

## Introduction

Aluminum hydride (alane) has received a great deal of interest in recent years due its possible use as a hydrogen storage material. Alane contains 10.1 weight % hydrogen which meets the 2015 target set by the DOE of 9 weight % hydrogen. The decomposition of alane to its elements has no side reactions and has a decomposition enthalpy of 10 KJ/mol H<sub>2</sub>.

Thermal decomposition begins above 60 °C, but is slow. Decomposition studies have shown an ideal temperature range of 130 – 150 °C but with added dopant of TiCl<sub>3</sub> or LiH decomposition can be achieved at an acceptable rate at <100 °C (1). This, accompanied with recognition that rehydrogenation is realistic, makes alane a contender for use as an ideal hydrogen storage material.

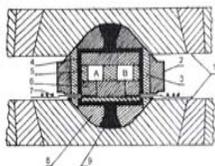


The synthesis of alane usually employs an organometallic preparation in an ether solution (2):



## Hydrogenation of Aluminum

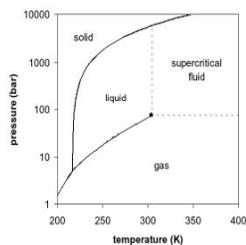
The first reported synthesis of aluminum hydride from its elements was reported by Kononov and Bulychev in 1995 using 2.5 GPa at 300 °C within two Bridgman anvils (3). This procedure is not energy efficient, however, it has set a precedent for high pressure reactions to lead the way in the quest for the reversible hydrogenation of aluminum to aluminum hydride. An innovative process is required with economical pressures, temperature and environmentally friendly solvents.



Construction of the high-pressure device:

- 1- Bridgman anvils (WC);
- 2- ring from lithographic stone (d<sub>inter</sub>= 18 mm, d<sub>ext</sub>= 30 mm);
- 3- container from lithographic stone (d<sub>inter</sub>= 12 mm, d<sub>ext</sub>=18 mm);
- 4- graphite heaters with caps (d<sub>inter</sub>= 10 mm);
- 5- holder with a sample (A) and standard (Al<sub>2</sub>O<sub>3</sub>) from NaCl (B);
- 6- thermocouple unit from NaCl;
- 7- thermocouples (d = 3 mm);
- 8- thermoisolators from lithographic stone;
- 9- graphite leads.

## Hydrogenation using Supercritical Fluids



Phase diagram of CO<sub>2</sub>.



CO<sub>2</sub>: P<sub>c</sub> = 73 bar; T<sub>c</sub> = 31 °C

Photo of meniscus at P<sub>c</sub> and T<sub>c</sub> CO<sub>2</sub> taken in Phase Monitor

80 bar H<sub>2</sub> in scCO<sub>2</sub> corresponds to 3 M H<sub>2</sub> concentration  
 corresponds to > 1000 bar H<sub>2</sub> in C<sub>6</sub>H<sub>6</sub>.

## Anyone for a Supercritical Fluid Cocktail?

Fluid	T <sub>f</sub> /°C	P <sub>f</sub> /bar	ρ/Kg
CO <sub>2</sub>	31	74	3
C <sub>2</sub> H <sub>6</sub>	32	49	100
C <sub>3</sub> H <sub>8</sub>	97	42	10
Me <sub>2</sub> O	127	54	15
SF <sub>6</sub>	45	38	50
CHF <sub>3</sub>	26	28	125

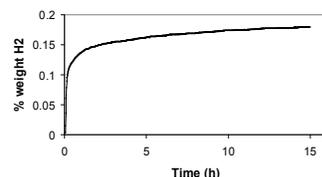
- Complete miscibility with permanent gases like H<sub>2</sub>
- Excellent thermal transfer properties
- Option to add co-solvents and solutes (e.g. donors and catalysts)

## SCF Manifold

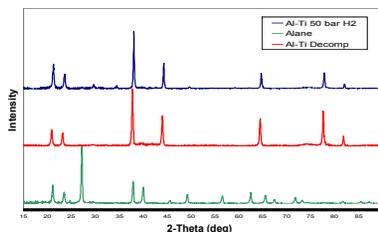


## SCF Hydrogenation Results

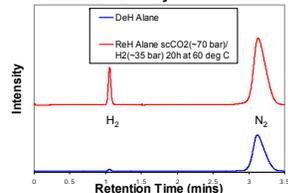
PCT plot showing decomposition of rehydrogenated Al doped with 2 mol % TiCl<sub>3</sub>



Stacked XRD plot of 2 mol % TiCl<sub>3</sub> doped α-Alane

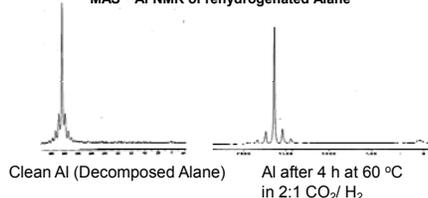


Stacked GC Analysis Plot of Alane



PV H<sub>2</sub> release from rehydrogenated sample heated in the Monel vessel ~0.2 wt% H<sub>2</sub>.

