



## Rh-based ternary catalyst for the catalytic dehydrogenation of hydrazine borane as a chemical hydrogen storage material

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This study focuses on the synthesis of the Zr-Ni-B-O supported Rh-based catalyst for the hydrogen generation from the hydrazine borane. Accordingly, adding a small amount of Rh to Zr-Ni-B-O had a significant effect on activity and selectivity in dehydrogenation of hydrazine borane. The characterization of the synthesized Rh-based catalyst was made by analyzing the electronic states of the catalyst surface (XRD, XPS) and measuring the surface area and pore size (BET). Furthermore, the catalytic hydrolysis experiments were conducted to evaluate the hydrogen generation performance of hydrazine borane. The results have demonstrated that 3.2 equivalents of (N<sub>2</sub>+H<sub>2</sub>) per mole of hydrazine borane (N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub>, HB) in alkaline solution within 7.7 min was released in the presence of Rh-based catalyst at 60°C. This approach will make a significant contribution to a decarbonization strategy for zero-carbon energy future.

Keywords: Hydrazine borane, hydrolysis, hydrogen, dehydrogenation, catalyst.

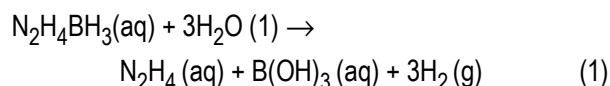
### Introduction

Current developments in the energy have shown that hydrogen will become the principal energy carrier of the future in a sustainable society. However, the major technical difficulty of hydrogen is the efficient and safe storage and release of hydrogen. Hydrogen can be stored as a compressed gas at high pressures, a liquid in tanks, and a solid involving the use of metal hydrides and/or chemical hydrogen storage materials<sup>1</sup>.

Recently, boranes and boron-nitrogen-hydrogen (BNH) compounds have been proposed for hydrogen storage applications. Among various hydrogen storage materials, hydrazine borane (HB) has attracted much attention due to its gravimetric high hydrogen storage capacity (15.4% by mass) and low molecular weight. Several studies have indicated that hydrazine borane was produced by salt metathesis using a BH<sub>3</sub> source (NaBH<sub>4</sub>, LiBH<sub>4</sub>), with a N<sub>2</sub>H<sub>4</sub> source (N<sub>2</sub>H<sub>4</sub>HCl, MgCl<sub>2</sub>·4N<sub>2</sub>H<sub>4</sub>), in an organic solvent (1,4-dioxane, hexane, THF, benzene) under room conditions<sup>2</sup>.

In general, the hydrogen stored in HB can be generated through hydrolysis in the presence of selective catalysts ac-

ording to the following equation (eq. (1))<sup>3</sup>:



The dehydrogenation mechanism of hydrazine borane depends on both the hydrolysis of BH<sub>3</sub> group and the decomposition of N<sub>2</sub>H<sub>4</sub> moiety<sup>4</sup>. Accordingly, a reaction between one (H<sup>δ-</sup>) of the [BH<sub>3</sub>-H]<sup>-</sup> and one protonic hydrogen (H<sup>δ+</sup>) of H<sub>2</sub>O takes place, which releases a first equivalent of H<sub>2</sub>. The second pathway includes (i) an intermolecular reaction between 2 (H<sup>δ-</sup>) of [BH<sub>3</sub>-H]<sup>-</sup> with [H-BH<sub>3</sub>]<sup>-</sup> or between 1 (H<sup>δ+</sup>) and 1 (H<sup>δ-</sup>) of [H<sub>4</sub>N<sub>2</sub>BH<sub>2</sub>-H] with [H-H<sub>3</sub>N<sub>2</sub>BH<sub>3</sub>] or (ii) an intramolecular reaction between 2 (H<sup>δ-</sup>) of [H<sub>2</sub>BH-H]<sup>-</sup> or between 1 (H<sup>δ+</sup>) and 1 (H<sup>δ-</sup>) of [H-H<sub>3</sub>N<sub>2</sub>BH<sub>2</sub>-H]<sup>5</sup>.

Different catalysts including reduced noble metal catalysts, bimetallic catalysts have been tested for hydrogen generation from the dehydrogenation of HB. Indeed, it has been reported that monometallic catalysts (Fe, Re, Ni, Cu, Co, Pt) are effective in the hydrolysis of BH<sub>3</sub> group, whereas Ru, Rh, and Ir based catalysts are found active in the decomposition of N<sub>2</sub>H<sub>4</sub> moiety<sup>5</sup>. Karahan *et al.* have demonstrated that RhCl<sub>3</sub> catalyst was used to release approximately 3

equivalents of H<sub>2</sub><sup>6</sup>. Furthermore, Yao *et al.* have found that NiPd nanoparticles modified with MoO<sub>x</sub> was an active catalyst for the dehydrogenation of HB<sup>7</sup>.

