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Application of Ionic Liquids in Hydrogen Storage Systems

Sebastian Sahler and Martin H.G. Prechtl

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1. Introduction

In the present world, individual mobility is mainly based on fossil hydrocarbons as transportable energy medium. Since there is a wide agreement on the future depletion of fossil resources, an alternative energy carrier, that can be transported efficiently, has to be found. One material, which is in many considerations suitable to fill this gap, is hydrogen. (Hamilton et al., 2009; Schlapbach & Züttel, 2001) The major advantages of hydrogen for these purposes are the low weight, the high abundance of the oxide, i.e. water, and the environmental benignity of the waste oxidation product, also water. The major hindrance for a widespread application of hydrogen in mobile applications is its low density in the gaseous state. Since the compression or liquefaction of hydrogen respectively the transportation of the denser forms of hydrogen is accompanied by a manifold of problems, i.e. severe disadvantages in especially gravimetric efficiency, alternatives are sought after. (Eberle et al., 2009; Felderhoff et al., 2007; Hamilton et al., 2009; Marder, 2007; Staubitz et al., 2010)

Since there are some materials that consist of an amount of hydrogen, that is high enough to compete with the aforementioned physical storage solutions, the storage of hydrogen in a chemical compound is discussed intensively lately. One important compound with one of the highest hydrogen contents possible is ammonia borane. The application of ammonia borane and its derivatives for hydrogen storage is matter of research in the last decade as well as a compound as simple as formic acid, which is in this sense the hydrogenation-product of carbon dioxide. (Fellay et al., 2008; Loges et al., 2008; Scholten et al., 2010; Stephens et al., 2007)

The application of ammonia borane itself is more efficient than elemental hydrogen, but nevertheless accompanied by some problems as well. Since there is a worldwide infrastructure suitable for the deployment of liquid fuels, a solid fuel bears certain

disadvantages competing with a liquid fuel. Another important aspect of fuels is the applicability, and here liquid fuels are also advantageous in comparison to solid fuels.

In conclusion it seems reasonable to search for a liquid fuel (-system). Regarding this assumption ionic liquids (ILs) promise advantages owing to their tunable physico-chemical properties. (Dupont & Suarez, 2006) Hydrogen-enriched materials or blends are as well in the focus of current research as catalytic decomposition. (Groshens & Hollins, 2009; Hugle et al., 2009; Jaska et al., 2003; Mal et al., 2011; Wright et al., 2011) ILs are investigated for their ability of supporting decomposition as well as solution of certain materials, including in some cases spent fuel products. (Bluhm et al., 2006; Wright et al., 2011) In some extent these approaches can be applied in combination. (Wright et al., 2011)

1.1. Ionic liquids

In the last two decades ionic liquids (ILs) have become very popular in various fields in chemistry. (Dupont et al., 2002; Dupont & Scholten, 2010; Dupont et al., 2011; Migowski & Dupont, 2007; Precht et al., 2010; Precht et al., 2011; Scholten et al., 2012) Their physico-chemical properties, i. e. non-flammable, non-volatile, highly solvating, in general weakly-coordinating, tunable polarity and good thermal stability make them highly attractive for various applications. (Dupont, 2004; Dupont & Suarez, 2006) Low melting (organic) salts are defined as IL if the melting point is below 100 °C. (Dupont et al., 2002; Hallett & Welton, 2011; Welton, 1999)

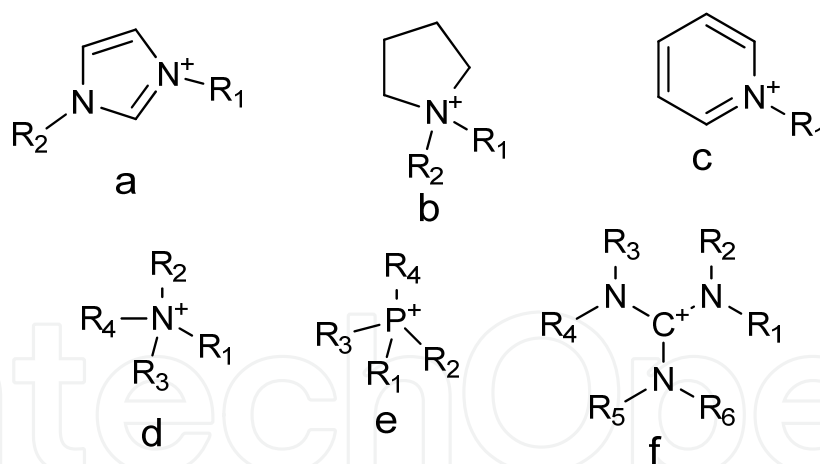


Figure 1. Selected examples for IL-cations: (a) imidazolium, (b) pyrrolidinium, (c) pyridinium, (d) ammonium, (e) phosphonium and (f) guanidinium. The side-chains are alkyl groups, which can also carry functionalities like alcohols, ethers, nitriles, etc. Usually weakly coordinating anions are used as counter-parts such as BF_4^- , PF_6^- , bistrifluoromethanesulfonylimide (NTf_2^-) etc.

The low melting points are a result of the reduced lattice energy originating from large ion-pairs and low symmetry of the cations (Figure 1). (Dupont, 2004; Dupont & Suarez, 2006; Krossing et al., 2006) Ionic liquids have been known since the early 20th century, though their predicted potential and wider application developed rapidly in the last two decades. For a more detailed historic introduction see the article by Wilkes. (Wilkes, 2002)

For different applications the physico-chemical properties of ILs can be modified by tailoring the cation and/or anion structures.(Chiappe et al., 2006; Cui et al., 2010; Fei et al., 2007; Yang et al., 2008; Zhao et al., 2004) It is possible to design the hydrophilicity or hydrophobicity, the viscosity as well as the coordinating properties, especially those implied by the anion. Another important aspect one has to keep in mind is the pK_a value, since especially in imidazolium-ILs the C₂-proton is fairly acidic(Dupont, 2011; Dupont et al., 2002; Precht et al., 2010; Welton, 1999) and metal ions form carbene complexes in some cases.(Xu et al., 2000) This can be avoided by protecting the C₂-position with a methyl group. Some ILs are able to stabilize certain homogenous and heterogeneous catalysts against decomposition or agglomeration, which can be of great benefit.(Precht et al., 2010)

The outcome of a reaction is strongly influenced by the solubility of the reactants, intermediates and products. In the particular case of dehydrogenation reactions, the reaction is influenced by the rather low solubility of hydrogen gas in ILs driving the equilibrium to the desired side.(Anthony et al., 2002; Jacquemin et al., 2006) In recent research ionic liquids have been employed not only as solvent in dehydrogenation reactions, but also as storage materials (vide infra).

