A multifaceted approach to hydrogen storage†

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The widespread adoption of hydrogen as an energy carrier could bring significant benefits, but only if a number of currently intractable problems can be overcome. Not the least of these is the problem of storage, particularly when aimed at use onboard light-vehicles. The aim of this overview is to look in depth at a number of areas linked by the recently concluded HYDROGEN research network, representing an intentionally multi-faceted selection with the goal of advancing the field on a number of fronts simultaneously. For the general reader we provide a concise outline of the main approaches to storing hydrogen before moving on to detailed reviews of recent research in the solid chemical storage of hydrogen, and so provide an entry point for the interested reader on these diverse topics. The subjects covered include: the mechanisms of Ti catalysis in alanates; the kinetics of the borohydrides and the resulting limitations; novel transition metal catalysts for use with complex hydrides; less common borohydrides; protic-ionic stores; metal ammines and novel approaches to nano-confined metal hydrides.

Introduction

The realisation of the hydrogen economy requires solutions to a number of problems involving production, transportation and fuel cells, but despite the significant progress made in the last decade, storage remains the key barrier to the implementation of the hydrogen economy1 in light vehicles.

The source of this barrier is the prevailing idea that consumers will not accept diminished performance compared to their fossil fuel powered cars, and that any replacement

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Table 1 Selected US Department of Energy revised targets for hydrogen storage (published 2009)²

<table>
<thead>
<tr>
<th>Units</th>
<th>2010</th>
<th>2015</th>
<th>Ultimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gravimetric capacity</td>
<td>wt% usable H₂</td>
<td>4.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>kg usable H₂ L⁻¹</td>
<td>0.028</td>
<td>0.04</td>
</tr>
<tr>
<td>Min/max operating temp</td>
<td>°C</td>
<td>-30/50</td>
<td>-40/60</td>
</tr>
<tr>
<td>Purity</td>
<td>% H₂</td>
<td>99.97 (dry)</td>
<td></td>
</tr>
<tr>
<td>System fill time</td>
<td>Minutes</td>
<td>4.2</td>
<td>3.3</td>
</tr>
</tbody>
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Note that these are system level efficiencies (i.e. including the tanks, piping, control systems etc., so the actual chemical store must be more efficient).

The second of the three broad categories, physisorption, consists of materials whose interaction with H₂ is characterised by the use of intermolecular forces which, as H₂ is non-polar, necessarily consist of the weaker London dispersion and dipole-induced-dipole interactions. Physisorption systems require very highly porous materials and the most widely studied systems reflect this: metal–organic-frameworks (MOFs), activated carbon, carbon nanotubes (and similar entities, including boron nitride analogues), zeolites, and specially crafted organic polymers.¹⁵ The enthalpy stabilisation of such systems is typically about 4–10 kJ mol⁻¹,¹⁶,²¹
far less than the entropy contribution of hydrogen gas at ambient temperature (~39 kJ mol⁻¹) and it is therefore necessary to cool these systems to around liquid nitrogen temperature (77 K, T*S(H₂) = 10 kJ mol⁻¹) to achieve acceptable performance. It is also possible to overcome the entropy barrier by storing at high pressure rather than low temperature, but these systems have very deficient capacities.²²

Increasing the enthalpy of adsorption allows it to occur at higher temperatures (nearer ambient) and/or improves capacity. This may be achieved by introducing groups with a higher affinity for H₂, typically involving dissociation of H₂ to H atoms, and so moves into the realm of chemisorption, a grey area between the second and third broad categories. A number of approaches have been investigated, such as doping carbon materials with boron,²³ doping with metals to create a ‘spill-over’ effect²⁴ or using ‘built-in’ features such as designing MOFs with more exposed cationic metal centres.²⁵ However, the increased enthalpy of adsorption manifests itself as greater heat generated on re-fuelling which may require additional components to prevent overheating, and thus a compromise must be struck. None of the physisorption systems meet the DOE targets.⁶

The third broad category, chemically bound hydrogen, is the subject of the main part of this paper. Materials containing chemically bound but easily released hydrogen typically offer high volumetric capacity and when comprised of the lighter elements may also provide a reasonable gravimetric range. There are many potential stores of this type including metal hydrides, complex hydrides,²⁶ amines and amides, ammonia boranes and their derivatives, and hydrocarbons, to list just a few general categories.

It is of course important that the hydrogen may be released from the store without too much difficulty, but for chemical stores, the corollary of easily released hydrogen is often difficult re-fuelling. There are plenty of substances, including many covered in this paper, that will release copious hydrogen upon reaction with water. The products of such reactions, however, are then too thermodynamically stable to be easily re-fuelled, requiring off-site regeneration which is expensive and often impractical.²¹ Instead, heating the hydrogen store to release its hydrogen with an entropic driving force is preferred and, if the thermodynamics are nicely balanced, allows reversible re-fuelling via lower-temperature, higher-pressure enthalpic stabilisation³ (see Fig. 1), though this does bring with it significant heat-management issues.

It is this approach, that the hydrogen should be released by heating the store (thermal decomposition), that is universally applied in the work set out here. In order to improve efficiency it is in practice required that the waste heat of the fuel cell be used to drive this hydrogen evolution, which, though not a prescription of the DOE,²⁸ establishes an additional target that the hydrogen should be evolved by heating to no more than about 90 °C.²⁹

However, for the most attractive stores either the thermal decomposition (hydrogen evolving) temperature is considerably higher than this or the refuelling (hydrogenation) temperatures and pressures are outside of the DOE targets. Where the cause of the problem lies in the kinetics rather than the thermodynamics, catalysts may present a solution, and much work has been done on developing suitable candidates. In 1997, Bogdanović and Schwickardi discovered that doping sodium alanate (NaAlH₄) with small amounts of Ti compounds could significantly improve the kinetics of hydrogen evolution and uptake.³⁰ Since then, considerable attention has been paid to Ti,³¹ and many other transition metals have also been investigated.³²

The HYDROGEN network’s approach to the hydrogen storage challenges was to provide new insight into longstanding, seemingly intractable problems, such as the mechanism of Ti catalysis in the alanates and the kinetics of the borohydrides, whilst also attempting to break ground in new areas such as the design of novel catalysts for metal hydride stores, and the use of MOFs to alter the properties of nano-confined metals. Thus, this paper aims to provide both in depth analysis of the more commonly found systems, and a flavour of some of the new approaches being tried (see Fig. 2 for an overview). The work uses both theoretical calculations and experimental techniques with a distinct emphasis on nano- and surface science approaches appropriate to the solid state.

In the first three sections, we are concerned with illuminating the fundamental processes involved in two key hydrogen storage systems, Ti doped alanates and the borohydrides, both examples of complex hydrides.³⁵ Slow kinetics are a fundamental problem with these materials, and we look in detail at attempts to expose the mechanisms of de- and re-hydrogenation in order to understand the origin of the problem. For the alanates (Sections I and II) this is the result of theoretical work across two research groups, whilst insight into the borohydrides (Section III) is gained from exhaustive work carried out by a third group over the last several years. These areas, particularly Ti/NaAlH₄, have received
considerable attention over the last decade, and further references can be found in these sections.

Modifying the catalysts with more sophisticated ligands has not received much attention, however. Even in related fields, such as the hydrolysis of NaBH₄, the transition metal catalysts are typically just mounted on a support, 33 and re-fuelling is still off-board. It is remarkable that such research is so rare, given that if we look at more ‘classical’ hydrogenation reactions, the design of highly intricate, tailored transition metal complexes is considered routine. Perhaps it has been assumed that the high mass of the complexes would prove too heavy for efficient storage, and whilst certainly an important concern, given a sufficiently active catalyst this problem is not insurmountable.

We consider this in the next part (Section IV), where we look first to theory to investigate how ‘orbital landscapes’ can be used to inform the design of transition metal complexes as catalysts for the reduction of hydrogen, an important step for refuelling stores such as the alanates and borohydrides. We then see how this has been applied experimentally in the early stages of work using macrocycles and chelates with Ni in the search for novel catalytic effects.

Continuing the search for new materials (Section V), this time for the store itself, we introduce an innovative screening study used to predict novel mixed metal borohydrides with improved properties, before looking at the experimental details of Y(BH₄)₃ and how crystal morphology and metastability can affect the kinetics of hydrogen evolution.

