

Supported nickel catalysts for the decomposition of hydrazine borane $N_2H_4BH_3$

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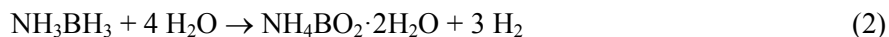
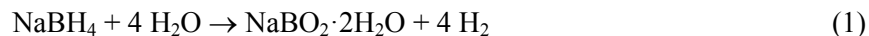
Abstract. In this work, we present the catalytic dehydrogenation of hydrazine borane $N_2H_4BH_3$ (HB) using supported nickel catalysts at 50°C. In the presence of monometallic nickel catalysts, the dehydrogenation of HB is a one-step reaction consisting of the hydrolysis of the BH_3 group only. The challenge is to activate nickel to make it reactive towards the N_2H_4 moiety of HB. A set of 52 catalysts were prepared by using 2 supports (Al_2O_3 and TiO_2), 5 nickel precursors and 3 preparation methods. For the first time, we show that the supported nickel catalysts are able to dehydrogenate the NH_3 moiety of HB. In our experimental conditions, the best results were obtained with 20 wt% Ni- Al_2O_3 and 20 wt% Ni- TiO_2 , with ca. 190 mL $H_2 + N_2$ generated over a total theoretical volume of 283 mL, suggesting H_2 selectivity of 37 and 32%, respectively. Both catalysts were then characterized by EDX, XPS, and XRD. Our achievement is the first step forward and opens new perspectives for developing catalysts for the total dehydrogenation of HB.

Keywords: chemical hydrogen storage; hydrazine borane; hydrolysis; supported nickel catalysts

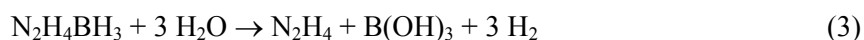
1. Introduction

Hydrogen as energy carrier is predicted to be a promising substitute of depleting and anthropogenic CO_2 -emitting fossil fuels. However, the development of the hydrogen economy is hindered by numerous scientific/technical key issues concerning production, storage, distribution, and end-use (Sartbaeva 2008). The storage problem is particularly problematic. Several solutions have been proposed to date. In addition to classical high-pressure (350-700 bar) and cryogenic-liquid storage ($-253^\circ C$), novel and innovative approaches have emerged. All concern materials. There is physical storage using adsorbents for cryo-adsorption (Lim 2010) and there is chemical storage involving, among others, hydrides, boranes, amides/imides, hydrocarbons and clathrate cages (Eberle 2009). Of the numerous compounds investigated (Hamilton 2009), boron- and/or nitrogen-based materials have shown to be attractive owing to high gravimetric hydrogen densities (Lu 2012) and their ability to dehydrogenate by hydrolysis in ambient conditions (Liu 2009, Demirci 2010). Sodium borohydride $NaBH_4$ (10.8 wt% H) and ammonia borane NH_3BH_3 (19.5 wt% H) are typical examples:

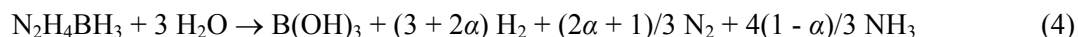
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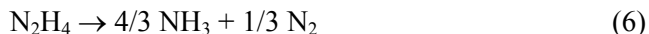
A recent example of boron- and/or nitrogen-based materials is hydrazine borane (HB; 15.4 wt%). Stable in room conditions and under inert atmosphere, it dehydrogenates in hydrolytic conditions at low temperature in the presence of a metal catalyst. Özkar and co-workers (Karahan 2011, Çelik 2012) showed that the BH_3 group of HB hydrolyzes in room conditions in the presence of rhodium or ruthenium catalysts



Demirci and co-workers (Hannauer 2011, Çakanyildirim 2012a) showed that, in addition to the hydrolysis of the BH_3 group, the partial dehydrogenation of N_2H_4 can be achieved in the presence of an active and selective Ni-based bimetallic catalyst at 50°C



Unfortunately, some ammonia is released because the N_2H_4 decomposition takes place *via* 2 parallel reactions



Recent progresses in the decomposition of hydrous N_2H_4 showed the importance of having reactive and selective nickel-based bimetallic or supported catalysts (Singh 2011, He 2012). Consequently, the current challenge with aqueous HB is to find a catalyst that (i) is active in the decomposition of the N_2H_4 moiety, (ii) is selective in the formation of H_2 (i.e., $0 < \alpha < 1$) and, (iii) ultimately, hinders completely the occurrence of the side-reaction given by Eq. (5) (i.e., H_2 -selective with $\alpha = 1$; Eq. (7))

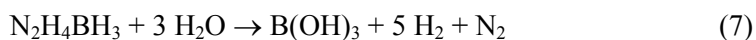


Fig. 1 gives a schematized view of these objectives. With regard to the recent literature dedicated to dehydrogenation of aqueous HB, we can assert that the challenge (iii) is not taken up yet.

