Supporting Information

A Facile One-Step Synthesis of Polymer Supported Rhodium Nanoparticles in Organic Medium and Their Catalytic Performance in the Dehydrogenation of Ammonia-Borane

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References cited herein are those independent from the main text.
Section 1: Experimental

Materials. Chloro(1,5-cyclooctadiene) rhodium(I) dimer ([Rh(µ-Cl)(1,5-cod)]2), ammonia-borane (H3NBH3, 97 %), carbodisulfide (CS2), deuterated tetrahydrofuran (THF-d8) and boron free quartz NMR tubes (Norell S-500-QTZ) were purchased from Aldrich. Hydrazine hydrate (N2H4.H2O) and hydrazine sulfate ((N2H6)SO4) were purchased from Merck. THF was distilled over sodium/benzophenone under argon and stored in the drybox (H2O and O2 < 1 ppm). Deionized water was distilled by a water purification system (Milli-Q System). All glassware and Teflon coated magnetic stir bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

Characterization. The chemical composition of the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Varian-Vista) after each sample was completely dissolved in the mixture of HNO3/HCl in a 1:3 ratio. Powder X-ray diffraction (XRD) patterns were acquired on a MAC Science MXP 3TZ diffractometer using Cu Kα radiation (wavelength 1.5406 Å, 40 kV, 55 mA). The XPS analysis was performed on a Physical Electronics 5800 spectrometer equipped with a hemispherical analyzer and using monochromatic Al Kα radiation (1486.6 eV, the X-ray tube working at 15 kV, 350 W and pass energy of 23.5 keV). ATR-IR spectra were taken on Vartex-70 spectrophotometer using Omnic software. TEM, HRTEM, and EDX analyses were done on a FEI Tecnai G² (X-Twin) microscope with an accelerating voltage of 120 kV (2 Å resolution). SEM-FEG images of the samples were taken by using Quanta 400 F Field Emission SEM. The nitrogen adsorption/desorption experiment was carried out at 77 K using a NOVA 3000 series instrument (Quantachrome Instruments). The sample was outgassed under vacuum at 373 K for 1 h before the adsorption of nitrogen.
MALDI-TOF analysis was carried out by using an Ultraflex-TOF/TOF mass spectrometer (Bruker Daltonics, Billerica, MA) in positive ion, reflector mode using a 25 kV accelerating voltage. External calibration is done using a peptide calibration mixture (4 to 6 peptides) on a spot adjacent to the sample. The raw data is processed in the FlexAnalysis software (version 2.4, Bruker Daltonics). The solid state $^{11}$B-NMR was performed on Bruker Biospin 300 MHz spectrometer in which chemical shifts were measured relative to external NaBH$_4$ (~41 ppm).

The solution NMR studies were carried out by using Avance DPX 400 MHz spectrometer (400.1 MHz for $^1$H NMR; 100.6 MHz and 128.2 MHz for $^{11}$B NMR). Si(CH$_3$)$_4$ and BF$_3$. (C$_2$H$_5$)$_2$O was used as the internal reference for $^1$H and $^{11}$B NMR chemical shifts, respectively.

Synthesis of Dihydrazine Sulfate ($\left(\text{N}_2\text{H}_5\right)_2\text{SO}_4$) and Hydrazine Borane ($\text{N}_2\text{H}_4\text{BH}_3$). Dihydrazine sulfate ($\left(\text{N}_2\text{H}_5\right)_2\text{SO}_4$) and hydrazine borane ($\text{N}_2\text{H}_4\text{BH}_3$) were prepared and identified according to literature procedures. The melting point of hydrazine borane: ~60 °C; (DP-MS) m/z = 46 (45.87 calculated for N$_2$H$_4$BH$_3$); $^1$H NMR (400.1 MHz, CD$_2$Cl$_2$) 5.1 ppm (t, 2, NH$_2$-NH$_2$-BH$_3$), 3.4 ppm (b, 2, H$_2$N-NH$_2$-BH$_3$), 1.2 ppm (t, 3, H$_2$N-NH$_2$-BH$_3$); $^{11}$B NMR (128.2 MHz, H$_2$O) -20 ppm (q, BH$_3$); ATR-IR (selected, cm$^{-1}$) 3310 (s), 3200 (s), 2840 (m), 2650 (m), 2370 (m), 2214 (m), 1620 (s), 1588 (m), 1435 (w), 1332 (m), 1150 (s), 910 (m), 747 (w) in agreement with the literature values.

