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Catalytic methanolysis of hydrazine borane: a new and efficient hydrogen generation system under mild conditions†

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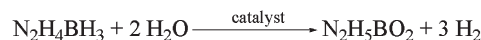
Safe and efficient hydrogen storage is a major obstacle for using hydrogen as an energy carrier. Therefore, intensive efforts have been focused on the development of new materials for chemical hydrogen storage. Of particular importance, hydrazine borane ($N_2H_4BH_3$) is emerging as one of the most promising solid hydrogen carriers due to its high gravimetric hydrogen storage capacity (15.4 wt%) and low molecular weight. Herein, we report metal catalyzed methanolysis of hydrazine borane ($N_2H_4BH_3$, HB) as a fast hydrogen generation system under mild conditions. When trace amounts of nickel(II) chloride ($NiCl_2$) is added to the methanol solution of hydrazine borane ([HB]/[Ni] $\geq$ 200) the reaction solution releases 3 equiv. of H_2 with a rate of 24 mol H_2 (mol Ni min)$^{-1}$ at room temperature. The results reported here also includes (*i*) identification of the reaction products by using ATR-IR, DP-MS, ^{1}H and ^{11}B NMR spectroscopic techniques and the establishment of the reaction stoichiometry, (*ii*) investigation of the effect of substrate and catalyst concentrations on the hydrogen generation rate to determine the rate law for the catalytic methanolysis of hydrazine borane, (*iii*) determination of the activation parameters (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$) for the catalytic methanolysis of hydrazine borane by using the temperature dependent rate data of the hydrogen generation.

Introduction

Hydrogen is a globally accepted clean energy carrier, which could overcome the world energy problem and reduce the environmental pollution caused by using fossil fuels as energy source.[1] However, the safe and efficient storage of hydrogen is still one of the most important and challenging problems in the hydrogen based energy policies.[2] Because of this concern, there has been a rapidly growing interest for the development of solid materials with high volumetric and gravimetric storage capacity for chemical hydrogen storage.[3] B–N compounds[4] such as ammonia–triborane,[5] ammonia–borane,[6] amine–borane adducts[6,7] and ammonium borates[8] are well suited for this

purpose due to their low weight, high gravimetric hydrogen storage capacity and inclination for bearing protic (N–H) and hydridic (B–H) hydrogens. In addition, it has been shown that hydrazine borane ($N_2H_4BH_3$, HB) with a gravimetric hydrogen storage capacity of 15.4 wt%, which is greater than the 2015 target of US Department of Energy (9 wt% hydrogen for a material to be practically applicable),[2] needs to be considered as another B–N compound that can be used for the storage of hydrogen.[9–12] Hydrazine borane can release its hydrogen very slowly up to 6.5 wt% upon heating to 150 °C in 16 h.[9] Additionally, recent studies[10–12] have shown that efficient hydrogen release can be achieved by its metal catalyzed dehydrogenation (Scheme 1) at room temperature in water. Although, the catalytic hydrolysis of hydrazine borane provides fast hydrogen generation under mild conditions, the instability of hydrazine borane towards the self-hydrolysis in water creates an important problem for using this system as a high performance hydrogen source to portable fuel cells.[10]

Herein, we demonstrate the catalytic alcoholysis of hydrazine borane by using nickel(II) chloride precatalyst in methanol, where hydrazine borane can not undergo self-alcoholysis. When trace amounts of nickel(II) chloride is added to the methanol solution of hydrazine borane ([HB]/[Ni] $\geq$ 200) the generation of 3

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†Electronic supplementary information (ESI) available: Fig. ESI-1: ^{11}B NMR spectrum of the reaction solution taken at the end of the hydrogen generation from hydrazine borane in a solution that contains 5 mL water and 5 mL methanol starting with $NiCl_2$ precatalyst; Fig. ESI-2: Volume of hydrogen *versus* time graph for the hydrogen generation from hydrazine borane in a solution that contains 5 mL water and 5 mL methanol starting with $NiCl_2$ precatalyst; Fig. ESI-3: XPS spectrum of bulk nickel isolated at the end of the methanolysis of hydrazine borane starting with $NiCl_2$ precatalyst; Fig. ESI-4: TEM image and TEM-EDX spectrum of the filtrate taken at the end of the methanolysis of hydrazine borane starting with $NiCl_2$ precatalyst; Fig. ESI-5: Catalytic methanolysis of hydrazine borane (400 mM in 10 mL methanol) starting with Ni(II)-2-ethyhexanoate (11.0 mM). See DOI: 10.1039/c2dt11867j

$$N_2H_4BH_3 + 2\,H_2O \xrightarrow{\text{catalyst}} N_2H_5BO_2 + 3\,H_2$$

Scheme 1 The catalytic hydrolysis of hydrazine–borane ($N_2H_4BH_3$) in water.[10–12]

equiv. of H_2 with a rate of 24 mol H_2 (mol Ni min)$^{-1}$ is observed at room temperature. The studies reported herein also deal with the identification of reaction products to write net reaction stoichiometry, investigation of reaction kinetics to establish the rate law and activation parameters (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$) for the methanolysis of hydrazine borane starting with nickel(II) chloride (NiCl$_2$) precatalyst.

