Complex hydrides for energy storage

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ABSTRACT

In the past decades, complex hydrides and complex hydrides-based materials have been thoroughly investigated as materials for energy storage, owing to their very high gravimetric and volumetric hydrogen capacities and interesting cation and hydrogen diffusion properties. Concerning hydrogen storage, the main limitations of this class of materials are the high working temperatures and pressures, the low hydrogen absorption and desorption rates and the poor cyclability. In the past years, research in this field has been focused on understanding the hydrogen release and uptake mechanism of the pristine and catalyzed materials and on the characterization of the thermodynamic aspects, in order to rationally choose the composition and the stoichiometry of the systems in terms of hydrogen active phases and catalysts/destabilizing agents. Moreover, new materials have been discovered and characterized in an attempt to find systems with properties suitable for practical on-board and stationary applications. A significant part of this rich and productive activity has been performed by the research groups led by the Experts of the International Energy Agreement Task 32, often in collaborative research projects. The most recent findings of these joint activities and other noteworthy recent results in the field are reported in this paper.

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Introduction

Hydrogen is the most abundant element in the universe accounting for ~90% of all atoms, and of ~15% of the atoms on the surface of earth, and it occurs in compounds like water, natural gas and biomass, but rarely as a free element. Hydrogen has the largest gravimetric energy density of all chemical substances, a factor ~3 higher than gasoline [1]. Thus, hydrogen remains likely the only solution that may allow today a large-scale energy storage and distribution [2]. Energy storage is considered a corner stone for implementation of a renewable energy system and it still remains an open issue for the use of hydrogen as energy carrier. So, the development of innovative hydrogen storage options, for instance in solid-state materials, is crucial. Magnesium constitutes the first generation material for solid-state hydrogen storage due to its virtually limitless abundance, low cost and reversibility of the absorption-desorption reactions, but unfavorable thermodynamics and slow kinetics has hampered industrial implementation [3–5]. In the past decades, complex hydrides have been deeply investigated as potential hydrogen storage materials owing to their very high gravimetric and volumetric H_2 capacities [1,6–9]. The name complex hydride indicates the presence of an anionic complex where hydrogen is covalently bonded to a metal or a non-metal, i.e.$[BH_4]^-$, $[AlH_4]^-$, $[NH_2]^-$, $[AlH_6]^{3-}$, $[NiH_4]^{4-}$, ionically combined to one or more alkali, alkali-earth, transition metal, or rare-earth metal cations. Although this class of materials has been known for a long time (the first report on metal amides dates back to the year 1809) [10], they were studied as potential hydrogen storage materials only starting from the 1960s [11] and the mechanisms and kinetics for hydrogen release and uptake are still debated [11]. Release of hydrogen often occurs at relatively high temperatures (i.e higher than 200 °C) and hydrogen uptake often takes place at high hydrogen pressures (i.e. higher than 50 bar), and these two processes are in most of the cases characterized by slow kinetics. Therefore, it has been proven difficult to find new high capacity H_2 storage materials, which simultaneously have fast release and uptake of hydrogen at moderate temperatures and pressures. Several strategies have been developed to improve the performance of complex hydrides as hydrogen storage materials. Reactive hydride composites, where two or more compounds react with each other during hydrogen release, may introduce new chemical reactions [12–15]. The total reaction will be the sum of the different chemical reactions, the hydrogen storage capacity will be the average of the reactants H_2 contents, and the thermodynamics (ΔH) may be improved if both exothermic and endothermic reactions are involved. A reduction of particle size together with surface effects are also explored in order to improve hydrogen storage properties, e.g. encapsulation in a nano-porous matrix, known as nanoconfinement [16,17]. Another strategy is to the develop new hydrides [18–21], that revealed a range of other interesting properties towards multi-functionality [9,20]. In this paper, the latest achievements concerning the above quoted topics will be briefly reviewed and discussed. Great attention will be paid to the description of the thermodynamic and kinetic aspects of the borohydrides-based systems and to the study of possible catalysts for their reactions, looking in detail at the catalytic mechanisms. The role of metal hydrides themselves as catalysts for hydrogenation and dehydrogenation reactions and for ammonia synthesis and decomposition will be discussed. Finally, original data on the reciprocal solubility of metal borohydrides in binary to quinary complex systems in solid and liquid states will be presented and discussed.

The paper is a collaborative work among international experts working on behalf of the International Energy Agency (IEA) Task 32 "H_2-Based Energy Storage", whose one of the aim is to address hydrogen-based energy storage by developing reversible or regenerative hydrogen storage materials [18].

New complex hydrides and their properties

A wide variety of metal borohydrides, $M_n(BH_4)_m$, where M represents one or more metals and m and n values depend on their charge, have been discovered and characterized during the past decade, revealing an extremely rich chemistry including fascinating structural flexibility and a huge range of compositions and physical properties.

Monometallic borohydrides

The complex anion $[BH_4]^-$ has covalent boron—hydrogen bonds, whereas the coordination to metals in the solid state is much more diverse. The heavier alkali metal borohydrides have predominantly ionic bonding with rock salt structures. However, most mono-metal borohydrides exist as framework structures with pronounced directional bonding and clearly some degree of covalence. In most cases, the BH_4^- tetrahedron shares an edge with the metal, i.e. bidentate coordination (η^2) [22]. An example is magnesium borohydride, which occurs as seven different polymorphs, all with bidentate coordination of four BH_4^- groups to each magnesium atom, forming framework structures [18]. Remarkably, these polymorphs have very different densities, e.g. $\gamma-$ and $\delta-Mg(BH_4)_2$ with, respectively, material densities of 0.55 and 0.99 g/mL and volumetric hydrogen densities of 82 and 147 g H_2/L [21]. Manganese borohydride shows similar building principles and framework structures to $Mg(BH_4)_2$, having slightly different stability ranges for porous and dense phases [23] as well as quite different accessibility of synthetic routes [24,25].

The most strongly polarizing cations form molecular monometallic borohydride with dominantly covalent bonding and directionality in the $M-BH_4$ coordination, e.g. Al^{3+} and Zr^{4+} with electronegativity χ_p ~1.5 and 1.3. The structure of zirconium borohydride consists of isolated neutral molecular complexes of $Zr(BH_4)_4$. These tetrahedral molecules are analogous to the methane molecule where each BH_4 complex coordinates via face sharing (η^3) to zirconium with one hydrogen dangling in the solid state in a primitive cubic unit cell. This results in weak intermolecular interaction and low sublimation temperature, T_{sub} $Zr(BH_4)_4$ = 29 °C [26].

