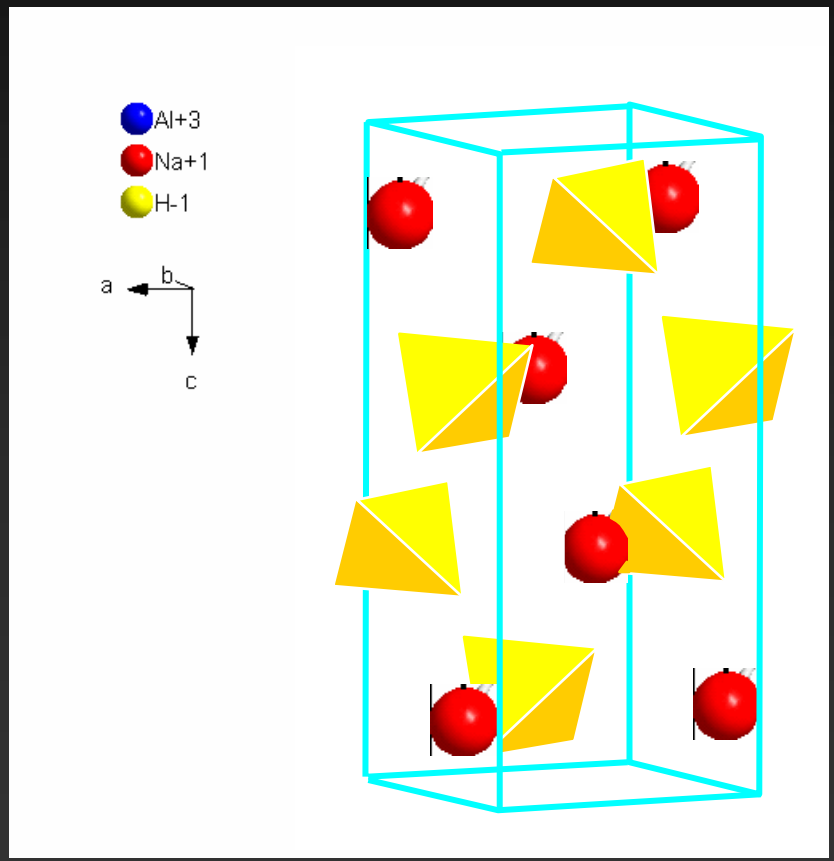
Property	Target
Gravimetric storage density	> 6.5 %
Volumetric storage density	> 6.5 %
De-/rehydrogenation kinetics	Dehydrogenation < 3 h Rehydrogenation < 5 min
Rehydrogenation pressure	< 5 MPa
Equilibrium pressure	Around 0.1 MPa near room temperature
Enthalpic effects	As low as possible (boundary condition reversibility at room temperature)
Safety	As high as possible, i.e. no ignition on exposure to air or water
Cycle stability	> 500
Memory effect	Ideally absent
Price	As low as possible (rough guideline: 100 €/kg H_2)

F. Schüth et al., Chem.Commun. 2249 (2004)

Layout

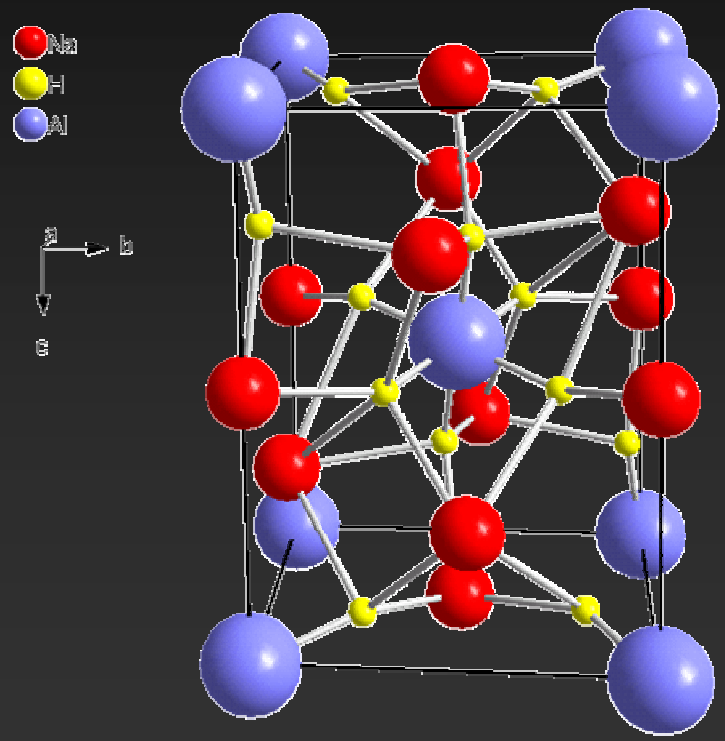
- $NaAlH_4$
  - » Materials synthesis
  - » Catalysts
  - » Mechanism
- Other alanates
- Perspectives

The relevant structures



$NaAlD_4$

B.C. Hauback et al., J.Alloys and Comp. 358, 142 (2003)

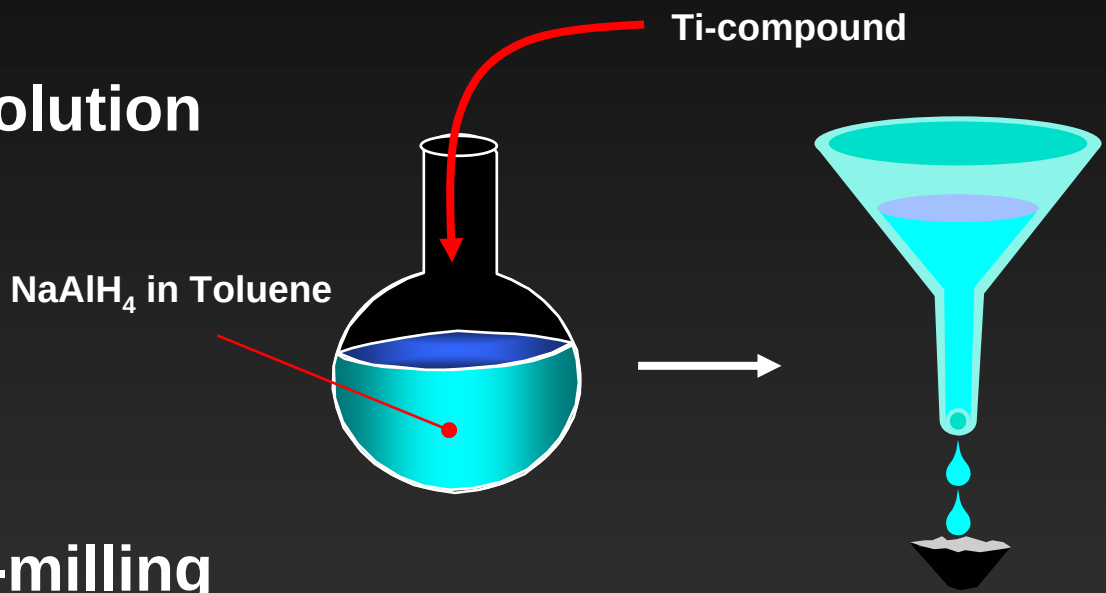


Na_3AlH_6

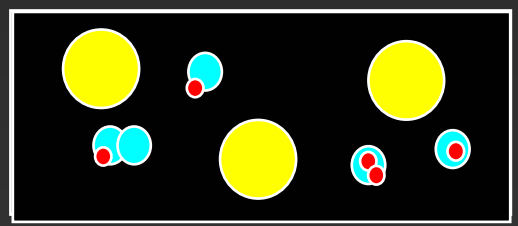
E. Rönnebro et al. J. Alloys and Comp. (2000), 299, 101

The doping procedure

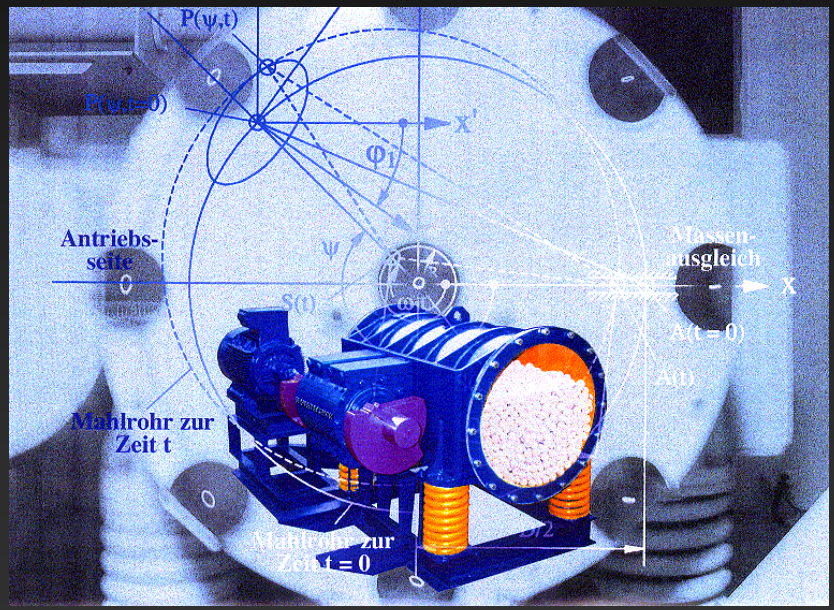
- From solution



- By ball-milling



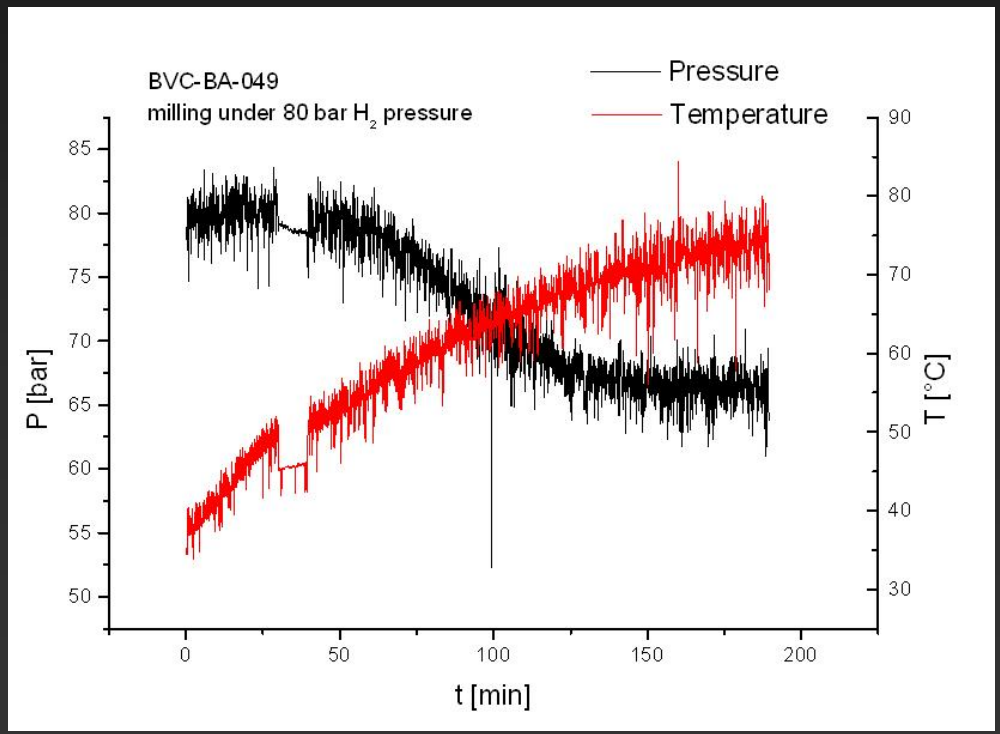
Ball milling scalable



- 10 kg Ti-doped $NaAlH_4$ prepared
- 4 x 2.5 kg batches
- Used as storage material for thermochemical heat storage for Stirling motor

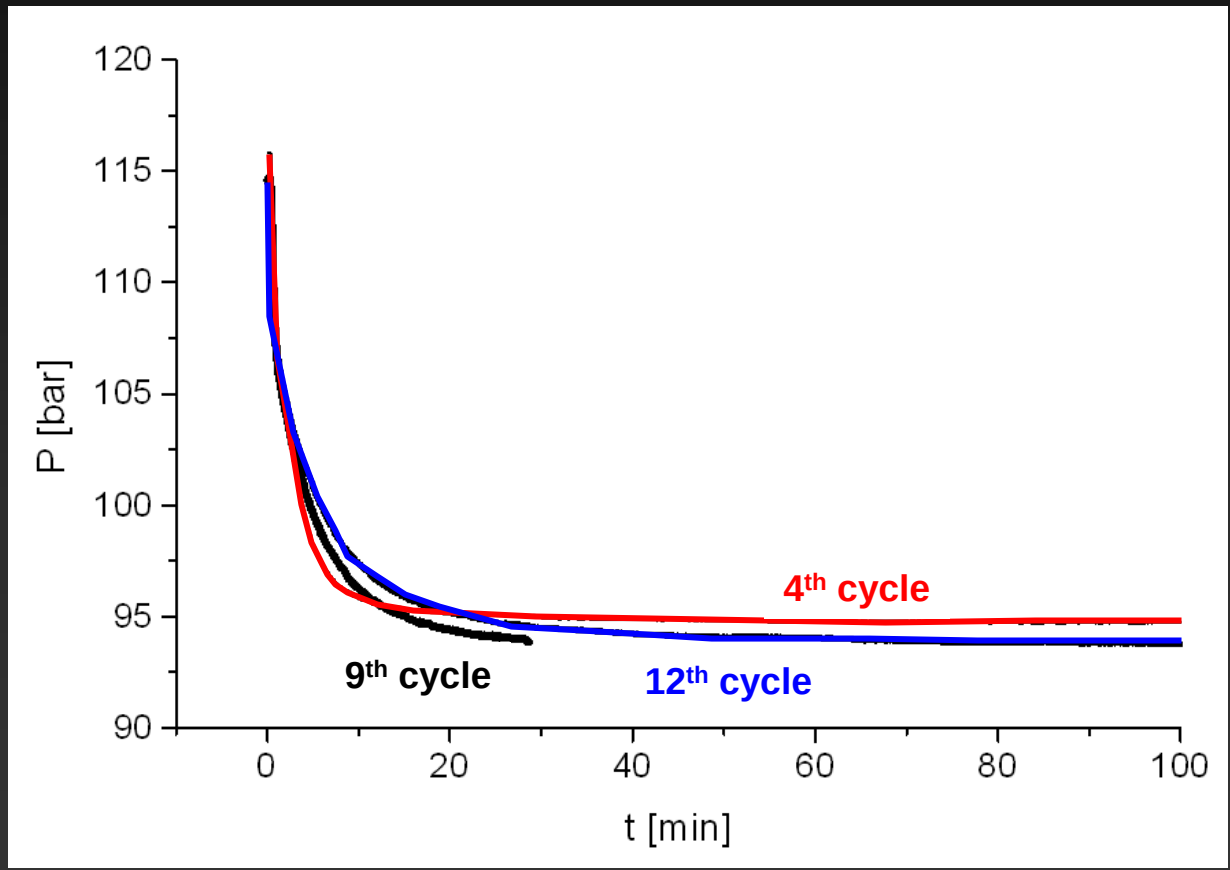
Hydrogenation during ball milling

$$NaH + Al + TiCl_3\ (cat.) \xrightarrow{H_2\ (80\ bar)} Ti{:}NaAlH_4$$



J.M. Bellosta von Colbe et al., submitted

Kinetics of directly synthesized material



J.M. Bellosta von Colbe et al., submitted

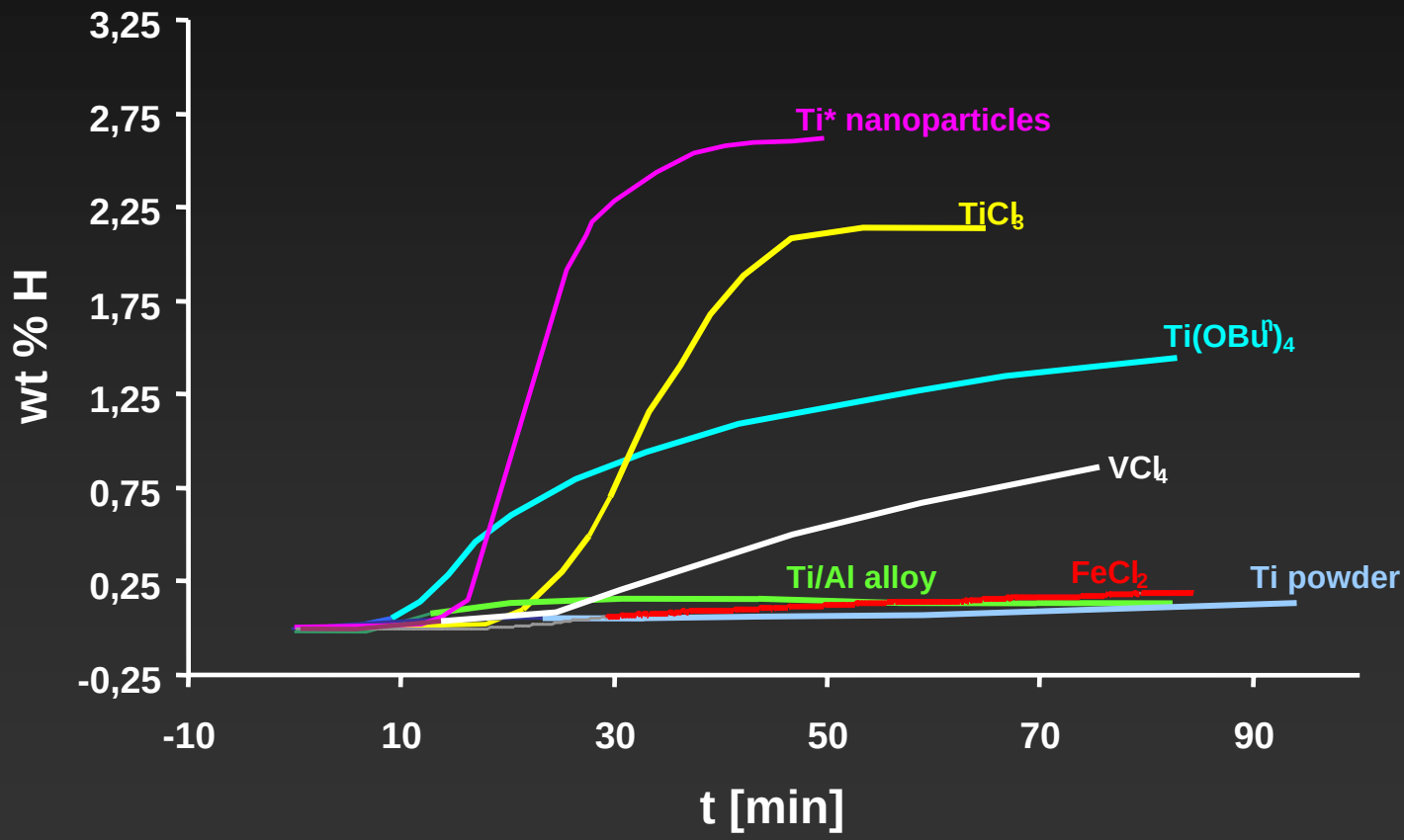
Layout

- $NaAlH_4$
  - » Materials synthesis
  - » Catalysts
  - » Mechanism
- Other alanates
- Perspectives

