IV.E.4 Aluminum Hydride: the Organic-Metallic Approach

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Project End Date: September 30, 2013

Overall Objectives

Develop onboard vehicle storage systems using aluminum hydride that meets all of DOE's targets for the proton exchange membrane fuel cell vehicle.

- Produce aluminum hydride material with a hydrogen gravimetric storage capacity greater than 9.7% (kg-H_2/kg) and volumetric storage capacity of 0.13 kg-H_2/L.

- Assist in developing aluminum hydride slurry storage systems for better than 6% hydrogen gravimetric material density, 0.07 kg-H_2/L volumetric hydrogen storage capacity, and well-to-wheels efficiencies greater than 60%.

Fiscal Year (FY) 2013 Objectives

Develop practical and economical processes for regenerating aluminum hydride.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) System Weight and Volume

(B) System Cost

(E) Charging/Discharging Rates

Technical Targets

Table 1 is a listing of the 2015 DOE hydrogen storage targets along with BNL's current 2013 aluminum hydride project status. The well-to-wheels efficiency listed in the table under the column for 2013 Status was taken from an independent analysis by Argonne National Laboratory on the alane adduct (AlH$_3$:TEA) storage system. The 0.0582 gravimetric storage parameter listed in Table 1 was a measured value obtained by decomposing 60 wt% alane slurries. The slurries consisted of aluminum hydride particles having a hydrogen content of 9.7 wt% that were suspended in liquid glycol. The gravimetric storage parameter was hydrogen material weight only, and did not take into account the balance of plant weight.

TABLE 1. Progress in Meeting Technical Hydrogen Storage Targets for Aluminum Hydride Regeneration

Storage Parameter	Units	2015 Target	2013 Status
Gravimetric	wt% H_2	0.055	0.0582
Volumetric	kg H_2/L	0.040	0.070
Fuel Flow Rate (temperature)	(g/s)/kW °C	0.02 80	0.02 80
Well-to-Wheels Efficiency	kW-H_2/kW	60%	>55%
Refueling Time	min	3.3	To Be Determined

FY 2013 Accomplishments

- Demonstrated direct synthesis of alane tertiary amines by reacting γ-AlH$_3$ in a diethylether solution with various tertiary amines, resulting in high yields of N-alkylpiperidine:alane, N-alkylmorpholine:alane, and N-alkylpyrrolidine:alane.

- Identified the N-ethylpiperidine:alane and N-ethylmorpholine:alane as being two compounds that improved yields, controllability and energy efficiency for recovering donor free aluminum hydride as compared to the previous 55% wells-to-wheels efficiency for recovering aluminum hydride from the triethylene:alane compound.

✧   ✧   ✧   ✧   ✧

INTRODUCTION

AlH$_3$ (alane) is a promising hydrogen storage material because of its high hydrogen capacity (10.1 wt% and 1.48 g/mL) and its low decomposition temperature

(<100ºC). The main challenge of using alane as a storage medium is finding methods for the cost- and energy-effective hydrogenation of aluminum back to donor-free AlH_3. Several synthetic methods that include reaction of $AlCl_3$ with alkali alanates, electrochemical synthesis from $LiAlH_4$ and $NaAlH_4$, and direct hydrogenation of Al metal all involve either expensive materials or very high H_2 pressures. These methods are therefore not practical for large-scale commercial manufacturing of aluminum hydride. Previous work at Brookhaven has shown a three-step alane regeneration pathway involving titanium catalyzed aluminum metal, hydrogen, and tertiary amines (Figure 1). In such a process a 2:1 adduct (amine)$_2$:AlH_3 (amine = Me_3N or $EtMe_2N$) is formed by hydrogenation of Al in a chemical reactor with an organic solvent at moderate temperatures and pressures. The 2:1 adduct is then transaminated with a second amine (nominally Et_3N) to yield the less stable Et_3N:AlH_3 compound. This compound is then decomposed under moderate heat and vacuum distillation to leave donor-free α-AlH_3. This additional chemical step of converting the 2:1 to a 1:1 adduct is necessary, since the 2:1 adducts directly decompose to aluminum metal. Although donor-free alane was identified in the product, the (Et_3N·AlH_3) decomposition step suffered from several drawbacks, including low yields of AlH_3, low energy efficiency, slow kinetics, and contamination of the product by varying amounts of Al metal.