In this work, we report a large screening of supported nickel catalysts for the dehydrogenation of HB. The objective was to find a nickel-based catalyst showing activity towards the dehydrogenation of the N_2H_4 moiety of HB. We opted for supported materials not to use noble metals. Our main results are discussed hereafter.

2. Experimental section

by adding some ammonium hydroxide (NH_4OH ; Sigma-Aldrich). For each procedure, NaBH_4 (mol ratio NaBH_4/Ni of *ca.* 8) was used as reducing agent. All of the supported Ni catalysts were washed with deionized water, dried at 80°C and then tested in dehydrogenation of $\text{N}_2\text{H}_4\text{BH}_3$. By this way, a set of 52 supported Ni catalysts were prepared. They are presented in Table 1.

A typical dehydrogenation experiment is as follows. The supported Ni 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 $50 \pm 1^\circ\text{C}$ and connected to a water-filled inverted burette (water colored in blue). A cold trap kept at 0°C is placed before the burette to trap H_2O in gaseous state. Should some NH_3 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 (90 mg in 4.5 mL) is injected in the reactor. The catalytic reaction starts. The H_2 evolution is monitored; it is especially video-recorded. For reproducibility, the dehydrogenation experiment is systematically done at least twice. The data are analyzed post-experiment and the evolution of $\text{H}_2 + \text{N}_2$ as a function of time is plotted. The gas (H_2 and, if any, N_2) generation rate (GGR) was determined by linearization of the curve over the range 0-50% of conversion of the BH_3 group of HB or over the range 0-50% of conversion of the N_2H_4 group of HB. GGR is given in mL/min. The selectivity in H_2 ($S(\text{H}_2)$, in %) was calculated by considering the reactions given by Eqs. (5) and (6).

Table 1. List of the 52 supported Ni catalysts prepared by using 5 different salts, 2 oxides, the same oxides but acid-treated (AT), and by applying 3 preparation routes (impregnation (IMP), incipient wetness impregnation (IWI) and precipitation (PCP)). For clarity, the 60 combinations of catalysts are denoted by numbers

		$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$	$\text{Ni}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$
Al_2O_3	IMP	1	2	3	4	5
	IWI	6	7	8	9	10
	PCP	11	12	13	14 ^b	15
AT- Al_2O_3	IMP	16	17	18	19	20
	IWI	21 ^a	22 ^a	23	24	25
	PCP	26 ^a	27 ^a	28	29 ^b	30
TiO_2	IMP	31	32	33	34	35
	IWI	36	37	38	39	40
	PCP	41	42	43	44 ^b	45
AT- TiO_2	IMP	46	47	48	49	50
	IWI	51 ^a	52 ^a	53	54	55
	PCP	56 ^a	57 ^a	58	59 ^b	60

^a Those supported catalysts were finally not prepared. They are not presented in the next tables.

^b In our conditions of precipitation, the reduction of Ni^{2+} from $\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$ did not occur.

The supported Ni catalysts that showed the best results in terms of mol number of $\text{H}_2 + \text{N}_2$ were analyzed by energy-dispersive X-ray spectroscopy (EDX; coupled with a SEM Hitachi S4500; Thermofisher 6213 detector; realized at 8 kV), X-ray diffraction (XRD; Bruker D5005 powder diffractometer, $\text{CuK}\alpha$ radiation, $\lambda=1.5406\text{\AA}$) and X-ray photoelectron spectroscopy (XPS; ESCALAB 250 Thermo Electron equipped with an $\text{Al K}\alpha$, $h\nu = 1486.6 \text{ eV}$).

From Table 2, the following observations stand out. With 8% of the supported Ni catalysts (i.e., 4 over 52), the preparation by precipitation did not lead to the formation of the catalysts because of the absence of reduction of the nickel cations. With 35% of the supported Ni catalysts (i.e., 18 over 52), < 3 mol H_2 per mol $N_2H_4BH_3$ are generated by hydrolysis of the BH_3 group. The conversion of the BH_3 groups is not total. Supporting nickel is in this case detrimental to the reactivity of the metal. With 17% of the supported Ni catalysts (i.e., 9 over 52), 3 mol H_2 per mol $N_2H_4BH_3$ are generated by the complete hydrolysis of the BH_3 groups of the HB molecules. With 40% of the supported Ni catalysts (i.e., 21 over 52), a reactivity towards the N_2H_4 moiety of HB is observed. In these cases, supporting nickel has activated the metal towards the N_2H_4 group.

