

Hydrogen Storage Using Ionic Liquid Media

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Abstract: The application of ionic liquids revealed a new dimension in many fields of chemistry. In the particular field of hydrogen storage system ionic liquids find application in several different ways. After a short introduction about the matter of hydrogen storage and its advantages and challenges, the different approaches of ionic liquid application in this field are presented. The different approaches can be classified into the application of ionic liquids as (i) solvent, as (ii) co-catalyst, as (iii) catalyst, as (iv) hydrogen storage material and as (v) stabilizing agent for nano particles. The benefit of ionic liquids for the system is discussed in this review.

Keywords: Ionic liquids, Hydrogen storage, Ammonia borane, Formic acid, Dehydrogenation, Catalysis.

1. INTRODUCTION

The majority of the world's transportation is based on limited resources of fossil oil as mobile energy medium. For the future, alternative materials for energy storage have to be found. An interesting material to overcome this problem is hydrogen gas [1-2]. Hydrogen has the advantages of low weight, thus, high energy density per kilogram, it is abundant in form of water and environmental benign as the combustion of hydrogen results in the formation of water. The drawbacks of molecular hydrogen are (i) the low density as gas, (ii) for the compression of gas the application of heavy pressure tanks is necessary and (iii) for cryogenic storage at low temperature in the liquid state efficient isolation is crucial [1, 3-6].

Alternatively to the storage in the molecular form, one can consider the storage of protic and hydridic hydrogen in organic or inorganic materials as a possibility to overcome the mentioned drawbacks. Such materials should contain reasonably high amounts of chemically bound hydrogen to compete with the physical storage of molecular dihydrogen. One of the highest hydrogen contents in weight percent (wt%) can be found in the Lewis pair ammonia borane (AB; >19 wt%). Ammonia borane (AB) and its derivatives have been under investigation for hydrogen storage since several years. Moreover, simple compounds such as CO₂ and its hydrogenation product formic acid (FA) are considered due to a decent content of hydrogen (4.4 wt%) [7-10]. Ammonia borane is more efficient than elemental hydrogen regarding the energy density (energy/volume ratio), but AB bears problems concerning regeneration and transportation. The established infrastructure for the distribution of energy carriers is designed for liquid fuels, thus, a solid energy carrier like AB has some disadvantages competing with liquid fuels.

In summary, it seems more convenient to find a new liquid fuel system. In this regard, ionic liquids (ILs) have promising advantages due to their variable physico-chemical properties [11]. Currently research focuses on hydrogen-enriched inorganic and organic materials and on catalytic dehydrogenation as well as regeneration of waste by hydrogenation [12-16]. ILs are interesting due to their ability to act as promoting agent for the dehydrogenation and in

certain cases to dissolve hydrogen carrier materials, as well as to solubilize specific spent fuel products [16-17]. In certain cases these properties are combined for application [16].

1.1. Ionic Liquids

Since the 1990s ILs changed from a "laboratory curiosity" to a very popular compound class in a broad range of research in natural science and especially in chemistry [18-24]. The physico-chemical properties of ILs – they are non-flammable, non-volatile, highly solvating, often weakly coordinating, have a tunable polarity and good thermal stability – make them attractive for a variety of applications [11, 25]. The definition has been established that salts with a melting point below 100°C are classified as ILs [24, 26-27].

The remarkable low melting points for ionic compounds are related to the reduced lattice energy due to large ion-pairs and low symmetry of the cations (Fig. 1) [11, 25, 28]. ILs are known since 1913, however their predicted potential for wide spread application only developed rapidly in the last two decades. A historical introduction can be found in the overview by Wilkes [29].

Tailoring the ion structures gives access to the tuning of the properties of the ILs [30-34]. Thus, it is possible to design ILs with defined hydrophilicity or hydrophobicity, viscosity as well as coordinating properties. Moreover, the acidity or basicity of the whole reaction system is important, since ILs based on imidazolium cations contain a quite acidic proton in the C₂-position [22, 24, 27, 35], therefore solvated metal species may form carbene complexes in certain cases [36]. This complexation can be suppressed by protection of the C₂-position with a methyl group. ILs are commonly used to stabilize and immobilize homogeneous and heterogeneous catalysts against decomposition or agglomeration [22].

The yield of a reaction is strongly influenced by the solubility of reactants, intermediates and products. In the case of hydrogen generation by dehydrogenation reactions, the driving force to push the equilibrium to the product side is based on the rather low solubility of gaseous hydrogen in IL [37-38]. Remarkably, ILs themselves have also been used as hydrogen storage materials and not simply as solvent for the substrates and catalysts.

1.2. Hydrogen-rich Molecules as Storage Media

Hydrogen storage materials have to fulfil several requirements. Since hydrogen can be stored in its molecular form as gas or liquid,

