Influence of Ti-dopants in $NaAlH_4$ on the performance of hydrogen storage applications

Aline LEON

FZK Karlsruhe, Institute for Nanotechnology (INT)
Department of Nanostructured Materials

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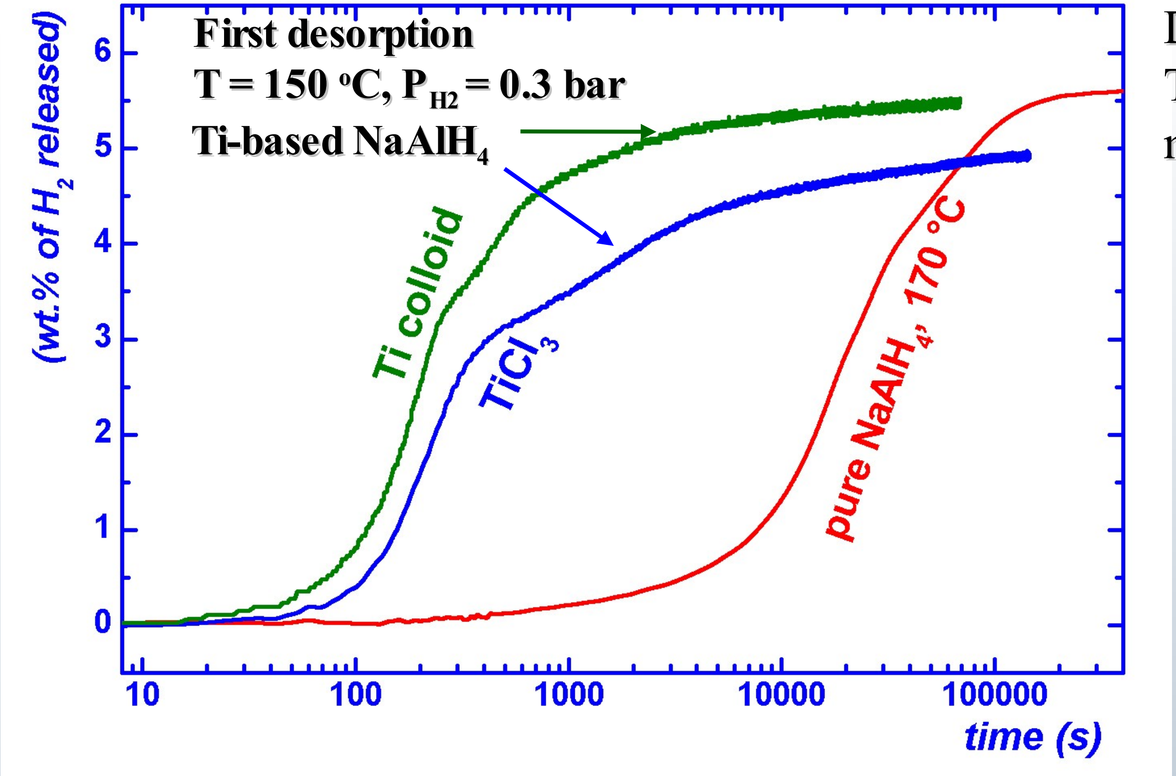
H-carrier: sodium alanate, $NaAlH_4$

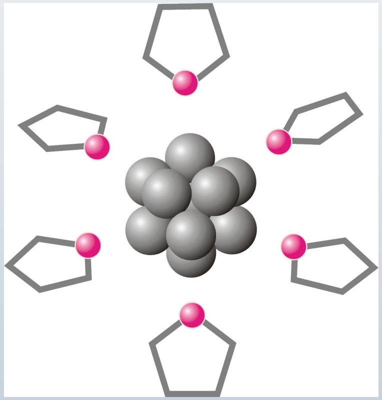
Isothermal decomposition kinetics

✓ Different Ti-based precursor



Doping with 5 mol.% Ti by ball milling 30 minutes

Ti_{13}·6THF



- **Importance of the nature of the Ti-based precursor**
- **Difference in the kinetics and the storage capacity**