Moving away from the complex hydrides allows us to introduce three alternative categories of store in the later sections. The first of these focuses on systems which retain the hydridic hydrogens common to the complex hydrides but introduce protic hydrogens as well: the protic-hydridic stores (Section VI). Work that revealed the ‘perverseness law’ is outlined, followed by an experimental analysis of the amidoboranes. Derivatives of ammonia borane 34,35 (NH₃BH₃), the amidoboranes (M⁺⁺(NH₃BH₃)x), have a subtly different character which may be tuned to some extent by the choice of metal, and indeed mixing of different metal cations. Since Xiong et al. 36 released their paper on sodium amidoborane in 2008, more than 100 articles on such systems have been published.

Moving on from the amidoboranes, we now remove the hydridic moiety altogether and discuss the metal ammines (M⁺⁺(NH₃)x) (Section VII). These metal complexes store hydrogen in the form of ammonia, so called ‘indirect storage’, which may then be catalytically reformed to produce hydrogen.37 The chief advantage over pressurised liquid ammonia is improved safety, with a significantly lower vapour pressure of the toxic gas. In this section we look in detail at a question relevant both to the advance of ammonia storage systems and potentially to inform other storage systems; what makes the kinetics of ammonia absorption and desorption so good?

The final two sections cover work playing on the phenomena associated with nano-confinement. We examine the potential for metal–organic frameworks to confine metals in order to make use of the improved properties of the resulting nanoparticles (Section VIII), presenting the very latest work on this area which is still under heavy research. Finally, we look at the development of the quartz-crystal microbalance technique with nanoparticles rather than thin films, thus allowing the study of confinement in all three dimensions, rather than just one (Section IX), with this highly sensitive technique.

Results and discussion

1. A theoretical model of H₂ reacting on Ti/Al(100) surfaces

The landmark discovery by Bogdanović and Schwickardi, 30 that pre-reacting NaAlH₄ with a titanium based compound improves the kinetics and reversibility of hydrogen absorption and desorption in sodium alanate (NaAlH₄), has motivated many attempts to elucidate the underlying mechanism. There is however still much left to be understood as to the precise catalytic role of Ti and it remains one of the key open questions in hydrogen storage.

The storage process can, in principle, be anticipated to take place through initial dissociation of H₂ to produce atomic hydrogen.35 Theoretically, molecular hydrogen dissociation on pure Al surfaces is found to be kinetically unfavourable. The lowest energy barriers for H₂ dissociation on pure Al surfaces are 1.28 eV on Al(111), 39 1.0 eV on Al(100), 40,41 and 0.70 eV on Al(110).42 As further discussed below, Ti/Al(100) surfaces represent a sensible choice for modelling H₂ dissociation on Al with Ti in it, and several Al(100) surfaces with different Ti coverages varying from 1/18 to 1 monolayer (ML) have been studied theoretically.40,41,43–45

Experiments show that Ti catalyses H₂ dissociative adsorption (and the reverse process, associative desorption) and isotope exchange experiments 46 on Ti-doped NaAlH₄ suggest that the diffusion of heavier hydrogen-containing species, such as AlH₃ or NaH, represents the rate limiting step in H₂ release and uptake. In agreement, 27Al in situ NMR spectroscopy experiments 47 reveal that a mobile species (evident at 105 ppm) carrying both Al and H atoms could provide the large scale metal-atom transport needed for rehydriding at ambient temperatures.

The fcc Ti lattice constant obtained from first-principles band-structure calculations 48 is found to be a = 4.08 Å, which is very close to the theoretical fcc Al lattice constant, a = 4.04 Å.40,49 Although the fcc phase of Ti has not been observed at any temperature in nature, matching lattice constants make the
pseudomorphic growth of an fcc Ti phase on Al(100) favourable at low Ti coverage.\textsuperscript{50,51} Low-energy electron diffraction (LEED) experiments by Kim \textit{et al.}\textsuperscript{50} show that, at low Ti coverage, Ti atom deposition on a clean Al(100) surface exhibits a \(c(2\times2)\) pattern, with the Ti atoms probably residing in the second layer of the substrate. Low-energy ion scattering (LEIS) measurements by Saleh \textit{et al.}\textsuperscript{52} confirm that the surface Al atoms do indeed float on top of the Ti film at low Ti coverage, up to 1/2 ML, because the initial Ti deposition does not change the LEIS results. When the Ti coverage is increased further, Ti adatoms are instead incorporated also into the top layer of the Al substrate. For instance, the fact that half of the Al LEIS peak area remains after 2 ML Ti deposition,\textsuperscript{52} together with the LEED experiments,\textsuperscript{50} suggests that in this case a \((2\times2)\)-Ti(Al(100)) alloy surface is formed, in which half of the top layer is composed of Ti atoms.

Returning to theory, the most stable Ti/Al(100) surface model to address the catalytic role played by titanium in hydrogenation and dehydrogenation of NaAlH\(_4\) was found to be 1/2 ML of Ti in the second layer of Al(100) surface, which has a \(\mathrm{H_2}\) dissociation barrier of 0.63 eV.\textsuperscript{41} Another slab model, which has, in total 1 ML of Ti in the first and third layer of Al(100), has an even lower \(\mathrm{H_2}\) dissociation barrier of 0.23 eV.\textsuperscript{41}

In our density functional theory (DFT) calculations on \(\mathrm{H_2} + \mathrm{Ti/Al(100)}\), we used the PW91 functional,\textsuperscript{53} which has been shown to give good results for \(\mathrm{H_2}\) dissociating on the Ni(110) alloy surface,\textsuperscript{54} to describe the exchange-correlation energy of the electrons. The PW91 functional should give results similar to the PBE functional\textsuperscript{55} used in ref. 40 to study \(\mathrm{H_2}\) dissociation on a 1/18 ML Ti/Al(100) surface. The RPBE functional,\textsuperscript{56} used in ref. 43 and 44, typically gives higher barriers than the PW91 functional, by about 0.25 eV. The ion cores were described by ultrasoft pseudopotentials.\textsuperscript{57} A plane wave basis set was used for the electronic orbitals, with a cutoff energy of 400 eV. The Brillouin zone was sampled by the Monkhorst–Pack\textsuperscript{58} method, using a set of \(12 \times 12 \times 1\) \textit{k}-points. The \((2\times2)\)-Ti/Al(100) slabs are obtained by replacing half of the Al atoms with Ti atoms in a specific layer(s) with a \((2\times2)\) pattern. The slab interlayer distances (initially \(2\) \AA) were relaxed by applying the quasi-Newton minimisation method in the slab optimisation, while they were subsequently kept fixed at their relaxed values in the calculations on \(\mathrm{H_2}\) dissociation. The slab geometries were converged to within 0.01 \AA, based on tests of adding more Al layers at the bottom of the 4-layer slab, going from 4 layers to 8 layers. The \(\mathrm{H_2}\) dissociation barrier heights presented were obtained using the adaptive nudged elastic band (ANEB) method.\textsuperscript{59} Both initial and final configurations have the same centre of mass \(x\) and \(y\) coordinates of the \(\mathrm{H_2}\) molecule. In all initial \(\mathrm{H_2}\) gas phase configurations, \(\mathrm{H_2}\) is 4.0 \AA above the surface, and parallel to the surface with a bond length of 0.755 \AA. Final dissociated \(\mathrm{H-H}\) configurations describe the relaxed atomic chemisorption minima on the slab.

The barrier height of \(\mathrm{H_2}\) dissociation on a pure Al(100) surface (Model-1) was found to be 1.03 eV employing a \((\sqrt{2}\times\sqrt{2})R45^\circ\) unit cell [0.96 eV when employing a \((2\times2)\) unit cell], with \(\mathrm{H_2}\) dissociating from the initial hollow site to the final two neighbouring bridge sites (Fig. 3(a)).

At 1/2 ML coverage, the energetically preferred structure has the Ti atoms present in the second layer with a \((2\times2)\) pattern (Model-2). At 1 ML coverage, the energetically preferred structure employing a four-layer slab model has the Ti atoms present in the first and third layers, again in a \((2\times2)\) structure, with the Ti atoms in the third layer being underneath the Ti atoms in the first layer (Model-3). In Model-2, the presence of Ti lowers the barrier for \(\mathrm{H_2}\) dissociation from 0.96 eV for a pure Al(100) surface (Model-1) to 0.63 eV with \(\mathrm{H_2}\) dissociating from bridge to top sites (Fig. 3(a)). The reactions for both Model-1 and Model-2 are endothermic processes, with chemisorption energies of 0.34 eV and 0.30 eV, respectively.

