# Effect of Ru/C and Ni/TiO<sub>2</sub> On the Hydrogen Generation from Metal Hydrides

Fahriye Dönmez and Nezihe Ayas

Abstract—Hydrogen is at a good level among all energy sources as a clean, renewable and sustainable energy source. Hydrogen has high energy intensity, an ideal energy carrier for the environment with zero emission and can be produced in a controlled way by selecting suitable catalysts from metal hydrides having a high content of hydrogen among the other production methods. In this study commercial (Ru/C) and synthesized (Ni/TiO<sub>2</sub>) catalyst was used in order to produce hydrogen from sodium borohydride. The activities of the synthesized catalysts were examined in the hydrolysis reaction and the results compared with the commercial catalyst. The effect of reaction parameters such as temperature and time, the amount of catalyst and the loading ratio of Ni on the support material on the hydrolysis reaction was examined.

*Index Terms*—Sodium borohydride, Ru/C, Ni/TiO<sub>2</sub>, nanocatalyst, hydrogen.

# I. INTRODUCTION

In recent years, there has been an unforeseen energy need. It is thought that energy demand increases day by day [1]. Fossil fuels cause damage to the environment also they will be insufficient for energy requirement in the future [2]. It is accepted that hydrogen energy can replace fossil fuels as a clean energy carrier [3]. Hydrogen is known as an ideal fuel with zero emission energy, harmless, and high energy density [4], [5]. Hydrogen is not regarded as an energy source because elemental hydrogen is rarely found in nature. The chemical energy carried by hydrogen per mass is three times higher than other chemical fuels. Because of that, hydrogen is accepted to be an important energy carrier [6].

Four main obstacles to the application of hydrogen and fuel cells have been proposed: hydrogen production, storage and distribution, and the high cost of fuel cells [7].

Hydrogen has the potential to lay the foundation for a clean and virtually unlimited energy system because it can be produced from a range of renewable and non-renewable sources, such as catalytic reforming, natural hydrolysis, chemical hydride hydrolysis, coal gasification, biomass pyrolysis and gasification, electrolytic or photocatalytic water partitioning [4], [6].

Storage of hydrogen as much as production of hydrogen is also an important issue, so it is necessary to use a suitable hydrogen source [8]. Factors to consider when evaluating storage systems include energy densities, cost, security, and ease of production.

Chemical hydrides, especially borohydrides, are currently being developed as storage alternatives; because they exhibit good energy densities but there is a need for cost-effective recycling methods to develop these options for selected fuel cell applications [7].

Hydrogen, which has many storage methods, can be safely stored in chemical hydrides and then hydrogen can be produced by hydrolysis. Therefore, there has been an interest on hydrolysis of chemical hydride, which is an alkaline or alkaline earth metal hydride [9]. Sodium borohydride is a member of borohydrides group. It is known to be stable in dry air, its solutions are not flammable; Production of hydrogen from sodium borohydride by hydrolysis is given by Equation 1 [10].

$$NaBH_4 + 2H_2O \xrightarrow{Catalyst} NaBO_2 + 4H_2$$
(1)  
$$\Delta H = -217 \text{ kj/mol}$$

2 moles of hydrogen are emitted from the water in the hydrolysis reaction of sodium borohydride. As a result, 1 mole of sodium borohydride is hydrolyzed with water to produce 4 moles of hydrogen [2]. Based only on the reactants, this refers to a gravimetric hydrogen storage capacity (GHSC) of 10.8% by weight [6]. The by-product sodium metaborate (NaBO<sub>2</sub>) is cleaner for the environment and can be reused after converting into NaBH<sub>4</sub> [11].

NaBH<sub>4</sub> self-hydrolysis occurs when the pH value of the solution is lower than 9, therefore NaOH is always supplemented to the solution as a stabilizer [12]. The reaction rate without the catalyst is very slow and in fact the reaction ends by adding sodium hydroxide in a small percentage into the solution. For this reason, sodium borohydride can be stored as an aqueous solution and transported as stable [13]. The base-balanced NaBH<sub>4</sub> solution produces significant amounts of hydrogen in ambient conditions while in contact with specific catalysts. An effective catalyst is considered to be the most important part of the NaBH<sub>4</sub> hydrolysis reaction [3], [8]. Adjustment of sodium borohydride hydrolysis reaction rate and the reaction control are based on determining the optimum level of the added catalyst [11].