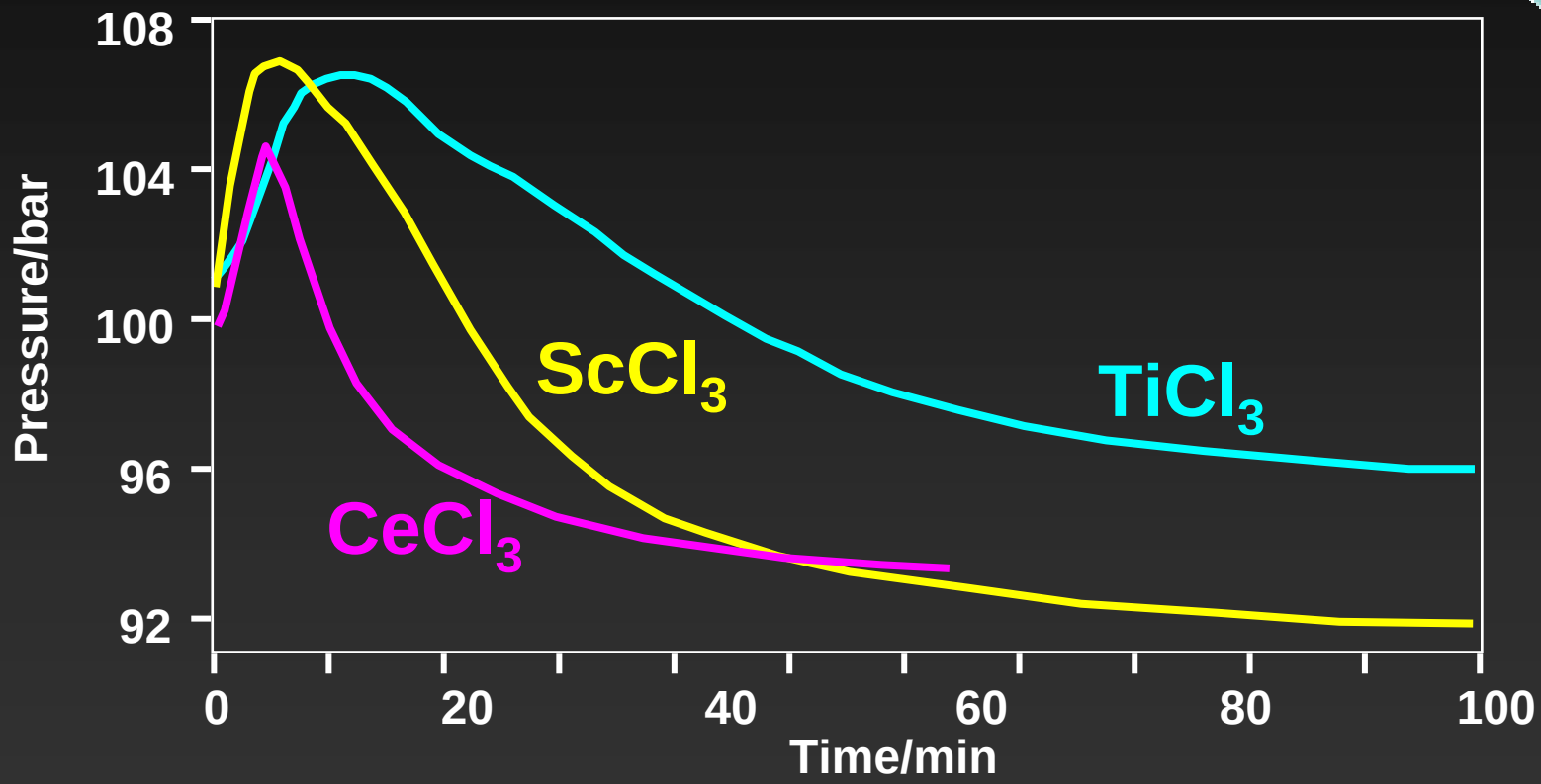
Catalyst systems investigated

- Titanium compounds
  - » Titaniumalkoxides
  - » Titaniumhalogenides
  - » Titanium colloids
  - » Titanium and titanium alloys
- Various transition and rare earth elements
- Carbon
- Diamond
- ...

Catalysts for the $NaAlH_4$ system: Rehydrogenation



New Systems

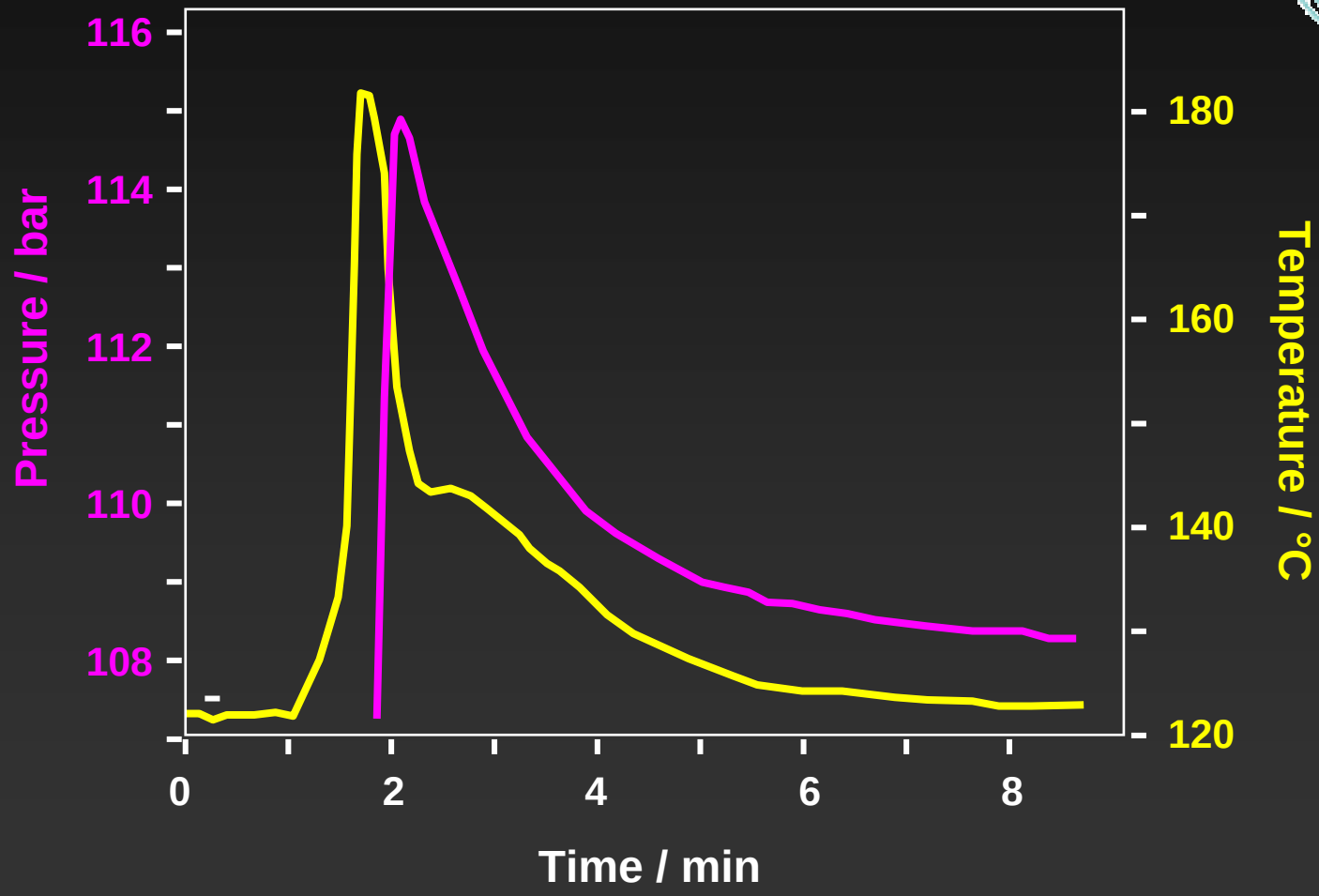


Very high capacity: 4.9 % for $ScCl_3$

Good kinetics at 50 bar: 2 % in 10 min, 3.9 % in 3h

B. Bogdanovic et al., submitted

Most advanced system



System heated to 120°C, then pressurized. Capacity: 3.2 %

Layout

- $NaAlH_4$
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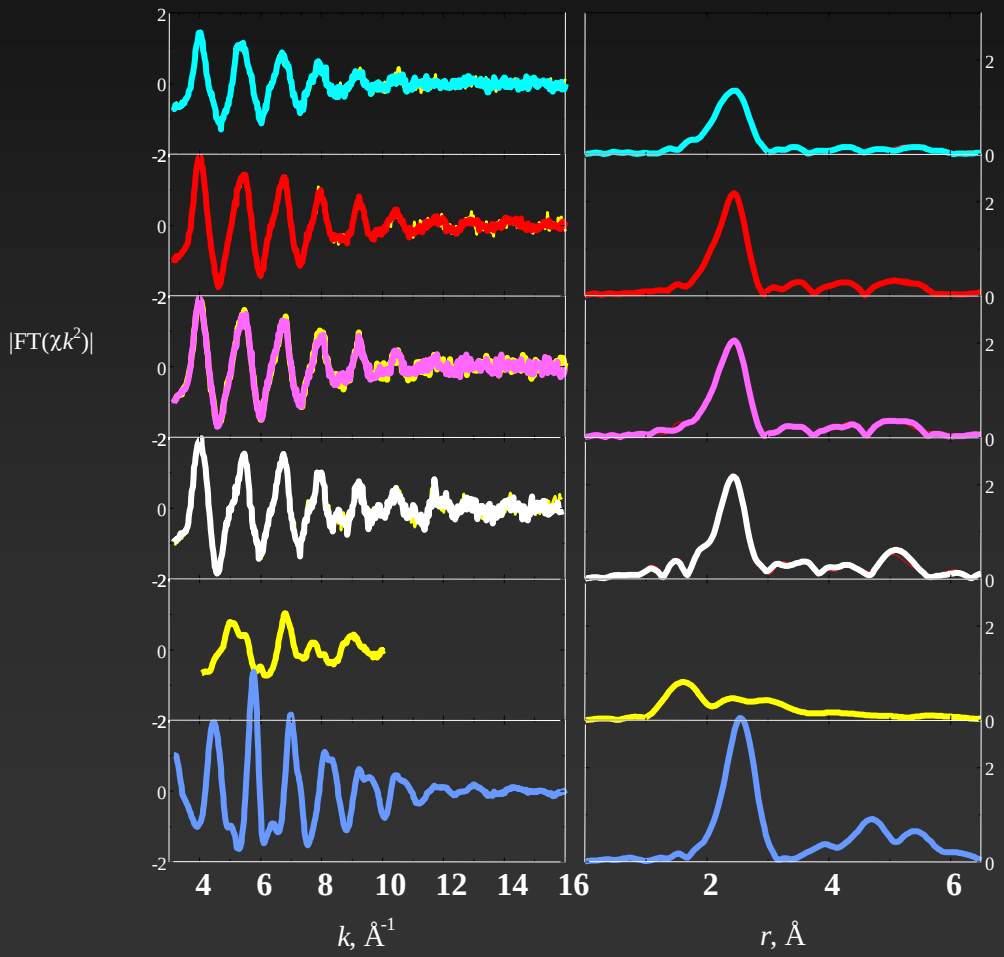
EXAFS Spectra of the Ti K-edge



after ball-milling

after 4 cycles dehy.

after 4 cycles hy.

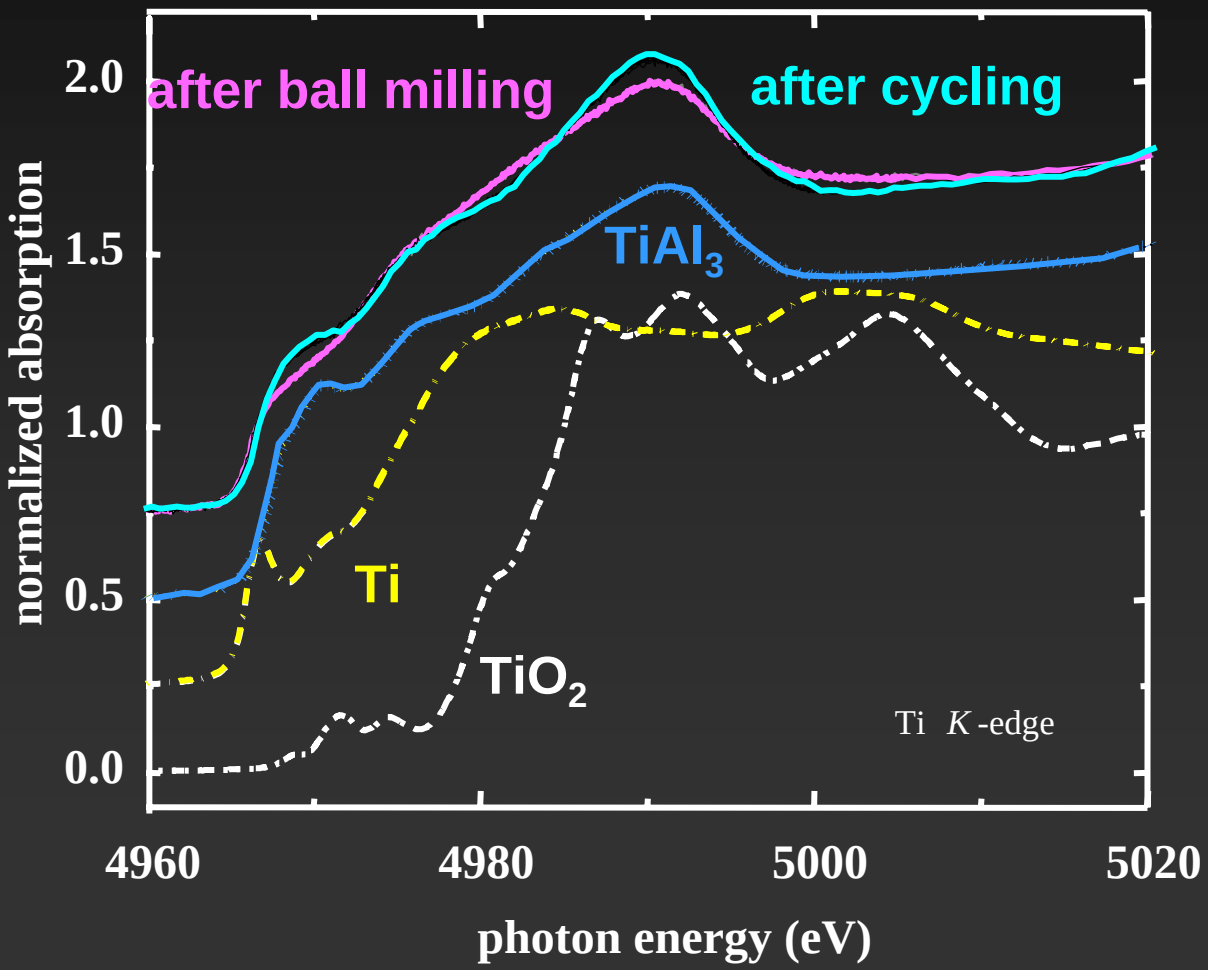
after 100 cycles

TiO_2

Ti metal foil

M. Felderhoff et al. Phys.Chem.Chem.Phys. 6,4369 (2004)

XANES spectra



All samples rather similar

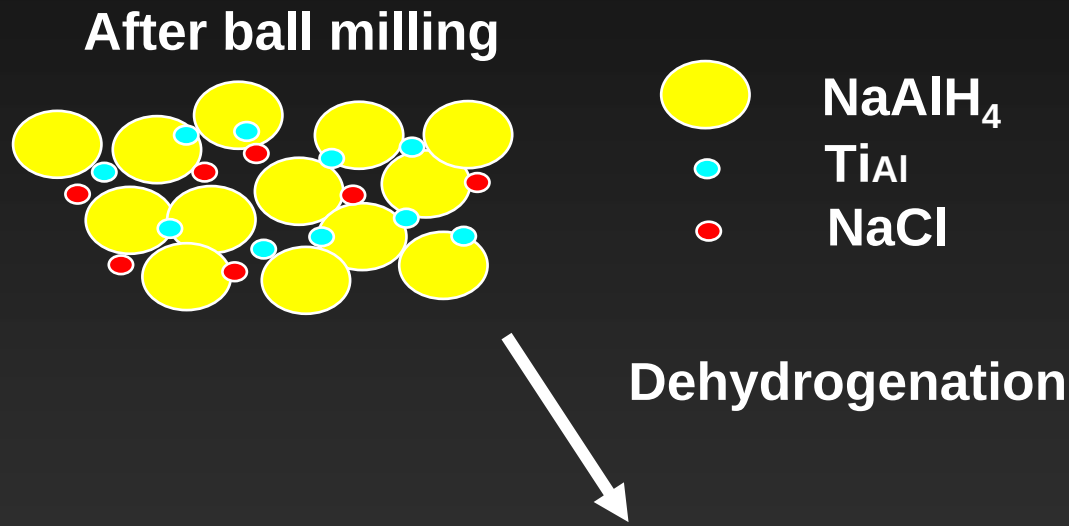
Ti zerovalent

Spectra resemble $TiAl_3$

Ti predominantly in Al-environment

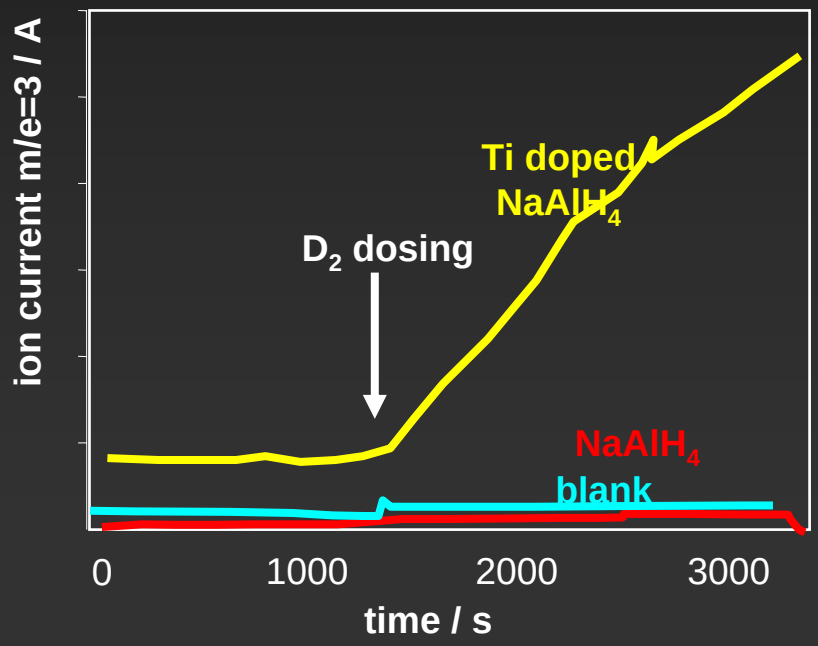
Status of the system during cycling

$3\ NaAlH_4 + TiCl_3 \longrightarrow Ti + 3\ NaCl + 3\ Al + 6\ H_2$



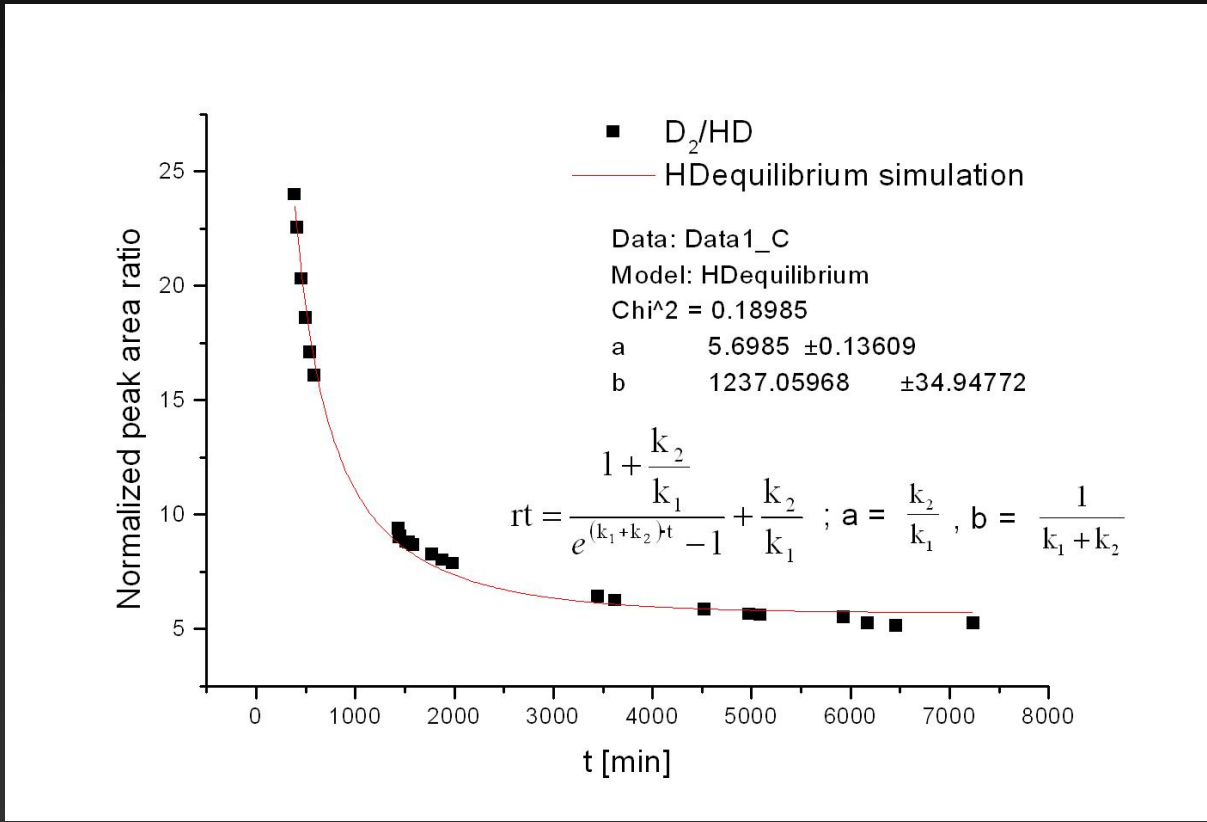
One role of titanium: H_2 dissociation

- DFT calculations point toward Ti/Al on surface as site for hydrogen dissociation (S. Chaudhuri, J.T. Muckerman, J.Phys.Chem.B. 109, 6952 (2005))
- Confirmed by isotope exchange experiments