Experimental

Materials

Nickel(II) chloride hexahydrate (99%), sodium borohydride (99%), tetrahydrofuran (99.9%), activated carbon, nickel(II)-2-ethylhexanoate and methanol (99%) were purchased from Aldrich. Nickel coated graphite powder (Ni : C = 3 : 2) was purchased from Alfa Aesar. Activated carbon supported nickel precatalyst was prepared by using solution impregnation technique.[13] Dihydrazine sulfate (98%) was purchased from Acros-Organics. THF and methanol was distilled over sodium–benzophenone and metallic magnesium respectively under argon and stored in the drybox (H_2O and O_2 < 1 ppm). NiCl$_2$·6H$_2$O was dehydrated at >100 °C in the oven. All glassware and Teflon coated magnetic stirrer bars were cleaned with acetone, followed by copious rinsing with distilled water before drying in an oven at 150 °C.

Characterization

All catalytic reactions and manipulations were performed under inert gas atmosphere using standard Schlenk techniques or in a Labsconco glovebox (H_2O and O_2 < 1 ppm) filled with dry nitrogen unless otherwise specified. ATR-IR spectra were taken on a Vartex-70 spectrophotometer using Omnic software. NMR spectra were recorded on a Bruker Avance DPX 400 MHz spectrometer (400.1 MHz for ^{1}H; 128.3 MHz for ^{11}B). TMS was used as internal reference for ^{1}H NMR chemical shifts. BF$_3$·(C$_2$H$_5$)$_2$O (^{11}B; 0 ppm (s), ^{1}H; 4.2 ppm, (q), OCH$_2$CH$_3$ and 1.4 ppm, (t), OCH$_2$CH$_3$) was used as external reference for ^{11}B NMR chemical shifts. Direct pyrolysis mass spectrometry (DP-MS) analyses were performed on a Waters Micromass Quattro Micro GC Mass Spectrometer with a mass range of 10–1500 Da and EI-ion source, coupled to a direct insertion probe by recording the 70 eV EI mass spectra at a mass scan rate of 1 scan s^{-1}.

Synthesis of hydrazine borane (N$_2$H$_4$BH$_3$)

Hydrazine borane (N$_2$H$_4$BH$_3$) was prepared and identified according to the procedure as described elsewhere;[14] the melting point of hydrazine borane: ∼60 °C; 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 (128.3 MHz, CH$_3$OH) −19 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.[14]

General procedure for the catalytic methanolysis of hydrazine borane and handling of hydrogen generation data

The catalytic methanolysis of hydrazine borane was performed using a Fischer–Porter (FP) pressure bottle. The F–P bottle was connected to a line through Swagelock 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. The progress of an individual methanolysis reaction was followed by monitoring the increase in the pressure of H_2 gas on the Lab View 8.0 program. The pressure *versus* time data was processed using Microsoft Office Excel 2003 and Origin 7.0 then converted into the values in proper units of volume of hydrogen (mL). In a typical experiment, 184 mg (4 mmol) N$_2$H$_4$BH$_3$ was dissolved in 7.0 mL methanol in a dry box (corresponding to a maximum amount of H_2 gas of 12 mmol = 322.9 mL at 25.0 ± 0.1 °C and 0.91 atm pressure in the F–P bottle). This solution was transferred with a 10 mL glass–pipette into the F–P bottle containing a new (5/16) in. × (5/8) in. Teflon coated magnetic stirrer bar. The F–P bottle was sealed and removed from the drybox and placed inside a constant temperature circulating water bath thermostated at 25.0 ± 0.1 °C. Next, the F–P bottle was attached to the line (which had already been evacuated for at least 30 min to remove any trace of oxygen and water present) *via* its TFE-sealed Swagelock Quick-Connects. Under nitrogen purging (14 mL dry N$_2$/s), a 3.0 mL methanol solution of catalyst in desired amount was added into a F–P bottle rapidly *via* a tap by using a 10 mL gastight syringe. The reaction was started (t = 0 min) by stirring the mixture at 1000 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 taken back into the drybox. An aliquot was then transferred into a quartz NMR sample tube, which was subsequently sealed and then brought out of the drybox. The ^{11}B NMR spectrum of this solution showed that N$_2$H$_4$BH$_3$ (δ = −19 ppm, (q)) is completely converted to N$_2$H$_5$B(OCH$_3$)$_4$ (δ = 9.5 ppm, (s)).[15] Next, the reaction solution was filtered into a Schlenk flask. The Schlenk flask was then sealed and brought outside the drybox and subjected to vacuum under liquid nitrogen vapour for condensation of a small amount of sublimed borate crystals. The borate crystals that condensed on the inner wall of the Schlenk flask in the vacuum were analyzed. ^{11}B NMR (δ = 9.5 ppm, s), ^{1}H NMR (δ = 3.9 ppm, (s) [N$_2$H$_5$]$^+$ and 3.3 ppm, (s) (OCH$_3$)$_4$) m/z = 167.4 (167.9 calculated for N$_2$H$_5$B(OCH$_3$)$_4$). ATR-IR (cm^{-1}) (597, C–H rocking), (950, B–O asymmetric stretching), (984, N–N stretching for N$_2$H$_5$$^+$), (1054, C–O stretching), (1192, C–H rocking), (1254, B–O deformation), (1381, B–O stretching), (1463, C–H deformation), (2895, C–H stretching), (3153, 3258, N–H stretching).[16]