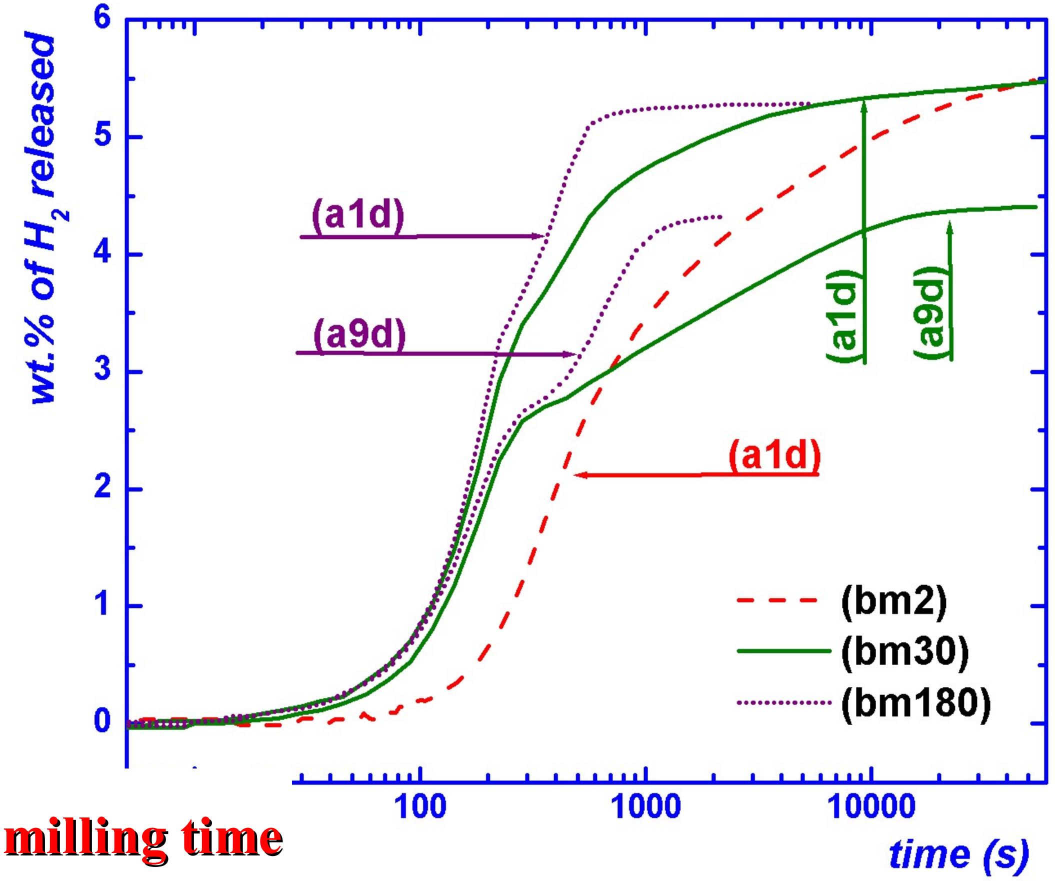
A. Léon et al., J. Phys. Chem. B, 110 (2006) 1192.

Isothermal decomposition kinetics

Different milling time

$NaAlH_4$ + 5 mol.% Ti
on the basis of $Ti_{13}\cdot 6THF$

T = 150 °C, P_{H2} = 0.3 bar



Kinetics depends on the milling time

But not the storage capacity !!!

A. Léon et al., J. Phys. Chem. B, 110 (2006) 1192.

Open questions

- ✓ How does the presence of Ti ease the thermal activation process?
- ✓ What is the relation between the structure and the properties?
- ✓ Ti at the surface or in the volume?

Key questions to improve the understanding and the efficiency of the material

Microscopic and long-range order analysis

- ✓ **HRTEM combined with EDX**
  - Homogeneous distribution of Ti with Al and Na
  - Al particle in the dehydrogenated state (300 nm)
  - No detection of Ti particles (size less than 0.8 nm)
- ✓ **SR-PXD** *(10 mol.% Ti on the basis of $TiCl_3$)*
  - No change in the unit cell dimensions
  - formation of a metastable phase ($Al_{0.85}Ti_{0.15}$) after 3 cycles

A. Léon et al., J. Alloys and Compd. 414 (2006) 190.
H. Brinks et al., J. Phys. Chem. B, 109 (2005) 15780.

Local structural-scale probe

To obtain complementary aspects of the crystal structure

XPS & XAS, local structural probe with elemental sensitivity

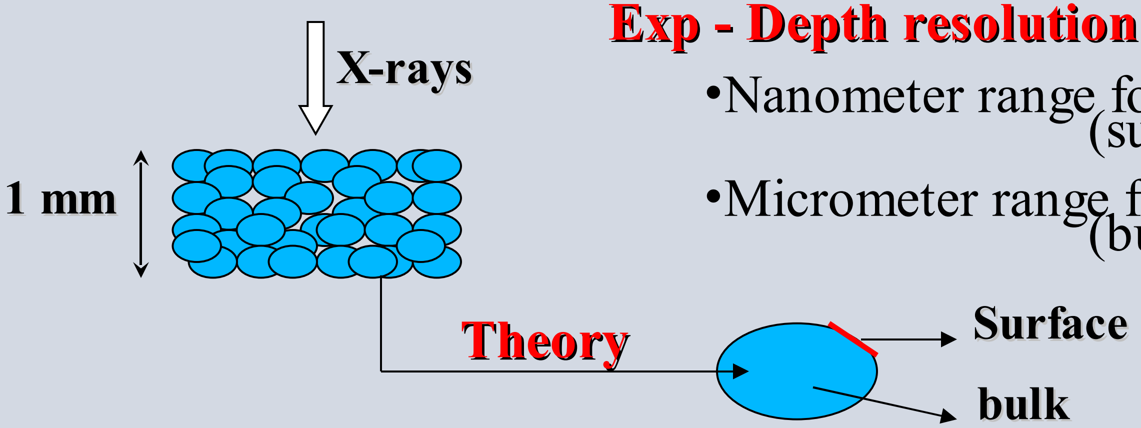
- Chemical state of the selected atom
- Number, type and distances of neighboring atoms
- Local deviations from the average structure

Surface and bulk

From experiment and theory,...

