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Mechanistic insights of metal acetylacetonate-aided dehydrocoupling of liquid-state ammonia borane NH_3BH_3

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Abstract. Ammonia borane NH_3BH_3 solubilized in organic solvent is a potential liquid-state chemical hydrogen storage material. In this study, metal acetylacetonates like $Fe(O_2C_5H_7)_3$, $Co(O_2C_5H_7)_2$, $Ni(O_2C_5H_7)_2$, $Pd(O_2C_5H_7)_2$, $Pt(O_2C_5H_7)_2$ and $Ru(O_2C_5H_7)_3$ are considered for assisting dehydrocoupling of ammonia borane in diglyme (0.135 M) at 50℃. The molar ratio between ammonia borane and metal acetylacetonate is fixed at 100. A protocol for the separation of the soluble and insoluble fractions present in the slurry is proposed; it consists in using acetonitrile to make the precipitation of metal-based compounds easier and to solubilize boron-based intermediates/products. The nature of the metal does not affect the dehydrocoupling mechanisms, the $^{11}B\{^1H\}$ NMR spectra showing the formation of the same reaction intermediates. The aforementioned metal acetylacetonates do mainly have effect on the kinetics of dehydrocoupling. Dehydrocoupling takes place heterogeneously and dehydrogenation of ammonia borane in these conditions leads to the formation of polyborazylene *via* intermediates like e.g., B-(cyclodiborazanyl) amine-borane and borazine. Our main results are reported and discussed herein.

Keywords: ammonia borane; dehydrocoupling; diglyme; metal acetylacetonate; thermolysis

1. Introduction

Ammonia borane NH_3BH_3 (30.87 g mol^{-1}) can be electronically compared to ethane CH_3CH_3 (30.07 g mol^{-1}) but the comparison ends there; these compounds have radically different physicochemical properties (Liu and Marder 2008). Ethane is gaseous in ambient conditions whereas ammonia borane is solid which opens up interesting application opportunities. Ammonia borane is indeed a promising chemical hydrogen storage material (Li *et al.* 2014). Another of its advantageous features is that it carries 19.6 wt% of hydrogen. Half of the hydrogen atoms are in protic form $H^{\delta+}$ (NH_3 group) and the other half are in hydridic form $H^{\delta-}$ (BH_3 moiety): for instance, Mulliken charges of +0.210 and −0.195 respectively were calculated (Palke 1972). By dint of these dissimilar hydrogen elements, there is intermolecular dihydrogen $N–H\cdots H–B$ bonding that rationalizes the solid state of the borane (Crabtree *et al.* 1996).

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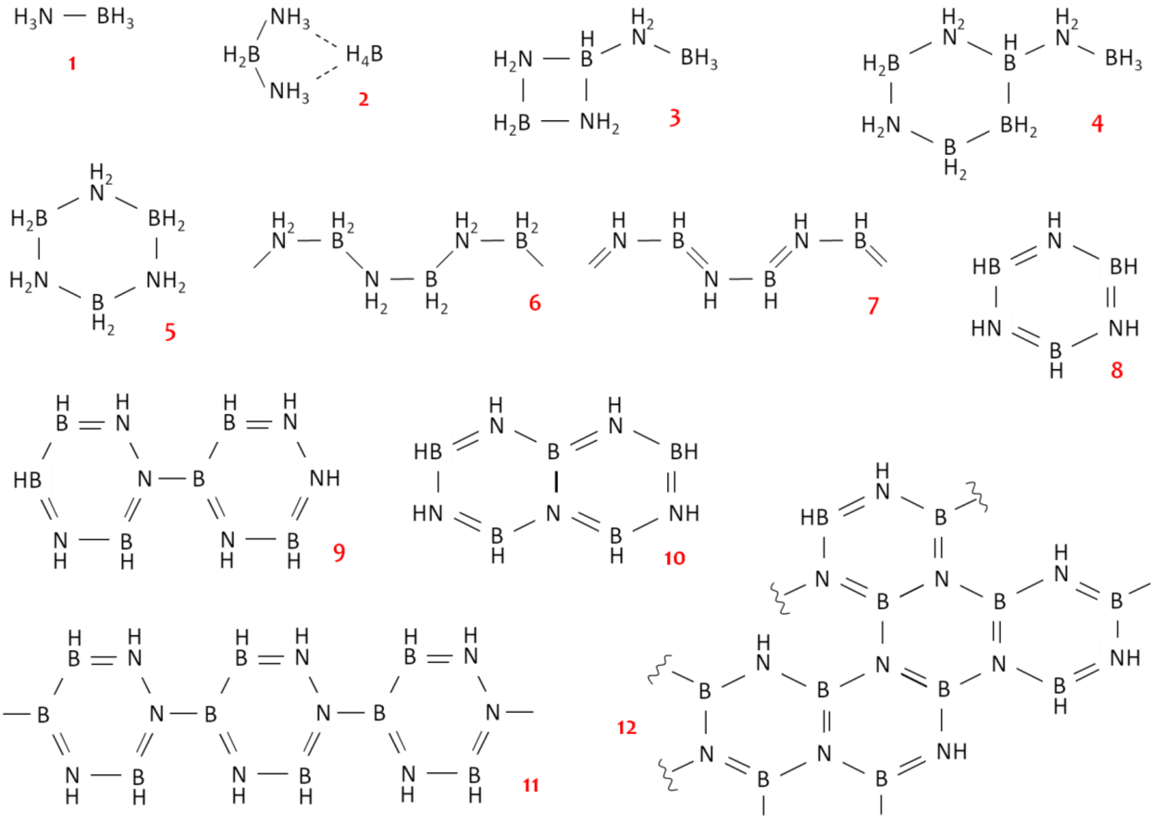


