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

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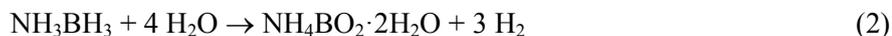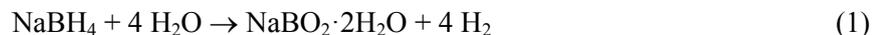
Abstract.   In this work, we present the catalytic dehydrogenation of hydrazine borane $N_2H_4BH_3$ (HB) using supported nickel catalysts at 50°C. In the presence of monometallic nickel catalysts, the dehydrogenation of HB is a one-step reaction consisting of the hydrolysis of the BH_3 group only. The 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
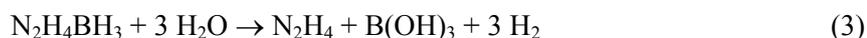
1. Introduction

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°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:
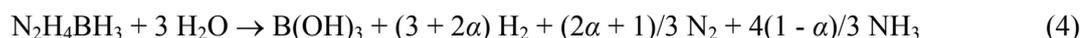
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$$NaBH_4 + 4\ H_2O \rightarrow NaBO_2 \cdot 2H_2O + 4\ H_2 \tag{1}$$

$$NH_3BH_3 + 4\ H_2O \rightarrow NH_4BO_2 \cdot 2H_2O + 3\ H_2 \tag{2}$$
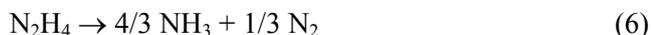
A recent example of boron- and/or nitrogen-based materials is hydrazine borane (HB; 15.4 wt%). Stable in room conditions and under inert atmosphere, it dehydrogenates in hydrolytic conditions at low temperature in the presence of a metal catalyst. Özkar and co-workers (Karahan 2011, Çelik 2012) showed that the BH_3 group of HB hydrolyzes in room conditions in the presence of rhodium or ruthenium catalysts

$$N_2H_4BH_3 + 3\ H_2O \rightarrow N_2H_4 + B(OH)_3 + 3\ H_2 \tag{3}$$

Demirci and co-workers (Hannauer 2011, Çakanyıldırım 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

$$N_2H_4BH_3 + 3\ H_2O \rightarrow B(OH)_3 + (3 + 2\alpha)\ H_2 + (2\alpha + 1)/3\ N_2 + 4(1 - \alpha)/3\ NH_3 \tag{4}$$

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

$$N_2H_4 \rightarrow 2\ H_2 + N_2 \tag{5}$$

$$N_2H_4 \rightarrow 4/3\ NH_3 + 1/3\ N_2 \tag{6}$$

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))

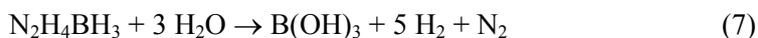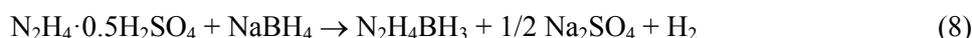$$N_2H_4BH_3 + 3\ H_2O \rightarrow B(OH)_3 + 5\ H_2 + N_2 \tag{7}$$

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

The synthesis of $N_2H_4BH_3$ is described in details elsewhere (Moury 2011). Typically, 264.34 mmol of hydrazine hemisulfate salt ($N_2H_4 \cdot 0.5H_2SO_4$, Sigma-Aldrich) and 264.34 mmol of sodium borohydride ($NaBH_4$, Acros Organics) were transferred in a round-bottom Schlenk flask in an argon-filled glove box (MBraun M200B, H_2O < 0.1 ppm, O_2 < 0.1 ppm). Then, under argon, 80 mL of anhydrous dioxane ($C_4H_8O_2$, Sigma-Aldrich) were added. The suspension of the solids in dioxane was favored by rigorous stirring, which is important to enable both materials to react. The evolution of the reaction was monitored by following the emission of H_2 passing through a bubble-counter. The reaction ceased after 48 h; $N_2H_4BH_3$ (soluble in dioxane) as main product and Na_2SO_4 (insoluble in dioxane) as by-product formed

$$N_2H_4 \cdot 0.5H_2SO_4 + NaBH_4 \rightarrow N_2H_4BH_3 + 1/2\ Na_2SO_4 + H_2 \qquad (8)$$

