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Metal-Free Coal Catalyst for Hydrogen Production: Synthesis and Performance Assessment

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Abstract: In this study, a coal-based catalyst produced by protonating phosphoric acid was used as a metal-free catalyst for hydrogen production from sodium borohydride ($NaBH_4$) methanolysis. Experiments were conducted with various acid concentrations, impregnation times, and carbonization temperatures and times in order to produce a metal-free coal catalyst with enhanced catalytic activity. The catalyst impregnated with 3M H_3PO_4 for 12 h and subsequently carbonized at 600°C for 90 min exhibited the highest catalytic activity. The hydrogen production at 60 °C methanolysis with 0.25 g of $NaBH_4$ catalyzed by a metal-free coal catalyst was found to be 11,854 mL $min^{-1}g_{.cat}^{-1}$. Additionally, the activation energy of the catalyst was determined to be 22.5 kJ mol^{-1}.

Keywords: Coal, Metal-free catalyst, Hydrogen, Phosphoric Acid, Sodium Borohyride, Methanolysis

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1. INTRODUCTION

Population growth, economic expansion, and urbanization are contributing to the demand for energy. Fossil fuels, which are widely accessible and easily extractable, have been the primary source of energy for industries and modern lifestyles since the 1800s. However, this reliance on hydrocarbon energy sources has harmful effects on the environment, such as acid rain, global warming, and climate change, as well as negative impacts on wildlife, plant life, and public health (Akpan & Akpan, 2012). Consequently, a global shift to cleaner and more sustainable renewable energy sources is necessary to mitigate the risks of climate change and its associated health impacts. The term "renewable energy" refers to energy that originates from natural sources and is regenerated over time. It originates from a wide range of self-sustaining natural sources, which include the kinetic energy of water, solar radiation, wind power, geothermal heat, and organic matter such as biomass (Güney, 2019; Panwar et al., 2011).

The intermittent and variable nature of renewable energy sources, along with the goal of reducing CO_2 emissions, presents a major challenge to their use in transportation. Consequently, energy storage has become an essential aspect of sustainable development (Amrouche et al., 2016; Bull, 2001; Najjar, 2011; Thellufsen et al., 2020). Hydrogen is regarded as a significant energy storage medium for fully utilizing renewable and sustainable energy (Dawood et al., 2020). A range of raw materials, including water, coal, natural gas, biomass, hydrogen sulfide, and boron hydrides, can be utilized for hydrogen production through various processes such as biochemical, thermal, electrolytic, or photolytic methods (Zhang et al., 2016). Hydrogen has the potential to address air pollution and global warming issues (Sürmen & Demirbas, 2002). However, challenges related to hydrogen transportation and storage arise due to its gaseous nature and behavior at normal temperatures and pressures. To address these challenges, a variety of hydrogen storage systems, such as compressed hydrogen, liquid hydrogen, and hydrogen bound to a storage material through chemical bonds like metal hydrides, are currently under development (Demirbas & Arin, 2004). Metallic borohydrides are a promising source of hydrogen due to their high hydrogen content and ability to be stored and transported under mild conditions (Hamilton et al., 2009; Lang et al., 2020; Yao et al., 2020). Among them, sodium borohydride ($NaBH_4$) is particularly attractive due to its ability to provide pure hydrogen without producing hydrocarbons or greenhouse gases. Hydrogen can be easily produced from $NaBH_4$ by hydrolysis at room temperature using catalysts. (Xu et al., 2012). Recent studies have focused on the advantages of methanolysis of borohydrides, including avoiding freezing issues associated with water, fast hydrogen generation potentially without the need for a catalyst, and reaction products that can be regenerated into sodium borohydride in a single step (Demirci et al., 2020). Equation 1 shows the chemical reaction of $NaBH_4$ and methanol, which is commonly referred to as methanolysis.

