

Hydrogen desorption kinetics in transition metal modified NaAlH_4

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Abstract

The compound NaAlH_4 has been proposed as a viable hydrogen storage media capable of supplying hydrogen at moderate temperatures and at rates required for fuel cell applications. A number of researchers have subsequently verified and enhanced the rate of dehydrogenation in this system using combined transition metal catalytic additions along with different methods of their introduction into the NaAlH_4 compound. The most potent catalytic addition identified thus far is TiCl_3 added through ball milling, however, ZrCl_3 and other transition metal chlorides have also been found useful. To this date, the role of the catalysts are still unknown as well as their disposition within the NaAlH_4 compound. This investigation has sought to identify the extent catalytic dehydrogenation reaction rate of a number of transition metal additions to NaAlH_4 at 120 °C. Two mol% catalysts were added, primarily as chlorides, in a number of valance states. High energy ball mill attrition of the catalyst and the alanate were made with optimum milling times determined. Comparison of dehydrogenation rates with ion radius has shown an optimum catalyst ion radius ratio to be readily identifiable as being midway between that of Al(III) and Na(I). Cation valance, while an important factor in hydrogen discharge kinetics, was shown not to be the primary contributing factor for catalytic activity.

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1. Introduction

In an effort to bring the ‘Hydrogen Economy’ to fruition through the introduction of fuel cell powered automobiles in the mid to long term timeframe, development of a hydrogen storage system will be required which meets both commercial and consumer requirements. The chemical media having the best potential to meet these very aggressive, but required goals at this time is NaAlH_4 . This compound has been shown capable of discharging a significant weight fraction of hydrogen since it was first synthesized in the early 1960s [1–4].

It has been shown by Bogdanović [5–7] and others [8–11] that through additions of various transition metal cations, such as, Ti^{3+} , Ti^{4+} , Zr^{4+} and Fe^{3+} to the sodium alanate, that rapid reaction temperatures can be lowered to ~100 °C. The initial work of Bogdanović and Schwickardi [6] as well as subsequent work by Zaluska et al. [10] have led to some insight as to the most active catalytic agents, but by no means has a thorough understanding of the catalyst been reported in the literature. To date, the addition of Ti^{3+} cations in the form of chlorides have been

demonstrated to hold the highest potential for rapid hydrogen release.

The rate of reaction for both hydrogen discharge and charge are second order (following a power law relation), as defined by Sandrock et al. [11] for purified Ti^{4+} and/or Zr^{4+} catalysts. For the following discussion, regeneration and degeneration rates will be averaged to first order kinetics. It is clear from their analysis that the decomposition of Na_3AlH_6 proceeds at a significantly slower rate than its predecessor reaction. Their hydrogen generation rate data indicates that at 80 °C and fully charged, this compound will generate 0.1 wt% h^{-1} of hydrogen gas, only a fraction of the amounts required for automotive application. A 50% discharged system, which is composed primarily of Na_3AlH_6 , will generate only 0.004 wt% h^{-1} , orders of magnitude slower than the required generation rate. More recent work by the same authors [12] has shown that substantial hydrogen generation rate increases can be achieved through increasing the dopant level.

The objective of this study is to screen the transition metal and rare earth elements to determine the highest performing cations in hydrogen discharge kinetics. Candidate catalysts were selected from across the transition metals including groups IVA–IVB and the rare earths. A

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number of catalysts were evaluated having differing ionic states to determine the role of valance of the catalysts.

2. Experimental procedures

Solid NaAlH₄ was purchased from Aldrich in granular form, having a designation 'tech grade, 90%'. The material was a fine grayish white powder. Analysis of major constituents indicated the as received material contained 68.66% NaAlH₄, 0.05% Na₃AlH₆ and 7.29% Al, 0.08% NaAlEt₂H₂ and 23.92% inert including oxides and hydroxides of sodium and aluminum (in wt%). A powder X-ray diffraction analysis was performed on incoming material and showed primarily NaAlH₄ with minor amounts of Al and trace amounts of Na₃AlH₆. The inert constituents are considered to be in the amorphous state. All chemicals were stored, measured and processed under a purified nitrogen atmosphere with an oxygen concentration measured and monitor at <10⁻⁵ ppmw in a glove box.

