## High-Extent Dehydrogenation of Hydrazine Borane $N_2H_4BH_3$ by Hydrolysis of $BH_3$ and Decomposition of $N_2H_4$

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## Experimental section

Hydrazine borane (N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>; HB) is synthesized as follows. Typically, 21.42 g (264.34 mmol) of hydrazine hemisulfate salt (H<sub>4</sub>N<sub>2</sub>·1/2H<sub>2</sub>SO<sub>4</sub>, Sigma-Aldrich) and 10 g (264.34 mmol) of sodium borohydride (NaBH<sub>4</sub>, Acros Organics) are suspended in 80 mL of anhydrous dioxane (puriss), Sigma-Aldrich), under an atmosphere of dry argon, and under stirring. The reaction mixture is kept under stirring overnight. Upon the completion of hydrogen evolution, the slurry is filtered under argon. Then, the solvent is removed under vacuum and upon the apparition of turbidity anhydrous *n*-pentane (≥ 99%, Sigma-Aldrich) is added to precipitate HB. The precipitate is then filtered and washed with *n*-pentane. The as-obtained material is a white solid (5.71 g; yield of 47%), and its purity is systematically verified by <sup>1</sup>H and <sup>11</sup>B solution-state NMR on a Bruker DRX-400 using a probe head BBFO+ such as: <sup>1</sup>H NMR (δ/ppm, 400.13 MHz, C<sub>4</sub>D<sub>8</sub>O, 298.51 K, *J*/Hz): 6.04 (s, 2H B-NH<sub>2</sub>) 3.54 (s, 2H, N-NH<sub>2</sub>), 1.48 (qua, 3H, <sup>1</sup>J (<sup>11</sup>B-<sup>1</sup>H) = 94,5 Hz); and <sup>11</sup>B NMR (δ/ppm, 128.38 MHz, C<sub>4</sub>D<sub>8</sub>O, 298.51 K, *J*/Hz): -15.03 (qua, <sup>1</sup>J (<sup>11</sup>B-<sup>1</sup>H) = 95 Hz). Water used for NMR analyses is Millipore milli-q water with a resistivity > 18 MΩ cm that has been degassed by bubbling argon for 30 min. For stability tests of HB in aqueous solution, the sample is kept under argon atmosphere.

The Ni<sub>1-x</sub>Pt<sub>x</sub> catalysts (with x = 0, 0.03, 0.07, 0.11, 0.17, 0.23, or 1) are prepared using a hexadecyltrimethylammonium bromide-aided (CTAB, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N(Br)(CH<sub>3</sub>)<sub>3</sub>,  $\geq$  98%, Sigma-Aldrich) coreduction method. To illustrate, the typical synthetic procedure for Ni<sub>0.97</sub>Pt<sub>0.03</sub> is described hereafter. An aqueous solution of nickel chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O,  $\geq$  99.999%, 0.130 g, 0.548 mmol), potassium tetrachloroplatinate (K<sub>2</sub>PtCl<sub>4</sub>,  $\geq$  99.99%, 0.008 g, 0.019 mmol) and CTAB (0.210 g, 0.576 mmol) is prepared by dissolution, subsequent sonication, and 5-min stirring. Millipore milli-q water with a resistivity > 18 MΩ cm was used. To 5 mL of this solution is then added dropwise 3 mL of aqueous solution of NaBH<sub>4</sub> (0.040 g, 1.052 mmol). Upon this operation, the solution is vigorously shaken for 2 min, resulting in the formation of a black suspension consisting of Ni<sub>0.97</sub>Pt<sub>0.03</sub>. It is centrifugated for 10 min at 11000 rpm. The supernatant is removed. The catalyst is dried at 80 °C

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for 15 min, grinded in an agate mortar under argon, and stored in an argon-filled glove box to be next used as catalyst. For the other  $Ni_{1-x}Pt_x$  nanocatalysts, the following amounts of  $NiCl_2 \cdot 6H_2O$  and  $K_2PtCl_4$  are used: 0.144 g (0.608 mmol) and 0.000 g (0.000 mmol) for Ni; 0.116 g (0.490 mmol) and 0.016 g (0.038 mmol) for  $Ni_{0.93}Pt_{0.07}$ ; 0.100 g (0.422 mmol) and 0.022 g (0.054 mmol) for  $Ni_{0.89}Pt_{0.11}$ ; 0.086 g (0.362 mmol) and 0.030 g (0.036 mmol) for  $Ni_{0.83}Pt_{0.17}$ ; 0.072 g (0.304 mmol) and 0.038 g (0.092 mmol) for  $Ni_{0.77}Pt_{0.23}$ ; 0.000 g (0.000 mmol) and 0.076 g (0.184 mmol) for Pt.

