Investigation of Hydrogen Production from Sodium Borohydride in the Presence of Ni/Al₂O₃

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Abstract. With the increasing trend towards the use of renewable energy and the encouragement of international agreements due to environmental effects, the world tends to provide the energy it needs from renewable sources. Hydrogen is an environmentally friendly energy carrier that is produced from various energy sources and can be a sustainable solution to energy needs. Catalyst evaluation studies are carried out in studies that release high purity hydrogen by hydrolysis of metal hydrides such as sodium borohydride (NaBH₄), and potassium borohydride (KBH₄). In this study, Al₂O₃ supported Ni catalysts were synthesized by the impregnation method and the catalysts were characterized by applying X-Ray Diffractometry (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), and Brunauer-Emmett-Teller (BET) methods. The performance of the catalysts was evaluated in the production of hydrogen by the hydrolysis of sodium borohydride. The influences of reaction temperature (20, 40, and 60 °C) and Ni content of the catalyst (20, 30, and 40 %) on the hydrolysis reaction was investigated under experimental conditions of 100 mg NaBH₄, 100 mg catalyst, 5 mL 0.25 M NaOH. The highest hydrogen yield (100%) and hydrogen production rate (364.3 mL/gcat.min) was obtained with 40% Ni/Al₂O₃ catalyst at 60 °C reaction temperature.

1. Introduction
The existent energy system based on fossil fuels to meet the increasing energy demand in the world is seen as the main cause of global climate change and air pollution [1]. Renewable clean energy should be promoted to develop more sustainable production methods, minimize waste, reduce air pollution from vehicles and reduce greenhouse gas emissions [2]. There is a growing interest in hydrogen-based technologies among alternative energy systems [1].

Technically, hydrogen is not an energy source, but it is an energy carrier like electricity. Hydrogen can be produced sustainably using fossil fuels, nuclear or renewable energy sources [3]. It also has the highest combustion energy per unit mass (lower calorific value 120 MJ/kg and higher calorific value 142 MJ/kg) compared to commonly used fuels [4]. Hydrogen is a renewable, abundant and more importantly, a clean fuel that provides only water vapor to the environment during combustion. In order to use hydrogen vehicles usable in the future, cost-effective, safe, efficient and practical hydrogen storage systems should be designed and developed for in-vehicle applications [5]. Hydrogen storage is recognized as one of the most critical problems to be solved before a technically and economically viable hydrogen fuel system can be installed. The main disadvantage of using hydrogen as a portable fuel is that large storage tanks are required due to the low hydrogen density [6].
In order to store pure hydrogen, storage systems have been developed in compressed gas, cryogenic liquid, storage in carbon materials, storage in metal hydrides and chemical hydrides. In particular, metal hydrides stand out as promising storage materials for the use of hydrogen in fuel cells [7]. Metal hydrides with high gravimetric hydrogen storage densities are known as 'one pass' in hydrogen storage systems due to the release of stored hydrogen when they come into contact with water [8]. In addition, since the reactions can be controlled by parameters such as water ratio, pH and catalyst, its use in portable applications is more advantageous than other storage methods [9]. Hydrogen storage as metal hydride has been the focus of concentrated research [10].

Sodium borohydride, which has a high hydrogen storage capacity of 10.8% by weight, stands out as potential materials for hydrogen storage [11]. NaBH₄ can produce twice the amount of hydrogen it stores through hydrolysis with water, and the by-product sodium metaborate (NaBO₂) is environmentally clean [12]. NaBH₄ has a slow rate of hydrolysis, and the rate of hydrolysis can be increased significantly in the presence of a suitable catalyst [13]. In addition, the rate of hydrolysis can be controlled with the catalyst and the hydrolysis reaction stops when the catalysts are removed [12]. Noble metals such as Pt, Rh, Pd, and Ru are commonly used as catalysts for NaBH₄ hydrolysis. However, the scarcity of natural resources for noble metals and the outcome elevated cost have led to the improvement of alternative catalysts. In the last few years, catalysts with low cost and good catalytic properties have been developed for hydrolysis of NaBH₄, particularly based on Co and Ni [14]. In addition, among the support material such as ZrO₂, SiO₂, TiO₂ or Al₂O₃, aluminium oxide can be used as a support material to increase the surface area and therefore the efficiency of the metal catalyst [15].

