



Development of Ni-Ti-B ternary catalysts for NaBH₄ hydrolysis reaction and evaluation of their catalytic activities

Scientific research paper

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ABSTRACT

Since it can be obtained from renewable sources and has a high heat value, hydrogen is a promising energy source. Chemical hydrides, such as sodium borohydride (NaBH₄), is used as hydrogen resources. This is due to their relatively high hydrogen content together with their recyclability. In this study, Ni-B catalysts with Ti addition were prepared for the hydrolysis reaction of NaBH₄. In the preparation of Ni-Ti-B catalysts, the chemical reduction technique was used. NiCl₂ salt was used as the Ni source, where TiCl₃ salt was preferred as the Ti source as the variations of the catalyst activities were determined. With the evaluation of the results, subsequent studies were carried out with the most effective Ti metal salt concentration. The effect of catalysts in different Ti/(Ni+Ti) molar ratios were examined according to the temperature, catalyst loading amount, NaBH₄ and NaOH concentrations. The microstructure and elemental analysis of each catalyst were explained by SEM-EDS. After determining the highest performance Ti/(Ni+Ti) molar ratio, the calcination process was performed at different temperatures. For Ni-B catalysts, 5 wt. % NaOH and 5 wt. % NaBH₄ were determined as the optimum fuel composition. Moreover, the Ti doped catalysts demonstrated longer durability and hydrogen production rate for hydrolysis of NaBH₄.

1 Introduction

Depletion of fossil fuels and long-term environmental effects of greenhouse gas emissions necessitate the shift from hydrocarbon fuels to renewable, environmental, and sustainable energy sources [1]. The combustion of

fossil fuels leads to the emission of various toxic gases such as unburned hydrocarbons, carbon monoxide (CO), and carbon dioxide (CO₂), which adversely affect the environment and increase global warming [2]. Therefore, many studies have been conducted on new sustainable energy sources including hydrogen. In

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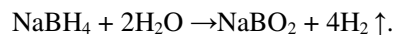
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modern society, hydrogen is a chemical substance that is used in large quantities in applications such as heating, transportation, mechanical power, rocket engines, fuel cells, oil production, electricity production, and synthetic chemical industries (ammonia synthesis) [3]. Therefore, hydrogen production is one of the major research fields in the renewable energy area. This is while hydrogen is an attractive energy carrier due to its significant properties such as high abundance, high energy density and environmentally friendly utilization [4]. Despite being a promising clean energy carrier with zero emission, its efficient and safe storage, remain as serious challenges that hinder its extensive usage [5-7].

For portable applications, high gravimetric and volumetric density of hydrogen storage is of major concern to the success of such applications. Moreover, hydrogen can be stored traditionally in pressurized tanks, by adsorption on high surface area, nanostructured materials (activated carbon, carbon nanotubes, metal organic frameworks (MOFs), etc.), and hydrogen storing alloys. But all of these methods have some drawbacks such as low volumetric and gravimetric storage, high energy consumption, and safety considerations [8].

Among various hydrogen storage systems, the hydrogen content existing in chemical hydrides (NaBH_4 , NaH , LiH , KBH_4 , NaAlH_4 , etc.) is much higher than that of metal hydrides. Hence, chemical hydrides are promising candidates for pure hydrogen production. Because the adsorption and desorption kinetics of these chemical hydrides are fast enough to provide continuous H_2 supply and possible transportation of hydrogen in the containing medium at atmospheric temperature and pressure conditions. Furthermore, hydrides can be recycled as they have relatively high hydrogen content [9]. Moreover, sodium borohydride (NaBH_4) is one of the promising compounds, which is relatively safer because of its non-flammability and higher hydrogen content (10.8 wt %) among different chemical hydrides [3]. In general, hydrogen generation from NaBH_4 obeys the catalytic hydrolysis mechanism as



The reaction efficiency for the hydrolysis reaction of the used catalyst is determined according to

$$\text{Efficiency (\%)} = \frac{V_{\text{H}_2 \text{theoric}}}{V_{\text{H}_2 \text{measured}}} \quad (1)$$

It can be obviously seen that, except hydrogen, there are no gaseous impurities generated. In addition, the reaction process can be easily controlled while the room temperature is competent for hydrolytic dehydrogenation. Therefore, hydrogen generation technology based on NaBH_4 hydrolysis is often applied to supply pure hydrogen for proton exchange membrane (PEM) fuel cell in portable power devices [10].

