

INVESTIGATION OF CATALYST FOR THE SYNTHESIS OF HYDRAZINE BORANE AS HYDROGEN STORAGE MATERIAL

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REFERENCE NO	ABSTRACT
HYST-02	This study focused on the synthesis of the hydrazine borane by using catalyst. A series of experiments were performed at different temperatures and time. Lab tests demonstrated that the highest hydrazine borane yield (% 89) was obtained at room temperature and 48 h. In addition, the effect of two types of catalyst (TiO ₂ and Ru/TiO ₂) on the reaction rate and reaction time of hydrazine borane synthesis was investigated. Titanium (IV) oxide catalyst displayed a remarkable performance in the hydrazine borane synthesis (%95 yield) by increasing reaction rate.

Keywords:
Hydrazine borane; hydrogen storage; amine borane; catalyst

1. INTRODUCTION

The need for energy is increasing day by day, and the current energy system is based on irreversible consumption of fossil fuels. Due to the limited availability of fossil fuels and environmental considerations, hydrogen energy is of great importance in renewable and sustainable energy sources in recent times. However, the most important issue that hinders the applicability of hydrogen is the storage of hydrogen [6].

Hydrogen is regarded as one of the best alternative energy carriers in the increasing demand for an efficient and clean energy source because of its abundance, high energy density and environmentally friendly. The reliable and efficient storage of hydrogen is important for the formation of a hydrogen-based energy infrastructure. Several studies have recently been carried out in the field of hydrogen storage materials. The most important application problem with boron compounds, which are considered as future hydrogen storage materials, is the rapid and controlled production of hydrogen required for fuel cells. Hydrogen production from boron compounds can be accomplished by catalytic solvolysis or dehydrogenation. Storing hydrogen efficiently and safely in future applications is a significant problem that must be solved in the prospect of a hydrogen-based economy. However by

nanoscience, designing new materials or catalysts to meet the requirements of the technology will increase the capacity of hydrogen storage [1, 7].

Hydrazine borane (N₂H₄BH₃) has been a new and promising boron-based hydride since 2010 with a hydrogen content of 15.4% by mass. The synthesis and thermal decomposition of hydrazine borane were first described by Ricker and Goubeau. According to their study, hydrazine borane was produced by reaction of hydrazine hemisulfate salt with sodium borohydride in dioxane at room temperature [3]. In addition, several different processes were investigated by reacting a borane source (such as NaBH₄, LiBH₄, etc.) with a hydrazine source (such as (N₂H₅)SO₄, N₂H₄.HCl, etc.) in an organic solvent (such as THF, 1,4-dioxane, benzene, etc.) under room conditions as seen in Table 1. Goubeau and Ricker found that the most efficient method to synthesize hydrazine borane involved sodium borohydride and hydrazine hemisulfate salt in dioxane. However, some challenges still remain for practical application of its synthesis, such as reaction kinetics. These studies showed that the reaction rate of hydrazine borane synthesis was slow and the reaction time was varied from 70 h and 8 days. It could be seen from the Table 1 that when the reaction time was decreased, the

yield of the hydrazine borane also decreased [8].

The work presented here is aimed at providing better understanding of the synthesis of hydrazine borane. Unlike previous research, we studied the reaction of hydrazine hemisulfate salt and sodium borohydride in dioxane with catalyst. The reaction was conducted by changing the parameters like temperature, time and the reactant mole ratio.

Table 1. The synthesis methods of hydrazine borane [3].

Source of N ₂ H ₄	Source of BH ₃	Solvent	Temperature	Time	Yield	Purity	Ref
(N ₂ H ₅)SO ₄	LiBH ₄	THF	40 ⁰ C	70 h			3
(N ₂ H ₅)SO ₄	NaBH ₄	Dioxane	30 ⁰ C		70-75%		3
(N ₂ H ₅)SO ₄	NaBH ₄	THF	30 ⁰ C	5-6 d			3
H ₂ N ₂ .HCl	NaBH ₄	Benzene	Room	6 d	76%	95%	5
H ₂ N ₂ .HCl	NaBH ₄	Hexane	Room	6 d	33%	95%	5
H ₂ N ₂ .HCl	NaBH ₄	THF	Room	1-3 d	72-98%		4
MgCl ₂ .4N ₂ H ₄	NaBH ₄	THF	Room	4 d	92%	98%	5
MgCl ₂ .4N ₂ H ₄	NaBH ₄	THF		8 d	83%		4
MgCl ₂ .6H ₂ O	NaBH ₄	N ₂ H ₄	0 ⁰ C	2 d	34%	98%	5
MgCl ₂ .6H ₂ O	NaBH ₄	N ₂ H ₄	0 ⁰ C	7 d	79%		4
H ₂ N ₂ .HCl	NaBH ₄	Dioxane	Room	2 d		87%	5
H ₂ N ₂ .HCl	NaBH ₄	THF	0 ⁰ C	3 d	67%		5
H ₂ N ₂ .HCl	Al(BH ₄) ₃	THF	0 ⁰ C	3 d			5
H ₂ N ₂ .HCl	KBH ₄	THF	Room	4 d	78%		5
(N ₂ H ₅)SO ₄	NaBH ₄	Dioxane	30 ⁰ C	3 d	81.6%	99.6%	8