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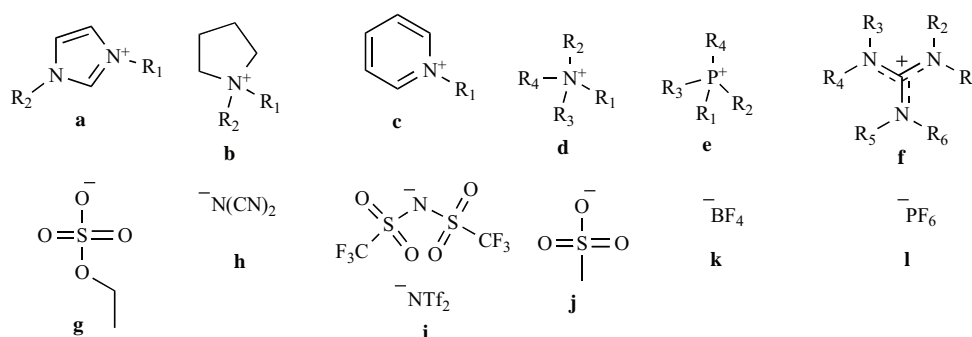
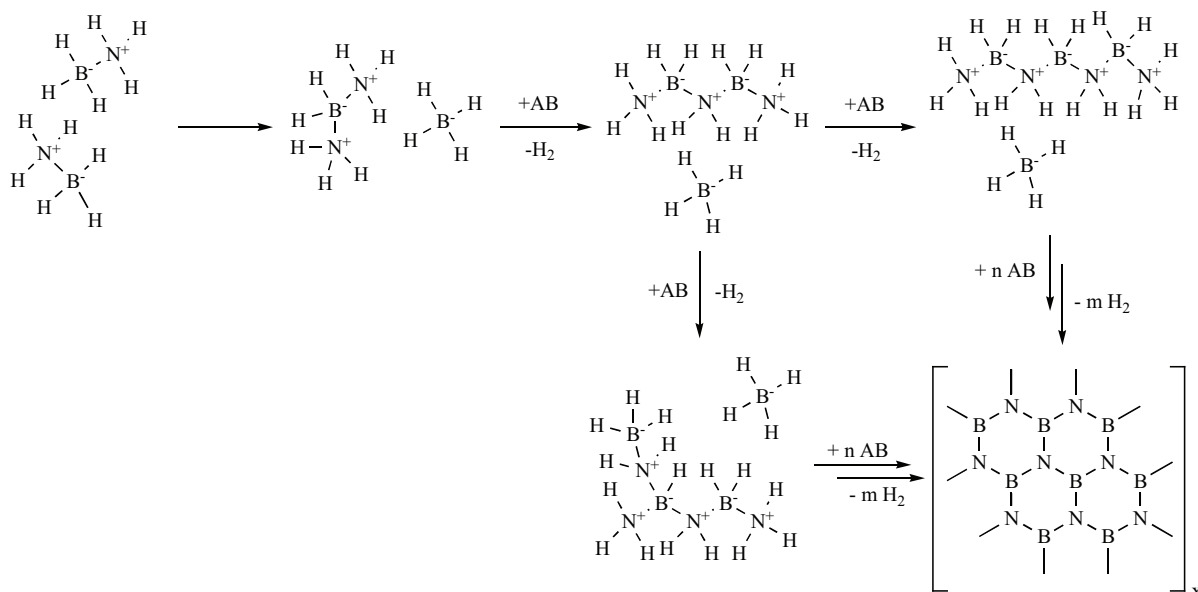


Fig. (1). Selected examples for IL-cations and anions: (a) imidazolium, (b) pyrrolidinium, (c) pyridinium, (d) ammonium, (e) phosphonium and (f) guanidinium. The side-chains R_{1-6} are alkyl groups, which can also carry functionalities like alcohols, ethers, nitriles, etc. Usually weakly coordinating anions are used as counter-parts (g-l): ethyl sulfate, dicyanamide, bistrifluoromethanesulfonylimide (NTf_2^-), methyl sulfonate (OMs^-), tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), etc.



Scheme 1. Decomposition pathways of AB.

such molecular materials must comprise advantages in comparison to molecular hydrogen. The disadvantageous properties of molecular hydrogen are the low density in the gaseous form and the requirements to store it as compressed gas or in the liquid state. The amount of hydrogen required for a 500 km travel (6 kg of H_2) would need a tank volume of around 67 m^3 under ambient conditions. Therefore, today 6 kg hydrogen is compressed into a tank with 260 litres volume at a pressure of 700 bar [4]. The total weight of such hydrogen tanks is 125 kg. This means the gravimetric efficiency is only 4.8 wt%. The cryogenic storage for liquid hydrogen is considered too inefficient in praxis due to evaporation of hydrogen. Moreover, problems arise from the required strong isolation of the tanks which results in further gravimetric inefficiency. In conclusion these disadvantages make it reasonable to store hydrogen in organic or inorganic materials where hydrogen is chemically bound in its protic and hydridic form. Thus, higher volumetric hydrogen density in the condensed phase is an obtainable target.

1.2.1. Ammonia Borane

The Lewis adduct of ammonia and borane is an interesting target compound and is in the focus of current research [6, 10, 17, 39-41]. This solid material is air and moisture stable and consists of 19.6 wt-% hydrogen. Its thermal treatment at $130 \text{ }^\circ\text{C}$ results in lib-

eration of 14 wt% of gaseous hydrogen [4]. Unfavorable byproducts which occur in course of the decomposition reaction are ammonia, diborane and borazine. These by-products are critical because of their high volatility causing contamination of the gas stream and lowering efficiency due to incomplete hydrogen release. The complete dehydrogenation of AB needs temperatures of $>500 \text{ }^\circ\text{C}$. The dehydrogenation results in oligoamino boranes, polyamino boranes and insoluble polyborazylene (Scheme 1), which is highly stable in mechanical, chemical and thermal means.

Since the temperature to decompose ammonia borane completely is high, complete dehydrogenation is undesired. Thus partial dehydrogenation of AB releasing $\sim 14 \text{ wt}\%$ of hydrogen is considered as efficient hydrogen storage material.