The cations added were all in the form of chlorides with the exception of Co³⁺ which was added as a fluoride. TiF₃ was also added as a catalyst to compare with CoF₃ to determine any effect of anionic species. Cation concentrations were constant at 2 mol%. All catalyst materials were purchased from Aldrich and had a designation of 99.99% or better. A summary of the catalysts added is given in Table 1. The catalysts were milled in a SPEX ball mill for the times indicated under a purified nitrogen atmosphere at nominally ambient temperatures.

Material was prepared using 2 mol% TiCl₃ as the catalyst. Milling times of 5, 10, 15, 30, 60 and 120 min were used. These materials were assessed for hydrogen desorption as described below and the optimum milling time of 15 min used for all subsequent catalyst mixing.

Immediately after ball milling, approximately 1 g of materials was placed into a modified Sievert's apparatus, immersed in a constant temperature oil bath at 120 °C, evacuated to 10⁻³ Torr, and backfilled with 1 bar of

purified hydrogen gas. All measurements were thus commenced within 30 min of milling and only on the first dehydride cycle. It was recognized that the possibility of partial dehydriding existed prior to specimen insertion into the measurement apparatus.

3. Results

A consistent processing procedure was required to be established in order to fairly evaluate the catalysts under consideration. The primary processing variable is the length of ball milling time which will affect not only homogeneity of catalyst dispersion, but also the powder particle size. The results of the previously described milling experiments are illustrated in Fig. 1a and b. The rate of hydrogen evolution is given as wt% h⁻¹ in both figures. The average rate over 5 min was measured and plotted continuously during the test in Fig. 1a while the average rate over the first hour of testing was measured and plotted in Fig. 1b as a function of milling time. This illustration indicates that an optimum milling time exists on the order of 15 min in duration. At shorter milling times, it is hypothesized that the catalyst is not homogeneously distributed through out the starting material and maximum catalytic action can not be attained. After catalyst dispersion, further milling allows for dehydriding to occur in milling and sample transfer. This dehydriding will skew the results towards lower dehydride rates and unfairly bias high rate catalysts. A constant milling time of 15 min was selected for all subsequent evaluations.

The results on dehydride rate evaluations of the various catalysts examined here are given in Fig. 2a–c, where plots of hydrogen discharge are given as wt% vs. time. A comparison of as received materials with that of material ball milled for 15 min shows a large increase in hydrogen desorption rate with milling. The as received material desorbs approximately 0.1 wt% H₂ initially at 120 °C and stops rapidly at that level. No further desorption is observed over nearly 70 h of testing. In comparison,

Table 1
Catalyst additions and resultant dehydrogenation rates

Addition	Rate (wt% h ⁻¹)		Addition	Rate (wt% h ⁻¹)		Addition	Rate (wt% h ⁻¹)	
	5 min	1 h		5 min	1 h		5 min	1 h
AgCl	0.26	0.09	GeCl ₄	0.50	0.10	TiCl ₂	3.98	2.38
CdCl	0.26	0.08	HfCl ₄	1.44	0.30	TiCl ₃	6.57	2.73
CeCl ₃	1.89	0.62	MnCl ₂	0.73	0.23	TiCl ₄	6.80	2.97
CoF ₃	1.06	0.27	MoCl ₃	0.87	0.24	TiF ₃	5.45	2.78
CrCl ₂	0.59	0.21	NbCl ₄	0.93	0.30	VCl ₂	0.72	0.46
CrCl ₃	0.25	0.15	PdCl ₂	0.34	0.15	VCl ₃	1.80	0.95
CuCl	0.39	0.11	PtCl ₄	0.33	0.13	VCl ₄	0.83	0.31
FeCl ₂	0.50	0.26	RhCl ₃	0.38	0.22	YbCl ₃	0.34	0.12
FeCl ₃	0.59	0.21	RuCl ₃	1.68	0.51	ZnCl ₂	0.77	0.17
GaCl ₃	0.22	0.07	SrCl ₂	0.34	0.07	ZrCl ₄	1.50	1.40
GdCl ₃	0.79	0.26						