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

Despite the various advantages, kinetically zero degradation processes are a drawback of the methanolysis of $NaBH_4$. To overcome this limitation, the focus has shifted towards the catalytic methanolysis of sodium borohydride (Wang et al., 2022). Various noble and non-noble metals, as well as their composites, have been studied in numerous studies as potential catalysts for the methanolysis of $NaBH_4$. Among them, noble metal catalysts are known for their exceptional catalytic activity, but their high cost and limited availability can limit their practical use (Yao et al., 2020). Carbon-based materials have become increasingly popular as catalysts or catalyst supports because of their cost efficiency and environmentally friendly characteristics in recent times. These materials include microalgal species (Duman et al., 2020; Inal et al., 2021; Karakaş et al., 2021), coffee waste (Akdemir et al., 2021; Kaya, 2020a), apricot kernel shells (Fangaj & Ceyhan, 2020), corn stalks (Bolat et al., 2021), cotton fibers (Ali et al., 2019), tea factory waste (Özarslan et al., 2021a; Özarslan et al., 2021b), pomegranate peels (Akdemir et al., 2022; Karakaş, 2021), banana peels (Karakaş et al., 2022), lake sludge (Bekirogullari et al, 2021), metallurgical waste sludge (Fangaj et al., 2020), and orange peels (Karakaş, 2022). Especially, metal-free catalysts provide numerous advantages over catalysts containing metals, stressing their abundance, cost-effectiveness, and sustainability. Additionally, they offer the benefit of reduced side reactions compared to metal catalysts, which are often susceptible to undesired oxidation or reduction reactions.

In this study, a metal-free coal-based catalyst was developed from phosphoric acid protonation for hydrogen production via methanolysis. Various experiments were carried out to enhance the catalytic activity of the catalyst by varying the acid concentrations, impregnation times, and carbonization temperatures and durations.

2. EXPERIMENTAL SECTION

2.1. Preparation of Metal-Free Coal Catalyst

The raw coal sample (petroleum coke) was supplied from Batman refinery and the coal catalyst was prepared by first grinding the coal to a size of 500 microns and washing it with 3M HCl, followed by rinsing with pure water. Then, the coal was treated with different concentrations of phosphoric acid (ranging from 1M to 7M) at 80 °C for 6-36 hours. After the impregnation process, the mixture was carbonized under N_2 atmosphere, with temperatures ranging from 500 °C to 800 °C and carbonization times of 30-90 min. Subsequently, kinetic studies were conducted at different solution temperatures (30-60 °C) to analyze the catalyzed methanolysis of $NaBH_4$. The catalyst's ability to be reused was evaluated by conducting five consecutive experiments. Before each experiment, the catalyst was separated, washed, and dried to prepare it for reused.

2.2. Procedure for Methanolysis Experiment

Methanol with a purity of ≥99.9% from Sigma Aldrich was used in the experiments. The reactions were conducted in a 50 mL flask equipped with a thermometer for temperature monitoring. The reaction mixture contained 0.25 g of $NaBH_4$ (98%, Sigma Aldrich) and 0.10 g of catalyst. To start the methanolysis reaction, 10 mL of methanol was added. The hydrogen gas generated was collected in a gas collection unit, and its volume was measured over a specific time interval.

3. RESULTS AND DISCUSSION

3.1. Characterization

Elemental analysis was performed using ICP-MS (Inductively Coupled Plasma Mass Spectrometry), which allows us to determine the elemental composition of the raw sample and H3PO4-coal, and the results are given in Table 1.

FTIR (Fourier Transform Infrared Spectroscopy) was conducted to characterize the material, providing insights into its molecular structure and chemical composition. These analyses contributed to a comprehensive understanding of the material's characteristics. As shown in Figure 1, the raw coal contains both aromatic and aliphatic hydrocarbons. The vibration bands at 2850 and 800 cm^{-1} are ascribed to the C–H in aliphatic hydrocarbons and aromatic hydrocarbons, respectively. The broad and intense bands at 1600 cm^{-1} is assigned to the aromatic like C=C stretching. In addition, after combustion with H3PO4, the characteristic peaks of the C–H stretching mode of the raw coal disappear while the peaks at the 1600 cm-1 stretching mode become broader, indicating that the raw carbon materials undergo a structural change.

Additionally, the vibration bands at 1000 cm^{-1} are attributed to P=O symmetric stretching, which confirm the successful attachment of–PO_4 onto the carbon matrix (Robinson, 1963).

3.2. Effect of H_3PO_4 Concentration on Metal-Free Coal Catalyst Performance

The performance of a metal-free coal catalyst was studied by treating it with four different concentrations of H_3PO_4 (1 M, 3 M, 5 M, and 7 M) and subjecting it to carbonization in an inert atmosphere. The catalysts were then incubated at 80 °C for 24 hours and carbonized in a 600 °C ash furnace for 90 minutes, as presented in Figure 2. The highest hydrogen production rate of 1856 mL $min^{-1}g_{.cat}^{-1}$ was achieved using 3M H_3PO_4, while the 1 M, 5 M, and 7 M H_3PO_4 treatments resulted in hydrogen production rates of 1080, 1651, and 1195 $min^{-1}g_{.cat}^{-1}$, respectively. Fangaj and Ceyhan (2022) investigated the use of apricot kernels activated with H_3PO_4 as a catalyst and found that the highest hydrogen production rate was achieved at a 15% acid concentration. However, the catalytic activity decreased at higher acid concentrations due to structural deformations in the catalyst. These results highlight the significance of optimizing acid concentration for maximizing catalytic activity.

