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Research Article

Investigation of Hydrogen Production from Sodium Borohydride Methanolysis in the Presence of Al_2O_3/*Spirulina Platensis* Supported Co Catalyst

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Abstract

In this study, Al_2O_3/*Spirulina Platensis* mixture was used for the first as support material. The aim is to demonstrate that microalgae can be used as a new, economic and environmental support agent to increase the efficiency of the catalysts that will be eventually used in the production of hydrogen. The strain was grown by preparing the culture medium containing all the necessary nutrients as described in the literature. To synthesize the catalyst for the production of hydrogen through methanolysis of sodium borohydride ($NaBH_4$), phosphoric acid (3M H_3PO_4) was used as the protonation agent for the selected strain. After achieving sufficient density, the strain was dried and mixed with Al_2O_3 in the ratio of 1/1. Modified Al_2O_3/*S. Platensis* mixture was finally blended with cobalt ions and the mixture was burned. As a result of this procedure Al_2O_3/*S. Platensis* supported Co catalyst was produced. The catalyst was prepared with the addition of different Co^{2+} metal concentrations, 10%, 20%, 30%, and 40% respectively. In the present study, the experiments were generally carried out with 10 ml methanol solution containing in 0.025 g $NaBH_4$ with 0.1 g catalyst at 30 °C. The hydrogen obtained in experimental studies was determined volumetric in the gas measurement system. Here, different $NaBH_4$ concentrations, catalyst amount and different temperature effects were investigated. The effect of the amount of $NaBH_4$ was investigated with 1%, 2.5%, 5%, and 7.5% ratio of $NaBH_4$ while the influence of the concentration of catalyst was carried out 0.05, 0.1, 0.15, and 0.25 g catalysts. To investigate the performance of the catalyst on hydrogen production with $NaBH_4$ methanolysis under different temperatures, 30, 40, 50 ve 60 °C, relatively. The experiments by using Al_2O_3/*S. Platensis* supported Co Catalyst reveal that the best metal ratio was 10% Co^{2+}. In addition, the maximum hydrogen production rate through methanolysis reaction of $NaBH_4$ by this catalyst was found to be 5747.1 $mLmin^{-1}gcat^{-1}$. Also, the activation energy was determined to be 34.67 kJ mol^{-1}. Moreover, different $NaBH_4$ concentrations, catalyst amounts and temperature studies of the fabricated catalyst were carried and it was discovered that there was no decline in the % of conversion for the synthesized catalyst.

Keywords: Sodium Borohydride; Al_2O_3/*S. Platensis* supported catalyst; Cobalt; Methanolysis

Al_2O_3/*Spirulina Platensis* Destekli Co Katalizörü Varlığında Sodyum Borhidrürün Metanolizinden Hidrojen Üretiminin İncelenmesi

Öz

Bu çalışmada, Al_2O_3/*Spirulina Platensis* mikroalg karışımı ilk kez destek maddesi olarak kullanılmıştır. Buradaki amaç yenilenebilir enerji kaynağı olan hidrojenin üretiminde kullanılan katalizörlerin etkinliğini arttıracak yeni, ekonomik ve çevreci destek maddesi olarak mikroalgin kullanılabileceğini ortaya koymaktır. Al_2O_3/*S. Platensis* destekli Co katalizörü hazırlanırken kullanılacak olan mikroalg (*Spirulina Platensis*) türü literatürde belirtilen kültür ortamı hazırlanarak büyütülmüştür. Sodyum borhidrürün ($NaBH_4$)

