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Regeneration Of Ammonia Borane Spent Fuel

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Introduction

A necessary target in realizing a hydrogen (H_2) economy, especially for the transportation sector, is its storage for controlled delivery, presumably to an energy producing fuel cell.¹ In this vein, the U.S. Department of Energy's Centers of Excellence (CoE) in Hydrogen Storage have pursued different methodologies, including metal hydrides, chemical hydrides, and sorbents, for the expressed purpose of supplanting gasoline's current > 300 mile driving range. Chemical H_2 storage has been dominated by one appealing material, ammonia borane (H_3N-BH_3 , AB), due to its high gravimetric capacity of H_2 (19.6 wt %) and low molecular weight (30.7 g mol⁻¹). In addition, AB has both hydridic and protic moieties, yielding a material from which H_2 can be readily released in contrast to the loss of H_2 from C_2H_6 which is substantially endothermic.² As such, a number of publications have described H_2 release from amine boranes, yielding various rates depending on the method applied.³⁻⁶ The viability of any chemical H_2 storage system is critically dependent on efficient recyclability, but reports on the latter subject are sparse, invoke the use of high energy reducing agents, and suffer from low yields.^{1, 7-10}

Summary of Results

Our group is currently engaged in trying to find and fully demonstrate an energy efficient regeneration process for the spent fuel from H_2 depleted AB with a minimum number of steps. Although spent fuel composition depends on the dehydrogenation method, we have focused our efforts on the spent fuel resulting from metal-based catalysis, which has thus far shown the most promise. Metal-based catalysts have produced the fastest rates for a single equivalent of H_2 released from AB and up to 2.5 equiv. of H_2 can be produced within 2 hours. While ongoing work is being carried out to tailor the composition of spent AB fuel, a method has been developed for regenerating the predominant product, polyborazylene (PB) which can be obtained readily from the decomposition of borazine or from nickel carbene catalyst dehydrogenation.¹¹ In this cycle, the PB is digested with benzenedithiol to yield two products which can both be converted to AB using Bu_3SnH and Bu_2SnH_2 as reductants. However, in a real world situation the process becomes more complicated for several reasons. Bu_2SnH_2 is thermally unstable and therefore not viable in a process scale operation. This has led to the development of Bu_3SnH as the sole reductant although this requires an additional amine exchange step in order to facilitate the reduction to an amine-borane which can then be converted to AB. The tin by-products also need to be recycled in order to maximize the overall energy efficiency and therefore minimize the overall cost of the process. In addition, on an industrial scale, the mass of the tin reductant generates significant cost due to the manipulation of the relatively large quantities involved so reducing the mass at this stage would be of vast significance. We will discuss further developments made to the tin recycle component of the cycle (including methods to minimize tin usage) and investigate new methods of reduction of the digested products, primarily focusing on lighter reductants, including lighter analogs of Bu_2SnH_2 and Bu_3SnH . These advances will have a

significant impact on the cost of production and therefore the viability of AB as a fuel.

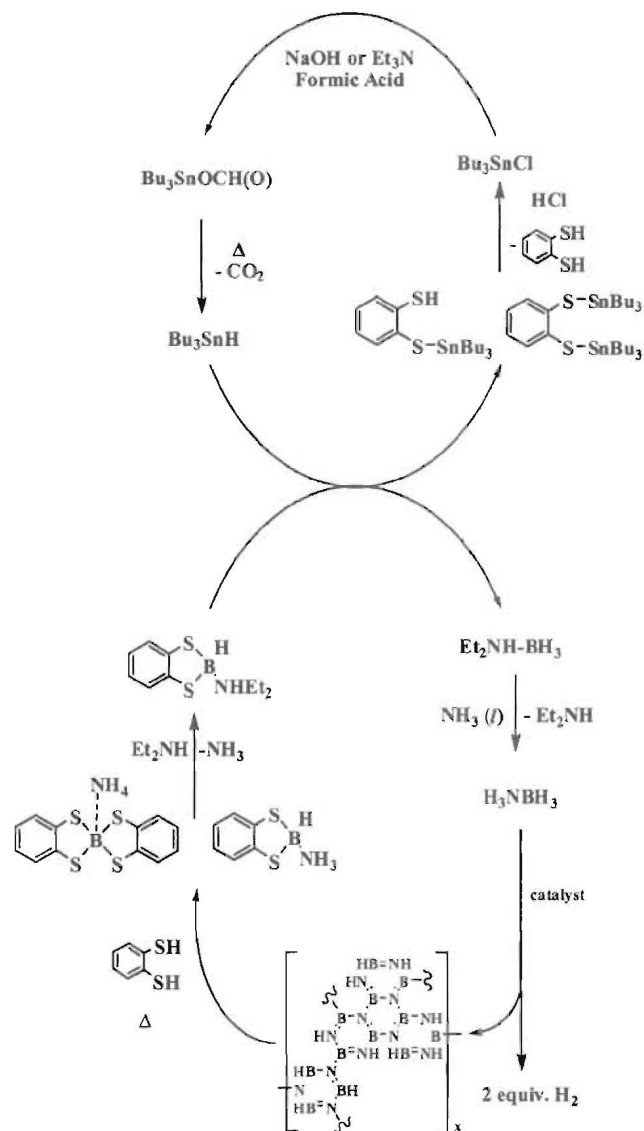


Figure 1. Regeneration of AB with tin and ortho-benzenedithiol recovery.

Conclusions.

Minimization of tin reagents and their recycle will contribute to reduction of the overall cost of AB regeneration and all stages of AB regeneration have been demonstrated.

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References

- (1) Stephens, F. H.; Pons, V.; Baker, R. T. *Dalton Trans.*, **2007**, 2613.
- (2) Matus M. H.; Anderson K. D.; Camaioni D. M.; Autrey S. T.; Dixon D. A. *J. Phys. Chem. A*, **2007**, *111*, 4411.
- (3) Bluhm M. E.; Bradley M. G.; Butterick III M.; Kusari U.; Sneddon L. G. *J. Am. Chem. Soc.*, **2006**, *128*, 7748.

- (4) Denney M. C.; Pons V.; Hebden T. J.; Heinekey D. M.; Goldberg K. I. *J. Am. Chem. Soc.*, **2006**, *128*, 12048.
- (5) Keaton R. J.; Blacquiere J. M.; Baker R. T. *J. Am. Chem. Soc.*, **2007**, *129*, 1844.
- (6) Stephens F. H.; Baker R. T.; Matus M. H.; Grant D. J.; Dixon D. A. *Angew. Chem. Int. Ed.*, **2007**, *46*, 746.
- (7) Sneddon L. G.; *Amineborane Hydrogen Storage* in Department of Energy Hydrogen Program Review. Can be found at http://www.hydrogen.energy.gov/pdfs/review06/st_3_sneddon.pdf 2006.
- (8) Sneddon L. G.; *Amineborane-Based Chemical Hydrogen Storage* in Department of Energy Hydrogen Program Review. Can be found at http://www.hydrogen.energy.gov/pdfs/review07/st_27_sneddon.pdf 2007.
- (9) Hausdorf, S.; Baitalow F.; Wolf G.; Mertens F. O. R. L, *Int. J. Hydrogen Energy*, **2008**, *33*, 608.
- (10) Ramachandran P. V. ; Gagare P. D. ; *Inorg. Chem.*, **2007**, *46*, 7810.
- (11) Davis, B. L.; Dixon, D. A.; Garner, J. C.; Gordon, J. C.; Matus, M. H.; Stephens, F. H., *Angew. Chem. Int. Ed.*, accepted for publication.