J.M. Bellosta von Colbe et al., submitted

Quantification



Analysis reveals that bulk hydrogen from alanate participates in exchange reaction

J.M. Bellosta von Colbe et al., submitted

Mass transfer

- Still an open issue
- Surface and bulk diffusion of alanates has been suggested
- Alanes have also been suggested as intermediates, as well as a Na_2AlH_5 species

Layout

- $NaAlH_4$
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  - » Mechanism
- **Other alanates**
- Perspectives

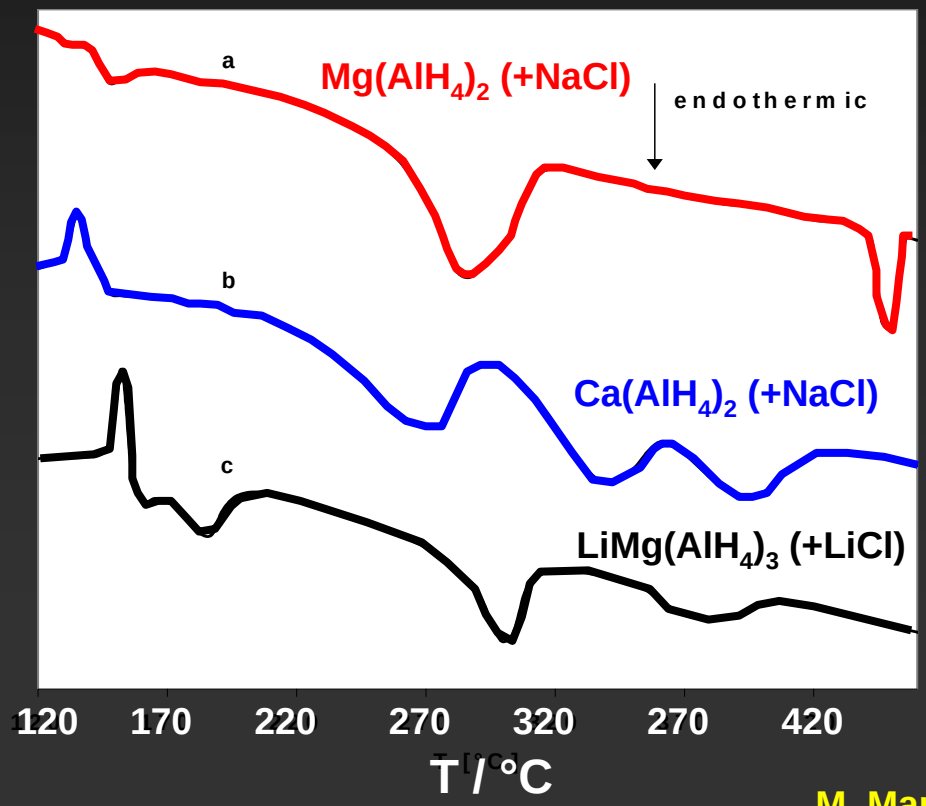
$Mg(AlH_4)_2$

- Structurally described (THF-adducts and neat compound) by the group of Fichtner (J.Alloys and Comp. 345, 286 (2002))
- Synthesized by metathesis of alanate precursors with magnesium halides in solvents
- Alternative: Ball milling of $NaAlH_4$ or $LiAlH_4$ with $MgCl_2$ (M.Mamatha et al., J.Alloys and Comp., in press)
- Titanium catalyzes decomposition as for $NaAlH_4$
- Thermodynamics unfavorable for hydrogen storage

Other alanates

- K_2NaAlH_6 Poster by Hauback et al.
- Solvent free metathesis via ball milling

  $NaAlH_4$ + metal halide ⟶ NaCl + metal alanate



DSC: none of the three alanates useful for storage

M. Mamatha et al., J.Alloys and Comp., in press

Layout

- $NaAlH_4$
  - » Materials synthesis
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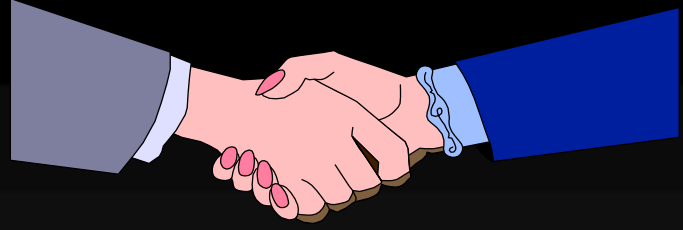
Perspectives

- The $NaAlH_4$ system is almost optimized, heat management seems to be limiting factor
- Low pressure rehydrogenation still an issue
- Other studied alanates thermodynamically unfavorable
- Titanium catalysis works for other alanates
- There is a wealth of alanates which has not been investigated yet

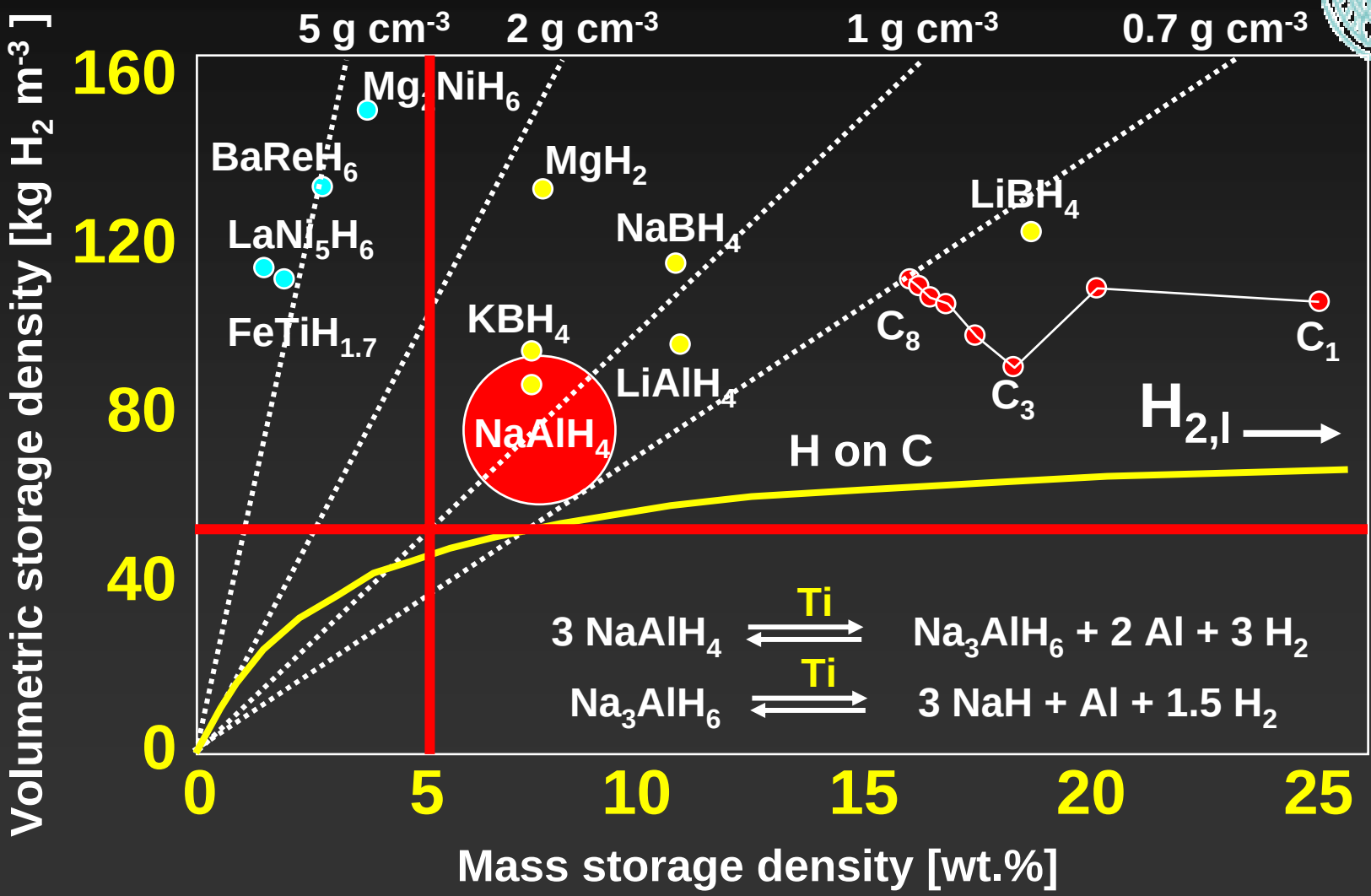


M. German
M. Härtel
T. Kratzke
M. Mamatha
A. Pommerin
K. Schlichte
W. Schmidt
M. Schwickardi
B. Spliethoff
A. Taguchi
J. von Colbe de Bellosta
C. Weidenthaler
B. Zibrowius

H. Bönnemann, Mülheim
S. Kaskel, Mülheim
W. Grünert, Bochum
K. Klementiev, Bochum
U. Eberle, Adam Opel AG
F. Mertens, Adam Opel AG
G. Arnold, Adam Opel AG

Adam Opel AG
Bomin Solar
FCI

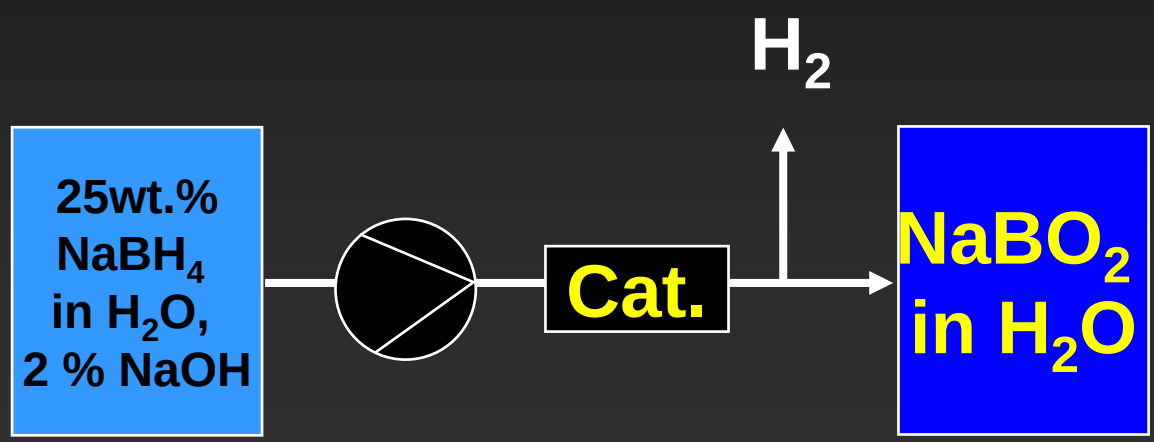
The „materials landscape“



Adapted from Schlapach and Züttel, Nature 414, 353 (2001)

Hydrolytic routes: Hydrogen on demand™

$$NaBH_4 + 2\,H_2O \longrightarrow 4\,H_2 + NaBO_2 \qquad 10.8\ \%$$



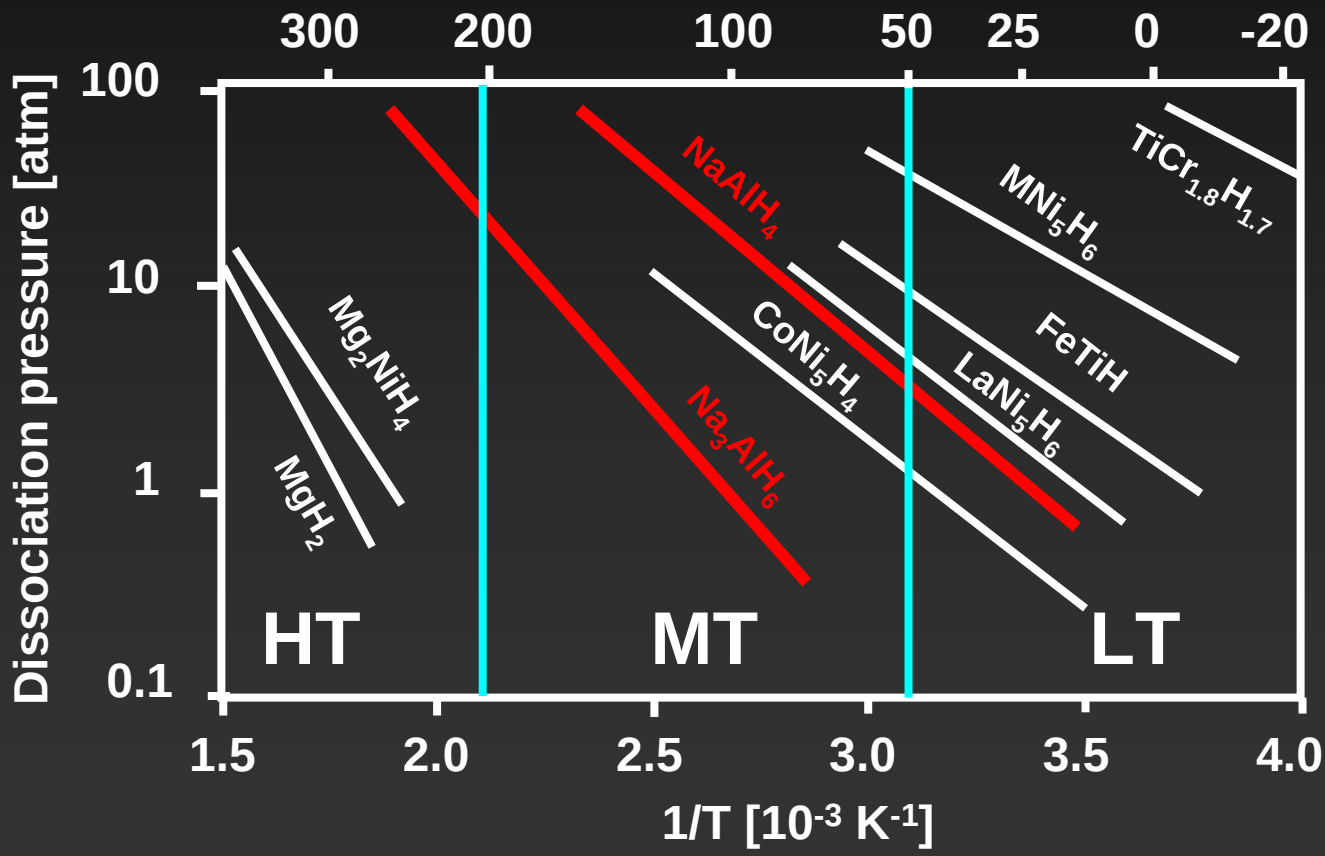
Advantages: Liquid fuel like conventional
no risk in absence of catalyst

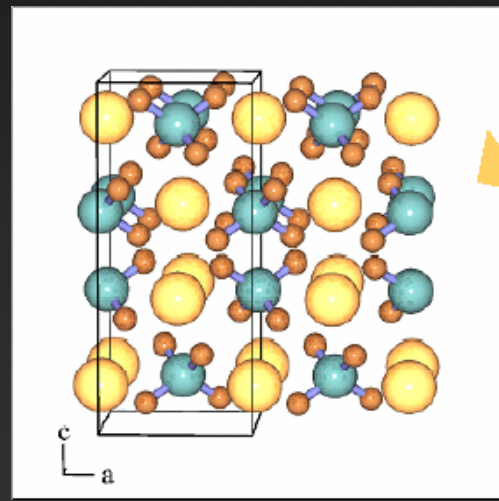
MILLENNIUM CELL

Problems with Hydrolytic Storage

- Modules have to be exchanged (solid)
- Quite difficult control problems (solid)
- Not very energy efficient
  - » production of alkali metals
  - » or production of metal hydrides
- Expensive, even if prices would drop
- Probably applications only in high-end niches

The alternative: reversible hydrides





B. Bogdanovic et al. J.Alloy Compd. 302, 36 (2000)

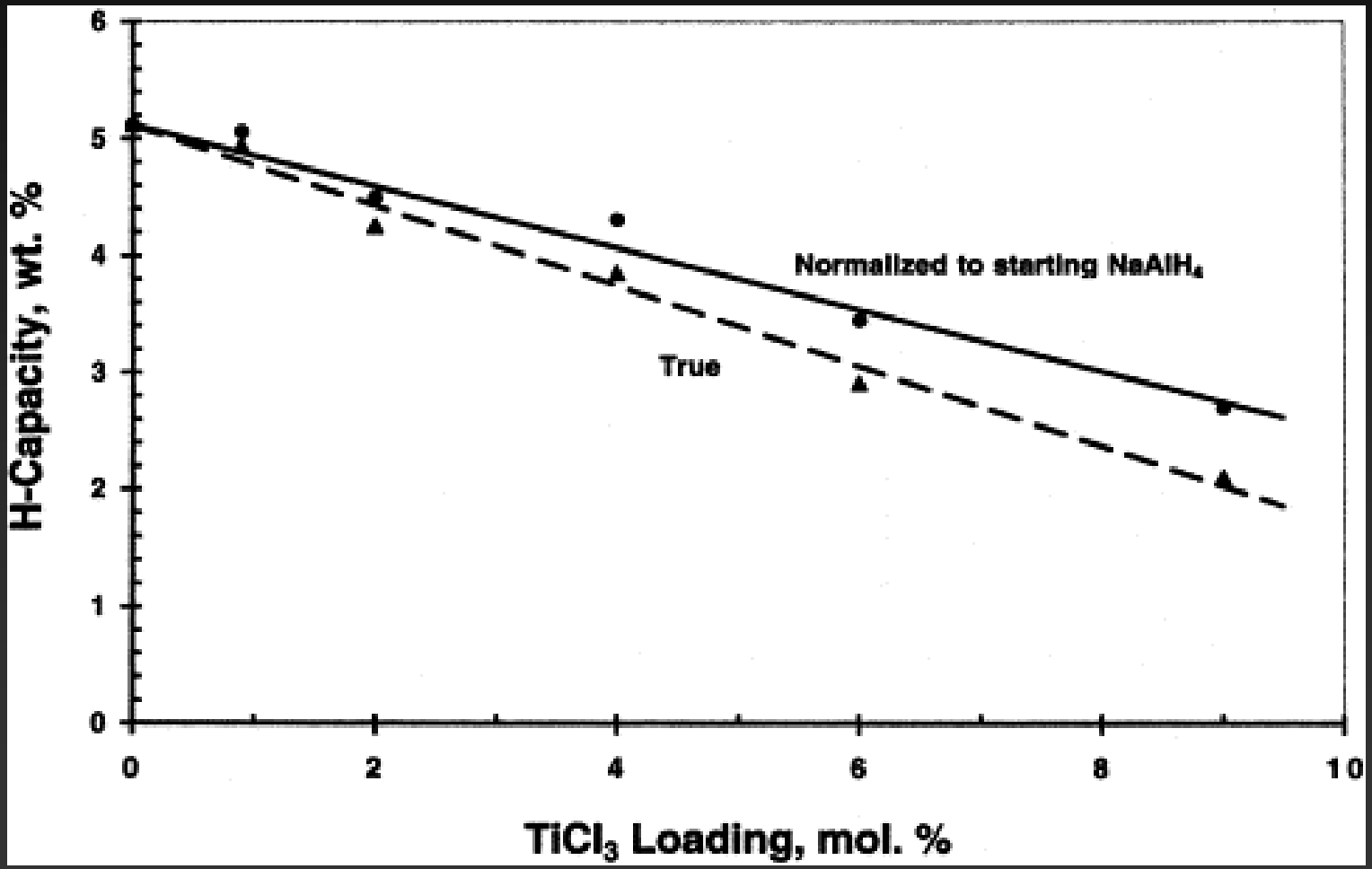
$NaAlH_4$ as storage material

- **Problem: $NaAlH_4$ is normally not reversible**
- **Solution: Catalysis of de-/rehydrogenation via metal doping**