The slurry was filtrated and the solvent removed under vacuum. The as-obtained $N_2H_4BH_3$ was finally stored in the argon-filled glove box and sampled for the dehydrogenation experiments.
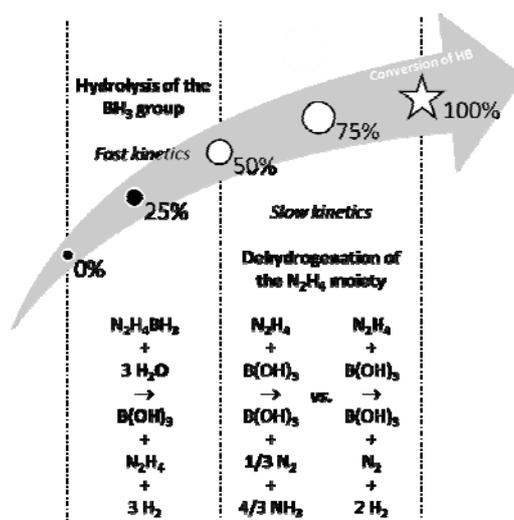

Fig. 1 Dehydrogenation of hydrazine borane $N_2H_4BH_3$, a two-step process

The supported Ni catalysts were prepared by using 5 different Ni salts (*cf.* Table 1; all from Sigma-Aldrich) and 2 commercial oxide supports: i.e., Al_2O_3 (Dispersal S, Condea, 100 m²/g, 0.8 cm³/g) and TiO_2 (P25, Degussa, 55 m²/g, 0.15 cm³/g). Both supports were used either as-received or after an acid-treatment according to a procedure reported elsewhere (Akdim 2009). Typically, the support was immersed in an aqueous solution of HCl (1 M) at room temperature for 1 h, separated, washed and finally dried at 105°C. It was reported that such treatment could enhance the reactivity of supported catalysts in hydrolysis of boron hydrides. For supporting Ni over the supports, 3 preparation procedures were applied in order to have a Ni content of 20 wt%: i.e., impregnation (IMP) in an excess of water; incipient wetness impregnation (IWI) where the volume of water is equal to the porous volume of the supports; precipitation (PCP) at pH = 10-11 adjusted

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 $N_2H_4BH_3$. 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 ± 1°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 H_2+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 ($S(H_2)$, 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

		$NiCl_2.6H_2O$	$Ni(NO_3)_2.6H_2O$	$NiSO_4.7H_2O$	$NiBr_2.3H_2O$	$Ni(SO_4)_2(NH_4)_2.6H_2O$
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 $NiBr_2.3H_2O$ did not occur.

The supported Ni catalysts that showed the best results in terms of mol number of $H_2 + N_2$ 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, CuKα radiation, λ=1.5406Å) and X-ray photoelectron spectroscopy (XPS; ESCALAB 250 Thermo Electron equipped with an Al Kα, hν = 1486.6 eV).

3. Results and discussion

Nickel is a good candidate to elaborate reactive and selective catalysts in dehydrogenation of HB. Up to now, pure nickel in the form of nanoparticles has shown to be active in hydrolysis of the BH_3 group of HB. Note that nickel has also shown to be a candidate of choice for hydrolysis of $NaBH_4$ (Christian 2012) as well as in hydrolysis of NH_3BH_3 (Metin 2010). However, nickel is inert in decomposition of the N_2H_4 moiety of HB (Hannauer 2011).

Alloying nickel with a small amount noble metal has a synergetic effect on the catalytic activity of the nanoparticles, with the occurrence of the reaction given by Eq. (4) where α tends to 1. With NiPt nanoparticles, up to 5.7 mol $H_2 + N_2$ were released at 50°C (Hannauer 2011). More recently, better results were obtained with a Rh_4Ni alloy nanocatalyst, which converted the hydrogen of HB to H_2, with 5.8 ± 0.2 equiv. $H_2 + N_2$ per HB released (Zhong 2012). This improvement has been mainly attributed to alloying and electronic effects, i.e., shifts of the d band centers of Ni and e.g., Pt or Rh (Çakanyıldırım 2012a).