Table 1. Chemical analysis of samples.

Element	**Raw-coal (ppm)**	**H_3PO_4-coal (ppm)**	**Element**	**Raw-coal(ppm)**	**H_3PO_4-coal(ppm)**
Li	0.2	8.5	Cu	1.6	46.0
B	10.4	18.8	Zn	17.0	109.7
Na	74.6	1098.7	Ga	7.1	1.4
Mg	145.8	450.0	As	21.4	40.5
Al	224.3	1533.8	Sr	6.5	3.8
P	57.9	21196.4	Ag	0.08	0.4
K	6705.5	11201.4	Cd	0.4	0.01
Ca	1032.9	627.8	Sb	4.3	5.8
Cr	21.0	96.9	Ba	11.7	7.8
Mn	4.0	12.7	Tl	0.2	0.03
Fe	320.6	446.7	Pb	1.1	4.4
Co	1.6	270.8	Bi	0.1	0.01
Ni	291.5	179.0			

3.3. Effect of Impregnation Time on Metal-Free Coal Catalyst Performance

The effect of impregnation time on the catalytic activity of methanolysis of $NaBH_4$ using metal-free coal catalysts at various times, including 6 h, 12 h, 24 h, and 36 h, was investigated through a series of experiments. According to the findings presented in Figure 3, the most significant efficiency in hydrogen production was obtained when the impregnation time was 12 hours, with a rate of 6588 mL $min^{-1}g_{.cat}^{-1}$. The lowest efficiency was recorded at the 24 h, with a rate of 1856 mL $min^{-1}g_{.cat}^{-1}$ and a reaction completion time of 8 min. Previous studies on hydrogen production from $NaBH_4$ methanolysis using different catalysts have shown that the most effective impregnation time is 24 hours. In a study by Saka et al. on hydrogen production from $NaBH_4$ methanolysis using $ZnCl_2$-treated Spirulina microalgala catalyst, the most effective impregnation time was found to be 24 h (Kaya et al., 2019). Therefore, obtaining the most effective catalyst at a 12 h impregnation time can be considered a cost-efficient option, in accordance with the previous findings.

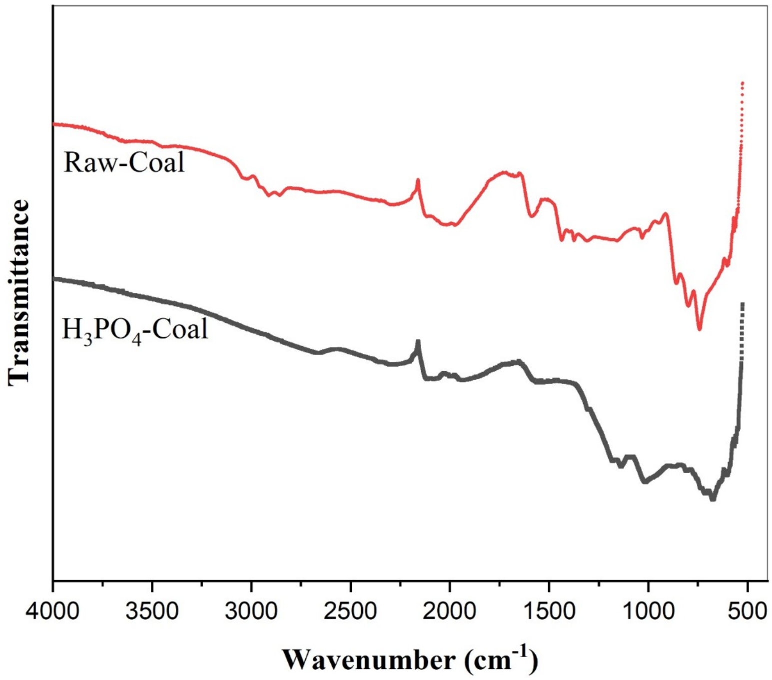

Figure 1: FT-IR spectra of samples.