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metanoliz reaksiyonundan hidrojen üretimi için katalizör destek maddesi olarak kullanılacak *S. Platensis* mikroalginin protonlanması için fosforik asit (3M H_3PO_4) kullanılmıştır. Daha sonra mikroalg, Al_2O_3 ile 1;1 oranında karıştırılarak destek maddesi olarak hazır hale getirilmiştir. Bu modifiye edilmiş Al_2O_3/*S. Platensis* karışımı destek maddesi, kobalt iyonları ile yakıldıktan sonra indirgenmiş ve Al_2O_3/*S. Platensis* destekli Co katalizörü elde edilmiştir. Al_2O_3/*S. Platensis* destekli katalizöre Co^{2+} metali ilavesi %10, %20, %30 ve %40 oranında eklenerek katalizör sentezi gerçekleştirilmiştir. Bu çalışmada, genel olarak deneyler 30 °C'de 0,025 g $NaBH_4$ içeren 10 mL'lik metanol çözeltisinde 0,1 g katalizör varlığında bozundurularak zamana bağlı hidrojen miktarları ölçülmüştür. Deneysel çalışmalarda elde edilen hidrojen, gaz ölçüm sisteminde hacimsel olarak belirlenmiştir. Yapılan deneylerde farklı $NaBH_4$ konsantrasyonları, katalizör miktarı ve farklı sıcaklık etkileri incelenmiştir. Deneylerde $NaBH_4$ miktarı incelenirken %1, %2.5, %5, ve %7.5 oranında $NaBH_4$ kullanılmış, katalizör miktarı etkinliği incelenirken ise sırasıyla 0.05, 0.1, 0.15, ve 0.25 g katalizör denenmiştir. Al_2O_3/*S. Platensis* destekli Co katalizörü varlığında $NaBH_4$ metanolizi ile hidrojen üretiminde, sıcaklık etkisini araştırmak için 30, 40, 50 ve 60 °C olmak üzere dört farklı sıcaklık deneyi yapılmıştır. Al_2O_3/*S. Platensis* destekli Co katalizörü kullanılarak gerçekleştirilen deneylerde en iyi metal oranının %10 Co^{2+} olduğu belirlenmiştir. Bunun yanı sıra $NaBH_4$'ün metanoliz reaksiyonundan elde edilen maksimum hidrojen üretim hızı 5747,1 $mLdak^{-1}gkat^{-1}$ ve katalizörün aktivasyon enerjisi 34.67 kJ mol^{-1} olarak belirlenmiştir. Aynı zamanda, üretilen katalizörünün yapılan farklı $NaBH_4$ konsantrasyonları, katalizör miktarları ve sıcaklık deneyleri için $NaBH_4$ dönüşüm %'sinde azalma olmadığı belirlenmiştir.

Anahtar Kelimeler: Sodyum Borhidrür, Al_2O_3/*Spirulina Platensis* Destekli Katalizör, Kobalt, Metanoliz

1. Introduction

Combustion of hydrocarbon-containing fossil fuels cause toxic waste such as unburned hydrocarbon, odor, CO and CO_2 which emits environmental impact and disrupts the ecological balance by creating environmental pollution. Therefore, finding and commercializing a long-term sustainable and environmentally friendly energy source becomes inevitable. In this sense, hydrogen, which is one of the alternative clean energy sources that will overcome environmental and energy problems in the future, gets increasing attention. Consequently, new technologies are being developed by making researches about its use as clean energy [1]. Hydrogen energy is produced from the conversion of chemical energy into electrical energy that is stored within H-H bonds. Consequently, it is an ideal fuel for PEM (Proton Exchange Membrane) fuel cells. Additionally, water or water vapor are the two main by-products of hydrogen burning reaction with oxygen. Therefore, it has no negative impacts on the environment unlike fossil fuels. However, one of the main problems with the use of H_2 gas as fuel is the insufficiency of storage efficiency [2]. The desired priority features in hydrogen fueled vehicles are safe production, transportation and storage of sufficient amount of H_2 gas. Therefore, sodium boron hydrides having high hydrogen gas storage capacity are very important in terms of hydrogen storage. According to the reaction given in Equation 1, half of the hydrogen gas produced is obtained from sodium borohydride and the other half is from methanol and methanolysis is important in terms of reacting faster than hydrolysis.

$$\boldsymbol{NaBH_4 + 4CH_3OH \rightarrow NaB(OCH_3)_4 + 4H_2} \quad (1)$$

However, there are several drawbacks encountered in the methanolysis of sodium borohydride [3-5]. Sodium borohydride degradation reactions are kinetically zero and the catalyst controls the rate of hydrogen production. However, use of catalyst containing precious metals such as Pt and Ru are not preferred due to being expensive. Therefore, attention has been drawn to synthesizing cheaper catalysts by applying different methods. This kind of studies are also very important for our country which has the richest boron mine in the world [6-10]. The activity of the catalyst is interrelated with its particle size and dispersion degree. One of the main potential route to optimize the particle size and dispersion degree is the use of support material. Several supporting material have been suggested in the literature such as SiO_2, carbon, nanotubes, activated carbon and Ni foam. However, these support material needs to be fabricated synthetically which increases the overall cost. Alternatively, biological materials can be utilized as support material to produce highly efficient catalysis which will eventually decreases the overall cost due to being abundant in the nature. In this study, Al_2O_3/*S. Platensis* supported Co catalyst was synthesized using Co^{2+} metal which relatively cheaper compare to precious metals. In the presence of this catalyst, $NaBH_4$ methanolysis experiments were examined for different sodium borohydride, different catalyst amounts and different temperatures. As a result of the obtained data, the results were evaluated, and kinetic parameters were determined.