Alloying is one of the approaches to modify the catalytic reactivity of a metal thanks to electronic effects. Another approach is to support the metal (in the form of nanoparticles) onto a support. Herein, we chose 2 well-known oxides as supports, i.e., alumina and titanium oxide. In a first stage, they were used as received. In a second one, they were acid-treated before the deposition of the nickel particles because, in a previous work, it was shown that acid-treating can have positive effects on the reactivity of a supported catalyst (Akdim 2009). With the objective to activate nickel towards the decomposition of the N_2H_4 moiety of HB, we prepared 52 supported Ni catalysts by using 5 different Ni salts and applying 3 preparation routes (Table 1).

The screening of the 52 catalysts was done by measuring the volume of gas ($H_2 + N_2$) generated as a function of time. In our experimental conditions, we used 90 mg $N_2H_4BH_3$. Therefore, assuming a total conversion of HB according to the reaction shown in Eq. (7), it was expected the evolution of 283 mL $H_2 + N_2$ in room conditions. Note that this volume can be decomposed as follows: 141.5 mL of H_2 released by hydrolysis of the BH_3 group of HB and as much by decomposition of the N_2H_4 moiety into H_2 (i.e., 94.3 mL) and N_2 (i.e., 47.2 mL). The main results are reported in Table 2. For clarity, the gas evolution curves are not presented for all of the 52 catalysts; they will be for the best catalysts (*cf.* hereafter).

Table 2. Volume of gas ($H_2 + N_2$) generated in the presence of the supported Ni catalysts at 50°C. In italic are shown the supported nickel catalysts active towards the N_2H_4 moiety of HB. In bold and italic are shown the best catalysts

		$NiCl_2.6H_2O$	$Ni(NO_3)_2.6H_2O$	$NiSO_4.7H_2O$	$NiBr_2.3H_2O$	$Ni(SO_4)_2(NH_4)_2.6H_2O$
Al_2O_3	IMP	130	118	125	135	*154*
	IWI	128	118	130	142	*164*
	PCP	120	120	122		95
AT-Al_2O_3	IMP	130	120	144	145	*150*
	IWI			*164*	*162*	***194***
	PCP			137		*150*
TiO_2	IMP	142	*160*	*155*	133	*158*
	IWI	135	*167*	*153*	143	*158*
	PCP	130	*162*	130		129
AT-TiO_2	IMP	145	*170*	148	145	*165*
	IWI			*185*	*163*	*165*
	PCP			***187***		*155*

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 $Ni(SO_4)_2(NH_4)_2.6H_2O$. Indeed, 10 over the 12 supported Ni catalysts showed reactivity towards the decomposition of the N_2H_4 moiety of HB. Second, the salts $NiCl_2.6H_2O$ do not lead to the formation of catalysts with acceptable reactivity in our experimental conditions. A same conclusion can be done for $Ni(NO_3)_2.6H_2O$ and $NiSO_4.7H_2O$ 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 $NiBr_2.3H_2O$. 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.
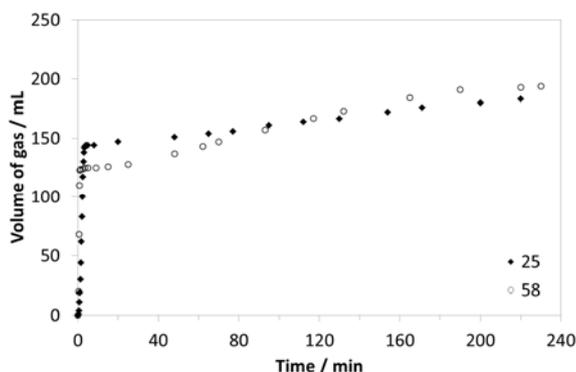
To sum up the results presented in Table 2, 52 supported Ni catalysts were envisaged, 48 were successfully prepared, 21 of them showed reactivity towards the decomposition of the N_2H_4 moiety of HB, and the highest gas volume was almost 190 mL with 2 of them (i.e., with **25** and **58**). Table 3 reports 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

HB.