Exp - Depth resolution

- Nanometer range for XPS (surface sensitive)
- Micrometer range for XAS (bulk analysis)



From the Ti side,...

Ti at the surface or in the volume?

Evolution of the atomic concentration of Ti from XPS

TiCl$_3$ doped NaAlH$_4$

(bm2)	2.8 at.% (± 10%)
(bm30)	0.6
(bm60)	0.5
(bm180)	0.4
(a1d)	0.3
(a1a)	0.4
(a8a)	0.4
(a9d)	0.4

Ti colloid doped NaAlH$_4$

(bm2)	3.4 at.% (± 10%)
(bm30)	3.0
(bm60)	2.3
(bm180)	1.3
(a1d)	1.7
(a1a)	0.8
(a8a)	0.5
(a9d)	0.6

No matter of the nature of the precursor

- **Ti does not remain at the surface upon milling or cycling**
- **Ti tends to a constant value of 0.5 at.% after cycling**
- **Ti concentration affects the kinetics but not the capacity**

Chemical state of Ti

- ✓ ***From XPS (binding energy) & XANES (edge position)***

$TiCl_3$ doped $NaAlH_4$

Before milling: Ti^{3+}

After milling: Ti^0

After cycling: Ti^0

Ti colloid doped $NaAlH_4$

Before milling: > Ti^0

After milling: > Ti^0

After cycling: Ti^0

► **No matter of the nature of the precursor Ti is in the metallic state after several cycles**

A. Léon et al., J. Phys. Chem. B, 110 (2006) 1192.

➢ *Local structure around Ti from EXAFS*

✓ *$TiCl_3$ doped Na-alanate*

- during milling: **strong distortion** of the local order
- first cycle under H_2: **distorted hcp structure**
- eight cycles under H_2: **formation of a Ti-Al inter-metallic**

✓ *Ti colloid doped Na-alanate*

- during milling: **no change** in the local structure
- first cycle under H_2 : **stripping off the oxygen atoms of THF** from the Ti metallic core
- eight cycles under H_2: **formation of Ti-Al inter-metallic**

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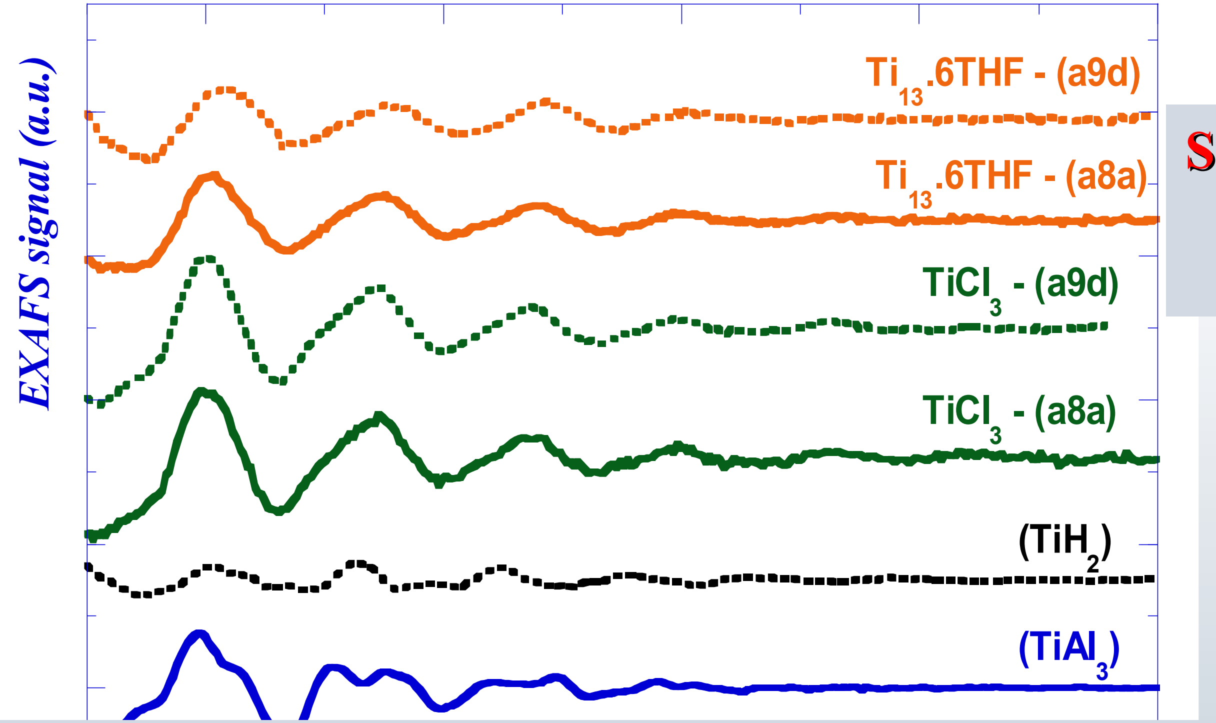
A. Léon et al., J. Phys. Chem. B, 110 (2006) 1192.