Model-3 seems to be the energetically most favourable model for \(\mathrm{H_2}\) dissociation. It has a late barrier of 0.14 eV (\(E_{\text{Ti-H}} = 1.50\) \AA) when employing a \((\sqrt{2}\times\sqrt{2})R45^\circ\) unit cell (the barrier is 0.23 eV when employing the \((2\times2)\) unit cell), see Fig. 3(b), with \(\mathrm{H_2}\) dissociating from top Ti to bridge sites. There is a deep molecular chemisorption well, with a depth of 0.45 eV, in front of the dissociation barrier (Fig. 3(b)).

Models with 1/4 to 1 ML coverages, with the Ti atoms present only in the first layer, have been found to exhibit even lower barriers to \(\mathrm{H_2}\) dissociation, but these show much less stable binding of Ti in Al(100) slabs, and the \(\mathrm{Ti-Ti}\) distances...
(exceeding 5.0 Å) in these structures are in disagreement with the values obtained in EXAFS experiments.\textsuperscript{43} At the Ti coverage of 1/4 ML with Ti in the top layer (Fig. 3(c)), employing a (2×2) surface unit cell (corresponding to model 4 of Muckerman and coworkers\textsuperscript{43}), the Ti binding energy is 1.0 eV per Ti atom higher (more unfavourable) than that in our Model-3. An ANEB barrier search performed by us shows that, for the 1/4 ML Ti covered slab for H₂ dissociation, a molecular chemisorption well appears above a top Ti atom (Fig. 3(c)), and the energy of this well is 0.50 eV lower than the gas phase energy. Next a barrier appears with a height that is 0.10 eV lower than the gas phase energy. The chemical reaction described is an exothermic process, with a chemisorption energy of −0.94 eV. A similar, low coverage study has been conducted for “isolated” Ti, in a 1/18 ML low coverage surface with Ti in the top layer, employing a (3√3×2√3)R45° unit cell.\textsuperscript{40} On this surface, the molecular chemisorption well also appears and the depth of the well is 0.30 eV. The barrier height is 0.10 eV lower than the gas phase energy. The energy of Ti for this case should also be close to the 1/4 ML coverage case. Thus, the results of the 1/18 ML Ti covered surface,\textsuperscript{40} employing a (3√3×2√3)R45° unit cell are in agreement with our results for the 1/4 ML Ti covered surface.

This study suggests that, to promote H₂ dissociation, the amount of Ti added should be high enough to provide, at least locally, a c(2×2)-Ti/Al(100) surface alloy with a Ti coverage of 1/2 ML, where Ti atoms are present in the second layer.

Model-3 discussed has a slightly higher binding energy than Model-2 by 0.23 eV per Ti atom, but it has a lower barrier for H₂ dissociation. Experimental growth of face-centered-cubic titanium on the Al(100) surface\textsuperscript{30–52} generally shows that Ti atoms prefer to be in the subsurface layer at low Ti coverage (less than 1/2 ML) and also in the surface layer at high Ti coverage (about 2 ML). The presence of the adsorbed hydrogen on the Ti/Al(100) surface could stabilise the surface Ti at a temperature of 200 °C.\textsuperscript{60} XRD experimental work by Kang \textit{et al.}\textsuperscript{61} confirmed that the metastable L1₂ type of TiAl₂ (a crystal type of Model-3) does have a catalytic effect on the reversible dehydrogenation in NaAlH₄. Thus, we conclude that Model-3 may be highly relevant to the description of H₂ dissociation on the Ti/Al(100) surface if the amount of Ti present is high enough.

II. Investigating the mechanism of hydrogenation in transition metal doped NaAlH₄: a cluster model

In the second of our theoretical studies\textsuperscript{62} on the mechanism of catalytic de- and re-hydrogenation in transition metal (Ti and Sc) doped sodium alanate (NaAlH₄), our principal aim was to design cluster model systems that would be small enough for the high level computational treatments to still be feasible, while simultaneously being sufficiently representative of the real-world bulk materials.

It is typically considered that the dehydrogenation of NaAlH₄ follows a two step process. In the first step NaAlH₄ undergoes a solid state conversion to Na₃AlH₆, which in turn decomposes to NaH. Both steps are accompanied by the evolution of H₂ and forming of the metallic Al phase. However, reasoning on the basis of earlier thermodynamic observations,\textsuperscript{5} Balema and Balema\textsuperscript{63} proposed a simpler one-step process of the threefold dehydrogenation:

\[
2\text{NaAlH}_4(\beta) \leftrightarrow 2\text{NaH}(\beta) + 2\text{Al}(\beta) + 3\text{H}_2(\beta)
\]

as a result of which the observed Na₃AlH₆ phase is assumed to form only subsequently, \textit{via} the side reaction of the NaAlH₄ reactant with the growing NaH phase.

For this study we employed density functional theory (DFT, B3LYP/6-31+G(d,p)) for the geometry optimisations and coupled cluster theory (CCSD(T)/6-311G(2df,p)) for the subsequent refinement of the energy profiles. In the calculations on the Ti-doped NaAlH₄ slabs we also used a periodic DFT approach at the BLYP/DZP level.

We commenced from an essentially simple stoichiometry (1) of the otherwise exceedingly complex solid state reaction. This inspired us to devise a model reaction system based on a minimal sensible number of atoms. In line with (1), this system consisted of two molecules of NaAlH₄ and one transition metal (TM) atom (Ti or Sc). Its particular configuration, from which an unconstrained geometry optimisation was then initiated, was assembled by placing the Ti (Sc) atom at the centre of the two NaAlH₄ units in a crystal-like configuration. During the optimisation, a remarkable coordination complex resulted, in which two H atoms end up residing solely on the TM centre, whereas four other hydrogen atoms bridge the TM and Al atoms in pairs. Such a 13 atom model system (M1, Fig. 4) was the starting point for studies into the possible manners of dehydrogenation and the corresponding role of the TM atoms in the process. Similar complexes were found in the periodic DFT studies of Liu and Ge,\textsuperscript{64} who placed Ti atoms in the interstices of the NaAlH₄ bulk, as well as in the DFT studies of Marashdeh \textit{et al.},\textsuperscript{65} who dealt with the interactions of Ti with medium-sized NaAlH₄ clusters.

Our calculations\textsuperscript{62} indicated that the H₂ production and its subsequent release from the model systems occurs according to a unique two-step mechanism, whose scheme is faithfully followed by the three successive dehydrogenations. In the first step, one of the H–Al bonds forming an Al–H–Ti bridge breaks, and the corresponding H atom combines with one of the hydrogens bonded solely to the TM (TS₁, Fig. 4). The two assemble into the H₂ molecule, which is not immediately released but, once formed, becomes side-on (η²⁻) bonded to the TM centre (M2, Fig. 4). In the second step, the H₂ ligand leaves the coordination sphere. The chemistry of η²⁻H₂ coordination complexes has been described previously,\textsuperscript{66} and their role in the context of dehydrogenation of the TM doped NaAlH₄ was also analysed in a recent study.\textsuperscript{67} Although the observed mechanism was completely analogous for the Ti and Sc centres, some considerable differences were seen in the reaction energy profiles.\textsuperscript{62}

We next confirmed that the model systems exhibit unambiguous kinetic stability when fitted into the (001) surface of the NaAlH₄ crystal. This was expected from the relative positions of the Al and Na atoms, which approximate retain their crystal-like configuration (Fig. 4). Thus only a minor local reorganisation of the crystal structure is brought about when the TM atom is placed in the surface interstice. However, the comparison between the gas and solid phase relative energies
III. Dynamic processes in solid and liquid borohydrides

As fellow members of the group of complex hydrides, the borohydrides have much in common with the alanates, discussed in Sections I and II, but present a different set of thermodynamic and kinetic opportunities and challenges. The lightest member, LiBH₄, has nearly 14 wt% hydrogen capacity, even allowing for one H to remain in the store as LiH, and over 90 g L⁻¹ volumetric capacity (ignoring powder packing inefficiencies). Unfortunately, though, the H₂ desorption temperatures are too high and the kinetics too slow. In a joint experimental and theoretical approach, we investigated the thermodynamic properties and the hydrogen sorption kinetics of the complex hydrides, paying special attention to the borohydrides.