Kilinc et al. synthesized an Al₂O₃ supported Ni-based complex catalyst containing 1% nickel for hydrogen production from NaBH₄ hydrolysis, and investigated its effect on the hydrolysis reaction. They found the Arrhenius activation energy as 27.29 kJ/mol for the Al₂O₃ supported nickel-based complex catalyst [16]. Li et al. prepared Ni-Co-P/γ-Al₂O₃ catalyst using electroless coating, and investigated its catalytic activity in the hydrolysis of NaBH₄ solution. The results of the study showed that the hydrogen production rate was highly dependent on the NaOH concentration, and the ratio of Co and Ni [12]. Lu et al. synthesized catalysts on different support materials TiO₂, Al₂O₃, and CeO₂ with the incipient-wet impregnation method, and investigated the activities of the obtained catalysts in sodium borohydride hydrolysis. They reported that they achieved the highest hydrogen production rate on sodium borohydride hydrolysis by using CoB/TiO₂ catalyst at 30 °C reaction temperature [17].

In this study, Ni/Al₂O₃ catalyst was synthesized as catalyst for hydrogen production by hydrolysis of alkali solution of sodium borohydride by weight 20, 30, and 40% Ni loading ratios by impregnation method, and the catalysts were characterized by XRD, XRF, SEM, and BET. The activity of catalysts in the production of hydrogen from the hydrolysis of alkaline NaBH₄ solution was also investigated.

2. Experimental and procedure

2.1. Materials
Aluminum oxide (Al₂O₃, alumina), Nickel (II) nitrate hexahydrate, sodium borohydride (NaBH₄) and sodium hydroxide (NaOH) were used in the experiments without any pre-treatment.

2.2. Catalyst synthesis
Ni/Al₂O₃ catalyst was synthesized using the impregnation method. Nickel (II) nitrate hexahydrate salt was dissolved in pure water with 1:5 catalyst:water ratio (wt/wt), Al₂O₃ support material was added and stirred for 3 hours in a magnetic stirrer heater at 70 °C. The obtained catalyst was aged for 1 night and the particle size was reduced after drying in an oven at 105 °C overnight. Then, it was calcined in the tube furnace at 550 °C with a heating rate of 2 °C/min for 3 hours under an air flow of 400 mL/min.

2.3. Catalyst characterization
The crystalline diffractogram of the catalysts were examined in the XRD equipment (Rigaku Rint 2200) operating at 40 kV voltage and 30 mA current. In the analyses, Cu-Kα was used as X-ray source and the film was shot at 2θ=15-85°. Analyses were carried out at a scan rate of 4°/min, and a scan
angle of 0.02°. Elemental analysis of the catalyst was made with a Rigaku ZSX model XRF device and the weight component ratio was obtained. The specific surface area of the catalysts was calculated using Brunauer-Emmett-Teller methods (Micromeritics, ASAP 2020). Catalysts were degassed under vacuum at 300 °C for overnight before the analysis. Morphological characterization of synthesized catalysts was operated using with scanning electron microscope by high-resolution method in 10 kV (TESCAN VEGA3). Before analyzing, the catalysts were sputter-coated with thin layers of Au/Pd in order to provide electron mobility.

2.4. Activity test
The catalytic activities of the catalysts were investigated on the NaBH₄ hydrolysis using the experimental setup given in our previous study [18, 19]. Briefly, the reaction was performed in a 250 mL flask. After the catalyst was added to the reactor, it was added onto the mixture of NaBH₄ and NaOH. The obtained hydrogen gas produced during the reaction was measured by water-gas replacement method and recorded. The catalysts were reduced to H₂/N₂ (20% H₂ by volume) at a flow rate of 400 mL/min for 30 minutes prior to use in hydrolysis experiments.

3. Results and discussions
3.1. Catalyst characterization
XRF results of Ni/Al₂O₃ catalysts are presented in table 1.

| Catalysts   | NiO (%wt/wt) | Al₂O₃ (%wt/wt) | Other component (%wt/wt) |
|-------------|--------------|----------------|--------------------------|
| 20% Ni/Al₂O₃| 22.65        | 76.19          | 1.16                     |
| 30% Ni/Al₂O₃| 35.44        | 62.55          | 2.01                     |
| 40% Ni/Al₂O₃| 46.78        | 51.48          | 1.74                     |

When the XRF results given in table 1 are examined, it is seen that the theoretical loading of nickel is above the theoretical value due to its oxide form, but it has been successfully loaded on the alumina support. It is clear that there is a reduction in the percentage of alumina in line with the enhancement in the nickel loading ratio.

XRD diffraction patterns of Ni/Al₂O₃ catalysts at different loading ratio are given in figure 1.