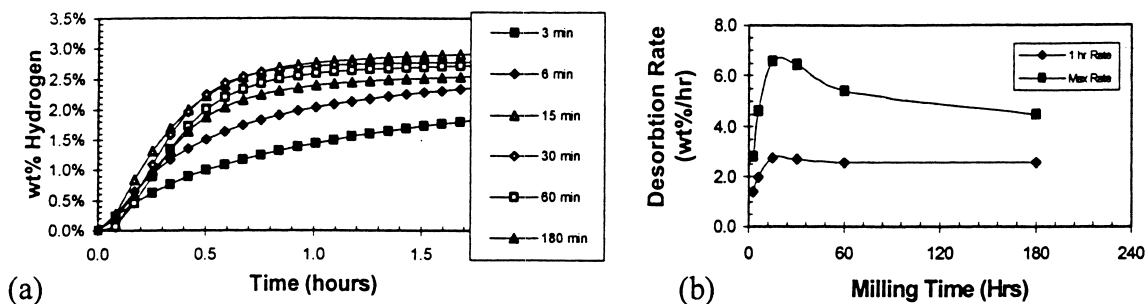


Fig. 1. The effect of milling time on dehydrogenation rate: (a) dehydrogenation curves and (b) 5-min and 1-h average rates.

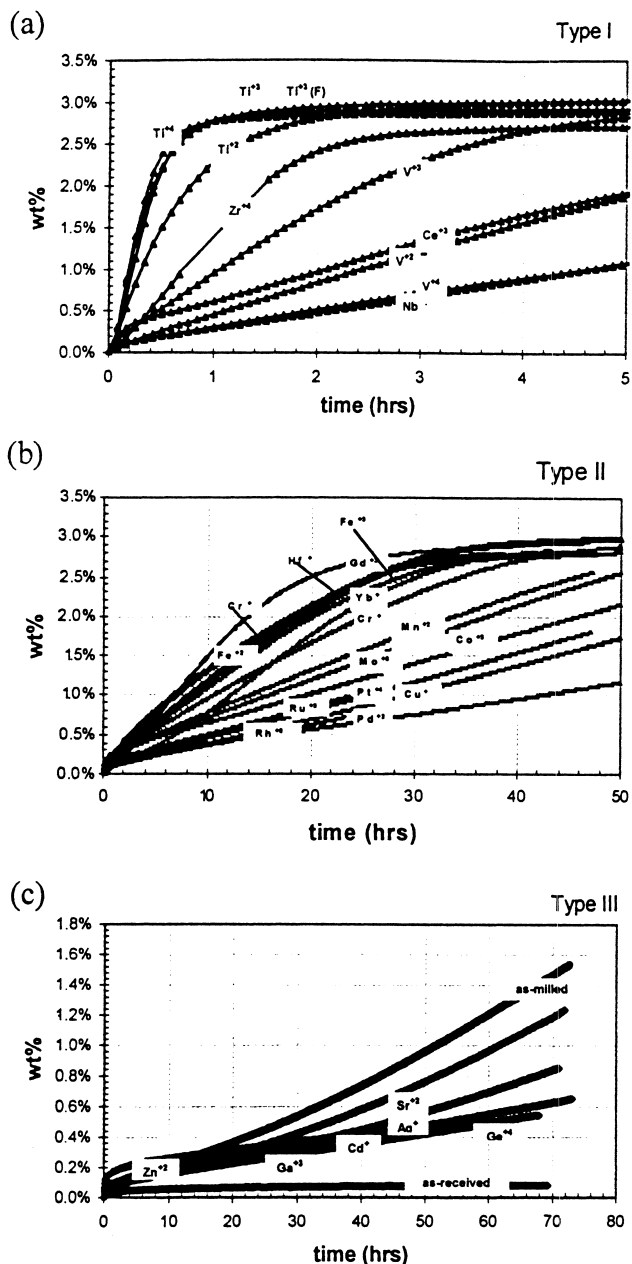


Fig. 2. Dehydrogenation curves for: (a) type I, highly active, (b) type II, moderately active, and (c) type III, inactive additives.

materials milled for 15 min continuously discharged hydrogen at a modest rate, \mathcal{R}_0 , of 0.02 wt\% h^{-1} for the duration of the over 70-h test. The enhanced discharge rate for milled specimens is attributed to the break up of surface contamination layers, and the reduction in particle size which may be anticipated from the ball milling process. The milled materials desorption curve is also observed to go through an inflection after approximately 10 h after which the rate increases continuously. The origin of inflection is not understood, but it may be attributed to a thin surface layer breakdown or the nucleation of metallic aluminum particles. Close examination of a number of other catalyst dehydride curves also illustrate this inflection