2. Material and Method

The microalgae (*Spirulina Platensis*) strain, which was used when preparing Al_2O_3/Spirulina Platensis supported Co catalyst, was grown as shown in Figure 1 by preparing the culture medium containing all the necessary nutrients as given in Bekirogullari et al. [1]. The microalgae biomass was precipitated by centrifugation at 4000 rpm, washed with purified water and placed in oven at 80 °C to dry. Then, 20 g of *Spirulina Platensis* was blended with 100 mL of 3M H_3PO_4 and placed in an oven at 75 °C for 24 hours and microalgae biomass was made ready for use. It was then mixed with Al_2O_3 by taking 1: 1 ratio of *Spirulina Platensis* and adding 10%, 20%, 30%, 40% $CoCl_2.6H_2O$, respectively. These mixtures were dissolved in 25 mL of water were first stirred with a speed of 200 rpm at 80 °C and then allowed to dry in an oven at 105 °C for 2 hours. These dried samples were then burned at 300 °C for 2 hours in the furnace apparatus shown in Figure 2a.

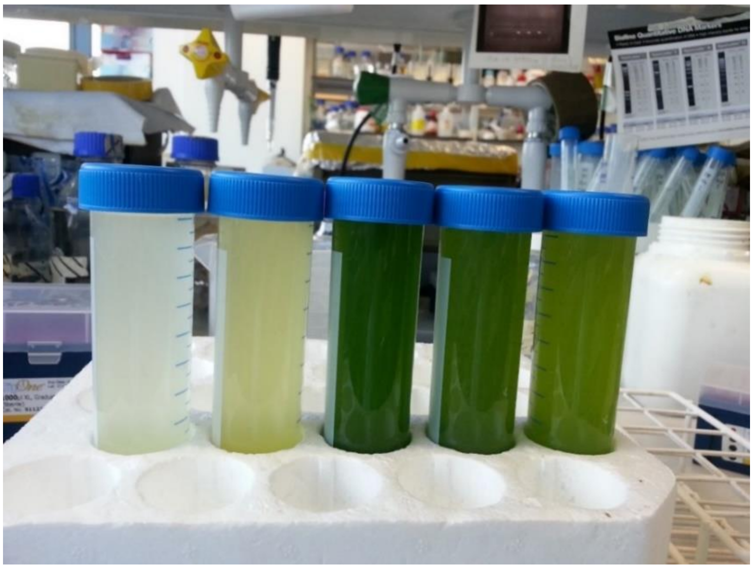

Fig 1. Cultivation of Microalgae Strain (*Spirulina Platensis*)

The prepared samples were dispersed with 20 mL of water and reduced by mixing with 5% 20 mL $NaBH_4$ solution in the presence of nitrogen gas. After reduction, Al_2O_3/*Spirulina Platensis* supported Co catalyst was filtered by vacuum pump and washed 3 times with deionized water and allowed to dry in an oven at 120 ° C in inert atmosphere for 2 hours. Finally, it was stored in an enclosed environment to prevent oxidation of the Al_2O_3/*Spirulina Platensis* supported Co catalyst. The system used for gas measurement in experimental studies is given in Figure 2b. The system consists of a reaction vessel, a gas collector and a thermostat used for temperature control. The amount of hydrogen gas obtained from the reaction in this system was recorded and plotted graphically.