1.2. Hydrogen-rich molecules as storage media

Suitable molecules for the storage of hydrogen have to fulfill several requirements. Since hydrogen is storable in elemental form as a gas or liquid, these molecular systems must bear certain advantages over storage as elemental hydrogen. The most impractical properties of elemental hydrogen are the low density of gaseous hydrogen and the high requirements to the storage system in case of compressed or liquid hydrogen. The amount of hydrogen (atmospheric pressure) required for a 500 km travel (6 kg) would require a tank volume of nearly 67 m³! To overcome this problem one is able to compress hydrogen into a reasonable volume. A 700 bar hydrogen storage tank is able to store the same amount of hydrogen in the volume of only 260 liters.(Eberle et al., 2009) Due to the severe pressure the tank has to withstand, the fuel including the tank weights 125 kg. This corresponds to a gravimetric efficiency of 4.8 %. Concerning liquid storage the losses due to boil off are considered too high for practical application, since they add up to the problems of a strongly isolated tank, i.e. gravimetric inefficiency. Since molecular hydrogen has these severe disadvantages, it seems reasonable to store hydrogen in a chemical way, where higher volumetric hydrogen density in the condensed phase is an obtainable target.

1.2.1. Ammonia Borane (AB)

One important molecule in the focus of research is the simple adduct of ammonia and borane (AB). (Ahluwalia et al., 2011; Al-Kukhun et al., 2011; Basu et al., 2011; Bluhm et al., 2006; Staubitz et al., 2010; Stephens et al., 2007) This solid Lewis pair is stable towards air and water and consists of 19.6 % hydrogen. When heating this compound to 130 °C it loses 14 % of its weight as hydrogen.(Eberle et al., 2009) Undesired side-products in the decomposition-reaction can be ammonia, diborane and borazine, where the last is a

standard decomposition product, that is only critical due to its high volatility contaminating the gas stream and lowering efficiency due to incomplete hydrogen release. For the complete dehydrogenation of AB temperatures of over 500 °C are required. The dehydrogenation of this compound leads via oligoamino boranes and polyamino boranes to insoluble polyborazylene (Figure 2), which is significantly stable in mechanical, chemical and thermal means.

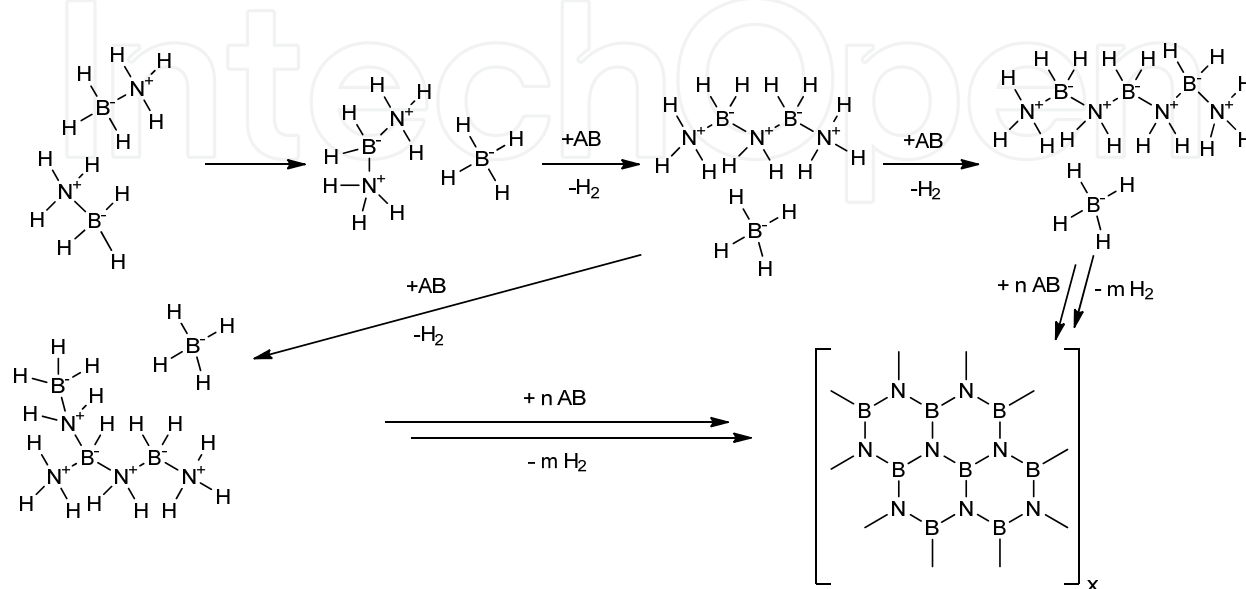


Figure 2. Decomposition Pathway of Ammonia Borane.

Since the temperature to decompose ammonia borane completely is so high and the according product is remarkably stable, complete dehydrogenation is undesired. As above mentioned, partial dehydrogenation leads to a capacity of around 14 wt% which is still enough to be considered as efficient hydrogen storage material.

Regarding the regeneration of spent fuel Sutton and co-workers recently presented meaningful results.(Sutton et al., 2011) The solution of AB spent fuel in liquid ammonia could be quantitatively reduced by hydrazine to yield AB, with gaseous nitrogen as the only by-product.

1.2.2. Ammonia Borane derivatives

Several derivatives of AB have been studied recently. The most important are: hydrazine borane (HB),(Hugle et al., 2009) guanidinium borohydride (GBH),(Groshens & Hollins, 2009) ethylenediamine bisborane (EDB),(Neiner et al., 2011) methylguanidinium borohydride (Me-GBH)(Doroodian et al., 2010) and different alkyl amine boranes (Figure 3).(Bowden et al., 2008; Mal et al., 2011) On the frontier between molecular and metal hydride storage materials are the metal amido borane compounds, which are not in the scope of this chapter.(Chua et al., 2011)

A derivative of AB with a comparable weight efficiency has been studied by Lentz and co-workers recently: hydrazine borane (HB).(Hugle et al., 2009) Much of the hydrogen content

of pure HB is thermally available, but the efficiency of release could be significantly improved by combining HB with the hydride-donor LiH: Though blending with LiH in 1:1 molar ratio lowers the theoretical gravimetric hydrogen density from 15.4 wt% to 14.8 wt% the actual release of hydrogen reached nearly 12 wt% at 150 °C in 4.5 h. The idea of combining HB with a hydride-donor arose from the fact that HB has an excess acidic hydrogen atom, since it consists of four acidic but only 3 hydridic hydrogen atoms. The released gas stream showed to consist of mainly hydrogen with an impurity of ammonia present in the range of <1%. The solid residue showed to be reactive towards water and completely insoluble in organic solvents. Hydrazine bisborane, a molecule very similar to HB, with a hydrogen content a little higher than HB, is not considered due to stability problems. The authors reported that rapid heating or temperatures above 160 °C lead to explosive decomposition.