The formation of the mentioned by-products is the major drawback and the regeneration of spent AB-based fuels is another major challenge. Recently, Sutton *et al.* presented encouraging results [42]. They dissolved AB spent fuel in liquid ammonia and reduced it with hydrazine resulting in the complete reformation of AB, with nitrogen gas as the only by-product.

1.2.2. Ammonia Borane Derivatives

In recent years, some derivatives of ammonia borane have been studied as hydrogen storage materials. The following materials are

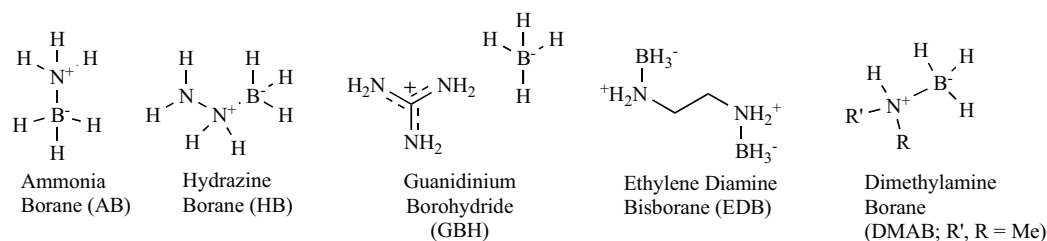


Fig. (2). Selected AB-related hydrogen storage materials.

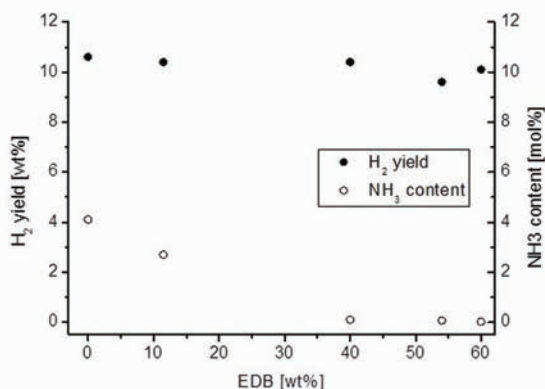


Fig. (3). GBH-EDB Self-Sustaining-Thermal-Decomposition. Mixture containing 60 wt% EDB is not self-sustaining [12].

considered as alternatives to AB: hydrazine borane (HB) [13], guanidinium borohydride (GBH) [12], ethylenediamine bisborane (EDB) [43], methylguanidinium borohydride (Me-GBH) [44] and different alkyl amine boranes (Fig. 2) [14, 45]. Another compound class between molecular and metal hydride storage materials are metal amido boranes, which are not discussed in this chapter [46].

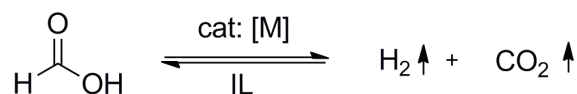
Lentz and co-workers studied hydrazine borane, which provides a comparable weight efficiency as AB [13]. The major part of the hydrogen content in HB is thermally accessible, but the hydrogen generation can be efficiently improved by mixing HB with lithium hydride. The molar 1:1-mixture of HB and LiH results in a blend material with a hydrogen content of 14.8 wt% in comparison to 15.4 wt% of neat HB. With this blend an experimental hydrogen release of ~12 wt% has been realized at 150 °C within 4.5 h. Blending HB with a hydride-donor is a consequent optimization, as pure HB consists of four acidic and three hydridic hydrogen atoms, thus, it contains one excess acidic hydrogen. The authors reported that they only found ammonia as impurity in the hydrogen gas stream in the range <1%. The solid by-products showed reactivity towards water and are insoluble in organic solvents. The double borane adduct of hydrazine, hydrazine bisborane, has a hydrogen content a little higher than HB, but is not considered due to stability problems. The authors reported rapid heating or temperatures above 160 °C caused explosive decomposition.

Groshens and Hollins reported remarkable results with guanidinium borohydride (GBH) and its blends [12]. In GBH, the protic moieties are incorporated in the guanidinium cation and the counter-ion contains the hydrides rendering a content of 10.8 wt% of hydrogen gas theoretically and 10.6 wt% experimentally. As the thermal decomposition is exothermic, the hydrogen generation reaction remains self-sustaining after initial heating. This material can nearly be completely dehydrogenated, though about 5 mol% ammonia is found in the gas stream. The idea of blending arises from the imbalance of protic and hydridic hydrogen atoms in GBH:

there are two surplus protic hydrogen atoms in GBH. As ideal hydride source for a GBH-blend, ethylene diamine bisborane (EDB) was chosen, carrying two excess hydrides. The hydrogen yields of GBH-EDB blends are high and the undesired ammonia formation is maintained on a low level, especially using an equimolar mixture GBH and EDB (Fig. 3). The 40:60 wt% GBH-EDB blend yields 10.1 wt% of hydrogen with a distinctly lower ammonia impurity of only 0.026 mol%. The major drawback of this material blend is its solid state. Pure EDB is also interesting in terms of high efficiency in comparison to the previously mentioned blend [43]. One advantage of this material is the high purity of the generated hydrogen as no impurities are detectable below 200 °C. The generation of hydrogen using EDB is comparably fast as ammonia borane based systems.

