

Hydrazine borane: synthesis, characterization, and application prospects in chemical hydrogen storage

Romain Moury^{1,+}, Georges Moussa^{1,+}, Umit B. Demirci^{1,2,*}, Julien Hannauer², Samuel Bernard¹, Eddy Petit¹, Arie van der Lee¹, Philippe Miele¹

[1] Institut Européen des Membranes, Université Montpellier 2, CNRS, UMR 5253, Laboratoire des Agrégats Interfaces et Matériaux pour l'Energie, Place Eugène Bataillon, F-34095 Montpellier Cedex 5, France

[2] Université Lyon 1, CNRS, UMR 5615, Laboratoire des Multimatériaux et Interfaces, 43 boulevard du 1 Novembre 1918, F-69622 Villeurbanne, France

* *Corresponding Author*

Dr. Umit B. DEMIRCI

Email: umit.demirci@iemm.univ-montp2.fr

Tel. +33 (0)4 67 14 91 60

Fax +33 (0)4 67 14 91 19

+ Romain Moury and Georges Moussa have an equal contribution in this work.

Electronic Supplementary Information

Materials. Hydrazine hemisulfate salt ($(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$) (Sigma-Aldrich), sodium borohydride NaBH_4 (Acros), anhydrous 1,4-dioxane (Sigma-Aldrich) and pentane (Sigma-Aldrich) were used as received. Hydrazine hemisulfate and sodium borohydride were stored and handled in an argon-filled glove box (MBraun M200B, $\text{H}_2\text{O} < 0.1$ ppm, $\text{O}_2 < 0.1$ ppm). The solvents were used under an argon flow to prevent pollution by moisture and air. Millipore milli-q water with a resistivity $> 18 \text{ M}\Omega \text{ cm}$ was used.

Synthesis 1. Synthesis 1 was performed according to 2 literature methods, the original one being from Goubeau and Ricker's work,^[1] and the second one being its modified version.^[2] Nevertheless, we brought few slight changes in the latter method. In the argon-filled glove box, hydrazine hemisulfate and sodium borohydride were separately, finely ground in agate mortars. Then, 21.59 g of hydrazine hemisulfate and 10.12 g of sodium borohydride were transferred in a 250 mL round-

bottom Schlenk flask. The glassware was then put in an argon-vacuum line and in an oil bath set at 30 °C to avoid pressure variations during the reaction. Then, 80 mL of dioxane was added under vigorous stirring. The reaction started immediately, H₂ evolved. The outlet of the Schlenk flask was connected to a bubble counter filled with paraffin oil, via a water-cooler and a flask used as trap for the paraffin oil. The reaction mixture was stirred until that the H₂ evolution ceased. After Schlenk filtration, the filtrate was transferred in a 250 mL round-bottom Schlenk flask and the solvent was slowly removed under vacuum till the apparition of a slight turbidity (solubility of HB). Pentane was then dropwise added to make HB precipitate. The solvents were removed by extraction. The crystals were washed several times with pentane and dried under vacuum in room conditions overnight. The as-obtained material is a white solid (5.7 g; yield 47%), with a purity of 99% verified by ¹H and ¹¹B solution-state NMR on a Bruker DRX-400 using a probe head BBFO+ such as: ¹H NMR (δ/ppm, 400.13 MHz, C₄D₈O, 25 °C, J/Hz): 6.04 (s, 2H B–NH₂), 3.54 (s, 2H, N–NH₂), 1.48 (q, 3H, ¹J_{HB} = 94.5 Hz); and, ¹¹B NMR (δ/ppm, 128.38 MHz, C₄D₈O, 298.51 K, J/Hz): -15.03 (q, ¹J_{BH} = 95 Hz).

Synthesis 2. An analogous procedure as for synthesis 1 was adapted. The main differences are as follows. In the glove box, hydrazine hemisulfate was suspended in 50 mL of dioxane in a 250 mL round-bottom Schlenk flask under stirring while sodium borohydride was suspended in 50 mL dioxane in an identical flask under stirring. The suspensions were mixed together. The mixture was then put in an argon-vacuum line. The reaction was performed 24 h. The as-obtained material (2.0 g; yield 16.6%) showed a purity of 51%, as verified by ¹H and ¹¹B solution-state NMR on a Bruker AV-300 (7.049 T). ¹H NMR (δ/ppm, probe head Dual ¹H/¹³C, 300.13 MHz, CD₃CN, 30 °C, J/Hz): 5.43 (s, 2H B–NH₂) 3.43 (s, 2H, N–NH₂), 1.42 (q, 3H, ¹J_{HB} = 95 Hz). ¹¹B NMR (δ/ppm, probe head BBO10, 96.29 MHz, D₂O, 30 °C, J/Hz): -17.2 (q, ¹J_{BH} = 95 Hz).