Even though extensive efforts have been made towards the understanding of complete dehydrogenation of hydrazine borane, it is still a challenge to find a suitable catalyst that exhibits high selectivity and high conversion for hydrogen generation<sup>8</sup>. Herein in this study, we investigate the synthesis and characterization of the Rh-based Zr-Ni-B-O catalyst and the catalytic activity of this ternary catalyst in liquid-phase dehydrogenation of hydrazine borane. Additionally, we highlight how this catalyst plays a key role to overcome the bottleneck in production of hydrogen.

## Experimental

### *Chemicals and materials:*

Hydrazine hemisulfate salt (≥ 98%), 1,4-dioxane (99.8%) and sodium hydroxide were purchased from Sigma-Aldrich. Sodium borohydride (≥ 98%), rhodium(III) chloride trihydrate (Rh ≥ 37), nickel(II) chloride hexahydrate and zirconium(IV) chloride were purchased from Merck. Deionized (DI) water was used throughout the experiments.

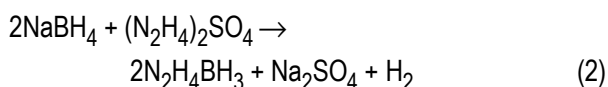
### *Instrument:*

The Rh-based ternary catalyst was characterized by XRD, XPS and BET. The X-ray diffraction (XRD) data was collected by a PAN analytical Empyrean model diffractometer in the 2θ range from 10° to 50° using Cu Kα radiation.

In addition, X-ray photoelectron spectroscopy (XPS) data was acquired with the Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer (XPS). The Brunauer-Emmett-Teller (BET) surface area and pore size measurements were determined by using the Quantachrome Autosorb-1 instrument.

### Synthesis of hydrazine borane:

The hydrazine hemisulfate salt ((N<sub>2</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and sodium borohydride (NaBH<sub>4</sub>) were transferred into a 100 mL three-necked round-bottom flask at room temperature. Then, 50 mL of 1,4-dioxane was added under vigorous stirring for 48 h. The reaction started immediately and the hydrogen gas evolved. After filtration, the solvent was removed and the as-obtained material was dried overnight under vacuum at 30°C<sup>9</sup>.



### *Rh-based ternary catalyst preparation:*

Rh-based ternary catalyst was synthesized by chemical reduction method. Briefly, 0.0085 M nickel chloride solution (NiCl<sub>2</sub>) and 0.065 M zirconium chloride solution (ZrCl<sub>4</sub>) was placed in a beaker, and 0.2 M sodium borohydride (NaBH<sub>4</sub>) was added dropwise as a reducing agent. The mixture was stirred in an ice bath. After all nickel and zirconium cations were reduced to metals, the mixture was centrifuged and washed to remove impurities. Lastly, rhodium(III) chloride solution (RhCl<sub>3</sub>, 0.04 mmol) was added to the mixture and the sample was dried overnight under vacuum. Then, the reactor tube containing the sample was subjected to activation at 400°C for 1.5 h by passing hydrogen and helium gases through the reactor at a rate of 50 ml/min. The as-obtained material was a black solid containing 2% Rh by mass.

### *Catalytic dehydrogenation of hydrazine borane:*

The catalytic hydrolysis experiments were conducted to test the performance of the catalyst as follows. Firstly, 0.05 g Rh-based ternary catalyst was introduced into the reactor consisting of a 50 mL round-bottom flask sealed with a rubber stopper. The reactor was placed in a constant temperature water bath at 25, 40 and 60°C on a magnetic stirrer and the outlet stream was connected to the water-filled gas-burette system. The fresh aqueous solution of 0.02 M HB was injected onto the catalyst and the hydrogen evolution was measured by recording the time. An additional experiment was performed to evaluate the effect of the 0.1 M NaOH solution on the dehydrogenation of HB. A 0.1 M solution of NaOH was used to dissolve 0.04 mmol HB. After completion of the reaction, the Rh-based catalyst was separated from the solution by filtration, washed with deionized water and dried at room temperature. Finally, the data were used to plot the time-variation of the mole number of H<sub>2</sub>+N<sub>2</sub> per mole of HB.

