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Catalyzed alanates for hydrogen storage

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Abstract

The discovery that hydrogen can be reversibly absorbed and desorbed from complex hydrides (the alanates) by the addition of catalysts has created an entirely new prospect for lightweight hydrogen storage. Unlike the interstitial intermetallic hydrides, these compounds release hydrogen through a series of decomposition/recombination reactions e.g.: $NaAlH_4 \Leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2 \Leftrightarrow NaH + Al + 3/2H_2$. Initial work resulted in improved catalysts, advanced methods of preparation, and a better understanding of the hydrogen absorption and desorption processes. Recent studies have clarified some of the fundamental material properties, as well as the engineering characteristics of catalyst enhanced sodium alanate. Phase transitions were observed real-time through in situ X-ray powder diffraction. These measurements demonstrate that the decomposition reactions occur through long-range transport of metal species. SEM imaging and EDS analysis verified the segregation of aluminum to the surface of the material during decomposition. The equilibrium thermodynamics of decomposition have now been measured down to room temperature. They show a plateau pressure for the first reaction of 1 bar at 33°C, which suggest that, thermodynamically, this material is ideally suited to on-board hydrogen storage for fuel cell vehicles. Room temperature desorption with slow but measurable kinetics has been recorded for the first time. Studies at temperatures approaching that found in the operation of PEM fuel cells (125–165°C) were performed on a scaled-up test bed. The bed demonstrated surprisingly good kinetics and other positive material properties. However, these studies also pointed to the need to develop new non-alkoxide based catalysts and doping methods to increase the capacity and reduce the level of hydrocarbon impurities found in the desorbed hydrogen. For this reason, new Ti–Cl catalysts and doping processes are being developed which show higher capacities and improved kinetics. An overview of the current state-of-the-art will be presented along with our own studies and the implications for the viability of these materials in on-board hydrogen storage applications.

Keywords: Metal hydride; Complex hydride; Catalysis; $NaAlH_4$; Na_3AlH_6; Hydrogen storage; Fuel cell

1. Introduction

It appears that the automobile industry is set to introduce hydrogen-powered fuel-cell vehicles in the near future [1]. To be practical, these vehicles will need a safe, lightweight and compact means of on-board hydrogen storage. Liquid, compressed gas and reformer-derived hydrogen all have well-known disadvantages [2]. For this reason, extensive efforts have been made to develop solid-state methods of hydrogen storage, including metal hydrides [2–4] and, more recently, nano-structured carbons [5–7]. Until recently, the development of a high capacity, lightweight metal hydride that could be used to reversibly store hydrogen under ambient conditions, seemed all but unattainable. That was until the pioneering work of Bogdanovic' and Schwickardi (1996) which showed that, by the addition of catalysts, the complex hydride $NaAlH_4$ could be made to reversibly release and absorb approximately 4 wt.% hydrogen under moderate conditions [8]. Thus, catalyzed hydride complexes show the greatest promise for meeting the requirements of on-board hydrogen storage.

The synthesis of $LiAlH_4$ in 1947 by Schlesinger [9] was followed by the discovery and study of many other complex hydrides [10–17]. $NaAlH_4$ was first synthesized by the process of reacting NaH with $AlBr_3$ ($AlCl_3$) in a THF solution [18]. Later, $NaAlH_4$ was directly synthesized from the elements under high-pressure hydrogen [19–21], and finally, it was produced through direct melt synthesis without using solvents [22]. While the potential use of complex hydrides for hydrogen storage had been considered [23], they were primarily developed for use as convenient and efficient chemical reducing reagents [24]. In the more general class of saline hydrides, compounds such as lithium hydride and particularly calcium hydride,

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have been used for lightweight hydrogen storage for over half a century. In a typical example, LiH and CaH_2 were widely employed as a portable means of storing hydrogen for inflating meteorological balloons [25]. However, in this case, hydrogen was generated by reacting the hydride with water. This is a reaction which cannot be reversed in any efficient or practical manner.

