

Catalytic dehydrogenation of hydrazine borane in aqueous solution

*Jean-Fabien Petit¹⁾, Çetin Çakanyıldırım²⁾, Umit B. Demirci³⁾, and Philippe Miele⁴⁾

IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM2), Université Montpellier 2, Place E. Bataillon, F- 34095, Montpellier, France

¹⁾ jean-fabien.petit@etud.univ-montp2.fr

ABSTRACT

In the field of chemical hydrogen storage, boron- and nitrogen-based materials have shown to be promising hydrogen-carriers owing to high gravimetric hydrogen densities. Recently emerged a novel material; it is hydrazine borane $N_2H_4BH_3$ with a gravimetric hydrogen density of 15.4 wt%. The present work focused on this material and particularly on its dehydrogenation in hydrolytic conditions. The challenge has been to search for a bimetallic catalyst that is able to dehydrogenate both the BH_3 and N_2H_4 groups of hydrazine borane in mild conditions. We therefore report the successful preparation and use of the bimetallic NiAg. This catalyst is able to totally hydrolyze the BH_3 group and then dehydrogenate the N_2H_4 moiety with a H_2 selectivity of almost 100%. This is the best performance we have ever obtained and reported.

1. INTRODUCTION

The attractiveness of the boron-nitrogen complexes in chemical hydrogen storage, especially the amine-boranes like ammonia borane NH_3BH_3 and hydrazine borane $N_2H_4BH_3$, lies into 3 main factors (Hamilton 2009): (i) boron and nitrogen are light elements, which is of high importance for the gravimetric hydrogen storage capacity of the compound; (ii) each of the atoms is able to bind 2/3 hydrogen elements; (iv) the B–H and N–H bonds are, respectively, hydridic $H^{\delta-}$ and protic $H^{\delta+}$, which may interact each other under heating to liberate H_2 (Moussa 2013).

With a gravimetric hydrogen density of 19.6 wt%, ammonia borane NH_3BH_3 has shown to be a promising candidate for chemical hydrogen storage. Its dehydrogenation by thermolysis or hydrolysis has been investigated. Nevertheless, the latter reaction has shown limitations (Ramachandran 2007), the most important one being the

¹⁾ Graduate student

²⁾ Assoc. Professor

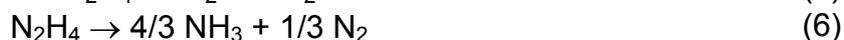
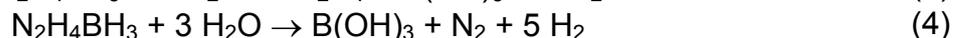
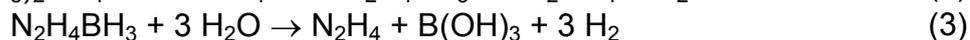
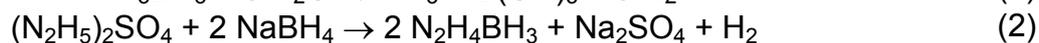
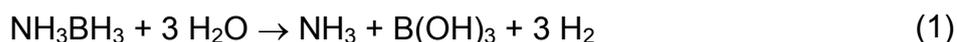
³⁾ Assoc. Professor

⁴⁾ Professor

evolution of unwanted ammonia NH_3 (Eq. 1).

Because the presence of NH_3 is detrimental to the purity of the generated hydrogen – the purity of H_2 is of importance for the fuel cell applications –, few strategies have been developed to address the issue (Sanyal 2011). The solution we have proposed is to replace the NH_3 moiety of NH_3BH_3 by another N-containing group, that is, hydrazine N_2H_4 . Accordingly, we synthesized hydrazine borane $\text{N}_2\text{H}_4\text{BH}_3$ (Goubeau 1961, Moury 2012) by salt metathesis (Eq. 2).