Nature of the Ti-Al intermetallic



Structure around Ti
~ 10 Al at 2.80 Å
~ 1 Ti at 3.88 Å

$TiAl_3$ bulk phase:
4 Al at 2.72 Å
8 Al at 2.88 Å
4 Ti at 3.85 Å

- **Significant difference in the fine structure**
- **Lack of long-range order**
- **Significant reduction of the Ti coordination number**
- **Relaxation to a single distance**

Ti-Al intermetallic is not $TiAl_3$ bulk phase

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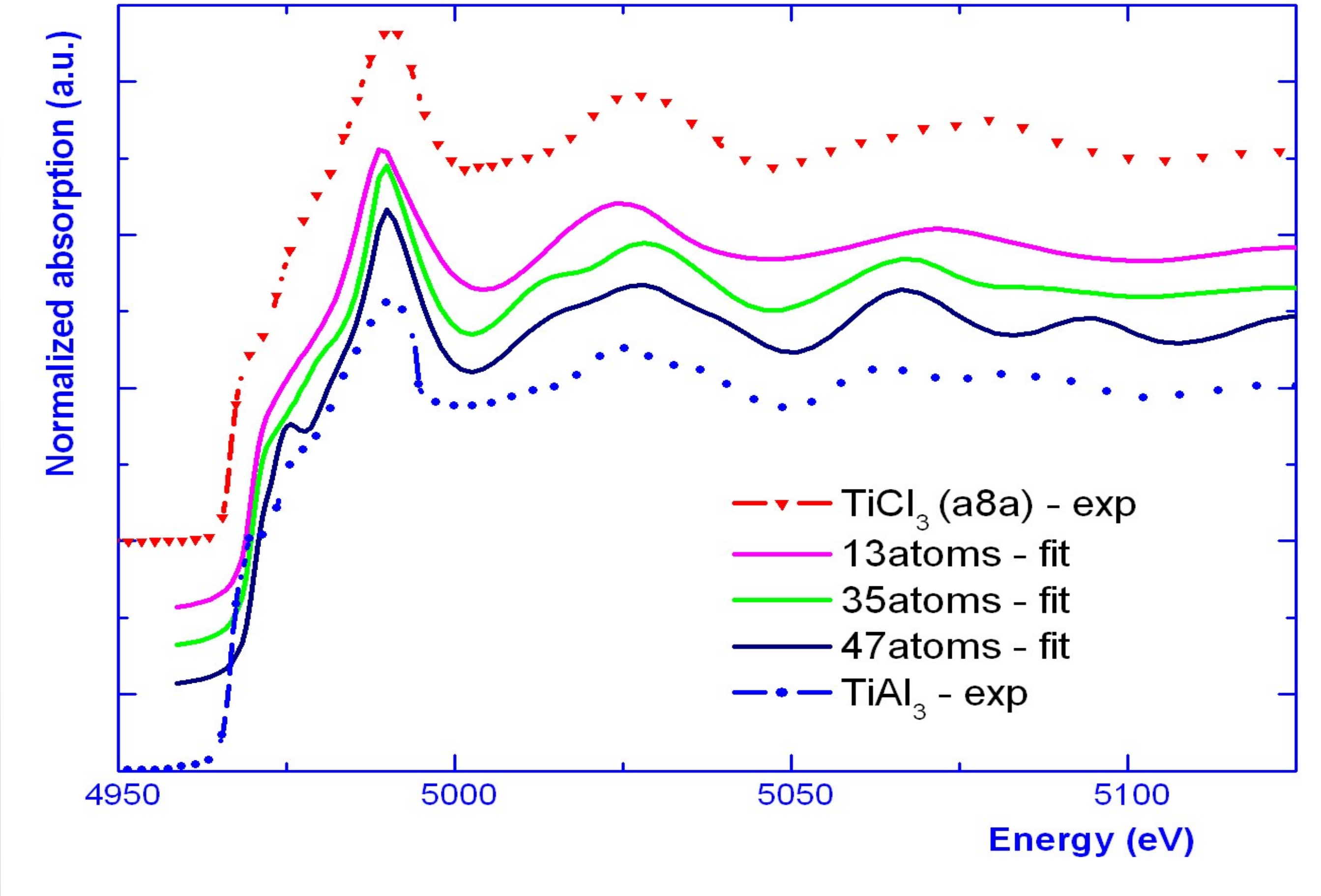
Nature of the Ti-Al intermetallic



Formation of Ti-Al cluster upon cycling under H_2

A. Soldatov, M. Fichtner, A. Léon, submitted (2006)

From the Al side,...