1 H 1.00794																1 H 1.00794	2 He 4.002602
3 Li 6.941	4 Be 9.012182											5 B 10.811	6 C 12.0107	7 N 14.00674	8 O 15.9994	9 F 18.9984032	10 Ne 20.1797
11 Na 22.989770	12 Mg 24.3050											13 Al 26.981538	14 Si 28.0855	15 P 30.973761	16 S 32.066	17 Cl 35.4527	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.955910	22 Ti 47.867	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938045	26 Fe 55.845	27 Co 58.933200	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.92160	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.90585	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.42	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.90447	54 Xe 131.29
55 Cs 132.90545	56 Ba 137.327	57 La 138.9055	72 Hf 178.49	73 Ta 180.9479	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.217	78 Pt 195.078	79 Au 196.96655	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.98038	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 (269)	111 (272)	112 (277)		114 (289) (287)		116 (289)		118 (293)

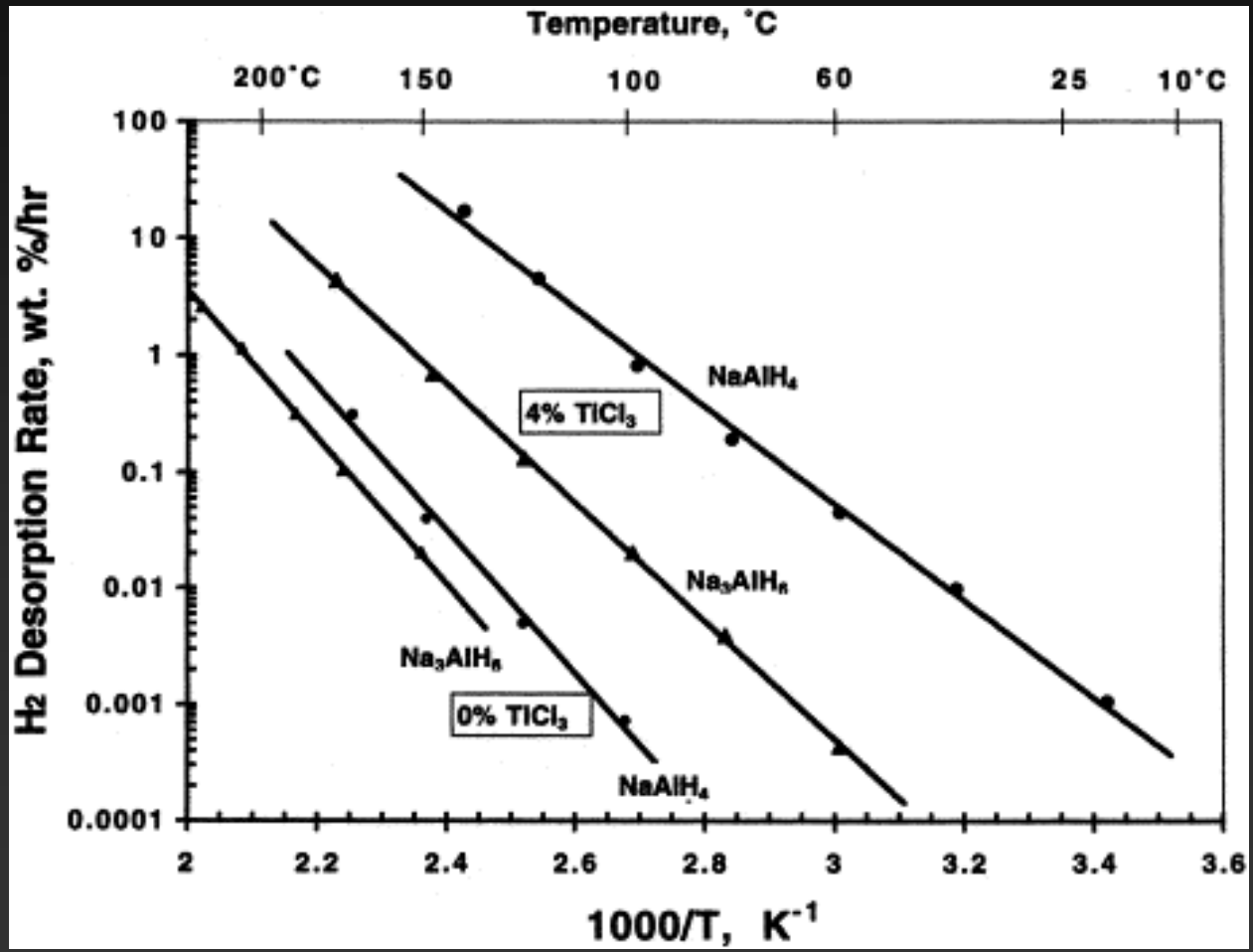
B. Bogdanovic, M. Schwickardi, J.Alloy Compd. 253-254, 1 (1996)

Choice of dopants



G. Sandrock et al. J.Alloy Compd. 339, 299 (2002)

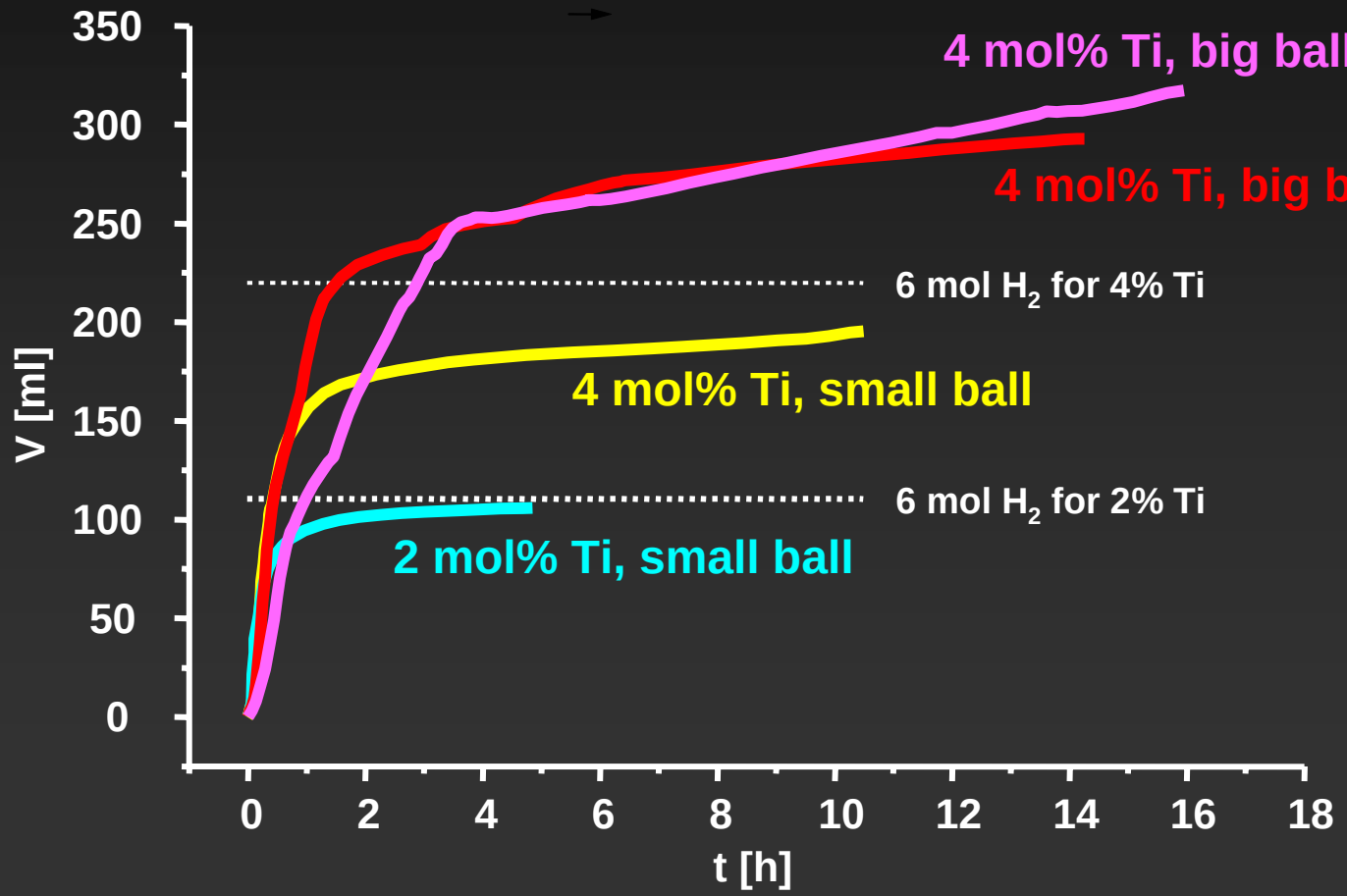
Effect of the catalyst during desorption



G. Sandrock et al. J.Alloy Compd. 339, 299 (2002)

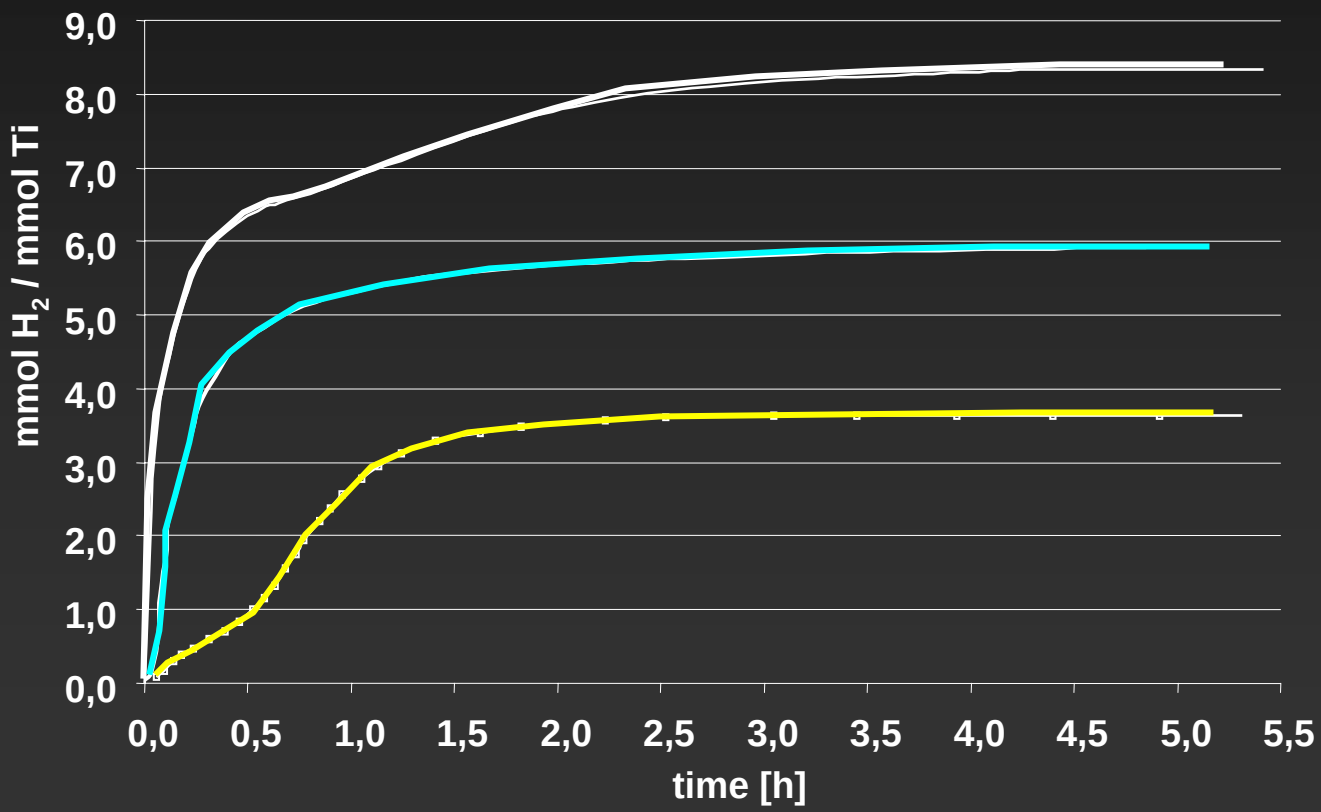
What happens during ball-milling?

$$3\ NaAlH_4 + TiCl_3 \longrightarrow Ti + 3\ NaCl + 3\ Al + 6\ H_2$$



B. Bogdanovic et al. J.Alloy Compd. 370, 104 (2004)

Different Ti-precursors

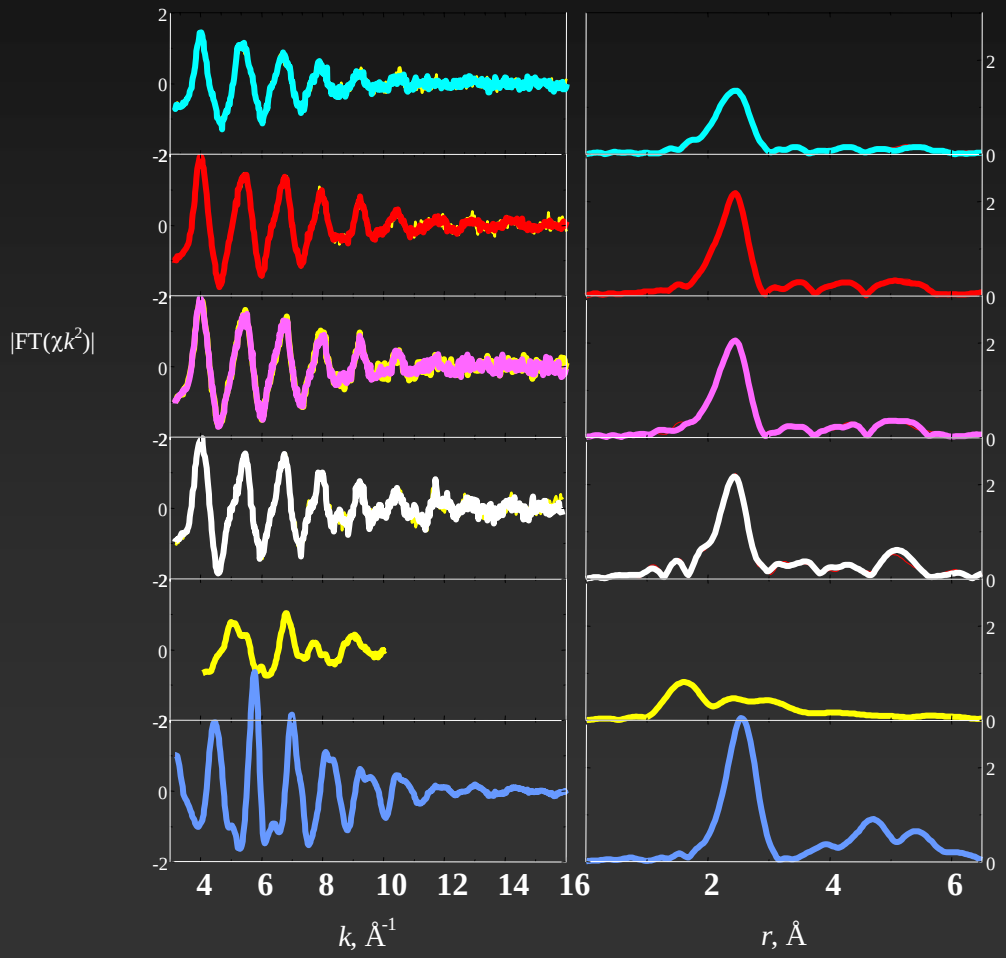


$TiCl_4 \xrightarrow{4\ NaAlH_4} 8\ H_2$

$TiCl_3 \xrightarrow{3\ NaAlH_4} 6\ H_2$

$TiCl_2 \xrightarrow{2\ NaAlH_4} 4\ H_2$

Lessons learned



Ti in all samples in essentially identical environment

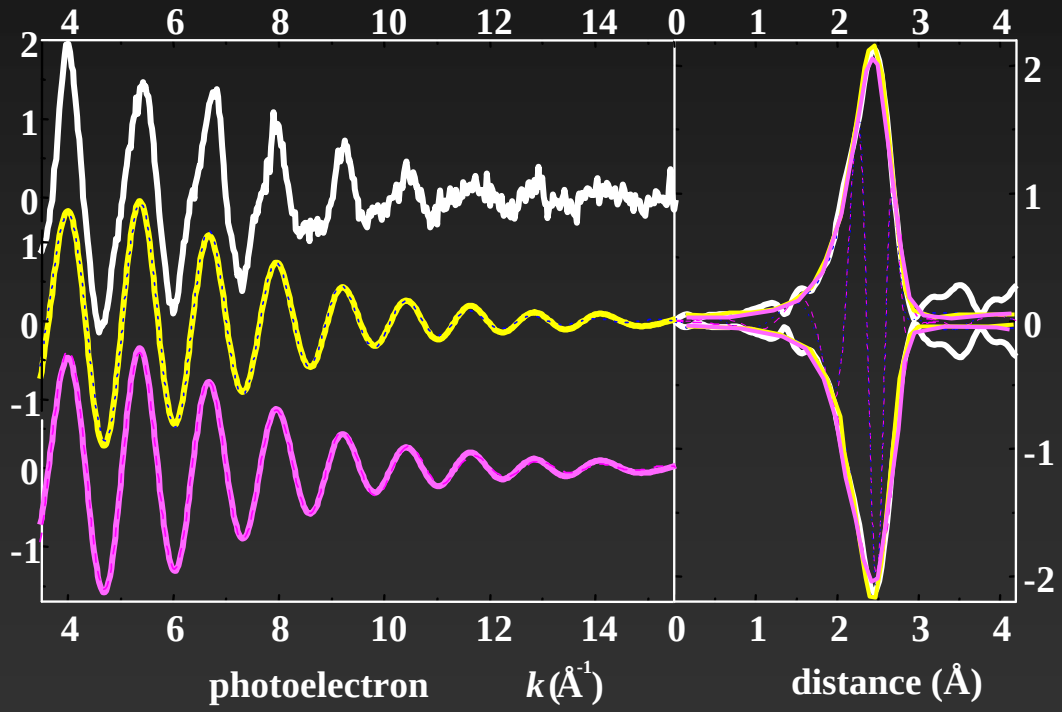
no oxidic environment, but first coordination sphere like Ti-metal

What is the atom in the first coordination shell?

Ti-2 4mol % $TiCl_3$ doped $NaAlH_4$ dehyd.