Hydrazine borane (denoted HB) is an attractive hydrogen storage material for several reasons, the most 3 important being as follows. First, it has a high gravimetric hydrogen density with 15.4 wt%. Second, its hydrolysis (Eq. 3) in the presence of a transition/noble metal-based catalyst does not lead to the formation of the unwanted NH_3 , while the free N_2H_4 remains in solution (Karahan 2011). Third, the N_2H_4 moiety can be dehydrogenated (Eq. 4) in the presence of an active and selective heterogeneous catalyst (Hannauer 2011, Çakanyıldırım 2013). Currently, we focus on this third aspect. However, the task is difficult as N_2H_4 is known to decompose according to 2 parallel paths as shown by Eq. 5 and Eq. 6; the latter reaction is unwanted.



In the present work, we report our last results on the preparation and catalytic characterization of a nickel-based bimetallic catalyst for the dehydrogenation of HB. The presence of a second metal, like silver in the present case, is crucial to make the catalyst active and selective in the dehydrogenation of the N_2H_4 moiety. Herein we show that, with NiAg as catalyst, almost 5 mol H_2 + 1 mol N_2 per mol HB can be liberated at 50 °C in a 2-step reaction involving first the hydrolysis of the BH_3 moiety of HB and second the dehydrogenation of the N_2H_4 group.

2. EXPERIMENTAL

The synthesis of HB is described in details elsewhere (Moury 2011). The synthesis of the NiAg catalyst was as follows. It was performed using a hexadecyltrimethylammonium bromide-aided (CTAB, $\text{CH}_3(\text{CH}_2)_{15}\text{N}(\text{Br})(\text{CH}_3)_3$, $\geq 98\%$, Sigma-Aldrich) co-reduction method (Singh 2010). An aqueous solution of nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\geq 99.999\%$, 243 mg), silver nitrate (AgNO_3 , $\geq 99.99\%$, 63 mg) and CTAB (0.210 g, 0.576 mmol) was prepared by dissolution, subsequent sonication, and 5-min stirring. Because AgNO_3 is light-sensitive, the preparation of the solutions was performed in a dark room. Millipore milli-q water with a resistivity $> 18 \text{ M}\Omega \text{ cm}$ was used. To this solution was then added dropwise 2 mL of

aqueous solution of NaBH₄ (0.4 g) stabilized by NaOH (0.5 M). Upon this operation, the solution was vigorously shaken for 2 min, resulting in the formation of a black suspension consisting of NiAg with 40 wt% of Ag. The slurry was maintained under stirring for 1 h under argon flow. Then, it was centrifugated for 10 min at 11000 rpm. The supernatant was removed. The catalyst was dried at 80 °C for 15 min, grinded in an agate mortar under argon, and stored in an argon-filled glove box to be next used as catalyst. The as-obtained catalyst was characterized by EDX, XRD and TEM.

A typical dehydrogenation experiment is as follows. The NiAg catalyst (20 mg) is introduced into the reactor, which consists in a 100 mL round-bottom flask sealed with a silicon septum. The reactor is placed in a water bath kept at 50°C and connected to a water-filled inverted burette. A cold trap kept at 0°C is placed before the burette to condensate H₂O in gaseous state. Should some NH₃ (formed by decomposition of the N₂H₄ group) evolve, a trap filled with an acidic solution (HCl, 0.1 M) is placed between the reactor and the cold trap. Then, the HB solution (50 mg in 4.5 mL) is injected in the reactor. The catalytic reaction starts and the H₂ evolution is monitored.

3. RESULTS

3.1. Experimental observations

In this work we present the results concerning the NiAg catalyst with a silver content of 40 wt%. The optimized elaboration procedure is described in the previous section. In fact, the silver content and the procedure was optimized by varying the silver content from 0 to 90 wt% and by changing the following experimental parameters: the CTAB amount from 50 to 260 mg, the NaBH₄ amount from 0.3 to 1 g, and the solution pH from 8 to 12 (by addition of NaOH and/or NH₄OH). The screening of the as-obtained NiAg catalysts was performed by following the volume of H₂ + N₂ liberated from HB in aqueous solution at 50°C. Depending on the catalysts, volumes of H₂ + N₂ varying from 78 to 155 mL was obtained.

It is worth of noting that silver nitrate is light-sensitive. It decomposes under the action of light. Therefore, the reaction flask must be kept far from light, *i.e.* in dark place, during all of the preparation stages till the reduction starts. In case the reactants could not be protected from light, metallic silver forms and appears on the flask wall during the reduction stage. This therefore does not permit to have the targeted contents and alloys.