The study of key thermodynamic parameters such as the heat or entropy of reaction requires the measurement and calculation of the reaction products and intermediates and their stability. A combination of DFT-calculations and pressure-composition isotherms for NaBH₄ revealed the reaction path, enthalpy and entropy of the decomposition of NaBH₄ (Δ_rH = +108 kJ mol⁻¹ of H₂ and Δ_rS = 133 J K⁻¹ mol⁻¹ of H₂, T = 650°C). The study of the decomposition reaction kinetics of LiBH₄ highlighted the importance of kinetic modelling including the pressure dependence of the reaction. To examine the origin of the slow kinetics, we investigated the hydrogen mobility in light weight complex hydrides in detail. The hydrogen mobility in the bulk of these compounds was measured as a function of temperature on a microscopic scale using inelastic and quasielastic neutron scattering. From the neutron studies on solid samples, rotational jump diffusion of a BH₄ tetrahedron is the dominant process in the solid. Within this process, no material is transported. The slow translational hydrogen transport rate was confirmed by macroscopic mobility measurements and nuclear magnetic resonance spectroscopy. The measurements give direct evidence of a macroscopic diffusion of BH₄⁻ ions as well as atomic exchange of hydrogen between the anions. In the liquid phase of LiBH₄ above 553 K, relatively fast translational diffusion of the BH₄⁻ units is found. The measured diffusion coefficients are in the 10⁻⁵ cm² s⁻¹ range at temperatures around 700 K. In the liquid, the atomic hydrogen deuterium exchange rate is comparable to the decomposition rate. Experiments using femtosecond spectroscopy complete the picture of the hydrogen dynamics in LiBH₄ shedding light on the energy transport in this system.

Fig. 5 summarises the various processes and depicts their relevance for hydrogen sorption. We estimate the characteristic length by which each process has proceeded within one second, which corresponds to a diffusion length for diffusion, or the velocity by which an atomic step (e.g. H–D exchange) would proceed through the solid. We compare these numbers to the characteristic speed needed to fill a hydrogen tank of around 100 l in 120 s (dashed line in Fig. 5). If the gas convection is fast enough between the grains, the corresponding velocity required for exchanging hydrogen in the grains to achieve the desired fuelling speed is shown in the grey band. As an ordinate we chose the characteristic energy of the process, either the activation energy or the energy needed to trigger the process. The figure demonstrates that processes not involving mass transport are very fast and thus cannot be rate-limiting. However, all processes involving mass transport are too slow in the solid to reach the rates required for a technical application. In the liquid, however, diffusion is fast enough.
In addition, the observed H–D-exchange as a measure of the rate of B–H bond breaking and formation is of the order of the decomposition rate. We therefore propose that the nucleation and growth of the solid products B and LiH are the rate-limiting step. The corresponding activation energies are relatively high resulting in a high temperature required to overcome these barriers and catalysts might be used to reduce these barriers.

IV. Investigating Ni complexes as novel hydrogen store catalysts

Slow kinetics need not be the end of a material if the thermodynamics are good; as we have seen with Ti/NaAlH₄, discovery of a catalyst may transform the prospects of a material. This was the subject of another investigation, attempting to design a new class of catalysts based on transition metal complexes leading to experiments involving nickel macrocycle complexes.

Formation of hydride stores using gaseous H₂ as reagent is formally a redox reaction:

\[ \text{H}_2(g) + 2e^- → 2\text{H}^+ \quad (\Delta H^\circ = +3.00 \text{ eV in the gas phase}) \] (2)

An initial study was carried out on the various possible spatial arrangements of frontier orbitals (‘orbital landscapes’, see Fig. 6) that may lead to the facile reductive splitting of H₂ by mono- or bi-nuclear catalysts made up of, or on the surface of solids containing, s, p, d or f-block metals. Using the insights obtained from this theoretical study, we began experimental work on developing a new class of late transition metal catalysts for use with complex hydrides, taking account of such orbital considerations.

Previous investigations of the transition metals typically involved elemental metal or simple salts, leaving little room for improvement beyond their inherent level. Instead, we targeted metal complexes, which afford the ability to tune the properties of the metal centre by judicious choice of ligand type and geometry, making new metal systems available (such as higher oxidation states) and offering the ability to further improve the performance of those showing promise. It had been previously reported that the value of the thermal decomposition temperature, \( T_{\text{dec}} \), is linked to the value of the standard redox potential for the \( \text{M}^{n+}/\text{M}^0 \) redox pair by a monotonic relationship. From this, it was hoped that using the well-known effects of ligation on a metal centre’s redox properties, new stable transition metal complexes with hydride, borohydride or even alanate ligands could be made. These should be stable enough to be introduced into complex hydride stores and may then show a catalytic role similar to that of Ti with the alanates.

Our first choice of metal was Ni, as the platinum group metals find myriad applications as hydrogenation catalysts, and whilst Pd and Pt present problems in terms of cost and availability, Ni is cheap, abundant, and also lighter than its group 10 congeners. For ligands, we decided to start with macrocycles, due to the greater stability they provide to the complex relative to separate monodentate groups and even open-chain polydentate ligands, thanks to the macrocyclic effect.

Results for Ni(cyclam)(BH₄)₂ (cyclam = 1,4,8,11-tetraazacyclotetradecane, a 14 member ring with 4 N donors, that forms strongly bonded complexes with Ni(II)) showed the validity of the approach, with the characterisation of two isomers, cis- and trans-, of a stable, easily synthesised Ni(II) complex with direct metal–borohydride coordination (Fig. 7). The stabilisation was impressive: Ni(BH₄)₂

سلح C:

\[ \text{Ni}(\text{BH}_4)_2 \]

Fig. 5 Overview of the dynamic processes in solid and liquid borohydrides, see text for details. The magnified region illustrates some microscopic processes taking place during formation and decomposition of complex hydrides.

Fig. 6 An example of reductive 2e⁻ activation of H₂ on a model PdPd₄ cluster. (a) HOMO of the d¹⁰ complex, Pd⁴(Pd⁴)₄ with the tetracoordinate Pd³ metal center (a butterfly coordination with four other Pd atoms), and the H₂ molecule far distant. (b) LUMO of H₂. (c) LUMO + 1 of the dihydride complex of the Pd₃ cluster, (H₂)₂Pd³(Pd³)₄. Reproduced with permission from ref. 79.

Fig. 7 Structure of cis-Ni(cyclam)(BH₄)₂ determined by single-crystal X-ray diffraction (H attached to C and N have been omitted for clarity).
(with no other ligands) decomposes below $-20\,^\circ C$, whilst trans-Ni(cyclam)(BH$_4$)$_2$ survives to $170\,^\circ C$. The slightly lower decomposition temperature of the cis isomer, at $140\,^\circ C$, was expected, as the two Ni bound bridging hydrogens are next to each other, providing a more viable decomposition pathway. The stabilisation of the inherently unstable Ni-BH$_4$ connection via ligation is the first indication that similar complexes of late transition metals may be utilised as hydrogenation catalysts on an equal footing with their unligated early transition metal counterparts.

The next systems investigated were the related 12 and 14 member thioether rings, 12aneS$_4$ and 14aneS$_4$ (12aneS$_4$ = 1,4,7,10-tetraazacyclododecane, 14aneS$_4$ = 1,4,8,11-tetraazacyclotetradecane). These systems showed considerably less stability in complex hydride hydrogen stores, reacting vigorously to form a black solid, and so proved less promising (though they were found to possess interesting magnetic behaviour with the facile addition/removal of two equivalents of water$^{84}$).

Attention is now focused on the tetraphosphine complex, Ni(PPh$_3$)$_2$(BF$_4$)$_2$ ($P_P$ = tri(2-diphenylphosphino)ethylphosphine). The PP$_3$ ligand is a chelate rather than a macrocycle, with the potentially advantageous property of enforcing a cis geometry, and is a logical next step in donor strength after amines and thioethers. It forms [NiH(PPh$_3$)]BF$_4$ by reaction with complex hydrides either in solution$^{85}$ or mechanochemical synthesis,$^{86}$ and has shown itself to be resistant to destruction even from such powerful reducing agents as LiAlH$_4$.

Though none of the systems yet tested have shown the required catalytic behaviour, the approach has been shown to be sound, and with a bewildering array of ligands, which may be combined with any of a number of metals, in numerous different geometries, it seems the field is wide open for exploration.

V. The less common borohydrides—in theory and practice

In this final section on the complex hydrides, we look at the network’s study of the less common borohydrides. The first area is an in depth experimental study of Y(BH$_4$)$_3$, investigating its synthesis, the hydrogen evolving thermal decomposition and the influence of phase-related phenomena, whilst the second is an innovative large scale screening for novel borohydrides with improved properties using theory.