2. MATERIALS AND METHODS

2.1.1. Materials

Hydrazine hemisulfate salt, 1,4-dioxane, ruthenium (III) chloride (Sigma-Aldrich); sodium borohydride and titanium (IV) oxide (Merck) were used as received.

2.1.2. Synthesis of Hydrazine Borane

In this study, the hydrazine hemisulfate salt and sodium borohydride were transferred into a 50 mL three-necked round-bottom flask. The flask was put in a hot plate set at temperature range from 23 to 40⁰C. Then, 25 mL of dioxane was added under vigorous stirring. The reaction started immediately and the hydrogen gas evolved. The mixture was kept under stirring for different times (24 to 96 h). It was then filtrated and the by-products were washed with 5 mL of dioxane. The solvent was removed and the filtrate was dried overnight under vacuum at 30⁰C. The as-

obtained material is a white solid verified by FTIR.

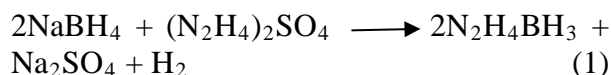
2.1.2. Synthesis of Ru/TiO₂ Catalyst

TiO₂ based Ru catalyst was synthesized by impregnation method. Firstly, 0.6% ruthenium (III) chloride solution was prepared and 33 ml was taken from the solution. The solution is then placed in the beaker and 3.8 g of titanium (IV) oxide is added. The mixture was stirred on a hot plate at 110⁰C until the solution evaporated. In order to reduce chlorides and other impurities, the reactor tube was subjected to activation at 500⁰C for 1.5 hours by passing hydrogen and helium gases through the reactor at a rate of about 50 cc/min. The as-obtained material is a white solid containing %5 Ru by mass.

3. RESULTS AND DISCUSSION

This study investigated the reaction of the hydrazine hemisulfate salt and sodium borohydride in dioxane by changing temperature, time and reactants mole ratio. In addition, the effect of two types of catalyst on the reaction rate was examined.

The synthesis procedure of hydrazine borane (Eq. (1)) in the literature is based on the reaction of sodium borohydride (NaBH₄) with hydrazine hemisulfate salt ((N₂H₄)₂SO₄) in dioxane at room temperature.



In the reaction, the borohydride reactant may be any stable ionic salt, such as a metal borohydride or a nitrogen-containing borohydride. The preferred reactants are the alkali metal borohydrides, such as sodium, lithium or potassium borohydride. For the hydrazine reactant, this may be hydrazine containing salt such as hydrazine hemisulfate salt [1, 2].

The reaction time may vary from 70 hours up to 8 days, depending on the selected reactants and the reaction conditions, such as the degree of agitation and the reaction temperature. As a solvent, an inert liquid for the reaction product should be used. Among the common inert liquid organic and inorganic solvents that can be used are C5 to C10 hydrocarbons, such as

benzene, heptane, and hexane. The preferred solvents are heterocyclic ethers, such as tetrahydrofuran, dihydropyran and dioxane because they facilitate the separation of the product from the reaction mixture depending on the insolubility of the non gaseous by-products. Therefore, separation of the hydrazine borane can be achieved by filtration and evaporation of the solvent [2, 6].

The results of the synthesis of the hydrazine borane are shown in the figures below. The data indicates that the best yield for the HB synthesis (%89) was obtained when the reaction temperature, reaction time and the reactant mole ratio were 23⁰C, 48 h and 0.9 respectively. In the literature, several processes for preparing HB were analysed, which especially based on the reacting a BH₃ source, such as NaBH₄, with a N₂H₄ source, either N₂H₄HCl or MgCl₂.4N₂H₄, in an organic solvent (dioxane, hexane, THF) at room temperature. The reaction time was changed from 2 to 8 days. After the solid was separated from the solvent by filtration or extraction, yields from 33 to 98% were obtained. In addition, Moury et al. found the best yield for HB as %80.3, when the reaction temperature and reaction time were 30⁰C and 72 h [7, 8].