Bimetallic borohydrides

Sodium potassium borohydride was found to be a solid solution $Na_xK_{1-x}BH_4$, $0 < x < 1$, stable in the temperature range

$200\,°C < T < 450\,°C$, but phase-separates into the monometallic borohydrides at RT [27]. The only stable cationic solid solution borohydride is made by very similar Mn^{2+} and Mg^{2+} cations [28]. Many bimetallic borohydrides have perovskite related structures [29,30]. However, bimetallic borohydrides often have more complex structures involving discrete complex anions formed as a consequence of the electronegativity difference between the two metals. The most electronegative metal form partly covalent bonds to BH_4 complexes, usually by edge sharing. The anionic complexes can be mononuclear, such as $[Sc(BH_4)_4]^-$ observed in $LiSc(BH_4)_4$, or binuclear, $[Zn_2(BH_4)_5]^-$ observed in $LiZn_2(BH_4)_5$ [31,32].

More recent series of alkali-metal aluminum borohydrides [33] illustrates the way to stabilize the liquid, pyrophoric and unstable borohydride of aluminum in stable solid bimetallic phases featuring versatile stability and decomposition properties. Complementary NMR studies show also different hydrogen dynamics [34].

Bicationic borohydrides containing ammonium were recently obtained for the first time, namely $(NH_4)Ca(BH_4)_3$ [35] and $NH_4[Al(BH_4)_4]$ [33]. They have different decomposition pathways, and very distinct from their monocationic counterparts.

Trimetallic borohydrides

Significantly smaller number of trimetallic borohydrides is described as compared to bimetallic compounds [36–40]. The first (discovered in 2013) trimetallic homoleptic borohydrides, $Li_3MZn_5(BH_4)_{15}$, M = Mg or Mn, are isostructural and reveal mixed cationic sites [39]. The framework of $Li_3MZn_5(BH_4)_{15}$ made of two mco-nets contains channels built from face sharing $[M(BH_4)_6]^{4-}$ octahedra. The framework type is related to bimetallic $LiZn_2(BH_4)_5$ with cation disorder (Li/Mg) on the Li-position. The two trimetallic compounds decompose via formation of the more stable mono- and bimetallic borohydrides [40].

Transition metal borohydrides

Mechanochemical treatment is a well-established method for the preparation of metal borohydrides [41], but only transition metals with d^0, d^5 or d^{10} electron configurations have sufficient stability for this approach [42]. A series of cadmium borohydrides, α-$Cd(BH_4)_2$, β-$Cd(BH_4)_2$, $KCd(BH_4)_3$ and $K_2Cd(BH_4)_4$ are formed by mechanochemical treatment of MBH_4–$CdCl_2$ mixtures (M = Li, Na or K) after only 20–30 min [43]. In contrast, iron and cobalt borohydrides were prepared by new low temperature, solvent-based synthesis methods, using dimethyl sulfide or liquid NH_3, which produce ammonia stabilized compounds, $[Fe(NH_3)_6](BH_4)_2$ and $[Co(NH_3)_6](BH_4)_2$, a solid solution, $[Co(NH_3)_6](BH_4)_{2-x}Cl_x$ (x ~ 1), and a bimetallic compound, $[Fe(NH_3)_6](Li_2(BH_4)_4)$ [44].

Rare earth metal borohydrides

A variety of mono- and bimetallic borohydrides and halides, also including rare earth metals, have been discovered during the past few years [9,45,46]. Among the rare earth metal borohydrides, $RE(BH_4)_3$, praseodymium can be considered at 'border line', due to its crystal chemistry, revealing five polymorphs. Moreover, the polymorphic transitions are strongly dependent on gas atmosphere (e.g. hydrogen or argon makes a significant difference) [47]. A major fraction (~95 wt%) of $Pr(BH_4)_3$ transforms directly to a rhombohedral polymorph, r-$Pr(BH_4)_3$, upon heating in argon ($p(Ar) = 1$ bar). However, hydrogen gas ($p(H_2) = 40$ bar) clearly facilitates, upon heating, polymorphic transitions α- → β- → β'- → β''- → r-$Pr(BH_4)_3$ of ~65 wt% of the sample. This also appears to be the first example of stepwise negative thermal expansion.

Metal borohydride derivatives

Metal borohydride derivatives created by anion substitution or by reactions with neutral molecules have also been intensively investigated, in particular new boron-nitrogen based hydrogen storage materials, which includes metal borohydrides coordinated to neutral H-rich molecules, such as NH_3, NH_3BH_3, N_2H_4 or ethylenediamine [48–53]. These new materials also show significant structural and compositional diversity, e.g. $Y(BH_4)_3 \cdot xNH_3$, x = 0, 1, 2, 4, 5, 6, 7 have structures that range from framework, layered, chain-like to molecular and cationic complexes [50].

Mechanism of hydrogen release and uptake in complex hydrides

A large number of new compounds have been synthesized and characterized during the last years [9,45]. However the reaction mechanisms for hydrogen absorption and desorption are complex and scarcely understood. In several cases, different reaction mechanisms have been proposed by the different authors for the same system. Thus, detailed spectroscopic studies and modeling, combined with theoretical investigations, are required to conclude on the nature of the decomposition products (see the recent example for manganese borohydride [54]).

The reaction mechanism for hydrogen release and uptake in complex hydrides has been extensively studied since Bogdanovic et al. [55] published hydrogen desorption and absorption at moderate conditions in Ti-catalyzed $NaAlH_4$. Lithium and sodium alanates, $LiAlH_4$ and $NaAlH_4$, are very well characterized, and release hydrogen via the intermediate formation of M_3AlH_6, M = Li or Na [18,56–60]. However, the heavier alkali metal alanates of potassium and rubidium are less well understood and follow a more complex hydrogen release mechanism, possibly involving other intermediates [61]. A number of other Al-based complex hydrides, e.g. polymorphs of alanes have also been synthesized and structurally characterized. Al-based bimetallic amidoboranes $M[Al(NH_2BH_3)_4]$ were recently reported for the first time, revealing complex decomposition pathway, along with a partial reversibility for M = Na [62,63]. Potential reversibility of ammonia borane complexed to aluminium borohydride, suggested on the basis of its endothermic dehydrogenation, is also ascribed to the ability of the strong Lewis acid Al^{3+} to coordinate both the initial hydrogenated species as well as their dehydrogenation products [51,64].

Starting materials, as well as intermediates and final products during hydrogen release, are typically crystalline,

and thus the crystal structures of the different hydrides during hydrogen desorption and absorption are in most cases well characterized [58,59].

On the other hand, the decomposition products may be also non-crystalline and thus difficult to characterize. Furthermore, no real catalysts that will break the B–H bonds have been identified for the borohydrides. Nevertheless, several additives have an effect on the kinetics for hydrogen release [65–67].