1.2.3. Formic Acid

The catalytic dehydrogenation of formic acid (FA) yielding equimolar amounts of dihydrogen and carbon dioxide has drawn some attention in the last years (Scheme 2). [9, 47-52] Formic acid contains only 4.4 wt% hydrogen, less than the previous mentioned materials. The abundance of carbon dioxide as substrate enhances the attraction of formic acid as simple and cheap hydrogen storage material. For synthetic applications formic acid is also suitable as hydrogen source for catalytic transfer-hydrogenation reactions [53-56].



Scheme 2. Reversible splitting of formic acid.

2. IONIC LIQUIDS IN HYDROGEN STORAGE SYSTEMS

ILs are interesting for different applications in the field of hydrogen storage due to their physico-chemical properties. For example, a low weight and hydrogen rich IL can be directly used as hydrogen storage material. Moreover ILs may be applied as solvent, as a promoting solvent for dehydrogenation, as co-catalyst or as stabilizer for e. g. metal nanoparticles.

2.1. ILs as Hydrogen Storage Materials

The GBH derivative Methyl-GBH contains one methyl group on a guanidinium nitrogen, and this modification results in a decrease of the melting point, hence, formation of an IL which is suitable as hydrogen source (Fig. 4) [44].

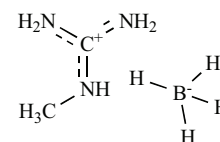
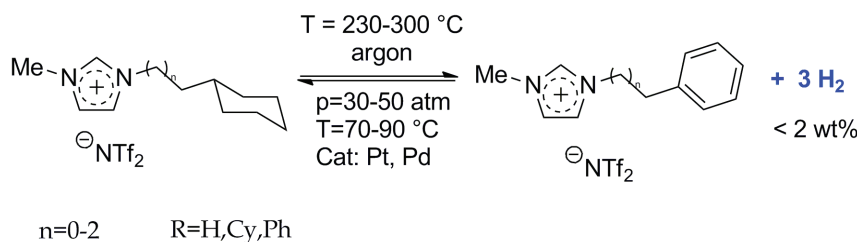
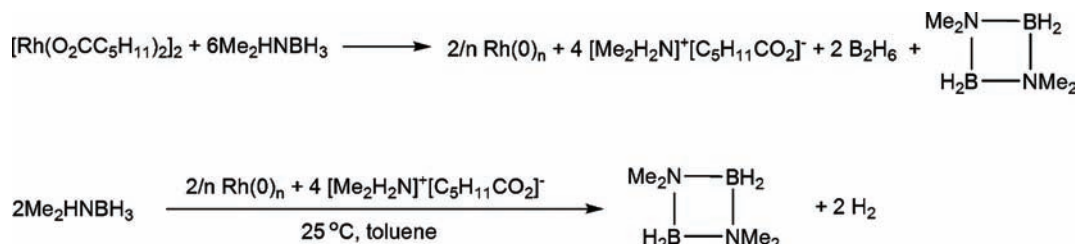


Fig. (4). Structure of methyl guanidinium borohydride (Me-GBH).



Scheme 3. Structure of cyclohexyl-ILs for hydrogen storage [58].



Scheme 4. Rhodium nanoparticle formation and catalytic decomposition of DMAB. Reprinted with permission from [59]. Copyright (2009) American Chemical Society.

Me-GBH contains smaller amounts of accessible hydrogen than GBH. The methyl group distorts the symmetry of the cation, thus, resulting in a lower melting point of this salt [57]. In particular, the Me-GBH is the first room temperature IL (m.p. -5°C) which can be easily dehydrogenated with a reasonably high hydrogen capacity of 9.0 wt%. However, kinetic studies focusing on thermal dehydrogenation at 75°C showed that the decomposition is too slow and ineffective for application. Moreover, the studies showed that the decomposition also causes mass loss which exceeds the theoretical capacity of the substrate, thus this cannot be assigned to hydrogen evolution. At higher temperatures ($>120^\circ\text{C}$) amounts of ammonia are detectable in the gas stream. The quantification of the hydrogen generation was calculated to be 9.0 wt% based on yields determined by TGA and volumetric measurements. The dehydrogenation product of Me-GBH is solid and insoluble in the IL. Additionally, Wilkinson's catalyst $[(\text{PPh}_3)_3\text{RhCl}]$ and FeCl_2 have been tested to improve the rate and extent of hydrogen generation with moderate success.

Another attempt to incorporate a hydrogen carrier into an IL was performed by attaching a side-chain containing a cyclohexyl moiety to an imidazolium cation [58]. Here, Pd/C was used at elevated temperatures during the cyclohexyl dehydrogenation and rehydrogenation process (Scheme 3). Even though storage capacity is too low, this work represents the first report where an IL has been applied as hydrogen storage material. The drawbacks of this system are the high temperatures (300°C) for fast dehydrogenation and the low hydrogen storage capacity. The thermal stability of some of the employed ILs is remarkable.

2.2. ILs as Stabilizing Agents for Nanoparticles for Catalytic Dehydrogenation

The dimethyl amino borane (DMAB) is an ideal model system for mechanistic studies, since the methyl groups suppress further dehydrogenation after one equivalent of dihydrogen is generated, hence, inhibits formation of oligomeric product mixtures. The catalytic dehydrogenation of disubstituted amino borane compounds leads to selective formation of cyclic dimers and trimers at room temperature [15]. The studies of these model systems are mechanistically important, rather than for the application as hydrogen storage materials owing to the lower accessible hydrogen content in comparison to the previously discussed materials. The dehydrogenation

of DMAB proceeds via the diammoniate of diborane to the cyclic dimer [59]. The application of excess DMAB in presence of dimeric rhodium(II)-hexanoate lead to the formation of Rh(0) nanoparticles and the IL dimethyl ammonium hexanoate (Scheme 4). These nanoparticles ($\sim 2 \text{ nm}$) show high activity for the catalytic dehydrogenation of DMAB at low temperature yielding high conversions (Scheme 4). The *in-situ* generated IL dimethyl ammonium hexanoate acts as protecting agent for the nanoparticles.

