

Lightweight and Robust Hydrogen Storage Materials for Automotive Fuel Cells

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A New Hydrogen Storage Material is Needed for Automotive Fuel Cells

- Current H₂ storage materials do not meet DOE requirements of 6 wt% (90% recoverable) and 1100 Wh/L. The weight capacity requirement is the most critical target. Candidate storage materials also have these characteristics:
 - Low charge/discharge temperatures
 - Absorption of heat produced during refueling
 - Method of heating the storage material during discharge
- High rate of absorption/desorption
- Resistance to contaminant gases (e.g. CO, H₂S, O₂, H₂O)

System	Wt% H ₂	H ₂ Vapor Pressure	Kinetics	O ₂ , H ₂ O	CO, H ₂ S
Mg	7.66	1 atm, 279°C	-	-	+
Mg ₂ Ni	3.59	1 atm, 255°C	+	+	+
FeTi	1.86	4.1 atm, 25°C	++	-	-
LaNi ₅	1.49	1.8 atm, 25°C	+	+	-
Pd	0.72	1 atm, 147°C	++	+	-

Why Alane?

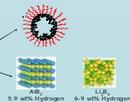
- Properties of Alane, [AlH₃],
 - 10% hydrogen by weight
 - Twice the hydrogen density (148 g/l) of liquid hydrogen (70.8 g/l at 20 K)
 - Nonvolatile crystalline solid
 - Structure is ionic (analogous to AF₃)
 - Molecular species unfavorable (AlH₃ Science 2003)
 - Free-flowing micro-crystalline powders
- Thermolysis of Alane
 - Begins to evolve H₂ at 60°C
 - Complete dissociation requires 200°C, depending on crystal size

Why Small Nanosize Aluminum?

- Thermodynamics
 - $\Delta H_f = -2.7$ kcal, $\Delta G_c = +11$ kcal
 - Calculations (at the PMP4 level of electron correlation) indicate that hydride formation from the reaction with hydrogen is thermodynamically favorable for small aluminum clusters (J. Phys. Chem. 1991, 95, 6519)
- Kinetics (catalysts are needed)
 - Alane is reversibly formed from the element in the 300-600°C range (Inorg. Chem. 1995, 34, 172)

Approaches to Forming Nanosize Aluminum

- Synthesize monodisperse aluminum nanoparticles using micelles as nanoreactors
- Investigate materials that store hydrogen in atomically thin two-dimensional layers

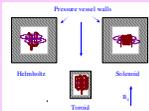


Materials Characterization Techniques

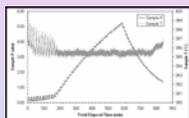
High-pressure NMR probe follows progress of aluminum-to-alane reaction



Toroid-pressure probes are more sensitive, yet are smaller than conventional NMR probes



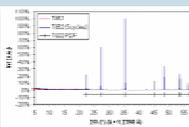
In-house fabricated automated Sievert's apparatus: Hydrogen uptake at hydrogen pressures up to 70 atm and temperatures up to 500°C



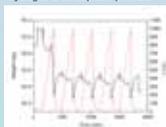
Operation of the apparatus has been verified using a titanium metal standard

Titanium Sample	mmoles H ₂	Avg T (°C)	Exp. wt% H ₂	Theo. wt% H ₂	Error
1	17.37	395.4	2.723	3.875	3.9%
2	16.03	294.8	2.370	3.876	13.1%

High-resolution X-ray diffraction at the APS: Phases present after hydrogen exposure



Thermal Gravimetric Analysis: Weight changes as a function of temperature during exposure to hydrogen at atmospheric pressure



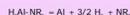
X-ray scattering at the APS will be used to determine nanoparticle size distribution

Aluminum Nanoparticles

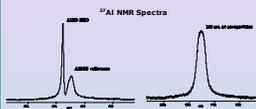
Goals

- A primary objective of this research is to determine how the thermodynamics for alane formation change with substrate size on the nanometer scale.
- Also investigated are strategies for the effective encapsulation of nanoparticulate aluminum and alane.
- This research seeks to develop hydrogenation catalysts for the activation of main group metals such as aluminum and magnesium

Thermodynamics for Alane-Amine System



- Reaction is readily followed in situ by ¹H and ²⁷Al NMR spectroscopy
- Results under 5000 psi of H₂
 - For T > 70°C the reaction proceeds to the right
 - $\Delta G = -4$ kcal at 65°C
 - Reaction appears to be autocatalytic and the mechanism is under investigation
- Experiments using H₂Al-NR₂ and D₂ in the gas phase are underway to provide additional evidence for chemical reversibility