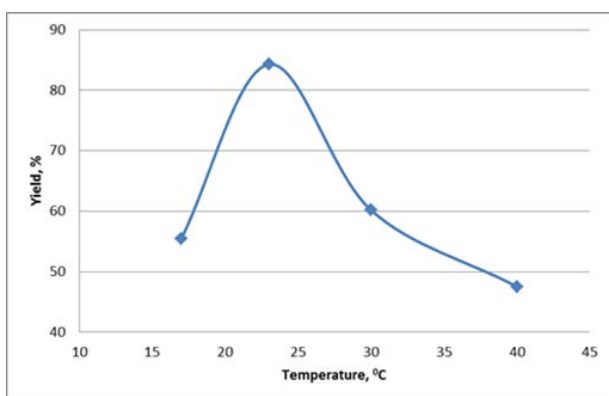


Fig. 1. The effect of temperature on the reaction yield. (t: 48h, mole ratio: 0.9)

To determine the influence of temperature on the reaction, it was varied in the range from 17 to 40⁰C. The results obtained are shown in Fig.1. It is evident that when the temperature is low and higher than the room conditions,

the hydrazine borane yields are low; for example, when the temperatures were 17⁰C and 40⁰C, the following yields are obtained 56 and 48% respectively. However, when the reaction occurs at room temperature, the highest yield is obtained. The rate of conversion to product in the reaction is greatly influenced by temperature.

The effect of the reaction time on the yield of hydrazine borane produced was also investigated. The reaction time was varied from 24 to 96 h. The results are shown in Fig. 2, which indicate that the reaction time substantially affects the yield of the hydrazine borane. With an increase in the reaction time from 48 to 72 h, the product yield rapidly decreased from %60 to %48. However, in the literature, the HB yield increases with the increase in the reaction time. This may be because of the fact that the reactant mole ratio was changed in this study [3-5].

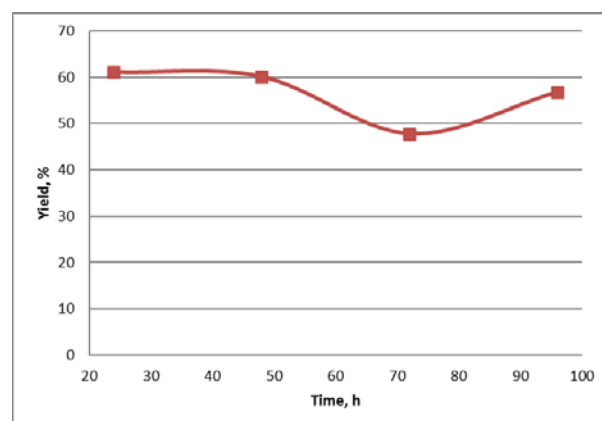


Fig. 2. The effect of time on the reaction yield. (T: 23⁰C, mole ratio: 0.9)

The results of the effect of reactant mole ratio on the reaction is presented in Fig.3. The results indicate that the reactant mole ratio affects the reaction yield. As the mole ratio of hydrazine hemisulfate to sodium borohydride increases, the reaction yield decreases until the mole ratio is 1. After that, the reaction yield increases by increasing the reactant mole ratio.

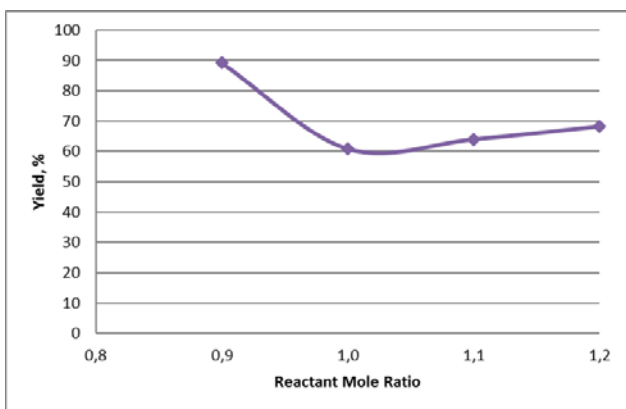


Fig. 3. The effect of reactant mole ratio on the reaction yield.
(T: 23⁰C, t: 48h)

In our study, different catalysts, titanium (IV) oxide and Ru/TiO₂ catalysts, were used to reduce the time and increase the yield. Comparing the reaction with and without catalyst as seen in Fig.4, these studies have shown that the maximum conversion is obtained as %95 using TiO₂. The addition of TiO₂ catalyst increased the reaction rate and the yield of HB. This is also established that under these experimental conditions, Ru/TiO₂ catalyst (%86) has lower yields compared to TiO₂ catalyst. This may be because of the side reactions, influencing the catalyst performance.

