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# Study of the activity of a novel green catalyst used in the production of hydrogen from methanolysis of sodium borohydride

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## ABSTRACT

Biomass is an important energy source because it is easily accessible, contributes to the protection of the environment, and can be easily used in industry. Biomass resources can be classified as plants, vegetable and animal wastes, urban and industrial wastes. Highly active catalysts can be prepared by physical and chemical activation methods. Here, *Microcystis aeruginosa* was used as a biomass source and a metal-free catalyst was synthesized. The production conditions were determined by burning the microsistis modified with 3M H<sub>3</sub>PO<sub>4</sub> at different temperatures (100, 200, 300 and 400 °C) and at different times (30, 45, 60 and 90 minutes). Parameters such as NaBH4 amount, catalyst amount and temperature of the synthesized MA-H<sub>3</sub>PO<sub>4</sub> catalyst that affect methanolization were investigated. In the kinetic calculations, the reaction order was found as n 0.18, activation energy 19.014 kj / mol and initial rate 4998.7 ml H<sub>2</sub>min<sup>-1</sup>g<sub>cat</sub><sup>-1</sup>. The reusability of the MA-H<sub>3</sub>PO<sub>4</sub> catalyst was tested 5 times and its stability determined.

## **1** Introduction

The need for energy used in every field in the world is increasing day by day. The limited reserves of fossil fuels used to meet energy needs in the world have increased the tendency towards alternative energy sources [1]. In addition, fossil fuels are not economically, ecologically and environmentally sustainable. This is an additional disadvantage of these fuels being limited [2]. Carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) emissions from the use of fossil fuels are among the main causes of global warming. Carbon dioxide emitted from many combustion sources, especially fossil fuels, provides a significant increase in greenhouse gas emissions [3,5]. In order to reduce these negative effects, it is important to find a sustainable, renewable and environmentally friendly energy source. [2]. Hydrogen, one of the alternative clean energy sources, has attracted the attention of researchers for the last decade [6]. The importance of reliability and lightness in the storage of hydrogen is highlighted by the storage of hydrogen in the hydride structure. In addition to being stable and safe NaBH<sub>4</sub>, in the long term it can be used easily in the dry and moisture free short term in aqueous form, making it ahead of other hydride compounds. The sodium boron hydride compound among the hydrides is used in studies because it contains more unit volume of hydrogen atoms than the others. Sodium borohydride, which contains 10,60% hydrogen in its

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structure, is a good hydrogen storage [7]. There are many studies in the literature to produce hydrogen from sodium borohydride [8, 12]. In addition, fuel cell issues have also been studied in the literature, apart from hydrogen production from sodium boron hydride [13, 18]

By methanolysis of NaBH<sub>4</sub> at room temperature, only a small percentage of the amount of H<sub>2</sub> expected to be obtained in theory can be obtained. However, the rate of methanolysis is increased by using a catalyst. For this reason, the reactions must be carried out in the presence of catalyst in order to quickly obtain all of the hydrogen in sodium borohydride. A catalyst must be developed for selective and efficient methanolysis. Catalyst development and utilization in the methanolysis of NaBH<sub>4</sub> is necessary to overcome the heat transfer limitations for this powerful endothermic hydrolysis reaction [4, 5, 20]. Researchers have drawn attention to the synthesis of cheaper catalysts by applying different methods such as the combination of support materials and 2–3 nonnoble metals in hydrogen production [23, 26].

Half of the hydrogen gas produced according to the reaction given in Equation (1) is obtained from sodium borohydride and the other half from methanol. Methanolysis reaction is preferred in the production of hydrogen from sodium borohydride. Because methanolysis occurs faster than hydrolysis reaction [20,21].

$$NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2$$
(1)

In this study, it was aimed to investigate the methanolysis performance of sodium borohydride in the presence of a sustainable and environmentally friendly metal-free catalyst. In addition, this study proposes that the use of organic materials that are abundant in nature, such as *Microcystis aeruginosa*, can be used directly as catalyst materials without the addition of any precious metals (Pt and Ru) and support materials to produce a highly efficient catalyst. Microalgae are preferred because of their simple development, use of CO<sub>2</sub> gas released into the atmosphere as a nutrient and have a faster growth rate than plants [22]. *Microcystis aeruginosa* strain was used as microalgae in this paper.