Hydrolysis reaction can be carried out using both homogeneous and heterogeneous catalysts. Acids are the homogeneous catalysts, but the non-reusability of acids and the difficulty to control hydrogen generation would limit their utilization. On the other hand, heterogeneous catalysts can initiate the reaction on demand without decreasing the pH which allows us to keep the solution for long term storage without any degradation [11]. Under the circumstance, a catalyst has a great importance to control the hydrogen generation rate (HGR). Many noble catalyst materials such as Ru and Pd, have been used for hydrolysis reaction [12, 13]. However, these noble catalysts are not viable for industrial applications because of their high cost and rare availability. The non-noble catalysts Co and Ni have better catalytic activity when used in their boride form because the metalloid increases the resistance of the active sites to oxidation by electron transfer [14]. However, as a result of the agglomeration of Co and Ni based catalysts, hydrogen production activities decrease. Techniques such as the use of different support materials and alloying with various transition metal have been developed to solve such problems [15]. So far, Co-W-B, Co-Cu-B, Co-Mn-B, Ni-Fe-B, Co-Mo-B, Co-Zn-B were developed for the catalytic hydrolysis of NaBH_4 to produce hydrogen [16-21]. In our previous studies, Co-Ti-B alloy catalysts were prepared by reducing the Ti^{+3} cation, obtained from TiCl_3 metal salt, and Ti^{+2} cation, obtained from TiCl_2 metal salt [8, 22].

In this study, different from the literature, Ni-Ti (III)-B catalyst was successfully prepared by chemical reduction of Ni⁺² and Ti⁺³ cations, simultaneously, for the first time and its catalytic properties for hydrolysis reaction are investigated.

2 Materials and methods

Nickel (II) chloride hexahydrate (NiCl₂.6H₂O, 97 %) was purchased from Alfa Aesar, while titanium (III) chloride (TiCl₃, 15 %), sodium borohydride (NaBH₄, min. 98 %), ethanol (C₂H₆O, technical grade) and EDTA were purchased from Merck.

2.1 Catalyst Preparation

Ni-Ti-B catalysts and pristine Ni-B powder catalysts were synthesized by the wet chemical reduction method. Firstly, various amounts of 0.02 M NiCl₂ solution stated in Table 1 were mixed with 80 ml distilled water in order to investigate the effect of concentration on catalytic activity of Ni-B catalysts. Secondly, Ni-Ti-B ternary alloys were synthesized with the obtained concentration that has the highest activity. After that, the desired amount of TiCl₃ solutions with 15 % purity, and EDTA, as complexing agent, were added to 28 ml 0,02 M NiCl₂ solution and 80 ml distilled water. The final solution was stirred at room temperature for 10 minutes before stirred in a cryostat for 30 minutes at 8°C. When the solution was vigorously stirred, an excess quantity of NaBH₄ aqueous solution was applied to the solution as a reduction agent. After the addition of reducing agent, the reaction solution was stirred for 5 minutes in the cryostat and 15 minutes at room temperature in order to ensure the complete reduction of nickel and titanium ions. The centrifugation process (Nüve, NF800) at 8000 rpm for 5 minutes was applied and repeated for all solutions. Then, the precipitated catalysts was washed twice respectively with distilled water and ethanol before being dried in a vacuum oven (Nüve, EV018) at 105°C for 2 hours. The grinding process was applied by using an agate mortar.

Table 1. Parameters for the preparation of Ni-B and Ni-Ti-B Triple Catalysts.

Catalyst Name	Contents
N1	NiCl ₂ (7 ml) / Distilled Water
N2	NiCl ₂ (14 ml) / Distilled Water
N3	NiCl ₂ (28 ml) / Distilled Water
T1	NiCl ₂ (28 ml) / TiCl ₃ (3 ml) / Distilled Water / EDTA
T2	NiCl ₂ (28 ml) / TiCl ₃ (6 ml) / Distilled Water / EDTA

2.2 Catalytic activity tests

Activity tests were performed using 20 mg of dry catalyst and 10 ml of alkaline NaBH₄ solution in a batch type reactor which was immersed into the thermostatic water bath had the temperature adjusted to 65 °C in order to control reactor temperature and stirred at 600 rpm with Teflon coated magnetic stirring bar. The experimental setup for catalytic activity tests was given in Fig. 1.



