

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 (N₂+H₂) per mole of hydrazine borane (N₂H₄BH₃, 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

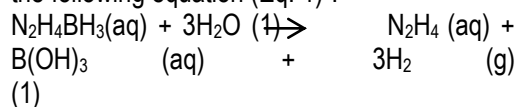
Introduction

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 materials¹.

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 BH₃ source (NaBH₄, LiBH₄), with a N₂H₄ source

(N₂H₄HCl, MgCl₂.4N₂H₄), in an organic solvent (1,4-dioxane, hexane, THF, benzene) under room conditions².

In general, the hydrogen stored in HB can be generated through hydrolysis in the presence of selective catalysts according to the following equation (Eq. 1)³:



The dehydrogenation mechanism of hydrazine borane depends on both the hydrolysis of BH₃ group and the decomposition of N₂H₄ moiety⁴. Accordingly, a reaction between one (H^{δ-}) of the [BH₃-H]⁻ and one protonic hydrogen (H^{δ+}) of H₂O takes place, which releases a first equivalent of H₂. The second pathway includes (i) an intermolecular reaction between 2 (H^{δ-}) of [BH₃-H]⁻ with [H-BH₃]⁻ or between 1 (H^{δ+}) and 1 (H^{δ-}) of [H₄N₂BH₂-H] with [H-H₃N₂BH₃] or (ii) an intramolecular reaction between 2 (H^{δ-}) of

[H₂BH-H] or between 1 (H^{δ+}) and 1 (H^{δ-}) of [H₃N₂BH₂-H]⁵.

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 BH₃ group, whereas Ru, Rh, and Ir based catalysts are found active in the decomposition of N₂H₄ moiety⁵. Karahan et al. have demonstrated that RhCl₃ catalyst was used to release approximately 3 equivalents of H₂⁶. Furthermore, Yao et al. have found that NiPd nanoparticles modified with MoO_x was an active catalyst for the dehydrogenation of HB⁷.

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 generation⁸. 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

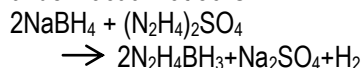
The Rh-based ternary catalyst was characterized by XRD, XPS and BET. The X-ray diffraction (XRD) data was collected by a PAN analytical Empyrean model diffractometer

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 ((N₂H₄)₂SO₄) and sodium borohydride (NaBH₄) 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°C⁹.



(2)

Rh-based ternary catalyst preparation

Rh-based ternary catalyst was synthesized by chemical reduction method. Briefly, 0.0085 M nickel chloride solution (NiCl₂) and 0.065 M zirconium chloride solution (ZrCl₄) was placed in a beaker, and 0.2 M sodium borohydride (NaBH₄) 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 (RhCl₃, 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 hours 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 H₂ + N₂ 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 literature⁹.

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 BH₃ group and the decomposition of N₂H₄ 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^{10,11}.

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-Ni-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 RuCl₃, RhCl₃, NiCl₂, Cu@SiO₂ nanoparticles, Ni_{0.7}Fe_{0.3}, group 4 metallocene alkyne complex, Rh_{0.5}(MoO_x)_{0.5} nanoparticles, CeO_x-modified RhNi nanoparticles and Ni_{0.6}Pd_{0.4}-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 counterparts¹². 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 PANanalytical Empyrean model diffractometer in the 2θ range from 10° to 50° using Cu Kα radiation, as displayed in Fig. 1. The acquired pattern showed a mostly amorphous material with few crystalline phases including rhodium, nickel-boron compounds and Zr(OH)₄. The peaks at 2θ = 46° and 56° were attributed to the semi-amorphous zirconium, while the peak at 2θ = 32° was assigned to the Zr(OH)₄, which are in line with the literature. On the other hand, the main peak at 2θ = 44° was related to the rhodium and nickel – boron intermetallic compounds (principally Ni₃B and Ni₂B),

indicating a rapid crystallization of Ni-B interactions. Eventually, these experimental data are in good agreement with the reference data^{13,14}.

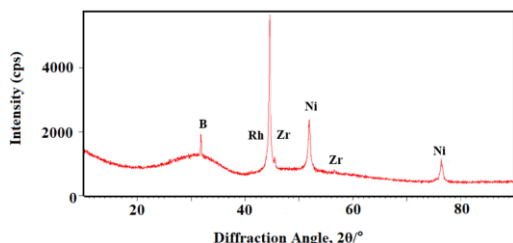


Fig. 1. The XRD Analysis of the Catalyst

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 °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 (ZrO₂nH₂O) on the catalyst^{15,16}. 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 BH₄⁻ and H₂O during the reduction of Rh⁺³, Ni⁺² and Zr⁺⁴ ions by sodium borohydride^{13,14}.