Since Bogdanovic' and Schwickardi's discovery, there have been considerable efforts to develop new catalysts, advanced methods of doping and materials processing, as well as a better fundamental and practical understanding of the hydriding mechanisms. Many of the important properties of these materials and the development of new catalysts (Ti- and Fe-alcoholates, (Fe, Ni)Cl_2, (V, RE)Cl_3, β-$TiCl_3$, and (Ti, Zr)Cl_4) were the focus recent research by the group of Bogdanovic' [26], and in particular, the Ph.D. thesis work of Tölle [27]. At the University of Hawaii, Jensen et al. developed an advanced catalyst doping technique in which liquid alkoxide catalyst precursors were mechanically homogenized with solid $NaAlH_4$. This method was used to produce materials with enhanced kinetics and improved reversible hydrogen capacities [28] compared with samples prepared using the original wet doping technique [8]. This homogenization technique was employed to dope $NaAlH_4$ with a double catalyst consisting of 2 mol.% each of the alkoxides $Zr(OPr^i)_4$ and $Ti(OBu^n)_4$. The two catalysts combined to give better overall dehydriding kinetics and a capacity of about 4.5 wt.% [29]. At McGill University, Zaluska et al. showed that hydrogen absorption and desorption kinetics could also be enhanced by mechanically grinding of the sodium alanates, as well as by using carbon as an additive in the milling process [30]. That work that supported the notion that reduced particle size plays an important role in improving kinetics. This was also confirmed by the observation of kinetic enhancement by decreasing the catalyzed $NaAlH_4$ particle size through precipitation using different solvents [26]. The mechanical milling technique was also employed to directly synthesis the alanates. This included the mechanical-alloying synthesis of Na_3AlH_6, Na_2LiAlH_6 [31], Li_3AlH_6 and $(Li–Na–B)_3AlH_6$ [32].

Collaborative research at Sandia National Laboratories (SNL) and the University of Hawaii (UH) has focused on the development and characterization of new hydrogen storage materials [33,34].

It is critical for the ultimate use of complex hydrides as practical hydrogen storage materials to gain a complete understanding of the mechanisms by which hydrogen is absorbed and desorbed in these materials. Unlike, the classic interstitial metallic hydrides, $NaAlH_4$ releases hydrogen through a series of decomposition reactions [35–37]:

$$NaAlH_4 \overset{3.7\ \mathrm{wt.\%}}{\Leftrightarrow} 1/3Na_3AlH_6 + 2/3Al + H_2 \overset{1.9\ \mathrm{wt.\%}}{\Leftrightarrow} NaH + Al + 3/2H_2 \quad \text{total} = 5.6\ \text{wt.\%} \qquad (1)$$

Dymova et al. were the first to make pressure vs. composition isotherm measurements (PCT) for the decomposition of undoped $NaAlH_4$ [38]. Two separate plateaus appeared in their measurements corresponding to the two decomposition reactions of Eq. (1). We recently verified this two-step process for the solid-state decomposition of catalyzed $NaAlH_4$ using dynamic in-situ X-ray diffraction [39]. Moreover, we also demonstrated the liquid-state decomposition of uncatalyzed $NaAlH_4$ (melting temperature 180°C) and showed the existence of an intermediate decomposition step which points to a polymorphic phase transition of Na_3AlH_6 [40,41]. The PCT measurements of Dymova [38] and later Bogdanovic' [8] provided equilibrium pressures from which the heats of decomposition of $NaAlH_4$ (liquid) and Na_3AlH_6 (solid) could be calculated. Equilibrium pressure measurements of the decomposition of catalyzed $NaAlH_4$ in the solid-state were made at Sandia National Laboratories [41] and also by Tölle and Bogdanovic' [26,27]. Advances in the catalytic activity of these materials now allow desorption measurements to be made down to room temperature [42]. These low temperature desorption measurements and, the resulting van't Hoff analysis will be presented in this paper.

Other important aspects of the decomposition/reformation processes that must be understood are the catalytic interactions and transport processes involved in the solid state reactions. The observed formation of sub-micron aluminum crystallites by in-situ X-ray diffraction experiments [39], as well as by a microscopic elemental analysis [26,27,43] demonstrates the existence of long-range transport of metal atoms. These transport phenomenon, the effects of particle size, and catalytic activity are some of the subjects of ongoing investigations [40,43].

The net reaction of Eq. (1) represents a theoretical reversible hydrogen capacity of 5.6 wt.%. The equilibrium thermodynamics of these reactions indicate the potential to liberate all of this hydrogen at above 1 atmosphere of pressure with temperatures of 110°C. Obtaining such values under practical conditions would be extremely valuable for the on-board storage of hydrogen in low-temperature fuel-cell vehicles. However, significant progress remains to be made in achieving the rapid hydrogen absorption and desorption kinetics required for vehicular applications. The work presented here summarizes recent cooperative activities between Sandia National Laboratories and the University of Hawaii to develop advanced catalyzed complex-hydride hydrogen-storage materials. In particular, our recent work focused on determining: (1) the positive as well as the detrimental aspects of our current catalysts-doping procedures; (2) the development of improved catalysts and doping methods; (3) engineering aspects; and (4) the fundamental properties of these materials. Further details of our joint work on the catalyzed alanates can be found elsewhere in this volume [33,34,40,43].