Transmission electron microscopy (TEM) analysis of reaction solution resulting from the methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

The sample used for the TEM experiment was harvested from the reaction solution. One drop of this colloidal solution was deposited on the chloroform cleaned, carbon coated Cu-TEM

grid and the solvent was then evaporated and analyzed by using Philips CM-12 TEM with a 70 mm lens operating at 100 kV and with a 2.0 Å point-to-point resolution. The elemental analysis was performed by using an energy dispersive X-ray (EDX) analyzer (KEVEX Delta series) mounted on a Hitachi S-800.

X-ray photoelectron spectroscopy (XPS) analysis of bulk nickel formed at the end of the methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

After the decantation of the supernatant solution at the end of the methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst, the precipitates were dried under vacuum for 2 h. The dried sample was collected in a screw-capped glass vial and used for XPS analysis. The X-ray photoelectron spectrum (XPS) was obtained by using a SPECS spectrometer equipped with a hemispherical analyzer and using monochromatic Mg Kα radiation (1250.0 eV, the X-ray tube working at 15 kV and 350 W) and pass energy of 48 eV.

Hydrogen generation from the hydrazine borane in methanol–water ($v/v = 1/1$) mixture starting with nickel(II) chloride precatalyst

The catalytic hydrogen generation from hydrazine borane ($[N_2H_4BH_3] = 400$ mM) in a 10 mL solution containing 5 mL H_2O and 5 mL CH_3OH was conducted at room temperature by using 5.0 mM $NiCl_2$ precatalyst at 25.0 ± 0.1 °C.

Kinetic studies for the catalytic methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

In order to establish the rate law for catalytic methanolysis of $N_2H_4BH_3$ using $NiCl_2$, two different sets of experiments were performed in the same way as described in the previous section. In the first set of experiments, $[N_2H_4BH_3]$ was kept constant at 400 mM (in 10 mL) and [Ni] was varied in the range of 1.0, 1.5, 2.0, 3.0, and 4.0 mM. In the second set of experiments, [Ni] was held constant at 2.5 mM (in 10 mL) while $[N_2H_4BH_3]$ was varied in the range of 100, 200, 300, 400 and 500 mM.

Determination of activation parameters for the catalytic methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst and self-methanolysis of hydrazine borane

The catalytic methanolysis of $N_2H_4BH_3$ starting with $NiCl_2$ precatalyst at constant $[N_2H_4BH_3]$ (400 mM in 10 mL) and [Ni] (2.5 mM) concentrations was performed at 10, 15, 20, 25 and 30 °C in the same way as described in previous sections. The values of the rate constants k_{obs} were determined for each temperature and used to obtain the activation energy E_a by using an Arrhenius plot as well as the enthalpy of activation $\Delta H^{\neq}$ and entropy of activation $\Delta S^{\neq}$ by using an Eyring–Polanyi plot. In a series of control experiments the methanolysis of hydrazine borane (400 mM in 10 mL) was investigated at 10, 15, 20, 25 and 30 °C in the absence of catalyst.

Testing the kinetic competence of bulk nickel(0) formed in situ during the methanolysis of hydrazine borane as an active catalyst in the methanolysis of hydrazine borane

At the end of the complete methanolysis of 100 mM $N_2H_4BH_3$ starting with 2.0 mM $NiCl_2$ in 10 mL CH_3OH at 25 ± 0.1 °C, the experiment was stopped and the F–P bottle was sealed, disconnected from the line and H_2 pressure was released. Then the F–P bottle was transferred back into the drybox, and the reaction solution was then filtered by using Dualex™ Millipore (200 nm) into a new 22 × 175 mm pyrex culture tube containing a new 5/16 in. × 5/8 in. Teflon coated magnetic stirrer. The culture tube was then sealed inside the F–P pressure bottle and brought outside the drybox and placed in a constant temperature circulating water bath. Next, the F–P bottle was attached to the line via its TFE-sealed Swagelock Quick-Connects and under nitrogen purging, 1 mL methanol solution of $N_2H_4BH_3$ (50.6 mg) was added into a F–P bottle rapidly via a tap by using a 10 mL gas-tight syringe. The reaction was started ($t = 0$ min) by stirring the mixture at 1000 rpm. Then, the hydrogen pressure was monitored for 2 h. In another control experiment the catalytic activity of isolated bulk nickel(0) metal was tested in the methanolysis of 100 mM $N_2H_4BH_3$ in 10 mL CH_3OH at 25 ± 0.1 °C.