Fig. 1 B-N-H compounds: 1 as ammonia borane; 2 as diammoniate of diborane; 3 as B-(cyclodiborazanyl) amine-borane; 4 as B-(cyclotriborazanyl) amine-borane; 5 as cyclotriborazane; 6 as polyaminoborane; 7 as polyiminoborane; 8 as borazine; 9 as diborazine; 10 as borazanaphtalene; 11 as *o*-polyborazylene; and, 12 as graphitic cross-linked polyborazylene

The development of ammonia borane in the field of solid-state chemical hydrogen storage is however hindered by issues relating to thermolytic decomposition. Under heating (e.g., over the temperature range 80-200℃), ammonia borane decomposes more than it dehydrogenates; high amounts of undesired gaseous by-products (e.g., borazine, diborane and ammonia) are released along with two equivalents of hydrogen (Hu *et al.* 1978). Concomitantly, a solid residue of complex nature, with the empirical formula $[BNH_x]_n$ where $x<2$, forms; as suggested elsewhere (Summerscales and Gordon 2013), it is likely a mixture of polyaminoborane $[H_2N–BH_2]_n$, polyiminoborane $[HN=BH]_n$, *o*-polyborazylene $[B_3N_3H_4]_{n/3}$ and graphitic cross-linked polymer $[B_3N_3H_y]_{n/3}$ with $y<4$ (Fig. 1).

The aforementioned decomposition scheme is not acceptable from an application point of view. The temperatures are too high. Hydrogen is not pure. The solid residue cannot be totally and properly rehydrogenated by chemical recycling (Wang 2012). In this context, strategies of destabilization of ammonia borane have been investigated with the purposes of decreasing the dehydrogenation temperature below 100℃, releasing pure hydrogen (while avoiding any by-products), and forming a solid residue of simple composition, ideally that of polyborazylene. Indeed, polyborazylene can be effectively reduced to ammonia borane by hydrazine in ammonia medium (Sutton *et al.* 2011). To date, five different destabilization strategies have been reported: i.e., solubilization in organic solvent or in ionic liquid; solubilization and addition of homogeneous catalyst; doping with solid-state oxidant or acid; nanoconfinement into the porosity of a host material; chemical modification towards the formation of derivatives like alkali amidoboranes (e.g., $LiNH_2BH_3$). All showed positive results but they all have their advantages and drawbacks (Wang 2012, Moussa *et al.* 2013).

By solubilizing ammonia borane in a suitable solvent, the intermolecular dihydrogen N−H···H−B network is disrupted (Shaw *et al.* 2008). This results in the destabilization of ammonia borane allowing then dehydrocoupling and hydrogen evolution at temperatures lower than 100℃. For example, a triglyme (b.p. 216℃) solution of 6 M ammonia borane is able to generate one equivalent of hydrogen in less than 1 h at 70℃, and with no induction period (Kostka *et al.* 2012). The dehydrogenation kinetics can besides be improved by using metal-based catalyst. For example, ammonia borane (0.4 M) in toluene (b.p. 110.6℃) is able to release one equivalent of hydrogen in less than 1 h when catalyzed by homogeneous ruthenium acetylacetonate-based catalyst and kept at 60℃ (Duman and Özkar 2013). From a mechanistic point of view, cyclic intermediates with singly dehydrogenated boron atoms are supposed to form and to subsequently polymerize towards the formation of polyborazylene. Cyclic intermediates like B-(cyclodiborazanyl) amine-borane, B-(cyclotriborazanyl) amine-borane and cyclotriborazane (Fig. 1) were indeed reported (Al-Kukhun *et al.* 2013, Kalviri *et al.* 2015).

In the present work, we focused on the thermolytic behavior (dehydrocoupling) of ammonia borane solubilized in an organic solvent with high boiling point, i.e., diglyme $C_6H_{14}O_3$ (b.p. 162℃), and in the presence of various metal acetylacetonates. Note that ethers such as glymes and tetrahydrofuran are suitable solvents for ammonia borane and polyborazylene (Moussa *et al.* 2013, Fazen *et al.* 1995). The main motivation of the study was to isolate, analyze and identify the reaction intermediates at the beginning of the process. There were thus three aspects that were specifically regarded: (*i*) the development of a protocol for the separation of the soluble and insoluble constituents of the reaction slurry; (*ii*) the analysis and identification of the reaction intermediates forming upon dehydrocoupling at conversion rates lower than 30%; (*iii*) the screening of several metal acetylacetonates as possible dehydrocoupling catalysts. Our main results are reported in details hereafter.