Fig. 1 The experimental setup for catalytic activity tests: 1. Magnetic stirrer 2. Temperature regulated water bath 3. Reactor 4. Washing bottle 5. Gas burette.

The volume of the hydrogen gas released during the reaction was measured via the decreasing of the water level in the gas burner, after passing through the wash bottle. During these experiments, both the total reaction time and the hydrogen generation time were measured separately. The amount of the hydrogen produced every one minute was noted and graphs of hydrogen produced by volume (ml) versus time were created.

3 Results and discussion

Initially, Ni-B binary catalysts which had been prepared with different nickel concentrations were synthesized, and their activities were tested using alkaline NaBH₄ solution (NaBH₄ (5 wt. %) and NaOH (5 wt. %)) at 338 K. The obtained HGR and reaction efficiency of the prepared catalysts are given in Table 2. The efficiency values given in Table 2 and Table 3, have been calculated according to Eq. (1).

Table 2. Determination of the total reaction time and efficiency (%) of catalysts.

Catalyst name	Reaction time(s)	Volume of H ₂ (ml)	Efficiency (%)
N1	1200	199	16,58
N2	1500	669	55,75
N3	1500	832	69,33

As it can be easily seen in Table 2, first of all, rising Ni⁺² concentration in the solution causes increase in the catalytic efficiency (%) and the generated H₂ volume in lower reaction times. Therefore, the optimum Ni⁺² was determined as N₃ (28 ml 0,02 M NiCl₂ and 80ml distilled water).

Ni-Ti-B ternary catalysts which had constant titanium amount were synthesized via simultaneous chemical reduction of Ni and Ti cations. The EDTA was used as complexing agent to reduce simultaneously Ti and Ni cations which have different electromotive forces. Figure 2 shows SEM images while Fig. 3 demonstrates the EDS analyses of Ni-B and Ni-Ti-B ternary catalysis. Nickel and titanium were obtained to be dominative components, while elements such as oxygen and sulfur were not found. This proves that nickel and titanium successfully co-reduce without oxidizing. Their activities were tested using the optimum fuel concentration determined above (5 wt. % NaBH₄ and 12,5 wt. % NaOH) at 338 K.

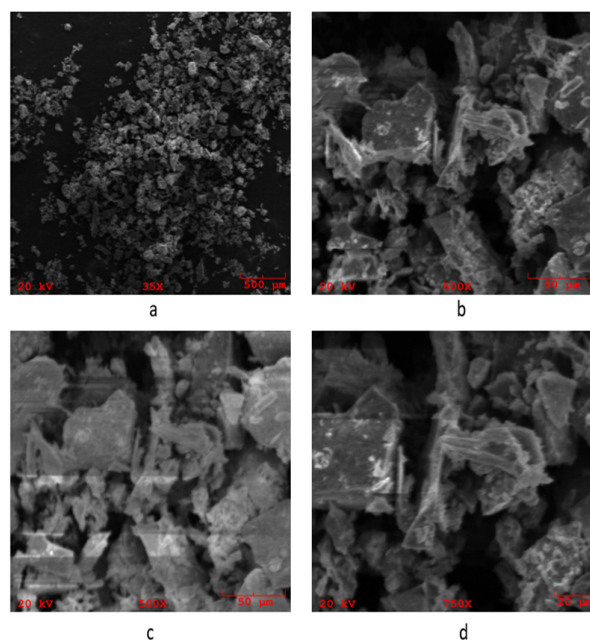


Figure 2. SEM images of Ni-Ti-B ternary catalyst. Panel a, catalyst microstructure under 35X magnification. Panel b, catalyst microstructure under 500X magnification. Panel c, catalyst microstructure under 500 X magnification. Panel d, catalyst microstructure under 750X magnification.