One example can illustrate the complexity of transformations induced by heat. $Mg(BH_4)_2$ has a high hydrogen capacity (14.5 wt%) and theoretically predicted hydrogen release at rather mild conditions [68,69]. It has the most complex structures and several polymorphs have been identified, including α-, β-, β'-, ε-, γ-, ζ-$Mg(BH_4)_2$ and amorphous Mg-borohydride [[65] and reference therein [70]]. By heating, α-$Mg(BH_4)_2$ transforms to the β-modification, whereas γ-, ζ- and amorphous $Mg(BH_4)_2$ undergo the phase transition via ε-to β'-$Mg(BH_4)_2$ before decomposition. This process begins from the β- or β'-polymorphs and its pathways depend on the polymorph and the experimental conditions. Many alternative reaction schemes have been proposed in the literature [65,71], and since amorphous phases may be involved, a complete understanding of the reactions is still missing. It has been found that a significant desorption of γ-$Mg(BH_4)_2$ starts at about 150 °C and complete desorption is obtained at 450 °C [65], see Fig. 1.

Both isotope exchange experiments with Raman spectroscopy and kinetic modeling indicate that bulk H diffusion is the rate-limiting step in dehydrogenation and re-hydrogenation reactions in $Mg(BH_4)_2$ [66,72]. Partial reversibility and cycling 3 times have demonstrated 2.5 wt% reversible hydrogen capacity with transition metal additives. It has also been shown that $Mg(BH_4)_2$ undergoes a reversible rehydrogenation to $Mg(B_3H_8)_2$ and MgH_2 at 200 °C with 2.5 wt% hydrogen involved [73].

From complex hydrides to complex hydride-based systems

Despite the relatively high gravimetric hydrogen content of most of the complex hydrides, due to thermodynamic and
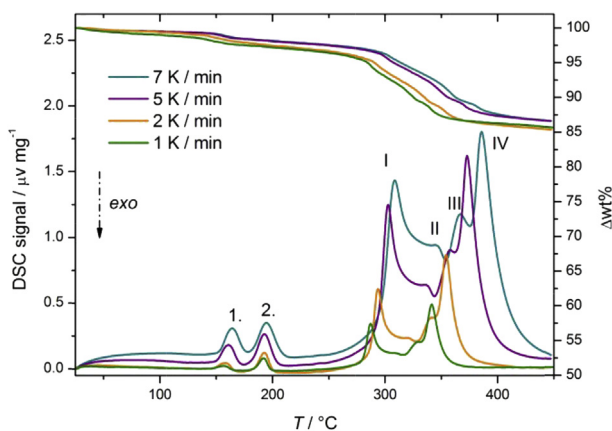
kinetic constrains, the hydrogen release takes place at temperatures that are too high for mobile applications. In addition, the reversibility of the dehydrogenation process is a barrier difficult to overcome. This is particularly true for the complex hydrides containing alkali or alkali-earth metal cations. In fact, the re-hydrogenation of the products of the thermally activated dehydrogenation of un-catalyzed complex hydrides can be achieved just partially if harsh temperature and hydrogen pressure are applied. The possibility to use complex hydrides (e.g. $NaBH_4$) for hydrogen generation through hydrolysis reaction was investigated since the 1950s [74,75]. However, recently the research on this topic has suffered a sensible decline due to the recommendation to "no go" for the aqueous solution of complex hydrides as hydrogen storage media for automotive application by the U.S. Department of Energy (DoE) [76].

Reactive hydride composites (RHCs)

The possibility to modify the thermodynamic properties of metal hydrides was reported for the first time in 1958. In that year G. G. Libowitz et al. reported that the alloy of Zr and Ni (ratio 1:1), once hydrogenated, displays, for a certain temperature, an equilibrium hydrogen pressure much higher than that of ZrH_2 [77]. This indicates that the decomposition enthalpy of $ZrNiH_3$ is lower than that of ZrH_2. Later, between 1967 and 1968 J J. Reilly et al. studying the hydrogenation properties of the alloys of Mg–Cu and Mg–Ni, described the possibility to modify the reaction enthalpy of a hydride by the addition of elements which, upon dehydrogenation, reversibly react with the starting hydride to form a new compound [12,13]. In particular, they proved that the reaction enthalpies of the $3MgH_2$–$MgCu_2$ system and of Mg_2NiH_4 are lower than that of pure MgH_2. Unfortunately, although alloying leads to a reduction of the dehydrogenation enthalpy, the gravimetric hydrogen capacity is significantly reduced. In the beginning of 2000s, propelled by the pioneering discovery of Bogdanovic and co-workers, the scientific community multiplied its efforts on developing hydrogen storage systems based on complex hydrides [55]. Similarly to the approach followed by G.G. Libowitz et al. and J.J. Reilly et al., P. Chen et al. [78], J.J. Vajo et al. [14] and G. Barkhordarian et al. [15] reported on the possibility to destabilize lightweight complex hydrides using a second hydride (RHCs systems). Compared with the complex hydrides they derive from, the RHC systems have the advantage of being reversible under moderate temperature and hydrogen pressure conditions and having a reduced reaction enthalpy without sacrifice the hydrogen storage capacity of the material. Since the publications of these pioneering works, several studies on RHC systems were carried out.

The first example reported in literature is $LiNH_2$ + LiH [14,78]. $LiNH_2$ and LiH alone decompose releasing hydrogen at temperature above 300 °C and 550 °C, respectively. However, $LiNH_2$ + LiH can be reversibly operated at temperatures around 250 °C and possesses a hydrogen capacity of about 6.5 wt %. For this system, the operating temperature could be reduced even further if the kinetic constrains that affect it could be overcome. In fact, the enthalpy and entropy associated to the dehydrogenation process being 38.9 kJ/mol H_2 and

Fig. 1 – DSC-TGA measurements of γ-$Mg(BH_4)_2$ at various heating rates, steps 1–2 indicate phase transitions, and I–IV decomposition. The figure is taken from Ref. [65] with permission from Elsevier.

111.98 J/K mol H_2, respectively, an equilibrium pressure of $p(H_2) = 1$ bar at 74 °C is expected [79].

Another appealing storage system based on amides is 2 $Mg(NH_2)_2$–4LiH [80,81]. This system decomposes following a two-step reaction which first leads to the formation of $Li_2Mg_2(NH)_2 + LiNH_2 + LiH$ and finally to the formation of $Li_2Mg(NH)_2$. Considering only the first reaction step, the replacement of $LiNH_2$ with $Mg(NH_2)_2$ leads to a reduction of the reaction enthalpy down to ca. 40 kJ/mol H_2 maintaining a still appreciable hydrogen storage capacity (4.2 wt %). However also in this case, despite the operating temperature of about 80 °C is expected, due to kinetic constrains, it is possible to cycle efficiently the material only at temperatures above 150 °C [81].