2. Experimental

Ammonia borane NH_3BH_3 (purity>97%), anhydrous diglyme $C_6H_{14}O_3$, anhydrous acetonitrile CH_3CN and anhydrous tetrahydrofuran C_4H_8O were all from Sigma-Aldrich and were used as received. Six metal acetylacetonates were purchased: $Fe(O_2C_5H_7)_3$, $Co(O_2C_5H_7)_2$, $Ni(O_2C_5H_7)_2$, $Pd(O_2C_5H_7)_2$, $Pt(O_2C_5H_7)_2$, and $Ru(O_2C_5H_7)_3$. They were from Strem Chemicals and Acros Organics. To prevent these chemicals from air and moisture, they were stored and handled in an argon-filled glove box (MBraun M200B, O_2<0.1 ppm, H_2O<0.1 ppm).

The dehydrocoupling experiment was performed as follows. In the glove box, ammonia borane (50 mg) was transferred in a round bottom two-neck Schlenk flask, followed by a mass of the selected metal acetylacetonate. The mole ratio between ammonia borane and the metal was kept as 100 to have slow kinetics. The flask was extracted from the glove box and installed on one of the vacuum/argon lines. Under argon flow, 12 mL of diglyme were added with the help of a syringe. The mixture was stirred and the flask immersed in an oil bath kept at 50℃. Though the boiling

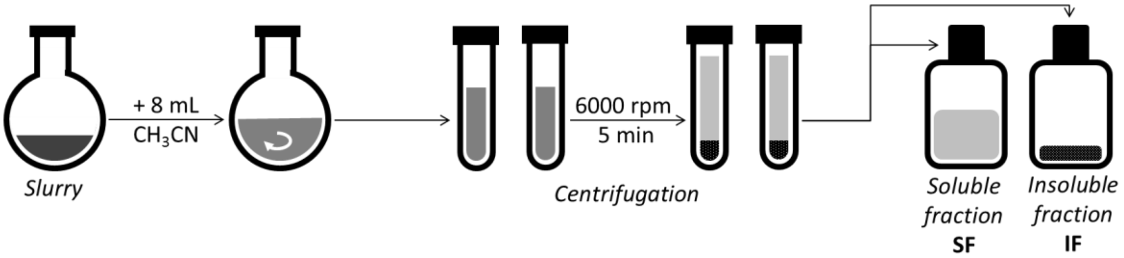


Fig. 2 Separation of the soluble (SF) and insoluble (IF) fractions of the slurry

point of diglyme is high (162°C), a condenser was used. The evolution of hydrogen was checked with the help of a bubbler located at the outlet of the condenser, which was therewith connected to an inverted burette. Dehydrocoupling was stopped upon the evolution of less than 0.3 equivalent of hydrogen (conversion rates lower than 30% assuming the release of one equivalent of hydrogen) in order to get and analyze the reaction intermediates at the early stages of the reaction. The as-obtained solution (consisting of diglyme, unreacted ammonia borane, reaction intermediates/products and catalyst) is called slurry herein. The slurry was then recovered and the soluble and insoluble fractions were separated. The separation procedure required optimization; more details are given in sub-section 3.1. The samples were finally analyzed by ^{11}B{^{1}H} nuclear magnetic resonance (NMR, Bruker AVANCE-300, 300.13 MHz, tetrahydrofuran-d8), and after solvent extraction, by Fourier transform infrared spectroscopy (FTIR, with attenuated total reflection sampling using a Nicolet 710 spectrometer, 32 scans and resolution of 4 cm^{-1}).

3. Results and discussion

3.1 Separation of the soluble and insoluble fractions

The separation of the soluble and insoluble fractions of the slurry after the dehydrocoupling experiments needed optimization. Centrifugation, which was done in the glove box to prevent the samples from oxidants, was inefficient for technical reasons. With our device, centrifugation is limited to 6000 rpm for 15-mL vials, and such a speed was not fast enough to make *in situ* forming black suspension precipitate. With smaller vials (1.5 mL), the centrifugation speed can be increased to 18000 rpm. However, despite a short centrifugation time (5 to 10 min), the vials heated. Heating was rather problematic because of the presence of unreacted ammonia borane that evolved (thermolytic dehydrogenation) with release of hydrogen and leading to opening of the vials. In some cases, heating was so high that melting of the vials occurred. Heating is mainly explained by exothermic decomposition of ammonia borane and atmosphere of argon which isobaric specific heat capacity is two times smaller than that of air.

Filtration in the glove box was tested in a second attempt. Syringe filters were specifically used. However, commercial filters (porosity 0.2 μm) were not efficient enough to trap the constituents of the black suspension. This approach was also not continued.

As alternative approach (Fig. 2), precipitation of the *in situ* forming black suspension was envisaged. Several organic solvents (acetonitrile, dicholoromethane, tetrahydrofuran and toluene) were used. Acetonitrile showed to be efficient in that. Typically, in the glove box, 8 mL of acetonitrile was added to the slurry and stirred. The mixture (20 mL) was transferred into two 15-mL vials and centrifuged at 6000 rpm for 5 min. This way, the soluble fraction was easily separated from the insoluble one. This procedure was then systematically applied. The samples are hereafter denoted SF-M with SF as soluble fraction and M as the metal of the metal acetylacetonate. The insoluble fraction was washed with tetrahydrofuran (10 mL) and, outside the glove box, the as-obtained sealed vial was ultrasonicated; this was done to solubilize any boron-containing solid that would have also precipitated. The samples are hereafter denoted IF-M with IF as insoluble fraction. The as-recovered black suspension was not analyzed because out of the scope of the present work.