From Table 2, other observations stand out when the results are compared on the basis of the nature of the nickel salts. First, the most appropriate Ni precursor is $Ni(SO_4)_2(NH_4)_2 \cdot 6H_2O$. Indeed, 10 over the 12 supported Ni catalysts showed reactivity towards the decomposition of the N_2H_4 moiety of HB. Second, the salts $NiCl_2 \cdot 6H_2O$ do not lead to the formation of catalysts with acceptable reactivity in our experimental conditions. A same conclusion can be done for $Ni(NO_3)_2 \cdot 6H_2O$ and $NiSO_4 \cdot 7H_2O$ even though better reactivity is reported. However, one of the most efficient catalysts (i.e., **58**) was prepared by using the latter precursor. Third, two problems are faced with $NiBr_2 \cdot 3H_2O$. It is difficult to reduce the nickel cations from this salt when the catalyst is prepared by precipitation and the reactivity of the successfully prepared supported Ni catalysts is not good at all.

From Table 2, the following last observations stand out when the results are compared on the basis of the nature of the support and of the preparation processes. First, acid-treating Al_2O_3 activates the supported Ni catalysts towards the decomposition of the N_2H_4 moiety of HB. A modification of the catalyst reactivity through such a treatment is consistent with the results of a previous work (Akdim 2009). In the field of the decomposition of hydrous N_2H_4 , it was reported that the presence of strong basic sites on Ni-Al hydrotalcite was at the origin increased H_2 selectivity (He 2012). In a first approach, this result might be seen in contradiction with our observation. However, surface basicity could also play an important role in the dehydrogenation of HB. We believe that the acid-treatment of the support is of benefit to the hydrolysis of the BH_3 group (Akdim 2009). Upon the completion of this reaction, the reaction medium reaches basic pH values (Çakanyıldırım 2012b), which is favorable to the dehydrogenation of the N_2H_4 moiety (Singh 2011). In addition, it is worthy of note that the metal surface is generally affected by the strong absorption of borates species during hydrolysis (Kim 2004). In other words, the acid-treatment would modify the support surface in such a way that, first, it would be more efficient in hydrolysis of BH_3 and second, it would show a state (in terms of adsorbed borates and thus basicity) increasing the reactivity towards the reaction (5). The second observation from Table 2 is as follows. Most of the supported Ni catalysts using TiO_2 show reactivity towards the decomposition of the N_2H_4 moiety of HB. In addition, the acid-treatment of this support slightly improves the reactivity of the supported Ni catalysts. Third, impregnation, and particularly the incipient wetness impregnation method, gives the most active catalysts.

To sum up the results presented in Table 2, 52 supported Ni catalysts were envisaged, 48 were successfully prepared, 21 of them showed reactivity towards the decomposition of the N_2H_4 moiety of HB, and the highest gas volume was almost 190 mL with 2 of them (i.e., with **25** and **58**). Table 3 reports the selectivity in H_2 for the 21 catalysts that showed an activity towards the N_2H_4 moiety. The selectivity changes within the range 6-37%. The best selectivity is obtained with the catalyst **25**, followed by **58** and **53**; they all show selectivity higher than 30%. Therefore, for the first time, it is shown that nickel can be active in the dehydrogenation of the N_2H_4 moiety of

The results presented heretofore show that supporting nickel over an oxide catalytically activates the Ni particles towards the decomposition of the N_2H_4 moiety of HB. Our strategy is thus validated. Though the selectivity values are lower than the best performance reported for bimetallic particles, they are high enough to open new perspectives for this kind of catalysts. Given the huge number of possibilities in terms of supports (e.g., carbonaceous nanostructures, metal oxides, carbides, nitrides...) and reducing agents, and in terms of experimental conditions (e.g., solvent, temperature...), we believe that there is a large room for improvement. Several challenges have to be taken up. Three of them, listed above, are as follows: (i) finding a catalyst active in the decomposition of the N_2H_4 moiety, (ii) finding a catalyst selective in the formation of H_2 and, (iii) hindering the occurrence of the unwanted side-reaction (Eq. (5)). In the present work as well as elsewhere (Hannauer 2011, Çakanyıldırım 2012a, Çakanyıldırım 2012b), we have taken up these 3 challenges but the third problem is not solved yet despite promising results. In addition, as shown in Fig. 2, there is a fourth issue/challenge. The kinetics of the second stage of the dehydrogenation (i.e., dehydrogenation of the N_2H_4 moiety) is too slow and thus not suitable from the application point of view. In our opinion, this is the most challenging aspect and many efforts will have to be dedicated in the near-future. It is crucial to improve the kinetics of the N_2H_4 dehydrogenation in order to have almost constant GGRs during the whole reaction. However, it is worth noting that we could address this problem only when the issues (iii) will be solved.