APPROACH

For this year the approach was to improve the well-to-wheels efficiency by studying the structures of 1:1 and 2:1 Lewis base stabilized alane tertiary amine adducts. In particular the project investigated the synthesis, characterization and thermal decomposition of various N-alkylpiperidine:alane, N-alkylmorpholine:alane and N-alkylpyrrolidine:alane compounds. The purpose of the study was to identify new energy efficient pathways for synthesizing alane. Alane tertiary amine adducts have a rich chemistry by possessing three types of structures (Figure 2). The type of structure depends on the steric hindrance of
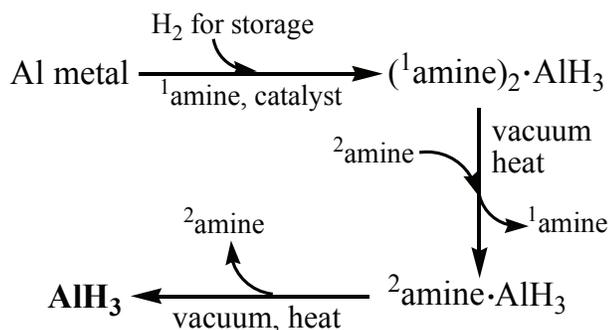
FIGURE 1. Three-step process for recovering aluminum hydride from amine:AlH_3.
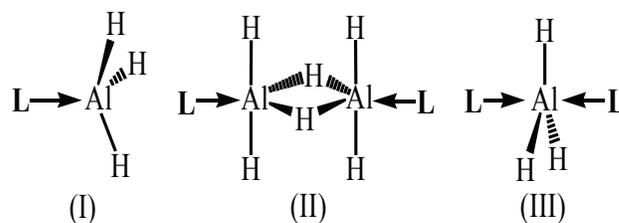
FIGURE 2. The three structure types of mono-dentate Lewis base alane compounds; (I) mono, (II) dimer, (III) bis.

the mono-dentate tertiary amine. These three structures are labeled the 1:1 mono-compound, the 1:1 dimer compound, and the 2:1 bis-compound. It is generally accepted that less steric hindered Lewis bases will form either 1:1 or 2:1 complexes with alane, but the bulkier hindered bases will yield only 1:1 compounds. These observations are relevant to the recovery of donor-free AlH_3, since only the 1:1 bulky ethyl bases such as the 1:1 triethylene:alane (Et_3N:AlH_3), the 1:1 N-ethylmorpholine:alane (NEM:AlH_3), as well as the 1:1 N-ethylpiperidine:alane (NEPi:AlH_3) have thus far afforded α-AlH_3 recovery under moderate heat and vacuum distillation removal of the tertiary amine.

RESULTS

Nuclear Magnetic Resonance (NMR) and Infrared (IR) Spectroscopy

At room temperature, both N-methylpiperidine:alane (NMPi:AlH_3) and NEPi:AlH_3 are viscous liquid; their identities were established by NMR and IR spectroscopy. The 1H NMR spectra confirmed that each adduct has one NMPi (or NEPi) molecule per AlH_3 moiety. In the IR spectra (Figure 3a), the Al-H absorptions are centered at 1,775 cm^{-1} for NMPi:AlH_3 and at 1,777 cm^{-1} for NEPi:AlH_3. It can be noted that the small difference in Al-H stretching frequencies between NMPi:AlH_3 and NEPi:AlH_3 may reflect the differences in the relative Lewis basicity of NMPi and NEPi. Although the 2:1 adducts $L_2$$AlH_3$ (L = NMPi or NEPi) were not isolated, in situ studies were performed to probe interactions between AlH_3 and N-alkylpiperidine. As shown in Figure 3a, addition of eight equivalent of NMPi into a solution of NMPi:AlH_3 (1 equivalent) caused the Al-H absorption to shift from 1,775 cm^{-1} to 1,712 cm^{-1}. This indicates the formation of (NMPi)$_2$:AlH_3. In contrast, NEPi:AlH_3 did not show any such changes, suggesting no or a negligible amount of (NEPi)$_2$:AlH_3 were formed under similar conditions. Such dramatic difference is due primarily to the steric effects from the ethyl group in NEPi. Similar difference was also observed for the N-alkylpyrrolidine:alane compounds. To further study the elusive nature of (NMPi)$_2$:AlH_3, a series of IR spectra of NMPi:alane under different conditions were recorded. As illustrated in Figure 3b, upon on addition of four equivalent
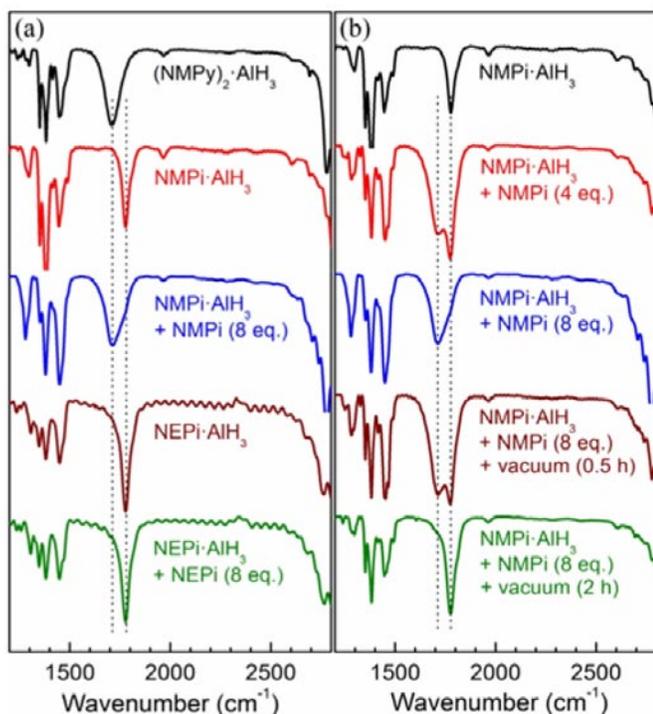
FIGURE 3. (a) IR spectra of NMPi:AlH$_3$ and NEPi:AlH$_3$ adducts in Et$_2$O; (b) IR spectra of NMPi:AlH$_3$ under different conditions of excess N-methylpiperidine.