Another important experimental point is the high sensitivity of the reactants to oxygen. The purity of the argon gas feeding to the reactor is extremely important. The catalyst activity highly depends on that. For example, we prepared 2 samples of NiAg, the first one under argon atmosphere and the second one in the presence of O₂. The catalyst exposed to O₂ showed to be much less efficient than the other one, with 82 mL H₂ + N₂ *versus* 155 mL H₂ + N₂, respectively.

3.2. Dehydrogenation of HB in the presence of NiAg

The results of dehydrogenation of HB in the presence of the NiAg catalyst are shown in Fig. 1, which represents the evolution of H₂ + N₂ per mol of HB as a function

of time. The first main observation is that almost 6 mol $H_2 + N_2$ per mol HB are generated (equivalent to 155 mL $H_2 + N_2$). It is difficult to state that exactly 6 mol formed as the presence of residual N_2H_4 or of NH_3 is difficult by the common techniques (Çakanyıldırım 2012). Furthermore, the experimental error (2%) due to our gas measurement system makes us cautious. However that may be, the present result is the best ever reported for the dehydrogenation of HB in aqueous solution at 50°C. Compared to our previous best bimetallic systems, NiAg has permitted to improve the H_2 selectivity up to almost 100%. In comparison, with NiPt, we obtained a selectivity of 93% (Hannauer 2011) and with NiRh the selectivity was 97% (Zhong 2012).

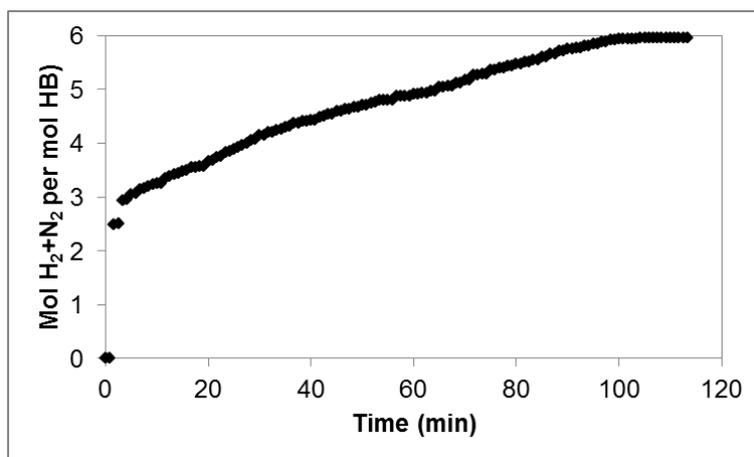


Fig. 1. Dehydrogenation of HB in the presence of NiAg at 50°C.

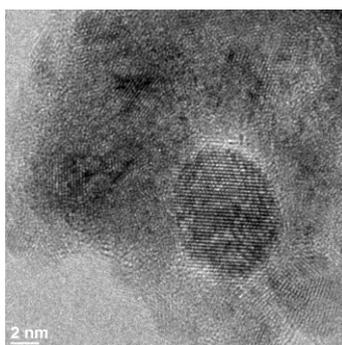


Fig. 2. TEM image of NiAg.

The evolution of $H_2 + N_2$ is not linear over the whole time range (Fig. 1). It can be divided into 2 parts. The first one is predominated by the hydrolysis of the BH_3 group of HB (Eq. 3), which is known to be a high-kinetic process (Çakanyıldırım 2012). This reaction is exothermic and takes place quite rapidly in the presence of any transition-

metal based catalyst. The second part corresponds exclusively to the dehydrogenation of N_2H_4 (Çakanyıldırım 2012). This stage is characterized by slower kinetics. This is an issue. In fact, the dehydrogenation of $N_2H_4BH_3$ has to overcome several challenges, that is: (i) finding an active and selective catalyst in the dehydrogenation of the N_2H_4 moiety; (ii) finding a stable and durable catalyst; (iii) finding a catalyst with which the whole dehydrogenation would show a constant dehydrogenation rate (Çakanyıldırım 2012). This 3rd issue should be worked when solutions to the 1st and 2nd ones will be found.