➢ Surface characteristics

✓ Evolution of the atomic concentration of Al from XPS

TiCl$_3$ doped NaAlH$_4$

	Al^{3+}	Al^{0}
(bm2)	18.1	3.4
(bm30)	20.1	4.6
(bm180)	20.2	1.4
(a1d)	12.6	3.4
(a1a)	14.4	2.1
(a8a)	13.8	2.2
(a9d)	11.1	4.8

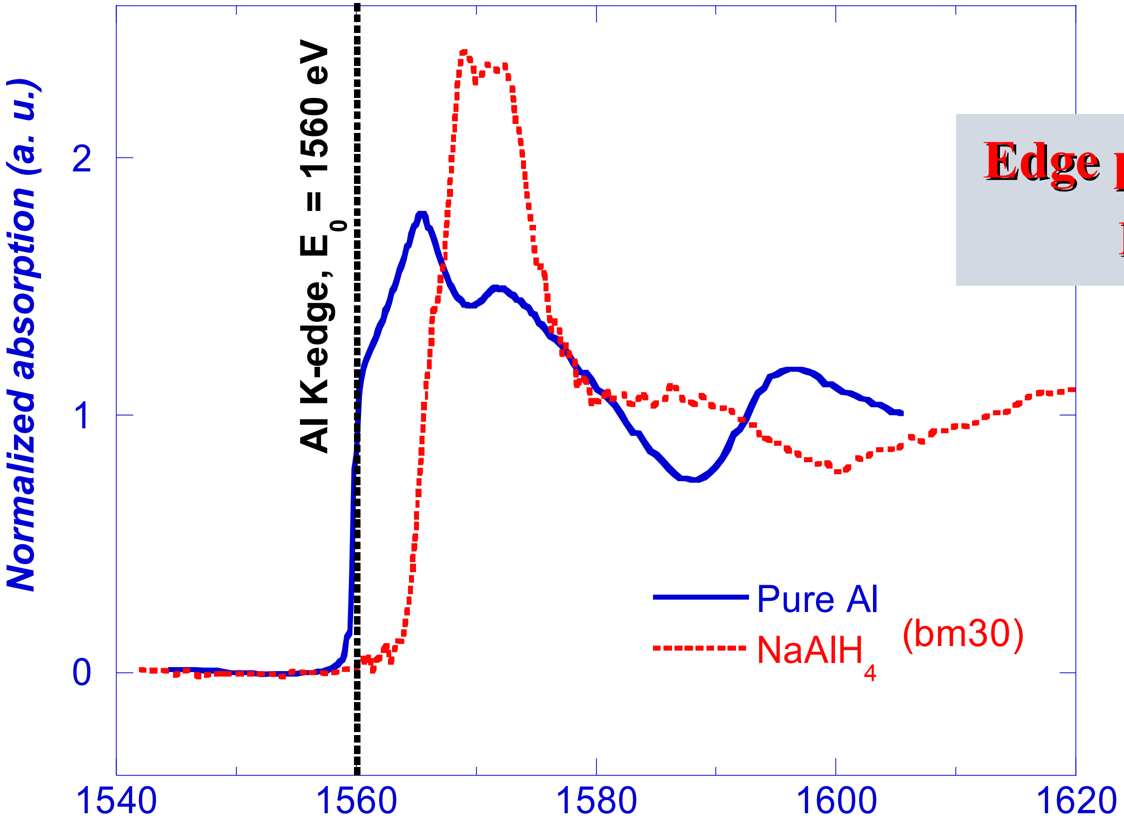
Ti colloid doped Na-alanate

	Al^{3+}	Al^{0}
(bm2)	13.5	
(bm30)	16.3	
(bm180)	14.3	
(a1d)	7.4	5.4
(a1a)	15.4	1.0
(a8a)	9.3	1.9
(a9d)	6.6	5.6

- Concentration of Al^{0} evolves with the phase transformations
- Presence of metallic Al at the surface after the absorption
- Electronic state of Al (2p) undergoes changes with cycling
- Al$_2$O$_3$ is below the detection limit

➢ Al K-edge XANES

✓ Metallic Al & $NaAlH_4$ (purified)