of NMPi into NMPi:AlH$_3$ (1 equivalent), a new peak at 1,712 cm^{-1} appeared. Further addition of NMPi (up to eight equivalent) generated more (NMPi)$_2$:AlH$_3$, as evidenced by the disappearance of NMPi:AlH$_3$ at 1,775 cm^{-1}. When this mixture was held under vacuum, the (NMPi)$_2$:AlH$_3$ absorption peak (1,712 cm^{-1}) decreased gradually with concurrent appearance of the NMPi:AlH$_3$ absorption peak. Thus, in the presence of excess NMPi, (NMPi)$_2$:AlH$_3$ is formed and exists in equilibrium with NMPi:AlH$_3$; however, it is not isolable because it readily loses under vacuum one NMPi molecule to form NMPi:AlH$_3$. Compared to more stable 2:1 adducts, such as (EtMe$_2$N)$_2$:AlH$_3$ and (NMPy)$_2$:AlH$_3$, the labile nature of the first NMPi molecule in (NMPi)$_2$:AlH$_3$ can be attributed to the increased steric hindrance of NMPi:

Thermal Decomposition

This year the project focused on studying the thermal properties (or decomposition pathways) of the 1:1 N-methylmorpholine:alane (NMM:AlH$_3$), NEM:AlH$_3$ and NEPi:AlH$_3$ compounds in order to replace the 1:1 Et$_3$N:AlH$_3$ compound in the recovery step for AlH$_3$. This replacement is beneficial because the separation of AlH$_3$ from Et$_3$N:AlH$_3$ is associated with several undesired processes, including evaporation loss of Et$_3$N:AlH$_3$ and formation of aluminum metal. Also it is worth recalling that all 2:1 amine:alane adducts previously studied in this project always decomposed directly to aluminum metal