Mercury (Hg(0)) poisoning of active catalyst in the catalytic methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

A typical methanolysis of 400 mM $N_2H_4BH_3$ (73.6 mg) starting with 1.0 mM $NiCl_2$ in 4.0 mL CH_3OH was performed at 25 ± 0.1 °C. When ~30% of conversion was reached, elemental mercury (Hg, 802 mg, ca. ~1000 equiv.) was added and the hydrogen pressure was monitored further for 3 h.

Determination of the catalytic lifetime of active catalyst in the methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

The catalytic lifetime of bulk nickel formed in situ during the methanolysis of hydrazine borane starting with the nickel(II) chloride precatalyst was determined by measuring total turnover number (TTO). Such an experiment was realized with [Ni] = 0.1 mM nickel and $[N_2H_4BH_3] = 400$ mM in 10 mL dry methanol at 25 ± 0.1 °C.
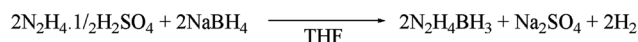
Testing the catalytic activity of different nickel catalysts in the methanolysis of hydrazine borane

The catalytic activity of different nickel catalysts (Ni(II)@activated carbon, Ni(0)@graphite powder and Ni(II)-2-ethylhexanoate, in all [Ni] = 11 mM) were tested in the methanolysis of hydrazine borane (400 mM) in 10 mL CH_3OH at 25 ± 0.1 °C.
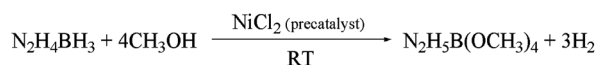
Results and discussion

Catalytic methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst

Hydrazine borane ($N_2H_4BH_3$) was prepared according to procedure described elsewhere,[14] which involves the reaction of

$$2N_2H_4.1/2H_2SO_4 + 2NaBH_4 \xrightarrow{\text{THF}} 2N_2H_4BH_3 + Na_2SO_4 + 2H_2$$

Scheme 2 The synthesis of hydrazine borane from the reaction of dihydrazine sulfate with sodium borohydride in THF at room temperature.[14]

$$N_2H_4BH_3 + 4CH_3OH \xrightarrow[\text{RT}]{\text{NiCl}_2 \text{ (precatalyst)}} N_2H_5B(OCH_3)_4 + 3H_2$$

Scheme 3 The catalytic methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst at room temperature.
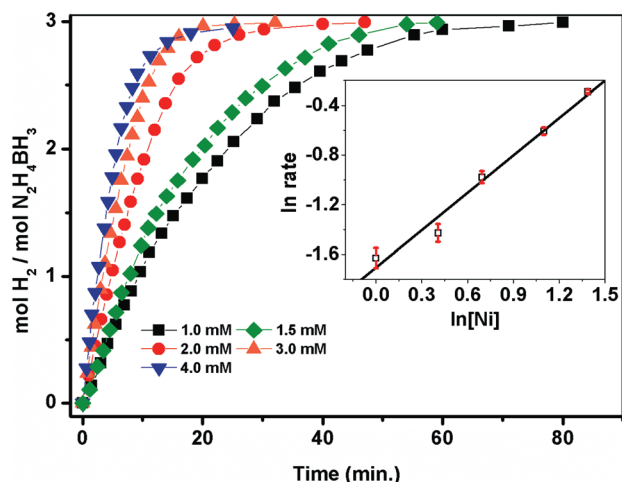

Fig. 1 (a) Plot of mol H_2/mol $N_2H_4BH_3$ *versus* time (min) for the catalytic methanolysis of 10 mL of 400 mM hydrazine borane ($N_2H_4BH_3$) starting with $NiCl_2$ with different nickel concentrations ([Ni] = 1, 1.5, 2, 3 and 4 mM) at 25.0 ± 0.1 °C (b) Inset: plot of the hydrogen generation rate *versus* the catalyst concentration, both in logarithmic scale, for the catalytic methanolysis of $N_2H_4BH_3$.

Fig. 2 ^{11}B NMR (128.3 MHz, unlocked, CH_3OH) spectra of hydrazine borane solution (up), and the reaction solution at the end of the catalytic methanolysis of hydrazine borane starting with $NiCl_2$ at 25.0 ± 0.1 °C (down).

dihydrazine sulfate with sodium borohydride in THF at room temperature (Scheme 2). The purity of the as-prepared hydrazine borane was checked by melting point determination, ATR-IR, DP-MS, ^{1}H and ^{11}B NMR spectroscopic methods and their results (*vide supra*) are in agreement with the previously reported literature data.[14]