Table 3. Selectivity in H$_2$ (S(H$_2$), in %) for the decomposition of the N$_2$H$_4$ moiety of HB for the active and selective supported Ni catalysts

		NiCl$_2$.6H$_2$O	Ni(NO$_3$)$_2$.6H$_2$O	NiSO$_4$.7H$_2$O	NiBr$_2$.3H$_2$O	Ni(SO$_4$)$_2$(NH$_4$)$_2$.6H$_2$O
Al$_2$O$_3$	IMP					9
	IWI					16
	PCP					
AT-Al$_2$O$_3$	IMP					6
	IWI			16	15	37
	PCP					6
TiO$_2$	IMP		13	10		12
	IWI		18	8		12
	PCP		15			
AT-TiO$_2$	IMP		20			17
	IWI			31	15	17
	PCP			32		10

Fig. 2 shows the gas evolution for the best 2 catalysts, i.e., **25** and **58**. Consistently with previous observations (Hannauer 2011), the gas evolution has a particular profile with a first stage characterized by a rapid evolution of gas and a second one showing slower kinetics (Fig. 1). The first stage is mainly due to the hydrolysis of the BH$_3$ group of HB, with a negligible or low contribution of the decomposition of the N$_2$H$_4$ moiety of HB; the second stage exclusively consists in the decomposition of N$_2$H$_4$ (Çakanyıldırım 2012b). The gas generation rates (GGRs, in mL/min) were calculated for each catalyst and each stage. In our conditions, the GGRs for stage 1 are *ca.* 36 and 41 mL/min for **25** and **58** respectively. Compared to the reactivity of pure Ni nanoparticles in the same experimental conditions, the GGRs for stage 1 are almost equivalent since rates of *ca.* 40 mL/min were reported elsewhere (Hannauer 2011). For **25** and **58**, the GGRs for stage 2 are *ca.* 0.3 and 0.2 mL/min, respectively. These rates are lower than those reported for the NiPt nanoalloys, i.e., 1.3-2.1 mL/min (Hannauer 2011).

Fig. 2 Evolution of H$_2$ + N$_2$ as a function of time for 25 and 58 at 50°C

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.
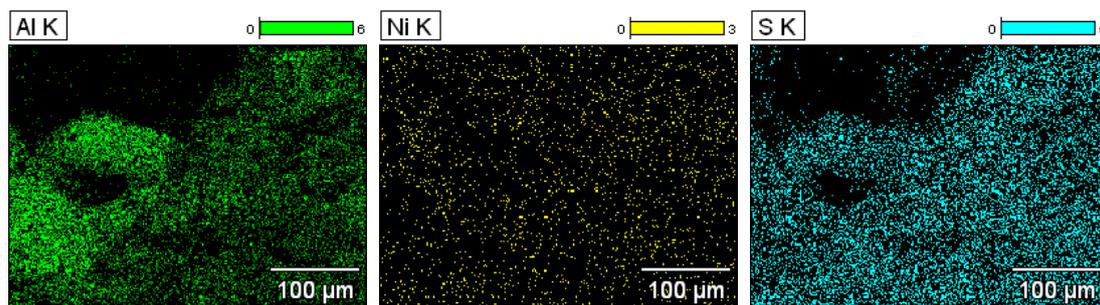

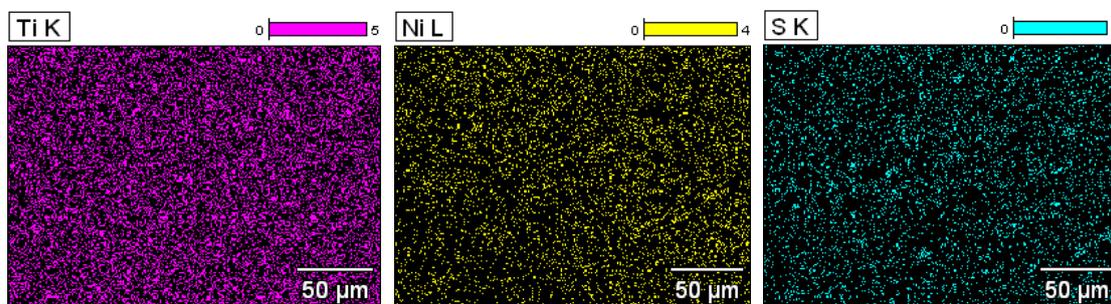Fig. 3. Mapping of 58 by EDX: distribution of Ni, Ti and S.