To accelerate the hydrogen generation reaction various catalysts have been developed, such as noble metals (Ru, Pt, Rh, Pd, Pt-Ru, Pt-Pd alloys) and non-noble transition metals or related compounds (Cu, Co, Ni, Co-B, Co-PB, Co-WB, Ni-Si0<sub>2</sub>, Fe-Ni alloys) [14].

It is known that noble metal catalysts have the most

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effective properties among the catalysts. The main disadvantage of noble metal catalysts is their high cost and their small number of quantities for use [2]. It is important to increase the reaction rate and reduce the use of excess catalyst. The catalyst must be of small particle size and well dispersed. As a result of which the efficiency of the catalyst increases [15].

Nanotechnology is a method of designing and synthesizing materials with particle size of 1-100 nm in a controlled manner [16]. It's one of the important fields of application is the catalyst production [17].

The role of nanoparticles in catalytic processes is important from an environmental, social, technological and scientific point of view because of their relevant properties such as activity, selectivity, endurance and reusability. The most important properties that nanocatalysts must possess are 100% selectivity, extremely high activity, low energy consumption and long life [18].

The performance of a catalyst is closely related to the particle size, because the surface structure and its electrolytic properties change as the particle size changes [19]. The reduction of the particle size increases the surface area and the activity [17].

The point to note in the nanocatalysis method is to clarify the structure of the prepared nanoparticle catalyst and to determine the mechanism [20].

In this study,  $Ni/TiO_2$  catalyst was synthesized by the impregnation method and its activity was tested on obtaining hydrogen from sodium borohydride then found results were compared with the result of commercial catalyst, Ru/C. In the experiments, a series of studies were carried out using different hydrolysis parameters such as temperature, reaction time, the amount of catalyst, and the loading ratio of Ni.

## II. EXPERIMENTAL

# A. Materials

Sodium borohydride (NaBH<sub>4</sub>, powder, 98.0%, Sigma-Aldrich), Ruthenium 5% on activated carbon, (Ru/C, powder, reduced, Alfa Aesar), Sodium Hydroxide (NaOH, pellets, 98.8%, VWR Chemicals), Titanium (IV) oxide (TiO<sub>2</sub>, powder, 99%, Sigma-Aldrich), Nickel (II) nitrate hexahydrate (N<sub>2</sub>NiO<sub>6</sub>H<sub>2</sub>0, 97% purity, Sigma-Aldrich) and distilled water was used in experiments. All the chemicals were used without any pre-treatment.

#### B. Catalysts

In the experiments, Ru/C as commercial catalyst and  $Ni/TiO_2$  synthesized by the impregnation method were used. Ru/C was used without any processing after purchase.

## C. Preparation of Ni/TiO<sub>2</sub> Catalysts

Ni/TiO<sub>2</sub> catalyst was synthesized using the impregnation method at the Ni loading ratio of 20, 30 and 40% (wt./wt.). The nickel (II) nitrate hexahydrate salt was dissolved in pure water, then the solution was stirred for 3 hours at stirring speed of 1000 rpm and at 70 °C with adding support material (TiO<sub>2</sub>). The sample was aged for a day at room temperature and then dried at 105 °C for 24 hours. The particle size was reduced and calcined in a tube furnace at a heating rate of 2 °C/min at 550 °C for 3 hours under an air flow rate of 400

mL/min.

Before being used in hydrolysis experiments, catalysts were reduced at 800 °C under a flow rate of 400 mL/min,  $H_2/N_2$  (20%  $H_2$  by volume) for 30 min.



Fig. 1. Impregnation steps of Ni/TiO2 catalyst.

#### D. Catalyst Characterization

*X-ray diffraction (XRD)* measurements were used to study the crystal structure of the synthesized nanocatalysts.

Each crystal phase has its own atomic sequence. XRD is based on the principle of breaking X-rays in a characteristic order according to these arrays. The resulting characteristic peaks define that crystal. In this context, XRD analysis was used to determine the distance between the structure and the layers of the catalysts produced.

XRD analyzes were performed with a Rigaku Rint 2200 X-ray diffractometer at 40 kV voltage and 30 mA currents at a scan angle of  $0.02^{\circ}$  and a scan rate of 4 %min. In the shootings, Cu-K $\alpha$  was used as X-ray source and the film was shot at  $2\theta = 15-85^{\circ}$ .