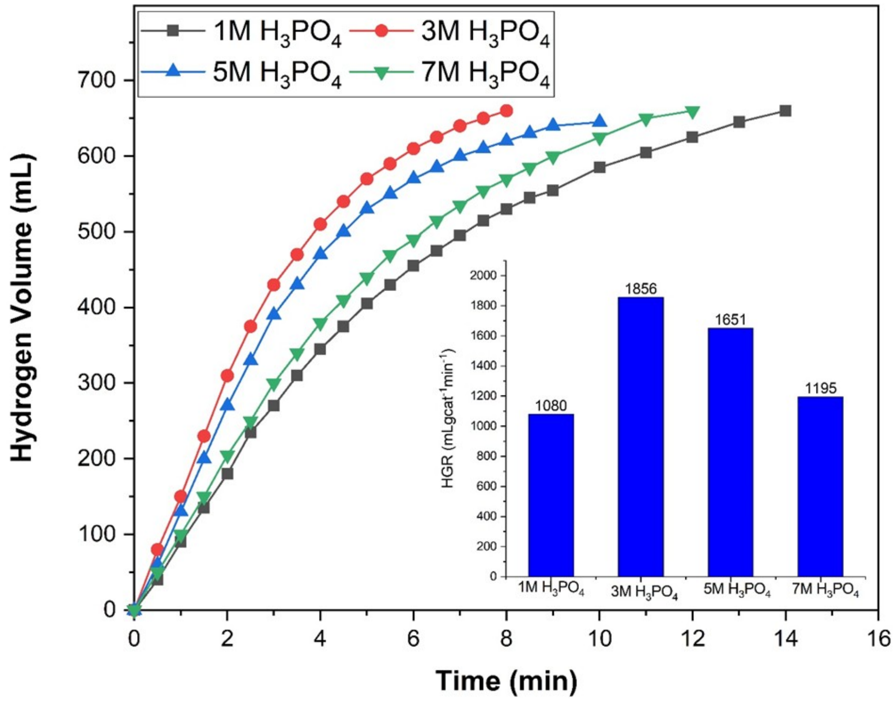

Figure 2: The effect of the concentration of H_3PO_4 on NaBH4 methanolysis [Reaction condition: 24 h impregnation time, 600 ºC carbonization temperature, 90 min carbonization time, 0.1 g catalyst, 10 mL methanol, 0.25 g $NaBH_4$, 30 ºC solution temperature.