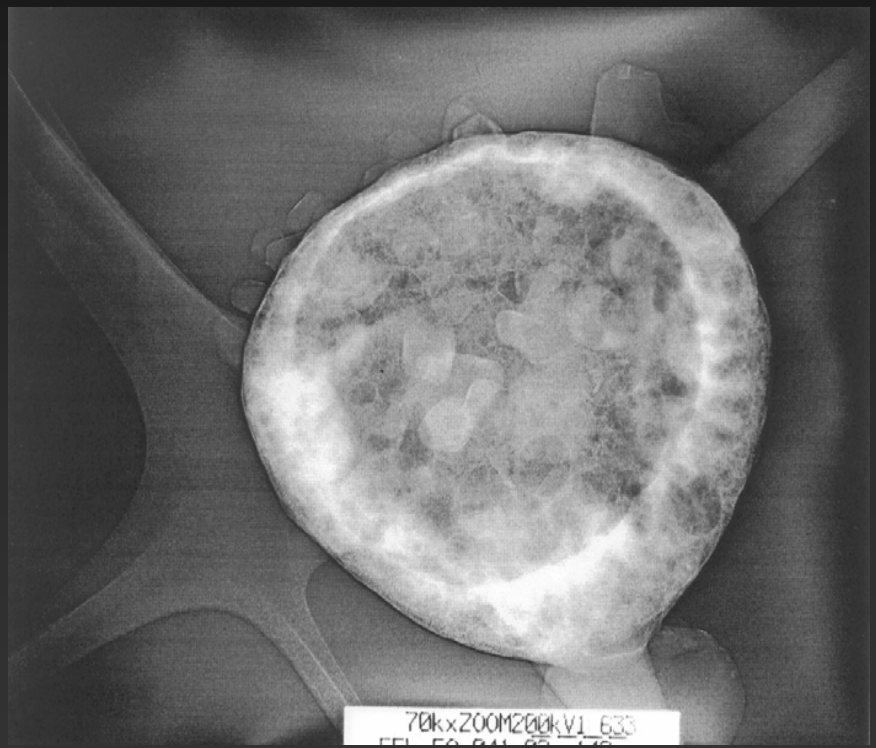
fit with Ti-Al

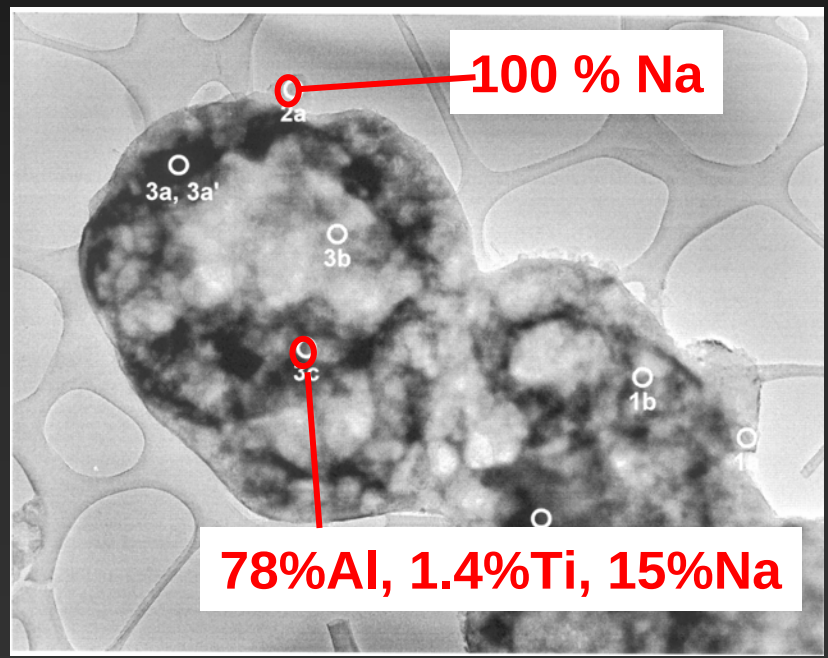
fit with Ti-Ti



the differentiation between these two contributions is impossible

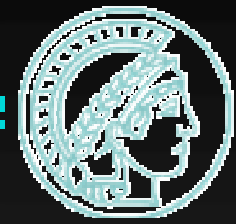
Decomposition reaction: morphologies



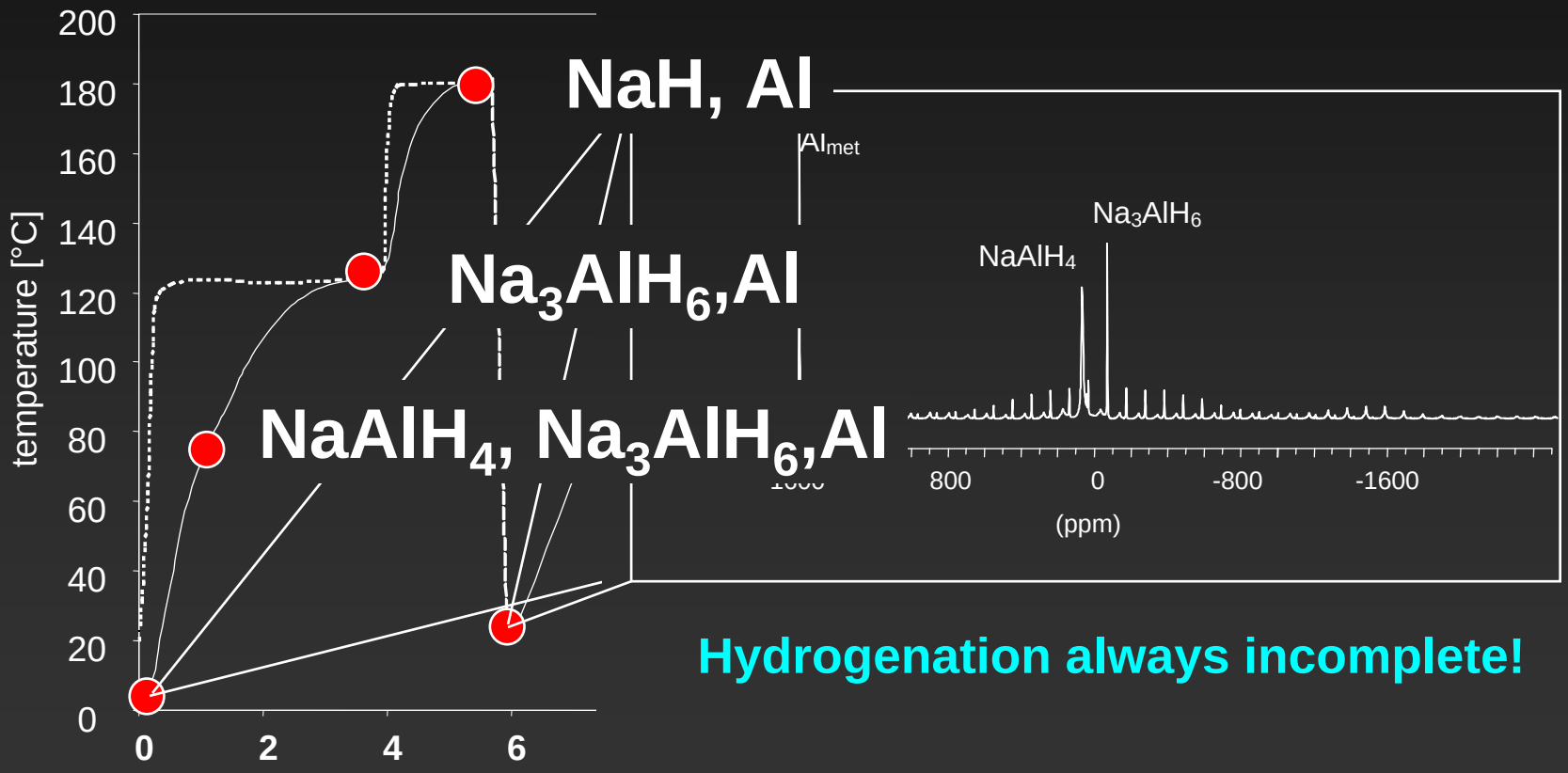


M. Felderhoff et al. Phys.Chem.Chem.Phys. 6,4369 (2004)

The decomposition process



$3\ NaAlH_4 \longrightarrow Na_3AlH_6 + 2\ Al + 3\ H_2 \longrightarrow 3\ NaH + 3\ Al + 4.5\ H_2$



Hydrogenation always incomplete!

B. Bogdanovic et al. J.Alloy Compd. 350, 246 (2003)

What happens during doping?

$$TiCl_4 + 4\,LiAlH_4 \xrightarrow{\text{Ether, -110 °C}} [Ti(AlH_4)_4] + 4\,LiCl$$

$$[Ti(AlH_4)_4] \xrightarrow{\text{1-3 days, r.t.}} Ti + 4\,Al + 8\,H_2$$

E. Wiberg, R. Usón, *Z. Naturforsch*., **1951**, *6b*, 392-393.

$$TiCl_4 + 4\,LiAlH_4 \xrightarrow{\text{ball-milling, 10 min}} Ti + 4\,Al + 8\,H_2 + 4\,LiCl$$

$$Ti + 4\,Al + 8\,H_2 + 4\,LiCl \xrightarrow{\text{1-3 days, r.t.}} TiAl_3 + Al$$

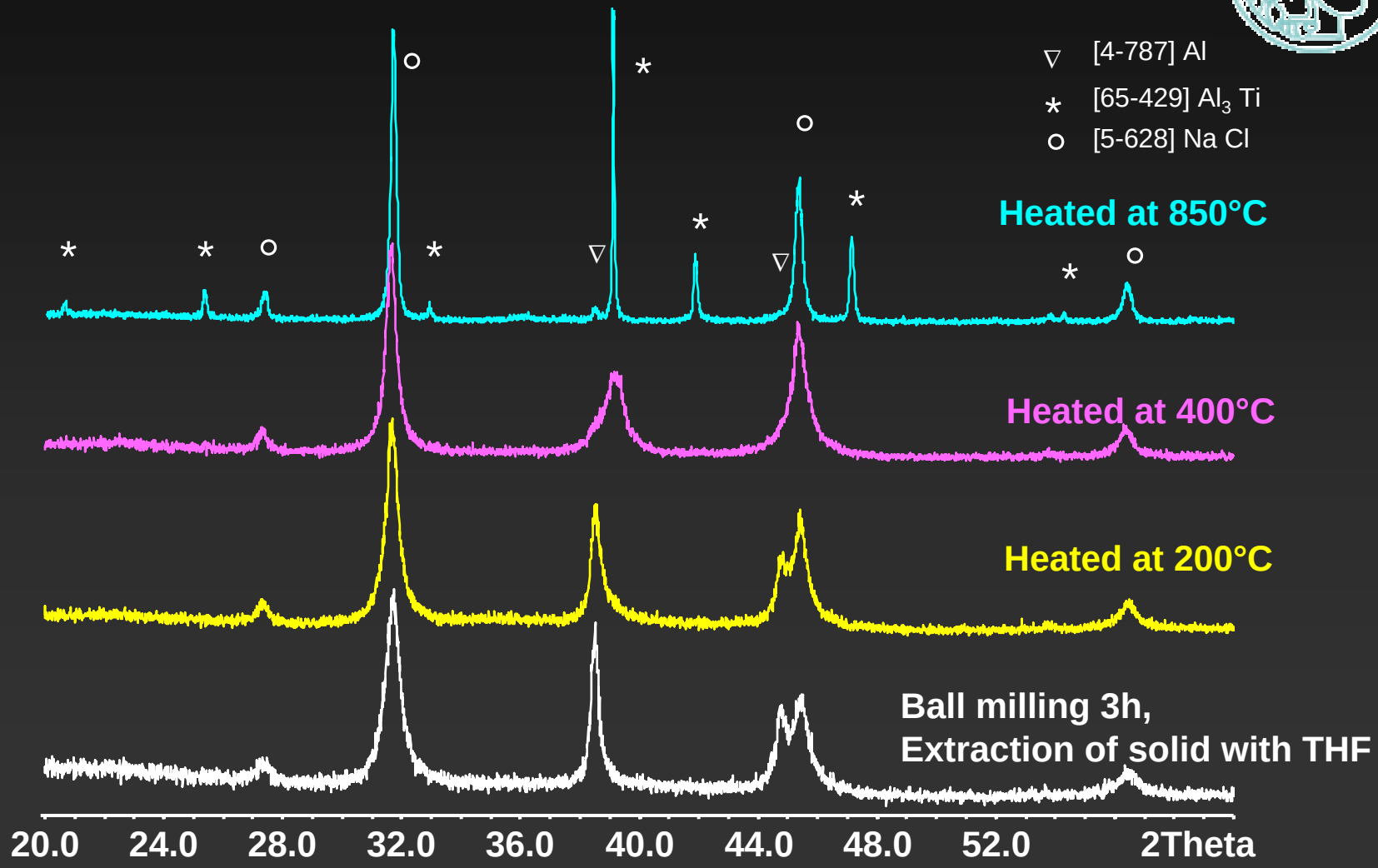
V.K. Pecharsky et al., *J. Alloys Comp*., **2001**, *329*, 108-114

$$TiCl_3 + 3\,NaAlH_4 \xrightarrow{\text{ball-milling}} Ti + 3\,Al + 3\,NaCl + 3\,H_2$$

$$TiCl_3 + 3\,NaAlH_4 \rightarrow [Ti(AlH_4)_3] \rightarrow TiAl_3 + 3\,NaCl + 6\,H_2$$

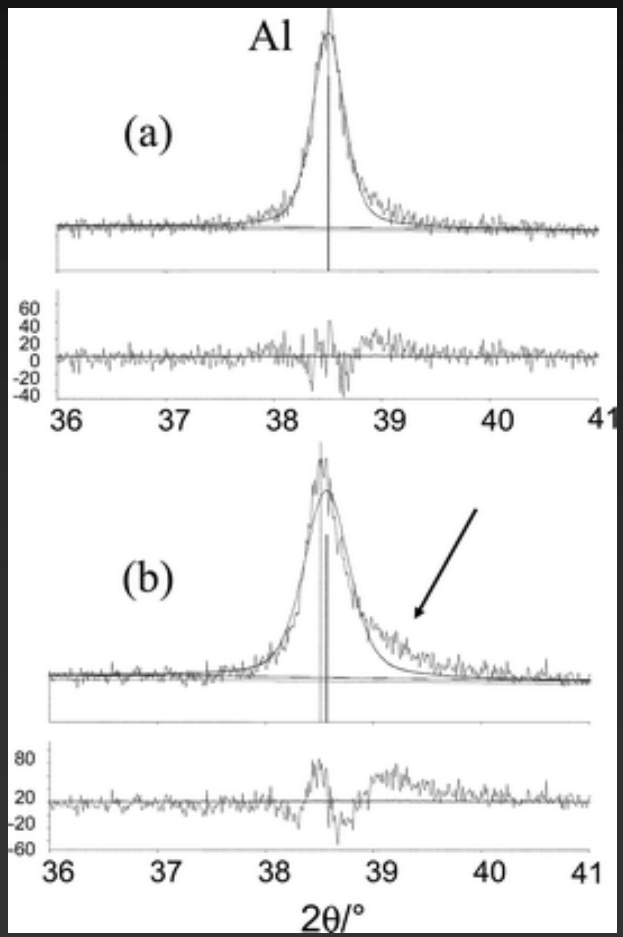
E.H. Majzoub, K.J. Gross, *J. Alloys. Comp*. **2003**, *356-357*, 363-367

Highly dispersed amorphous Ti after doping



C. Weidenthaler et al. Phys.Chem.Chem.Phys. 5, 5149 (2003)

First indication for alloy formation at 200°C

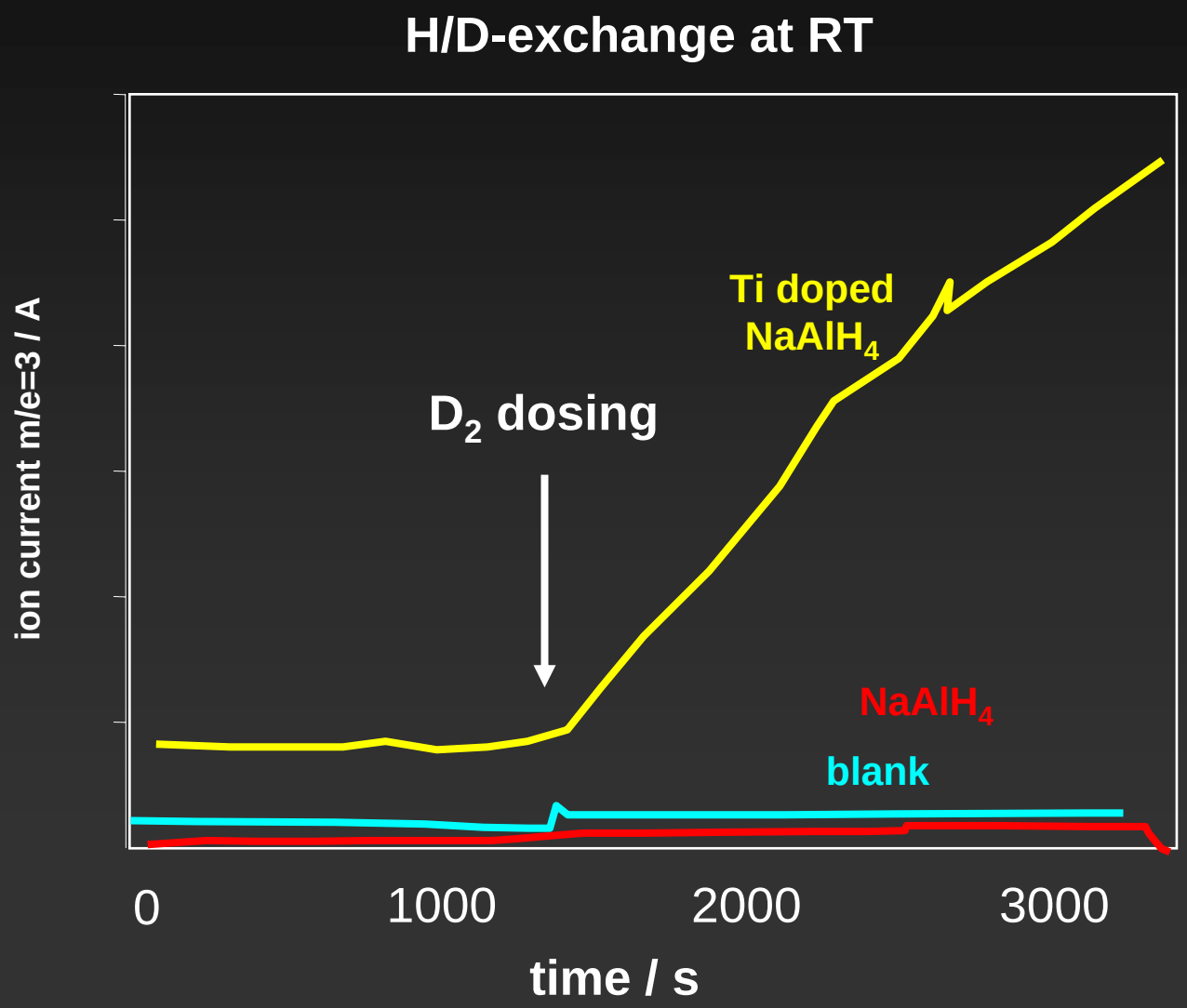


Al-reflection at 38.5° 2θ at RT

after heating to 200 °C

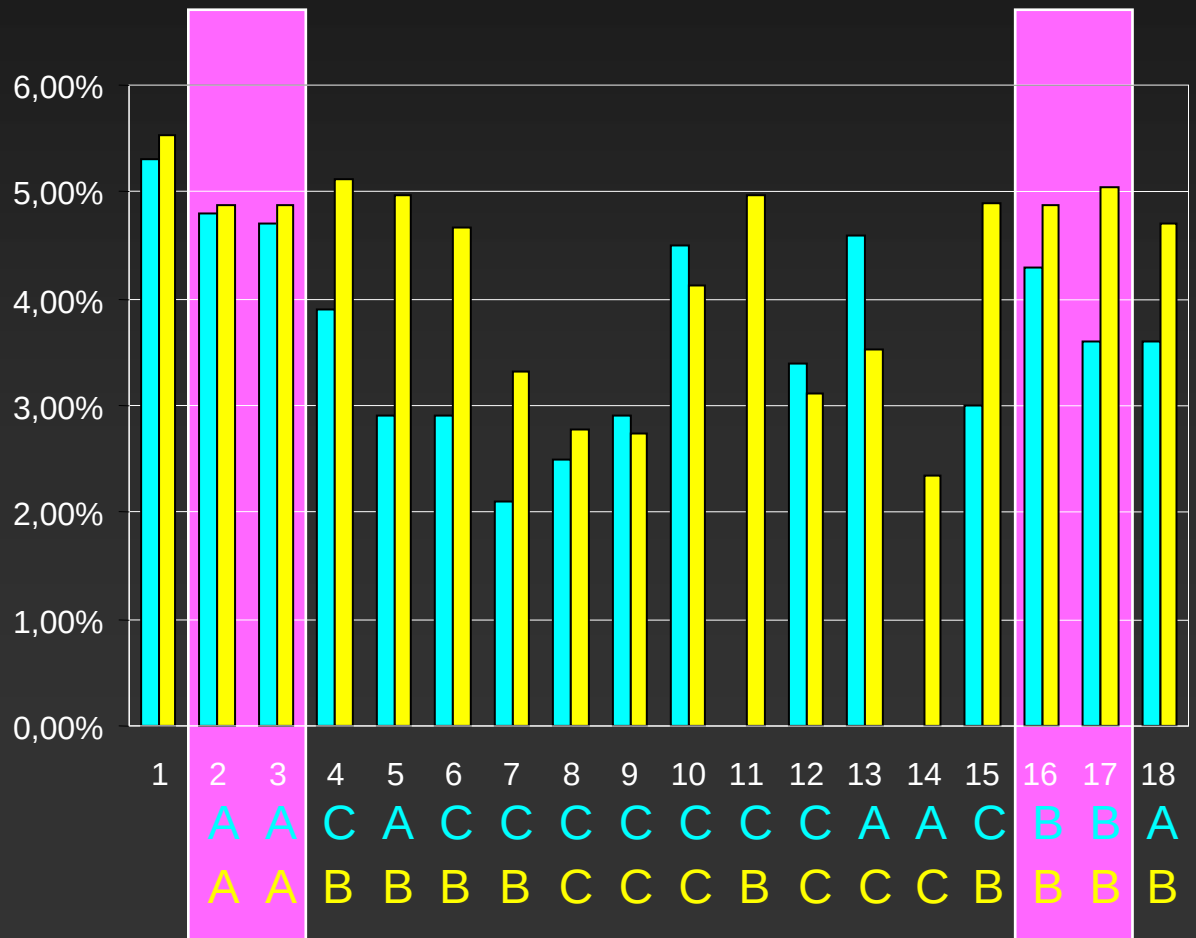
$TiAl_3$ at higher temperatures

Action of the catalyst



Improved system: storage capacity

- **TiN-nanoparticles are surprisingly good catalysts with high cycle stability**