Later, these works were followed by reports on the discovery of RHC systems based on borohydrides. The first system was 2$LiBH_4$–MgH_2 [82–86]. This system has a theoretical reversible hydrogen storage capacity of 11.5 wt % as well as values of reaction enthalpy and entropy (46 kJ/mol H_2 and 104 J/K mol H_2, respectively) which imply an equilibrium pressure of 1 bar hydrogen at 170 °C. However, as for the $LiNH_2$–LiH system, also in this case, due to kinetic constrains, the operating temperature (>300 °C) is usually much higher than expected. The key for the reversibility of this system is the formation upon dehydrogenation of MgB_2 (rather than stable boron containing phases such as $Li_2B_{12}H_{12}$ and amorphous boron) and its unexpectedly good kinetic properties of rehydrogenation [82].

A similar RHC system based on borohydrides is 2$NaBH_4$–MgH_2 [87–90]. Despite a rather high hydrogen storage capacity (i.e. 7.8 wt %) it has a relatively high overall reaction enthalpy of 62 kJ/mol H_2 which results in an equilibrium hydrogen pressure of 1 bar at 350 °C. Moreover, due to phase segregation phenomena it is only partially reversible upon cycling.

The hydrogen storage properties of the RHC systems 4$LiBH_4$–5Mg_2NiH_4 [91] and 4$NaBH_4$–5Mg_2NiH_4 [92] were sporadically investigated. However, due to their low hydrogen storage capacity and high thermodynamic stability they are not considered any more as potential hydrogen storage materials. Recently, the $Ca(BH_4)_2$–2.5Mg_2NiH_4 system was also investigated [93,94]. Despite its poor hydrogen storage properties, this system evidenced unique kinetic properties. In fact, in this system, during dehydrogenation, the formation of $MgNi_{2.5}B_2$ is observed as the only B-containing phase. Apparently, Mg_2Ni/Mg_2NiH_4 accept boron atoms from $CaB_{12}H_{12}$ and amorphous boron, which are usually irreversible decomposition products of $Ca(BH_4)_2$, to form $MgNi_{2.5}B_2$. This phase in turn readily donates the boron atoms back to form again $Ca(BH_4)_2$ upon re-hydrogenation.

A mixture of Mg_2NiH_4 with a eutectic mixture of borohydride has been tested to understand the role of liquid borohydride in the tailoring of RHC, however similar results to the previously described systems have been obtained [95].

Recently new ternary amide-borohydride-hydride RHC systems with appealing hydrogen storage properties were proposed. J. Hu et al. [81] reported on the improvement of the kinetic and thermodynamic properties of the $Mg(NH_2)_2$–LiH system obtained by the addition of 0.1 mol of $LiBH_4$. In fact, for this system, a theoretical dehydrogenation temperature of 70 °C at 1 bar of hydrogen pressure is expected and a reduction

of the operating temperature from 180 °C to 140 °C was achieved. Among others, the key factor enabling the tuning of the kinetic properties of this system appears to be the formation of $Li_4(BH_4)(NH_2)_3$ [96] upon dehydrogenation. This phase possesses an extremely high Li^+ conductivity and being in molten state under operating temperature conditions it ensures fast mass transport within the system and high surface contact between reactants [97–100]. It is interesting to notice that varying the quantity of $LiBH_4$ contained in the system a fine tuning of its hydrogen storage properties is possible. For this reason a systematic investigation of the effect of the $LiBH_4$ content in the 6 $Mg(NH_2)_2$–9LiH system was recently carried out. Astonishingly, for the 6 $Mg(NH_2)_2$–9LiH–12$LiBH_4$ system the measured reaction enthalpy is of only 24 kJ/mol H_2, thus a theoretical equilibrium pressure of 1 bar hydrogen at room temperature is expected [100]. Also in this case, kinetic constrains impair the dehydrogenation and re-hydrogenation reactions occurring at the theoretically expected temperature and hydrogen pressure. However, for the first time it has been possible to reversibly operate a RHC system below 100 °C, thus matching the operative temperature target established by the DoE for vehicular fuel cell applications [101]. A similar system has been employed in a solid-state hydrogen tank to be used as Auxiliary Power Unit [102].

Composite materials of complex hydrides

Other than the RHC strategy, various composites with complex hydrides have been studied to decrease the dehydrogenation temperature and the pressure for re-hydrogenation [7,103] and will be shortly reviewed in this section.

Complex hydrides on carbon support

One strategy is to make nanocomposite hydrides, which have reduced diffusion length to optimize the thermodynamics and kinetic of hydrogen absorption and desorption. Furthermore, it can be considered as an important strategy to control dynamics, reversibility and equilibrium pressure for hydrogen storage [104]. However, the high surface of nanoscaled materials often causes agglomeration of particles. The agglomeration from structured nanomaterials can be prevented by using various supports. Carbon has been reported as a suitable support material for nano-sized complex hydrides [105,106]. Carbon supports physically adsorb hydrogen and the hydride contains chemically absorbed hydrogen. The combination of these two active species increases the total hydrogen storage density [107].

The most commonly used method to prepare nano-sized complex hydrides on a carbon support is ball milling [42]. In the case of a composite of porous carbon and $LiBH_4$, hydrogen desorbs at 330 °C with a reversible capacity of 6.0 wt% [108]. The ball milling method gives a wide distribution of particle size. Therefore, $NaBH_4$ can be synthesized directly on carbon to form nano-sized $NaBH_4$ of 6 nm and it shows different levels of dehydrogenation depending on the types of carbon used as support. The dehydrogenation temperature is reduced to 100–150 °C and the reversible hydrogen storage capacity is more than 5.0 wt% [109,110]. Another approach to achieve

nanoscale size in complex hydrides is to infiltrate the material into a porous support. This approach, that can greatly improves the hydrogen absorption kinetics of the complex hydrides, will be described in details in paragraph 6.1.