With a view to implementation the procedure we optimized and reported above could be easily scaled up and applied for larger volumes of slurry recovered upon ammonia borane dehydrocoupling, provided recycling of the inorganic solvents is considered.

3.2 Screening of the metal acetylacetonates

Six metal acetylacetonates were selected as potential catalysts. The metals (M) were: iron, cobalt and nickel from the 3d row of the periodic table; nickel, palladium and platinum as metals with $n\mathrm{d}^8$ valence state (n=3, 4 and 5); and, ruthenium for comparison. Elsewhere, ruthenium acetylacetonate showed to be an efficient precursor of *in situ* forming homogeneous catalyst (not identified yet) for ammonia borane dehydrocoupling; the homogeneous character was unequivocally demonstrated with the help of the mercury poisoning test (Duman and Özkar 2013).

Palladium acetylacetonate was found to be much reactive towards ammonia borane, even in the glove box when both solids were put into contact without solvent. For evident safety reasons, palladium acetylacetonate withheld from the present study. Similar observations were reported for solid-state palladium chloride put into contact with ammonia borane (Toche *et al*. 2012).

The catalytic effect of the other metal acetylacetonates was compared by monitoring the hydrogen evolution with time (over a maximum of 2 hours). The main objective was to define the time at which the dehydrocoupling reaction could be stopped upon the evolution of less than 0.3 moles of hydrogen per mole of ammonia borane (conversion rates lower than 30%) to get and analyze the reaction intermediates at the early stages of the reaction. The hydrogen evolution curves are shown in Fig. 3. The most efficient metal acetylacetonate is $Ru(O_2C_5H_7)_3$ with the release of one equivalent of hydrogen in less than two hours. This is in good agreement with the results reported by Duman and Özkar (2013) where one equivalent of hydrogen was liberated in about 70 min at 60°C (mol ratio NH_3BH_3/Ru of 160). In our conditions, $Ru(O_2C_5H_7)_3$ is followed by far from $Pt(O_2C_5H_7)_2$ and then the other metal acetylacetonates. For the solution-state $^{11}B\{^1H\}$ NMR experiments, dehydrocoupling was thus stopped after 15 and 30 min of reaction for $Ru(O_2C_5H_7)_3$ and $Pt(O_2C_5H_7)_2$, and after 3 hours for the others.

3.3 Analyses of the insoluble fractions

The samples IF-Fe, IF-Co, IF-Ni, IF-Pt and IF-Ru were analyzed by solution-state $^{11}B\{^1H\}$ NMR (Fig. 4(a)). The spectra show a quartet of normalized intensity 1:2.6:2.6:1 centered at δ between −24 and −22 ppm (coupling constant $^1J_{B-H}$ of 96 Hz) that is typical of unreacted ammonia borane (Shaw *et al.* 2008). The quartets do not appear at the same chemical shift; this is explained by the likely presence of traces of metals which magnetic properties may lead to such shifts. An additional signal at δ between +19 and +21 ppm is observed. It might be attributed due to