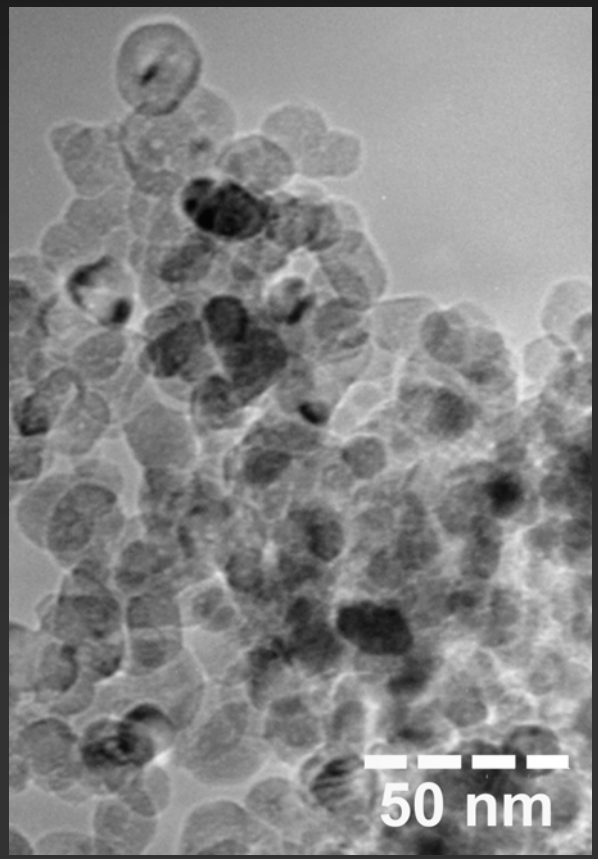


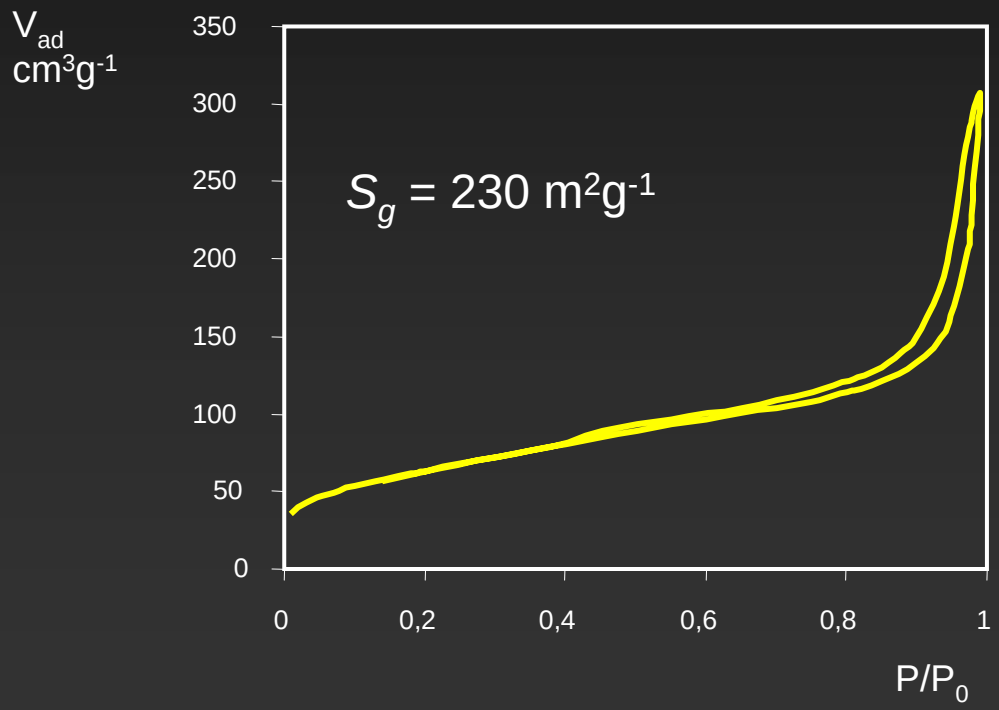
Coll. Ti
nano-TiN

Rehydrog. at

A: 105°C/140 bar
B: 170°C/130 bar
C: 100°C/50 bar

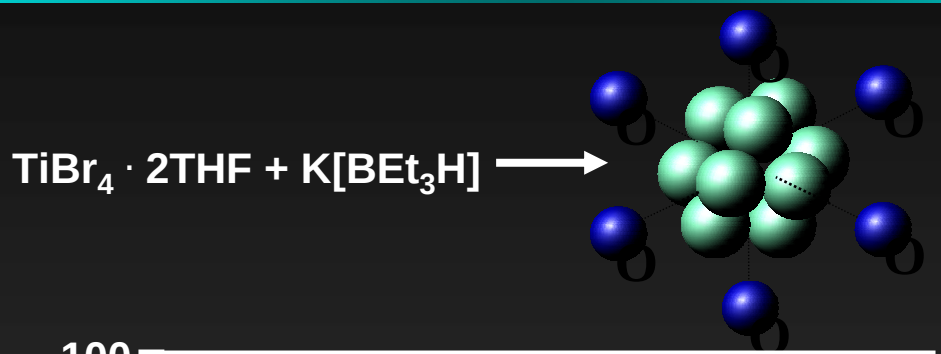
The catalyst Nano-TiN

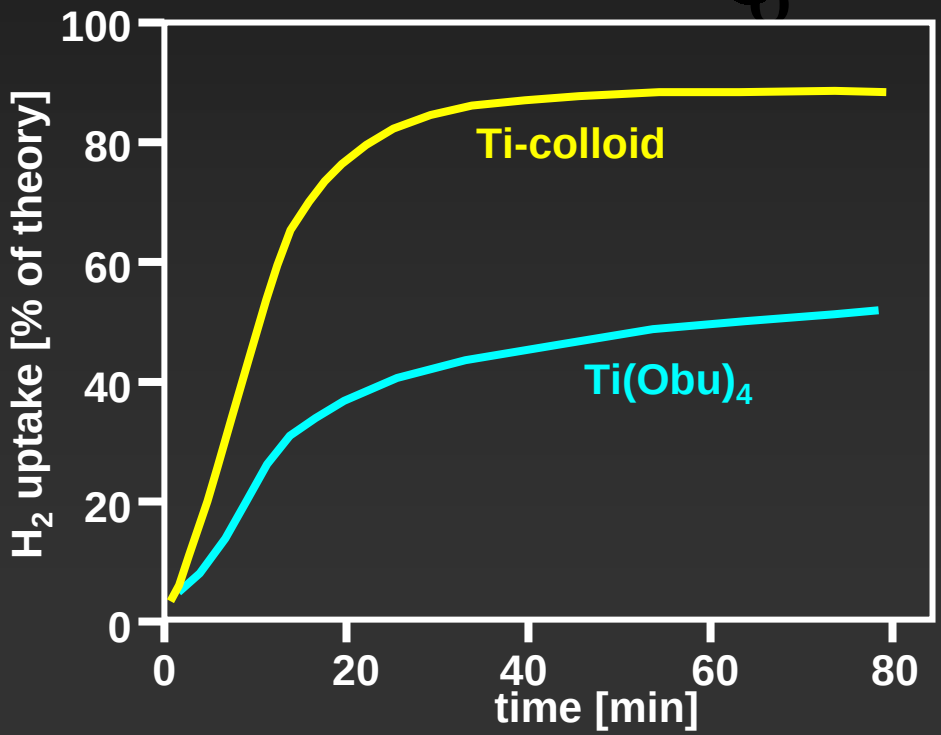




S. Kaskel et al., J. Mater. Chem. 2003, DOI:10.1039

Improved system: kinetics





B. Bogdanovic et al. Adv.Mater. 15, 1012 (2003) and DE-A-10163697.0

Direct Synthesis

First described system for ball-milling hydrogenation up to 160 bar

simultaneous measurement of pressure and temperature during the milling process and wireless data transmittance

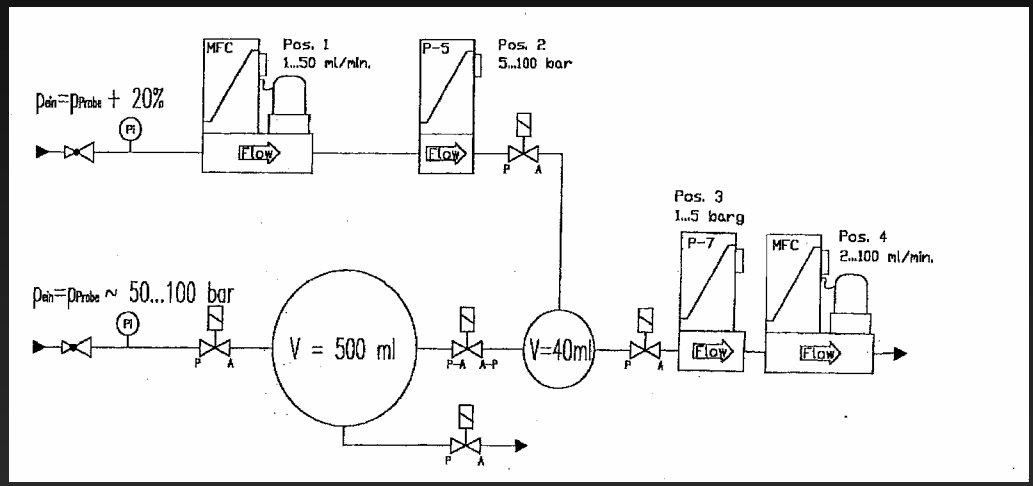
Advantages

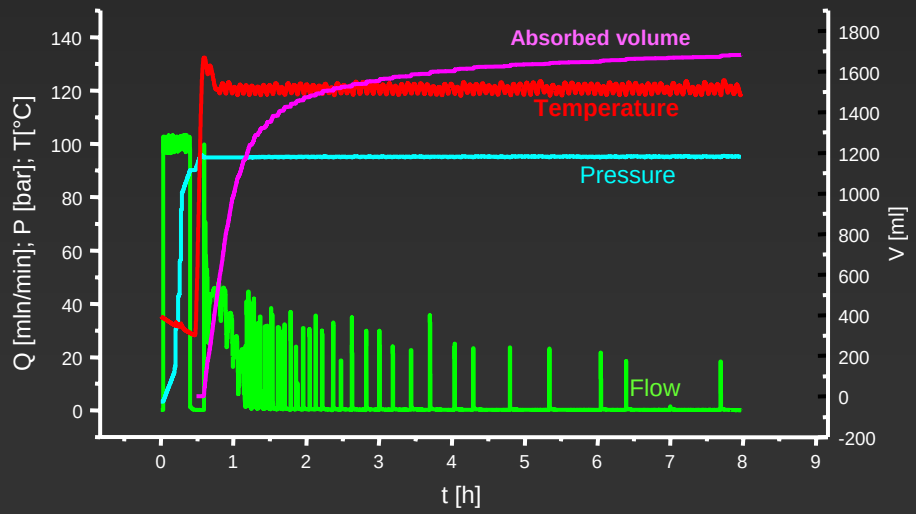
observation of start and end of the hydrogenation process

extremly homogenous distribution of the catalyst - fast kinetics!!