In-Situ Preparation of Rh@PAB During the Dehydrogenation of Hydrazine Borane. The in-situ formation of polymer entrapped Rhodium nanoparticles and the concomitant dehydrogenation of hydrazine borane were performed in a Fischer-Porter (F-P) pressure bottle connected to a line through Swagelock tetrafluoroethylene (TFE)-sealed quick connects and to an Omega PX-302 pressure transducer interfaced through an Omega D1131


digital transmitter to a computer using the RS-232 module as described elsewhere. The progress of an individual dehydrogenation reaction was followed by monitoring the increase in the pressure of H₂ gas on the LabVIEW 8.0 program. In a typical experiment, 5 mmol N₂H₄BH₃ (230 mg) was weighted and taken into a new 22 × 175 mm pyrex culture tube containing a new 5/16 in. × 5/8 in. The culture tube was then sealed inside the F-P bottle, which was brought outside the drybox and placed inside a constant-temperature circulating water bath thermostated at 25.0 ± 0.1 ºC. Next, the F-P bottle was connected to the line, which had already been evacuated for at least 30 min to remove any trace of oxygen and water present, via its Swagelock TFE-sealed quick connects. Under nitrogen purging (15 mL of dry nitrogen/s), 1.0 mL of 7.5 mM [Rh(µ-Cl)(1,5-cod)]₂ was added to the F-P bottle rapidly via tap of bottle by using a 10 mL pyrex volumetric pipet, which had been nitrogen-flushed three times. The reaction was started (t=0 min) by stirring the mixture at 600 rpm. When no more hydrogen generation was observed, the experiment was stopped, the F-P bottle was sealed and disconnected from the line, and the hydrogen pressure was released. Then the F-P bottle was transferred back into the drybox. An approximately 0.5 mL aliquot of the reaction solution in the culture tube was withdrawn with a 9 in. glass Pasteur pipet and added to 1 g of THF-d₈ in an individual glass ampule. The solution was then transferred into a quartz NMR sample tube, which was subsequently sealed and then brought out of the drybox. The ¹¹B NMR spectrum of this solution was found to be silent. The insoluble product formed at the end of the reaction was taken into a new Schlenk tube by simple decantation and brought outside the drybox. Then, it was dried 3 h under vacuum (10⁻³ Torr) for characterization.

3 (a) Zahmakiran, M.; Özkar, S. Langmuir 2008, 24, 7065; (b) Zahmakiran, M.; Özkar, S. Langmuir 2009, 25, 2667.
Testing the Catalytic Activity of Rh@PAB in the Hydrolytic Dehydrogenation of Ammonia-Borane and Determination of Activation Energy. The same system described in the previous section was used in all of these experiments. In a typical experiment, 2 mmol H$_3$NBH$_3$ (63.6 mg) was dissolved in 10 mL water. This solution was transferred with a 50 mL glass-pipette into the FP bottle thermostated at 25.0 ± 0.1 ºC. Then, Rh@PAB (6.8 mg with 1.5 wt.% Rh) was transferred into the FP bottle. The experiment was started by closing the FP bottle connected to the pressure transducer and turning on the stirring at 1000 rpm simultaneously. The same experiment was also performed at 10, 15, 20 and 30 ºC to determine activation energy $E_a$. In all experiments, the conversion of ammonia-borane to ammonium metaborate was also checked by comparing the intensities of signals of ammonia-borane and metaborate anion at $\delta = -23.9$ and 9 ppm, respectively, in the $^{11}$B NMR spectra of the solution.

Reusability of Rh@PAB in the Hydrolytic Dehydrogenation of Ammonia-Borane. After the first run of hydrolysis of 2 mmol H$_3$NBH$_3$ (63.6 mg), catalyzed by Rh@PAB (6.8 mg with a rhodium content of 1.5 wt.%, [Rh] = 0.1 mM) at 25 ºC, the catalyst was isolated by vacuum (10$^{-3}$ Torr), and dried under N$_2$ gas purging at room temperature then bottled under nitrogen atmosphere and transferred into the drybox. The isolated and bottled samples of rhodium nanoparticles catalyst were weighted and used again in the hydrolysis of 2 mmol H$_3$NBH$_3$. The same methodology was followed up to the third reuse and in all the result was expressed as turnover frequency (TOF).
Section 2: Results

Figure S-1. Solid-state $^{11}$B NMR (240 MHz) spectrum of THF-insoluble product formed at the end of the dehydrogenation of hydrazine borane starting with [Rh(μ-Cl)(1,5-cod)]$_2$ precatalyst in THF at 25 °C. Asterisks indicate the formation of negligible amount of BO$_x$ species.
Figure S-2. MALDI-TOF MS spectra (a) in the m/z range of 0-5500 (b) 1440-2540 of THF-insoluble product formed at the end of the dehydrogenation of hydrazine borane starting with [Rh(µ-Cl)(1,5-cod)]$_2$ precatalyst in THF at 25 °C.
Figure S-4. (a) XPS survey spectrum (b) high resolution Rh 3d XPS spectrum of Rh@PAB.

Figure S-5. STEM image and EDS spectra of the selected regions as indicated in STEM image of Rh@PAB.
**Figure S-6.** (a) TEM image (b) high resolution TEM image of Rh@PAB harvested at the end of the 5th reuse in the hydrolytic dehydrogenation of ammonia-borane.