The catalysts can be broken down into three categories, type I, very active, type II, moderately active and type III, inactive or passivating. Type I catalysts shall be defined as having an overall average hydrogen discharge rate, $\mathcal{R} > 0.15 \text{ wt\% h}^{-1}$, type II as having $0.15 > \mathcal{R} > \mathcal{R}_0$, and type III having $\mathcal{R} < \mathcal{R}_0$. It should be noted that categorizations such as this are purely for convenience of analyzing large sets of data. There is no inherent difference in the hydrogen discharge kinetics between these three categories of additions. Fig. 2a–c illustrate the relative dehydride kinetics for types I, II and III catalyst, respectively. Type I are the obvious candidates for further dehydride rate studies and include the IVA metals composed of the three titanium valence cations Ti^{2+} , Ti^{3+} and Ti^{4+} and Zr^{4+} (with the notable exception of Hf^{4+}); the VA metals composed of the three vanadium cations V^{2+} , V^{3+} and V^{4+} and Nb^{4+} , and the rare earth Ce^{3+} . The titanium additions have long been identified as the most active catalysts originally by Bogdanović and Schwickardi [5,6] and additionally, Zr^{4+} by Jensen and co-workers [8,9] and this work confirms the earlier assertions. Bogdanović had also cited the iron and vanadium compounds as active catalysts along with the rare earths and refractory metals. No other references have been identified citing active catalytic agents.

The type II catalysts are weak activation agents, and include the VIA, VIIA and VIIIA transition metals including the cations Cr^{3+} , Mn^{2+} , Fe^{2+} , Co^{3+} , and the associated heavy elements. Gd^{3+} , another rare earth metal rounds out this less active group.

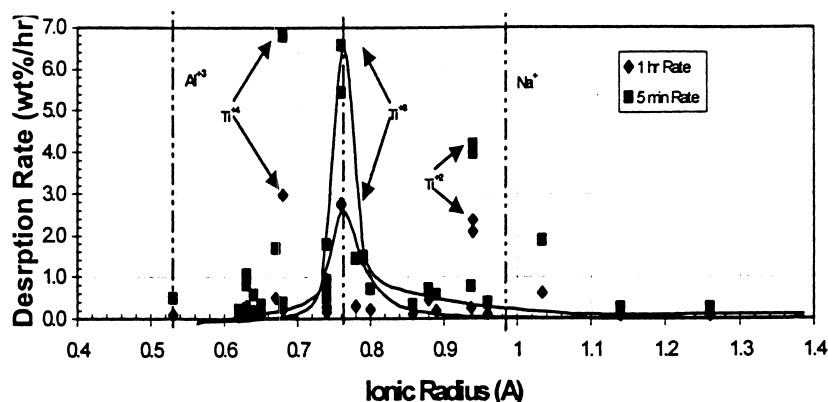


Fig. 3. Dependence of hydrogen desorption rate on ionic radius.

Those additions which resulted in hydrogen discharge rates below that of as milled NaAlH_4 are considered passivators, and actually slow dehydrogenation kinetics, at least at the test temperature of 120°C . These elements include the IB, IIB, IIIB and IVB metals and semi metals as well as the alkaline earth, Sr^{2+} . Many of these additions resulted in the inflected discharge rate curve with a steadily increasing discharge rate after 20 h at temperature. Many of these compounds yielded an overall low hydrogen discharge rate after 20 h of testing but showed an initial high discharge rate. This phenomenon indicates a mechanism change, possibly spurred by a surface blocking of hydrogen. Further investigation would need to be conducted to determine the cause and mechanism of the inflection.

When the discharge reaction was given time to come to completion, the majority of tests resulted in weight fractions of hydrogen discharged ranging between 2.8 and 3.0 wt%. Two notable exceptions were for Zr^{4+} and V^{4+} additions. No ready explanation can be given for these two anomalies. It may be suggested, however, that the materials were somehow discharged prior to testing either by milling or heat exposure which was not documented. Further investigation will be needed to clarify these results.

A ready source of CoCl_3 could not be found so CoF_3 was used in its place. In order to determine if there was any effect of anion species on dehydrogenation rate, a sample of TiF_3 was also evaluated. As can be identified in Fig. 3b, the type I catalysts, TiCl_3 and TiF_3 doped materials behaved in a nearly identical manner. It can thus be concluded that anion species has no effect on dehydride kinetics.