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

The best catalysts, i.e., **25** and **58**, were then characterized. The presence of nickel was first verified by EDX (Figs. 3 and 4). For both catalysts, the amount of nickel was consistent with the target 20 wt% and the metal was observed to be homogeneously supported over the support. The presence of nickel was also confirmed by XPS. The binding energy for Ni 3p3/2 was found to be 67.4 and 67.3 eV for **25** and **58**, suggesting the presence of NiO on the catalyst surface. As the samples were handled in ambient conditions after preparation, the supported nickel particles oxidize. By EDX (Figs. 3 and 4), the presence of sulfur was also detected for both materials. This sulfur is from the nickel salts used, i.e. $Ni(SO_4)_2(NH_4)_2.6H_2O$ and $NiSO_4.7H_2O$, respectively, suggesting that sulfate anions remain strongly adsorbed over the catalyst surface. This could explain why the supported Ni catalysts prepared with the sulfate salts are better in terms of activity towards the N_2H_4 group of HB than the chloride, bromide and nitrate salts. This is consistent with literature. By the addition of the sulfate group, metal oxides develop the ability to catalyze reactions characteristic of very strong acid catalysts at low temperatures (Brown 1999). Typical examples are as follows: SO_4^{2-}/ZrO_2, SO_4^{2-}/SnO_2, SO_4^{2-}/TiO_2, SO_4^{2-}/Al_2O_3, SO_4^{2-}/SiO_2, *etc.* (Arata 1990). The sulfated metal oxides are known as superacidic heterogeneous catalysts.
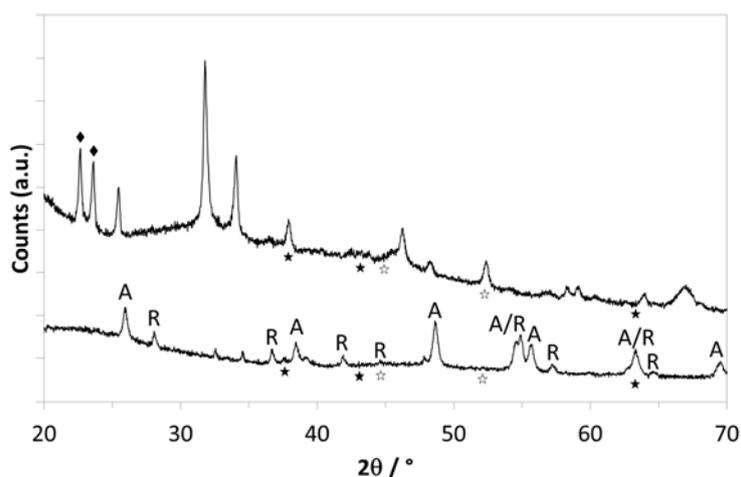

Fig. 5 XRD patterns of 25 (top curve) and 58 (bottom curve). For 58, A denotes anatase TiO_2 (ICDD 00-002-0406), R denotes rutile TiO_2 (ICDD 01-088-1175), and the peaks with no attribution are ascribed to brookite TiO_2 (ICDD 01-076-1934). For 25, most of the peaks are ascribed to Al_2O_3 (ICDD 00-003-0915) but 2 peaks are attributed to Na_2SO_4 (ICDD 01-089-4751; shown by black rhomb). The white and black stars indicate the 2θ values at which Ni (01-070-0989) and NiO (00-002-1216) should diffract, respectively

The catalysts **25** and **58** were then analyzed by XRD. The patterns are shown in Fig. 5. With respect to **25**, most of the peaks were attributed to alumina (ICDD 00-003-0915) but two of them to Na_2SO_4 (ICDD 01-089-4751). This is consistent with the observation of sulfur by EDX. With respect to **58**, the presence of mainly anatase and rutile TiO_2 is suggested. Traces of brookite are also proposed. The pattern was compared to the reference patterns of these crystalline phases (i.e., ICDD 00-002-0406, ICDD 01-088-1175, ICDD 01-076-1934, respectively). For both materials, it is difficult to assert that nickel in metallic state (Ni, ICDD 01-070-0989) or in oxidized state (NiO,

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 $NiSO_4.7H_2O$ and $Ni(SO_4)_2(NH_4)_2.6H_2O$ respectively, the supporting of Ni being done by incipient wetness impregnation and precipitation respectively. With both, *ca.* 190 mL H_2 + 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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