The resulting patterns were compared with the Joint Committee on Powder Diffraction Standards (JCPDS) to identify the crystallite phases of metal oxides.

The mean crystalline size of the oxide phase of the catalysts and the metallic phase of the reduced catalysts was calculated from the full width at the half maximum (FWHM) of intense X-ray diffraction peaks using Debye Scherrer's equation.

$$D = \frac{\kappa \times \lambda}{\beta \times \cos\theta} \tag{2}$$

where *D* is the mean size of the ordered crystallite (nm), 0.9 <K <1.0 is a correction factor for the shape of the sample,  $\lambda$  the wavelength of the X-ray (0.154 nm for Cu-K $\alpha$ ),  $\theta$  Bragg angle,  $\beta$  is known as the line broadening at half the maximum intensity (FWHM).

#### E. Hydrogen Generation Measurement

The catalytic activities of the prepared catalysts were tested on hydrolysis of the sodium borohydride solution (Fig. 2). The hydrolysis reaction was carried out in the 250 mL three-necked glass using a water bath and magnetic stirrer. First, the catalyst was placed in the glass flask, and then NaBH<sub>4</sub> solution, equilibrated with NaOH was added. The amount of hydrogen gas generated during the reaction was measured by the volume change method and recorded as a time-dependent. 100 mg NaBH<sub>4</sub> and 5 mL 0.25 M NaOH were used in all experiments.



Fig. 2. Experimental setup for hydrogen generation (1- Three neck flasks 2-Thermometer 3- Thermostatic bath 4- NaBH<sub>4</sub>+NaOH solution 5- Catalyst 6-Graduated cylinder 7- Sink).

In order to determine the appropriate amount of catalyst, hydrolysis experiments were carried out using different amounts of (30-100 mg) Ru/C catalyst.

Experiments were performed at different temperatures (20, 40 and 60  $^{\circ}$ C) in order to observe the effect of the temperature.

To determine the effect of nickel loading rate, experiments were carried out with 20, 30 and 40% (wt./wt.) nickel loading rate.

## III. RESULTS AND DISCUSSION

## A. XRD Analysis

A powder XRD analysis was used to study the structural and crystalline properties of the as-prepared catalysts and the diffraction patterns are shown in Fig. 3.

In the XRD diffraction pattern results, according to the literature, the diffraction peaks at  $2\theta = 25.88^{\circ}$ ,  $37.92^{\circ}$ ,  $48.16^{\circ}$ ,  $54.24^{\circ}$ ,  $62.92^{\circ}$ ,  $70.94^{\circ}$ ,  $75.24^{\circ}$ ,  $83.08^{\circ}$  belong to TiO<sub>2</sub>. Both anatase and rutile phases were identified in the TiO<sub>2</sub> support. However, the rutile phase was dominant, and this could be attributed to the annealing temperature used for the synthesis of catalysts. Furthermore, the diffraction peaks at  $2\theta = 37.4^{\circ}$ ,  $43.44^{\circ}$ ,  $63.00^{\circ}$ ,  $79.72^{\circ}$  belong to NiO. There, the diffraction peaks at  $2\theta = 63.00^{\circ}$ ,  $37.4^{\circ}$  can be attributed both to the TiO<sub>2</sub> of the spinel structure and the NiO, since the diffraction patterns of the two oxides are very close.

As expected, an increase in the nickel content caused an increase in the intensity of the main diffraction peak at  $2\theta = 37.4^{\circ}$ , suggesting a better crystal formation. For the higher nickel contents signals at  $2\theta = 43.44^{\circ}$  and  $63.00^{\circ}$  were observed. It was also observed that the peaks of TiO<sub>2</sub>, notably at  $2\theta = 37.92^{\circ}$  and  $48.16^{\circ}$ , became less intense with the increase in the nickel content.

The XRD diffraction patterns of the catalysts show that the peak intensities of NiO and TiO<sub>2</sub> are high. Moreover, the intensities of the peaks in the catalysts were found to change considerably after nickel loading with respect to the amount of nickel in the catalysts. The intensity of the peaks related to TiO<sub>2</sub> in the catalysts was significantly reduced after nickel loading, denoting their lower crystallinity. This indicates that the incorporation of nickel prevented the crystalline growth of TiO<sub>2</sub>. However, with increasing amounts of nickel, the intensity of the peaks corresponding to NiO increased, denoting their improved crystalline features.