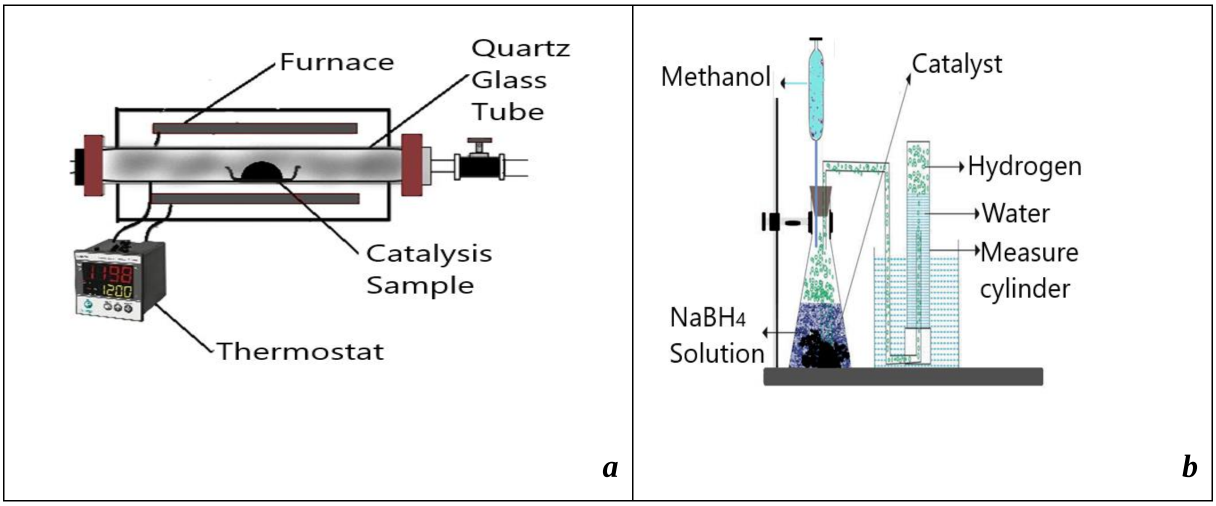

Fig 2. Furnace System Scheme for Catalyst Preparation ***(a)*** Hydrogen Gas Measurement Scheme ***(b)***

3. Results and Discussion

3.1 Investigation of Metal Effect (Co^{2+})

In this study, experiments were carried out in the presence of 0.1 g of catalyst in 10 mL methanol solution containing 0.025 g $NaBH_4$ at 30 °C. Fig 3 shows the activity of Al_2O_3/*Spirulina Platensis* supported Co catalyst containing 30% Co^{2+} and pure Al_2O_3 catalysts containing 30% $Co^{2+.}$ As can be seen from Figure 3, the Al_2O_3/Spirulina Platensis supported Co catalyst yielded better than the catalyst synthesized using pure Al_2O_3. While the Al_2O_3/*Spirulina Platensis* (1:1) supported Co catalyst reduces the solution with the same concentration in about 13 minutes, the reaction completion time of the catalyst containing the pure Al_2O_3 appears to be about 24 minutes. According to these results, *Spirulina Platensis* microalgae strain contributed positively to Al_2O_3 supported Co catalyst. The results of metal addition (%10, %20, %30, %40) to Al_2O_3/*Spirulina Platensis* supported catalyst are given in Fig 4.

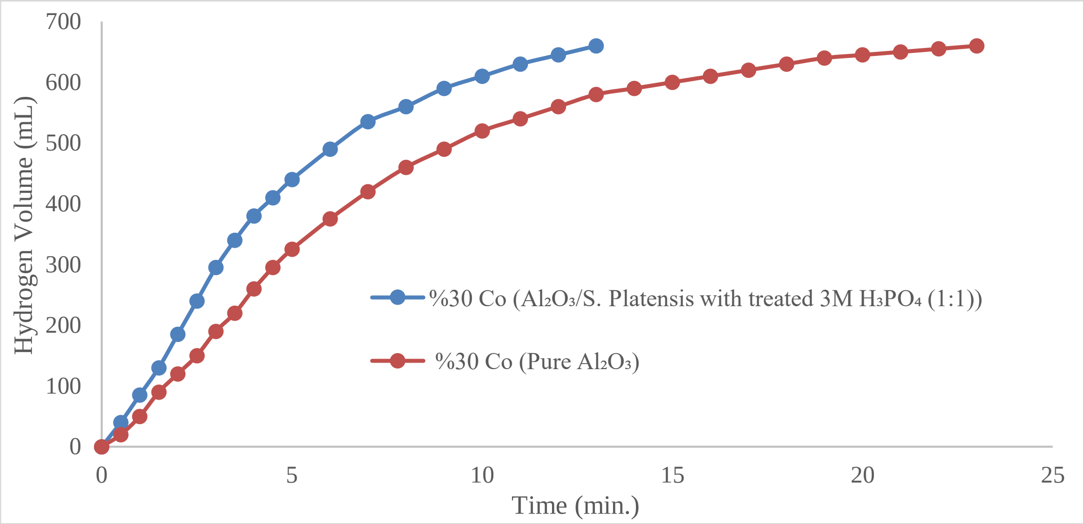

Fig 3. The variation of hydrogen production rate with time in methanol solvent medium (% 2,5 $NaBH_4$, w_{cat}=0,1 g, T=30 ºC, Vsolution=10 mL

As can be seen from Fig 4, increasing Co metal ratios addition to Al_2O_3/*Spirulina Platensis* supported catalyst had a negative effect on the rate of hydrogen production. The best result for the Al_2O_3/*Spirulina Platensis* supported catalyst was the catalyst containing 10% cobalt. The reaction completion time for this catalyst was approximately 11 minutes. On the other hand, with the effect of increasing metal ratios, it is seen that the reaction completion time is about 17 minutes for the catalyst containing 40% Co. As can be seen, the best metal ratio in Al_2O_3/*Spirulina Platensis* supported Co catalyst is %10 Co^{2+}.

