Borohydrides Hot Paper

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Hydrogen Storage Materials: Room-Temperature Wet-Chemistry Approach toward Mixed-Metal Borohydrides**

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Dedicated to Professor Ingo Krossing

Abstract: *The poor kinetics of hydrogen evolution and the irreversibility of the hydrogen discharge hamper the use of transition metal borohydrides as hydrogen storage materials, and the drawbacks of current synthetic methods obstruct the exploration of these systems. A wet-chemistry approach, which is based on solvent-mediated metathesis reactions of precursors containing bulky organic cations and weakly coordinating anions, leads to mixed-metal borohydrides that contain only a small amount of "dead mass". The applicability of this method is exemplified by $Li[Zn_2(BH_4)_5]$ and $M[Zn(BH_4)_3]$ salts (M = Na, K), and its extension to other systems is discussed.*

The efficient storage of hydrogen is one of the most pressing problems related to utilization of the lightest element as an energy carrier.[1] Metal borohydrides contain large amounts of hydrogen compared to other groups of inorganic compounds (up to 24.5 wt% for NH_4BH_4)[2] and have been intensely examined as potential materials for hydrogen storage.[3] The properties of metal borohydrides that limit their applicability as hydrogen storage materials (such as temperature of H_2 release[4] and reversibility) can be tuned-up to some extent by the substitution at the metal or ligand site or by the preparation of complex materials,[5] e.g. $LiK(BH_4)_2$,[4] $M[Sc(BH_4)_4]$, M = Li, Na, K,[6] $Li_3MZn_5(BH_4)_{15}$, M = Mg, Mn.[7]

The most frequently used synthetic pathway toward unsolvated single- and mixed-metal borohydrides consists of a mechanochemical reaction between a metal halide and an alkali metal borohydride.[3] For example:

$$MnCl_2 + 2\,NaBH_4 \rightarrow Mn(BH_4)_2 + 2\,NaCl \quad (1)$$

$$2\,ZnCl_2 + 5\,LiBH_4 \rightarrow Li[Zn_2(BH_4)_5] + 4\,LiCl \quad (2)$$

The method can be easily extended to mixtures of the three substrates.

The mechanochemical (high-energy milling) method, although very convenient for the initial screening of a wide variety of single- and mixed-metal borohydrides,[10] has serious drawbacks, which hamper the application of this method on an industrial scale. One key disadvantage is the presence of halide-containing by-products in the sample [Equations (1)[8] and (2)[9]]. This "dead mass" usually constitutes 40–60 wt% of the composite, which dramatically decreases the effective hydrogen content and often influences the thermal decomposition process, for example, through the formation of halide-substituted borohydrides.[6c,11] For example, the total hydrogen content of $Li[Zn_2(BH_4)_5]$ decreases from 9.5 wt% to less than 5.3 wt% (i.e. below the 2017 US Department of Energy limit of 5.5 wt%) for the composite product obtained according to Equation (2). The separation methods based on the difference of buoyancy of the products or solubility of borohydrides in ethereal solvents either do not work or lead to ether-solvated products.[12] Most ethers contribute even more to the dead mass than alkali metal halides, they compromise the purity of the evolved H_2 gas, and they often cannot be removed without thermal decomposition of the borohydrides, especially those which evolve H_2 in the desirable low-temperature range (60–100 °C).[13]

On the other hand, the synthesis of pure mixed-metal borohydrides at room temperature from single-metal precursors [for example Equation (3)] is severely restricted by the thermodynamics of the reaction, the reactivity of the precursors, and their availability in an uncontaminated form.[14]

$$M^2(BH_4)_x + y\,M^3BH_4 \rightarrow M^3{}_y[M^2(BH_4)_{x+y}] \quad (3)$$

Indeed, the reported purity of the mixed-metal borohydrides prepared according to this method did not exceed 80 wt%, that is, about 45 wt% for the metastable $NaK(BH_4)_2$,[15] 71 wt% for $K[Al(BH_4)_4]$,[16] and 77.5 wt% for $LiK(BH_4)_2$.[4]

Herein we present a novel room-temperature wet-chemistry approach (Scheme 1) toward mixed-metal borohydrides based on solvent-mediated ion-exchange (metathesis) reactions in organic solvents. This method allows the preparation of desired high-purity products virtually free from the "dead

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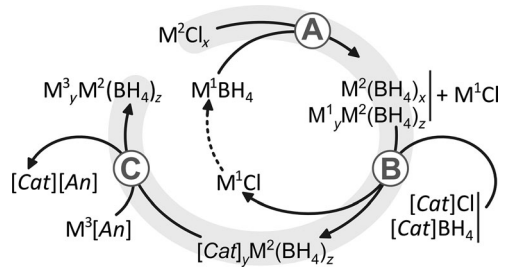

Scheme 1. Synthesis of mixed-metal borohydrides, $M^3_y[M^2(BH_4)_z]$, $z = x + y$. For zinc compounds prepared this way: M^1 = Li, M^2 = Zn, M^3 = Li, Na, K, [*Cat*] = $[Ph_4P]$ or $[nBu_4N]$, [*An*] = $[Al\{OC(CF_3)_3\}_4]$ or $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$.