Complex hydrides in ionic liquids

The general properties of ionic liquids are (1) no boiling point, (2) the vapor pressure close to zero, (3) thermal stability at high temperatures, (4) possibility of dissolution in various organic, inorganic, metallic and polymeric substances, and (5) various physicochemical properties such as density, viscosity, solubility, hydrophobicity depending on the combination of cation and anion [111]. Ionic liquids were studied both as a hydrogen source and as a solvent to further assist hydrogen generation from hydrogen storage materials. Dupont et al. [112] reported that a hydrogen atom can be reversibly added to 1-alkyl(aryl)-3-methylimidazolium N-bis(trifluoromethanesulfonyl) imidate molecule of an ionic liquid by using Pd/C catalyst and it can store up to 30 g/L of hydrogen. Recent research on hydrogen storage using ionic liquids concerns mainly the amine borane group. Amine borane releases a significant amount of hydrogen at temperatures below 200 °C and the theoretical hydrogen content is 19.6 wt% [113]. Prechtl and Sahler [114] studied ionic liquids for hydrogen production from amine borane derivatives, in particular hydrogen yields related to cations in ionic liquids, giving rise to 3.0 wt% of hydrogen. Sneddon et al. [115] reported the dehydrogenation properties of the amine borane with ionic liquid depending on amine borane structure. The ionic liquid changes the structure of the amine borane group to desorb hydrogen at low temperature (95 °C) with hydrogen yields of 5.4 wt%. Banerjee et al. [116] has studied the reaction kinetics of the hydrogen storage pathway for composites of six different ionic liquids and amine borane. In addition, Li et al. [117] synthesized a composite from $NaBH_4$ and an ionic liquid (bmimNTf2). The composite is liquid and releases more than 70% of the theoretical hydrogen content at temperatures as low as 180 °C. The dehydrogenation proceeds as an exothermic reaction compared to the endothermic dehydrogenation of the pure complex hydride, this difference is attributed to a destabilization due to the charge transfer of the cation from $NaBH_4$ to the ionic liquid. The ionic liquid was investigated to assist in the formation of the intermediate during dehydrogenation, but the role of the ionic liquid has not been clarified. Further investigations of physical properties in ionic liquids are required in order to apply them as hydrogen storage materials.

The influence of nanoconfinement and catalysis

It has been well recognized that none of the complex metal hydrides in its pure form fulfills the requirements in terms of functionality for applications such as in reversible hydrogen storage. Next to composites made by ball-milling, as discussed in the previous section, nanostructured metal hydride composites made by confining the metal hydride in a porous matrix, or adding a second phase as a catalyst or promoter, can greatly enhance the hydrogen absorption and desorption

kinetics and cyclability, albeit at the expense of hydrogen storage capacity [16,17,118,119]. Progress until 2015 can be found in other reviews [17,18,120,121]. Hence, after a few introductory remarks, in this paper we focus on developments and publications on this topic from 2015 onwards.

Nanoconfinement

It was discovered almost a decade ago that confining complex metal hydrides such as $NaAlH_4$, $LiBH_4$ or $NaBH_4$ in a nanoporous scaffold, typically a carbon-based scaffold, greatly enhances the hydrogen uptake and release kinetics and cyclability for reversible hydrogen storage [122–130]. The scaffold, often consisting of a high surface area carbon material, allows for the preparation of small crystallites, stabilizes them against further growth, and might provide nuclei for phase transitions [131]. Also electronic interaction with carbon might play an important role [132]. Recently also $LiAlH_4$ was confined in high surface area graphite, showing remarkably lowered desorption temperatures and reversibility [133].

The phase stability is also affected by nanoconfinement in carbon materials, but typically not in a favorable manner. The generally attractive interaction between the (molten) complex metal hydride and the carbon scaffold material, as evidenced by the generally spontaneous infiltration of carbon matrices with complex metal hydrides upon melting [134], stabilizes the metal hydride with respect to its decomposition products such as LiH, B and Al [135,136]. A notable exception is when the decomposition products such as Li or Na can be stabilized by intercalation into the carbon scaffold. For instance, it was demonstrated that the equilibrium decomposition temperature of $LiBH_4$ in a porous carbon scaffold under 1 bar H_2 pressure was lowered by 150 °C compared to macrocrystalline $LiBH_4$ (Fig. 2a), which was explained by the favorable intercalation into carbon of the Li decomposition product [137] shifting the equilibrium from complex metal hydride to the (partially) intercalated decomposition products. Typically the quest has been to destabilize metal hydrides, as their enthalpies of formation are generally too negative for practical applications. However, a few complex metal hydrides are too unstable, and nanoconfinement might be used to stabilize them. An elegant proof of principle was recently reported for $Ti(BH_4)_3$. This unstable complex metal hydride which normally rapidly decomposes at room temperature, was stable for at least a month when confined in a metal organic framework and kept under Ar atmosphere (Fig. 2b)] [138].

Other authors have explored whether chemical modification of the carbon scaffold might be beneficial. Oxygen-containing surface groups decrease the reversible capacity by gradual reaction with the active material, while if the carbon material is properly purified and the dangling bonds are hydrogen-terminated, over 95% reversibility can be achieved for nanoconfined $NaAlH_4$ [139]. Modifying the carbon scaffold with nitrogen functionality did have a large impact, but overall did not lead to an improved performance for nanoconfined $LiBH_4$ or $NaAlH_4$ [106,140]. Fluorographite led to faster hydrogen release from $Mg(BH_4)_2$ in the presence of $LiBH_4$, probably due to the formation of some stable fluoro-compounds such as MgF_2 and LiF, but reversibility was poor [141]. These studies show
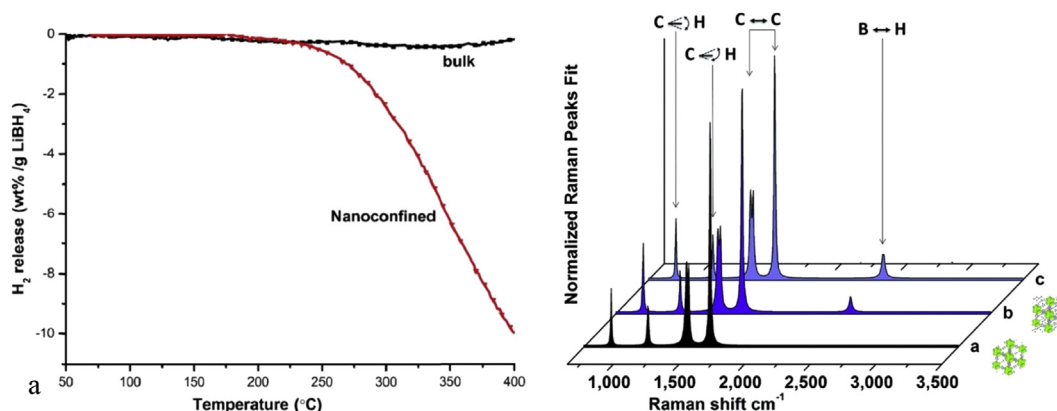
Fig. 2 – Two examples of how nanoconfinement can change the stability of complex metal hydride materials. (a, left) H_2 release from macrocrystalline $LiBH_4$ and from $LiBH_4$ confined in a nanoporous carbon scaffold, measured at $p(H_2) = 1.1$ bar H_2 and heating with 3 °C/min, showing how nanoconfinement destabilizes and lowers the 410 °C equilibrium temperature under 1 bar H_2 with ~150 °C [137]; (b, right) Raman spectra showing how the normally at room temperature unstable $Ti(BH_4)_3$ is stabilized by confinement in a MOF, (a) empty MOF, (b) MOF loaded with $Ti(BH_4)_3$, (c) the same sample after 1 months storage in Ar at RT [138].

that control over the nature and amounts of surface groups on the carbon scaffold offers an important strategy to tune hydrogen sorption properties, but often comes at the expense of reversible capacity due to side reactions.