A typical hydrogen (and nitrogen) generation measurement is performed as follows. In an argon-filled glove box, 20 mg of Ni<sub>1-x</sub>Pt<sub>x</sub> is introduced into the reactor consisting of a 100 mL round-bottom flask sealed with a silicon septum. The reactor is placed in a water bath thermostated at 50 °C and connected to a water-filled inverted burette. To trap any evolving ammonia (NH<sub>3</sub>), a trap filled with a HCL (0.1 M) solution is placed between the reactor and the inverted burette. For gas characterization, the acid trap is replaced by a cold trap to condensate steam. The room temperature was 20 °C. To start the catalytic reaction, 4.5 mL of water (Millipore milli-q water with a resistivity > 18 MΩ cm) containing 90 mg of HB (mol ration H<sub>2</sub>O/HB of 127.34) is injected into the reactor and the H<sub>2</sub> evolution is measured. No stirring is used, except that induced by H<sub>2</sub> evolution. The experiments are video-recorded and are afterwards analyzed to plot the evolution of H<sub>2</sub>+N<sub>2</sub> as a function of time. The hydrogen (and nitrogen) generation rate (HGR) is determined by linearization of the N<sub>2</sub>H<sub>4</sub> group. HGR may be given either in mL min<sup>-1</sup> or in mL min<sup>-1</sup> g<sup>-1</sup>(catalyst). The gases evolving are analyzed by a Thermo VG Prolab quadrupole mass spectrometer (MS) in the course of the reactions; the MS capillary is connected to the tube allowing the gas to escape from the reactor to event.

The Ni<sub>1-x</sub>Pt<sub>x</sub> nanocatalysts, after utilization in dehydrogenation of HB, were characterized by various techniques. After the completion of reaction, the catalyst is separated from the solution by centrifugation (11000 rpm, 10 min), washed twice with 10 mL of deionized water and dried at 80 °C for 15 min. Chemical analysis is done by ICP-AES (ACTIVA<sup>TM</sup> Horiba Jobin Yvon). Morphology identification is done by using a JEM 2010 (Cs = 0.5 mm) transmission electron microscope (TEM; operating at 200 kV) equipped with energy-dispersive spectroscopy (EDS) LINK-ISIS (spatial resolution of 1 nm). High resolution transmission electron microscopy (HRTEM) is performed with a 200 kV JEOL 2010 microscope, with a point resolution of 0.195 nm (coefficient of spherical aberration Cs = 0.5mm) equipped with energy-dispersive spectroscopy (EDS) LINK-ISIS (spatial resolution of 1 nm). Further analytical work was performed on a 200 kV JEOL 2010F field-emission microscope, with a point resolution of a 200 kV JEOL 2010F field-emission microscope, with a point coefficient of spherical aberration Cs = 0.5mm). The samples are suspended in ethanol before deposition onto carbon coated copper grids for microscopic analyses. Crystalline state and phase composition are also controlled by powder X-ray diffraction using Bruker D5005 powder diffractometer (CuK $\alpha$  radiation,  $\lambda$ =1.5406Å). X-ray photoelectron

spectroscopy (XPS) was performed at "Science et Surface", in Ecully, France, using a PHI Quantera SXM spectrometer equipped with an Al K $\alpha$ , h $\nu$  = 280 eV, 47.7 W; the spectrometer binding energy (BE) scale was calibrated using the position of C 1s core level, 284.8 eV). The BEs were ascribed based on data available online at http://www.lasurface.com and http://srdata.nist.gov/xps/.

## Table 1S

Hydrogen/nitrogen generation rates (HGRs) stemming from the H<sub>2</sub> evolution profiles (in Figure 1a).