mass" (i.e. metal halides or coordinated solvents), thus representing a substantial advantage over the currently used methods.[17]

The advantages of the new method will be illustrated using the above-mentioned example of complex zinc borohydrides (Scheme 1). Initially, the complex borohydride precursors [*Cat*][$Zn(BH_4)_3$] and [*Cat*][$Zn_2(BH_4)_5$], where [*Cat*] denotes a bulky organic cation, such as $[Ph_4P]^+$ or $[nBu_4N]^+$, were prepared from the commercially available reagents. This synthesis was achieved via inorganic intermediates (synthesized in step A, for example, according to Equation (2)), which form the precursors in step B. For example:

$$Li[Zn_2(BH_4)_5] + [Cat]Cl \rightarrow [Cat][Zn_2(BH_4)_5] + LiCl \quad (4)$$

Steps A and B may be conveniently combined into a one-pot mechanochemical reaction, as it has been tested for the preparation of the precursors containing the $[Zn(BH_4)_3]^-$ anion.

$$ZnCl_2 + 2\,NaBH_4 + [Cat]BH_4 \rightarrow [Cat][Zn(BH_4)_3] + 2\,NaCl \quad (5)$$

In both cases the organic precursors are easily extracted with a solvent such as CH_2Cl_2, $CHCl_3$, or toluene, in which metal halides are not soluble.[18] Inorganic mixed-cation borohydrides are prepared in step C, which involves a metathesis reaction in CH_2Cl_2.

$$M[An] + [Cat][Zn_2(BH_4)_5] \rightarrow M[Zn_2(BH_4)_5]\downarrow + [Cat][An] \quad (M = Li) \quad (6)$$

$$M[An] + [Cat][Zn(BH_4)_3] \rightarrow M[Zn(BH_4)_3]\downarrow + [Cat][An] \quad (M = Na, K) \quad (7).$$

A mononuclear $Li[Zn(BH_4)_3]$ decomposes in situ to the more stable compounds.

$$M[An] + [Cat][Zn(BH_4)_3] \rightarrow {}^1/_2\,M[Zn_2(BH_4)_5]\downarrow + {}^1/_2\,MBH_4\downarrow + [Cat][An] \quad (M = Li) \quad (8)$$

The precipitated mixed-cation borohydrides are then easily separated from the solution of [*Cat*][*An*]. Here, [*An*] denotes a bulky, weakly-coordinating anion, such as $[Al\{OC(CF_3)_3\}_4]^-$ or $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$.

The purity of a hydrogen storage material is essential for its prospective use as H_2 source. We verified the purity of our as-prepared samples [Equations (6)–(8)] using FTIR spectroscopy and powder X-ray diffraction, PXD. The purity of the H_2 gas that evolved upon heating was monitored using time-resolved mass spectrometry (MS). We will focus here on the mixed-metal borohydride with the largest hydrogen content (M = Li), which has been carefully studied in the past (for Na and K samples see the Supporting Information). The samples prepared using dry [Eq. (2)] and wet [Eq. (6)] procedures are denoted as **D_Li2.5** and **W_LiC**, respectively (see Table S1 in the Supporting Information for the description of these and other important samples.

The PXD pattern of sample **W_LiC** (Figure 1) is dominated by the signals from $Li[Zn_2(BH_4)_5]$ and is virtually free from the LiCl by-product (ca. 0.2 wt % according to a Rietveld analysis), while only traces of organic impurities are visible in the FTIR spectrum (Figure S14, Supporting Information).[19]

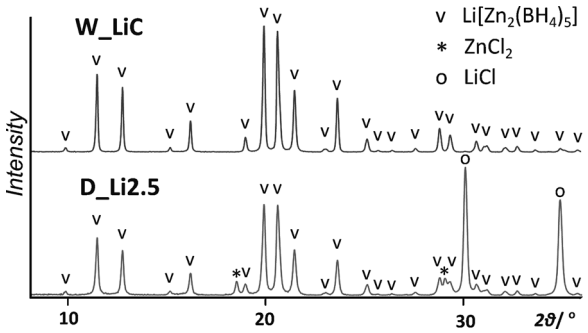

Figure 1. PXD patterns ($Cu_{K\alpha}$ radiation) of the samples of $Li[Zn_2(BH_4)_5]$: **W_LiC** (blue) and **D_Li2.5** (red). Note the significant contamination of mechanochemically prepared sample (**D_Li2.5**) by LiCl and $ZnCl_2$.