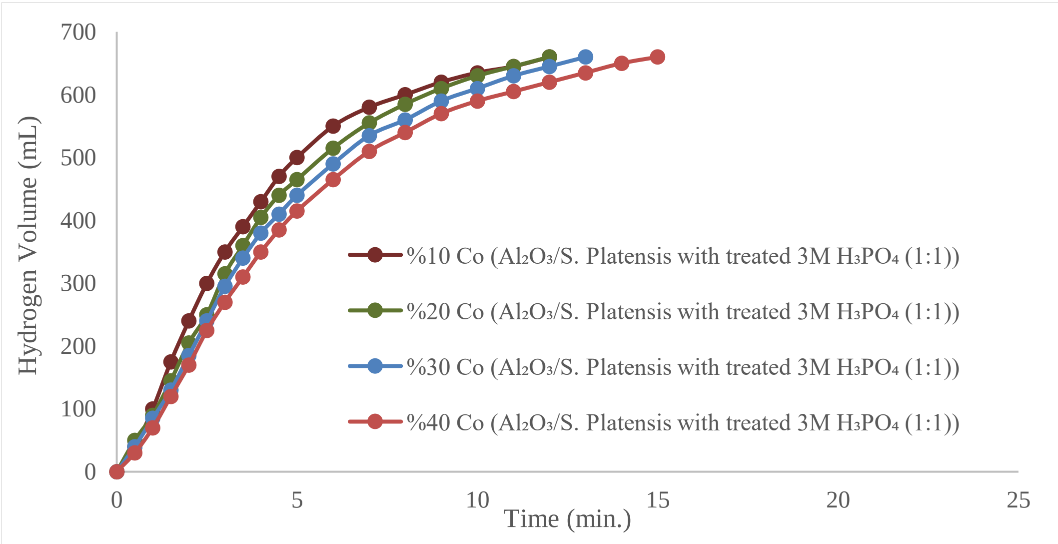

Fig 4. Variation of the hydrogen production rate over time in different solvent media (% 2,5 $NaBH_4$, w_{cat}=0,1 g, T=30 ºC, Vsolution=10 mL) .

3.2 Catalyst Amount Effect

The rate of hydrogen from sodium boron hydride depends on the catalyst that will be used. In another word, it essentially depends on the amount of catalyst used, as well as the catalyst type. Therefore, the effect of different catalyst amounts on $NaBH_4$ solution was investigated in the second stage of this study. When the catalyst activity was examined, different amounts of catalyst were used under the same temperature and in the presence of the same $NaBH_4$ concentration. The change in the amount of hydrogen production over time is plotted in Fig 5.