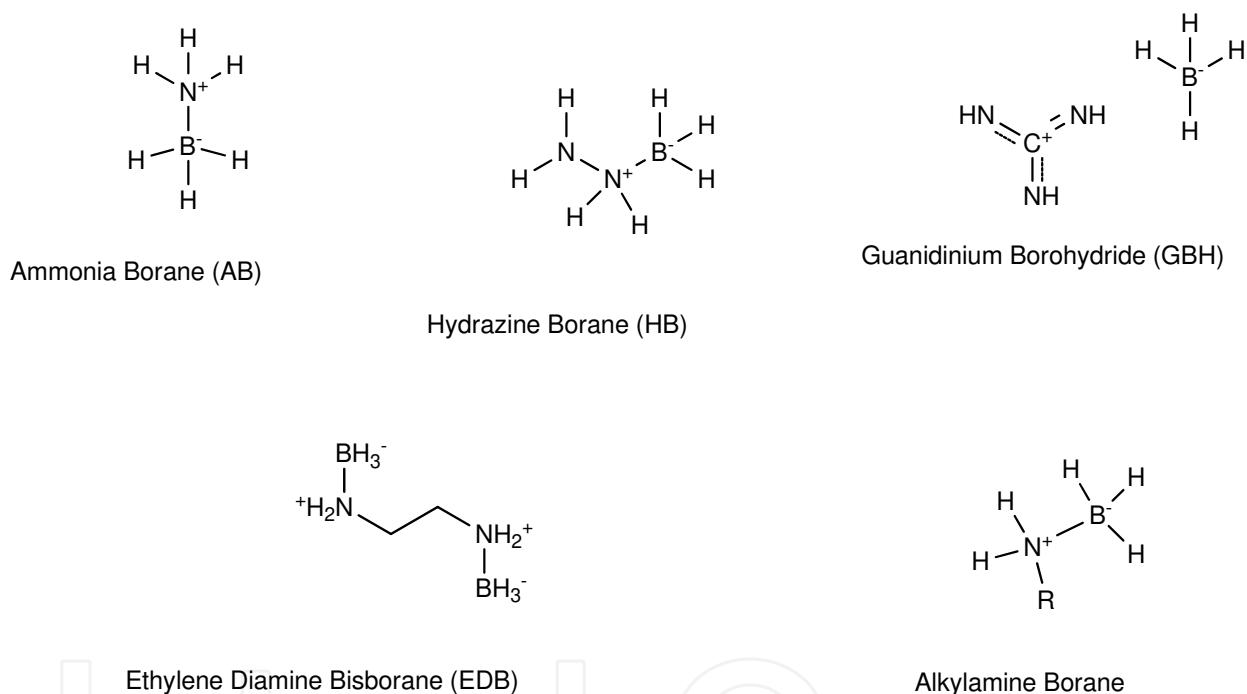


Figure 3. Structures of selected molecular hydrogen storage materials.

Guanidinium borohydride (GBH) and blends containing GBH were investigated by Groshens and co-workers showing remarkable results. (Groshens & Hollins, 2009) The material consists of the guanidinium ion contributing acidic protons and borohydride for hydridic hydrogen atoms. As this material consists only of light weight atoms and hydrogen, the theoretical capacity is 10.8 wt%. The exothermic reaction results in a self-sustaining decomposition when initiated by a heat source. Nearly quantitative release of hydrogen was observed with a distinct impurity of ammonia of about 5 %. The imbalance of acidic and hydridic hydrogen atoms is a factor susceptible to improvement by blending. The material of choice for blending was ethylene diamine bisborane, which contributes two excess hydridic hydrogen atoms to the mixture. As shown in figure 4 the blending results in the maintenance of hydrogen yield, while suppressing the formation of undesirable

ammonia. This effect is exceptionally strong in the mixtures containing approximately equimolar amounts of both materials.

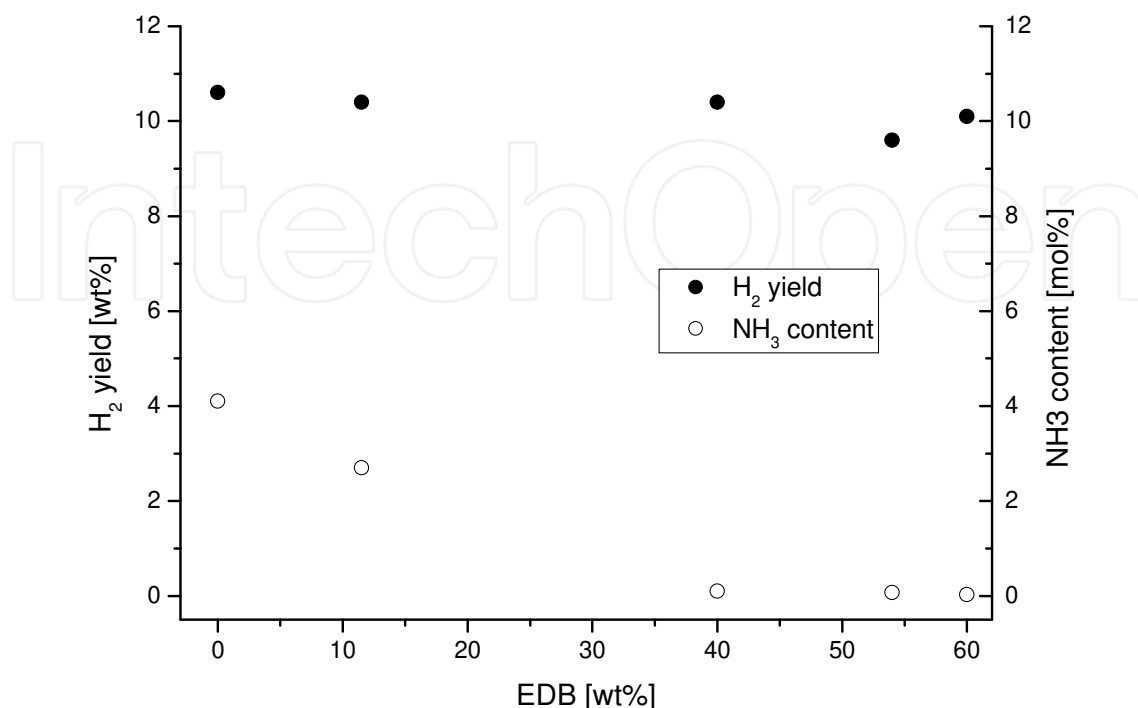


Figure 4. GBH-EDB Self-Sustaining-Thermal-Decomposition. Mixture containing 60 wt% EDB is not self-sustaining. (Groshens & Hollins, 2009)

In comparison to pure GBH, that decomposes with an impurity of ammonia of 4.1 mol% in the gas stream, resulting in a hydrogen yield of 10.6 wt%, the 40:60 wt% mixture of GBH and EDB releases 10.1 wt% of hydrogen with an impurity of ammonia as low as 0.026 mol%. The solid state of this material(-blend) is one major drawback.