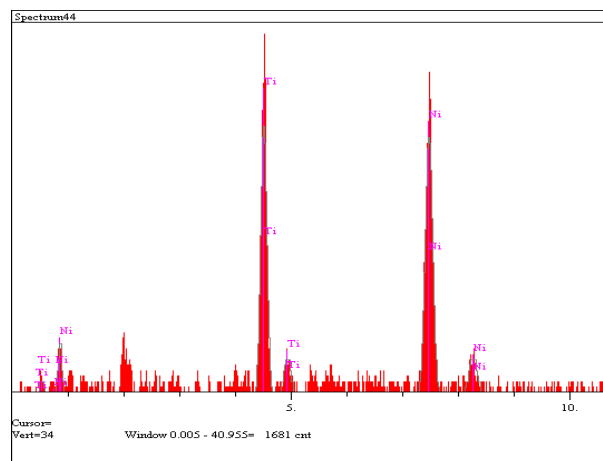


Figure 3. EDS spectra of Ni-Ti-B catalysts.

Figure 4 shows the hydrogen released volume as a function of reaction time for N₃ coded Ni-B catalyst.

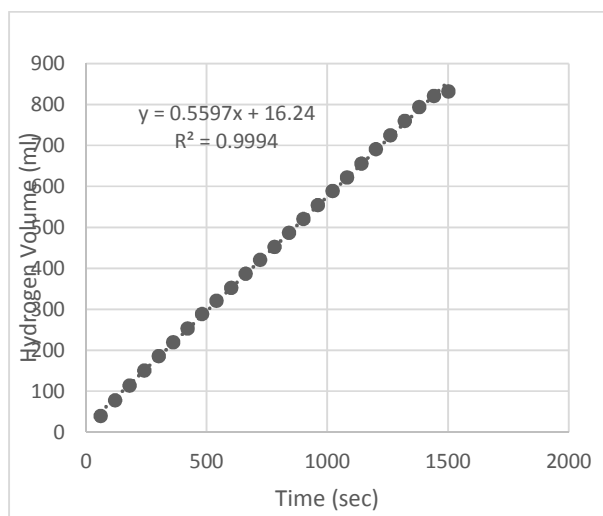


Figure 4. Hydrogen released volume as a function of reaction time from 10 ml fuel solution (5 wt. % NaBH₄ and 5 wt. % NaOH) at 338 K in the presence of 20 mg Ni-B.

Figure 4 shows that the hydrogen production starts immediately without an induction time after addition of fuel. Moreover, the amount of hydrogen generation is almost linearly proportional ($R^2=0,9994$) to the reaction time for the Ni-B, revealing the constant generation rate of hydrogen and stable catalytic activity of the catalyst. Usually the NaBH₄ solution used for hydrolysis is a combination of NaBH₄ and NaOH. In the literature, it has been shown that both the NaOH and NaBH₄ concentrations significantly effect the rate of hydrogen production of the used catalysts. Jeong et al. studied 20 wt. % NaBH₄ + 5 wt. % NaOH for Co-B. Aydin et al. studied 8 wt. % NaBH₄ and 7.5 wt. % NaOH solution for Co-B catalyst supported on graphene. Ding et al. studied 7 wt. % NaOH + 7 wt. % NaBH₄ fuel solutions for their catalysts [8, 17, 23]. The effect of both NaOH and NaBH₄ concentration on the hydrolysis reaction rate was examined via conducting a series of experiments. As given in Table 3, to investigate the NaOH effect, we tried different initial concentrations of NaOH while keeping the NaBH₄ concentration at 5 wt. %. Similarly, to clarify the optimum NaBH₄ concentration, we kept the NaOH concentration at 5 wt. %.

Table 3. Determination of total reaction time and efficiency (%) of fuels with different concentrations.

Catalyst name	Fuel content	Reaction time(s)	Volume of H (ml)	Efficiency (%)
N3	0.5g NaOH 1g NaBH ₄	1500	657	54,75
N3	1g NaOH 1g NaBH ₄	1500	832	69,33
N3	2g NaOH 1g NaBH ₄	1380	926	77,16
N3	2.5g NaOH 1g NaBH ₄	1500	1012	84,33
N3	1g NaOH 0.5g NaBH ₄	840	535	44,58
N3	1g NaOH 2g NaBH ₄	1500	640	53,33

As can be seen in Table 3, the optimum fuel concentration for Ni-B catalyst that we synthesized is determined at 5 wt. % NaBH₄ and 12,5 wt. % NaOH, with hydrogen released volume as a function of the reaction time where for this fuel composition is shown in Fig. 5.