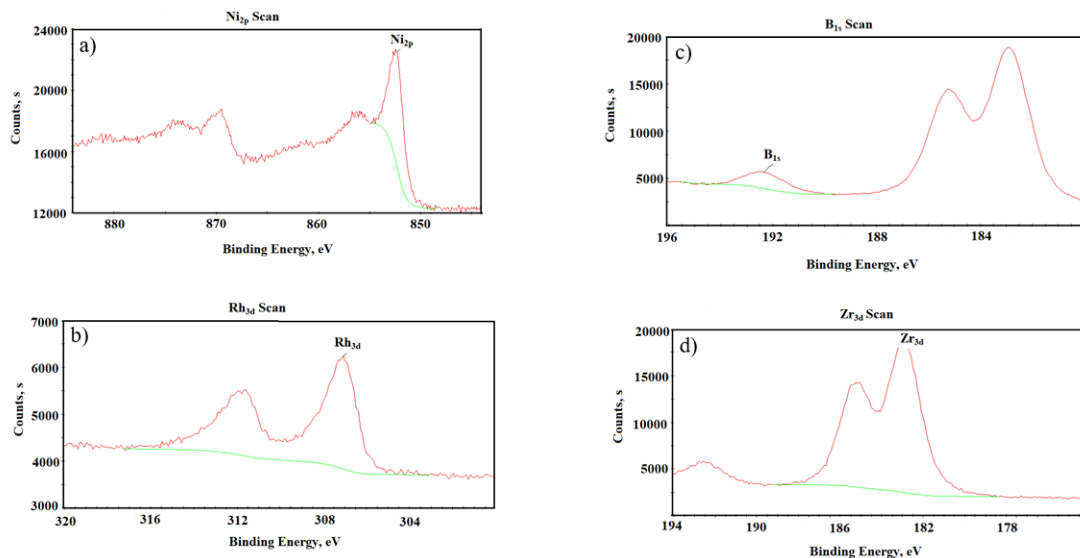


Fig. 2. The XPS Analysis of the Catalyst a) Ni_{2p}, b) Rh_{3d}, c) B_{1s}, d) Zr_{3d}

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 m²/g, 0.036 cm³/g and 11.5 Å, respectively.

The catalytic activity of as-prepared catalyst was examined on the dehydrogenation of N₂H₄BH₃ at different temperatures (25 °C, 40 °C and 60 °C), and the results were given in Fig. 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 $[H_3BOH]^-$ that is the key factor for the heterogeneous hydrolysis¹⁷. 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 $(N_2+H_2)/HB$, 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 $(N_2 + H_2)$ per mole of HB within 7.7 min in the presence of Rh-based catalyst at 60 °C¹⁸.

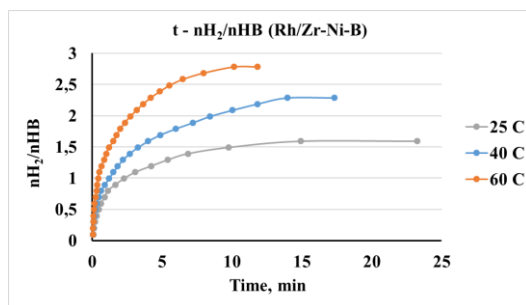


Fig. 3. Catalytic Performance of Rh-based catalyst for Hydrogen Generation from HB

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

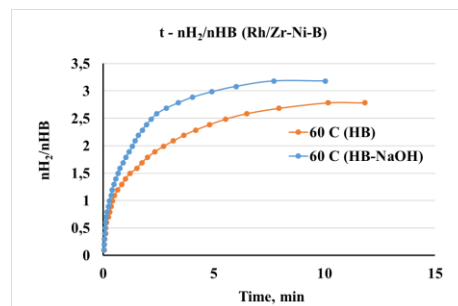


Fig. 4. Catalytic Performance of Rh-based catalyst for Hydrogen Generation from HB- H_2O and HB-NaOH

zirconium, nickel and rhodium salts by using $NaBH_4$ 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_2+H_2) per mole of HB was released within 7.7 min from the catalytic hydrolysis of hydrazine borane at 60 °C.

Acknowledgements

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