Synthesis 3. For this synthesis, the procedure applied in synthesis 2 was modified. In the glove box, hydrazine hemisulfate was suspended in 50 mL of dioxane in a 500 mL three-necked round-bottom flask under vigorous stirring and put in the argon-vacuum line. The amount of hydrazine hemisulfate (21.58 g) was chosen to be in slight excess of that of sodium borohydride (9.99 g). Sodium borohydride was transferred in a 250 mL dropping-funnel and added to the hydrazine hemisulfate suspension under argon flow. The mixture was stirred 48 h, and then filtrated. The solid by-products were washed with dioxane, which was kept and added to the filtrate. The solvent was removed under vacuum at 30 °C (oil bath), then the as-obtained HB dried overnight at 30 °C. The crystallization with pentane was discarded. The as-obtained material (8.7 g; yield 72.5%) had a purity of 98.3%. ¹H NMR (δ/ppm, probe head Dual ¹H/¹³C, 300.13 MHz, CD₃CN, 30 °C, J/Hz): 5.44 (s, 2H B–NH₂) 3.44 (s,

2H, N–NH₂), 1.42 (q, 3H, ¹J_{HB} = 95 Hz). ¹¹B NMR (δ/ppm, probe head BBO10, 96.29 MHz, D₂O, 30 °C, J/Hz): -17.2 (q, ¹J_{BH} = 95 Hz).

Synthesis 4. The procedure was adapted from synthesis 3. In the glove box, 21.59 g of hydrazine hemisulfate and 10.12 g of sodium borohydride were transferred in a 500 mL three-necked round-bottom flask. In fact, while we were working on finding the solubility of HB in dioxane, we found that the experimental conditions used before did not enable the solvation of all formed HB. Hence, the volume of solvent was increased to 150 mL; 50 mL were used to wash the solid by-products. The HB formed was thus solubilized in 200 mL of dioxane. The as-obtained material (9.1 g; yield 74.7%) had a purity of 94.8%. ¹H NMR (δ/ppm, probe head Dual ¹H/¹³C, 300.13 MHz, CD₃CN, 30 °C, J/Hz): 5.45 (s, 2H B–NH₂) 3.44 (s, 2H, N–NH₂), 1.42 (q, 3H, ¹J_{HB} = 95 Hz). ¹¹B NMR (δ/ppm, probe head BBO10, 96.29 MHz, D₂O, 30 °C, J/Hz): -17.3 (q, ¹J_{BH} = 95 Hz).

Synthesis 5. Synthesis 5 was considered on the basis of syntheses 2 and 4. Hydrazine hemisulfate was suspended in 100 mL of dioxane in a 500 mL three-necked round-bottom flask under stirring while sodium borohydride was suspended in 50 mL of dioxane in a 250 mL round-bottom Schlenk flask under stirring. The sodium borohydride suspension was transferred in the other under high flux of argon. The reaction was then stirred 24 h. 50 mL of dioxane were used to wash the solid during filtration. The as-obtained material (9.9 g; yield 81.3%) showed a purity of 94.9%. ¹H NMR (δ/ppm, probe head Dual ¹H/¹³C, 300.13 MHz, CD₃CN, 30 °C, J/Hz): 5.44 (s, 2H B–NH₂) 3.44 (s, 2H, N–NH₂), 1.42 (q, 3H, ¹J_{HB} = 95 Hz). ¹¹B NMR (δ/ppm, probe head BBO10, 96.29 MHz, D₂O, 30 °C, J/Hz): -17.3 (q, ¹J_{BH} = 95 Hz).

Synthesis 6. We considered the optimizations of the previous syntheses. In the glove box, 21.59 g of hydrazine hemisulfate and 10.12 g of sodium borohydride were transferred in a 500 mL three-necked round-bottom flask. The flask was put in the argon-vacuum line and 150 mL of dioxane was added. The mixture was kept under stirring for 48 h at 30 °C. It was then filtrated and the by-products washed with 50 mL of dioxane. The filtrate was dried under vacuum overnight. The as-obtained material (9.8 g; yield 80.3%) had a purity of 99.6%. ¹H NMR (δ/ppm, probe head Dual ¹H/¹³C, 300.13 MHz, CD₃CN, 30 °C, J/Hz): 5.45 (s, 2H B–NH₂) 3.44 (s, 2H, N–NH₂), 1.42 (q, 3H, ¹J_{HB} = 95 Hz). ¹¹B NMR (δ/ppm, probe head BBO10, 96.29 MHz, D₂O, 30 °C, J/Hz): -17.3 (q, ¹J_{BH} = 95 Hz). With respect to yield, our various attempts did not enable to get values higher than ~82% because some matter spatters on the glassware during drying and some dried matter is lost during the transfer into vials, being pasted onto the Schlenk flask.

References.

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SupMat - Hydrazine borane: synthesis, characterization, and application prospects in chemical hydrogen storage

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The below figure is integrated as 3D content in this pdf-file. The molecule can be manipulated with the mouse, just by holding the left mouse button down on the molecule and shifting it gently. By holding the right mouse button down on the molecule and shifting the cursor up and down, the molecule can be zoomed in and zoomed out. There are more options accessible with a right-click on the molecule. Adobe Reader 7.0 or better is needed.