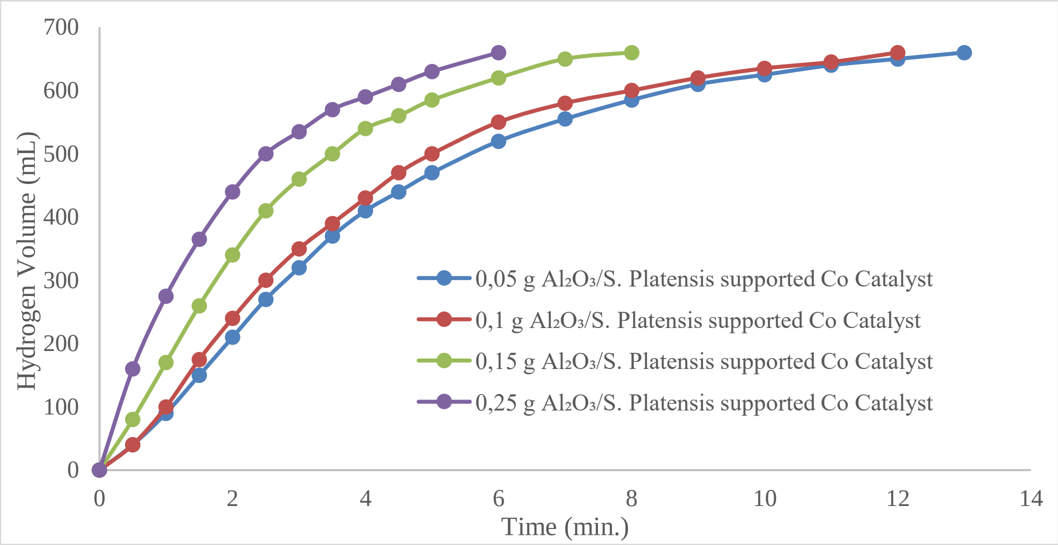

Fig 5. The effect of different amounts of Al_2O_3/*Spirulina Platensis* supported Co catalyst on the degradation of sodium borohydride (% 2,5 $NaBH_4$, T=30 ºC, Vsolution=10 mL)

As can be seen in Fig. 5, increasing the amount of catalyst, generally increases the rate of hydrogen production. Hydrogen production rate increase is due to the increase in the active areas of the catalyst in proportion to the amount of catalyst. With the increase in the amount of catalyst used, the reaction time of sodium borohydride is reduced and the rate of hydrogen production increases. In Fig 5, the experiment performed using 0.25 g of catalyst in the same sodium borohydride concentration solution was completed in about 6 minutes, while the experiment performed using 0.05 g of catalyst was completed in 13 minutes. The reaction times of other used catalysts (0.1g and 0.15g) ends in 12 minutes and 8 minutes, respectively. Thus, it is possible to say that this reaction is a catalyst-controlled reaction and the speed increases depending on the amount of catalyst.

3.3 Effect of $NaBH_4$ Amount

The effect of Al_2O_3/*Spirulina Platensis* supported Co catalyst on different $NaBH_4$ concentrations was investigated and the results are shown in Fig 6. As can be seen in Fig 6, the reaction rate increases with increasing $NaBH_4$ concentration. In the reaction of 7.5% of the $NaBH_4$ solution, it is seen that the amount of hydrogen produced increases as well as the increase of the reaction rate. In another $NaBH_4$ solution, which have a lower concentration, the rate of hydrogen production decreases proportionally and it is observed that the amount of hydrogen obtained depending on the concentration also decreases. Thus, in experiments carried out using constant temperature and constant catalyst amount, the hydrogen production rate and the amount of hydrogen obtained are generally reduced in the presence of different amounts of sodium borohydride.

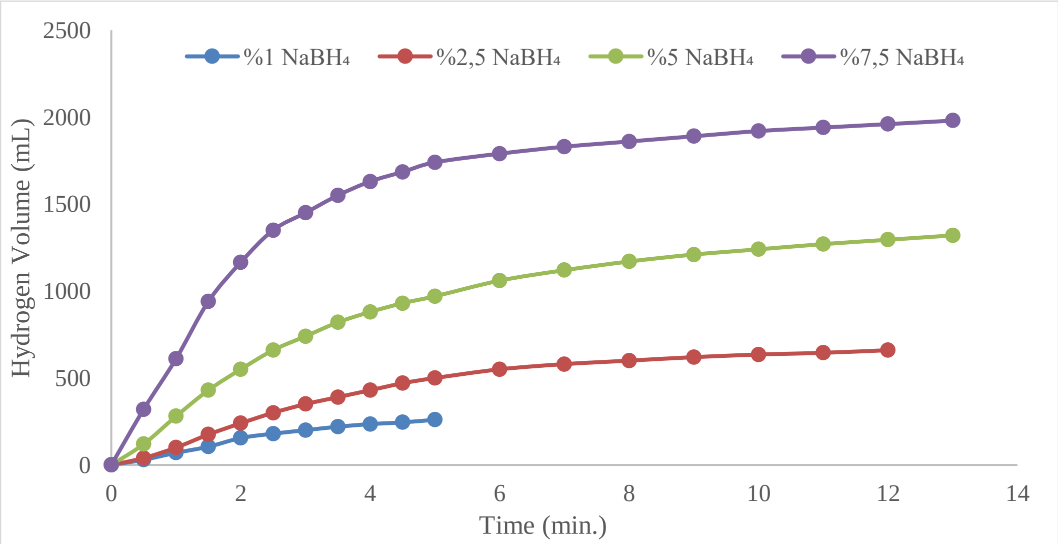

Fig 6. Investigation of the effect of different sodium boron hydride concentrations on the hydrogen production rate in the presence of Al_2O_3/*Spirulina Platensis* supported Co catalysts (w_{cat}=0,1 g, T=30 ºC, Vsolution=10 mL)