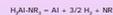


Future Work on Nanoparticulate Aluminum

- Measure additional T/P data points to determine ΔH and ΔS
- Determine the particle size distribution by X-ray scattering (R. Wharles, CHM) under T/P conditions established by in situ NMR
- Investigate the effect of hydrogen atom transfer catalysts
- The alane/amine literature approach exhibits poor control over the particle size
 - Synthesize monodisperse aluminum particles by the reaction of alane/amine complexes within the cores of micelles of known dimensions using amphiphilic diblock copolymer surfactants in nonaqueous media
- Determine thermodynamics and kinetics for hydrogen storage as a function of particle size with focus in determining which particle size is required to fine-tune the thermodynamics so that the equilibrium hydrogen partial pressure crosses one atmosphere near 100°C

Synthesis of Nanoparticulate Aluminum

- Literature method for producing nanoparticulate aluminum (J. Am. Chem. Soc., 1998, 120, 10847)



- Amines function as surface active agents for the stabilization of metal nanoparticles (Chem. Mater. 2003, 15, 935)

Thermodynamics for aluminum nanoparticulate hydrogenation are comparable to that of transition metal dimers



Future Work: Metal Radical Species Are Potential Hydrogen Atom Transfer Catalysts

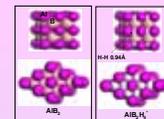
- Successful approach for the hydrogenation of transition metal dimers with strong M-M bonds (Inorg. Chem. 1994)
 - $M_2(CO)_4 + H_2 \rightarrow 2 HMn(CO)_5$
- Based on radical species such as Co(CO)₄ or V(CO)₆
 - $Co_2(CO)_8 \rightarrow 2 Co(CO)_4$
- That form molecular hydrogen complexes
 - $Co(CO)_4 + H_2 \rightarrow (H_2)Co(CO)_4$
- Which serve as "hydrogen" atom donors
 - $Co(CO)_4 + Mn_2(CO)_{10} \rightarrow (CO)_4CoH + HMn(CO)_5 + Mn(CO)_5$

Layered Boride Structures

MB₂ (M = Mg, Al, Ti) Materials Have Potential for Storing ~8 wt% H₂

- Boron layers are structurally similar to graphite except each B has one fewer electron
- Preliminary DFT calculations show a trend for the hydride materials to be more stable

- Initial TGA studies under one atmosphere of hydrogen using AlB₂, MgB₂, TiB₂ CoB₂ indicated a weight increase. Further characterization using high-resolution XRD at the APS showed that oxides were formed.



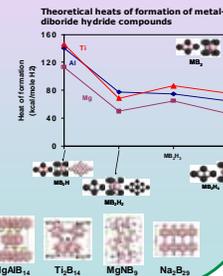
Material	Wt% H storage based on metal hydride only	Wt% H storage based on Al/Ti wt% only	No. of H atoms per B or Ti atom
AlB ₂	4.25 (2)	8.97	2.028
TiB ₂	5.25 (2)	7.97	2.078
MgB ₂	2.82 (2)	5.48	4.403

The heat of formation of the hydrides has been calculated for several known and proposed hydrogen storage materials

Compound	ΔH_f (kcal/mol H ₂)
Fe	-10.998 (8.82)
Mn	-12.013 (8.848)
MgH ₂	-280.565 (17.87) (14.268)
CaH ₂	-196.019 (19.27) (14.268)
MgH	174.519
CaH	144.660
Mg ₂ H ₂ (metal)	94.660

Future Work on Light Element Materials

- High pressure (70 atm, 1000 psia) testing apparatus is now operational
 - Critical to elucidating the hydriding properties of these materials
- First samples will be the MB₂ and MB₃ materials → leading samples AlB₂ and TiB₂
- Other nitrides, phosphides, and borides: Li₃P, B₂P₃, ZrB₃
- Surface doping the samples with ppm levels of Pd may be necessary to promote H₂ dissociation



Summary

- The ²⁷Al NMR resonance is a useful diagnostic tool for nanoparticulate aluminum formation because it is shifted by 1600 ppm from molecular alane complexes
- The ²⁷Al NMR results indicate that it is feasible to measure the thermodynamics and kinetics for Al nanoparticle hydrogenation at modest temperatures (60–125°C) and hydrogen pressures under 5000 psi in the presence of trialkyl amines
- Boride based materials are demonstrated to increase in weight under H₂ at ~850°C but, then lose weight by a second reaction process at temperatures near 1000°C
- High-pressure (70 atm, 1000 psia) testing apparatus is now complete and will be used to measure the hydrogen capacities of target materials containing aluminum, boron, and magnesium in atomically thin two-dimensional layers