Consequently, the mass spectrum of gases that evolved during thermal decomposition showed only trace signals from impurities (i.e. occluded solvent and organic precursors, Figure 2). The total ion current from hydrogen, diborane, and higher boranes (the main gaseous decomposition products of zinc-containing borohydrides) exceeds the total ion current from organic impurities by more than two orders of magnitude (Figure S19). On the other hand, the sample **D_Li2.5** contains as much as 43.8 wt % of LiCl and 3.4 wt % of $ZnCl_2$ (and some unreacted $LiBH_4$). Obviously, the most visible difference between the TGA and DSC profiles of the two samples is related to their different $Li[Zn_2(BH_4)_5]$ content; the mass loss of a nearly pure **W_LiC** sample is much larger than that of a highly contaminated **D_Li2.5** sample (i.e. 24.6 wt % vs. 14.3 wt % within the range of 75–150 °C), the same holds true for the corresponding DSC signals. Interestingly, the decomposition process of the sample **W_LiC** is slightly shifted toward lower temperatures (e.g. the most intense DSC peaks of **W_LiC** and **D_Li2.5** occur at 121.0 °C and 124.3 °C, respectively) pointing to smaller kinetic obstacles for H_2 gas evolution for the LiCl-free system. This observation is contrary to what would be expected simply on

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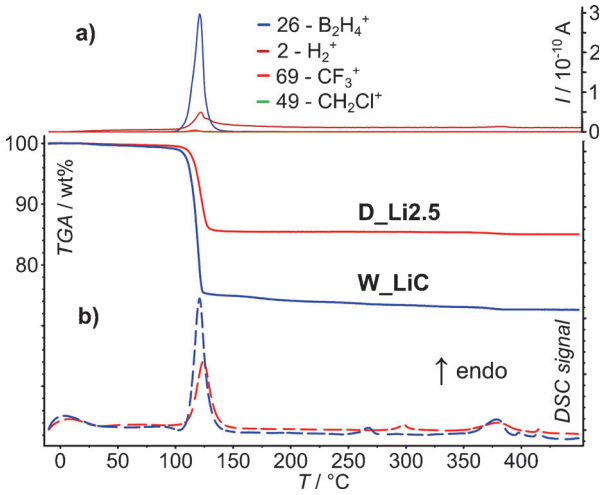

Figure 2. a) Temperature-resolved mass spectrum of the gases that evolved during the thermal decomposition of $Li[Zn_2(BH_4)_5]$ (only **W_LiC**). The ions that result in the most significant maxima in ion current have been specified. b) TGA and DSC profiles of contaminated (**D_Li2.5**) and pure (**W_LiC**) $Li[Zn_2(BH_4)_5]$ samples.

the basis of the crystallite size, which is larger for the sample prepared by precipitation (an estimate from the Scherrer equation gives a more than 50% larger average crystallite size for the sample **W_LiC** as compared to **D_Li2.5**).

Next, the technicalities and limitations of the new method are discussed. The use of volatile and weakly coordinating dichloromethane as the reaction medium enables an easy desolvation. This is a critical issue, especially for the thermally less stable borohydrides that could not be prepared in their desolvated form using typical ethereal, organic sulfide, or amine solvents. Simultaneously, the moderate polarity of CH_2Cl_2 restricts the choice of precursors for the mixed-metal borohydrides. While the borohydrides that contain large organic cations, $[Cat]^+$, are very soluble in CH_2Cl_2, the solubility of many common precursors that contain alkaline metal cations, M[*An*], is insufficient. The successful metathesis in CH_2Cl_2 has been enabled only by the application of the M[*An*] precursors that contain weakly coordinating anions, such as $[Al\{OC(CF_3)_3\}_4]^-$ or $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$.[20] As a result of the large volume of the anion and significant shielding of the negative charge by the bulky, fluorine-rich substituents, the salts that contain these anions show a small lattice enthalpy (even for the tiny and hard Li^+ cation), which enhances their solubility in the weakly solvating solvents and renders them an excellent source of "naked" metal cations.[21] Our preliminary results indicate that the method described here may easily be transferred to other combinations of metal (M^2, M^3) and organic ([*Cat*]) cations, because soluble complex borohydrides, $[Cat]_y[M^2(BH_4)_z]$, have been reported for selected metals M^2, for example, $[Ph_4P][Zn(BH_4)_3]$, $[Ph_4P]_2[Mg(BH_4)_4]$, $[Et_4N][Al(BH_4)_4]$.[23] These compounds can be conveniently synthesized either in solvent-mediated reactions, or in a one-pot mechanochemical process followed by the extraction as for $[Cat][Y(BH_4)_4]$.[18] These organic mixed-cation borohydrides are typically more thermally stable than the parent metal borohydrides,[1b] which further facilitates their use for the synthesis of $M^3_y[M^2(BH_4)_z]$.[11,23b]

In summary, we have described a wet-chemistry method for the synthesis of complex metal borohydrides at room temperature. This method eliminates the "dead mass" problem that occurs when the mechanochemical synthesis is used as an exclusive synthetic tool, or when ethereal solvents are applied. The new method is quantitative, scalable, leads to borohydride products of high purity, and eliminates the need to use toxic B_2H_6 for the synthesis.[22] Use of low-boiling solvents such as CH_2Cl_2 (which may circulate in a closed system in an industrial setting) also renders the method energy efficient.[24,25] The described method, which works neatly for bimetallic borohydrides, complements the recently developed approach for the synthesis of unsolvated monometallic borohydrides with dimethyl sulfide as the solvent.[26]

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