#### 2. Meterial and methods

The Microcystis aeruginosa was collected as described in the literature and dried for experiments [20]. Catalyst synthesis from the Microcystis aeruginosa was carried out in two steps. In the first step, the Microcystis strain was treated with 3M H<sub>3</sub>PO<sub>4</sub> acid. Chemical activation was achieved by keeping the sample treated with acid for 1 day at 80 °C. Then, the sample was washed with distilled water and dried, and the second activation process was performed. The second stage activation process was carried out using the carbonization method. The sample treated with acid was burned in an ash furnace at different temperatures (100, 200, 300 and 400 °C) and at different times (30, 45, 60 and 90 min) and carbonization process was carried out. The resulting catalyst was named MA-H<sub>3</sub>PO<sub>4</sub>.The hydrogen gas released during the methanolysis reaction was read from a measure by setting a water trap. The volume of hydrogen released over time was recorded. The production scheme of the catalyst and the setup used in the experiment are given in Figure 1 (a, b). After determining the optimum combustion time and temperature, parameters affecting methanolysis were investigated.



**Figure 1.** *a)* Furnace system scheme for catalyst preparation, b)hydrogen gas measurement scheme [4,14]

#### 3. Results

#### 3.4. Burning Temperature Effect

In order to examine the effect of burning temperature on methanolysis reaction, methanolysis reaction was carried out by adding 100 mg MA-H<sub>3</sub>PO<sub>4</sub> catalyst, which was burned at different temperatures for 45 minutes, to the solution medium consisting of 2.5% NaBH<sub>4</sub> and 10 ml of methanol at 30 °C. The time-dependent hydrogen production graph of the burning temperature is given in Figure 2. As seen in the figure, while the combustion temperature was increased from 100 °C to 400 °C, the burning time was set as 45 minutes. The modified MA-H<sub>3</sub>PO<sub>4</sub> catalyst, which was burned at 300 ° C for 45 minutes, completed the methanolysis reaction in the shortest time.



Figure 2. Time dependent hydrogen production graph of burning temperature (30 °C, 2.5% NaBH4, 10 ml methanol and 0.1 g catalyst)

## 3.5. Burning Time Effect

After determining the burning temperature, the effect of burning time on methanolysis reaction was investigated. The methanolysis reactions of the modified MA-H<sub>3</sub>PO<sub>4</sub> catalyst fired at 300 ° C for different times under the same conditions (2.5% NaBH<sub>4</sub>, 10 ml methanol, 0.1 g catalyst, 30 °C) are given in Figure 3. Figure 3 shows the time dependent hydrogen production graph in the presence of MA-H<sub>3</sub>PO<sub>4</sub> catalyst. As can be seen in the figure, the methanolysis reaction was completed in the shortest time in the presence of the catalyst with a burning time of 45 minutes.



**Figure 3.** *Time dependent hydrogen production graph of burning time (30 °C, 2.5% NaBH*<sub>4</sub>, 10 ml methanol and 0.1 g catalyst)

#### 3.6. Catalyst Amount Effect

Experiments were carried out to examine the effect of the amount of catalyst on the methanolysis reaction. The methanolysis reaction was carried out at  $30 \degree C$  in the presence of % 2.5 NaBH<sub>4</sub>, 10 ml methanol and different amounts of MA-H<sub>3</sub>PO<sub>4</sub> catalyst. Figure 4 shows the time dependent hydrogen production graph in the presence of MA-H<sub>3</sub>PO<sub>4</sub> catalyst. As can be seen in the figure, as the amount of catalyst increases, the completion time of the methanolysis reaction decreases. While the catalyst amount is 0.05 g, the methanolysis reaction is completed in 3.75 minutes, when the amount is increased to 0.25 g, the methanolysis reaction is completed in 1.5 minutes.