Other scaffolds than carbon were investigated using innovative preparation techniques. Buckley et al. used porous Mg as a reactive scaffold to be melt-infiltrated with $LiBH_4$ [142]. Aguey-Zinsou coated LiH nanoparticles, made by wet-chemical synthesis (hydrogenation of lithium naphthalenide) with Ni, which acted as scaffold and catalyst at the same time [143]. In a similar manner, nanoscale $LiAlH_4$ coated with Ti was prepared [144].

Complex metal hydrides can also be co-confined with another metal hydride, such as in the combinations MgH_2–$LiBH_4$ [130,145,146], Mg_2NiH_4–$LiBH_4$ [147], $LiBH_4$–MgH_2–$TiCl_4$ [148], and with another complex hydride, like reported recently in the combinations $LiBH_4$–$Ca(BH_4)_2$ [149,150], $LiBH_4$–$NaAlH_4$ [151], $2LiBH_4$–$NaAlH_4$ [152], $LiBH_4$–$NaBH_4$ [153] and $LiBH_4$–KBH_4 [154]. Eutectic melting composites have received special interest, because they are readily infiltrated in a porous matrix [154–156]. Bulk and nanoconfined $0.68LiBH_4$–$0.32Ca(BH_4)_2$ mixtures have hydrogen storage capacities of 5.4 wt % H_2 and 3.7 wt % H_2 stable from the second to the fifth H_2 release, close to the calculated hydrogen contents of $LiBH_4$ in the $0.68LiBH_4$–$0.32Ca(BH_4)_2$ system. The decomposition products of $Ca(BH_4)_2$, e.g. CaH_2 and CaB_6, appear to facilitate the full reversibility of $LiBH_4$.

In most cases the nanoconfinement led to better cycling stability and faster kinetics, especially in the first few cycles. Understanding these systems is a challenge, due to the presence of a multitude of different phases. Theoretical investigations, such as based on the Calphad method for the assessment of thermodynamic properties combined with *ab initio* calculations, are increasingly able to validate experimental results and provide a complete description of the thermodynamic properties of mixtures of complex metal hydrides (see Solubility in borohydrides) [157].

Catalysts and additives for hydrogen ab- and desorption

Two decades ago Bogdanovic reported how a few percent of a Ti-based compound greatly accelerates the hydrogen desorption from $NaAlH_4$, as well as the subsequent hydrogen absorption [55]. Since then, a wide range of catalysts has been explored to enhance the kinetics of hydrogen absorption and release in complex metal hydrides. However, detailed understanding of the mechanism by which these catalysts operate is still lacking. The additives are often added as salts, for instance as chlorides or oxides, and by ball milling. Although in practice the metal cations will be reduced to metallic form by most of the complex metal hydrides, it is not easy to distinguish catalytic effects in the classical sense (for instance, the impact of additives on the microstructure of complex metal hydrides, the effect of anions, the reaction between the additives and the complex metal hydride itself., etc.). Nevertheless a wide range of additives, mostly based on transition metals, is known to enhance hydrogen absorption and desorption kinetics and reversibility.

In a few cases, well defined transition metal catalysts have been added, which allows a more detailed study of the mechanism. An example where the mechanism was studied in more detail was for carbon-supported metallic Ni nanoparticles added to $LiBH_4$. It was shown that the nickel nanoparticles are converted to a nanosized nickel boride phase with variable nickel to boron ratio, acting as a flexible boron store and probably as a nucleus for phase transformations [158]. In a recent study, L. Chen et al. explored 5–15 nm Fe, Co and Ni metallic catalysts being added to the $2LiBH_4$–MgH_2 system [159]. They showed that in-situ FeB, CoB, and $MgNi_3B$ were formed, with the last identified as the most effective catalyst for this system. Starting from metal-organic frameworks highly dispersed but stable metal nanoparticles can be obtained [106,160,161]. Metal-organic framework derived cobalt nanoparticles improved the reversibility in the $LiBH_4$–$2LiNH_2$ system, being stabilized against growth during cycling

by the pyrolyzed carbon resulting from the decomposition of the original metal organic framework [161].

Using metal hydrides as catalysts

Another recent development is that the complex metal hydrides themselves can be explored as hydrogenation, dehydrogenation or isomerization catalysts. The group of Schüth was the first to report that Ti and Ce-doped $NaAlH_4$ (synthesized via mechanical milling) catalyzes the gas phase hydrogenation of unsaturated hydrocarbons, such as DPA (diphenylacetylene) and stilbene [162]. They showed that at 130 °C and 100 bar hydrogen, the DPA was fully hydrogenated to the saturated product within 3 h. The bulk or pristine $NalAH_4$ is not active in this reaction, just as it does not exhibit reversible hydrogen uptake and release, therefore in this case the transition metal doping with Ti or Ce seemed crucial. However, more recently Bramwell et al. showed that $NaAlH_4$ confined in nanoporous carbon without any transition metal additives is an active catalyst for hydrogenation of a wide range of terminal and internal alkynes and alkenes [163]. In both cases, the catalysts were only active under conditions corresponding to those for reversible hydrogen uptake.

The same is true for another reaction that was tested, namely the formation of methane during the hydrogenation of CO_2 using a $ZrCoH_x$ catalyst [164]. Cobalt is probably in a reduced state, but the availability of hydrogen from the metal hydride was essential to observe methane production. Catalyst activities were not reported, so no comparison with more standard CO_2 hydrogenation catalysts (or non-catalytic reduction of CO_2 by complex hydrides [165]) is possible, but it is clear that the presence of hydrides enhanced the catalytic activity. The state of the catalyst was also important for carbon-supported Rh-based nanoparticles with an average size of 1.0 nm, which were tested for the selective hydrogenation of butadiene [166]. RhH_x was consistently more active than Rh, which was predominantly ascribed to electronic effects: it was hypothesized that Rh–H bonds at the surface were stabilized by the presence of subsurface hydrogen.

Attracting much attention is the use of complex metal hydride-based catalysts for ammonia decomposition and synthesis. David et al. reported that $NaNH_2$ and non-stoichiometric $LiNH_2$ were very active catalysts for NH_3 decomposition [167], however only when used in a steel reactor, which suggested that the presence of additional transition metal was essential. Alternatively good activities were obtained by combining nanoconfined Ni and $LiNH_2$ nanoparticles confined in a carbon scaffold [168]. The group of Chen systematically investigated the combination of LiH/$LiNH_2$ with a range of transition metals, and showed that for instance lithium amides combined with Mn can rival the activity of conventional Ru/CNT catalysts for ammonia decomposition [169]. Even more excitingly, they also showed that the same type of catalysts could be used effectively for ammonia synthesis (Fig. 3), for which they propose a concerted mechanism involving both the transition metal (nitride) and LiH/$LiNH_2$ [170].