Before starting the catalytic methanolysis of hydrazine borane, its stability against the self-methanolysis was checked at 10, 15, 20, 25 and 30 °C. Unlike the aqueous solutions of sodium borohydride, dimethylamine borane, and ammonia triborane, the methanol solution of hydrazine borane shows great stability against self-methanolysis as determined by ^{11}B NMR studies.[10] We selected nickel(II) chloride as a precatalyst for the methanolysis of hydrazine borane because of (i) its previously demonstrated activity in the dehydrogenation of analogous ammonia–borane,[17] (ii) high natural abundance of nickel as a first row transition metal, (iii) its fairly low price. Fig. 1 shows the plots of the mol H_2/mol $N_2H_4BH_3$ *versus* time during the catalytic methanolysis of 400 mM hydrazine borane solution in the presence of $NiCl_2$ precatalyst in different nickel concentrations at 25.0 ± 0.1 °C. A linear hydrogen generation starts without observable induction period and continues until the consumption of hydrazine borane. It is worth noting that 3 equiv. of H_2 generation from the methanolysis of hydrazine borane (mol H_2/mol $N_2H_4BH_3$ = 3 corresponds to 28.5% of total hydrogen content of hydrazine–borane) can be achieved even at high substrate/precatalyst ratio (~400) at 25.0 ± 0.1 °C (Scheme 3).

The hydrogen generation rate was determined from the linear portions of the plots for each experiment with different catalyst
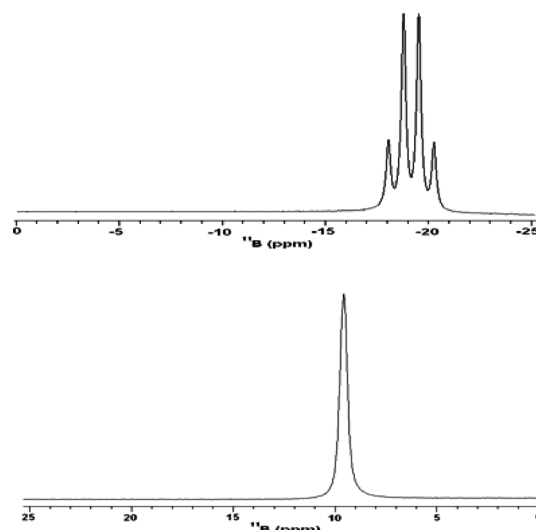
concentration and found to be in the range of 11.8–44.9 mL H_2 min^{-1}, at precatalyst concentrations [Ni] = 1.0–4.0 mM. The plot of hydrogen generation rate *versus* nickel concentration, both on logarithmic scales (Fig. 1 inset), gives a straight line, the slope of which is found to be 1.03 indicating that the methanolysis of hydrazine borane starting with nickel(II) chloride precatalyst proceeds in first order with respect to the nickel concentration. ^{11}B NMR spectrum of the reaction solution at the end of the reaction showed that $N_2H_4BH_3$ ($\delta = -19$ ppm, q) is completely converted to $N_2H_5B(OCH_3)_4$ ($\delta = 9.5$ ppm, s)[15] (Fig. 2) and the crystals of $N_2H_5B(OCH_3)_4$ condensed on the inner wall of the Schlenk flask were isolated and further characterized by ATR-IR and DP-MS spectroscopic methods (*vide supra*). It should be noted that a control test using acid/base indicators was performed to check whether ammonia liberation occurs during the methanolysis of hydrazine borane and ammonia evolution was not observed in detectable amounts.[18]

In another control experiment we carried out hydrogen generation from hydrazine–borane in a solution that contains a (1 : 1) mixture of methanol and water starting with nickel(II) chloride precatalyst. It was found that in the presence of water the hydrazine borane preferentially undergoes hydrolysis rather than methanolysis.[19] The effect of hydrazine borane concentration on the rate of its catalytic methanolysis was also studied by varying the substrate concentration in the range of 100–500 mM while keeping the catalyst concentration constant ([Ni] = 2.5 mM) at 25.0 ± 0.1 °C (Fig. 3). The plot of hydrogen generation rate *versus* hydrazine borane concentration, both on logarithmic scales, indicates that the catalytic methanolysis in the presence
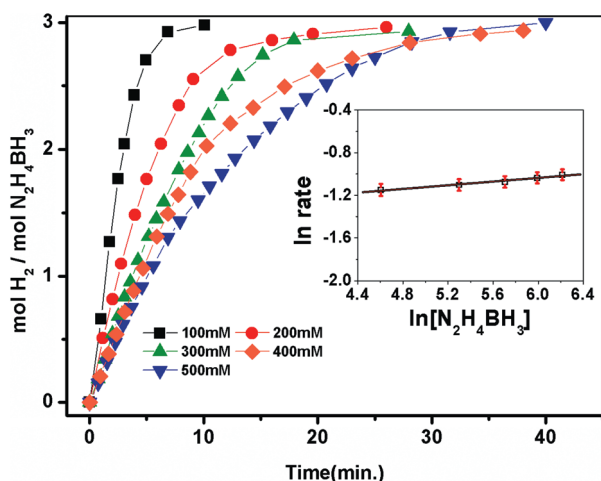
Fig. 3 Plot of mol H_2–mol $N_2H_4BH_3$ *versus* time (min) for the catalytic methanolysis of hydrazine borane ($N_2H_4BH_3$) starting with $NiCl_2$ precatalyst ([Ni] = 2.5 mM in 10 mL CH_3OH), with different hydrazine borane concentrations ([$N_2H_4BH_3$] = 100, 200, 300, 400 and 500 mM) at 25.0 ± 0.1 °C. Inset: plot of the hydrogen generation rate *versus* the substrate concentration, both in logarithmic scale, for the catalytic methanolysis of $N_2H_4BH_3$ starting with $NiCl_2$ precatalyst.