The decomposition of pure EDB is comparably efficient to that of the blend mentioned above. (Neiner et al., 2011) The characteristics in decomposition are especially interesting due to the purity of released hydrogen without additives. No volatile by-products are released up to a temperature of 200 °C. In addition the decomposition achieves release rates comparable to AB.

1.2.3. Formic acid

In recent years catalytic splitting of formic acid into hydrogen and carbon dioxide has drawn some interest (Figure 4). (Boddien et al., 2011; Enthaler et al., 2010; Johnson et al., 2010; Scholten et al., 2010; Tedsree et al., 2011; Yasaka et al., 2010; Zhao et al., 2011)

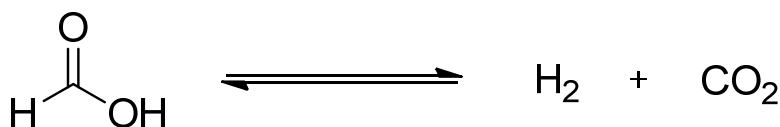


Figure 5. Reversible splitting of formic acid.

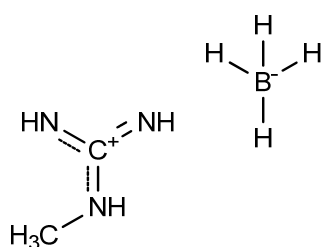
Though the hydrogen storage capacity of 4.4 wt% stays behind that of several other materials, the simplicity and wide availability of carbon dioxide as educt make formic acid attractive for hydrogen storage. In chemical means formic acid can be utilized as hydrogen source for catalytic hydrogenation reactions. (Blum et al., 1972; Bulushev & Ross, 2011; Kawasaki et al., 2005)

2. Ionic liquids in hydrogen storage systems

The unique physico-chemical properties of ILs make it possible to use them for different applications in hydrogen storage systems. The most simple one is to use a low molecular weight, hydrogen rich IL as hydrogen storage material. This approach has been realized in two different ways, which are presented below. Other possible applications are as inert solvent, as a catalytically active solvent, as a co-catalyst or as a stabilizing agent e.g. for nanoparticles, as presented afterwards.

2.1. ILs as hydrogen storage materials

Introducing one methyl group into a GBH molecule results in the first reported IL that can be efficiently dehydrogenated (Figure 6). (Doroodian et al., 2010)



Methylguanidinium Borohydride (Me-GBH)

Figure 6. Structure of methyl guanidinium borohydride.

Me-GBH has a storage capacity slightly reduced in comparison to GBH. Rieger and co-workers modified GBH by introducing a methyl group. As the methyl group lowers the cation's symmetry and, consequently, lowers the melting point, (Mateus et al., 2003) this salt is an IL, i.e. liquid below 100 °C. Furthermore with a melting point of -5 °C Me-GBH is the first room temperature IL that can be readily dehydrogenated with a reasonable gravimetric efficiency having a theoretical capacity of 9.0 wt%. Kinetic investigations by Rieger and co-workers about the thermal decomposition (75 °C) showed the decomposition of this material to be insufficiently slow and too inefficient for application. In the course of the decomposition some mass loss exceeding the theoretical capacity of the substrate is observed and consequently cannot be assigned to hydrogen evolution. Temperatures above 120 °C result in a detectable ammonia amount in the gas stream. The authors reported around 9 wt% hydrogen yield determined by TGA and volumetric quantification. The dehydrogenation product is solid and insoluble in the IL. To improve the rate and extent of hydrogen generation Wilkinson's catalyst ((PPh₃)₃RhCl) and FeCl₂ were employed with moderate success.

Initial attempts using an imidazolium IL containing a cyclohexyl moiety as hydrogen carrier were reported by Dupont and co-workers.(Stracke et al., 2007) This group used commercial palladium on charcoal catalyst and rather harsh conditions in the dehydrogenation/hydrogenation cycles. Despite the theoretical storage capacity of this system being insignificant, this was the first report of an IL being employed as hydrogen storage material. Chemically this procedure is based on the reversible dehydrogenation of a cyclohexyl group (Figure 7).

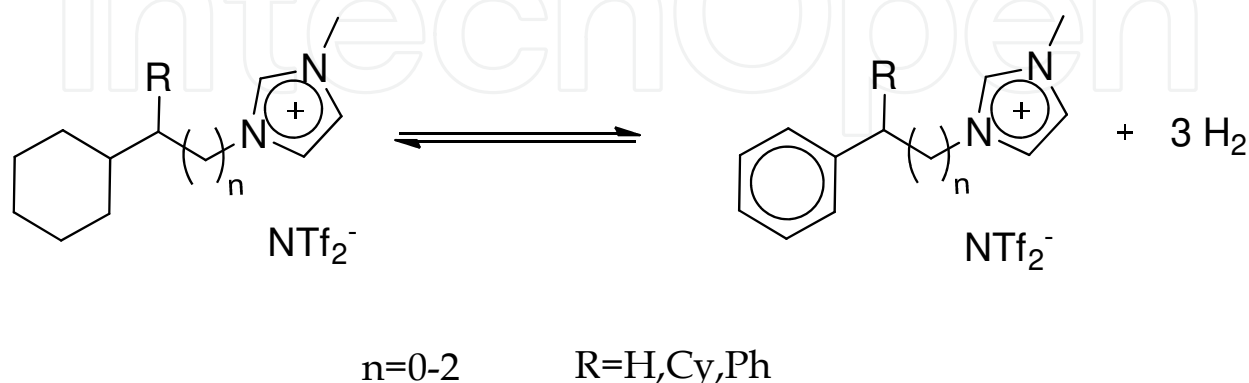


Figure 7. Structure of cyclohexyl-ILs for hydrogen storage by Dupont and co-workers.(Stracke et al., 2007)

The strong thermal stress (300 °C), required for fast dehydrogenation, and low weight efficiency are the most severe drawbacks of this system. The thermal stability of some of the employed ILs is remarkable.