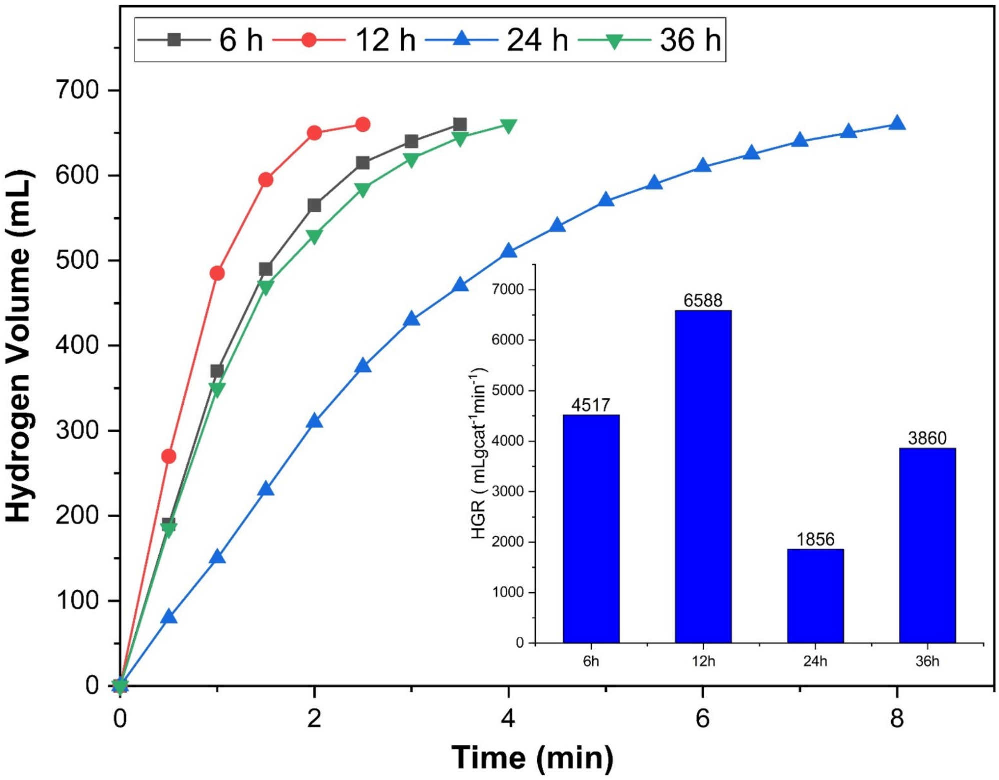

Figure 3: The effect of the impregnation time on $NaBH_4$ methanolysis [Reaction condition: 3M H_3PO_4, 600 ºC carbonization temperature, 90 min carbonization time, 0.1 g catalyst, 10 mL methanol, 0.25 g $NaBH_4$, 30 ºC solution temperature.

3.4. Effect of Carbonization Temperature on Metal-Free Coal Catalyst Performance

The effect of different carbonization temperatures on the experimental results was presented in Figure 4. The carbonization process was conducted at four different temperatures, specifically 500 °C, 600 °C, 700 °C, and 800 °C. It was clear that increasing the temperature from 500 ºC to 600 ºC could significantly improve the activity of metal-free coal catalysts. However, increasing the calcination temperature from 600 ºC to 800 ºC caused a decrease in the catalytic activity. It has been suggested that the reduction in catalytic activity at higher temperatures may be due to loss of active OH groups via dehydration and dihydroxylation (Fitzgerald et al., 1997). The highest hydrogen production efficiency of 6588 mL $min^{-1}g_{.cat}^{-1}$ was recorded for the coal catalyst obtained at 600 ºC. Karakaş et al. reached the similar conclusion in their methanolysis experiments using Spirulina Platensis waste-supported Pd-Co catalyst and identified the most efficient carbonization temperature as 600 ºC (Karakaş et al., 2021).

3.5. Effect of Carbonization Time on Metal-Free Coal Catalyst Performance

The catalytic activity of $NaBH_4$ methanolysis is highly dependent on the carbonization time. As shown in Figure 4, different carbonization times were studied by experimenting with 30, 60, 90, and 120 minutes. Figure 5 indicates that the production of hydrogen increases gradually with increasing carbonization times up to 90 minutes. However, further increases caused a decrease in the catalytic activity. The highest efficiency for hydrogen production was achieved at 90 minutes, with a recorded rate of mL $min^{-1}g_{.cat}^{-1}$. Using a manganese catalyst supported by *Microcystis aeruginosa*, Duman et al. (2020) investigated the $NaBH_4$ methanolysis process. They determined that 45 min was the best carbonization time for the reaction, demonstrating the significance of determining an appropriate reaction time for maximizing effectiveness.