## Results and discussion

In this study, hydrazine borane (HB), as one of the most promising hydrogen carriers, was synthesized by the reaction of hydrazine hemisulfate salt and sodium borohydride in 1,4-dioxane at room temperature, as seen in eq. (2). After the reaction, the impurities were separated from the HB by filtration and the solvent was evaporated because hydrazine borane (HB) is soluble in 1,4-dioxane, while the by-product

(sodium sulfate) is not. It has been found that the results for HB are in good agreement with the literature<sup>9</sup>.

Hydrogen was obtained from aqueous solution of hydrazine borane in the presence of catalyst. The dehydrogenation reaction takes place in two steps; the hydrolysis of  $\text{BH}_3$  group and the decomposition of  $\text{N}_2\text{H}_4$  moiety of hydrazine borane. However, the problems arising in the hydrolysis of HB were the slow reaction rate and the evolution of undesirable by-products such as hydrazine<sup>10,11</sup>. Accordingly, this Rh-based ternary catalyst has been studied to overcome these challenges.

Rh-based catalyst was prepared by facile chemical reduction of zirconium, nickel and rhodium salts with sodium borohydride as a reducing agent. The addition of Rh to Zr-N-B-O catalyst has been found to promote the hydrogen generation from hydrazine borane. So far, however, there has been no research on the employment of Rh/Zr-Ni-B-O as the catalyst for the hydrolysis of HB. In the literature, several catalysts including  $\text{RuCl}_3$ ,  $\text{RhCl}_3$ ,  $\text{NiCl}_2$ ,  $\text{Cu@SiO}_2$  nanoparticles,  $\text{Ni}_{0.7}\text{Fe}_{0.3}$ , group 4 metallocene alkyne complex,  $\text{Rh}_{0.5}(\text{MoO}_x)_{0.5}$  nanoparticles,  $\text{CeO}_x$ -modified RhNi nanoparticles and  $\text{Ni}_{0.6}\text{Pd}_{0.4}\text{-MoO}_x$  nanocatalyst have exhibited excellent catalytic activity towards hydrogen production from hydrazine borane. Interestingly, many studies have confirmed that bimetallic catalysts surpass than monometallic counterparts<sup>12</sup>. Thus, it is worth pointing out to the effectiveness of Rh/Zr-Ni-B-O catalyst in comparison to the monometallic and bimetallic systems for catalytic dehydrogenation of HB. Rhodium has been selected as a noble metal to activate Zr-Ni-B-O towards the decomposition of hydrazine. The catalyst was characterized by powder X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS) and the Brunauer-Emmett-Teller (BET).

To better understand the structure of the Rh-based catalyst, the XRD data was collected on a PANalytical Empyrean model diffractometer in the  $2\theta$  range from  $10^\circ$  to  $50^\circ$  using  $\text{Cu K}\alpha$  radiation, as displayed in Fig. 1. The acquired pattern showed a mostly amorphous material with few crystalline phases including rhodium, nickel-boron compounds and  $\text{Zr}(\text{OH})_4$ . The peaks at  $2\theta = 46^\circ$  and  $56^\circ$  were attributed to the semi-amorphous zirconium, while the peak at  $2\theta = 32^\circ$  was assigned to the  $\text{Zr}(\text{OH})_4$ , which are in line with the literature. On the other hand, the main peak at  $2\theta = 44^\circ$  was re-