2. Sample preparation and experimental details

Some results are reproduced here from published data of the work at the Max-Planck-Institut für Kohlenforschung and McGill University. Sample preparation for those results are described briefly in the figure captions and details can be found in the accompanying references. Much of the collaborative efforts of Sandia National Laboratories and the University of Hawaii were done using double catalysts of Ti- and Zr-alkoxides. The homogenization technique developed at the University of Hawaii [28] was generally employed for sample preparation. This consisted of adding 2 mol.% each of liquid $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ to solid $NaAlH_4$ which had been purified from (THF) solution and vacuum dried. The mixture was ground together with a mortar and pestle and finally milled in a SPEX® mixer/mill for 30 s. Sandia National Laboratories also tested samples which were mechanically milled under argon for 3 and 8 h, as well as samples which were doped with other catalysts (specifically; β-$TiCl_3$).

Low temperature kinetics, plateau pressures, and capacity measurement were obtained volumetrically using samples of approximately 1.5 g. Reversible hydrogen capacity data is presented in terms of wt.% hydrogen with respect to the combined weight of $NaAlH_4$ and the catalysts. Special air-less techniques were developed at Sandia National Laboratories to be able to characterize these catalyzed alanate materials using X-ray diffraction [33,40], scanning electron microscopy (SEM), electron dispersive spectroscopy (EDS) and Auger elemental analysis [43].

Engineering property studies were performed at Sandia National Laboratories on a ‘scaleup’ reactor bed designed to simulate the heat transfer and gas impedance conditions that might be found in real hydrogen storage applications. The bed was loaded with 100 g of Ti/Zr-alkoxide catalyzed $NaAlH_4$ (78 g of $NaAlH_4$ and 22 g or 2 mol.% each of $Ti(OBu^n)_4+Zr(OPr^i)_4$) prepared in collaboration with the University of Hawaii [33].

3. Results and discussion

Sandia National Laboratories together with the University of Hawaii initially examined the use of liquid alkoxide catalysts and the homogenization doping procedure. This has practical advantages over the ‘wet-chemistry’ methods of doping the alanates in solution. Namely, the precipitation and drying steps are avoided. In addition, intimate mixing as well as particle size reduction can be achieved through mechanical milling leading to improved kinetics. However, we also found that the Ti/Zr-alkoxide catalyst doping procedure has significant drawbacks. These are: (1) the alkoxide based catalysts are heavy, 2 mol.% of each catalysts results in a 22 wt.% overall burden on the total material; (2) the liquid catalysts contaminate the desorbed hydrogen with hydrocarbons; (3) oxygen from the decomposition of the alkoxide catalysts contaminates the active material, resulting in a lower than theoretical reversible capacity. All of these considerations lead to the need to develop non-hydrocarbon-based catalysts. For this reason, we are now investigating the catalytic properties of the titanium-halides. Recent experiments on $NaAlH_4$ doped with 2 mol.% β-$TiCl_3$ have shown reversible hydrogen capacities approaching the theoretical limit with no degradation in kinetic properties and significantly reduced gas impurities [33]. These materials desorb 3 wt.% hydrogen in 100 min at 125°C and absorb 4.2 wt.% hydrogen in an hour at the same temperature with an applied hydrogen pressure of 91 bar. Using X-ray diffraction, it was discovered that the β-$TiCl_3$ catalyst precursor decomposes during the mechanical milling process to form NaCl and a dispersed titanium-based catalyst [40]. In a parallel investigation at the University of Hawaii, samples were catalyst doped by homogenization milling with liquid $TiCl_4$. TPD measurements gave results very similar to that found for the Ti-alkoxide catalyst [34]. The nature of the titanium-based catalysts is the focus of current investigations.