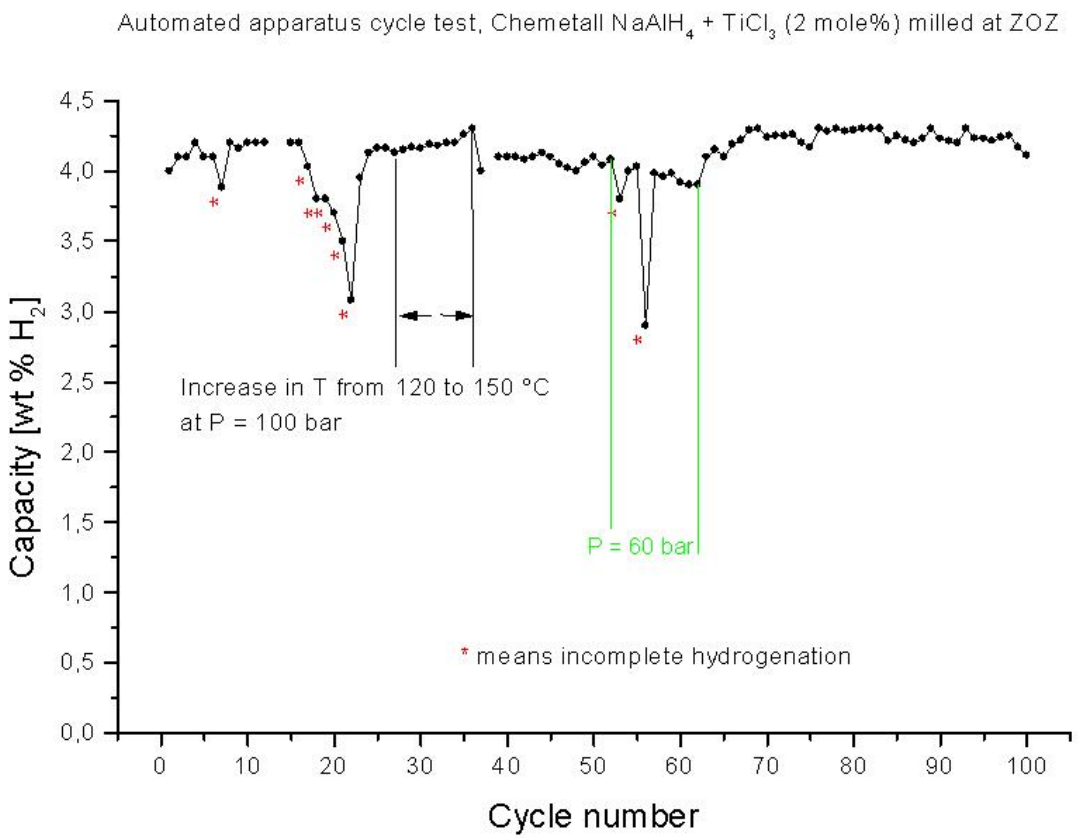
preparation of new materials

Automated test rig

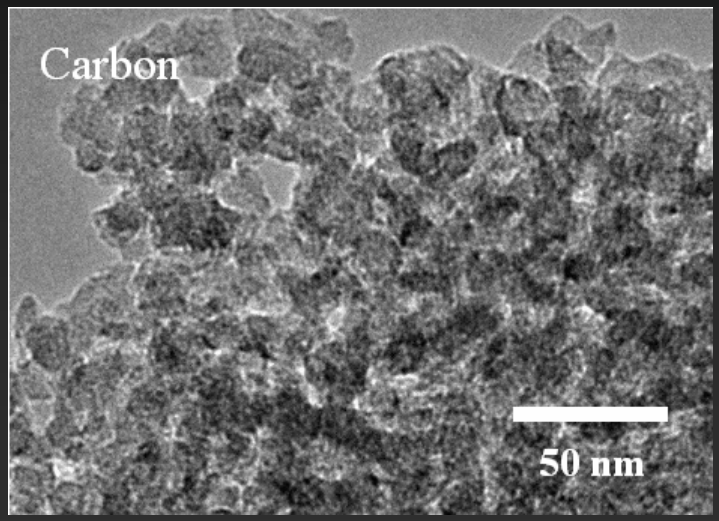




Cycle Stability

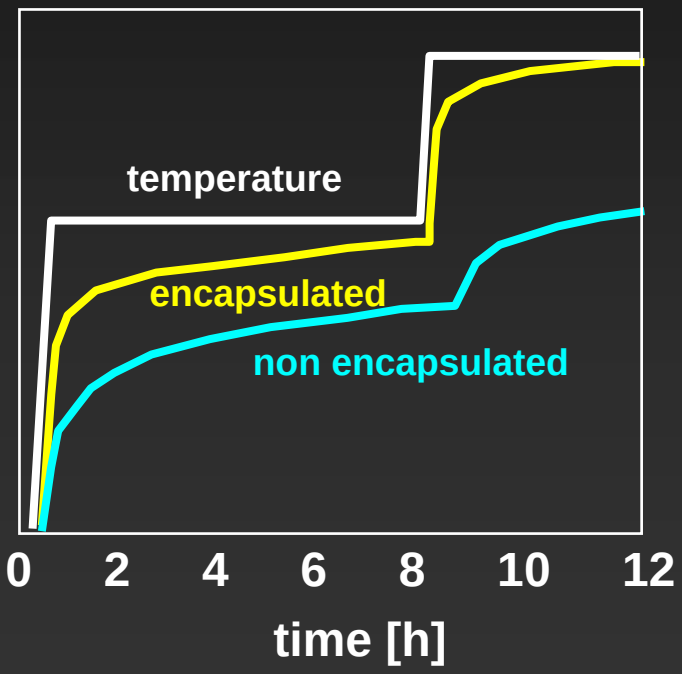


Encapsulation in porous matrices



Carbon aerogel

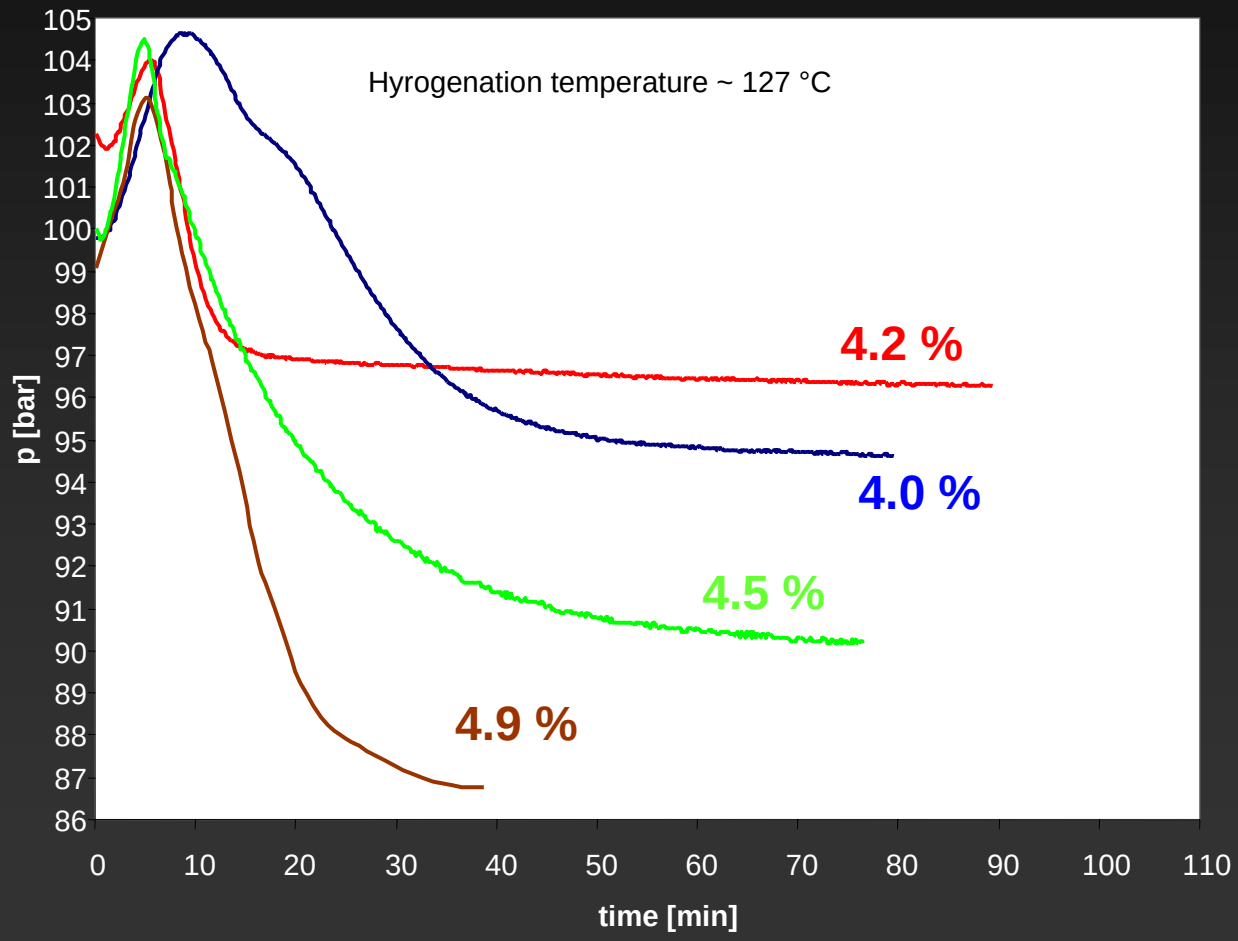
$NaAlH_4$ in THF



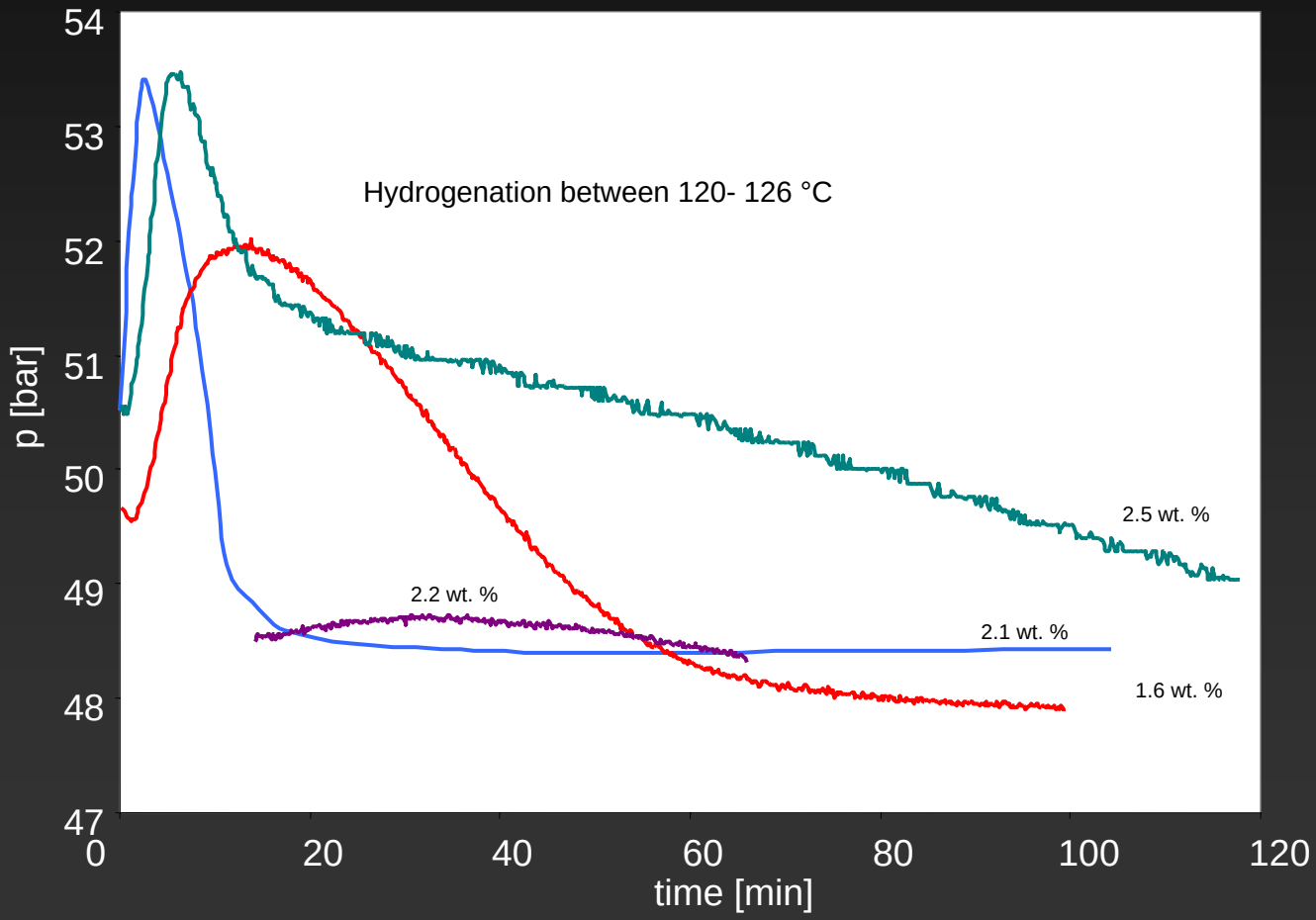
Safety problems appear to be manageable

$NaAlH_4$ after switching from argon to Air

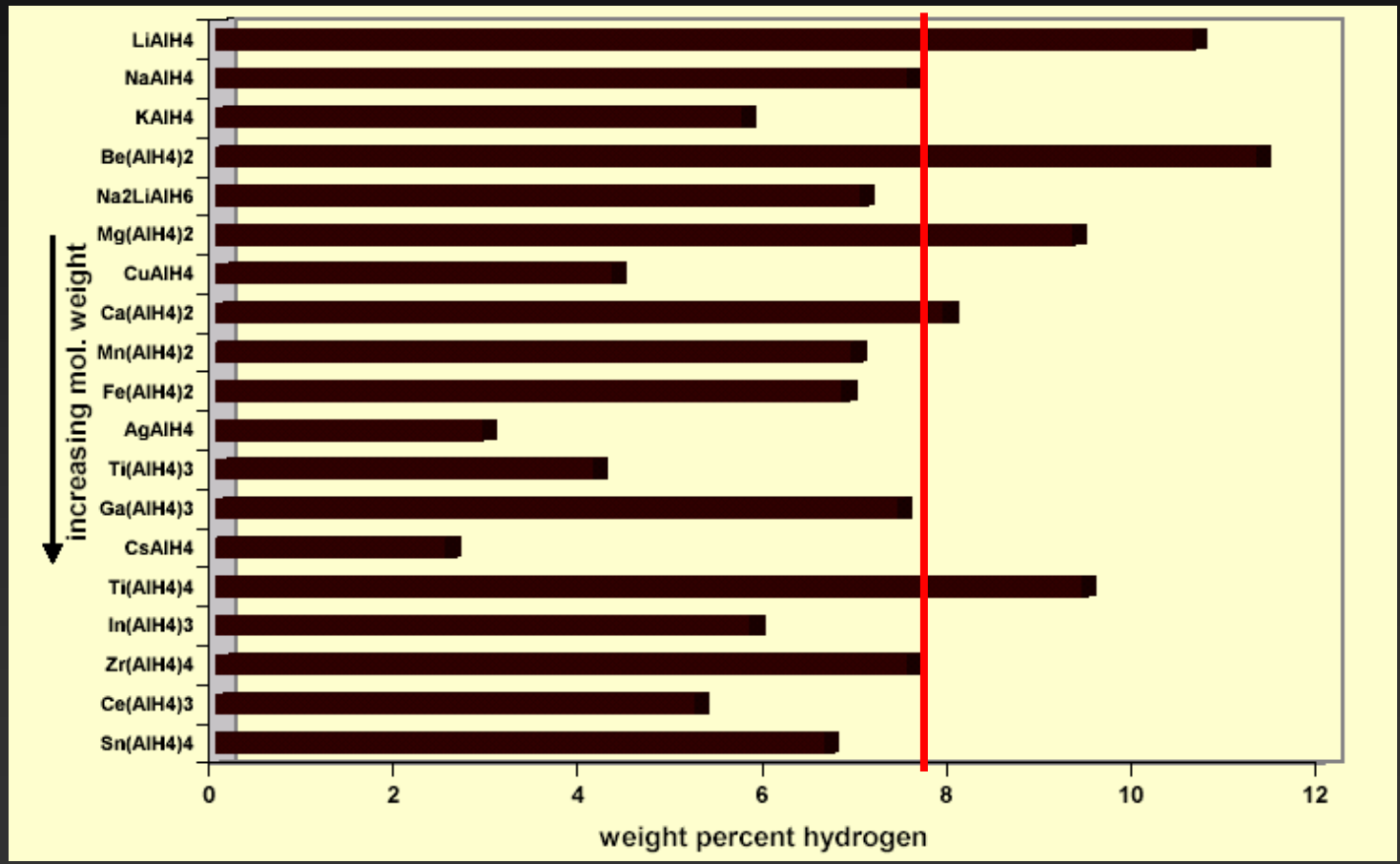
State-of-the-art systems



Mild conditions



Other Alanates



G.J. Thomas

Other alanates?

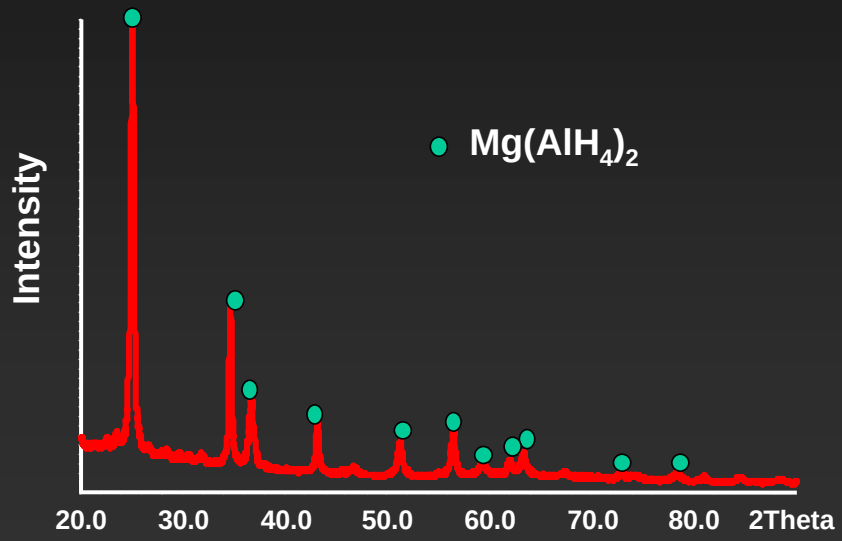
- **Other alanates: $Mg(AlH_4)_2$, $LiMg(AlH_4)_3$…**
- **Synthesized in our laboratory by various pathways**

$$MgCl_2 + 2\,NaAlH_4 \xrightarrow{\text{Ball milling}} Mg(AlH_4)_2 + 2NaCl$$

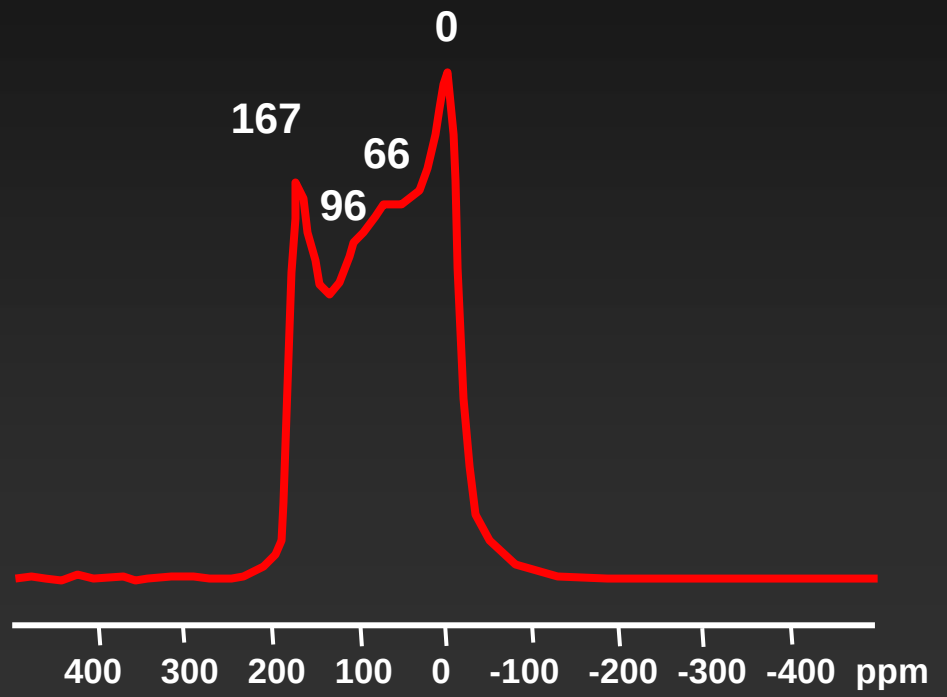
$$MgCl_2 + 2\,LiAlH_4 \xrightarrow{\text{Ball milling}} Mg(AlH_4)_2 + 2LiCl$$

$$Mg(AlH_4)_2 + 2\,NaCl \xrightarrow[\text{Soxhlet}]{Et_2O} Mg(AlH_4)_2 \cdot Et_2O \xrightarrow{60°C} Mg(AlH_4)_2$$

$Mg(AlH_4)_2$



XRD



^{27}Al NMR

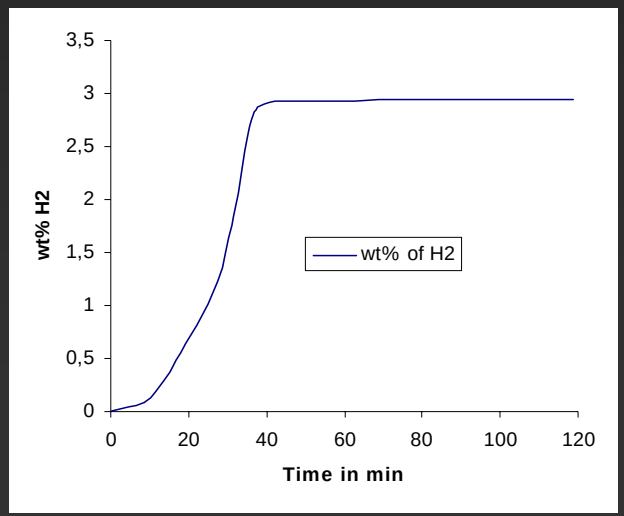
According to M. Fichtner et al.,
J.Alloys and Compounds 345, 286 (2002)

$Mg(AlH_4)_2$ as storage material?

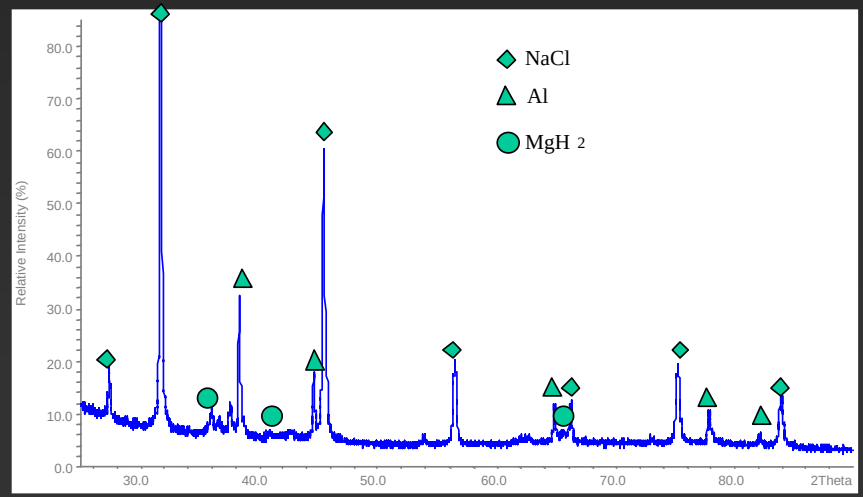
- ΔH_f around 0 kJ/mol

- **But titanium catalyzes hydrogen release!**

$$MgCl_2 + 2NaAlH_4 \xrightarrow{\text{Ti* ball milling}} MgH_2 + 2Al + 3H_2\uparrow + 2NaCl$$