Although Y(BH$_4$)$_3$ is a hydrogen-rich compound (9.1 wt% H), and the evolved H$_2$ is not significantly contaminated with B$_x$H$_y$, it would not serve as a practical large-scale hydrogen store as it has some serious drawbacks. Firstly, H$_2$ is evolved at too high a temperature for use with PEM fuel cells.$^5$ Secondly, this system releases only 76% of its total H content below 400 $^\circ$C. Thirdly, the thermal decomposition of Y(BH$_4$)$_3$ turns out to be a complicated multi-step process which is likely to result in problems with reversibility (i.e. with refuelling). Another issue hampering potential application of yttrium compounds as H$_2$ stores is related to the price of yttrium, which—albeit two orders of magnitude cheaper than the lightweight scandium—is still considered to be a rather expensive metal.$^87$

However, Y(BH$_4$)$_3$ is still interesting as a potential parent compound for some modified borohydrides of superior hydrogen content, as mixed-cation borohydrides,$^{88}$ or proton-hydride hydrogen stores, e.g. Y(BH$_4$)$_3$-xNH$_3$. Such systems are still of interest for on-board hydrogen storage in helping to understand how the properties of hydrogen storage materials can be tuned by manipulating crystal structure or composition (and might be of some significance for small-scale applications where the cost of materials is of less importance). Recently, numerous novel metal borohydrides have been synthesised and investigated,$^{89,90}$ but the only universal method used for the preparation of solvent-free transition metal borohydrides is mechano-chemical metathesis of transition metal halide and alkaline metal borohydride:

$$MX_n + nM'BH_4 \rightarrow M(BH_4)_n + nMX$$ (3)

Such a synthesis presents several serious drawbacks including difficulties in scaling-up to industrial quantities, and produces a by-product alkali metal halide (M’X) which is difficult to separate and therefore decreases the amount of hydrogen stored, as well as possibly influencing the thermal decomposition mechanism, complicating its study.$^{91}$

In our study,$^{92}$ we investigated a broad spectrum of previously published and novel methods of synthesis of solvent-free Y(BH$_4$)$_3$. Thirteen reaction pathways failed to deliver the desired product. Dry Y(BH$_4$)$_3$ (in a fine mixture with LiCl) could only be obtained by brief high-energy disc milling of the LiBH$_4$ and YCl$_3$ precursors, as recently reported.$^{90}$ Interestingly, the other possible analogous reactions: YCl$_3$ + NaBH$_4$, YF$_3$ + LiBH$_4$ and YF$_3$ + NaBH$_4$ did not lead to the expected metathesis products.

Upon investigating the behaviour of Y(BH$_4$)$_3$, we found$^{92}$ that slow thermal decomposition of Y(BH$_4$)$_3$ starts above 160 $^\circ$C (temperature ramp at 10 K min$^{-1}$) with a significant acceleration of hydrogen evolution above 200 $^\circ$C (Fig. 8).

Traces of boranes were detected in the evolved H$_2$ using time resolved infrared spectroscopy and mass spectrometry. The nature of the solid state decomposition products depends on the initial sample composition as well as the other reaction conditions. With increasing temperature, other groups have detected powder X-ray diffraction reflections from YH$_3$, YH$_2$, and YB$_4$$^{89,94}$ together with unidentified intermediates, while in our investigations only amorphous thermal decomposition products have been observed. During the heating to ca. 200 $^\circ$C
a phase transition takes place to a novel cubic polymorph,\textsuperscript{92} later shown to adopt the \textit{Fm\textsuperscript{3}c} space group.\textsuperscript{94}

The high-temperature polymorph of yttrium borohydride is metastable under ambient conditions, and could be prepared by heating \( \text{LT-Y(BH}_4\text{)}_3 \) up to 194–216 °C followed by rapid cooling. The HT-form of \( \text{Y(BH}_4\text{)}_3 \) decomposes at lower temperature than the as synthesised LT-form,\textsuperscript{95} releasing roughly the same amount of \( \text{H}_2 \) (ca. 3.5 wt% up to 400 °C, molar ratio ca. 1 : 3 \( \text{Y(BH}_4\text{)}_3 : \text{LiCl} \)). In addition, the apparent activation energy calculated using the Kissinger approach\textsuperscript{96} (at the maximum of thermal decomposition rate) is remarkably higher for the HT polymorph, than for the HT form. The striking 3-fold difference of activation energy connected with the first step of thermal decomposition (at ca. 200–260 °C) gives evidence for significant kinetic improvement of the thermal decomposition process due to the LT \( \rightarrow \) HT phase transformation. Our study of the non-isothermal kinetics of the thermal decomposition process of \( \text{Y(BH}_4\text{)}_3 \) testifies how strongly the phase transitions may influence \( \text{H}_2 \) desorption from borohydride stores of \( \text{H}_2 \) fuel.\textsuperscript{95}

The challenge for the future is to apply these lessons to systems where the stability of either the hydrogenated or depleted phase is a problem, but where the cost of materials is less of an issue.

Now looking at an entirely different group of less common borohydrides and a different methodology for studying them; we briefly examine theoretical predictions for the properties of ternary (mixed cation) borohydrides determined by large scale screening.

As already discussed, the borohydrides have very attractive volumetric and gravimetric capacities, but to summarise the problems of the binary metal borohydrides: the alkali metal based compounds are too stable, the alkali earth compounds are kinetically too slow and practically irreversible, whilst the transition metal borohydrides are either unstable or irreversible. These contrasting characteristics, however, present the possibility that the mixing (alloying) of these borohydrides might provide a material with optimised properties. For this purpose, a computational screening study was performed to find the most promising ternary metal borohydrides using DFT.\textsuperscript{77} Alloys were produced by mixing one alkali metal atom, Li, Na, or K (\( \text{M}_1 \)) with one alkali, alkaline earth or 3d/4d transition metal atom (\( \text{M}_2 \)) plus two to five\( \text{BH}_4\) groups, \textit{i.e.}, \( \text{M}_1\text{M}_2(\text{BH}_4)_{2-5} \), using a number of model structures with trigonal, tetrahedral, octahedral and free coordination of the metal borohydride complexes. This screening study predicted 20 structures out of 753 as being potentially stable. These contrasting characteristics, however, present the possibility that the mixing (alloying) of these borohydrides might provide a material with optimised properties. For this purpose, a computational screening study was performed to find the most promising ternary metal borohydrides using DFT.\textsuperscript{77} Alloys were produced by mixing one alkali metal atom, Li, Na, or K (\( \text{M}_1 \)) with one alkali, alkaline earth or 3d/4d transition metal atom (\( \text{M}_2 \)) plus two to five\( \text{BH}_4\) groups, \textit{i.e.}, \( \text{M}_1\text{M}_2(\text{BH}_4)_{2-5} \), using a number of model structures with trigonal, tetrahedral, octahedral and free coordination of the metal borohydride complexes. This screening study predicted 20 structures out of 753 as being potentially stable. Amongst them, \( \text{M}_1(\text{Al/Mn/Fe})(\text{BH}_4)\text{, (Li/Na)}\text{Zn}(\text{BH}_4)\text{, and (Na/K)}\text{Ni/Co}(\text{BH}_4) \) alloys were found to be the most promising. Several of the alloys have been experimentally synthesised,\textsuperscript{96} showing the use of screening techniques to find potential candidate materials for hydrogen storage is a valuable tool.

VI. Amidoboranes as proton–hydride hydrogen stores

Proton–hydride stores retain the hydridic hydrogens in common with the complex hydrides discussed until now, but include protic hydrogens too, giving them quite different properties. The coupling reaction between protons and hydride anions (where both species are bound in various chemical compounds or within a single phase) usually leads to the facile evolution of\( \text{H}_2 \). The reverse process, heterolytic activation of\( \text{H}_2 \):

\[
\text{H}_2(g) \rightarrow \text{H}^+ + \text{H}^- \quad (\Delta H^0 = +17.35 \text{ eV in the gas phase}) \quad (4)
\]

(\text{which is formally a disproportionation reaction}) is thus more difficult to achieve than homolytic activation:

\[
\text{H}_2(g) \rightarrow 2\text{H}^* \quad (\Delta H^0 = +4.50 \text{ eV in the gas phase}) \quad (5)
\]

Despite reaction (4) being thermodynamically uphill, heterolytic activation may indeed be achieved if the resulting proton and hydride anion form sufficiently strong chemical bonds to other elements in the reaction products. This happens for many second period p-block elements, but there are also a wide variety of transition-metal-based synthetic molecules known to be capable of heterolytically activating\( \text{H}_2 \) under quite mild conditions. Some recently developed systems include phosphine complexes of Ru, Ni, Pd, and Pt, nitrosyl derivatives of Re, mononuclear Ir species, Rh-S and Ti-S compounds, Ir\textsubscript{2}–S, binuclear Ru–W–S, NiFe–S, and many polynuclear cluster complexes,\textsuperscript{101} to mention just a few.