of $NiCl_2$ precatalyst is zeroth order with respect to the substrate concentration. Taking both results together, the rate law for the catalytic methanolysis of hydrazine borane starting with $NiCl_2$ precatalyst can be given as;

$$-d[N_2H_4BH_3]/dt = +d[H_2]/3dt = k_{obs}[Ni]$$

The methanolysis of hydrazine borane was also carried out at various temperatures in the range of 10–30 °C starting with the initial substrate concentration of 400 mM $N_2H_4BH_3$ and precatalyst concentration of [Ni] = 2.5 mM in order to find activation parameters (E_a, $\Delta H^{\#}$, and $\Delta S^{\#}$) by using Arrhenius[20] and Eyring[21] equations. Fig. 4a shows the plots of stoichiometric ratio of generated H_2 to $N_2H_4BH_3$ *versus* time at various temperatures. As expected, the hydrogen generation rate from the catalytic methanolysis of hydrazine–borane starting with $NiCl_2$ precatalyst increases with increasing temperature. It is noteworthy that the catalyst is active in the methanolysis of hydrazine borane even at 10 °C. The values of the observed rate constants, k_{obs}, determined from the linear portion of plots at five different temperatures were used in the construction of Arrhenius (Fig. 4b) and Eyring (Fig. 4c) plots to calculate the activation parameters; Arrhenius activation energy E_a = 65 kJ mol^{-1}, activation enthalpy $\Delta H^{\#}$ = 63 kJ mol^{-1} and activation entropy $\Delta S^{\#}$ = −79 J mol^{-1} K.

Kinetic competence of bulk nickel metal as true heterogeneous catalyst formed *in situ* during the catalytic methanolysis of hydrazine borane starting with nickel(II) chloride

During the catalytic methanolysis of hydrazine borane starting with $NiCl_2$ precatalyst colloidal nickel(0) may initially be formed in the reaction solution by the reduction of $NiCl_2$ with hydrazine borane. However, the only stabilizing agent present in
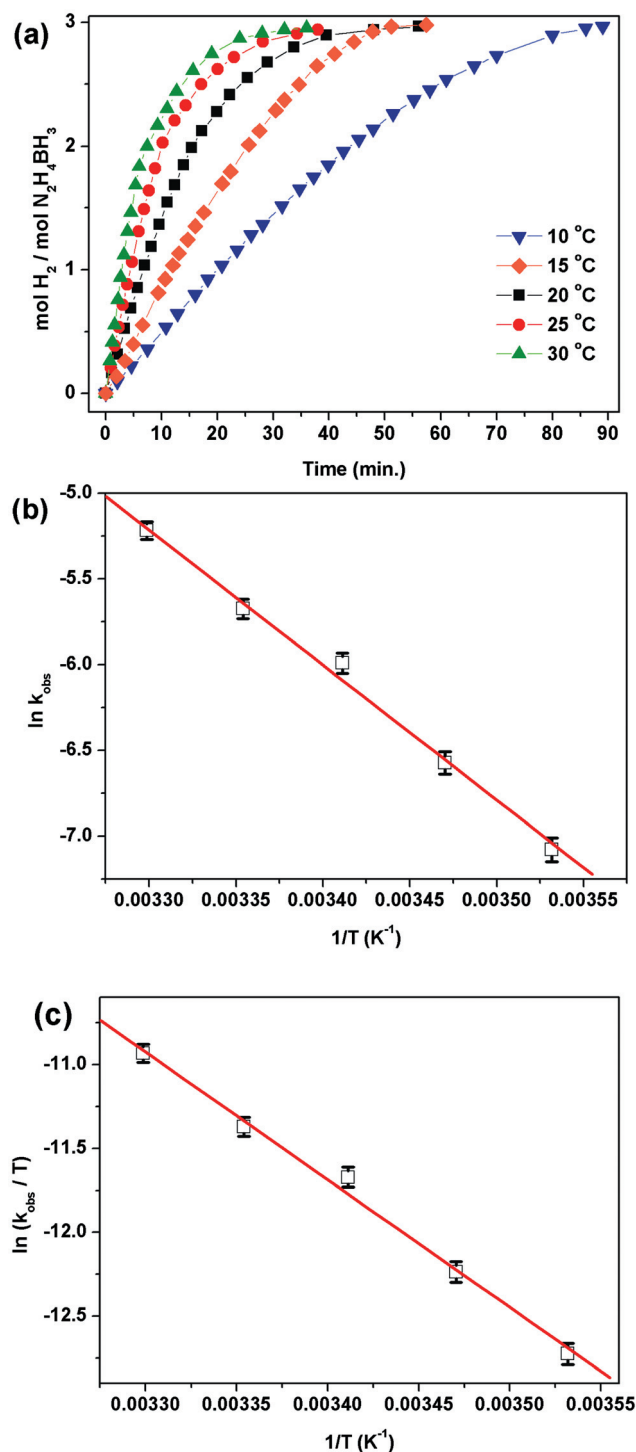