Hydrogen evolved during milling

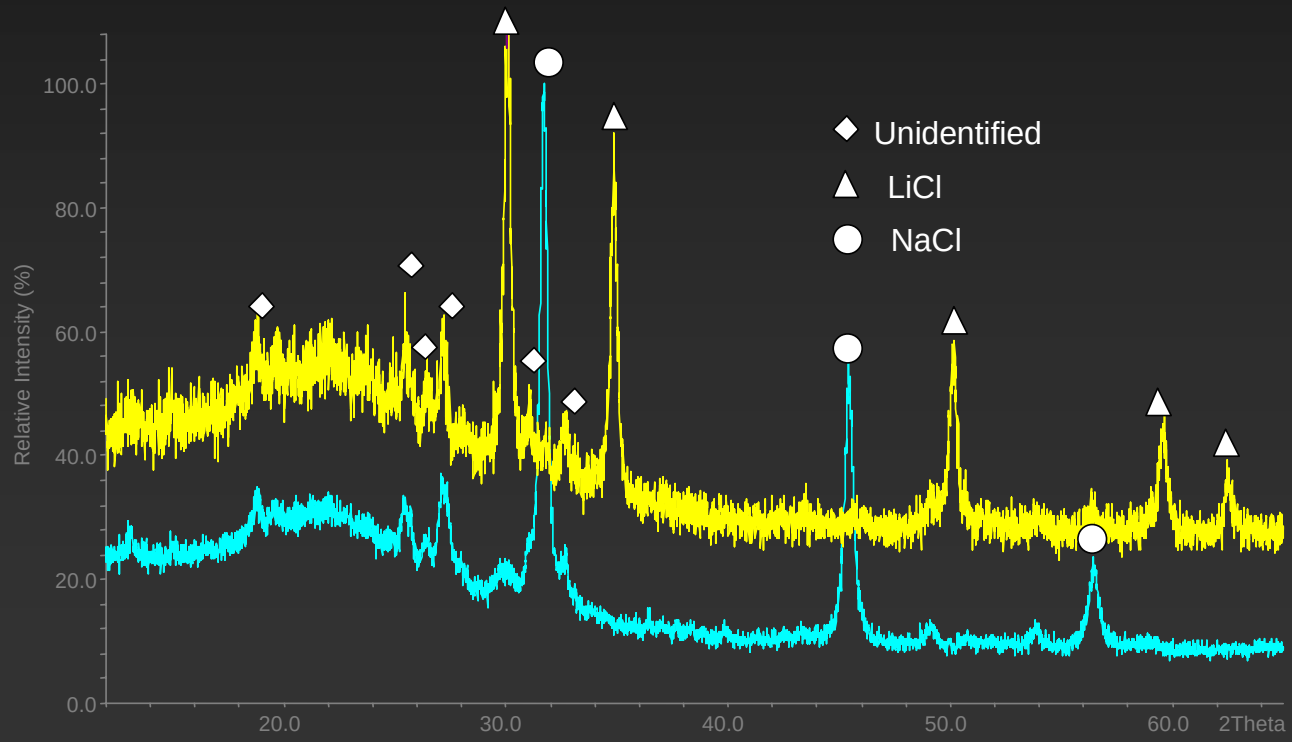


XRD after milling

XRD measurements $Ca(AlH_4)_2$

$$CaCl_2 + 2\,NaAlH_4 \xrightarrow{\text{Ball milling}} Ca(AlH_4)_2 + 2NaCl$$

$$CaCl_2 + 2\,LiAlH_4 \xrightarrow{\text{Ball milling}} Ca(AlH_4)_2 + 2LiCl$$



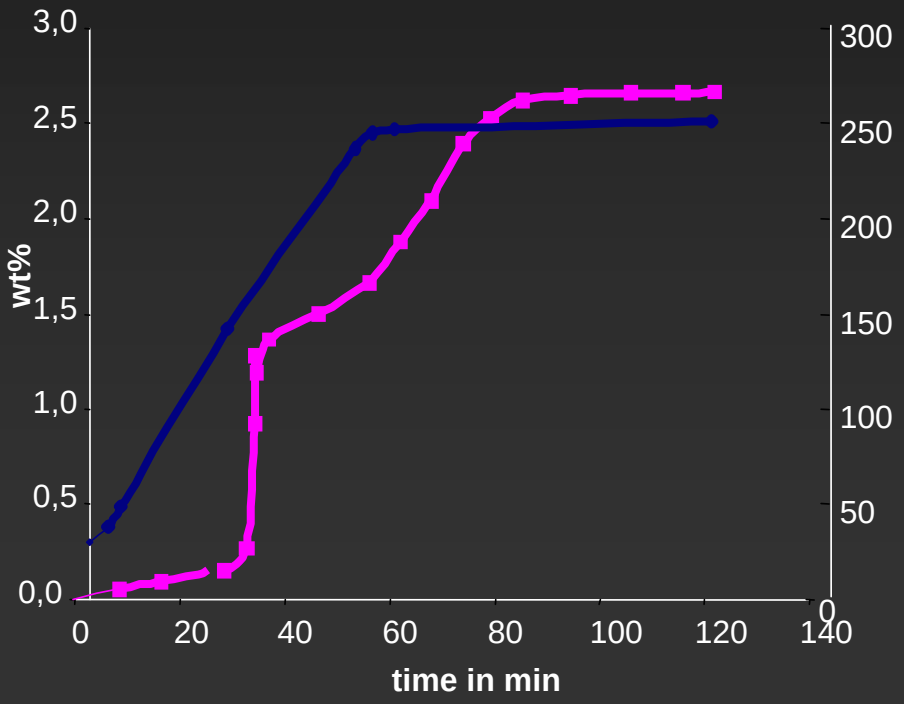
Thermovolumetric measurements

$$Ca(AlH_4)_2 + 2NaCl \xrightarrow{250^oC} CaH_2 + 2Al + 3H_2\uparrow + 2NaCl$$

$$Ca(AlH_4)_2 + 2LiCl \xrightarrow{250^oC} CaH_2 + 2Al + 3H_2\uparrow + 2LiCl$$

Expected: 3.0 wt%

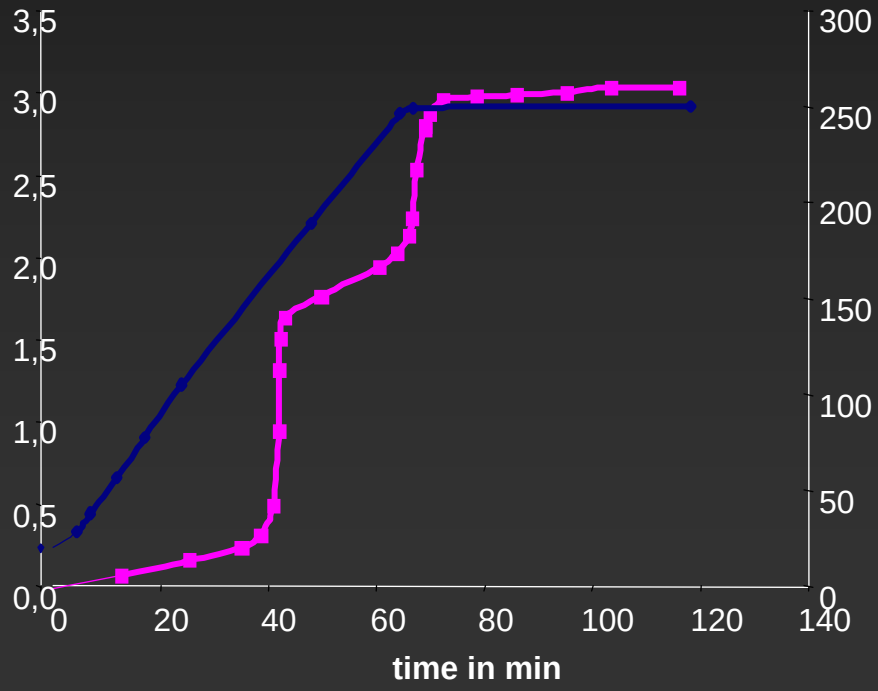
Found : 2.9 wt%



Thermal dissociation of $Ca(AlH_4)_2$ -2NaCl mixture

Expected: 3.3 wt%

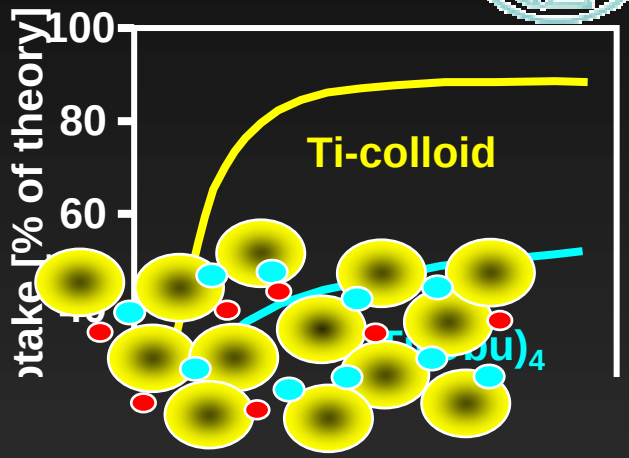
Found : 3.0 wt%



Thermal dissociation of $Ca(AlH_4)_2$ -2LiCl mixture

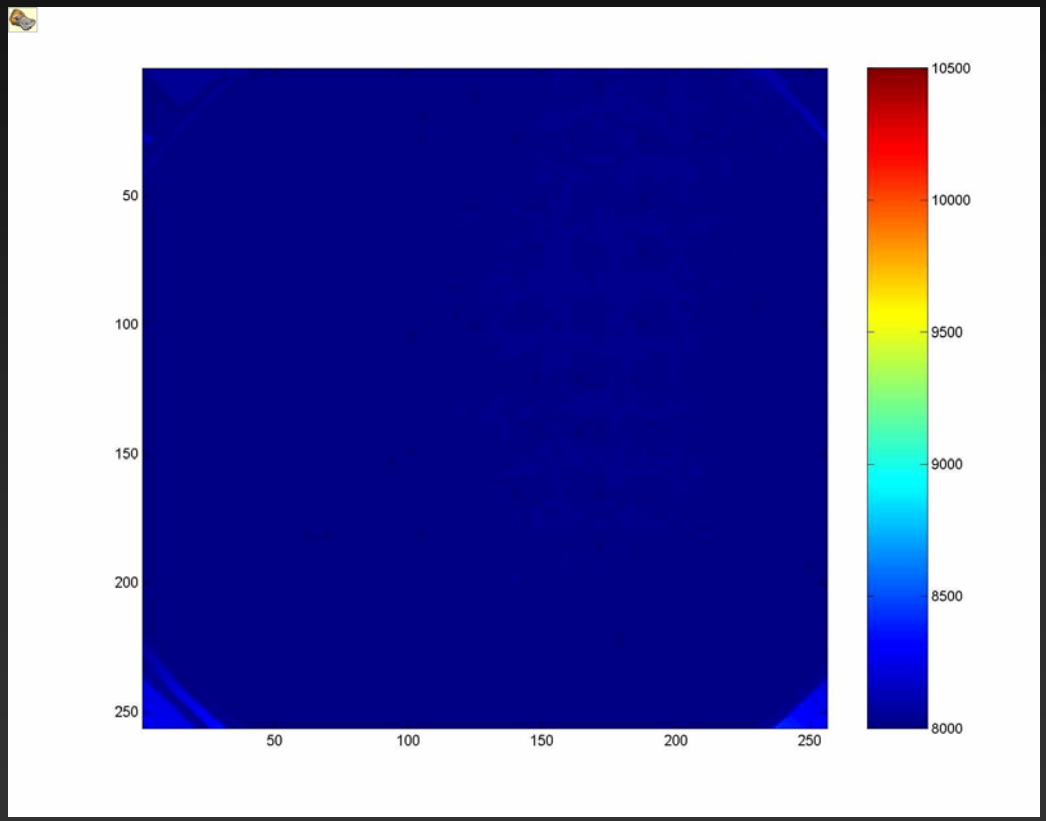
Summary and Outlook

- Titanium catalyzed hydrogen storage in $NaAlH_4$ at present most advanced reversible solution
- Changes of the system during cycling beginning to be understood
- So far no other promising alanate identified
- Innovation potential in improved catalysts, hydrides with higher storage capacity



!!!

Possible Search Methodology: High Throughput Experimentation



- Prepare metal/catalyst library in inert atmosphere
- Expose to hydrogen
- Record thermal signature with thermography
- Integrate to obtain estimate on enthalpy

Courtesy of J. Klein/A. Haas/S. Schunk, hte AG

More Common Light Metal Hydrides

Hydride	theo. Capacity/%	$\Delta G(298)/kJmol^{-1}$
LiH	12.5	-70
NaH	4.2	-33
BeH_2	18.2	+20 (?)
MgH_2	7.6	-36
AlH_3	10.0	+15 (?)
$LiAlH_4$	10.5	-60 (?)
$LiBH_4$	18.3	-143.5
$NaAlH_4$	7.4	(+4)
$NaBH_4$	10.6	-123.8

Hydrolytic One-Way Processes

- Either alkali metals or better metal hydrides are hydrolyzed with water

$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2} H_2$$

$$NaH + H_2O \longrightarrow NaOH + H_2$$

- Alkali metal or hydride has to be packaged

- Process is irreversible under consumer conditions, thus only one-way

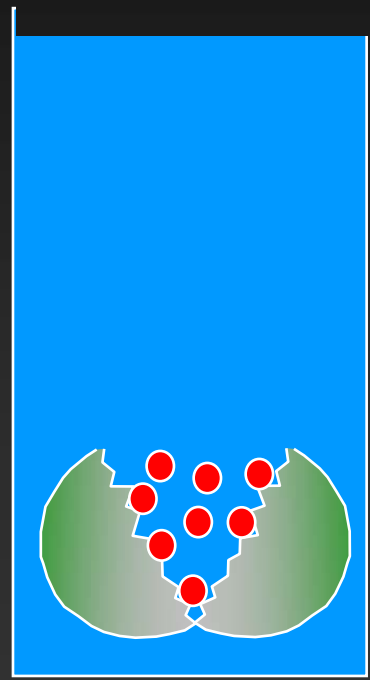
Some Possible Hydrolysis Reactions

Reaction	theoretical wt % H_2 evolved from reactants (hydride + water)
$LiH + H_2O \rightarrow LiOH + H_2$	7.7
$CaH_2 + 2\,H_2O \rightarrow Ca(OH)_2 + 2\,H_2$	5.2
$LiAlH_4 + 4\,H_2O \rightarrow LiOH + Al(OH)_3 + 4\,H_2$	7.3
$LiBH_4 + 4\,H_2O \rightarrow LiOH + H_3BO_3 + 4\,H_2$	8.6
$NaAlH_4 + 4\,H_2O \rightarrow NaOH + Al(OH)_3 + 4\,H_2$	6.4
$NaBH_4 + 4\,H_2O \rightarrow NaOH + H_3BO_3 + 4\,H_2$	7.3

Release from: **- solid hydrides**
- stabilized solutions

D. Browning, http://www.h2net.org.uk/PDFs/Stor2000/H2nettalk_Nov00.pdf

The Powerball concept



$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2} H_2$$

$$NaH + H_2O \longrightarrow NaOH + H_2$$

Na-balls coated with polyethylene which are broken under water for hydrolysis

http://www.powerball.net

Complex boron hydrides

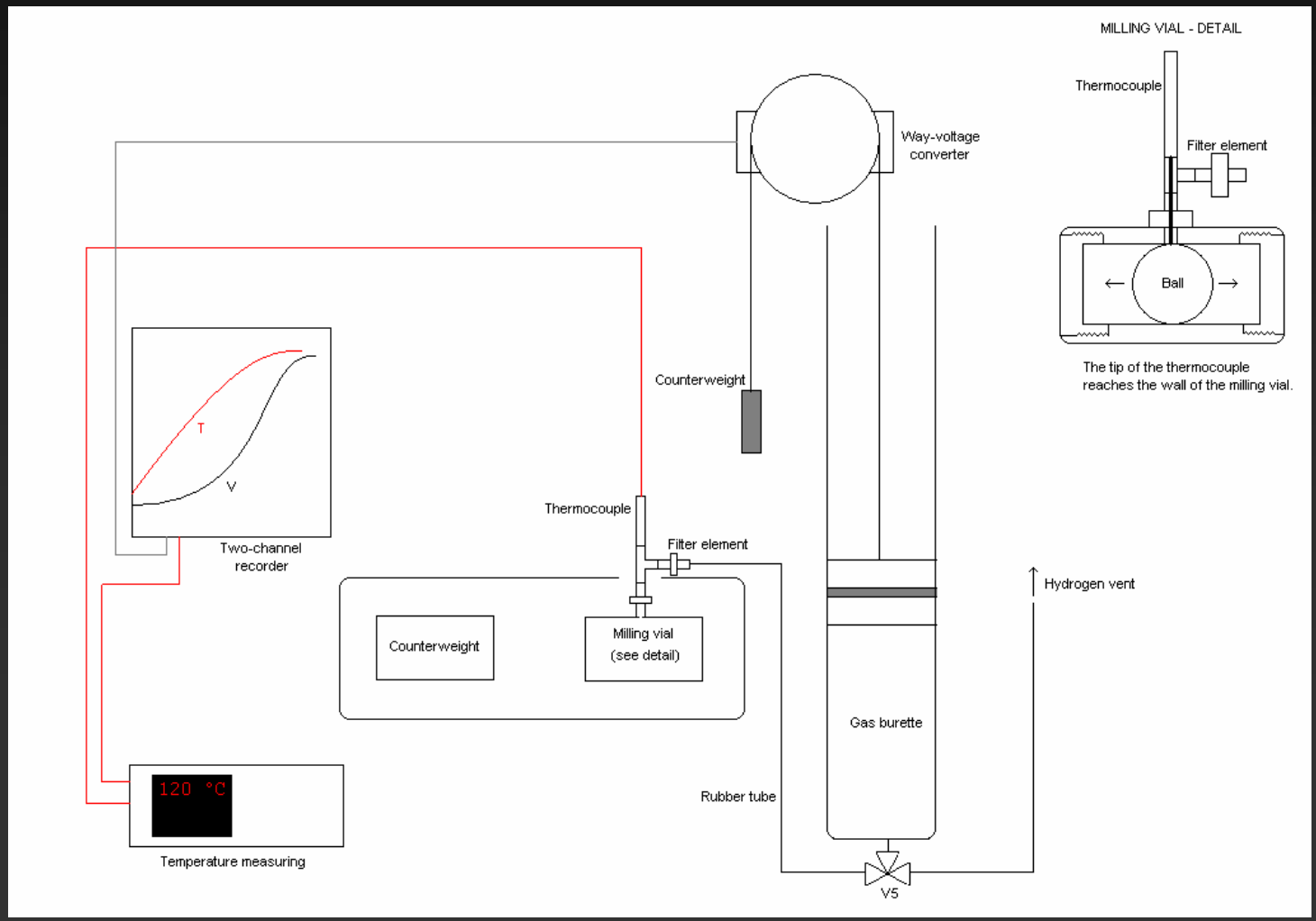
- In principle more attractive due to higher storage capacity
- More conventional ones are too stable
- So far no catalysis reported
- Question of boron hydride (volatile) release unclear

How to search for new hydrides?

- Look for right enthalpic effect initially
- Entropy of decomposition reaction dominated by formation of gaseous H_2 ($\Delta S \cdot 298K = 39$ kJ/mol H_2)
- For $\Delta G = 0$ at 298 K → $\Delta H \approx 40$ kJ/mol H_2)

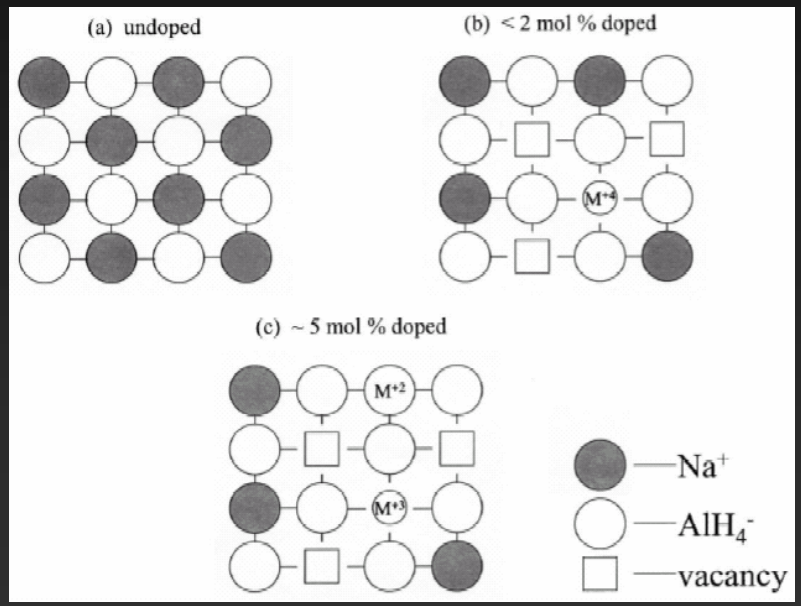
→ Look for hydrides with moderately negative heat of formation

Following gas evolutin during ball milling

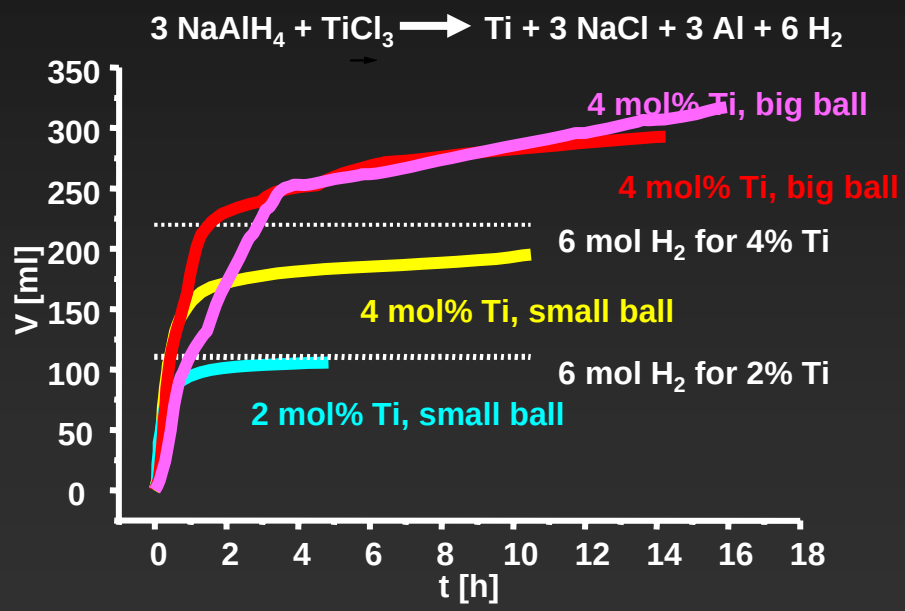


State of the catalyst

Framework substitution model



D. Sun et al. J.Alloy Compd. 337, L8 (2002)



Low crystal-chemical probability

There is no high valency titanium

Status of Ti-doped $NaAlH_4$

- Possibility of reversible storage capacity around 5 wt% has been demonstrated
- Rehydrogenation in less than 10 minutes has been achieved at around 100 bar
- Rehydrogenation pressure still too high (2.5 h at 61 to 45 bar)
- Catalyst improvement still seems possible
- Safety issues need to be addressed
- Cost issues of catalysts need to be addressed