Over the last decade, several important lightweight hydrogen storage materials have been developed that are able to attach hydrogen via the heterolytic splitting of\( \text{H}_2 \).\textsuperscript{102} The thermal decomposition of these systems proceeds according to the following representative equations, listed here with their standard reaction enthalpy values,\( \Delta H^0 \):

\[
\text{LiH} + \text{Li}_2\text{NH} \rightarrow \text{Li}_3\text{N} + \text{H}_2 \quad (\Delta H^0 = +1.20 \text{ eV}) \quad (6)
\]

\[
\text{LiH} + \text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{H}_2 \quad (\Delta H^0 = +0.47 \text{ eV}) \quad (7)
\]

The majority of reactions evolving hydrogen from proton–hydride stores require thermal activation and proceed with reasonable speed only at elevated temperatures; for example, the reaction depicted in eqn (6) proceeds only at temperatures above 325 °C, the one shown in eqn (7) above 150 °C.

Our work\textsuperscript{103} has helped to systematise important properties of proton–hydride stores, noting that a fatal ‘perverseness law’ applies: the higher the effective H content (\textit{i.e.}, that which is released as\( \text{H}_2 \)), the higher the temperature needed to desorb it completely (Fig. 9). The increase in\( T_{\text{dec}} \) simply reflects the progressive thermodynamic stabilisation of the proton–hydride store and the decreasing polarisation of\( \text{H}_2^+ \) as the effective H content increases. Take for example the\( \text{NH}_2\text{BH}_3 \) family: the absolute values of the effective charges on the hydride anion and proton are smaller for\( \text{NHBH}_d \text{H}_3 \) than the corresponding values for\( \text{NH}_2\text{BH}_4 \), electrostatic\( \text{H}^+–\text{H}^- \) coupling is therefore more difficult for the former species and thus requires a higher temperature to desorb\( \text{H}_2 \).\textsuperscript{104}

Regrettably, most proton–hydride stores offering hydrogen release at the mildest temperatures (for example\( \text{Mg(NH}_3\text{)}_2(\text{BH}_4\text{)}_2 \)) do so exothermically and thus are not on-board reversible. Despite this, the amidoboranes seemed worthy of further investigation thanks to a number of promising attributes, such as their high hydrogen content (8–13.5%) and low temperature of hydrogen evolving decomposition, under 100 °C (see Table 2). Currently the amidoboranes of the alkali metals (Li, Na, K)\textsuperscript{76,105–109} and alkali earth metals (Ca, Sr),\textsuperscript{110–112}
transition metals (Y, Yb, Eu)\textsuperscript{113,114} as well as bi-metallic compounds (Na–Li, Na–Mg)\textsuperscript{115,116} are known.

For the systems we investigated, the alkali metal amidoboranes, LiAB, NaAB and NaLi(AB)\textsubscript{2} are easily synthesised in a one step dry mechanochemical reaction using AB as a precursor:

\[
\text{LiNH}_2 + \text{NHBH}_3 \rightarrow \text{LiNH}_2\text{BH}_3 + \text{NH}_3
\]

\textsuperscript{(8)}

\[
\text{NaH} + \text{NHBH}_3 \rightarrow \text{NaNH}_2\text{BH}_3 + \text{H}_2
\]

\textsuperscript{(9)}

\[
\text{LiH} + \text{NaH} + 2\text{NHBH}_3 \rightarrow \text{NaLi}[(\text{NH}_2\text{BH}_3)_2] + 2\text{H}_2
\]

\textsuperscript{(10)}

Yttrium amidoborane is synthesised by milling LiAB with YCl\textsubscript{3} in a metathetical reaction:

\[
3\text{LiNH}_2\text{BH}_3 + \text{YCl}_3 \rightarrow \text{Y(NH}_2\text{BH}_3)_3 + 3\text{LiCl}
\]

\textsuperscript{(11)}

The synthetic procedure used meant it was not necessary to purify the alkali metal amidoboranes, but for Y(AB)\textsubscript{3}, all attempts at separation from the LiCl by-product were unsuccessful, reducing its effective hydrogen capacity to 4.9%.

The amidoborane products react vigorously with water, unlike ammonia borane. These amidoboranes have similar thermal properties—they all decompose at temperatures below 100 °C in an exothermic reaction, precluding them from being on-board reversible, (cf. Fig. 1). Our work also shows the evolved hydrogen is significantly contaminated with ammonia which would cause poisoning of the fuel cell membrane and catalyst,\textsuperscript{117} and deplete the store. Decomposition is preceded by an endothermic process of intermolecular transition which was discussed in detail for the case of NaAB. The exemplary results of a TGA/DSC experiment on NaLi(AB)\textsubscript{2} are shown in Fig. 10.

The crystal structure space group of Y(NH\textsubscript{2}BH\textsubscript{3})\textsubscript{3} was determined to be C\textsubscript{2}/c with lattice parameters of 13.189 Å, 7.822 Å, 14.874 Å and b = 92.42°,\textsuperscript{113} whilst infrared spectroscopy suggests that a considerable interaction takes place between BH\textsubscript{3} groups and Y\textsuperscript{3+}, leading to a marked lowering of the bridging (BH) stretching frequency in comparison with LiNH\textsubscript{2}BH\textsubscript{3}.\textsuperscript{113}

VII. Ammonia dynamics in magnesium ammines

As the hydridic half of the amidoboranes, BH\textsubscript{3}, provided the link from the complex hydrides, the protic part now leads us to look at storing hydrogen in molecules of ammonia.\textsuperscript{118} NH\textsubscript{x}BH\textsubscript{x} may be catalytically reformed onboard\textsuperscript{119} to produce H\textsubscript{2} and inert N\textsubscript{2}, so called ‘indirect storage’, whilst the ammonia itself may be stored in metal ammine complexes, whose chief advantage over pressurised liquid ammonia is improved safety, with a significantly lower vapour pressure\textsuperscript{38} of the toxic gas.

The complexes may be pressed into high density tablets,\textsuperscript{120} allowing volumetric densities close to the theoretical crystal density whilst still offering fast and reversible ammonia absorption and desorption. The origin of the fast kinetics, that is, the mechanism of NH\textsubscript{3} transport in the bulk, was the subject of this study, principally based on theory but additionally supported by experimental results.

In a theoretical study of such materials, one usually starts from the experimentally available crystal structures. If, however, the experimental data is not available, either crystal structure...
Fig. 11 Minimum energy paths for double NH₃ rotations in low (LT) and high (HT) temperature structures of Mg(NH₃)₆Cl₂. HT has the highest rotation barrier. Reproduced by permission of the Royal Society of Chemistry from ref. 125.

Fig. 12 Cartoon illustrating the two competing mechanisms, along the chain and interchain (shown for MgCl₂(NH₃)₂, purple—Mg, green—Cl, blue—N, white—H).

any direction results in the same barrier height as individual rotations: first one NH₃ rotates 120° and stops, then the other NH₃ starts to rotate another 120°. A similar rotation pattern exists in HT. In addition to the hexaamine Mg complexes, we also calculated the NH₃ rotation barriers in the diammine and monoammine complexes and found a barrier of 0.02 eV and 0.04 eV, respectively, showing a free rotation of NH₃.

Quasielastic neutron scattering data, used to identify C₃ rotations of NH₃, for the hexaamine complex at 80, 90 and 100 K display an Arrhenius temperature dependence with an activation energy of 0.09 eV, in agreement with the calculated rotation barrier for LT.

The expectation that the desorption of NH₃ from the Mg complex is limited by bulk diffusion of NH₃ was investigated by locating the lowest activation barriers for NH₃ transfer in Mg(NH₃)₆Cl₂ with n = 6, 2, 1.

Diffusion barriers were calculated for each of the many possible NH₃ diffusion pathways considered in the hexaamine complex, and found to lie in the range 0.52–0.60 eV. For the long-range transport path, an additional step involving a ~90° reorientation of an NH₃ molecule, with a barrier of 0.10 eV, must also be considered. With the diammine complex two competing long-range diffusion pathways exist: along the chains and between the chains (see Fig. 12 and animations in the ESI†). The activation energy for the “along the chain” path, 0.88 eV, is 0.15 eV lower than the interchain paths. Similar to the diammine complex, both the “along the chain” and interchain paths are possible long-range transport methods for the monoammine Mg complex. The lowest barrier, 0.90 eV, was obtained for the along the chain path. All the calculated barriers agree with the experimental desorption enthalpies, therefore, the fast absorption and desorption process observed experimentally is explained on the basis of a diffusion limited process for n = 6, 2, 1.