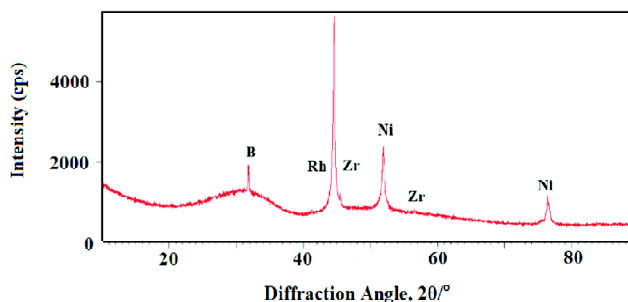


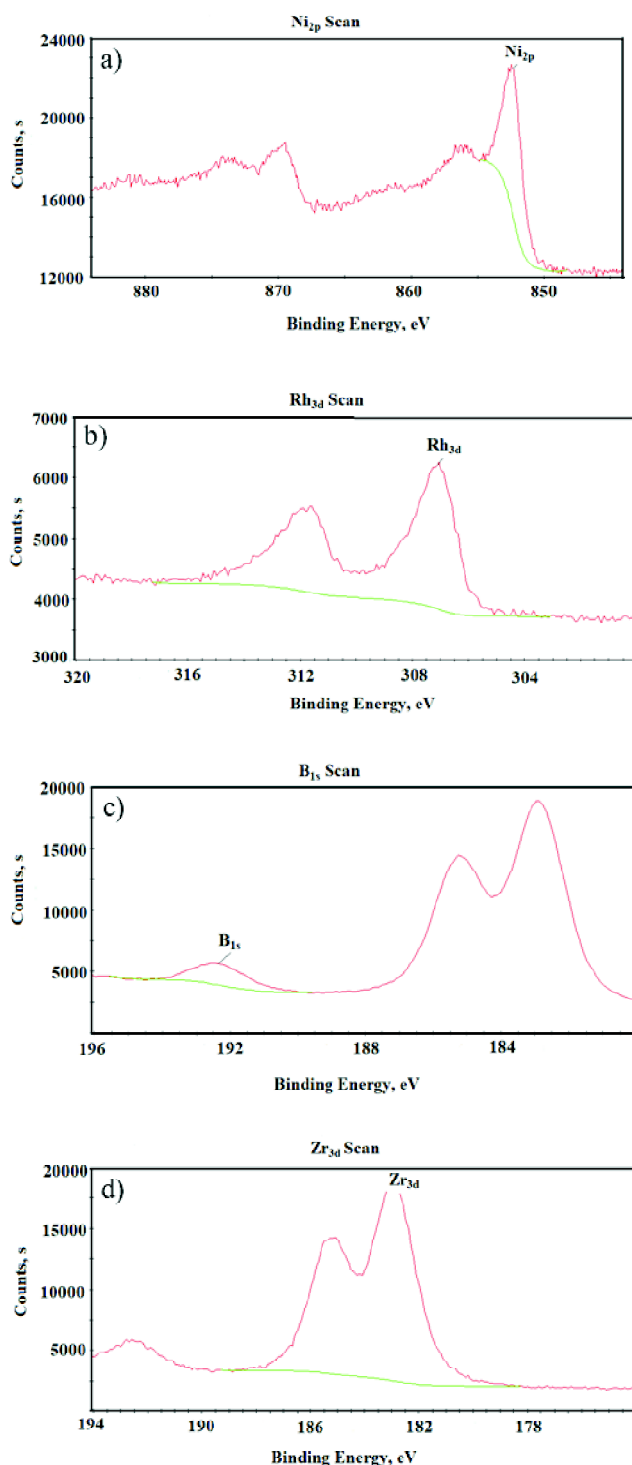
Fig. 1. The XRD analysis of the catalyst.

lated to the rhodium and nickel-boron intermetallic compounds (principally  $\text{Ni}_3\text{B}$  and  $\text{Ni}_2\text{B}$ ), indicating a rapid crystallization of Ni-B interactions. Eventually, these experimental data are in good agreement with the reference data<sup>13,14</sup>.

In addition, the compositions and the electronic state of each element on the surface of the catalysts were studied by XPS, and the results were shown in Fig. 2. Before the XPS analysis, the sample was degassed in the pretreatment chamber at  $300^\circ\text{C}$  for 3 h and then it was transferred into the analyzing chamber. The survey XPS spectrum for as-synthesized catalyst has indicated the co-existence of Ni-B, Zr and Rh. As seen in Fig. 2a, absorption bands located at 855 eV and 875 eV were assigned to Ni  $2p_{3/2}$  and Ni  $2p_{1/2}$ , whereas the peak at 307 eV was attributed to Rh. On the other hand, the peaks at 182 eV and 185 eV were assigned to the Zr  $3d_{5/2}$  and Zr  $3d_{3/2}$  binding energy levels, respectively. Previous researches have revealed that the peak appeared at 182 eV might be due to the oxidation of zirconium, which results in the formation of an amorphous/hydrous zirconia ( $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ ) on the catalyst<sup>15,16</sup>. Moreover, the peak with the binding energy around 192.5 eV was related to the presence of the oxidized B species. This may lead to the interaction between  $\text{BH}_4^-$  and  $\text{H}_2\text{O}$  during the reduction of  $\text{Rh}^{3+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zr}^{4+}$  ions by sodium borohydride<sup>13,14</sup>.

To analyze the surface area and pore size of the catalyst, multipoint BET measurements were further carried out. The specific surface area of the catalyst was determined by physical adsorption of the nitrogen gas on the surface of the solid. Consequently, the specific surface area, pore volume and average pore size were measured as  $125 \text{ m}^2/\text{g}$ ,  $0.036 \text{ cm}^3/\text{g}$  and  $11.5 \text{ \AA}$ , respectively.