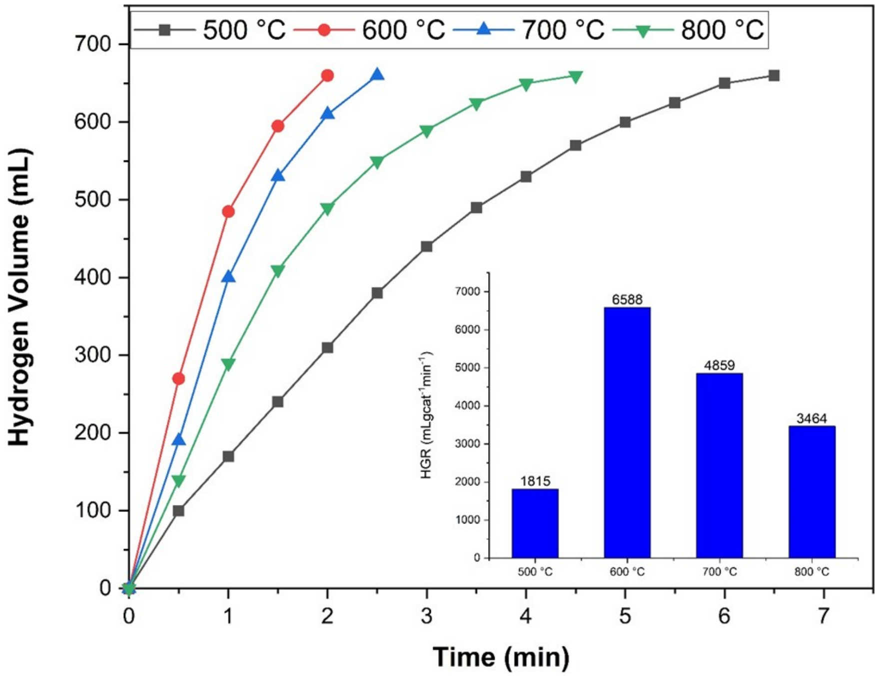

Figure 4: The effect of the carbonization temperature on $NaBH_4$ methanolysis [Reaction condition: 3 M H_3PO_4, 12 h impregnation time, 90 min carbonization time, 0.1 g catalyst, 10 mL methanol, 0.25 g $NaBH_4$, 30 ^oC solution temperature.

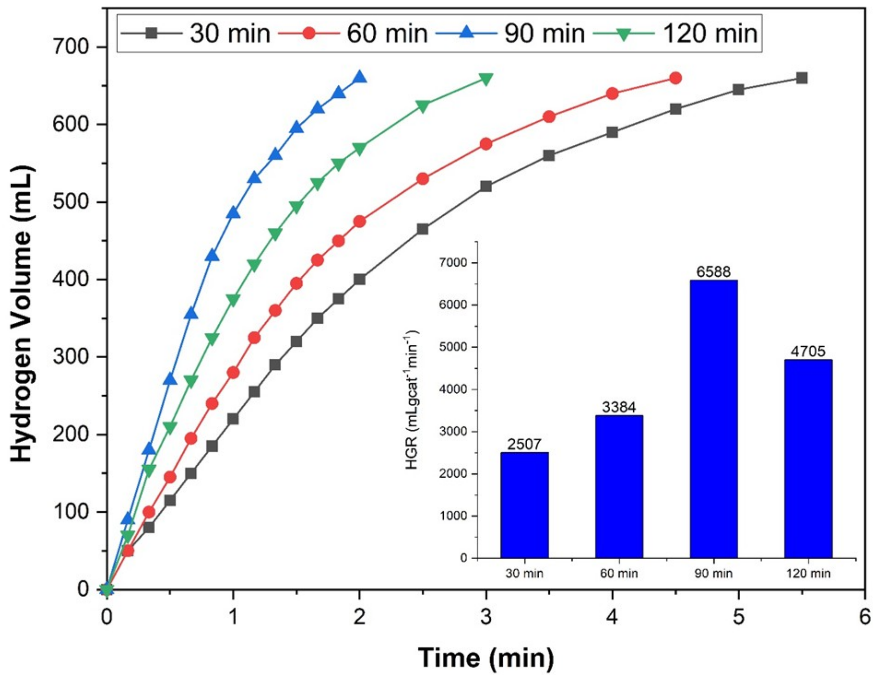

Figure 5: The effect of the carbonization time on $NaBH_4$ methanolysis [Reaction condition: 3M H_3PO_4, 12 h impregnation time, 600 ^oC carbonization temperature, 0.1 g of catalyst, 10 mL of methanol, 0.25 g of $NaBH_4$, 30 ^oC solution temperature.

3.6. Effect of Solution Temperature on Metal-Free Coal Catalyst Performance

The study examined the impact of solution temperature on the catalytic performance of metal-free coal catalyst in the methanolysis of $NaBH_4$. The experiment was carried out at four different temperatures: 30, 40, 50, and 60 ^oC, and the results were presented in Figure 6. The graph shows the hydrogen volume produced versus reaction time and the hydrogen production rate (HGR) for the methanolysis of $NaBH_4$ with 0.25 g of $NaBH_4$, 10 mL of methanol, and 0.1 g of catalyst at varying temperatures. According to the experimental results, the HGR increased gradually with increasing temperature and the highest efficiency (11854 mL $min^{-1}g_{.cat}^{-1}$) was determined at the highest temperature of 60 °C. Previous research has shown that there is a linear relationship between temperature and HGR ratio. One of these was the study in which coffee waste was used as a catalyst for the methanolysis of $NaBH_4$, and a hydrogen production rate of 13332 mL $min^{-1}g_{.cat}^{-1}$ was achieved at 60°C (Kaya, 2020b). Similarly, the pomegranate peel supported NH_2/PdMnAg catalyst showed hydrogen production yields of 7209.4, 8689.6, 10324 and 11334 $min^{-1}g_{.cat}^{-1}$ at 30°C, 40°C, 50°C and 60°C, respectively (Karakaş, 2021).