VIII. Loading metal–organic frameworks (MOFs) with alane nanoparticles

In these final two sections we come full circle, turning to the metal hydrides, close cousins of the complex hydrides we started with. Nano-particles of these materials possess considerably different physical properties from those of the bulk material,
which may be of benefit in a hydrogen store. The field has received a lot of attention in recent years, so first we look at its application to alane and a novel method for nano-confinement for hydrogen storage, before, in the next section, moving on to developments in measuring these effects.

Aluminium hydride (AlH₃) is known as an excellent single-use hydrogen storage material having both high volumetric and gravimetric hydrogen storage density. This compound releases hydrogen in one decomposition step under mild conditions, however, the direct hydrogenation of aluminium metal to aluminium trihydride requires very high pressures (about 1 GPa) making it an impractical hydrogen storage material for onboard applications. Engineering of a new nanostructured aluminium hydride could solve this problem as it is well known that entering the nanosize regime can significantly modify the physical and chemical properties of materials. Many theoretical studies have suggested that nanosized aluminium hydride clusters would show differences from bulk alane, especially in terms of their thermodynamic stability. When aluminium hydride particles are scaled down to nanodimensions, the dehydrogenation enthalpy becomes less negative, making the system more stable. The number of both aluminium and hydrogen atoms in a cluster along with the configuration of hydrogen atoms on the surface of the aluminium cluster are factors determining the thermodynamic stability of an aluminium hydride nanosystem. Moreover, Cox et al. demonstrated that Al₆ clusters are reactive towards hydrogen and are able to dissociate a H₂ molecule. Electronic structure calculations on Al clusters reproduce this finding. These calculations also showed that the Al hexamer is the smallest cluster that is reactive towards H₂ because it exhibits a singlet ground state, which is not reactive towards H₂. In contrast, the Al dimer and tetramer both exhibit triplet ground states with significant barriers towards H₂ dissociation. In addition, Kawamura et al. stated that the weak bonding of hydrogen with Al clusters together with the low density of aluminium could be of interest for hydrogen based fuels in the nano-sized form.

To produce alane nanoparticles with well-defined sizes and shapes a template-directed synthesis using metal-organic frameworks (MOFs) as scaffold materials was employed. MOFs are crystalline and porous solids, formed by an extended network of metal ions (or metal clusters) coordinated to multidentate organic molecules. The unique combination of properties like the presence of strong metal-ligand interactions, tunable pore size and shape, finely controlled dimensionality and tailored functionality of their coordination space, not only differentiate MOFs from other porous compounds but also makes them suitable templates for encapsulating nanoparticles. A successful incorporation of a wide range of transition metals in numerous MOFs has been the subject of extensive study over recent years. This triggered us to examine the hypothesised effect of spatial confinement on the thermodynamic and kinetic properties of the alane nanoparticles embedded in the cavities of a MOF material.

Zeolitic imidazolate framework-8 (ZIF-8) was chosen as a template for the inclusion of aluminium hydride particles. The ZIF-8 topology (Fig. 13) results from the association of 2-methylimidazolate (MeIM) ions with tetrahedrally coordinated Zn²⁺ ions to form a sodalite-type structure. The ZIF-8 pore openings are much smaller than the interior dimensions, which should limit nanoparticle mobility. In addition, the remarkable thermal stability (up to 450 °C) of this material would enable hydrogen desorption from aluminium hydride without the framework collapsing.

Using a solution infiltration method (employing dimethyl-ethylamine alane—a precursor more commonly used in the metal-organic chemical vapour deposition of aluminium) we show, for the first time, the successful loading of aluminium hydride into the porous ZIF-8 matrix. The obtained nanocomposite, denoted as alane@ZIF-8, contained 1.14 wt% Al, and was characterized by various analytical techniques.

The structure of the porous template remained intact after the loading procedure, as confirmed by PXRD measurements. Furthermore, no crystalline phases of aluminium or aluminium trihydride were observed in the diffractogram of the composite material. However, the relative intensities of the low angle reflections diminished compared to the unloaded ZIF-8, which strongly suggests the presence of alane particles in the porous matrix. FTIR spectroscopy was used to confirm the existence of aluminium hydride in the synthesized sample. The new bands located at 1844 cm⁻¹ with a shoulder at 1868 cm⁻¹ and at 656 cm⁻¹ were assigned to Al–H stretching and H–Al–H deformation modes, respectively. The position of the alane nanoparticles in the alane@ZIF-8 sample was further investigated by examining the level of guest species pore infiltration using low-pressure Ar adsorption measurements at 87 K. The specific surface area and the pore volume values were calculated using the BET method decreased for the loaded material and compared to the empty matrix. This finding suggests that pores of ZIF-8 are partially filled with alane nanoparticles. Further examination of the accessibility of the void space in the alane@ZIF-8 sample revealed that the loaded sample exhibits a bimodal pore size distribution (see Fig. 14): those two contributions were assigned to empty and partially occupied pores in the composite material. Since hydride particles are lacking contrast under transmission electron microscope imaging, the accurate size of the alane particles could not be determined. However, the distribution...
of the aluminium hydride in the alane@ZIF-8 sample was analyzed by the X-ray mapping of aluminium and showed that the examined area was covered uniformly with aluminium.

Considering the small window aperture in ZIF-8, the diffusion of the dimethylethylamine alane precursor is expected to be limiting and consequently leading to the loading of the first layers of micron-sized ZIF-8 particles with guest molecules. Taking the TEM results into account it is speculated that the alane nanoparticles are deposited in the outermost pores of the template. The hydrogen evolution and uptake of this novel material is still the matter of research, but this result represents an important step in the realisation of high performance hydrogen storage materials based on nano-alane.

IX. Refining the quartz-crystal microbalance technique for use with nanoparticles

Experimental investigation of such nano-scale effects, however, brings significant challenges, and the development of highly sensitive techniques for probing these systems is of great utility. While conventional hydrogen storage measurement systems are designed for bulk materials and typically require at least tens of milligrams of material, the hydrogen uptake in nanomaterials such as thin films or nanoparticles can be measured accurately and sensitively with a quartz crystal microbalance (QCM). QCM has traditionally been used to monitor the thickness of thin films deposited under vacuum in physical vapour deposition systems due to its high mass sensitivity (< 1 ng cm⁻²). The technique exploits the (inverse) piezoelectric effect, which is found in certain materials including quartz. To this end, the piezoelectric material is sliced into a thin plate with a suitable crystallographic orientation, and metallic electrodes are evaporated on both front and backside. An AC voltage applied across the electrodes induces a shear deformation of the crystal. Since the oscillation frequency of the quartz crystal resonator is disturbed by small changes in mass, adsorption and desorption processes can be monitored with high precision by measuring the change in resonance frequency. For sufficiently thin ad-layers, which have the same or similar acoustic properties as quartz and which are rigidly coupled to the sensor surface, the change in resonance frequency is directly proportional to the mass change on the crystal, as first described by Sauerbrey.

The QCM can be operated at any pressure from high-vacuum conditions up to the highest pressures of interest for hydrogen storage materials. The accessible temperature range, on the other hand, is typically limited to temperatures below around 250 °C due to issues with signal stability and gradual loss of piezoelectric response at higher temperatures.

Earlier investigations have shown that the QCM technique is useful to measure both the thermodynamics and kinetics of hydrogen uptake in metal thin films, where one dimension of the hydrogen storage material is confined to the nanoscale. In order to study the full potential of nano-confinement effects on the kinetics and thermodynamics of the hydrogenation/dehydrogenation process of hydrogen storage materials, however, it is necessary to scale down all three dimensions, i.e. to work with nanoparticles.

When fabricating such structures one must take into account two aspects: (1) The crystal has a limited sensitivity (about 1 ng Hz⁻¹ for an SC-cut crystal operating at its base frequency of 10 MHz). In order to enhance the signal, it is desirable to place as many nanoparticles on the crystal as possible. (2) The surface area of the crystal is also limited, thus placing too many nanoparticles too close to each other would lead to the loss of the 3D-nano effect and the resulting system would behave as if only one-dimensionally confined (i.e. a thin film).

By depositing a relatively thick porous layer on a standard, flat QCM sensor, both the above criteria can be satisfied. Such a porous matrix can incorporate many more nanoparticles than the flat crystal surface and also acts as the spacer between them, thus ensuring an enhanced 3D-nano effect (Fig. 15). The porous matrix must ideally be inert, adhere well to the quartz crystal and grant access for hydrogen gas to all nanoparticles.

As silica and alumina have been widely used and studied in the catalysis field as support materials, we fabricated 50 to 1200 nm thick layers by spin-coating from sols and suspensions. The total surface area of such a porous film can be up to 1000 times larger than the geometrical surface area of the crystal itself.