From these recent developments, it is clear that, although in many cases the details of the mechanism are not yet fully understood, metal hydrides do represent a class of materials that is highly interesting to explore as an alternative for the present (de)hydrogenation catalysts, which are often based on scarce and expensive transition metals.

Solubility in borohydrides

Complex hydrides are characterized by a cationic and an anionic sublattice, as expected for ionic compounds. Solubility of complex hydrides in the solid state can be obtained in a single or in both sublattices. Generally, complex hydrides show different crystal structures at room temperature and often are subjected to polymorphic phase transitions upon heating, eventually leading to melting before decomposition. Mixtures of complex hydrides may show the formation of solid solutions, i.e. cationic or anionic fully disordered structures. On the other hand, as already described before, they can form compounds, i.e. cationic or anionic ordered structures. These compounds can be bimetallic, trimetallic or multimetallic, and they can show different anions in the structure. A systematic description of compounds observed upon mixing complex hydrides is reported in Ref. [9]. In the following, an overview of solubility in both cationic and anionic sublattices for borohydrides will be presented and the role of chemical bonds and coordination in the crystal structure will be highlighted.

Binary combinations between borohydrides or with halides have been extensively investigated, showing the formation of solid solutions, resulting from cationic [28,171–173] or anionic [174–182] substitutions, as well as hydrogen-fluorine exchange [183–186]. For some binary and ternary mixtures of borohydrides, corresponding thermodynamic properties and phase diagrams have been recently assessed, allowing the determination of the enthalpy of mixing in solid and liquid phases [173,186].

Examples of cationic solid solutions in binary borohydrides are limited to the $Mg(BH_4)_2$–$Zn(BH_4)_2$ [171], $Mg(BH_4)_2$–$Mn(BH_4)_2$ [28], $LiBH_4$–$NaBH_4$ [153] and $NaBH_4$–KBH_4 [27] systems. In other cases, a nearly full immiscibility is observed [150,154,156,157,187–191], suggesting structural and electronic constrains in the formation of solid solution in cationic sublattice in the case of borohydrides. Considering the $LiBH_4$–$NaBH_4$–KBH_4 system, $LiBH_4$ can form a cubic phase with limited solid solubility in $NaBH_4$ and KBH_4. No solid solutions have been observed in the orthorhombic and hexagonal phase, except for the $LiBH_4$–$NaBH_4$ system, where an extensive dissolution of $NaBH_4$ in the hexagonal phase has been observed. The higher solubility in the hexagonal phase with respect to the orthorhombic one in $LiBH_4$ is likely related to structural factors, such as the higher available free volume, fast reorientation of the BH_4^- anion and more favorable coordination in the hexagonal structure with respect to that in the orthorhombic one, allowing an easier cationic exchange and motion. Recently, an explorative investigation of a quinary borohydride mixture showed a limited interaction of the different borohydrides in the $LiBH_4$–$NaBH_4$–KBH_4–$Mg(BH_4)_2$–$Ca(BH_4)_2$ system in the solid phase [192].

Fig. 4a resumes available information on the cations interactions in the solid phase in the $LiBH_4$–$NaBH_4$–KBH_4–$Ca(BH_4)_2$–$Mg(BH_4)_2$ system. It can be observed that, in addition
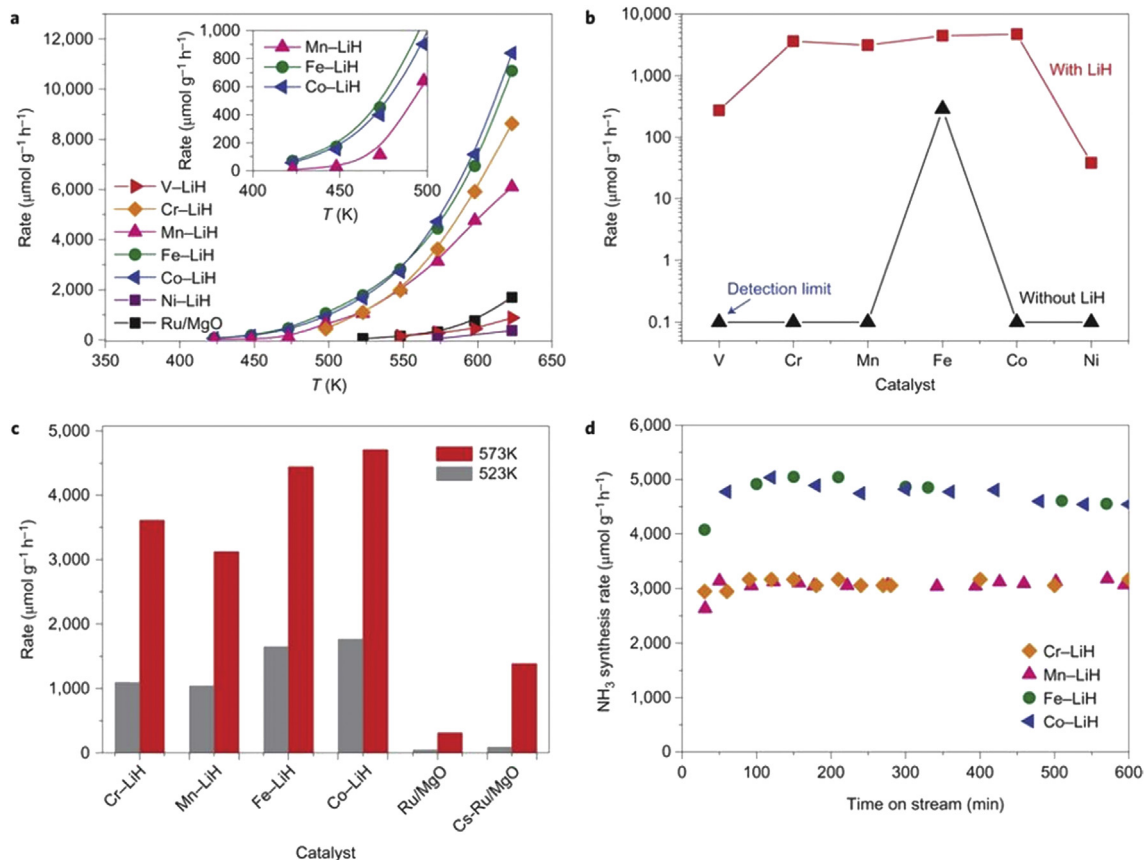
Fig. 3 – Catalytic performance of TM(N)–LiH nanocomposites; (a) NH$_3$-synthesis rate as a function of temperature, reaction conditions: N$_2$:H$_2$ = 1:3 with a WHSV of 60,000 mL g^{-1} h^{-1}; pressure, 10 bar. (b) comparison of the activities of the TM with and without LiH at 573 K; (c) activities of Cr–, Mn–, Fe– and Co–LiH composites, Ru/MgO and Cs-promoted Ru/MgO (Cs–Ru/MgO) catalysts at 523 and 573 K (d) activity evolution with time for Cr–, Mn–, Fe– and Co–LiH at 573 K. Reproduced with permission from Ref. [170].
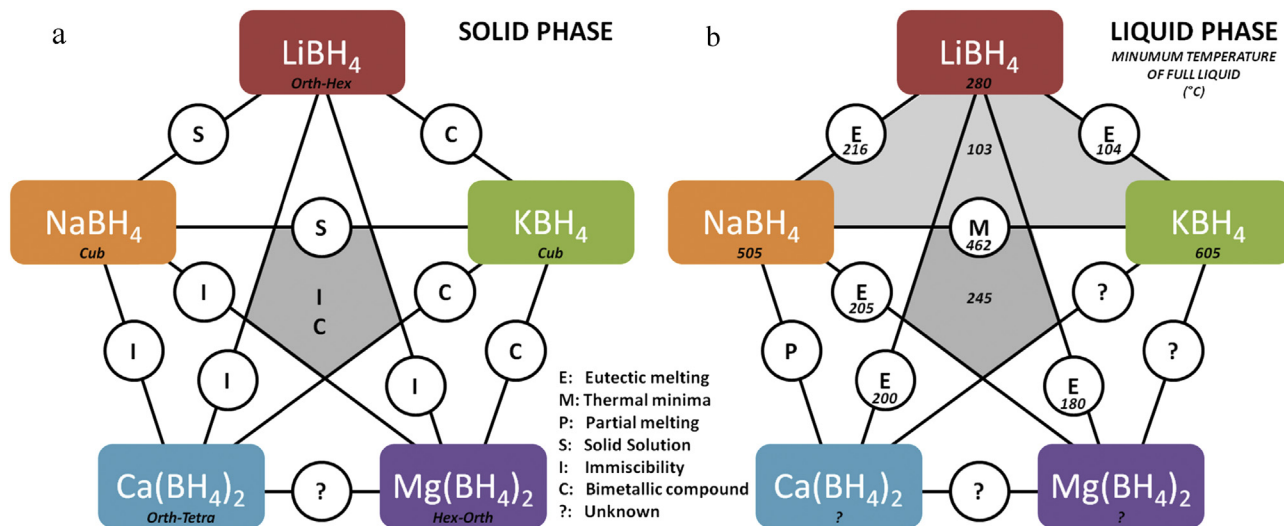