2.3. ILs as Active/Supporting Solvents

In other studies it has been shown that certain ILs are capable to act as promoting solvents for the dehydrogenation of amine boranes (Figs. 5 and 6) [17, 60].

The IL-promoted dehydrogenation of AB in IL mixtures consisting of 50 wt% of AB at 85°C shows that certain ILs are capable to release more than two equivalents of hydrogen gas per AB (Fig. 6; A-C). Most ILs promote dehydrogenation significantly, even though the initial rates of generated H_2 are not related to the overall amount of released hydrogen. Only in one case (Entry J) the IL does not show any promoting effect, hence the dehydrogenation efficiency is equivalent to the thermal decomposition of neat ammonia borane (Fig. 6).

The dehydrogenation of AB promoted by $[\text{BMIM}]\text{Cl}$ was studied in more detail [60]. The in-depth studies showed that reaction rates as well as total hydrogen yield can be further improved (Fig. 7). At a rather low temperature of 85°C the hydrogen yield of AB can be significantly enhanced in presence of $[\text{BMIM}]\text{Cl}$ in a 50 wt% mixture, in comparison to neat ammonia borane, also regarding weight-efficiency in both systems (Fig. 7 – left).

Interestingly, the gas analyses revealed that only residual amounts of borazine are present, this indicates that borazine formation is suppressed or it completely dissolves in the IL. As shown above, $[\text{BMIM}]\text{Cl}$ efficiently promotes dehydrogenation and the induction period is precluded completely. These advantages remain when IL concentration is lowered to 20 wt%. The IL supported H_2 generation from AB at 75°C yields an equal amount of H_2 as the decomposition of neat AB at 85°C . Moreover, in IL the reaction is faster and no induction period occurs. The reaction is quite sensitive towards process temperature, where hydrogen yield increases

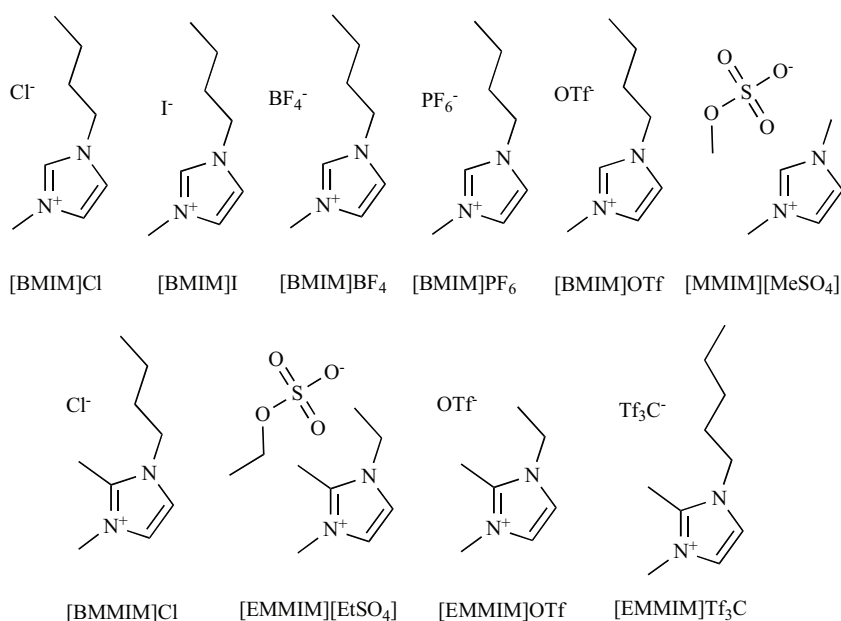


Fig. (5). Structures of ILs applied as promoting media of AB dehydrogenation [60].