Edge position in $NaAlH_4$

E_0 = 1565.5 eV

Al in $NaAlH_4$:

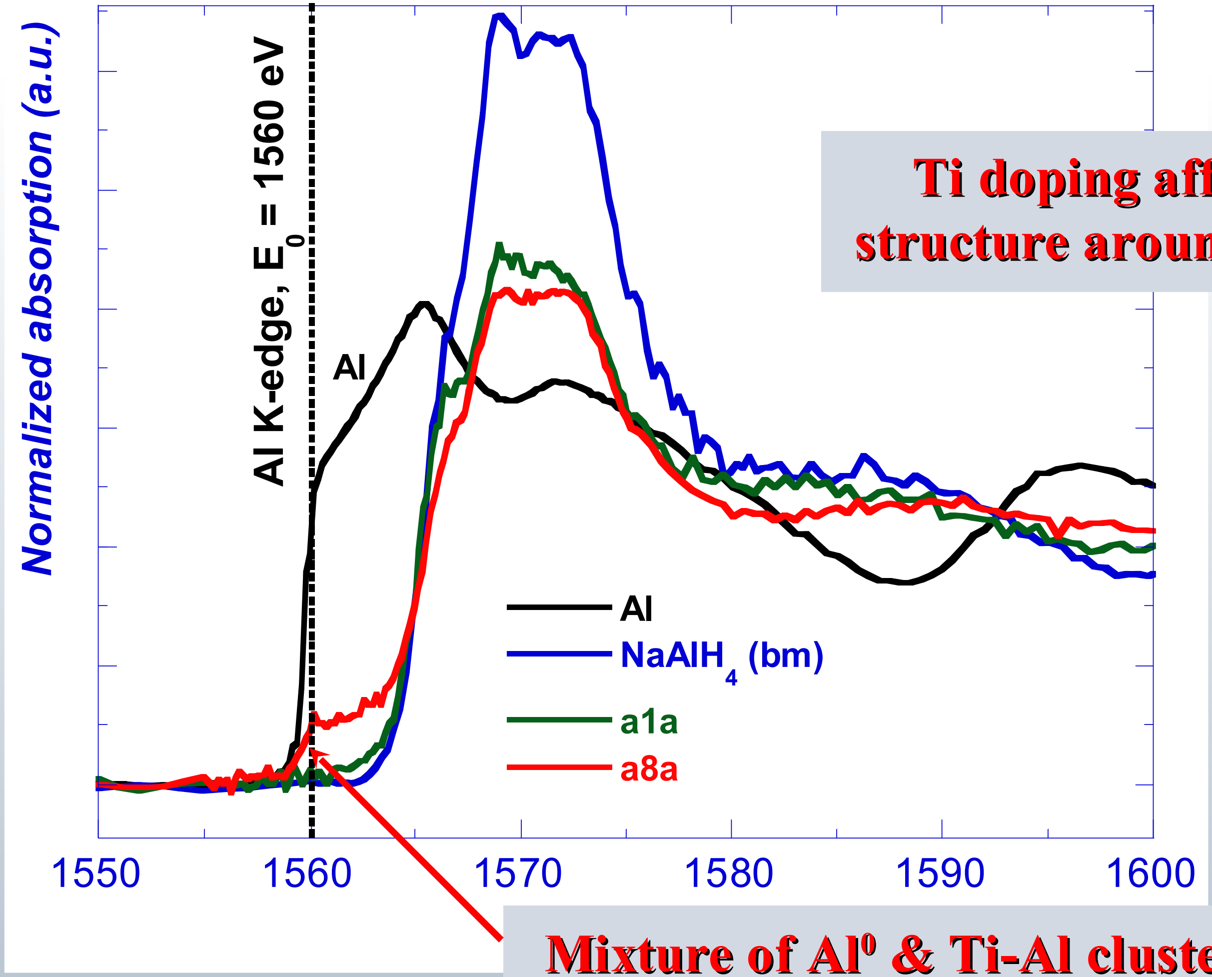
is in a higher valence state than Al^0

is in a four-fold coordinated geometry

A. Léon et al., J. Phys. Chem. B, submitted

➢ Al K-edge XANES

✓ $TiCl_3$ doped Na-alanate



Ti doping affects the local structure around Al in $NaAlH_4$

Mixture of Al^0 & Ti-Al cluster

Indication of molecular-scale inhomogeneities within the average structure of Na-alanate

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Novel $Al_xTi_{(1-x)}$ nanocomposite

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➢ *Knowledge transfer to design a novel material*

✓ *Fundamental studies*

- Avoid the reduction of Ti particles and go directly to the steady state
- Avoid the consumption of a significant Al fraction during doping and the formation of bimetallic entities (cycling)

To gain stability

in the kinetics and the reversible storage capacity*

✓ *Design of the novel material*

- Ti should be bound to an element preventing the shift to the metallic state
- Use of one of the decomposition product to synthesize a new Ti containing phase