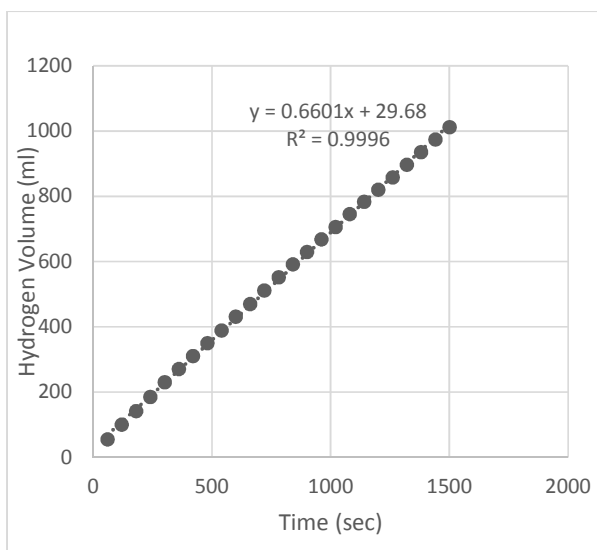


Figure 5. Hydrogen volume-time graph of optimum fuel content (5 wt. % NaBH₄ and 12,5 wt. % NaOH).

In comparison with Fig. 4 and Fig. 5, as a result of usage of optimum fuel composition, the slope of the graph increases from 0,55 to 0,66 due to higher hydrogen generation rate of Ni catalyst. Moreover, similar to Fig. 4, the constant generation rate of hydrogen and stable catalytic activity of the catalyst still continues. Figure 6 shows the hydrogen released volume as a function of the reaction time for both Ni-B and ternary Ni-Ti-B catalysts.

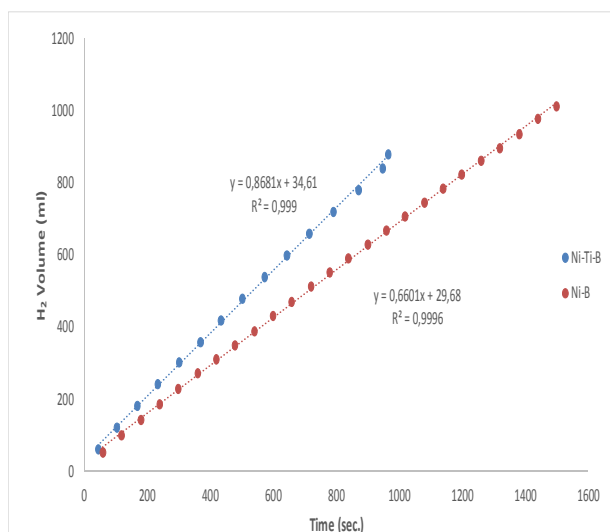


Figure 6. Hydrogen released volume as a function of the reaction time from 10 ml fuel solution (5 wt.% NaBH₄ and 12,5 wt.% NaOH) at 338 K in the presence of 20 mg catalyst.

As it can be easily seen in Fig. 6, the total reaction time is shortened with the addition of titanium which results in higher HGR. On the other hand, the total released hydrogen volume decreases for the ternary Ni-Ti-B due to leakage which is generally an observed problem because of the high reaction rate [8].

4 Conclusions

For the first time, Ni-Ti-B ternary catalysts were synthesized with constant amount of titanium by the chemical reduction method in order to use in hydrolysis of alkaline NaBH₄ solutions. For Ni-B catalysts, the optimum fuel composition was defined as 5 wt. % NaBH₄ with 5 wt. % NaOH. The Ni-Ti-B catalysts were compared with undoped Ni-B, catalysts which were prepared under the same conditions. Even small amounts of Ti enhanced the catalytic activity according to the volume of released hydrogen as a function of time. The EDS results did not show any oxygen or any unknown element peak; this means that the Ni and Ti ions were absolutely reduced. However, the efficiency (amount of the produced hydrogen) and strength decreased due to leakage. Additionally, the Ti-doped catalysts have longer durability and hydrogen production rate.

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