Fig. 4 (a) Plot of mol H_2/mol $N_2H_4BH_3$ *versus* time (min) for the catalytic methanolysis of hydrazine borane ([$N_2H_4BH_3$] = 400 mM in 10 mL CH_3OH) starting with $NiCl_2$ ([Ni] = 2.5 mM in 10 mL CH_3OH) at different temperatures 10, 15, 20, 25 and 30 °C. (b) Arrhenius plot (y = 20.7 ¬ 7877 x). (c) Eyring plot (y = 14.2 ¬ 7617 x) for the catalytic methanolysis of hydrazine borane.

the system is the weakly coordinating chloride ion which cannot provide enough stabilization for nickel(0) nanoparticles against aggregation.[22] Therefore, the formation of bulk nickel at the end of the methanolysis reaction is unavoidable in such a system.
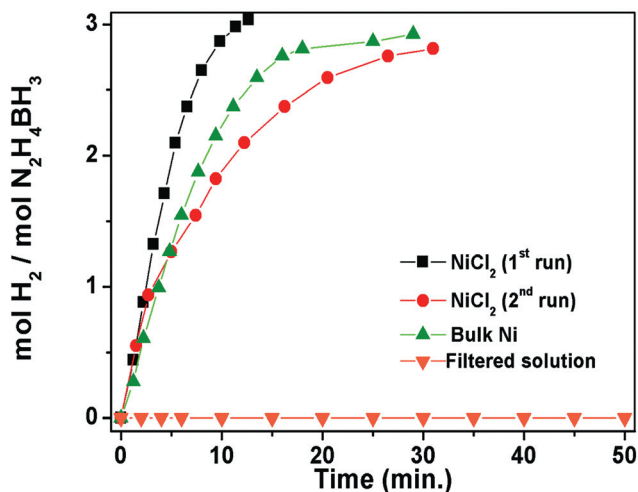
Fig. 5 Plots of mol H_2/mol $N_2H_4BH_3$ *versus* time for four separate methanolysis experiments; the squares (■) and circles (●) stand for the methanolysis of $N_2H_4BH_3$ starting with 2 mM $NiCl_2$ and 100 mM $N_2H_4BH_3$ in 10 mL methanol for the first and second run, respectively. The triangles (▲) stand for the methanolysis of $N_2H_4BH_3$ starting with the bulk nickel metal isolated after the first run of methanolysis, and the inverse triangles (▼) stand for the filtrate obtained from the filtration of reaction solution after the first run of methanolysis at 25.0 ± 0.1 °C.

The oxidation state and elemental surface composition of the resulting bulk nickel were investigated by using X-ray photoelectron spectroscopy (XPS). Survey XPS spectrum shows the reduction of Ni(II) in precatalyst ($NiCl_2$) to Ni(0) during the methanolysis of hydrazine borane (Fig. ESI-3†).[23,24] The question here is which one of two species is acting as catalyst in the methanolysis of hydrazine borane: (*i*) the initially formed soluble chloride stabilized nickel(0) nanoparticles or (*ii*) the bulk nickel metal that becomes visible at the end of the methanolysis. The following two separate experiments were performed to determine which one of these two species is responsible for the observed catalysis. First, the reaction solution formed at the end of the reaction was filtered through a micropore filter to remove bulk nickel (but not the nanoparticles). Then the catalytic activity of the filtrate was tested in the methanolysis of hydrazine borane by the addition of a fresh substrate. In such an experiment, the reaction solution showed no activity (Fig. 5). This is an expected result as transmission electron microscopy (TEM) analysis of the same solution confirmed the absence of nanosized nickel particles resulting from their agglomeration in the embryonic stage[25] to bulk nickel. Moreover, the TEM-EDX spectrum of the same solution showed that the solution was free from nickel (Fig. ESI-4†). Next, the catalytic activity of the bulk nickel isolated after the first run was tested by the addition of fresh hydrazine borane. The bulk metal showed nearly the same initial activity that was observed in the first run starting with $NiCl_2$ precatalyst. These results clearly indicate that the bulk nickel formed *in situ* during the methanolysis of hydrazine borane is the true kinetically competent catalyst.