MAS <sup>27</sup>Al NMR of rehydrogenated Alane



## Stabilizing Adducts

It has been suggested that employing a stabilizing adduct during hydrogenation of aluminum could aid the formation of aluminum hydride. Alane is a Lewis acid which reacts readily with Lewis bases that have a high donor strength. Many adducts of alane have been theoretically studied, chemically synthesized and characterized over the past 60 years including carbenes, phosphines, amines and various oxygen donors.

Under high pressures of hydrogen the alane adduct can be formed and then removed by thermal decomposition. E. C. Ashby reported a triethylenediamine (TEDA) alane complex which was directly synthesized at high pressure (350 bar) in organic solvents from aluminum, hydrogen and TEDA (4). Graetz et al. recently reduced the required pressure for Ashby's experiment to less than 600 psi using aluminum doped with 2 mol % TiCl<sub>3</sub> (5). Although the TEDA alane has been synthesized, it can not be removed to leave pure alane.

Use of donor co-solvent to stabilize the alane intermediate:  
 $\text{Al} + 1.5 \text{H}_2 + \text{L} \rightarrow \text{L} \cdot \text{AlH}_3 \rightarrow (\text{AlH}_3)_x$   
 $\text{Al} + 1.5 \text{H}_2 + 2\text{L} \rightarrow 2\text{L} \cdot \text{AlH}_3 \rightarrow (\text{AlH}_3)_x$

Decomposition of Alane adduct intermediate:  
 $\text{L} \cdot \text{AlH}_3 \rightarrow (\text{AlH}_3)_x + \text{L} \rightarrow \text{Al} + 1.5 \text{H}_2$   
 $2\text{L} \cdot \text{AlH}_3 \rightarrow (\text{AlH}_3)_x + 2\text{L} \rightarrow \text{Al} + 1.5 \text{H}_2$

## DFT Calculations

DFT calculations (B3LYP) have been performed on various nitrogen and oxygen donors to ascertain the ideal ligand to act as a leaving group to produce pure alane. According to the calculations, oxygen donors require less energy in formation and decomposition whilst nitrogen donors are more thermodynamically stable.

### Oxygen Donor Ligands

1:1 Complexes	ΔH <sub>c</sub> (kJ/mol)	1:2 Complexes	ΔH <sub>c</sub> (kJ/mol)
AlH <sub>3</sub> .Et <sub>2</sub> O	-71.52	AlH <sub>3</sub> .2Et <sub>2</sub> O	-87.07
AlH <sub>3</sub> .MeOEt	-77.68	AlH <sub>3</sub> .2MeOEt	-99.29
AlH <sub>3</sub> .Me <sub>2</sub> O	-83.18	AlH <sub>3</sub> .2Me <sub>2</sub> O	-113.69
AlH <sub>3</sub> .Dioxane	-84.40	AlH <sub>3</sub> .2Dioxane	-116.88
AlH <sub>3</sub> .THF	-93.13	AlH <sub>3</sub> .2THF	-122.02

### Nitrogen Donor Ligands

1:1 Complexes	ΔH <sub>c</sub> (kJ/mol)	1:2 Complexes	ΔH <sub>c</sub> (kJ/mol)
AlH <sub>3</sub> .Et <sub>3</sub> N	-89.05	AlH <sub>3</sub> .2Et <sub>3</sub> N	-90.92
AlH <sub>3</sub> .Me <sub>3</sub> N	-108.13	AlH <sub>3</sub> .2Me <sub>3</sub> N	-145.90
AlH <sub>3</sub> .Pyridine	-109.24	AlH <sub>3</sub> .2Pyridine	-142.12
AlH <sub>3</sub> .TEDA	-115.38	AlH <sub>3</sub> .2TEDA	-155.40
AlH <sub>3</sub> .Quinuclidine	-118.37	AlH <sub>3</sub> .2Quinuclidine	-156.04

## Conclusions and Future Work

Low level hydrogenation of Al (max 0.4 weight % H<sub>2</sub>) has been achieved using different combinations of SCFs.

Occurrence of hydrogenation has been confirmed by MAS <sup>27</sup>Al NMR spectroscopy, gas chromatography, and isothermal desorption studies.

A new station has been built that is designated for SCF reactions.

DFT studies have been conducted on 1:1 and 2:1 adducts of alane that can stabilize hydrogenation reactions.

Alternative SCFs and cocktails will be explored to improve hydrogen uptake by the stabilization of alane or intermediate.

New sources of 'activated' aluminum will be investigated, as well as new types and methods of doping.

Alternative sources of catalysts and initiators will also be screened.

## Acknowledgements

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## References

- (1) J. Graetz, *J. Phys. Chem. B* **2005**, 109, 22181. (2). F.M. Brower, N.E. Matzek, P.F. Reigler, H.W. Rinn, C.B. Roberts, D.L. Schmidt, J.A. Snover, K. Terada, *J. Am. Chem. Soc.* **1976**, 98, 2450. (3) S. Kononov and Boris M. Bulychev, *Inorg. Chem.* **1995**, 34, 172. (4) E.C. Ashby, *J. Am. Chem. Soc.*, **1964**, 86, 1882 (5) J. Graetz, *J. Phys. Chem. C*, **2007**, 111 (51), 19148