Fig. 4 – Summary on the cation interactions in the LiBH$_4$–NaBH$_4$–KBH$_4$–Mg(BH$_4$)$_2$–Ca(BH$_4$)$_2$ system, both in the solid (a) and liquid (b) phases. In Fig. 4a, crystal structures of pure borohydrides, including allotropic transformations and the effect of interactions, are reported. In Fig. 4b, melting temperature of pure borohydrides, as well as minimum temperature for the existence of full liquid in mixtures, are reported, together with the description of the melting reactions.

to the previously reported interactions, no miscibility is observed in other binary or higher combinations. Thus, KBH_4 strongly interacts with other borohydrides to form bimetallic compounds or solid solutions.

An anionic substitution of the BH_4^- group by halides is widely favored in binary systems. In $LiBH_4$—LiBr [179] and $LiBH_4$—LiI [174], hexagonal solid solutions are stable at room temperature and they have been widely explored and characterized. A limited orthorhombic solid solution is present in the $LiBH_4$—LiBr system, while possible solid solutions in the cubic structure have never been characterized in details. In the $LiBH_4$—LiCl system [180,181], no significant solubility in the orthorhombic and cubic phases is evidenced, while in the hexagonal phase limited solubility is detected at high temperatures. A solubility in the solid state is confirmed for many binary systems between borohydrides and metal halides: $NaBH_4$—NaCl [175,178], $NaBH_4$—NaBr [193], $Ca(BH_4)_2$-CaX_2, X = Cl, Br, I [172,177], $Mg(BH_4)_2$—$MgCl_2$ [9], $Mg(BH_4)_2$—$MgBr_2$ [9]. In case of metal borohydride-borofluorides composites, MBH_4-MBF_4 with M = Li, Na, K, a hydrogen-fluorine exchange occurs and short-lived $MBH_{4-x}F_x$ species are formed, but fast decomposition to metal fluoride, diborane and *closo*-borane is observed [183,184,186,194].

Full solubility is generally observed for complex hydrides in the liquid phase. In case of immiscibility among complex hydrides, a eutectic melting can be observed [155,157,172,173]. For the quinary $LiBH_4$—$NaBH_4$—KBH_4—$Mg(BH_4)_2$—$Ca(BH_4)_2$ borohydride mixture, a multi-cation liquid phase has been observed for the first time, underling a strong interaction among borohydrides that could be probably related to entropy effects [192].

Fig. 4b summarizes the melting reactions occurring in the $LiBH_4$—$NaBH_4$—KBH_4—$Ca(BH_4)_2$—$Mg(BH_4)_2$ system, evidencing the lowest temperature for the occurrence of a single liquid phase. Generally, in the liquid phase, a full solubility in the cation sublattice is observed, with a stabilization of the liquid mixture with respect to pure liquid borohydrides, as evidenced by the occurrence of eutectics or thermal minima.

Conclusions

The present paper represents the most recent achievements on complex hydrides-based materials for hydrogen and energy storage obtained by the Experts of the workgroup ''Complex and liquid hydrides'' operating in the frame of the International Energy Agency (IEA) Task 32 ''H_2-Based Energy Storage''. In particular, the synthesis of new complex hydrides and the results of their deep physical, chemical and structural characterization are reported. The strategies to improve thermodynamics of H_2 release and uptake by the reactive hydrides composites approach, the preparation of composites (with carbon supports and ionic liquids) and nanoconfinement are reported. Advantages and drawbacks of the different methods are discussed and the characteristics of each system are commented. The role and mechanism of action of metal hydrides acting as catalysts for hydrogenation, dehydrogenation and ammonia decomposition are discussed. Finally, the solubility in hydrides systems both in solid and in liquid state is considered from both the theoretical and the experimental point of view and the results on different mixed systems are shortly reviewed and discussed.

Acknowledgments

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