3.4 Temperature Effect

In order to reveal the influence of temperature on hydrogen production from $NaBH_4$ methanolysis reaction catalyzed by Al_2O_3/*S. Platensis* supported Co catalyst, temperature experiments were performed at four different temperatures (30, 40, 50 and 60 °C). 0.1 g Al_2O_3/*S. Platensis* supported Co catalyst (10% Co) and 2.5% $NaBH_4$ were used to carry out temperature experiments. The temperature experiments results containing both the hydrogen volume and the reaction rates are plotted in Fig 7, while the 1/T graph versus lnK is shown in Fig 8. As shown in Fig 7, increasing the temperature from 30 to 60 °C decreases the completion time of the reaction while increasing the produced hydrogen volume. It was found that the time that is required to complete the reaction at the aforementioned temperatures are 5, 12, 12.7 and 13 minutes, respectively. In the meantime, at the specified temperatures the maximum hydrogen production rates were determined as 1309.9, 2246, 3231.6 and 5747.1 mL $min^{-1}g.cat^{-1}$, respectively. Arrhenius equation was applied to determine the activation energy of $NaBH_4$ methanolysis catalyzed by Al_2O_3/*S. Platensis* supported Co catalyst:

$$lnk = lnA - \frac{Ea}{RT} \quad (2)$$

here k is the reaction rate constant, A is the reaction constant, Ea is the activation energy (kJ/mol), T is the temperature (K) and R is the ideal gas constant. The lnk versus 1/T plot for the methanolysis reaction is linear. The activation energy was found by reading the slope of the straight line, 34,67 kJ mol^{-1}. As can be seen Al_2O_3/*S. Platensis* supported Co catalyst has low activation energy. These results clearly emphasize the superiority of Al_2O_3/*S. Platensis*-supported Co catalyst used in the production of hydrogen by $NaBH_4$ methanolysis.

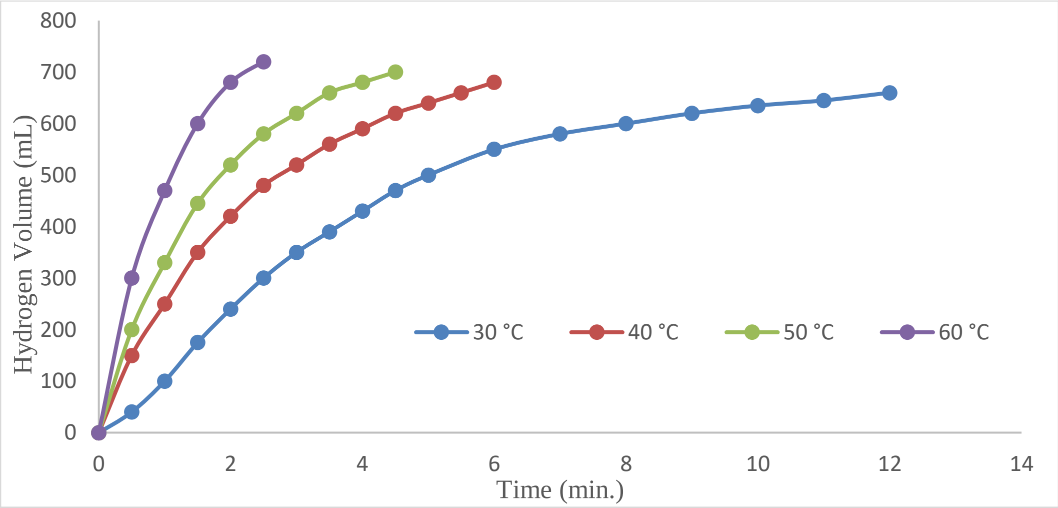

Fig 7. Variation of methanolysis in the presence of Al_2O_3/*Spirulina Platensis* supported Co catalyst in sodium boron hydride solution at different temperatures (w_{cat}=0,1 g, %0.25 $NaBH_4$, Vsolution=10 mL)