The activation energy in the hydrogen production reaction of the metal-free coal catalyst treated with 3M H_3PO_4 in the methanolysis of $NaBH_4$ was determined by applying the Arrhenius' equation (2):

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

Equation (2) consists of the reaction rate constant (k), reaction constant (A), activation energy (Eα) measured in kJ mol^{-1}, temperature (T) in K, and the ideal gas constant (R). The Arrhenius (ln(k) vs 1/T plot) plot for the methanolysis of $NaBH_4$ catalyzed are given in Figure 7.

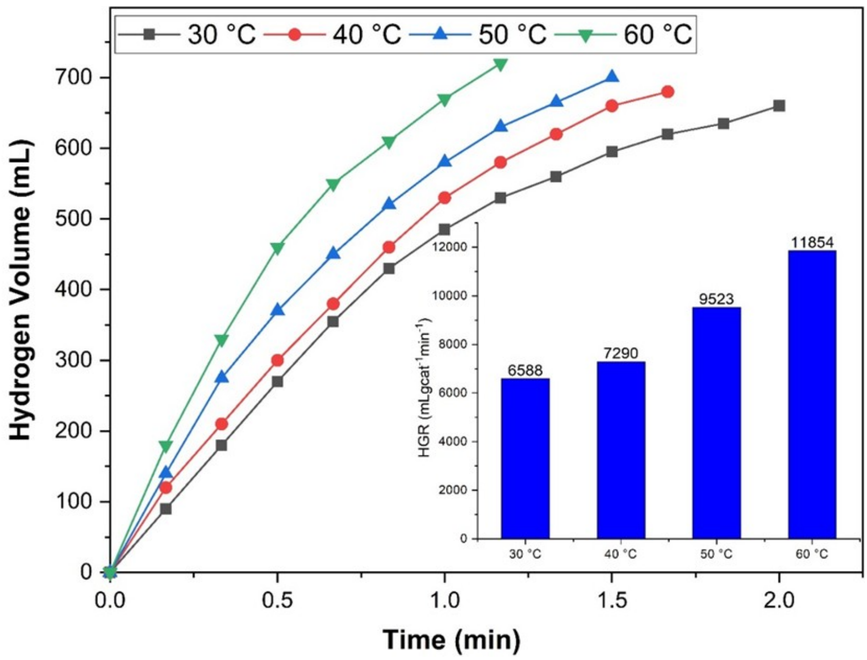

Figure 6: The effect of the solution temperature on $NaBH_4$ methanolysis [Reaction condition: 3 M H_3PO_4, 12 h impregnation time, 600 ºC carbonization temperature, 0.1 g of catalyst, 10 mL of methanol, 0.25 g of $NaBH_4$.

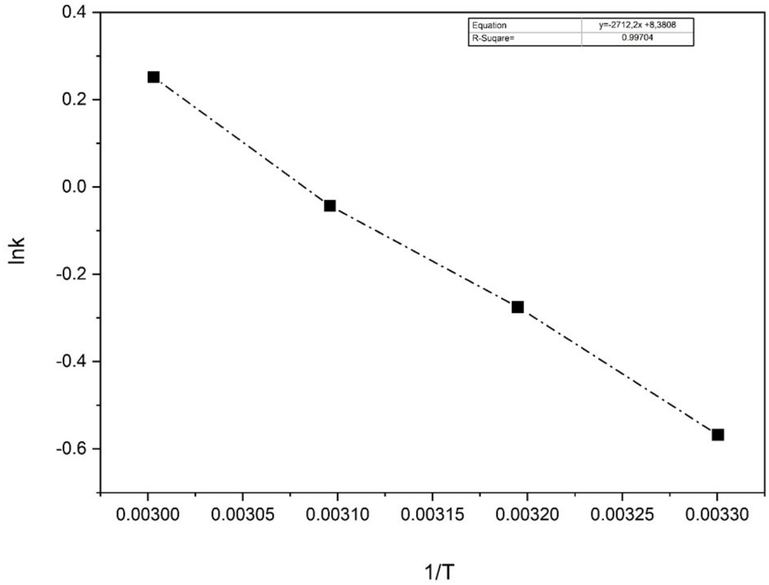

Figure 7: Arrhenius' plot for the metal-free coal-based catalyst for methanolysis of $NaBH_4$

The activation energy of the metal-free coal catalyst for sodium boron hydride methanolysis hydrogen production was found to be 22.5 kJ mol^{-1}, which is very close to the 24 kJ mol^{-1} poly (Castor Oil) (p(CO)) organo-particle (Dudu et al., 2022)

3.7. Catalytic Stability of Metal-Free Coal for the Methanolysis of $NaBH_4$

In addition to having remarkable catalytic activity, a methanolysis catalyst must also have great stability, in addition to being both cost-effective and eco-friendly. Therefore, the stability performance of metal-free coal catalyst was conducted in five consecutive methanolysis reactions. The stability test produced a histogram of the cycle time and hydrogen generation rate, as illustrated in Figure 8.