![Figure 1. XRD diffraction pattern of Ni/Al₂O₃ catalyst (▲: NiO, ●: Al₂O₃).](image-url)
According to the XRD diffraction patterns of the calcined catalysts given in figure 1 are examined, it is clear that the peak intensities of NiO and Al₂O₃ increase depending on the Ni ratio. In XRD diffraction patterns, it is seen that NiO characteristic peaks are 2θ=37.2°, 62.8°, 75.16°, 79.04° and Al₂O₃ characteristic peaks are 2θ=36.36°, 44.56°, 66.28°. In the Al₂O₃ peaks, a decline was observed in the peak intensities as the Ni ratio increased.

The physicochemical properties of catalysts are presented in table 2.

| Catalysts      | BET Surface Area (m²/g) | Pore volume (cm³/g) | Pore size (nm) |
|----------------|-------------------------|---------------------|---------------|
| γ-Al₂O₃        | 163.21                  | 0.26                | 7.4           |
| 40% Ni/Al₂O₃  | 79.96                   | 0.13                | 6.4           |

As can be noticed from table 2, the BET surface area of γ-Al₂O₃ was 163.21 m²/g, and it diminished dramatically with the increase in the loading amount of Ni, proving evidence that the impregnation of metal and calcination process results in coating the surface of support material and blockage of small pores which could account for the loss of surface areas.

Figure 2 indicates the SEM images to examine the surface morphology of catalysts.

![SEM images of a) 30% Ni/Al₂O₃ and b) 40% Ni/Al₂O₃ catalysts.](image)

According to the SEM images the Ni was loaded onto the support materials. SEM images of nano catalysts have a very global structure consistent with the literature. As seen in figures, as the nickel loading ratio increases from 30% to 40% Ni, floccule textures are formed on the catalyst surface. In addition, it is seen that the floccule structures and agglomeration formed on the catalyst surface with 40 wt% Ni/Al₂O₃ catalyst exhibit a homogenous distribution and completely cover the Al₂O₃ surface and display a compact structure.

3.2. Activity test
Ni/Al₂O₃ catalysts were synthesized by the impregnation method by weight 20, 30, and 40% Ni loading ratios. Other parameters (reaction temperature 20 °C, amount of catalyst 100 mg, amount of NaBH₄ 100 mg, 5 mL 0.25 M NaOH) were kept constant to analyse the activity in hydrogen production. The results obtained on the effect of nickel loading ratio on hydrogen production at 20 °C are given in figure 3, and the effect of reaction temperature on hydrogen production are given in figure 4. The summary of activity test results is given in table 3.
In the figure 3, the effect of different nickel loading ratio on the hydrogen yield was examined, depending on the increased nickel content, it is seen that the yield obtained with 30% nickel catalyst, produces 2 times better results than the 20% nickel loaded catalyst. It is clear that 96.67% hydrogen yield was obtained with 40% nickel catalyst with a hydrogen production rate of 40.83 mL/g cat.min. As seen in figure 4, the effect of reaction temperature on hydrogen yield was investigated at 20, 40, and 60 °C. With the increase of the reaction temperature, the hydrogen production rate increased, and the hydrolysis time decreased. As the temperature increased from 20 °C to 40 °C, the hydrogen yield reached 100%, and the hydrogen production rate reached 170.55 mL/g cat.min. With the temperature being 60 °C, the reaction hydrogen production rate increased approximately 2 times, and the highest hydrogen production rate was obtained at 60 °C as 364.29 mL/g cat.min.

### 4. Conclusions

In this study, Ni/Al₂O₃ catalyst was synthesized by the impregnation method and their properties were characterized by XRD, XRF, SEM, and BET. Activity studies were tested by weight 20, 30, 40% nickel catalyst and 20, 40, 60 °C reaction temperatures and it was observed that as the temperature increased, the hydrogen yield and hydrogen production rate increased, and the reaction time shortened. When the results were compared with the literature, the synthesized catalyst offered promising results. In future studies, this study can be improved by using different synthesis methods and trying different catalyst active substances.

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**Figure 3.** Effects of Ni loading ratio on hydrogen production (100 mg catalyst, 100 mg NaBH₄, 5 ml 0.25 M NaOH, 20 °C).

**Figure 4.** The effects of temperature on hydrogen production (100 mg 40% Ni/Al₂O₃, 100 mg NaBH₄, 5 ml 0.25 M NaOH).

**Table 3.** Summary of activity results.

| Nickel loading ratio (%) | Hydrogen yield (%) | Hydrogen production rate (mL/g cat.min) |
|--------------------------|--------------------|----------------------------------------|
| 20                       | 33.33              | 17.35                                  |
| 30                       | 66.67              | 34.00                                  |
| 40                       | 96.67              | 40.83                                  |
| Reaction temperature (°C) |                    |                                        |
| 20                       |                     |                                        |
| 40                       | 100.00             | 170.55                                 |
| 60                       | 100.00             | 364.29                                 |
5. References

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