Nanocatalyst Ni <sub>1-x</sub> -Pt <sub>x</sub>	HGR for the BH <sub>3</sub> hydrolysis		HGR for the N <sub>2</sub> H <sub>4</sub> decomposition	
	$(mL H_2 min^{-1})$	$(mL H_2 min^{-1} g^{-1})$	$(mL H_2/N_2 min^{-1})$	$(mL H_2/N_2 min^{-1} g^{-1})$
x = 0.00	59.3	2965	0.1	5
x = 0.03	40.0	2000	1.3	65
x = 0.07	35.9	1795	2.1	105
x = 0.11	32.4	1620	2.1	105
x = 0.17	34.3	1715	1.5	75
x = 0.23	32.9	1645	1.8	90
x = 1.00	11.1	555	0.0	0.0



**Figure 1S**. <sup>1</sup>H (top) and <sup>11</sup>B (bottom) solution-state NMR spectra of HB in THF-d8. The attribution of the signals is given in the experimental section. These spectra show that HB is synthesized with a purity of >99%.



**Figure 2S**. <sup>1</sup>H solution-state NMR spectra of HB in water. The spectrum of fresh HB and that of HB after 3 weeks of storage under argon atmosphere at room temperature are showed in the top figure. Because a broadening of the signal at  $\delta$  4.03 ppm was observed, a further test was performed to better understand this. The bottom figure shows the spectrum of a solution consisting of fresh HB to which a small amount (3, 6 or 9 vol%) of hydrous hydrazine was added; the spectra clearly show a similar broadening of the signal at  $\delta$  4.07 ppm. The broadening is thus attributed to the presence of free N<sub>2</sub>H<sub>4</sub> in the solution after a 3-week storage (hydrolysis of some HB; see Fig. 3S).



**Figure 3S**. <sup>11</sup>B solution-state NMR spectra of HB in water: fresh state, after 3 weeks of storage under argon atmosphere at room temperature, and after reaction in the presence of  $Ni_{0.89}Pt_{0.11}$ . The boron-based by-products consist of a mixture of borates and polyborates as suggested in references [1,2]. Further studies are required to identify the species and catch the equilibriums occurring, such a work being out of scope of the present communication.



**Figure 4S**. Time profile of the mass spectrometric analysis of the gases evolved from the dehydrogenation of HB in the presence of the  $Ni_{0.89}$ -Pt<sub>0.11</sub> nanocatalyst at 50 °C. For convenience, the top figure only shows the peaks ascribed to H<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O. For information, the bottom figure also displays the original curves where the peaks relative to Ar are showed.



Figure 5S. TEM images (left) and EDS spectra (right) of the  $Ni_{0.89}$ -Pt<sub>0.11</sub> nanocatalyst recovered after reaction: magnifications of 5 nm (a), 10 nm (b), and 100 nm (c).



Figure 6S. SAED of the  $Ni_{0.89}Pt_{0.11}$  nanocatalyst recovered after reaction.



**Figure 7S**. XRD patterns of the Ni (ICDD 03-065-0380), Pt (ICDD 01-087-0640) and Ni<sub>0.89</sub>Pt<sub>0.11</sub> nanocatalysts after dehydrogenation of HB at 50 °C. The peaks centered at around  $2\theta = 34$  and  $60^{\circ}$  might be ascribed to Ni(OH)<sub>2</sub>·0.75H<sub>2</sub>O (ICDD 00-038-0715).



**Figure 8S**. XPS spectra (overall, B 1s, O 1s, Ni 2p, and Pt 4f) for the Ni<sub>0.89</sub>Pt<sub>0.11</sub> nanocatalyst recovered after reaction. The colors indicate the materials before and after the 1 to 5 argon sputtering processes: red = surface; navy blue =  $1^{st}$  sputtering; light blue =  $2^{nd}$  one; green =  $3^{rd}$  one; pink =  $4^{th}$  one; and orange =  $5^{th}$  one.

## References

- (1) C.G. Salentine, Inorg. Chem. 1983, 22, 3920.
- (2) J. Hannauer, U.B. Demirci, C. Geantet, J.M. Herrmann, P. Miele, Phys. Chem. Chem. Phys. 2011, 13, 3809.