Pre-cleaning of the crystal and deposition of adhesion layers is necessary in order to improve sticking of the porous support. The thickness and porosity could be measured quickly, reliably and non-destructively by a spectroscopic ellipsometer (J.A. Wollam Co., Inc.). Silica films contained about 40% pore volume, while the porosity of alumina films was about 70% by volume. We demonstrated the feasibility of this approach by choosing palladium as a well-studied model material for reversible hydrogen storage. The porous templates were impregnated with an aqueous solution of a complex palladium salt, [Pd(NH₃)₄][NO₃]₂. The salt was reduced to metallic Pd in a hydrogen–argon gas mixture.

![Fig. 15 Schematic depiction of the concept of porous supports.](image-url)
stream at 130–400 °C. The resulting structures were inspected by TEM, and ICP-MS was used to determine the palladium content. The observed plateau pressure of 7 Torr measured upon hydrogenation at 298 K corresponds well to literature data for nanocrystalline Pd. 41

Since the response of the QCM sensor not only depends on hydrogen uptake but also on changes in the gas environment (e.g. pressure, viscosity, temperature), the template response had to be calibrated prior to Pd loading. In order to avoid uncertainties associated with this calibration procedure, we investigated the usefulness of a dual QCM setup, where two resonators are fabricated onto one and the same crystal (Fig. 16). Using one resonator as a measurement resonator and the second one as a reference, all frequency changes occurring due to changes in the environment can be corrected for. The performance of these dual QCM sensors with respect to critical issues such as crosstalk between the resonators was tested by studying hydrogen uptake in a well-studied model system (thin Pd films). Non-mass related frequency changes could be compensated for to some extent, but additional fine-tuning is required.

In summary, we have shown that the quartz crystal microbalance technique is a suitable tool for the investigation of nanostructured hydrogen storage materials, which can be deposited onto quartz sensors and the thermodynamic properties of which are compliant with the temperature and pressure range accessible to QCM. Both thin films and nanoparticles may be studied, where high-surface area porous supports provide an improved signal-to-noise ratio in the latter case. Non-mass related contributions to the QCM frequency response are present and must be compensated for, either by calibrating the system in separate “dummy” runs, or using a dual sensor setup.

Conclusions

Though the conclusive breakthrough has not arrived, progress has certainly been made. Building on the experimental evidence, our studies using periodic models have suggested the critical role the sub-surface dispersal of Ti in Al has for H2 dissociation 41 and so for the regeneration of spent NaAlH4, with at least a local, sub-surface 1/2 monolayer of Ti required to promote H2 dissociation. The optimisation of this dispersal, including during cycling, could provide useful improvements to the storage system and this work provides additional pointers for experimental investigations. Cluster models have provided useful insights into the mechanism of hydrogen release from these systems, suggesting the formation of an η2-H2-transition metal complex followed by evolution of H2, though the integration of these gas-phase models into more realistic representations remains challenging. 62

When considering systems with problematic kinetics, such as the group I borohydrides, we need to know precisely what is rate-limiting in order to design a catalyst. The determination of the physical limits of a system such as the borohydrides requires thorough and painstaking investigation 72–78 but such studies allow us to reveal that, for the borohydrides, solid state mass transport is too slow for use in cars. In the liquid, where fast translational motion overcomes the mass transport problems, we propose that nucleation and growth of the decomposition products are rate-limiting, and may benefit from catalysis. In contrast to this, the metal ammines show fast ammonia desorption kinetics, and indeed we have found they are rate limited only by the bulk diffusion of ammonia. 125

Designing catalysts is another important issue that must be dealt with. Trial and error can certainly provide useful starting points, but it would be lucky indeed if it returned a perfect candidate as far as improvement of kinetics is concerned. It is far more likely that any promising catalyst will require fine-tuning to squeeze the best possible performance out of a system, and that is where transition metal complexes excel. We have shown that we can move beyond simple inorganic salts of the transition metals, using common organic ligands to insert Ni2+ into highly reducing hydrogen stores and maintain this oxidation state, and even attach borohydride groups to Ni2+ that remain stable to 170 °C. 83 The deep understanding available in the coordination chemistry community combined with the sheer enormity of permutations available suggests this could be a profitable seam of knowledge to mine.

Unfortunately, we do not always have the detailed knowledge required to inform serious attempts at ab initio material design. Large scale screening, either theoretical as shown here or experimental, certainly has its place in providing both viable candidates and inspiration for further thinking. We have outlined above the prediction of novel stable ternary borohydrides with promising decomposition energies, with the (Li|Na|K)(Al|Mn|Fe)(BH4)4, (Li|Na)Zn(BH4)3 and (Na|K)(Ni|Co)(BH4)3 systems predicted to be most propitious. 97 NaZn(BH4)3 has already been synthesised, 98 as well as Li–Zn, Na–Zn, Na–Mn borohydrides in 1:2 and 2:1 stoichiometries (see ref. 99 and references therein) and Li3Al(BH4)3. 100 Certain Sc and Zr based mixtures which fell outside the 0.2 eV alloy stability criteria have also been synthesized successfully. 99 It is to be hoped that the others will follow, helped along by the knowledge gained at the coalface by experimentalists, such as the exhaustive investigation of fourteen possible pathways to Y(BH4)3, mentioned here. 92

Though much of our work has aimed to open new areas for research it is also important to narrow the bounds by signalling those areas that look less promising. So far all the amidoboranes studied evolve H2 below 100 °C, but do so exothermically, 36,105–109 mandating less-than-ideal off-board regeneration of the spent fuel, whilst issues with ammonia contamination must also be resolved. If off-board regeneration becomes feasible, however, their prospects may improve.
Finally, it is important to remember that the development and refinement of experimental and computational techniques is crucial. The quartz crystal microbalance has long been known as a valuable tool for characterising the thermodynamics and kinetics of hydrogen storage in one-dimensionally confined materials (thin films). We have developed porous support structures which extend the technique’s scope towards three-dimensionally confined hydrogen storage materials, i.e. nanoparticles, an important advance for their study. We have also seen from the example of the metal ammines how first-principles structure determination, such as the predicted monoclinic $C2/m$ symmetry for low-temperature $\text{Mg(NH}_3\text{)}_6\text{Cl}_2$, can be a powerful tool to model diffusion kinetics$^{125}$ where there is no experimentally available structure.

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References

26. The “complex hydrides” are the large group of compounds consisting of hydrogen bound to a metal (or boron) to form a hydridic anion, and another metal cation. In hydrogen storage these most commonly take the form $M_AH_n$, where $M$ is the metal cation and $A$ is B or Al, to which the hydrogen is bound to form $BH_x^-$ or $AlH_y^-$ anions.
28. Note, the DOE targets do specify that the hydrogen must not operate above 100 °C. One of the goals for PEM fuel cells is to operate at higher temperatures (using a different class of membrane), even up to 200 °C, so the challenge for the store may become easier as further progress is made in fuel cells. For a very accessible introduction to the subject, see L. Gubler and G. G. Scherer, Desalination, 2010, 250, 1034.
In the literature, Li$_2$(B$_{12}$H$_{12}$) has been discussed extensively:


The research also provided further curiosities, such as the highly unusual complex [Ni(H$_2$O)$_6$][Ni(SO$_4$)$_2$(cyclam)]·2H$_2$O, where all weaker field ligands (H$_2$O) bind to one Ni, and the considerably stronger field ligands (SO$_4$-$^2$, cyclam) bind to a second Ni centre. See A. J. Churcard, M. K. Cyrański and W. Grochala, *Acta Crystallogr.*, Sect. C: Cryst. Struct. Commun., 2010, 66, m263.


While the average abundance of Sc and Y in the Earth’s crust is 86 A. J. Churchard and W. Grochala, in preparation.

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122 The SA approach was also applied to Mg(BH₄)₂¹²³ and LiBH₄,¹²⁴ the SA optimizations successfully yielded the previously proposed Pmnn and F222 symmetry structures of Mg(BH₄)₂.¹²⁴ Further relaxations at the DFT level indicated that these two phases are isoeNERgetic. For LiBH₄, a new stable orthogonal structure with Pmna symmetry was found, which is 9.66 kJ mol⁻¹ lower in energy than the proposed Pmnm structure. For the previously investigated high temperature phase, a new monoclinic P2₁c structure was proposed, which is 21.26 kJ mol⁻¹ over the ground-state energy and showed no lattice instability. Moreover, six new and stable structures were found lower in energy than the reported orthorhombic structure.