3.1. Thermodynamics

Reasonably high kinetics at low temperatures allowed us to reliable determine equilibrium desorption plateau pressures down to room temperature for the decomposition of $NaAlH_4$. These data are plotted in Fig. 1 in the form of a van’t Hoff plot ($\ln P$ vs. $1/T$) and compared to the data

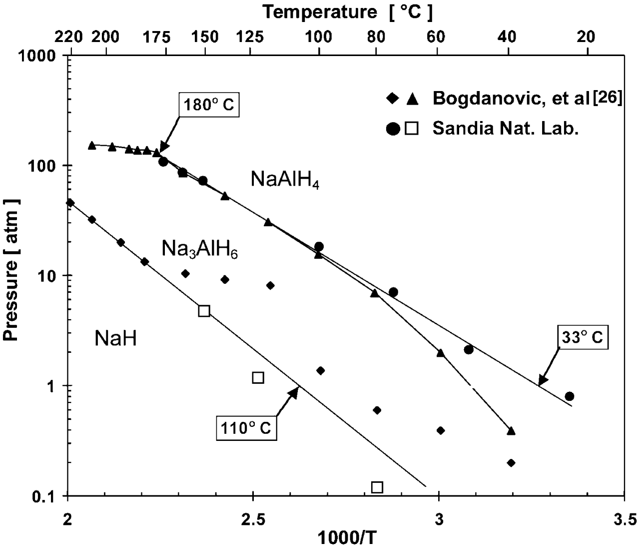


Fig. 1. van’t Hoff diagram showing equilibrium pressures as a function of temperature for the $NaAlH_4 \Leftrightarrow 1/3(\alpha\text{-}Na_3AlH_6)+2/3Al+H_2$ and the $\alpha\text{-}Na_3AlH_6 \Leftrightarrow 3NaH+Al+3/2H_2$ reactions. Samples doped with 2 mol.% each of the liquid catalysts of $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$. Plateau pressure data are also plotted from measurements made by Bogdanovic’ et al. [26].

previously published by the Bogdanovic' et al. [26]. Our low temperature data is a good agreement with the extrapolation of our previous high temperature data [41]. Thus, it has now been shown that the temperature required for an equilibrium desorption pressure of 1 bar from catalyzed $NaAlH_4$ is 33°C. This is a very convenient temperature for PEM fuel-cells and other applications.

The Na_3AlH_6 plateau pressure is also shown in Fig. 1. Because of the relatively low pressures and kinetics involved, the low-temperature Na_3AlH_6 van't Hoff data are not as reliable as the $NaAlH_4$ data. Be that as it may, the 1 bar van't Hoff temperature for Na_3AlH_6 is estimated to be about 110°C. This temperature is somewhat higher than desired for PEM fuel cells and future work will aim at lowering this temperature. This can only be accomplished by direct modification of the thermodynamic properties of Na_3AlH_6.

3.2. Kinetics

Some of the more recent β-$TiCl_3$ catalyst results are compared with our earlier Ti/Zr-alkoxide data in Fig. 2 (desorption) and Fig. 3 (absorption). Also shown are published kinetics measurements made by the groups at the Max-Planck-Institut für Kohlenforschung [26,27] and McGill University [30]. It is important to note that these results were collected using different catalysts or additives, as well as different sample quantities, sample holders, and measuring techniques. Thermal effects, such as temperature variations due to the heat of reaction and thermal conductivity will strongly influence kinetics, and may be substantially different between the various measurements. Variations in the measured hydrogen capacities may be the result of an incomplete absorption or desorption prior to measuring, as well as the amount and type of catalyst loading. Thus, a qualitative comparison of the different materials is not possible. However, some general qualitative conclusions can be made. They can be summarized as follows. First, the combined results from these four independent laboratories validate the reversibility and high capacities of these materials regardless of the specific methods of sample preparation or catalysts used. At least 3 wt.% of hydrogen can be desorbed at 125°C in under 5 h. On a weight basis this is still nearly twice the capacity of low temperature commercial metal hydrides. At higher temperatures (160°C) the capacity increases to nearly 5 wt.% or three times better than commercial materials. A second observation, which is consistent for most of the desorption measurements, is the appearance of a change in the desorption rate at about 3 wt.%. At this point the materials are giving off hydrogen through the second reaction of Eq. (1). This demonstrates the universally slower kinetics of the second reaction. A third observation is that the rates of hydrogen absorption and desorption are highly temperature dependent. Finally, it is apparent that both particle size and the type of catalysts used strongly influence hydrogen absorption and desorption rates.