upon heating. This fact suggests limiting the scope of the investigation to only 1:1 compounds. It was found that the 1:1 NMM:AlH$_3$ (solid) is stable up to 80°C, and no reaction was observed below 80°C. However at 85°C, NMM:AlH$_3$ gradually decomposed to a grey solid, which was confirmed to be aluminum metal by X-ray diffraction (XRD) analysis. Thus, NMM:AlH$_3$ is not suitable for the separation and recovery of donor free AlH$_3$. Decomposition of NEM:AlH$_3$ was also studied in a similar manner. In the temperature range of 20 to 55°C, no reaction occurred. Between 60 and 70°C and under reduced pressures (~20 mm Hg), NEM:AlH$_3$ readily changed to a grey solid with significant loss of mass. XRD analyses showed the formation of α-AlH$_3$ with a small amount of Al metal (Figure 4). Compared to that of NMM:AlH$_3$, the decomposition of NEM:AlH$_3$ to give alane could be attributed to the greater steric hindrance and the decreased Lewis basicity of NEM. Further increasing the reaction temperature (>75°C) of NEM:AlH$_3$ gave mostly Al metal with a trace amount of (or no) α-AlH$_3$. Thus, the ideal temperature range for the separation of AlH$_3$ from NEM:AlH$_3$ is between 60 and 70°C. As a result, unlike Et$_3$N:AlH$_3$, which requires a metal hydride additive (such as LiH or LiAlH$_4$) as catalyst or seed for the decomposition, NEM:AlH$_3$ and NEPi:AlH$_3$ do not require any catalyst in the alane recovery process. Thus, no external hydride impurities are introduced into the product for the NEM:AlH$_3$ and NEPi:AlH$_3$ reactions. Although a small amount of α-AlH$_3$
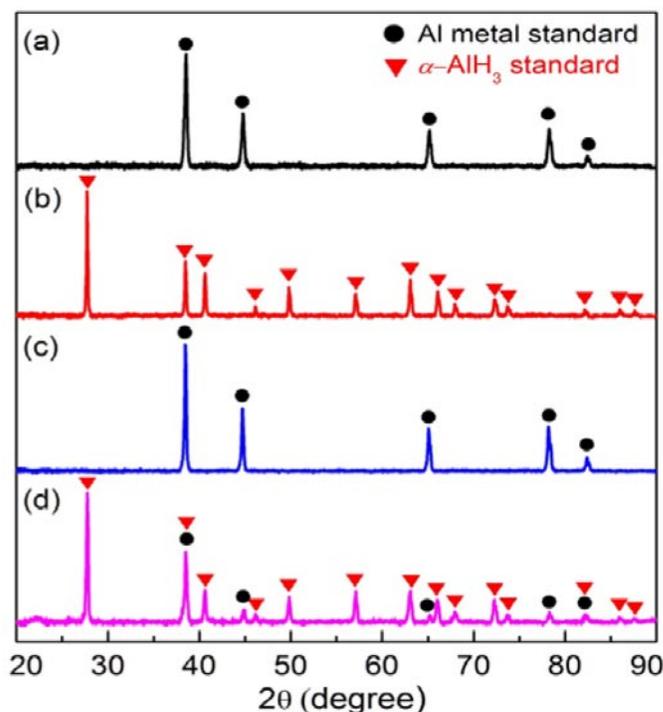
FIGURE 4. XRD patterns of the decomposition products of NMM·AlH$_3$ and NEM·AlH$_3$: (a) Al metal (standard); (b) α-AlH$_3$ (standard); (c) the NMM:AlH$_3$ decomposition product; (d) the NEM:AlH$_3$ decomposition products.

(as seed/catalyst) can hasten the reaction to some extent. We note that the alane product from NEM:AlH$_3$ and NEPi:AlH$_3$ may contain a small amount of Al metal; however, the yield and selectivity of these two reactions are significantly improved compared to Et$_3$N:AlH$_3$. Thus, NEM:AlH$_3$ and NEPi:AlH$_3$ are both better intermediates than Et$_3$N:AlH$_3$ for the separation and recovery of alane.

CONCLUSIONS

The thermal decomposition pathways of NMM:AlH$_3$, NEM:AlH$_3$ and NEPi:AlH$_3$ have been elucidated this year. It was shown that the efficiency for recovering AlH$_3$ from tertiary amine alanes greatly improves when incorporating either the NEM:AlH$_3$ or NEPi:AlH$_3$ compounds into the synthesis process, rather than using the TEA:AlH$_3$ compound. The main conclusion reached was that the 1:1 NMM:AlH$_3$ compound decomposes directly to aluminum metal, while the 1:1 NEM:AlH$_3$ and 1:1 NEPi:AlH$_3$ compounds can be selectively transformed to donor free AlH$_3$. Therefore by combining the transamination of (DMEA)$_2$:AlH$_3$ with either NEM:AlH$_3$ or NEPi:AlH$_3$, we have established a new separation pathway for the recovery of donor free AlH$_3$. This new pathway has improved yields, selectivity, and energy efficiency. More importantly, because of the fast reaction kinetics (even at room temperature), the new pathway can be combined with hydrogenation of Al metal to prepare donor-free AlH$_3$. The process still involves multiple chemical steps, but requires only a one-pot reactor. Achieving the synthesis of donor-free AlH$_3$ in a single pot reactor would significantly reduce cost. However, whether aluminum hydride would meet DOE's hydrogen fuel cost target awaits further validation testing.

FY 2013 PEER-REVIEWED PUBLICATIONS

1. Ni, Chengbao; Yang L.; Muckerman J.T.; Graetz J.; N-Alkylpyrrolidine Alane Compounds for Energy Applications, *J. Phys. Chem. C.*, Jan. (2013) 117, p2628.

2. Ni, Chengbao; Wegrzyn J.; Zhou W-M; Celebi Y.; N-Alkylpiperidine Alane Compounds and Their Applications in Alane Regeneration, *Int. J Hydrogen Energy*, Aug. (2013).

3. Ni, Chengbao; Yang L.; Muckerman J.T.; Graetz J.; Aluminum Hydride Separation Using N-Alkylmorpholine, *J. Phys. Chem. C.*, June (2013) 117, p14983.