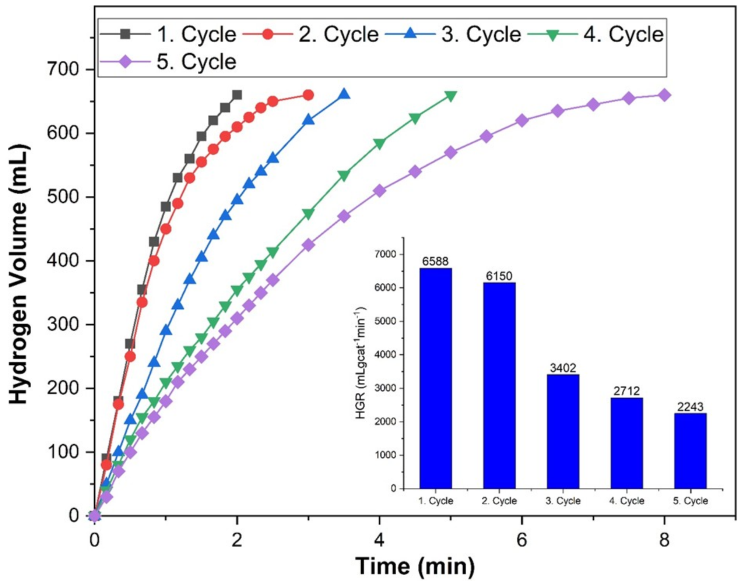

Figure 8: Reusability of metal-free coal catalyst in methanolysis of $NaBH_4$ at solution temperature of 30 ^oC

According to the findings, the hydrogen generation rate decreased gradually with an increase in the number of cycles. At the 5th cycle, the HGR of the coal catalyst without metal was found to be 2243 mL $min^{-1}g_{.cat}^{-1}$. The possible reasons for the decrease in efficiency seen in repeated experiments may be due to mass loss during catalyst preparation or loss of properties during washing. Xu et al. produced hydrogen from $NaBH_4$ methanolysis using a Co/Al_2O_3 catalyst and measured its efficiency through repeated experiments. It was founded that the catalyst surface became smoother after five consecutive experiments, with a loss in the active material content and changes in the surface composition (Xu et al., 2012). Demirci et al. employed porous carbon particles as a catalyst without metal for hydrogen production via $NaBH_4$ methanolysis. A set of experiments was carried out, where 0.0965 g of $NaBH_4$ was added to 50 mg of catalyst mixed with 20 mL of methanol, repeated five times. The results indicated that the regeneration process could help slow down the decline in catalytic activity after each use. (Demirci et al., 2020).

4. CONCLUSION

Hydrogen (H_2) as a renewable energy is considered as a promising energy carrier for future applications due to its eco-friendly fuel with high energy density features. Catalytic methanolysis of $NaBH_4$ is a significant process for hydrogen H_2 production. An innovative methodology in which carbon-based materials are used as direct catalysts as an alternative to metal-based catalysts has been widely accepted for its cost-effectiveness and environmentally friendly approach. In this study, hydrogen production through $NaBH_4$ methanolysis using metal-free coal was performed. Different H_3PO_4 concentrations were used in the catalyst preparation, and the most efficient acid concentration was determined to be 3 M. Then, experiments were conducted on different impregnation times, carbonization temperatures, and durations. The most efficient catalyst conditions were determined as 3 M phosphoric acid, 12 h impregnation time, 600 °C carbonization temperature and 90 min of carbonization time. The catalyst exhibited a hydrogen production efficiency of 11854 mL $min^{-1}g_{.cat}^{-1}$, and its activation energy was determined to be 22.5 kj mol^{-1}, according to the findings. The evaluation of prepared metal-free coal as a catalyst is very promising. It is believed that this material can be further modified by different chemical and thermo processes to obtain even more efficient catalysts.

5. CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the study.

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