2.2. ILs as stabilizing agents for nanoparticles for catalytic dehydrogenation

Dimethyl amine borane (DMAB) is another derivative of AB able to decompose releasing hydrogen. It has been studied for mechanistic investigations, since the two additional methyl groups inhibit further dehydrogenation after the first equivalent of hydrogen. The group of Manners investigated catalytic dehydrocoupling of different disubstituted amine boranes for the selective formation of cyclic dimers and trimers at ambient temperatures.(Jaska et al., 2003) These investigations were found to be important for mechanistic considerations in the dehydrogenation of amine boranes (see section 2.2.1). The dehydrogenation of DMAB proceeds via the diammoniate of diborane to the cyclic dimer.(Zahmakiran & Ozkar, 2009) The group of Özkar found DMAB to reduce the dimeric rhodium(II)-hexanoate to rhodium(0) forming Rh-clusters and dimethyl ammonium hexanoate (Figure 8).

The formed nanoclusters (~2 nm) were tested for catalytic activity in the dehydrogenation of dimethyl amine borane and found to be highly active. The *in-situ* generated IL dimethyl ammonium hexanoate was found to act as protecting agent for the nanoparticles.

2.3. ILs as active/supporting solvents

Another interesting option is the employment of an ionic liquid (IL) as active solvent supporting the dehydrogenation of AB.(Bluhm et al., 2006; Himmelberger et al., 2009)

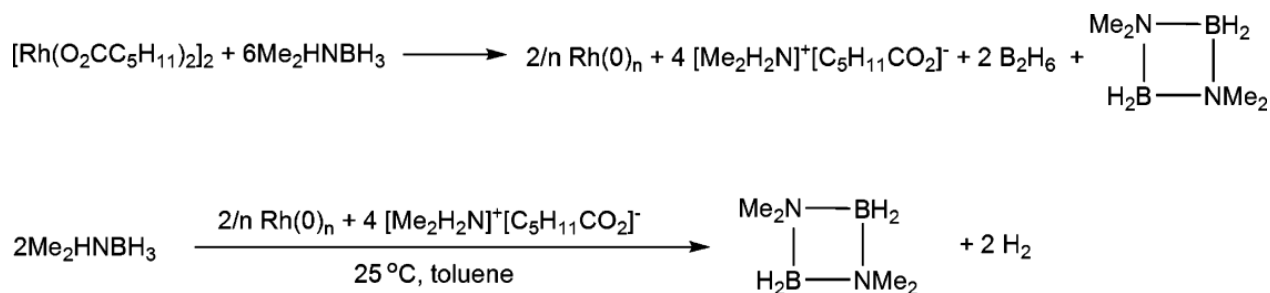


Figure 8. Rhodium nanoparticle formation and catalytic decomposition of dimethyl amine borane. Reprinted with permission from (Zahmakiran & Ozkar, 2009). Copyright (2009) American Chemical Society.

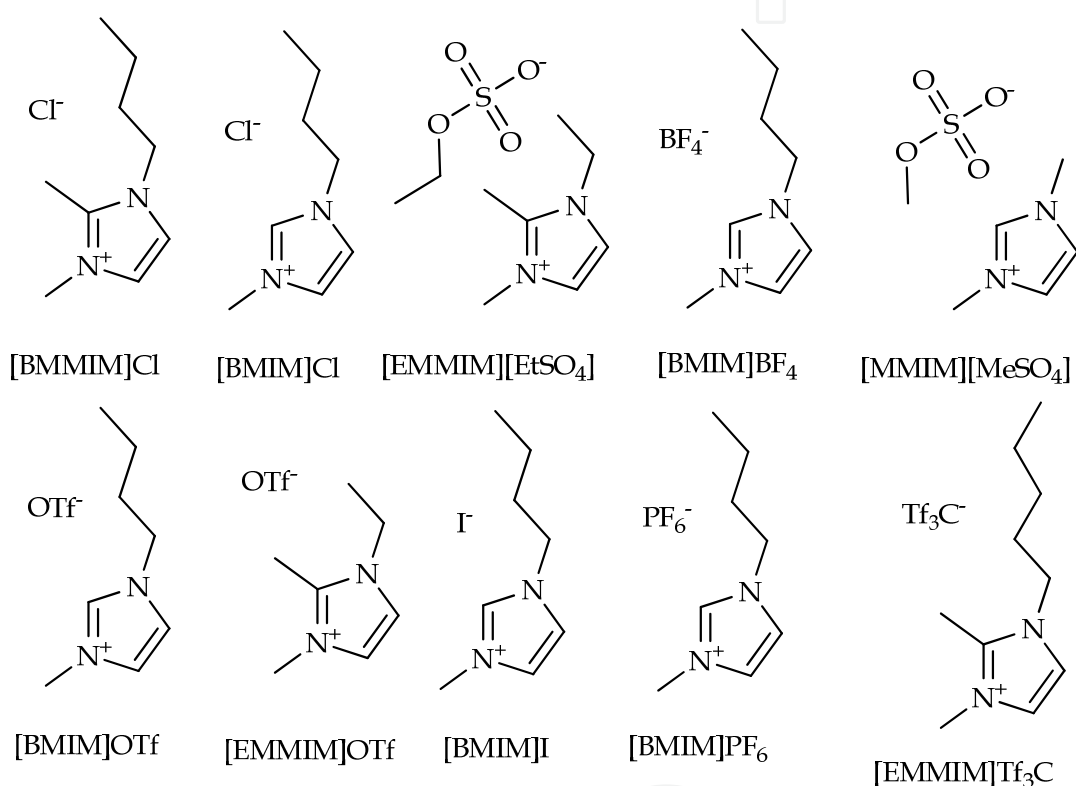


Figure 9. Structures of employed ILs by Sneddon and co-workers. (Himmelberger et al., 2009)

Figure 10 displays the hydrogen release results from Toepler pump measurements of the decomposition reactions of 50 wt% of AB in different ILs at 85 °C. Whereas the decomposition in pmmimTf₃C is comparable to the decomposition of neat AB (compare Figure 11(left)), every other tested IL improves the hydrogen yield significantly, though initial rates of hydrogen release do not relate strictly to the amount of overall released hydrogen.

Deeper investigations were conducted on the decomposition of AB in 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl). The application of this IL results in enhanced kinetics (Figure 11) and improved hydrogen yield. As shown in figure 11 (left) the hydrogen yield at a temperature as low as 85 °C can be more than doubled by addition of [BMIM]Cl implicating that a 50 wt% mixture of AB and [BMIM]Cl has a better weight-efficiency than pure AB.