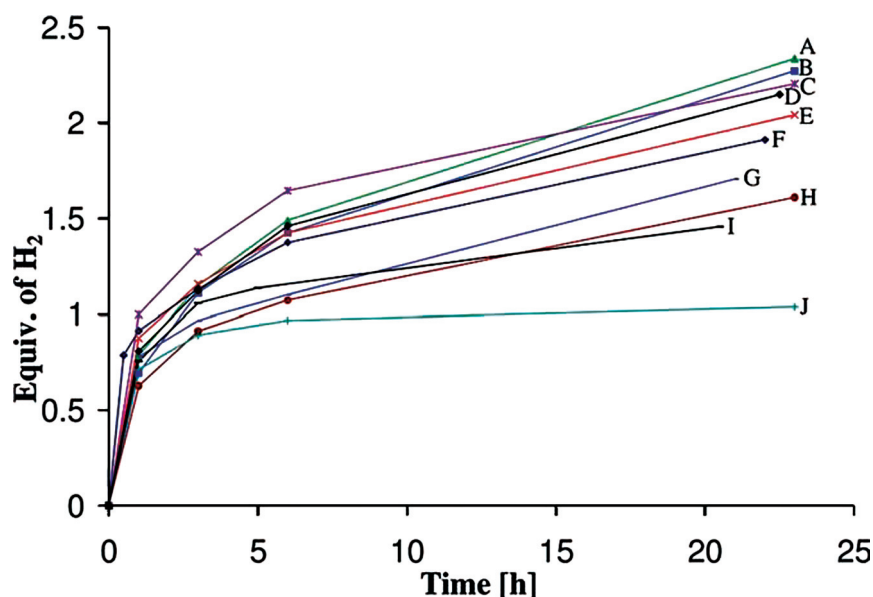


Fig. (6). H₂-release measurements (Toepler pump) of the reaction of 50 wt% AB (250 mg) at 85 °C in 250 mg of (A) [BMMIM]Cl, (B) [BMIM]Cl, (C) [EMMIM][EtSO₄], (D) [BMIM]BF₄, (E) [MMIM][MeSO₄], (F) [BMIM]OTf, (G) [EMMIM]OTf, (H) [BMIM]I, (I) [BMIM]PF₆, and (J) [PMMIM]Tf₃C. Reprinted with permission from [60]. Copyright (2009) American Chemical Society.

slightly and reaction time is significantly shorter. At 85 °C 2.1 equivalents of H₂ are released within ~4.1 hours, in comparison, at 110 °C 2.3 equivalents H₂ are released in less than 0.5 hours.

2.4. ILs as Solvents for Catalytic AB Dehydrogenation

Certain metal complexes are suitable to catalyse the dehydrogenation of ammonia borane based materials, thus reaction rate and process temperature can be improved, which are crucial for hydrogen storage systems in transportation [15, 61]. In combination with ILs as promoting solvents for the dehydrogenation of AB derivatives, the catalytic dehydrogenation can be further accelerated. For example transition metal based pre-catalysts, such as Rh, Ru, Pd or

Ni, decrease the process temperature of AB dehydrogenation significantly (45-85 °C) and hydrogen yield is improved at the same time (Fig. 8) [16].

The applied metal precursors have not been further investigated regarding the active species, however, most of them are known to form metal nanoparticles in presence of a reductant or undergo thermal decomposition in ILs [23]. Therefore, one may consider that at least in some cases metal(0) nanoparticles play a role in the catalytic dehydrogenation of ammonia borane. The reaction monitoring showed that the majority of the applied precursors (5 mol%) undoubtedly accelerate the reaction and improve yields significantly.

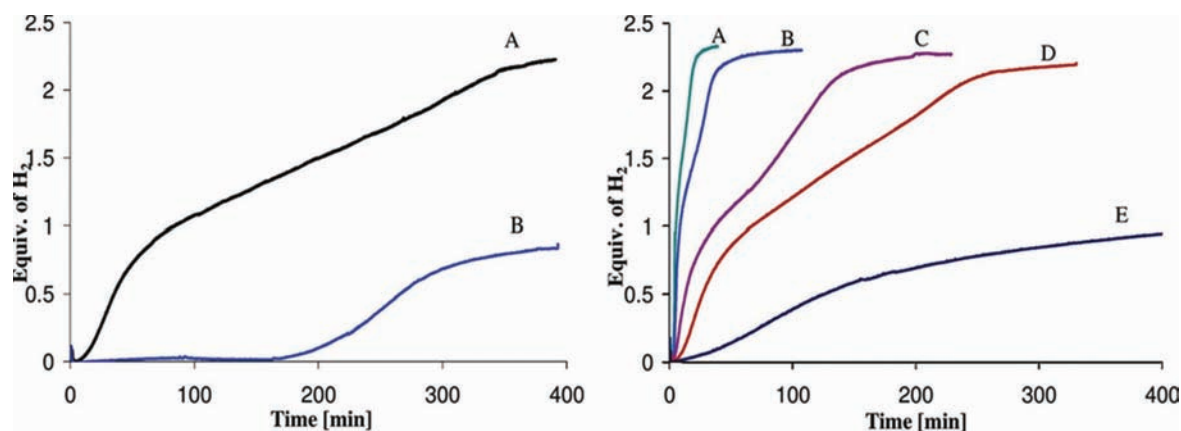


Fig. (7). (Left) H_2 -release measurements at 85 °C of: (A) 50 wt% AB in [BMIM]Cl and (B) solid-state AB (Right) H_2 -release measurements of 50 wt% AB in [BMIM]Cl at (A) 110 °C, (B) 105 °C, (C) 95 °C, (D) 85 °C, and (E) 75 °C. Reprinted with permission from [60]. Copyright (2009) American Chemical Society.