**Figure 4.** *Hydrogen production graph with time of catalyst amount effect (30 °C, %2.5 NaBH*<sub>4</sub> *and 10 ml methanol)* 

#### 3.7. NaBH<sub>4</sub> Concentration Effect

In order to examine the effect of the amount of NaBH<sub>4</sub> on the hydrogen production rate, experiments were carried out at 30  $^{\circ}$ C, in the presence of 10 ml of methanol, 0.1 g of MA-H<sub>3</sub>PO<sub>4</sub>

catalyst and different concentrations of NaBH<sub>4</sub> (1%,2.5%, 5% and 7.5% by weight). Figure 5 shows the time dependent hydrogen production graph in the presence of MA-H<sub>3</sub>PO<sub>4</sub> catalyst. As the amount of NaBH<sub>4</sub> increases in the methanolysis reaction environment, the hydrogen production rate is expected to increase. As seen in the figure, as the amount of NaBH<sub>4</sub> increases, the rate of hydrogen production increases. Consequently, the completion time of the reaction without methanol increases.



**Figure 5.** Hydrogen production graph with time of NaBH<sub>4</sub> amount effect (30 °C, 0.1 g catalyst and 10 ml methanol)

## 3.8. Temperature Effect

Experiments were carried out in the presence of 2.5% NaBH<sub>4</sub>, 10 ml methanol and 0.1 g MA-H<sub>3</sub>PO<sub>4</sub> catalyst at different temperatures (30-60 °C) to investigate the effect of temperature on the methanolysis reaction. Figure 6 shows the time dependent hydrogen production graph in the presence of MA-H<sub>3</sub>PO<sub>4</sub> catalyst. As seen in the figure, as the temperature increases, the reaction completion time decreases. Because as the temperature increases, the number of collisions between molecules increases and the kinetic energy of the molecules also increases. Consequently, the reaction rate increases and the reaction completion time decreases. As seen in the figure, when the temperature is increased from 30 °C to 60 °C, the completion time of the methanolysis reaction decreases from 2.5 minutes to 1.3 minutes.



**Figure 6.** Hydrogen production graph with time of temperature effect (2.5 % NaBH<sub>4</sub>, 0.1 g catalyst and 10 ml methanol)

## 3.9. Finding the constant k at different temperature values

Considering that the hydrolysis reactions occurring at different temperature values in order to determine the reaction rate constant (k) take place at the nth degree;

$$\begin{array}{l} -r_A = k^* C_A{}^n \tag{2} \\ dC_A/dt = -r_A \tag{3} \end{array}$$

Equation 1 and Equation 2 are combined If  $t_0 = 0$ ,  $t_1 = t$  and  $C_{A0}$  are integrated in  $C_A$  boundary conditions, the following equation is obtained.

$$(1/n-1)^{*}(1/C_{A^{n-1}}) = k^{*}t + (1/n-1)^{*}(1/C_{A0^{n-1}})$$
(4)

The term graph on the left side of Equation 4 against time is plotted and the value k is calculated from the slope of the obtained line. These graphs are drawn for each temperature at which the hydrolysis reaction takes place. With the trial and error method [8, 9], the reaction order was determined by taking the value that gives the highest regression coefficient n. Calculated reaction rate constant values of hydrolysis reaction at different temperatures are given in Table 1.The reaction order was found as n = 0.18 by trial and error method.

#### 3.10. Calculation of activation energy;

Arhenius equation;

$$k = A^* e^{-E/RT} \tag{5}$$

If ln of both sides of equation 5 is taken, equation 6 is obtained:

$$lnk = lnA - E/RT \tag{6}$$

The values calculated at different temperatures with the help of Equation 6 are given in Table 1. If the lnk versus 1 / T graph is drawn using the values given in the calculated table 1, the slope gives the activation energy and the graph in Figure 7 is obtained. The E / R value is found from the slope of this graph.