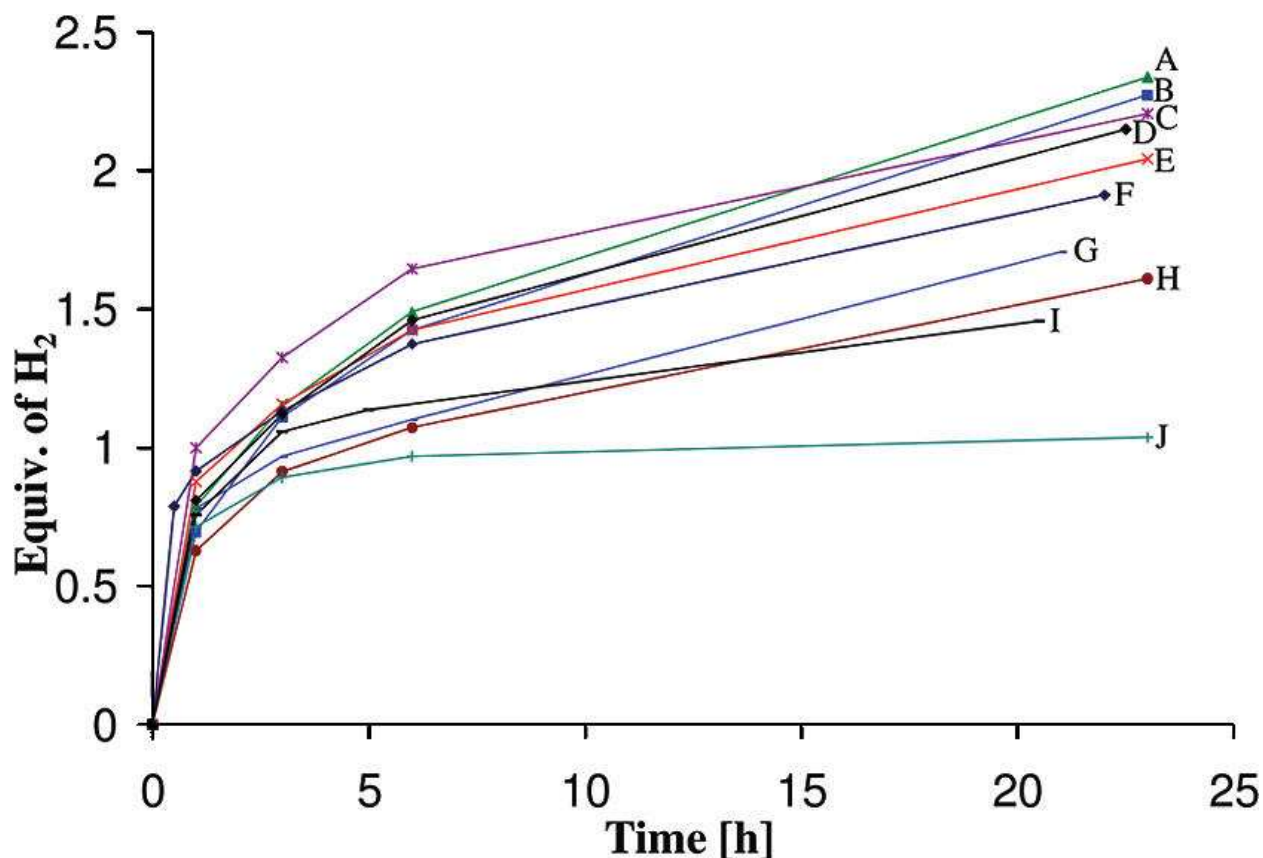


Figure 10. H₂-release measurements (Toepler pump) of the reaction of 50 wt% AB (250 mg) at 85 °C in 250 mg of (A) [BMMIM]Cl, (B) [BMIM]Cl, (C) [EMMIM][EtSO₄], (D) [BMIM]BF₄, (E) [MMIM][MeSO₄], (F) [BMIM]OTf, (G) [EMMIM]OTf, (H) [BMIM]I, (I) [BMIM]PF₆, and (J) [PMMIM]Tf₃C. Reprinted with permission from (Himmelberger et al., 2009). Copyright (2009) American Chemical Society.

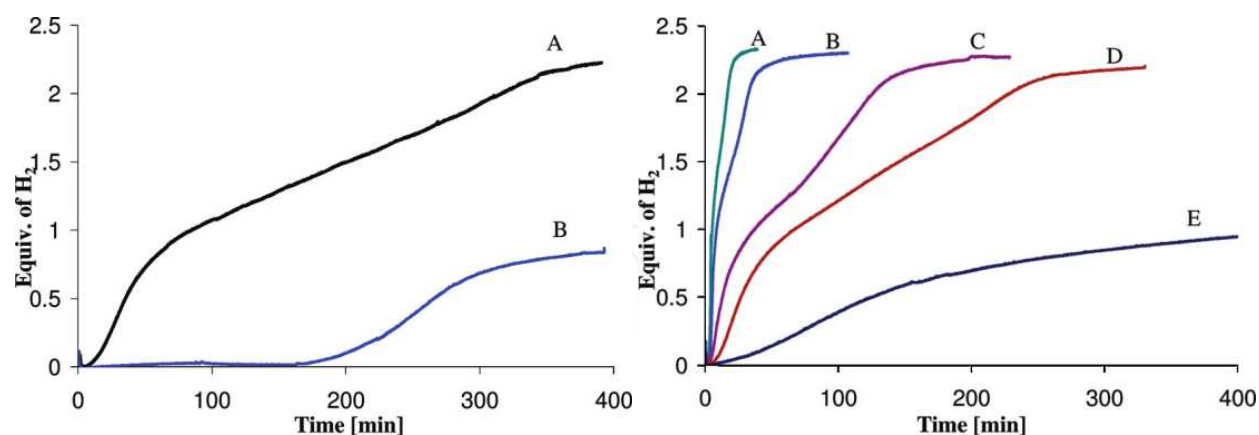


Figure 11. (Left) H₂-release measurements at 85 °C of: (A) 50-wt% AB in [BMIM]Cl and (B) solid-state AB (Right) H₂-release measurements of 50-wt % AB in [BMIM]Cl at (A) 110 °C, (B) 105 °C, (C) 95 °C, (D) 85 °C, and (E) 75 °C. Reprinted with permission from (Himmelberger et al., 2009). Copyright (2009) American Chemical Society.

Only trace amounts of volatile borazine are identified in the gas stream indicating that its formation is suppressed or borazine is soluted readily by the IL. As can be seen, the addition of [BMIM]Cl prevents induction times and promotes dehydrogenation. This effect persists,

if the amount of IL is reduced to 20 wt%. In direct comparison, the promoted dehydrogenation at 75 °C releases an equal amount of hydrogen as neat AB at 85 °C but without the induction time. An increase in temperature leads to a slight increase in quantity of hydrogen and an intense acceleration: The dehydrogenation at 85 °C results in a release of about 2.1 equivalents of hydrogen in 250 minutes and at 110 °C approximately 2.3 equivalents are released in less than 30 minutes.