3.3. Characterization of NiAg

The fresh NiAg catalyst was *ex-situ* characterized by various techniques. It can be observed by TEM (Fig. 2) that NiAg consists of agglomerated almost-spherical crystalline nanoparticles of <10 nm.

By powder XRD (Fig. 3), the crystalline structure was analyzed. The XRD pattern of NiAg shows that the peaks can be referenced to a face-centered cubic (FCC) unit cell. The 2θ values of 38.1, 44.25 and 64.5° can be indexed to the diffractions of (111), (200) and (220) crystal planes, respectively (ICDD 00-004-0851).

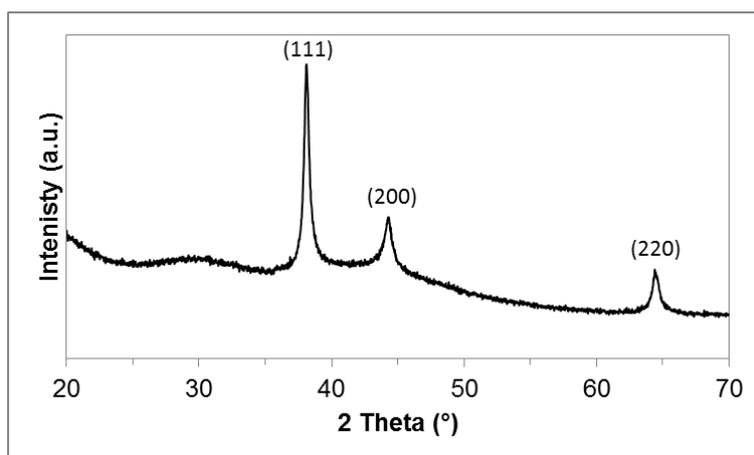


Fig. 3. XRD pattern of NiAg.

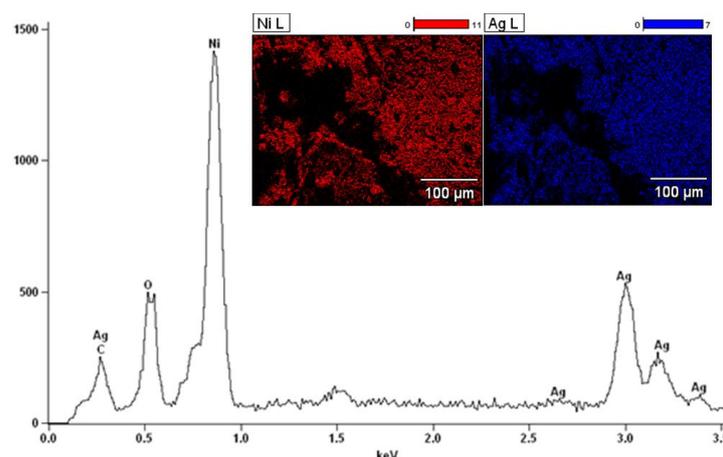


Fig. 4. EDX results for NiAg, with mapping images in insert.

An EDX analysis (Fig. 4) of the sample at randomly focused areas has revealed metal (Ni and Ag) contents in good agreement with the nanoparticles composition targeted (*i.e.* 60 and 40 wt%, respectively). This was besides confirmed by ICP analysis.

3.4. Issue

As reported in the sub-section 3.1, the synthesis of the NiAg nanoparticles is very sensitive to the experimental parameters. The reproducibility is thus arduous. Such problems can be seen as signs of the instability of the NiAg nanoparticles. In fact, the NiAg is not stable at all. A second utilization of the catalyst shows deteriorated catalytic activity, with only half of the expected gases generated and with slower kinetics.

Better understanding the reasons of the good activity of NiAg is now crucial to work on the stability of this catalyst. *In-situ* and post-reaction characterizations by using surface techniques have to be considered. Works are in progress.

4. CONCLUSIONS

In our efforts of finding a bimetallic catalyst active in the total dehydrogenation of hydrazine borane, we have found that the system NiAg with 40 wt% of Ag is one likely candidate. Almost 100% of H₂ selectivity was measured in our experimental conditions, which is the best performance ever reported. However, the catalyst has a limited stability, not enabling a second use. Works are in progress to improve this feature.

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