Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft

Institute of Nanotechnology

Transformation Mechanisms of Alanate Composites

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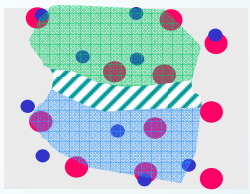
Our proposition for a model:

*The **Overall Kinetics** is a consecutive reaction of*

Fast Chemisorption step	*Fast H transport*	*Slow Phase Transformation*
dissociation / recombination of H_2 *Ti containing surface*	*mobile H species or jumping* *Enhanced by Ti induced defects*	*Materials transport in the solid* *Ti induced defect structure*

H ? , AlH_3?



Why ?

Chemisorption Step / observations:

- *Isotope Scrambling of H2/D2 on the surface of Ti-doped $NaAlH_4$ (MPI-KF, Mühlheim)*

But: Noble metal catalysts have no advantage although Pd, Pt have 3 orders of magnitude better chemisorption properties than Ti !

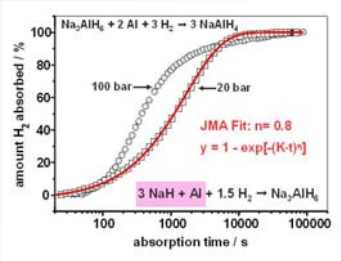
H transport / observations:

- *^{1}H NMR experiments: Mobility of H is greatly enhanced with Ti-doped $NaAlH_4$ (MPI Stuttgart + Forschungszentrum Karlsruhe)*
- *There is a fast mobile H-species with 10^{11} jumps/s at room temperature (Universities di Roma, Genua & Hawaii)*

Defects and Phase Transformation / observations:

- *Rate limiting step is diffusion in the solid (Forschungszentrum Karlsruhe)*
- *Anelastic spectroscopy indicates point defect relaxation and stoichiometric defects (Univs. di Roma, Genua & Hawaii)*
- *There are indications for Al→Ti substitution and defects in XRD patterns of doped SAH (Forschungszentrum Karlsruhe).*

=> Ti plays multiple roles in the material; what we see in the kinetics is the Ti induced enhancement of the solid transport !



Kinetics

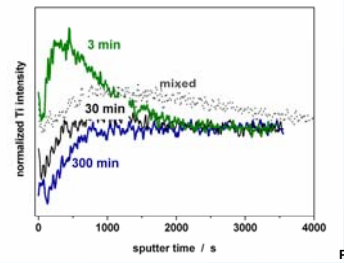
Rate limiting step is **diffusion in the solid!**

(Avrami coefficient: 0.8)

XRD

Possible substitutions of Ti for Al or Na inside the $NaAlH_4$ structure and the **presence of defects** have been checked by Rietveld refinement -> Slight preference for Ti at Al, not Na sites.

Occupation number	R_{Bragg}
No Ti fully occupied site	27.6
No Ti Al=1.003(5)	27.5
No Ti Na=0.996(6)	27.7
Ti=0.042(7) Al=0.958(7)	27.4
Ti=0.026(7) Na=0.974(7)	27.8



Ti depth profile (SNMS)

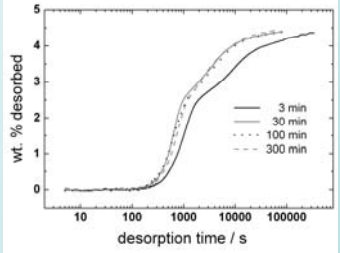
Depletion of Ti at the outer surface of longer ball-milled samples. Ti is driven into the material by ball milling.

Kinetics

There are *correlations* between

1. the amount of Ti **in** the material,
2. the deviations in the XRD pattern, and

the reaction rate!



Further reading:

- M. Fichtner, *Nanotechnological Aspects in Materials For Hydrogen Storage*, Advanced Engineering Materials 6 (2005) 232
- M. Fichtner, P. Canton, O. Kircher, A. Léon, *Nanocrystalline Alanates – Phase Transformations, and Catalysts*, J. Alloys Compounds (in press)
- A. Léon, O. Kircher, J. Rothe, and M. Fichtner, *Chemical State of Ti in $NaAlH_4$ Doped With $TiCl_3$ Using X-Ray Absorption Spectroscopy*, J. Physical Chemistry B 108 (2004) 16372