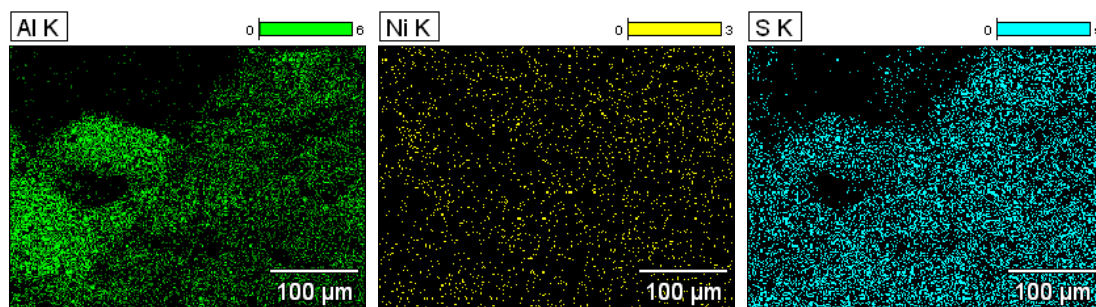


Fig. 3. Mapping of 58 by EDX: distribution of Ni, Ti and S.

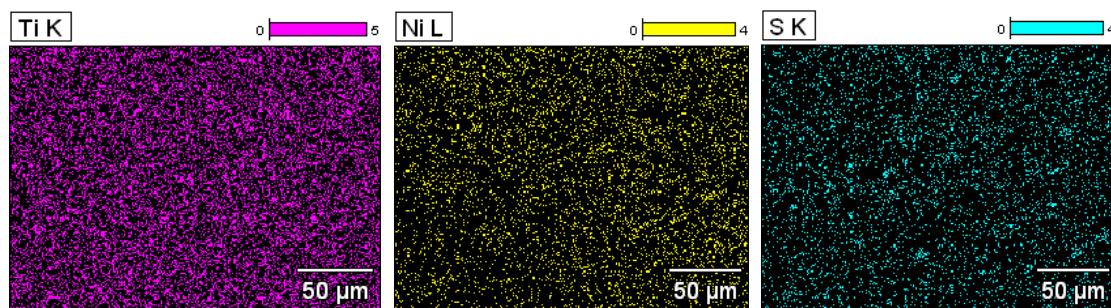


Fig. 4 Mapping of 58 by EDX: distribution of Ni and Ti

ICDD 00-002-1216) diffracted. The nickel particles on the oxides surface are likely amorphous. This would be in agreement with previous reports that showed that the reduction of Ni^{2+} or Co^{2+} by NaBH_4 leads preferably to amorphous particles (Walter 2008, Arzac 2011, Nie 2012).

4. Conclusions

Hydrazine borane stores 15.4 wt% H. Attractively, it is able to liberate step by step all of its hydridic and protic hydrogens in hydrolytic conditions, provided an active and selective metal-based catalyst is used. The challenge is to hydrolyze the BH_3 group of HB, which takes place with most of the transition metals, and right after dehydrogenate the N_2H_4 moiety, which is more difficult. Preparing such selective catalytic material was the objective of the present work. To avoid the use of noble metal in alloys while improving the reactivity of nickel, we chose to support this cost-effective metal on common oxides, i.e., Al_2O_3 and TiO_2 .

Of the 52 supported Ni catalysts prepared (by combinations of supports, Ni precursors and synthesis methods), 21 showed to be reactive towards the N_2H_4 moiety of HB. Making nickel reactive in this reaction is a promising achievement. The decomposition of N_2H_4 into NH_3 predominates in our experimental conditions. The best results were obtained with 20 wt% Ni- Al_2O_3 and 20 wt% Ni- TiO_2 , the supports of which being acid-treated and used as received respectively, the Ni precursors being $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Ni}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ respectively, the supporting of Ni being done by incipient wetness impregnation and precipitation respectively. With both, ca. 190 mL $\text{H}_2 + \text{N}_2$ (NH_3 was trapped in an acidic bath) were generated over a total of 283 mL, suggesting H_2 selectivity of 37 and 32% respectively.

Our achievement is the first step forward. Therefore, it opens new perspectives for developing cheap, reactive and selective catalysts for dehydrogenation of hydrazine borane and we are firmly convinced that the present work is the first of many. Further, we believe that nickel is a candidate of choice for a large-scale study.

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