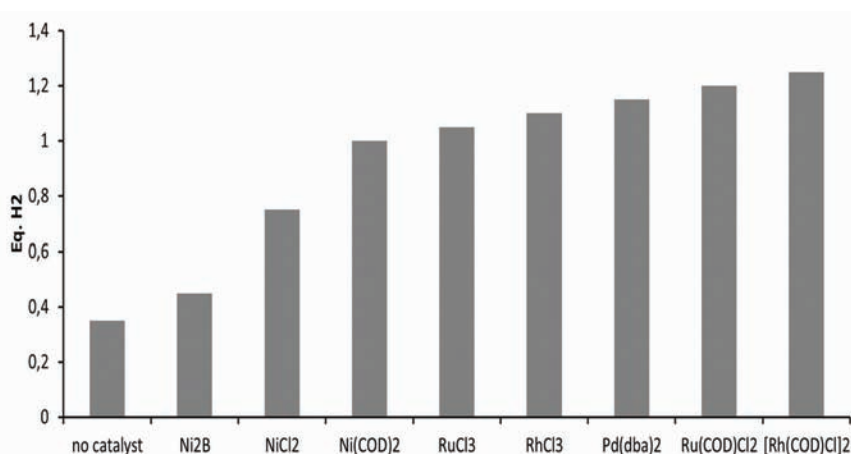
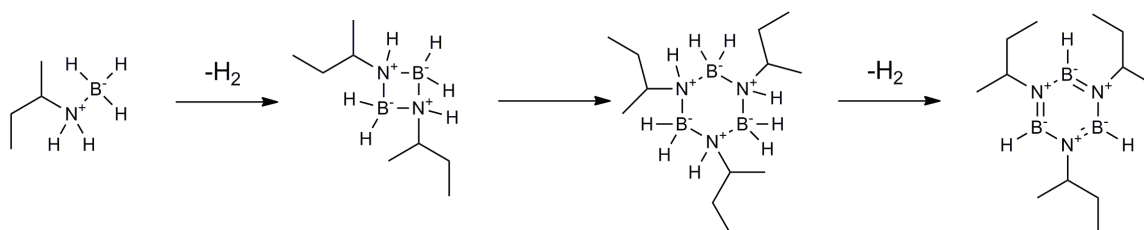


Fig. (8). Hydrogen evolution from AB-decomposition at 65 °C after 4 h catalyzed by different metal catalyst-precursors. Adapted from Ref. [16].



Scheme 5. Trimerisation of SBAB to the corresponding borazine derivative during hydrogen production [14].

Another derivative of AB, sec-butyl amine borane (SBAB), blended with AB can be dehydrogenated catalytically in IL [14]. Interestingly, the dehydrogenation of this blend in [EMIM][EtSO₄] leads via trimerisation to a soluble mono-molecular borazine derivative and oligomerisation to insoluble polyamino boranes is suppressed completely (Scheme 5). The weight efficiency drops down to 5 wt% due to the alky chain. This catalytic dehydrogenation used 1 mol% [RuCl₂(PMe₄)₃] at 80 °C. Details about the gas stream purity have not been reported.

2.5. FUNCTIONALIZED ILS FOR CATALYTIC DECOMPOSITION OF FORMIC ACID

Functionalised ILs have different applications as task-specific designer solvents for example in the dehydrogenation of formic acid (see Scheme 2). In this example a basic amine-functionality is

incorporated into the IL side-chain. The imidazolium-based ILs with a 1-(N,N-diethylamino)-ethyl-3-methylimidazolium cation ([Et₂NEMIM]⁺) (see Fig. 9) act as solvent for the catalyst, are miscible with formic acid and the amine-functionality acts as immobilised basic co-catalyst in the dehydrogenation of formic acid (Fig. 9) [9, 62].

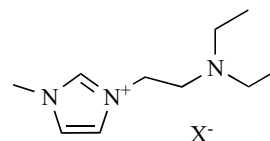
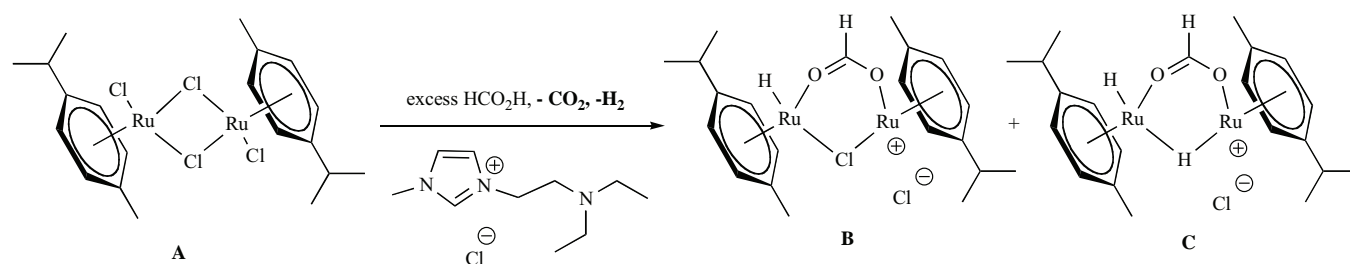


Fig. (9). Structure of the amino-functionalized ILs containing [Et₂NEMIM]⁺ [9, 62].

Several anions (Cl⁻, BF₄⁻, OTf⁻, NTf₂⁻ and HCO₂⁻) with this cation were tested for the catalytic dehydrogenation of formic acid



Scheme 6. Reactivity of $[(p\text{-cymene})\text{RuCl}_2]_2$ **A** in presence of formic acid and $[(\text{Et})_2\text{NEMIM}]\text{Cl}$.