4. Discussion

In trying to understand which catalysts are most effective in enhancing the hydrogen discharge kinetics of NaAlH_4 , we will investigate the utility of Vegard's Law [12]. The 5-min and 1-h average rates of hydrogen

discharge are plotted in Fig. 3 as a function dopant ionic radii (in Å) [12]. A clear dependence of ionic size and hydrogen discharge rate is apparent. Very low rates of hydrogen discharge are observed for dopants with radii significantly larger or smaller than 0.76 \AA . The cation showing the maximum activity is TiCl_3 , as noted previously having this ionic radius. With the radius of Na^+ being 0.97 \AA and that of Al^{3+} being 0.51 \AA , Ti^{3+} at 0.76 \AA is nearly at the midpoint radius, 0.74 \AA , between these two constituent ions, a remarkable occurrence. Based on these observations, cations having a radius in the range of $0.73\text{--}0.80 \text{ \AA}$ should hold the highest potential for enhanced hydrogen discharge rate.

As with any phenomenological model, the variances from the model are as important as the conformances. In this case both Ti^{2+} and Ti^{4+} cations are the most prominent. Both of these ions have significantly different ionic radii from 0.74 \AA . They, however, display high hydrogen discharge rates. This observation can not be readily explained at this time. However, the charge state of the cations after they are incorporated into the NaAlH_4 lattice is not known. If they incorporate as Ti^{3+} ions with a subsequent loss or gain of electrons in the milling process, this would at least partially explain this observation. Why Ti^{4+} leads to a significantly increased discharge rate than Ti^{3+} and why Ti^{2+} leads to an inferior discharge rate still can not be answered. The magnitude of these rates differences is not accounted for by Cl^- variations since TiCl_2 would go to form less NaCl than either the tri- or quarto-valent cations.

The other cations which show higher discharge rates than anticipated based solely on their ionic radii are the group VIIIA metals Co^{3+} , Fe^{3+} , Ru^{3+} and Pd^{2+} and the rare earth Ce^{3+} . The most anomalous cation additions were Ce^{3+} and Ru^{3+} . Materials doped with 2% of these elements achieved much higher hydrogen discharge rates than others having similar ionic radii. No hypothesis for this behavior can be put forth at this time.

Bogdanović [6] has performed the most comprehensive study of different dopant species to date. These results are

in very good agreement with those presented here. A relative ranking of the effectiveness of dopants leads to essentially identical conclusions between these two works with the exception of Ti^{2+} cation. The present study concludes that this addition is very active while the aforementioned work indicated it to be only moderately active. Bogdanović [6] introduced Ti^{2+} through an organometallic precursor which has subsequently been shown [9] to result in slower kinetics than through halide milling, explaining the differing results.

Four of the cations studied were introduced in various valance states. These were titanium as Ti^{2+} , Ti^{3+} , Ti^{4+} ; vanadium as V^{2+} , V^{3+} , V^{4+} ; chromium as Cr^{2+} and Cr^{3+} and iron as Fe^{2+} and Fe^{3+} . As noted previously, the order of activity for the titanium ions is: +4, +3 and +2; for vanadium ions it was +3, +2, +4; for chromium ions it was +2 and +3 and for iron ions +3 and +2. valance in and of itself is not a driving factor in determining activity of the catalyst additions. Ionic radius appears to be a more prominent indicator of catalytic activity.

5. Conclusions

- Ball milling of as-received NaAlH_4 activates it so as to allow desorption of hydrogen at a significant rate.
- The use of ball milling in the preparation of halide catalyzed NaAlH_4 specimens proved very efficient in preparing 1 g sample quantities. An optimum milling time of 15 min was observed with inhomogeneous distribution of catalyst occurring after shorter milling times and partial dehydrogenation occurring after longer milling times for 2 mol% TiCl_3 catalyzed compounds.
- Metal cation catalysts were added as both chlorides and fluorides. No difference was observed between these species leading to the conclusion that the anions do not play a role in NaAlH_4 catalysis.
- The most active cation additions were found to be (in

order of activity) Ti^{4+} , Ti^{3+} , Ti^{2+} , Zr^{4+} , V^{3+} , Ce^{+3} , V^{2+} , V^{4+} and Nb^{4+} .

- The cation radius was found to be primarily indicative of catalyst dehydrogenation activity. Cations with ionic radii in the range of 0.76 Å, the midpoint between the ionic radii of Al^{3+} and Na^+ , were most active.
- Cation valance in and of itself played no direct role in catalytic activity.

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