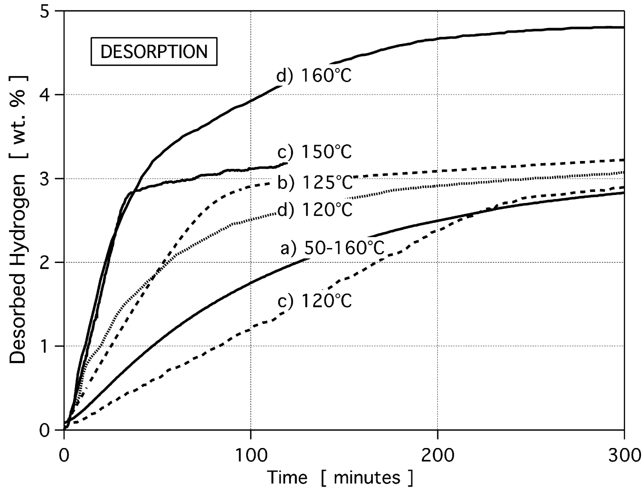


Fig. 2. A compilation of $NaAlH_4$ hydrogen desorption kinetics measurements from different authors: (a) 1st desorption (50–160°C) of 100 g scale-up bed $NaAlH_4$ doped by mechanical mixing for 30 s with 2 mol.% each of the liquid catalysts of $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ (SNL/UH); (b) 3rd desorption (125°C) of 2 g $NaAlH_4$ doping by mechanical milling for 3 h with 2 mol.% β-$TiCl_3$ (SNL); (c) desorption (120 and 150°C) of $NaAlH_4$ milled together with 10 wt.% carbon for 2 h [30]; (d) 1st desorption (120 and 150°C) of $NaAlH_4$ precipitated from THF using pentane then doped with 2 mol.% $Ti(OBu^n)_4$ in toluene, filtered and dried under vacuum [26].

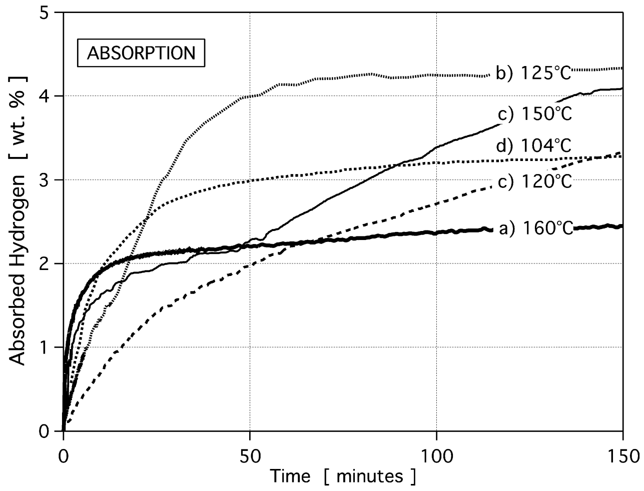


Fig. 3. A compilation of $NaAlH_4$ hydrogen absorption kinetics measurements from different authors: (a) 4th absorption (160°C, 174 bar) of 100 g scale-up bed $NaAlH_4$ doped by mechanical mixing for 30 s with 2 mol.% each of the liquid catalysts of $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ (SNL/UH); (b) 2nd absorption (125°C, 91 bar) of 2 g $NaAlH_4$ doping by mechanical milling for 3 h with 2 mol.% β-$TiCl_3$ (SNL); (c) absorption (120 and 150°C, 89 bar) of $NaAlH_4$ milled together with 10 wt.% carbon for 2 h [30]; (d) 8th absorption (104°C, 83 bar) of $NaAlH_4$ precipitated from THF using pentane then doped with 2 mol.% $Ti(OBu^n)_4$ in toluene, filtered and dried under vacuum [27].

In addition to enhanced kinetics at 80–150°C, we made the rather surprising observation that hydrogen desorption could be measured even down to room temperature. As would be expected, the initial desorption rate was found to be strongly dependent on particle size. While the desorption rates are low (0.016 wt.%/h), room temperature desorption from these high-capacity materials should prove of great interest for certain low-rate hydrogen-powered applications.

3.3. Reversible hydrogen capacity

The initial desorption from our alkoxide catalyzed samples gave gas capacities in excess of the theoretical 5.5 wt.% value (6 wt.%). This is believed to come from large quantities of impurities gases derive from the alkoxide catalyst precursors in addition to the desorbed hydrogen. Further cycles demonstrate a lower-than-expected capacity for all of the samples we have tested with the liquid alkoxide catalysts (both absorption and desorption capacities were about 3 wt.%). X-ray diffraction measurements clearly showed that the low capacity is due mainly to an inability to completely recharge to a composition of 100% $NaAlH_4$. X-ray diffraction measurements also demonstrated that the samples could be fully desorbed to sodium hydride and aluminum. The mechanism for this incomplete recharging phenomenon is uncertain. It may have been due to an inhomogeneous distribution of the catalysts or impurity effects. Despite this, the capacity problem has now been overcome through the application of titanium-halide catalysts.