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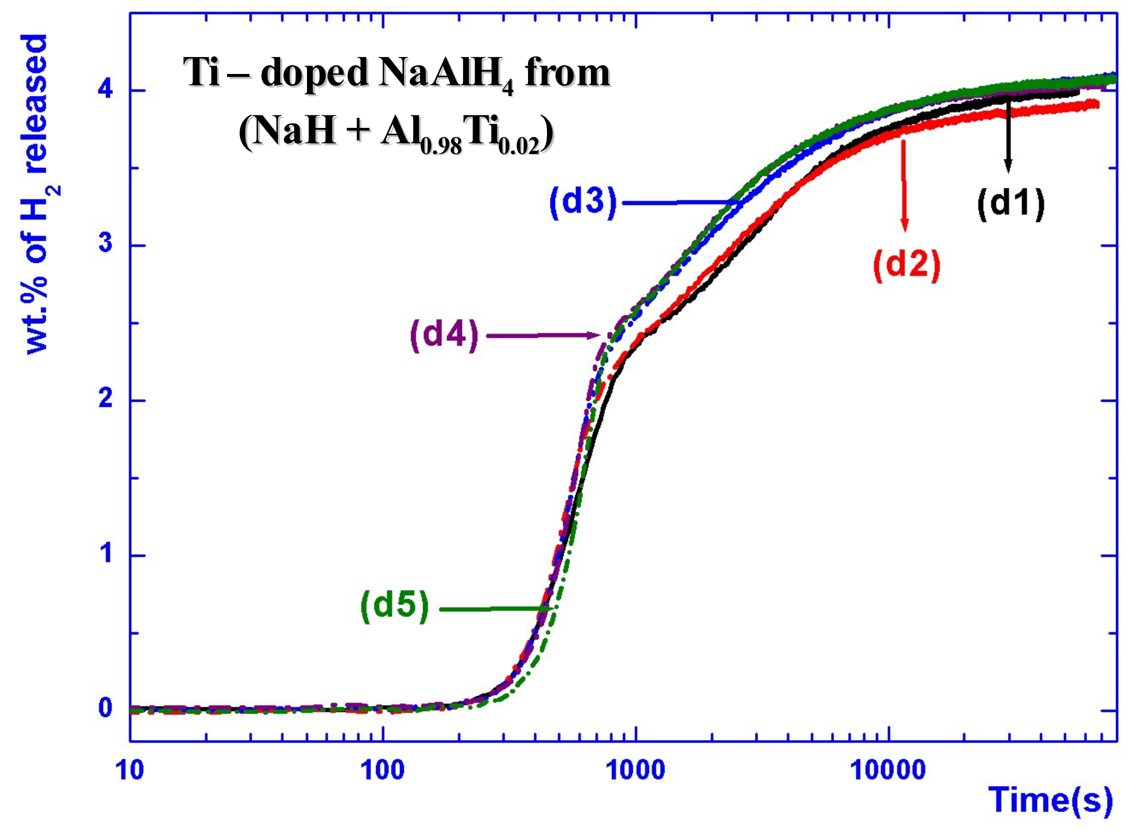
**H. Brinks et al., J. Phys. Chem. B, 110 (2006) 2740.*
N. Eigen et al., J. Alloys and compd., (2006)