Table 1. Calculated k values at different temperatures

T (°C)	k	1/T	Lnk
30	0.43731	0.0033	-0.82711
40	0.5349	0.003195	-0.62568
50	0.6598	0.003096	-0.41582
60	0.8699	0.003003	-0.13938



Figure 7. Lnk- 1 / T Arrhenius plot of MA-H<sub>3</sub>PO<sub>4</sub> catalyst

In the calculations made, the activation energy of the MA- $H_3PO_4$  catalyst was calculated as 19,014 kj / mol. In optimum conditions, the initial rate of the MA- $H_3PO_4$  catalyst was calculated as 4998.1 ml  $H_2 \min^{-1}g_{cat}^{-1}$ .

## 3.11. Reusability of MA-H<sub>3</sub>PO<sub>4</sub> Catalyst in Methanolysis Reaction

Reusability experiments were performed in the presence of 30 °C, 10 ml methanol, 2.5% NaBH<sub>4</sub> solution and 0.1 g MA- $H_3PO_4$  catalyst. In Figure 8 obtained as a result of the experiments, a time dependent hydrogen production graph is given. As seen in the figure, when the catalyst is used repeatedly, the completion time of the methanolysis reaction increases. The reason for this behavior is thought to be due to the fact that NaBO2 formed in the environment during methanolysis was not completely cleaned and blocked active surfaces. [27]. It is also due to the reduced amount of catalyst when the catalyst is washed for reuse. Despite all these negativities, when MA-H<sub>3</sub>PO<sub>4</sub> was used even for the 5th time, methanolysis reaction completed its conversion 100%. This shows the stability of the catalyst.



Figure 8. Reusability graph of MA-H<sub>3</sub>PO<sub>4</sub> catalys

## 4. Conclussions

Hydrogen energy, which can be an alternative to fossil fuels and environmentally friendly energy solutions, is shown among the most suitable renewable energy sources. This work aims to produce a stable and environmentally friendly catalyst to be used in hydrogen production. Microcystis aeruginosa strain was used as a biomass source. After the microcystic was modified with acid, it was transformed into a catalyst using the carbonization method. In experiments, it has been found that optimum conditions for carbonization are 300 °C and 45 minutes. Parameters affecting methanolysis were examined. In the kinetic calculations, the reaction order was found as 0.18, the activation energy as 19.014 kj / mol and the initial rate as 4998.7 ml H<sub>2</sub> min<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>. The reusability was tested 5 times to determine the stability of the catalyst. Although MA-H<sub>3</sub>PO<sub>4</sub> was used 5 times, it continued its catalytic activity. In Table 2, activation energies and initial speeds of some organic wastes or biomass-based and metal contaning catalysts in the literature are given. As seen in the table, MA-H<sub>3</sub>PO<sub>4</sub> catalyst showed better activity than metal-containing catalysts.

**Table 2.** Comparison of activation energies and initial rate of catalysts in the literature

Catalyst	İnitial Rate (ml H2min <sup>-</sup> <sup>1</sup> g <sub>cat</sub> <sup>-1</sup> )	Activation Energy (kj/mol)	Reference
DSCG-CH <sub>3</sub> COOH	3171.4	25.23	[5]
PC-PEI <sup>+</sup>	4040	23.82	[28]
Co-Fe-B (Water)	1300	31	[29]
CVMS-H <sub>3</sub> PO <sub>4</sub> _CuB	6500	23.79	[30]
Co-P/CNTs-Ni foam	2430	49.94	[31]
Co/Al <sub>2</sub> O <sub>3</sub>	4400	21.9	[32]
MA-H <sub>3</sub> PO <sub>4</sub>	4998.7	19.014	This study

In conclusion, using biomass-based catalyst for hydrogen production from sodium borohydride is important for the environment and sustainable energy. In addition, the production of catalysts from biomass is both environmentally friendly and economical. Microsystis microalgae was used as a biomass source in this study. An environmentally friendly catalyst has been developed using microalgae. The catalyst obtained as a result of the activation processes showed higher catalytic activity than many catalysts in the literature.

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