3.4. Practical studies, applications oriented materials properties

A scaleup bed containing 100 g of $NaAlH_4$ doped with Ti/Zr-alkoxides (2 mol.% each) was tested at Sandia National Laboratories. The bed was tested through five absorption/desorption cycles. Hydrogen absorption was conducted at pressures ranging from 122 to 210 bar and nominal absorption temperatures of 125–165°C. Desorption was performed at 150–165°C against a 1 bar back-pressure. In addition to capacity and rate measurements, exothermic (charging) and endothermic (discharging) thermal effects were recorded. The desorbed hydrogen was monitored for gaseous impurities and a small sample was removed after the fourth desorption cycle for XRD and SEM/EDS analysis. The volume change of the alanate was measured over the last desorption cycle. Detailed results from these tests are presented in an accompanying paper [33]. The following are some highlights of that study.

3.4.1. Discharge and recharge rates

Desorption of hydrogen occurred rapidly at 150–165°C, with about two thirds of the hydrogen (30 st.l) discharging in 3 h. The absorption of hydrogen over a range of applied pressures and starting temperatures was more rapid than we had expected. Most of the hydrogen was absorbed in the first hour, even for the lowest pressure and starting temperature (125°C, 122 bar). Charge and discharge curves for the scale-up bed are presented in Figs. 2 and 3 (curves a).

3.4.2. Thermal effects

The higher than expected initial charging kinetics, combined with limited heat transfer, resulted in large exothermic temperature excursions (Fig. 4), as is common with many hydrides. In this example, 174 bar of hydrogen was applied to the fully desorbed bed which had been equilibrated to 155°C. Within 1 min, the exothermic hydriding reaction produced an internal temperature of 234°C (the van't Hoff temperature for $NaAlH_4$ at this pressure). This is well above the melting point of $NaAlH_4$ (182°C). Therefore, any $NaAlH_4$ produced during this thermal excursion formed directly in the liquid phase. As

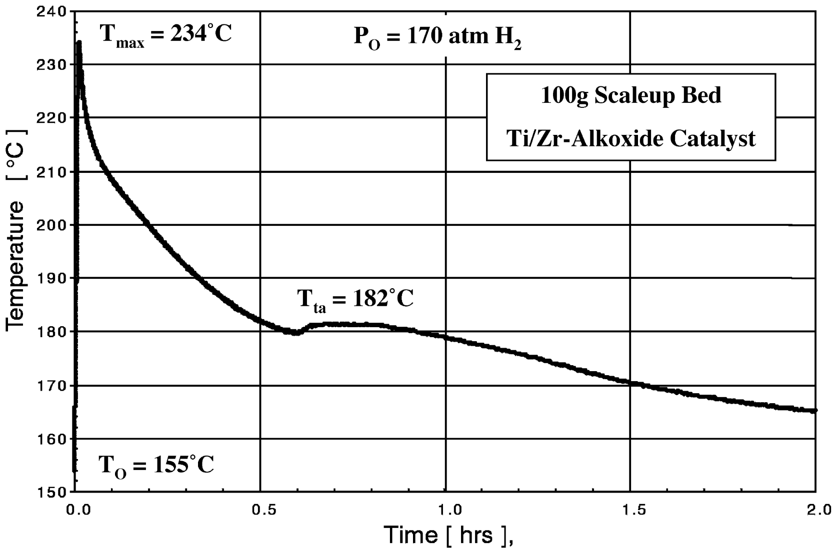


Fig. 4. Temperature excursion in 100 g scale-up test bed during the fourth hydrogen absorption cycle (initial: $T=155$°C, $P=174$ bar).

the bed cooled a thermal arrest occurred at 182°C due to solidification (Fig. 4). This confirms that liquid $NaAlH_4$ was formed during the initial stages of charging.

It is natural to ask if such melting could be detrimental to the subsequent performance of the alanate bed. Our observations indicated no negative effects of partially melting the alanate at least three times. In fact, partial melting may have beneficial side effects. We opened the reactor between cycles 4 and 5 and found that the bed material had been sintered into a porous, solid mass. Such a structure may have distinct advantages for actual applications. In particular, such a sintered structure would reduce particulate migration, increase packing densities, allow expansion, provide a constant internal gas impedance, increase thermal conductivity and enhance some safety aspects of the materials.