2.4. ILs as solvents for catalytic AB dehydrogenation

Employing a metal complex as catalyst is an option to improve reaction kinetics and optimize low temperature application for the demands of hydrogen-storage materials for transportation applications.(Alcaraz & Sabo-Etienne, 2010; Jaska et al., 2003) This idea was combined with the idea of using ILs as supporting solvents. Sneddon and co-workers reported that ILs, loaded with different precious metal (Rh, Ru, Pd) or Ni-based pre-catalysts, decrease the onset temperature (45–85°C) of AB-decomposition significantly improving hydrogen yield at the same time (Figure 12).(Wright et al., 2011)

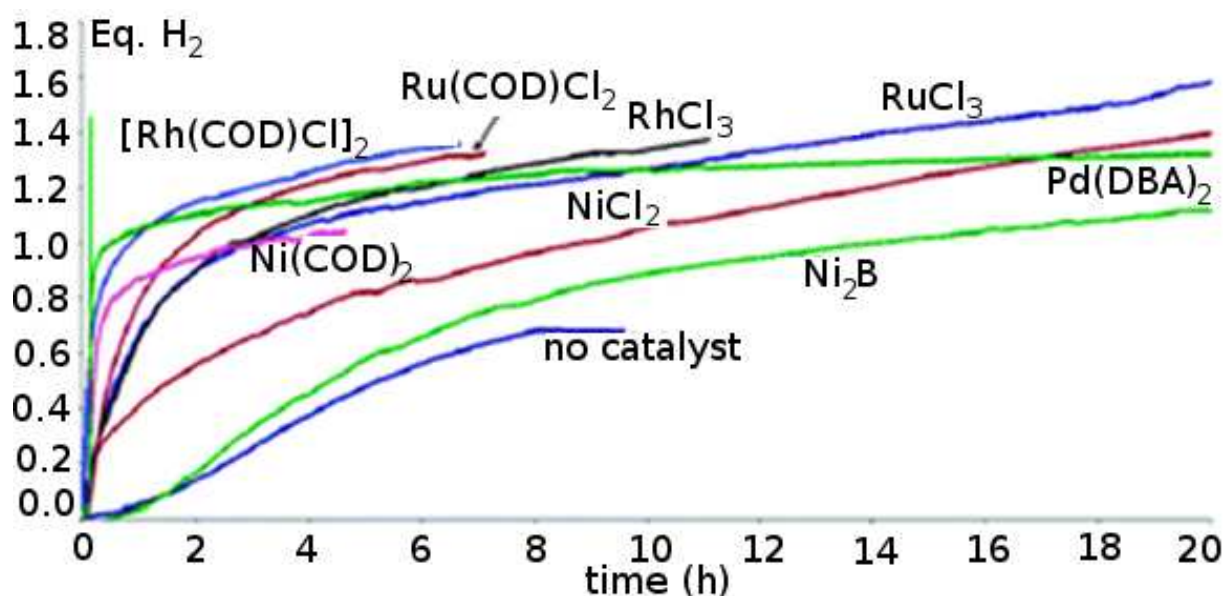


Figure 12. Hydrogen evolution from AB-decomposition at 65 °C catalyzed by different metal catalyst-precursors. Reproduced from (Wright et al., 2011) with permission of The Royal Society of Chemistry.

Though there were no deeper investigations concerning the active species, many of the precursors are known to form nanoparticles when being treated with a reducing agent.(Migowski & Dupont, 2007) This leads to the assumption that metal(0)-nanoparticles are involved in at least some of the catalyses. It is clearly visible that many of the employed precursors evoke a severe acceleration of hydrogen release as well as improving yield significantly as well. The shown results were obtained in experiments with 5 mol% of the respective catalyst.

In recent work Baker and co-workers employed another substrate blend for catalytic decomposition in IL.(Mal et al., 2011) The utilized mixture consisted of AB and sec-butyl

amine borane (SBAB). The decomposition of this blend in the IL 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) leaves only a solution of products behind. The formation of insoluble polyamino borane is effectively hindered. Instead the formation of the cyclic (formal trimeric) borazine derivative is observed (Figure 13).

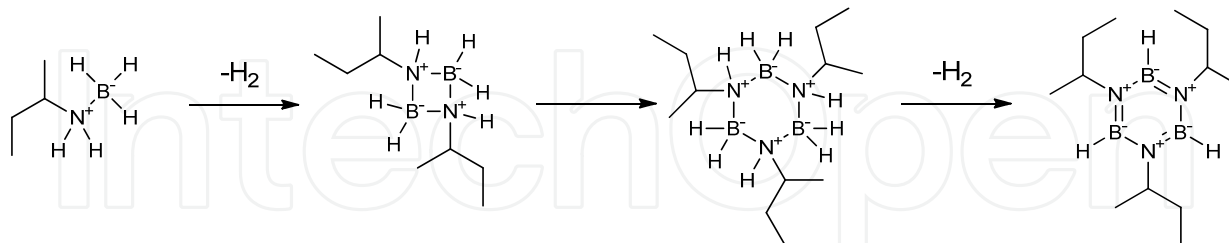


Figure 13. Observed decomposition products of SBAB decomposition. (Mal et al., 2011)

The alkyl group decreases the gravimetric efficiency to 5 wt%. This value was achieved by a metal catalyzed dehydrogenation reaction at 80 °C employing 1% RuCl₂(PMe₄)₃ as catalyst-precursor. Concerning the purity of the released hydrogen no investigations have been reported yet.

2.5. Functionalized ILs for catalytic decomposition of formic acid

A very interesting application of ILs is the utilization as solvent and base at the same time. In the decomposition of formic acid this can be realized by the employment of the amine-functionalized imidazolium-IL **1** (Figure 14). (Li et al., 2010; Scholten et al., 2010)

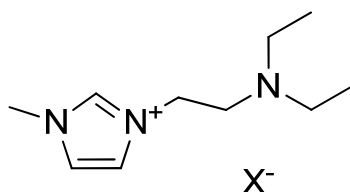


Figure 14. Structure of amino-functionalized IL **1**. (Li et al., 2010; Scholten et al., 2010)

While the Dupont group reported only about the application of the chloride IL **1**, the Shi-group used various anions, i.e. BF₄⁻, OTf⁻, NTf₂⁻ and HCOO⁻. Both groups used the catalyst (-precursor) [(p-Cymene)RuCl₂]₂, investigations of the Dupont group suggested the formation of hydrogen bridged and hydrogen/formate bridged Ru(p-Cymene)-Dimers. The group of Shi, Deng and co-workers reported varying TOFs up to 36 h⁻¹ without additional base and up to 627 h⁻¹ with additional base. The group of Dupont and co-workers reported TOFs of up to 1684 h⁻¹ without additional base.