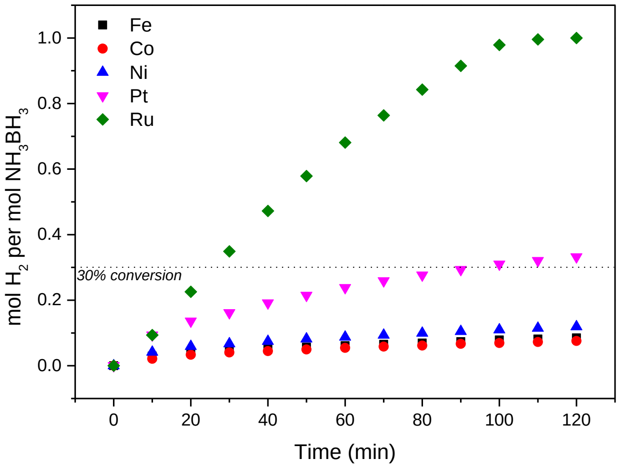


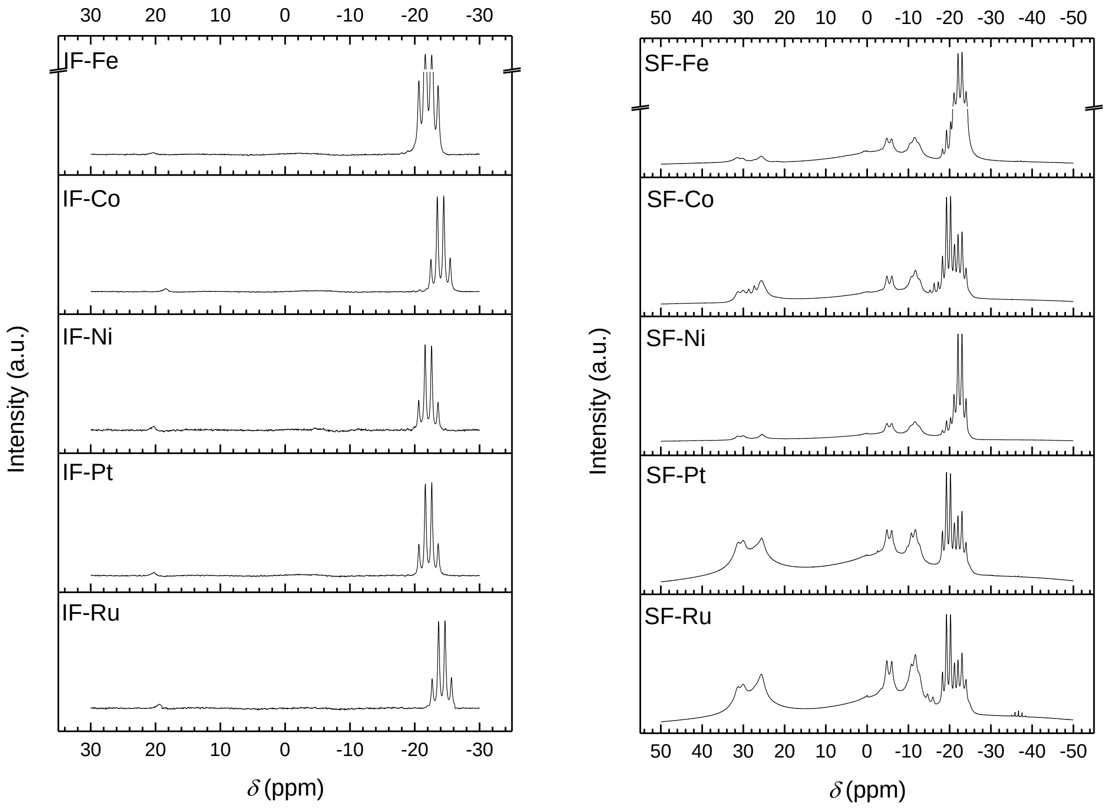
Fig. 3 Time evolution of hydrogen release by dehydrocoupling of ammonia borane (0.135 M) solubilized in diglyme, at 50°C and in the presence of metal acetylacetonate (mol ratio NH_3BH_3/M of 100; with M as Fe, Co, Ni, Pt or Ru for the metal of the acetylacetonate salts)

tetrahydrofuran-soluble polyborazylene (Fazen *et al.* 1995, Kalviri *et al.* 2015), though the chemical shift is generally reported at slightly higher values (*ca.* +25 ppm). From these results, two main observations stand out. First, a fraction of ammoniaborane has dehydrogenated in high extent towards the formation of polyborazylene, suggesting the generation of more than one mole of hydrogen per mole of ammonia borane. Second, the separation procedure is efficient in separating the metal-based compounds from the boron-based intermediates/products.

3.4 Analyses of the soluble fractions

The samples SF-Fe, SF-Co, SF-Ni, SF-Pt and SF-Ru were analyzed by solution-state $^{11}B\{^{1}H\}$ NMR (Fig. 4(b)). The spectra show several signals with different intensity from δ –28 ppm to δ +35 ppm, except for that of SF-Ru where an additional signal can be seen at δ –36.7 ppm. The spectra are quite similar, showing overall the same signals. In Fig. 5 is reproduced the magnified spectrum of SF-Ru where the signals are ascribed to the molecules presented in Fig. 1. The attribution was performed with the help of previous NMR-dedicated works (Wang and Geanangel 1988, Baker *et al.* 2012, Erickson *et al* 2015, Glüer *et al.* 2015, Kalviri *et al.* 2015, Zhao *et al.* 2015).

The spectrum of SF-Ru is characterized by two overlapping quartets for δ from –28 to –17 ppm. They are likely followed by a quartet centered at around δ –15 ppm. They are attributed to $–BH_3$ environments like those found in ammonia borane, B-(cyclodiborazanyl) amine-borane and B-(cyclotriborazanyl) amine-borane. At more negative chemical shifts (δ –36.7 ppm), there is a quintet of small intensity (coupling constant $^{1}J_{B–H}$ of 65 Hz); it is generally observed for the anion BH_4^- of the intermediate diammoniate of diborane $[H_2B(NH_3)_2][BH_4]$. At δ –11.5 ppm, there is a triplet ascribed to the N_2BH_2 environment of cyclotriborazane and the aforementioned cyclic compounds. The doublet at δ –5.3 ppm is due to N_3BH of B-(cyclodiborazanyl) amine-borane and B-(cyclotriborazanyl) amine-borane. Finally, three signals at positive chemical shifts are found at δ



(a) Spectra of IF-Fe, IF-Co, IF-Ni, IF-Pt, IF-Ru (b) Spectra of SF-Fe, SF-Co, SF-Ni, SF-Pt, SF-Ru

Fig. 4 Solution-state $^{11}B\{^1H\}$ NMR spectra; for clarity, the *y* axis of the spectrum of SF-Fe is broken