3.4.3. Hydriding volume changes

Large volume changes associated with lattice expansion during classic metal hydride formation poses significant engineering problems. For this reason, we measured the volume change of the catalyzed alanate in the scaleup bed from the beginning to the end of fifth desorption cycle. The volume contracted by -14.7%, which is reasonably close to the theoretical value calculated from X-ray densities for the complete dehydriding reaction (-16.5%) [33]. Unlike the traditional hydrides, alanates have the distinct advantage of being fully hydrided in the as-received state. Therefore, fully packed beds can be constructed, which simplifies bed design and allows higher volumetric system densities to be achieved.

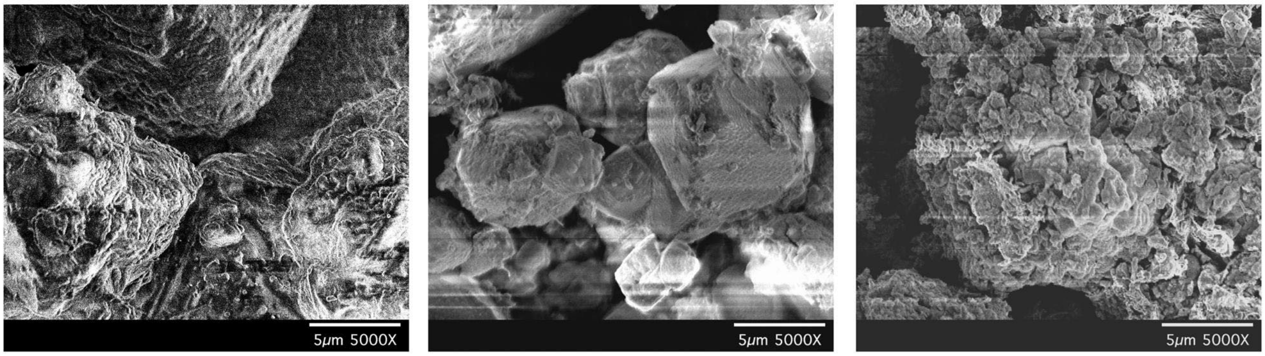
3.4.4. Impurity gases

The composition of the desorbed gases were examined regularly by RGA (Residual Gas Analysis [Mass Spectroscopy]) and occasionally using GC (Gas Chromatography). Typical RGA spectra of the desorbed gasses showed not only hydrogen but also significant hydrocarbon impurities along with the ubiquitous background RGA peaks for H_2O, CO and CO_2. GC analysis taken after the second cycle showed that butane and propane were present in the hydrogen. It appears that the liquid $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ catalysts decompose during cycling releasing significant amounts of gaseous impurities. PEM fuel cells will not tolerate even low levels of impurity gases, especially hydrocarbons that lead to the formation of CO. It was these results in particular that led us to concentrate on the development of inorganic catalysts.

3.5. Fundamental studies, catalysis and transport mechanisms

SEM images of the Ti/Zr-alkoxide catalyzed alanates at different stages of desorption are presented in Fig. 5. These show the pronounced changes in morphology that occur during the two-stage desorption process (Eq. 1). This is indicative of the segregation of the constituent phases. Surface EDS analysis was also used to examine the samples for impurities effects. Measurements taken after the homogenization process clearly showed the presence of large amounts of residual oxygen introduced by the $Ti(OBu^n)_4 + Zr(OPr^i)_4$ catalysts [43]. The surface oxygen was still present, albeit at lower levels after desorption. Thus, some capacity loss may be attributed to the formation of oxides or hydroxides.

Dynamic in-situ X-ray diffraction measurements were made during the decomposition of both catalyzed and pure $NaAlH_4$ (Fig. 6) [39]. The formation of relatively narrow aluminum diffraction peaks was observed. Thus, aluminum must segregate according to Eq. (1) to form crystallites with dimensions on the order of 1000 Å or larger. This implies the long-range transport of metal species. Surface EDS verified this concept by showing an increasing overall aluminum concentration on the surface of the powder particles during decomposition [36]. In addition, Auger analysis demonstrated that most of the catalyst remains at the material's surface [39]. This raises the question of how aluminum hydride anions paired with sodium cations in an



a) $NaAlH_4$ ⇨ b) $1/3\ Na_3AlH_6 + 2/3Al + H_2$ ⇨ c) $NaH + Al + 3/2H_2$

Fig. 5. SEM images showing changes in morphology that occur during the decomposition of $NaAlH_4$ doped with 2 mol.% each of the liquid catalysts $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$.