In investigations of the Dupont group the amount of IL in the system seemed to play an important role, since after a required amount additional IL decreases the efficiency of the system remarkably. Addition of more formic acid proved the durability of this easy system in 6 recycling experiments. The high activity of the first run could not be sustained in subsequent runs. Nevertheless the slightly reduced activity remained constant for the subsequent runs except the 5th (Figure 15).

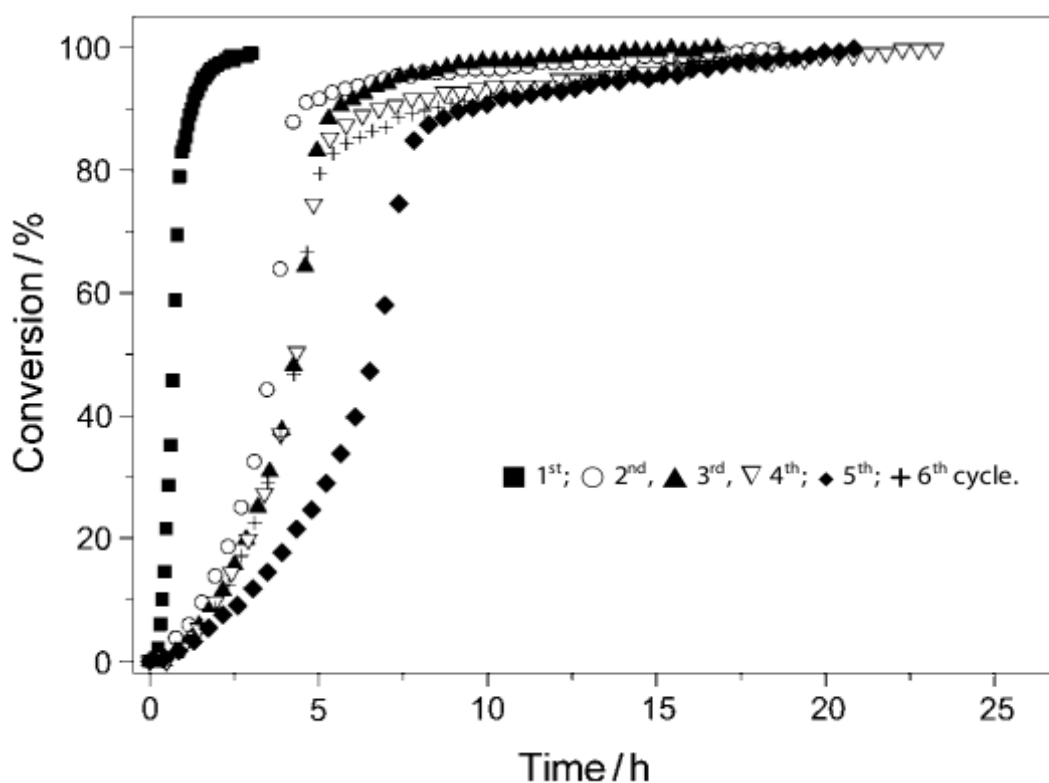


Figure 15. Reaction profiles for formic acid decomposition catalyzed by [(p-cymene)RuCl₂] in IL **1** (Cl⁻) at 80 °C for 6 cycles. Reprinted with permission from (Scholten et al., 2010). Copyright (2010) John Wiley and Sons.

The same catalyst (-precursor) was investigated in another context: The solubilization and decomposition of biomass especially cellulose-based ones. Different ILs can be employed to solvate the carbohydrate feedstock and the [(p-Cymene)RuCl₂]₂ complex (-precursor) is suitable for dehydrogenation. (Taccardi et al., 2010) Detailed investigations by Wasserscheid et al. showed that this reaction proceeds via the thermal decomposition of glucose to formic acid and subsequent catalytic decomposition of formic acid by the Ru complex. Some ILs, in this case for example 1-ethyl-3-methylimidazolium methyl-methylphosphonate, are able to solute wood. The soluted biomass can be thermally decomposed at 180 °C and the resulting formic acid can be split into hydrogen and CO₂ by the Ru-complex (Figure 16).

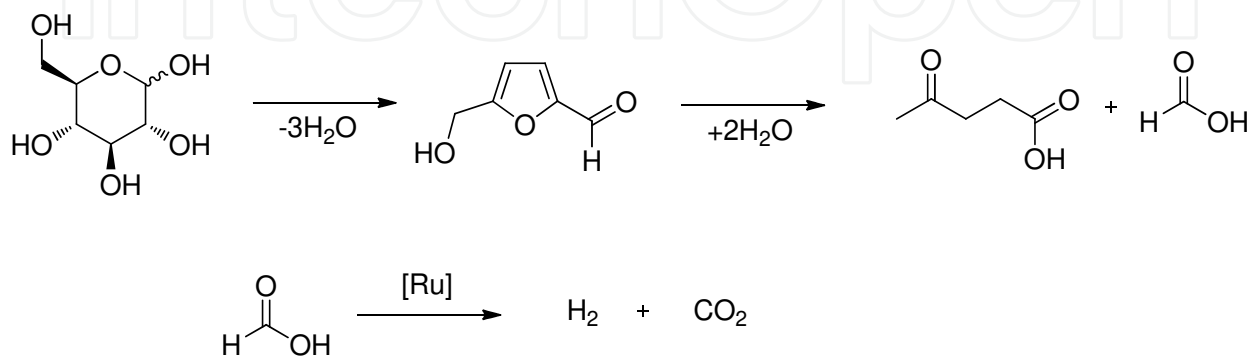


Figure 16. Thermal decomposition pathway of glucose and subsequent catalytic splitting of formic acid in IL. (Taccardi et al., 2010)

The thermal stability of the employed IL is remarkable and important in this application.

3. Conclusion and outlook

In the field of molecular hydrogen storage materials, ILs add interesting aspects in different meanings. Besides the application of ILs as (molecular) hydrogen storage materials, they can act in several other ways: They can be utilized as inert solvents, as solvents which support dehydrogenation, i.e. active solvents, as promoting agent/base or as a combination of these aspects. Especially the unique solubilization properties of ILs show considerable promise to find a liquid hydrogen storage system that remains liquid after dehydrogenation. One important aspect one has to keep in mind, when considering the application of ILs, is the addition of weight into the system, which, in general, lowers the gravimetric efficiency. This 'weight penalty' is the most severe drawback in the discussed applications of ILs.

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