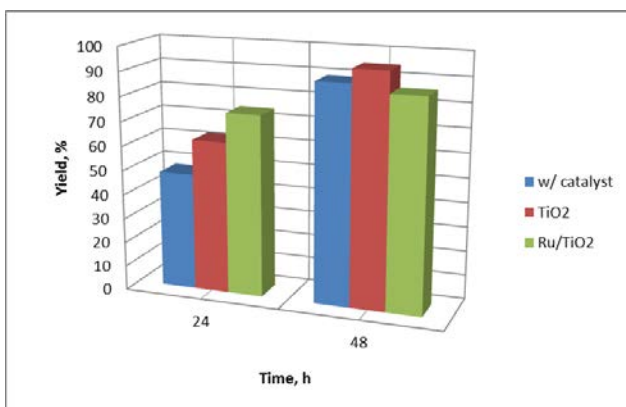


Fig. 4. The effect of catalysts on the reaction yield.
(T: 23⁰C, t: 48h, mole ratio: 0.9)

Additionally, the molecular structure of HB was analyzed by Fourier transform infrared spectroscopy (FTIR). The FTIR spectrum of hydrazine borane with several vibration bands has been shown in Fig.5. In this figure, there are several bands in the N–H and B–H

stretching regions over the range 2600–3500 and 2100–2600 cm⁻¹. Two small bands are observed in the B–H stretching region (1915 and 2015 cm⁻¹), indicating the strong interactions between H of BH₃ and other elements. At 1590 and 1620 cm⁻¹, two sharp very strong bands are seen in the N–H asymmetric bending region. In addition, there are two strong bands at 1435 and 1335 cm⁻¹, corresponding to the N–H symmetric bending region and several bands in the B–H bending region (1100 - 1300 cm⁻¹). Two sharp bands at 1045 and 980 cm⁻¹ correspond the N–H rocking region. The band at 910 cm⁻¹ is assigned to the BN–N asymmetric and N–N symmetric stretching region; whereas a medium band at 750 cm⁻¹ occurs in the B–N stretching region and in the BN–N symmetric stretching region [8].

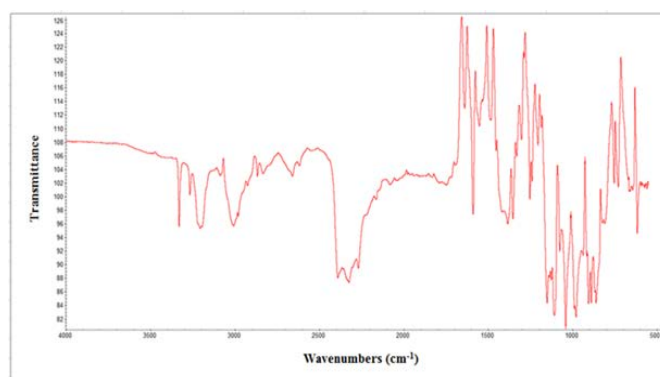


Fig. 5. The FTIR spectrum of the hydrazine borane.

This data coincides with that reported in the literature as shown in Fig. 6, and therefore supports the molecular structure of HB [9].

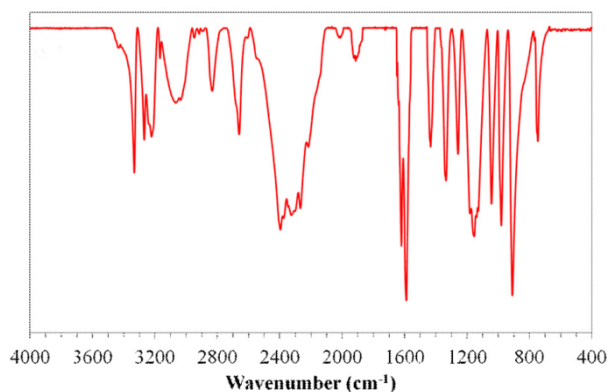


Fig. 6. The FTIR spectrum of the hydrazine borane in the literature [9].

4. CONCLUSIONS

This study evaluated the synthesis of the hydrazine borane with and without the presence of catalyst. The results showed that the synthesis of hydrazine borane was affected by the temperature, time and reactant mole ratio.

The highest yield (%89) for the HB synthesis was obtained, when the reaction temperature, reaction time and the reactant mole ratio were 23⁰C, 48 h and 0.9 respectively. In addition, two types of catalyst were investigated in the study and the best results were obtained (%95) when titanium (IV) oxide was used as the catalyst.

The molecular structure of the hydrazine borane was analyzed by using Fourier Transform Infrared (FTIR) Spectroscopy. This was consistent with the data given in the literature.

Acknowledgements

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Nomenclature

<i>HB</i>	Hydrazine borane
<i>THF</i>	Tetrahydrofuran
X_1	Temperature
X_2	Time
X_3	Reactants mole ratio

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