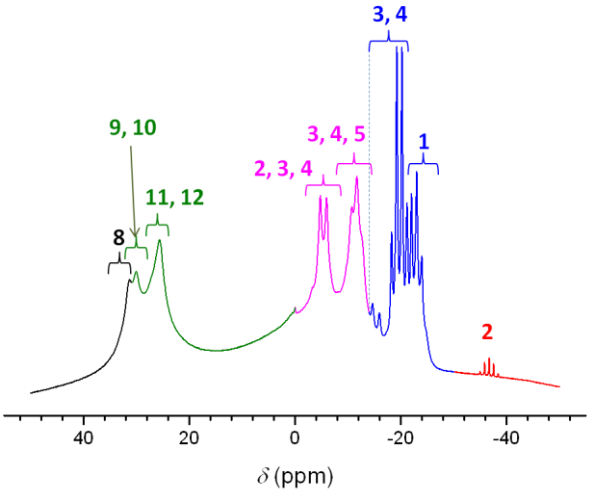


Fig. 5 Identification of the reactions intermediates/products (Fig. 1) on the basis of the spectrum of SF-Ru

+25.5, +30 and +31.3 ppm. They can be ascribed to polyborazylene, a dimer of borazine (diborazine or borazanaphtalene) and borazine respectively.

The spectrum of SF-Co (Fig. 4(b)) shows additional signals between δ+25 and +35, maybe due to a more complex composition in terms of borazine, diborazine, borazanaphtalene and polyborazylene. With respect to SF-Fe, SF-Ni and SF-Pt, the spectra do not show the quartet at δ −15 ppm. Otherwise, they resemble that of SF-Ru.

In our conditions, the composition of the soluble fractions appears to be roughly independent of the nature of the metal acetylacetonate (). The soluble fractions consist of singly dehydrogenated intermediates like B-(cyclodiborazanyl) amine-borane and/or B-(cyclotriborazanyl) amine-borane, and twice and more dehydrogenated products like borazine, dimer(s) of borazine and polyborazylene. Borazine and derivatives as well as polyborazylene are generally reported as dehydrogenation products of B-(cyclodiborazanyl) amine-borane and/or B-(cyclotriborazanyl) amine-borane (Al-Kukhun *et al.* 2013).

The samples SF-Fe, SF-Co, SF-Ni, SF-Pt and SF-Ru were subjected to solvent extraction (under vacuum) and drying 18 h under dynamic vacuum to be analyzed by FTIR. The spectra were found to be typical of dehydrogenated ammonia borane. They are not reported herein being similar to and characteristic of spectra reported elsewhere (Toche *et al.* 2012, Al-Kukhun *et al.* 2013, Duman and Ö zkar 2013). It was observed broadened signals due to the following modes, i.e., N–H stretching (3600-3000 cm^{-1}), B–H stretching (2600-2000 cm^{-1}), N–H deformation (1700-1300 cm^{-1}), B–H deformation (1300-1000 cm^{-1}) and B–N stretching (900-600 cm^{-1}).

Our results are in accord with the dehydrogenation scheme summarized in Fig. 6. Dehydrogenation of ammonia borane in diglyme is stepwise, with the first step being dehydrocoupling of three molecules towards the formation of B-(cyclodiborazanyl) amine-borane and/or cyclotriborazane. By reaction with another ammonia borane molecule, the cyclic intermediate B-(cyclotriborazanyl) amine-borane forms. Through further dehydrogenation, with evolution of two or three moles of hydrogen depending on the intermediate, borazine forms and is believed to dehydropolymerize into polyborazylene compounds *via* dimers and other oligomers.

Important information stemming from the solution-state $^{11}B\{^1H\}$ NMR spectra of SF-Fe, SF-Co, SF-Ni, SF-Pt and SF-Ru is that, in our conditions, the mechanisms of ammonia borane dehydrocoupling seems to be roughly independent on the metal nature. The catalysts have mainly an effect on the reaction kinetics only (Fig. 3).

Formations of borazine and afterwards of polyborazylene imply evolution of two and more than two moles of hydrogen per mole of ammonia borane, respectively. Therefore, the presence of borazine and polyborazylene in the soluble fractions (i.e., for conversions lower than 30%) indicates that dehydrocoupling takes place heterogeneously: one part of ammonia borane dehydrogenates in high extent whereas the other part remains unreacted. This may be explained by the limited number of catalytic sites. Homogeneous dehydrocoupling would require one catalytic site for three ammonia borane molecules if the formation of the “trimers” B-(cyclodiborazanyl) amine-borane, cyclotriborazane and borazine are taken into account.

5. Conclusions

The use of metal acetylacetonates (i.e., $Fe(O_2C_5H_7)_3$, $Co(O_2C_5H_7)_2$, $Ni(O_2C_5H_7)_2$, $Pd(O_2C_5H_7)_2$, $Pt(O_2C_5H_7)_2$ and $Ru(O_2C_5H_7)_3$) to assist thermolytic dehydrocoupling (50℃) of ammonia borane solubilized in diglyme (0.135 M) has been proposed in this study:

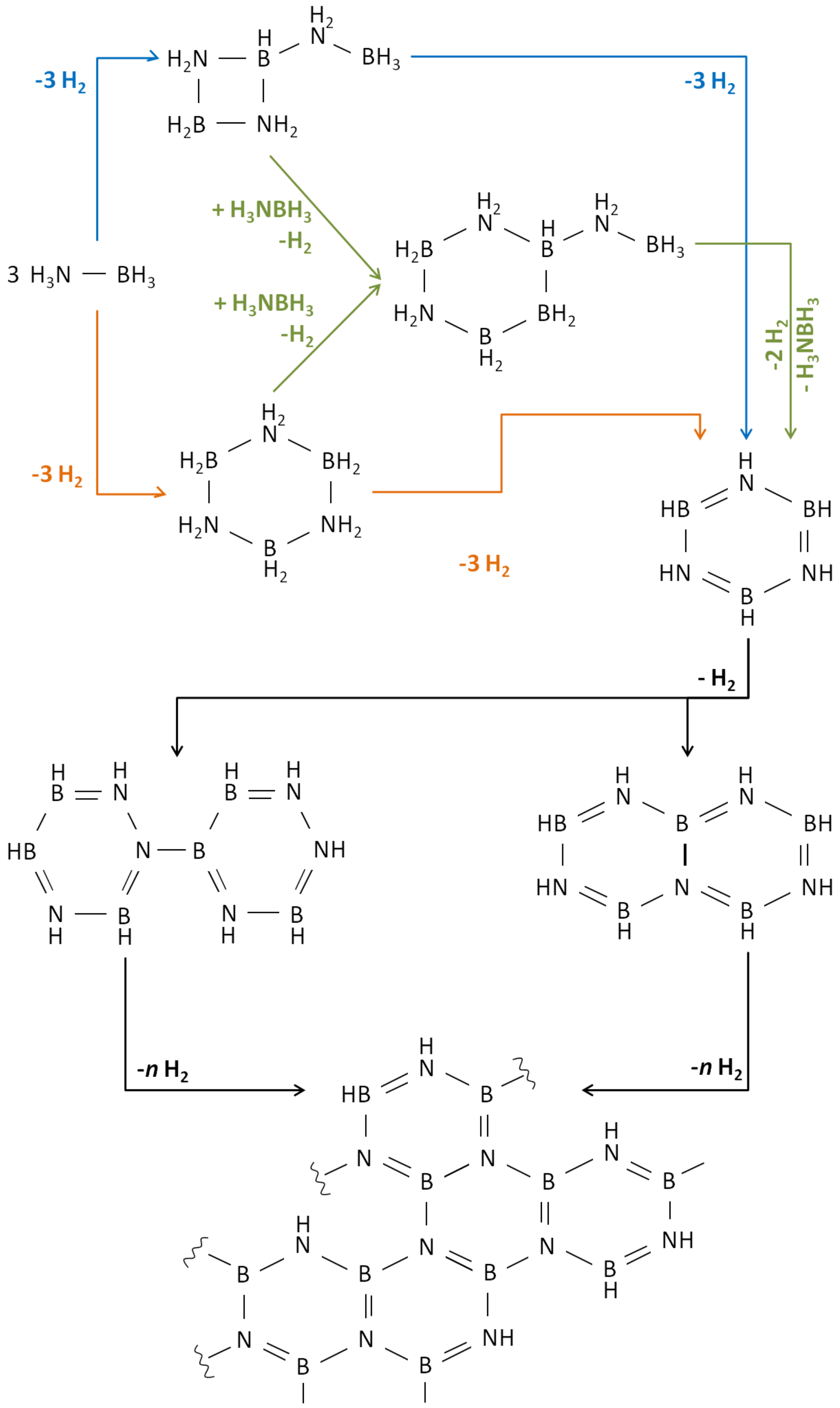


Fig. 6 Mechanisms of dehydrocoupling for ammonia borane in solution in diglyme

- Palladium acetylacetonate readily reacts with ammonia borane, even when mixed together in solid state in the argon filled glove box. Such reactivity makes it unsuitable for dehydrogenation of ammonia borane.
- A protocol for the separation of the soluble and insoluble fractions after dehydrocoupling was proposed. Acetonitrile is used to precipitate the metal-containing fraction and by centrifugation the soluble boron-based compounds are separated.
- The mechanisms of ammonia borane dehydrocoupling are roughly independent on the metal nature of the acetylacetonate salts. The same reaction intermediates and products were observed by NMR. Metal acetylacetonates catalyze ammonia borane dehydrocoupling by accelerating the reaction; they mainly have effect on the kinetics.
- Ammonia borane in diglyme dehydrogenates and polymerizes towards the formation of polyborazylene, *via* intermediates like B-(cyclodiborazanyl) amine-borane, B-(cyclotriborazanyl) amine-borane), cyclotriborazane, borazine and dimers of borazine.
- Dehydrocoupling takes place heterogeneously, one part of ammonia borane dehydrogenating, the other part remaining unreacted. This is due to the limited number of catalytic sites, that is, 1 for 100 molecules of the borane in our conditions.

Further works are required, especially focusing on catalyst with the target of fully converting ammonia borane to polyborazylene, which is a recyclable product. Closing the hydrogen cycle with ammonia borane is strictly required to take the next step, that of scale-up. Another field could have interest in such easy production of polyborazylene, since this polymeric material is a precursor of boron nitride-based ceramics (Fazen *et al.* 1995).