Fig. 3. X-Ray diffraction patterns of Ni /  $I1O_2$  catalyst synthesized by impregnation method ( $\blacktriangle$  NiO,  $\bullet$  TiO<sub>2</sub>).

The average particle size was calculated using Equation 2 is given in Table I.

Catalysts	Ni Loading	Crystalline size
	(wt./wt.)	(nm)
20% Ni/TiO <sub>2</sub>	20/30	7.5
30% Ni/TiO <sub>2</sub>	30/40	6.4
40% Ni/TiO <sub>2</sub>	40/60	6.8

The average particle size of  $Ni/TiO_2$  catalysts was calculated as 6.9 nm. Furthermore, Scherrer calculations prove the nanocrystalline properties of the synthesized catalysts.

# B. Activity Test

The amount of hydrogen generated in the experiments were recorded according to the amount of catalyst and temperature.

# C. Effect of Ru/C Catalyst Quantity on Hydrogen Generation

Hydrogen formation and the reaction time due to the amount of catalyst used is given in Fig. 4.



Fig. 4. Effect of catalyst amount on hydrogen generation (Ru/C, 100 mg NaBH<sub>4</sub>, 5 mL 0.25 M NaOH, 20 °C).

As shown in Fig. 4,  $H_2$  production does not occur at room temperature without the catalyst and reaction time decreases with the catalyst. 100%  $H_2$  yield was achieved at all conditions in varying reaction times, depending on the amount of catalyst.

# D. Effect of Temperature on Hydrogen Generation

Change in  $H_2$  yield with temperature without using a catalyst at the constant reaction time of 45 minutes (Fig. 5).



catalyst, 100 mg NaBH<sub>4</sub>, 5 mL 0.25 M NaOH).

As shown in Fig. 5, hydrogen has started to generate after 40 °C, the highest H<sub>2</sub> yield (38.91%) was obtained at 60 °C. Fig. 6, shows the results of experiments carried out using Ru/C catalyst.



Fig. 6. Effects of reaction temperature on hydrogen generation (50 mg Ru/C, 100 mg NaBH<sub>4</sub>, 5 mL 0.25 M NaOH).

The theoretical amount of H<sub>2</sub> (257 mL) was obtained at three different temperatures. At the temperature of 20 °C, the theoretical amount of hydrogen was reached in 10 minutes and it was reached in almost 2 minutes at 40 and 60 °C (Fig. 6).

#### E. Effect of Ni/TiO<sub>2</sub> Catalyst on Hydrogen Generation

The results of the activity tests with the  $Ni/TiO_2$  catalyst are given in Fig. 7.



Fig. 7. Effect of Ni content in Ni/TiO<sub>2</sub> catalyst on hydrogen generation (60 °C, 100 mg NaBH<sub>4</sub>, 100 mg catalyst, 5 mL 0.25 M NaOH).

According to Fig. 7, when the catalyst containing 20% and 30% Ni was used, maximum yield (85% and 93%, respectively) was reached almost in 45 minutes while 95% yield was achieved in 23 minutes with the 40% Ni loaded catalyst.

#### IV. CONCLUSION

In this study, a parametric study was carried out in the hydrolysis experiments with Ru/C. As a result of the experiments, the increasing amount of catalyst the decreased the reaction period from 22 minutes to 10 minutes. After determining the best amount of catalyst, the temperature parameter was tried and the increasing temperature the decrease the reaction time from 10 minutes to 2 minutes.

Then Ni/TiO<sub>2</sub> catalyst was synthesized by the impregnation method. According to the activity results, the reaction time decreased with the Ni content from 45 minutes to 20 minutes.

While 100%  $H_2$  generation was achieved at 60 °C using Ru/C. The approximate yield (95%  $H_2$  generation) was achieved at the same reaction condition using synthesized Ni/TiO<sub>2</sub> catalyst (40%Ni loaded). Considering the high cost of Ru/C, Ni/TiO<sub>2</sub> is the promising catalyst when the  $H_2$  yield reaches to 100%.

This research can be improved by using a different catalyst synthesis method, active and support material, loading ratio and NaOH concentration.

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