The heterogeneous nature of catalytically active bulk nickel was also confirmed by mercury poisoning experiment (Fig. 6). It is well known that metallic mercury can poison heterogeneous metal catalysts by amalgamating them or being adsorbed on their
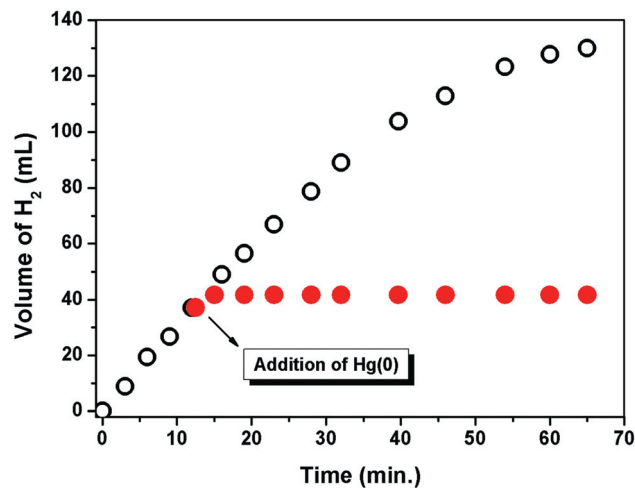

Fig. 6 Plot of volume of hydrogen (mL) *versus* time (min) for Hg(0) poisoning experiment starting with 400 mM $N_2H_4BH_3$ (73.6 mg) in the presence of the 1 mM $NiCl_2$ in 4.0 mL CH_3OH at 25 ± 0.1 °C and 1000 equiv. Hg(0) was added when ~30% conversion had been achieved.

surface; this is the single most widely used test of homogeneous *versus* heterogeneous catalysis.[26] The suppression of catalysis by mercury is considered to be compelling evidence for heterogeneous catalysis.[25] In addition to the nickel(II) chloride precatalyst we also used different nickel catalysts; Ni@activated carbon, Ni@graphite and Ni(2-ethylhexanoate)$_2$ for the catalytic methanolysis of hydrazine borane under the same conditions (at room temperature and high [substrate]/[catalyst] ratio) to investigate their catalytic behaviour in this reaction. Our initial studies indicated that supported nickel catalysts as classical heterogeneous catalysts (where the active nickel can provide only a low percentage of atoms as catalytically active surface sites)[26] cannot catalyze the methanolysis of hydrazine borane, whereas nickel(II)-2-ethylhexanoate provide the generation of 2.8 equiv. of H_2 per $N_2H_4BH_3$ within 40 min after an induction time of 1 h (Fig. ESI-5†). The formation of bulk nickel was still observed at the end of the methanolysis of hydrazine borane starting with Ni (2-ethylhexanoate)$_2$ precatalyst.

In another experiment we determined the catalytic lifetime of this catalytically active bulk nickel in hydrogen generation from the catalytic methanolysis of hydrazine borane. A catalyst lifetime experiment was started with a 10 mL methanol solution of 0.1 mM $NiCl_2$ and 400 mM $N_2H_4BH_3$. As the active catalyst, bulk nickel provides 11 200 turnovers in hydrogen generation from the methanolysis of hydrazine borane over 17 h before deactivation (Fig. 7) at 25.0 ± 0.1 °C. The initial turnover frequency is 1430 h^{-1}.

Conclusion

In summary, we report here, for the first time, the catalytic methanolysis of hydrazine borane at room temperature. The methanol solution of hydrazine borane is stable against self-methanolysis. Starting with nickel(II) chloride precatalyst, rapid hydrogen generation can be achieved from the methanolysis of hydrazine borane. It was shown that bulk nickel formed *in situ*
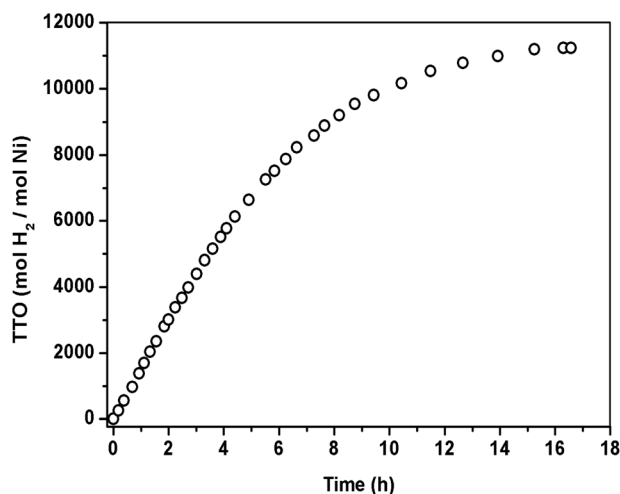
Fig. 7 Plot of total turnover number (TTO) *versus* time for the methanolysis of hydrazine borane ($N_2H_4BH_3$) with a 10 mL methanol solution of 0.1 mM $NiCl_2$ and 400 mM $N_2H_4BH_3$ at 25.0 ± 0.1 °C.

during the reaction is the true kinetically competent heterogeneous catalyst in hydrogen generation from the methanolysis of hydrazine borane. Bulk nickel provides an initial TOF value of 1430 h^{-1} for this reaction at room temperature. The catalytic methanolysis of hydrazine borane can enable rapid and controllable hydrogen generation at ambient temperatures. Therefore, it possesses high potential to find application as a high performance hydrogen source for portable fuel cells. Our initial efforts in terms of heterogenization of nickel precatalyst by using activated carbon and graphite showed that these catalysts are inactive in this reaction. The development of highly stable and catalytically active supported or support-free metal nanoparticle catalysts remains a challenging issue for the transition of the existing system to flow-through reactors that can be used for continuous hydrogen generation for on-board systems.

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