Acknowledgments

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References

Al-Kukhun, A., Hwang, H.T. and Varma, A. (2013), “Mechanistic studies of ammonia borane dehydrogenation”, *Int. J. Hydrogen Energy*, **38**, 169-179.

Baker, R.T., Gordon, J.C., Hamilton, C.W., Henson, N.J., Lin, P.H., Maguire, S., Muriguesu, M., Scott, B.L. and Smythe, N.C. (2012), “Iron complex-catalyzed ammonia-borane dehydrogenation. A potential route toward B–N-containing polymer motifs using earth-abundant metal catalysts”, *J. Am. Chem. Soc.*, **134**, 5598-5609.

Crabtree, R.H., Siegbahn, P.E.M., Eisenstein, O., Rheinhold, A.L. and Koetzle, T.F. (1996), “A new intermolecular interaction: unconventional hydrogen bonds with element-hydride bonds as proton acceptor”, *Acc. Chem. Res.*, **29**, 348-354.

Duman, S. and Ö zkar, S. (2013), “Hydrogen generation from the dehydrogenation of ammonia-borane in the presence of ruthenium (III) acetylacetonate forming a homogeneous catalyst”, *Int. J. Hydrogen Energy*, **38**, 180-187.

Erickson, K.A., Stelmach, J.P.W., Mucha, N.T. and Waterman, R. (2015), “Zirconium-catalyzed amine borane dehydrocoupling and transfer hydrogenation”, *Organometall.*, **34**, 4693-4699.

Fazen, P.J., Remsen, E.E., Beck, J.S., Carroll, P.J., McGhie, A.R. and Sneddon, L.G. (1995), “Synthesis, properties and ceramic conversion reactions of polyborazylene. A high-yield polymeric precursor to boron nitride", *Chem. Mater.*, **7**, 1972-1956.

Glüer, A., Förster, M., Celinski, V.R., der Günne, J.S., Holthausen, M.C. and Schneider, S. (2015), "Highly active iron catalyst for ammonia borane dehydrocoupling at room temperature", *ACS Catal.*, **5**, 7214-7217.

Hu, M.G., Geanangel, R.A. and Wendlandt, W.W. (1978), "The thermal decomposition of ammonia borane", *Thermochim. Acta*, **23**, 249-255.

Kalviri, H.A., Gärtner, F., Ye, G., Korobkov, I. and Baker, R.T. (2015), "Probing the second dehydrogenation step in ammonia-borane dehydrocoupling: characterization and reactivity of the key intermediate, B-(cyclotriborazanyl)amine-borane", *Chem. Sci.*, **6**, 618-624.

Kostka, J.F., Schellenberg, R., Baitalow, F., Smolinka, T. and Mertens, F. (2012), "Concentration-dependent dehydrogenation of ammonia-borane/triglyme mixtures", *Eur. J. Inorg. Chem.*, **2012**, 49-54.

Li, H., Yang, Q., Chen, X. and Shore, S.G. (2014), "Ammonia borane, past as prolog", *J. Organomet. Chem.*, **751**, 60-66.

Liu, Z. and Marder, T.B. (2008), "B−N versus C−C: how similar are they?", *Angew. Chem. Int. Ed.*, **47**, 242-244.

Moussa, G., Moury, R., Demirci, U.B., Şener, T. and Miele, P. (2013), "Boron-based hydrides for chemical hydrogen storage", *Int. J. Energy Res.*, **37**, 825-842.

Palke, W.E. (1972), "Calculation of the internal rotation barrier and its derivative in BH_3NH_3", *J. Chem. Phys.*, **56**, 5308-5312.

Shaw, W.J., Linehan, J.C., Szymczak, N., Heldebrant, N.J., Yonker, C., Camaioni, D.M., Baker, R.T. and Autrey, T. (2008), "In situ multinuclear NMR spectroscopic studies of the thermal decomposition of ammonia borane in solution", *Angew. Chem. Int. Ed.*, **47**, 7493-7496.

Summerscales, O.T. and Gordon, J.C. (2013), "Regeneration of ammonia borane from spent fuel", *Dalton Trans.*, **42**, 10075-10084.

Sutton, A.D., Burrell, A.K., Dixon, D.A., Garner III, E.B., Gordon, J.C., Nakagawa, T., Ott, K.C., Robinson, J.P. and Vasiliu, M. (2011), "Regeneration of ammonia borane spent fuel by direct reaction with hydrazine and liquid ammonia", *Science*, **331**, 1426-1429.

Toche, F., Chiriac, R., Demirci, U.B. and Miele, P. (2012), "Ammonia borane thermolytic decomposition in the presence of metal (II) chlorides", *Int. J. Hydrogen Energy*, **37**, 6749-6755.

Wang, J.S. and Geanangel, R.A. (1988), "^{11}B NMR studies of the thermal decomposition of ammonia-borane in solution", *Inorg. Chim. Acta*, **148**, 185-190.

Wang, P. (2012), "Solid-state thermolysis of ammonia borane and related materials for high-capacity hydrogen storage", *Dalton Trans.*, **41**, 4296-4302.

Zhao, Q., Li, J., Hamilton, E.J.M. and Chen, X. (2015), "The continuing story of the diammoniate of diborane", *J. Organometall. Chem.*, **798**, 24-29.

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