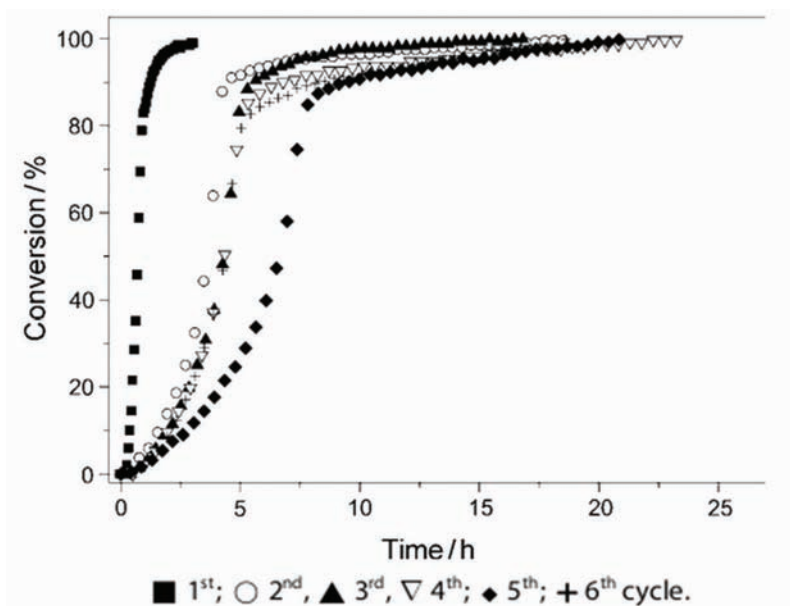


Fig. (10). Reaction profiles for formic acid decomposition catalyzed by $[(p\text{-cymene})\text{RuCl}_2]$ in $[(\text{Et})_2\text{NEMIM}]\text{Cl}$ at 80 °C for 6 cycles. Reprinted with permission from [9]. Copyright (2010) John Wiley and Sons.

with the dimeric ruthenium pre-catalyst $[(p\text{-cymene})\text{RuCl}_2]_2$ **A**. Depending on the reaction conditions and the used IL the TOFs varied from 36 h^{-1} (no add. base) to 627 h^{-1} (add. base). Further studies showed that in presence of formic acid the dichloro-bridged ruthenium dimer **A** is converted into the corresponding formate/chloro-bridged $[(p\text{-cymene})\text{RuCl}(\text{HCO}_2)]_2$ **B** and formate/hydride-bridged $[(p\text{-cymene})\text{RuH}(\text{HCO}_2)]_2$ **C**. This indicates that in the catalytic cycle formate-bridged ruthenium dimers play a crucial role (Scheme 6). The reported TOFs of up to 1684 h^{-1} were calculated with the assumption of a dimeric ruthenium complex species. Notably no monomeric ruthenium species have been detected.

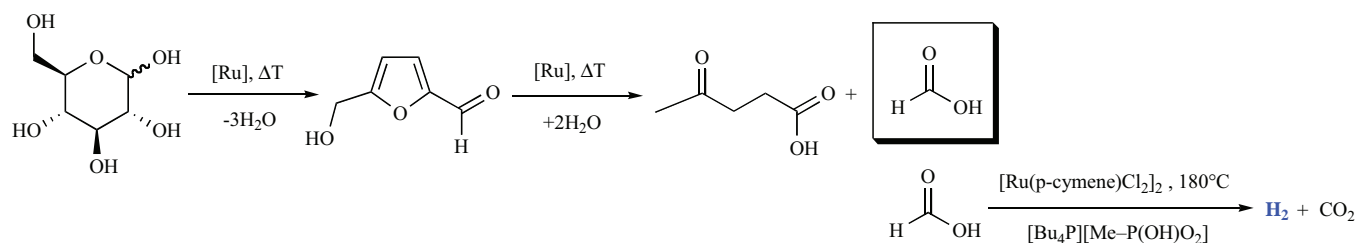
It has been shown that small IL amounts result in a more efficient system than high co-catalyst loadings. Due to the high viscosity of the pure IL, the mixtures viscosity increases in the course of the reaction. The viscosity may be accounted for the decelerated reaction resulting from higher co-catalyst, i.e. IL, loadings. The robustness of this system has been shown in six recycling experiments that were conducted without any precautions against air or moisture. After the high activity in the first run, the reaction monitoring showed similar profiles for the next runs, except the fifth (Fig. 10).

The catalyst precursor $[(p\text{-cymene})\text{RuCl}_2]_2$ in IL can also be applied in the dehydrogenative conversion of biomass, such as cellulose(-derivatives). Some strongly solvating ILs are suitable to dissolve these (in classical solvents hardly soluble) materials. Thus,

these substrates become accessible for homogeneous dehydrogenation [63]. Studies about the dehydrogenation of these carbohydrates revealed that e.g. glucose is not converted into the corresponding dehydrogenated product, but it undergoes thermal decomposition releasing formic acid which is then catalytically converted into CO_2 and H_2 . Moreover, wood was dissolved in the IL 1-ethyl-3-methylimidazolium methyl-methylphosphonate, thermally converted into formic acid at 180 °C and subsequently dehydrogenated by the ruthenium complex (Scheme 7). The high process temperatures necessitate ILs with high thermal stability.

3. CONCLUSION AND OUTLOOK

The research field of molecular hydrogen storage materials still provides several challenges to be overcome. ILs seem to be capable to resolve some aspects in different points. Besides the rare examples of ILs as hydrogen storage materials, they serve in several ways for the hydrogen generation: (I) application as highly thermally and chemically stable solvents, (II) promoting solvents for dehydrogenation of the hydrogen-rich substrates, (III) co-catalyst in case of incorporation of a Lewis-base, and (IV) the superior solubilisation properties of ILs are promising aspects in search of liquid hydrogen storage systems which remain liquid after complete hydrogen release. The only drawback of ILs as additive to pure or blended hydrogen storage materials is the additional weight in the system, resulting in a lower gravimetric efficiency. However, it has been shown that this drawback can be fully compensated as the IL-



Scheme 7. Thermal conversion of glucose and catalytic dehydrogenation of formic acid in IL [63].

based systems gave much higher hydrogen yields in shorter reaction times than the dehydrogenation of neat hydrogen-rich materials.

CONFLICT OF INTEREST

The author(s) confirm that this article content has no conflicts of interest.

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