Isothermal decomposition kinetics

✓ Cycling under H_2

$NaH + Al_xTi_{(1-x)} \rightarrow$ Ti-doped $NaAlH_4$

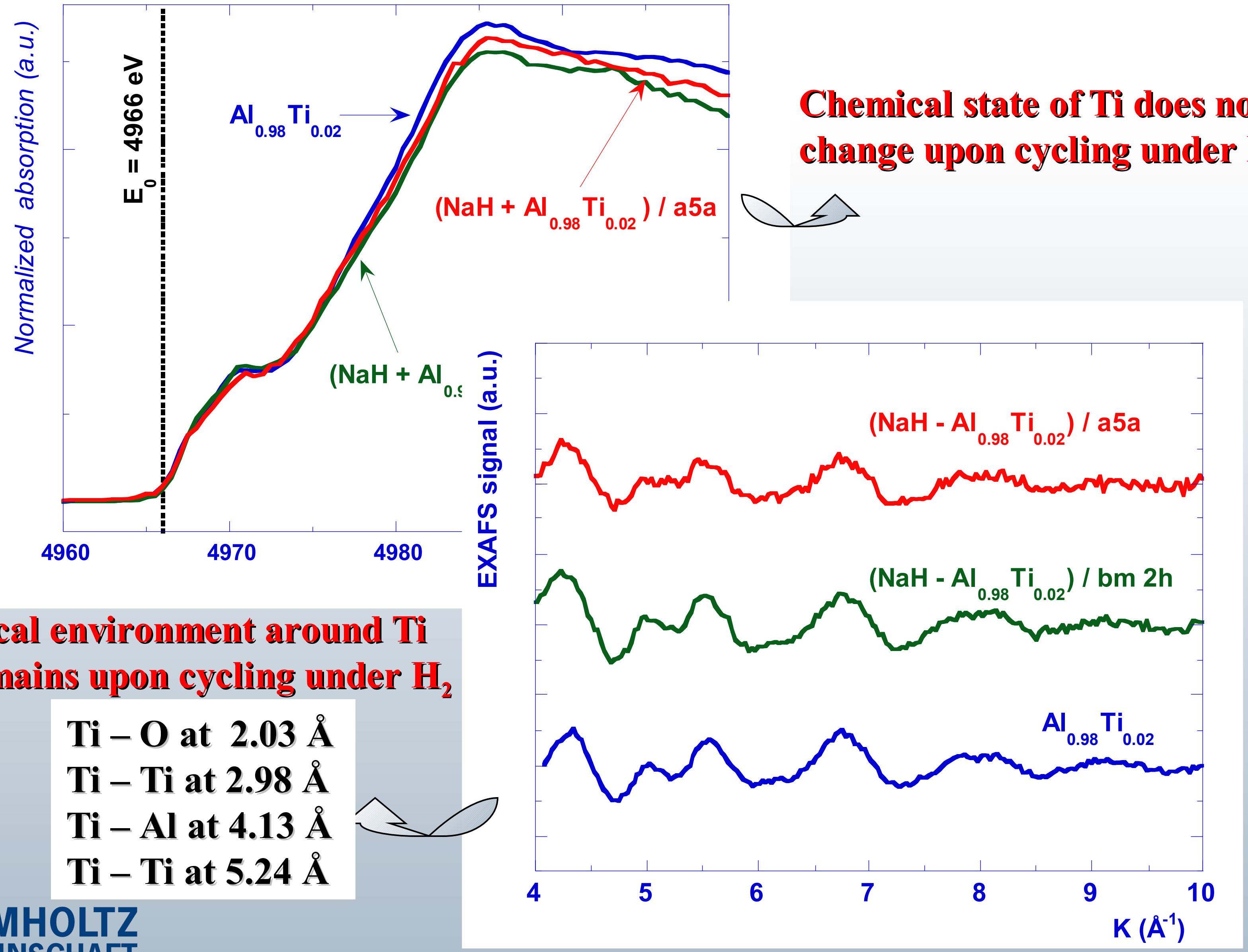
P_{H2} = 100 bar, T = 100 °C



- **Kinetics is improving with increasing number of cycles**
- **Reversible storage capacity is stable around 4 wt.% H_2**

M. Fichtner et al., patent DE 10 2005 037 772.6

XAS investigations



Chemical state of Ti does not change upon cycling under H_2

Local environment around Ti remains upon cycling under H_2

Ti – O at 2.03 Å
Ti – Ti at 2.98 Å
Ti – Al at 4.13 Å
Ti – Ti at 5.24 Å

Summary as concerns Ti,...

XPS analysis

- Ti is depleted at the surface (XPS, SIMS, and SNMS)
- Ti is in the metallic state after several cycles no matter of the nature of the precursor
- $TiAl_3$ alloy, TiO_2, TiH_2 are not present at the surface
- Electronic state of Ti ($2p_{3/2}$) line is less sensitive to the reversible reaction under hydrogen

XAS analysis

- XANES confirms the chemical state obtained from XPS
- Formation of a Ti-Al cluster after several cycles no matter of the nature of the precursor
- Local structure around Ti is not the $TiAl_3$ bulk phase

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Summary as concerns Al,...

XPS analysis

- Al concentration at the surface evolves with the reaction
- Al_2O_3 is not present at the surface
- Electronic state of Al(2p) line is sensitive to the reversible reaction under hydrogen

XANES analysis

- XANES confirms the higher valence state of Al in $NaAlH_4$
- Local structure around Al evolves with the presence of Ti
- Presence of molecular-scale inhomogeneities in the average structure of $NaAlH_4$

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➢ Summary and conclusion,...

▶ **Multidisciplinary approach on nanoscale H_2 storage material**

- Gain knowledge on the ongoing transformation processes around Ti
- Synthesize a novel $Al_xTi_{(1-x)}$ nanocomposite as starting material for $NaAlH_4$
- Stabilize the kinetics and the reversible hydrogen storage capacity upon cycling
- Kinetics comparable to the $TiCl_3$ doped $NaAlH_4$

► **Efficiency of the novel material to be improved**
(by varying key parameters like annealing temperature,...)

► **Mechanism involved and identity of the effective catalyst**
(to be determined,…)

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Beam-time allotment

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EU-IP "StorHy"

Hydrogen Storage for Automotive Application

Contract No. 502667