

Systems of assisted hydrogen evolution from chemical hydrides.

Sherzod Madrahimov

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Ecological, political, and economical issues associated with natural hydrocarbon resources, especially their dwindling supply and their effect on global climate, are prompting increasing research on renewable energy sources. A nearly ideal candidate as the basis of a renewable energy technology is the conversion of water to H_2 using electricity or sunlight.¹ However, the development of a lightweight and compact system to store large amounts of hydrogen is one of the biggest scientific and technological challenges that must be overcome before it will be possible to switch to a “hydrogen economy”.^{2,3} For transportation applications, the current goal is to develop a system of controlled H_2 release that would provide vehicles with a traveling range of ~500 km without refueling. It should operate at temperatures below 350 K, which would allow for utilization of heat generated during operation of polymer electrolyte membrane (PEM) fuel cells. The recharging of the system with hydrogen should be reversible under mild conditions. Alternatively, if the recharging is thermodynamically irreversible, the system should produce environmentally benign dehydrogenation products that can easily be chemically rehydrogenated. Several approaches have been investigated over the years, with systems based on chemical hydrides having the most desirable operating temperature range and hydrogen storage capacity by weight.³

Elemental transition metals and intermetallic alloys are known to form complex hydrides that release hydrogen reversibly under mild conditions.^{4,5} These compounds, however, are not suitable for hydrogen storage due to their low hydrogen content by weight (0.5-2.5%).⁵ Some complex hydrides of lighter elements such as aluminum, most notably $LiAlH_4$, $NaAlH_4$, and $KAlH_4$, undergo stepwise dehydrogenation at elevated temperatures (>200°C).^{6,7} In 1997 Bogdanovic and Schwickardi reported that dehydrogenation and rehydrogenation of $NaAlH_4$ in the solid state is catalyzed by 2 mol% Ti.⁸ Jensen and his group showed that the performance of this system improves, due to smaller particle size, if Ti(III) or Ti(IV) salts are incorporated into the system through ball milling (Figure 1).⁹ Later, the same group showed that $NaAlH_4$ prepared by milling NaH and Al under 10 bar H_2 pressure showed better hydrogen storage capacities during cyclic dehydrogenation/rehydrogenation tests.¹⁰

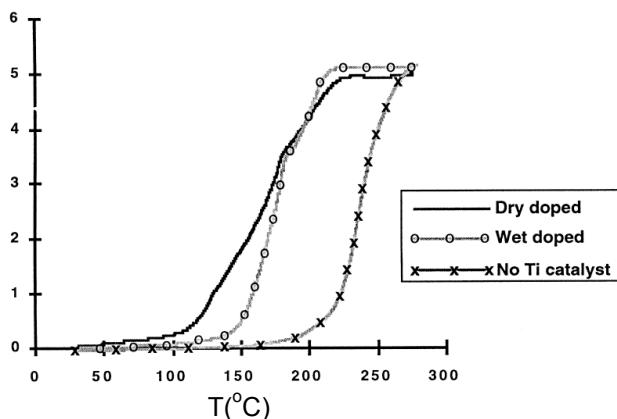


Figure 1. Thermal programmed desorption (2 °C/min) of hydrogen from undoped $NaAlH_4$ (“no Ti catalyst”), from $NaAlH_4$ doped with titanium via a THF suspension (“wet doped”), and from $NaAlH_4$ doped dry with titanium (“dry doped”).

Another interesting candidate for hydrogen storage is ammoniaborane (AB). Its high hydrogen content (19.6%) makes it an attractive candidate to satisfy DOE target of 9.0% hydrogen release by weight for the entire system.¹¹ However, unfavorable thermodynamics prevent direct rehydrogenation of AB dehydrogenation products.¹² So, viable ways to regenerate AB chemically must be developed, in order to use AB as a hydrogen storage material.

Goldberg and coworkers reported that 1 equivalent of H₂ is released from a THF solution of AB at room temperature in the presence of catalytic amounts of H₂Ir(POCOP), where POCOP is the 2,6-bis(di-tert-butylphosphinoxy)phenyl ligand (Figure 2).¹³ Computational studies concluded that the catalysis depends on the hydridic and protonic nature of the B-H and N-H groups in AB, respectively¹⁴.

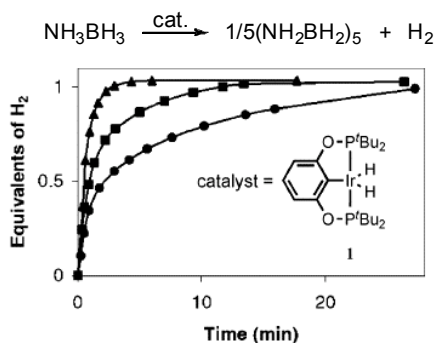


Figure 2. Amount of H₂ evolved from NH₃BH₃ with 0.25 mol% Ir catalyst (●), 0.5 mol% Ir catalyst (▲), and 1 mol% Ir catalyst (■).

Baker and coworkers reported an unprecedented 18% by weight H₂ release at 60 °C from a 25% solution of AB in diglyme catalyzed by 10% mol of a nickel N-heterocyclic carbene catalyst. The same group developed acid catalyzed and Lewis acid catalyzed dehydrogenation of AB in diglyme, which at 60 °C produces up to 1.3 equivalent of H₂.¹⁶

The catalyzed release of hydrogen from chemical hydrides, especially AB, is promising approach to developing hydrogen storage systems due to the low operating temperature and high hydrogen content. A drawback is that it currently is difficult to regenerate AB from its dehydrogenation products.

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