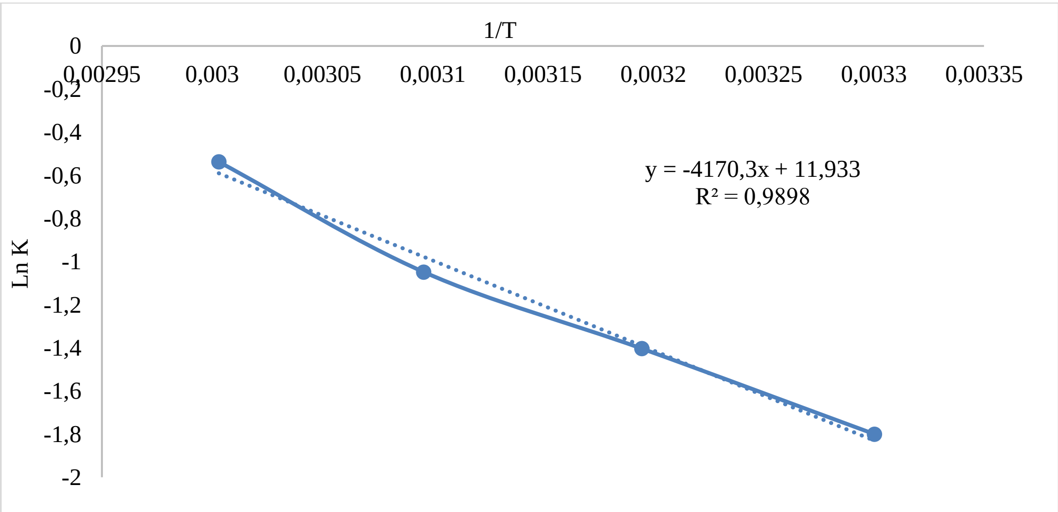

Fig 8. Kinetic graph of Al_2O_3/*Spirulina Platensis* supported Co catalyst (w_{cat}=0,1 g, %0.25 $NaBH_4$, Vsolution=10 mL)

Table 1 present maximum hydrogen production rates and activation energies obtained from cobalt containing catalysts with different supported materials. As can be seen from the table use of biological material as support materials can significantly improve the hydrogen production rate. These results point out the importance of use of abundant biological resources as support material.

Table 1. The maximum hydrogen production rates and activation energies of $NaBH_4$ methanolysis by catalysts obtained using different support materials in the literature

Catalyst	**Maximum hydrogen production rate ($mLmin^{-1}gcat^{-1}$)**	**Activation energy ($kjmol^{-1}$)**	**References**
Co-B/tSepiolite	424.3		[11]
Co-CFC catalyst	1119		[12]
Co-P/CNTs-Ni foam	2430	49.94	[13]
Ru5Co/C	2586	23.82	[14]
Co/Al2O3	4400	21.9	[15]
Co-B catalyst supported on C. Vulgaris microalgal strain treated with HCl	13215	25.22	[1]
Al_2O_3/*Spirulina Platensis* supported Co catalyst	5747.1	34.67	**This study**

4. Conclusions and Recommendations

Hydrogen energy is one of the most important renewable and environmentally friendly energy solutions that has been proposed to replace the fossil fuels. Currently, hydrogen production is still under development due to its storage, production cost and more environmentally friendly production methods. This study aims to produce a more stable and environmentally friendly catalyst that will be used in the production of hydrogen energy. In the present study, in order to produce hydrogen through methanolysis reaction of $NaBH_4$, Al_2O_3/*Spirulina Platensis* supported Co catalysts was fabricated. To synthesize the catalyst for the production of hydrogen through methanolysis of sodium borohydride ($NaBH_4$), phosphoric acid (3M H_3PO_4) was used as the protonation agent for the selected strain. Different concentrations of Co ions (10% to 40%) were used to define most efficient catalyst with optimal Co ions and the optimal Co concentrations was found to be 10%. In order to analyze the efficiency of the produced catalyst, experiments with different $NaBH_4$ concentrations, catalyst amount and different temperature were carried out. The maximum production rate for the produced catalysts was found to be 5747,1 mL $min^{-1}gcat^{-1}$. In every usage the synthesized catalyzed showed a moderately decent performance by producing nearly same amount of hydrogen through methanolysis reaction of $NaBH_4$ with 100% conversion. Moreover, the influence of temperature on the hydrogen production through reaction of $NaBH_4$ methanolysis was performed. With the aid of temperature experiments, the activation energy for the *S. Platensis* microalgal strain-supported Co-B catalyst from the slope of lnk versus 1/T and it was found to be 34.67 kJ mol^{-1}. The results showed that the use of microalgae biomass as support material is a long-term promising candidate. Consequently, this work shows both importance of hydrogen energy and production of efficient catalyst.

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