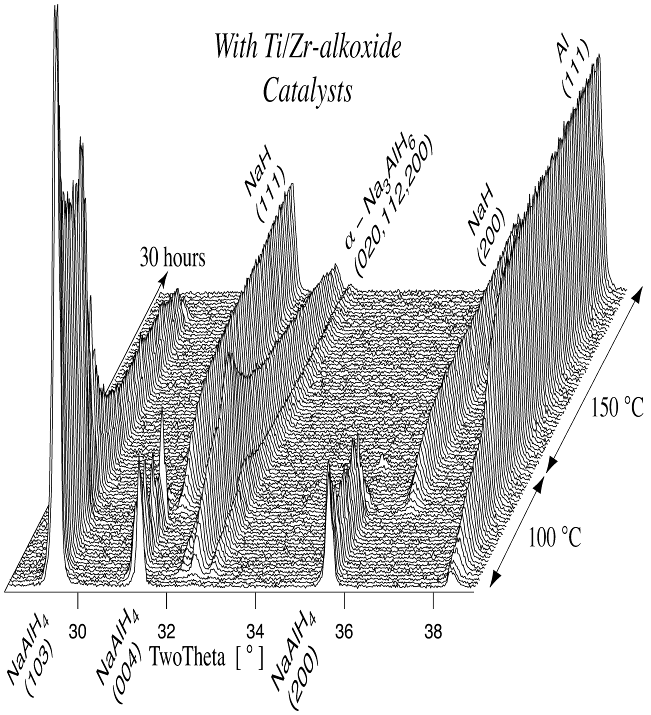


Fig. 6. Dynamic in-situ X-ray diffraction measurements taken during decomposition of $NaAlH_4$ mechanically mixed with 2 mol.% each of the liquid catalysts of $Ti(OBu^n)_4$ and $Zr(OPr^i)_4$ [39].

ionic solid could be influenced by catalytic sites that are immobilized at the particle surface. One speculation is that the transported species is a more mobile hydride such as AlH_3 [39]. The low melting point of $NaAlH_4$ demonstrates the weak nature of the ionic bond. It is possible that local disproportionation of $3NaAlH_4$ into Na_3AlH_6 and $2AlH_3$ takes place. The AlH_3 then transports to the catalytic site where it dissociates into Al and H_2. However, it should be noted that none of these mechanistic concepts have been verified experimentally.

4. Conclusion and outlook

This overview has covered some of the recent advances in the development of catalyzed sodium-alanates as lightweight hydrogen storage materials. These materials are now realizing reversible capacities in excess of 4.2 wt.%. The current state of the art allows the desorption of 3 wt.% hydrogen in a little over 1 h at 125°C. Precise plateau pressure measurements demonstrate that thermodynamically these materials are ideally suited to practical applications. The catalyzed $NaAlH_4 \Leftrightarrow 1/3Na_3AlH_6 + 2/3Al + H_2$ reaction delivers 1 bar hydrogen at 33°C.

These are important achievements; however, a great deal of progress remains to be made. In particular: (1) The slow dehydriding and rehydriding kinetics remain a significant barrier to applications such as fuel cell vehicles. Titanium-halide catalysts and dry doping procedures are showing promise, especially in overcoming the impurity and capacity related constraints of the previous alkoxide based catalysts, but kinetics must still be improved. (2) Completing the second desorption step $1/3Na_3AlH_6 + 2/3Al + H_2 \Leftrightarrow NaH + Al + 3/2H_2$ is necessary to obtain a full 5.6 wt.% theoretical capacity. Unfortunately, Na_3AlH_6 releases 1 bar hydrogen at about 110°C, which is a little too stable for many applications. Elemental substitution must be explored as a means to de-stabilize this reaction. (3) Long-term cycling studies will be needed to ensure the viability of these materials for reversible hydrogen storage. (4) Safety is an important issue that must be addressed. These compounds are highly reactive with water and air. Small amounts of water or oxygen as impurities are unlikely to be a significant problem. However, engineering solutions or material modifications will be required to reduce the hazards associated with a full exposure to air or water. (5) Finally, progress has been made in understanding the fundamental processes that take place in these solid-state reactions. Long-range transport of metal species appears to play an important role in the overall reaction kinetics. For the moment, however, the nature of the transported species and the role of the catalysts remain a mystery.

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