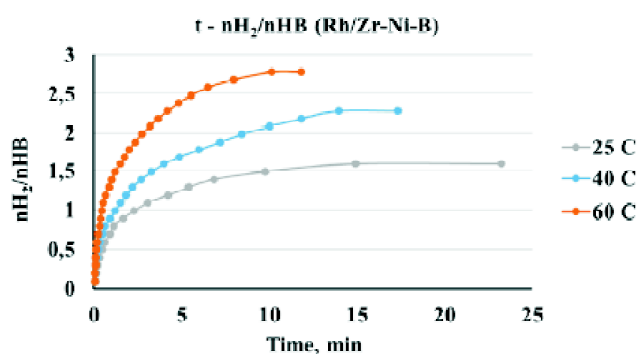
The catalytic activity of as-prepared catalyst was exam-



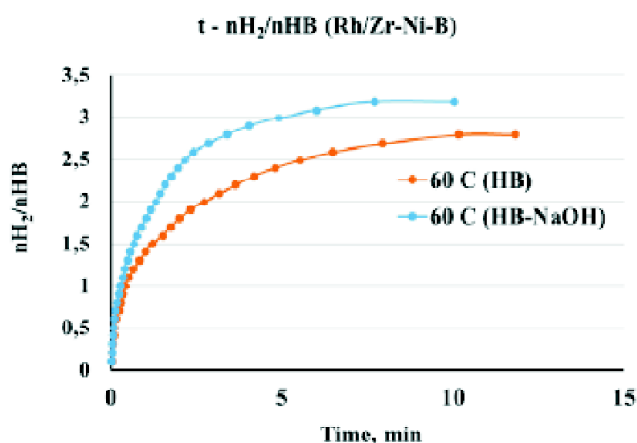
**Fig. 2.** The XPS analysis of the catalyst: (a) Ni<sub>2p</sub>, (b) Rh<sub>3d</sub>, (c) B<sub>1s</sub>, (d) Zr<sub>3d</sub>.

ined on the dehydrogenation of N<sub>2</sub>H<sub>4</sub>BH<sub>3</sub> at different temperatures (25°C, 40°C and 60°C), and the results were given

in Figs. 3 and 4. In catalytic experiments, 0.05 g of Rh/Zr-Ni-B-O catalyst was used for the hydrolysis of the aqueous hydrazine borane solution. Fig. 3 represented the hydrogen production from HB solution, while Fig. 4 displayed the hydrogen evolution from HB in an alkaline (0.1 M NaOH) solution. It was apparent that a rapid hydrogen generation was observed without the induction period. Recent studies have demonstrated that the alkaline solution could promote the hydrogen evolution from the decomposition of hydrazine. This may be owing to the formation of instable intermediate [H<sub>3</sub>BOH]<sup>-</sup> that is the key factor for the heterogeneous hydrolysis<sup>17</sup>. As can be seen from Fig. 3, with the increase of the temperature from 25°C to 60°C, the kinetics of the dehydrogenation reaction was improved. At 60°C, the release of hydrogen for the alkaline solution (Fig. 4) was higher than for the experiment reported here (2.8 equivalents of ((N<sub>2</sub>+H<sub>2</sub>)/



**Fig. 3.** Catalytic performance of Rh-based catalyst for hydrogen generation from HB.



**Fig. 4.** Catalytic performance of Rh-based catalyst for hydrogen generation from HB-H<sub>2</sub>O and HB-NaOH.

HB, 10.2 min). Furthermore, the use of 0.1 M NaOH solution has led to complete hydrolysis of hydrazine borane, which yielded 3.2 equivalents of (N<sub>2</sub>+H<sub>2</sub>) per mole of HB within 7.7 min in the presence of Rh-based catalyst at 60°C<sup>18</sup>.

### Conclusions

In summary, this study presented an overview of the synthesis of the Rh-based ternary catalyst for the hydrogen evolution from the HB. Accordingly, Rh-based ternary catalyst was prepared from simultaneous reduction of zirconium, nickel and rhodium salts by using NaBH<sub>4</sub> as a reducing agent. The characterization of the Rh-based ternary catalyst was analyzed by using XRD, XPS and BET methods. Besides, the catalytic properties of Rh-based ternary catalyst were tested in the dehydrogenation of HB. As a result, more than 3 equivalents of (N<sub>2</sub>+H<sub>2</sub>) per mole of HB was released within 7.7 min from the catalytic hydrolysis of hydrazine borane at 60°C.

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