Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi
Afyon Kocatepe University – Journal of Science and Engineering
https://dergipark.org.tr/tr/pub/akufemubid

Araştırma Makalesi / Research Article
DOI: https://doi.org/10.35414/akufemubid.1398395
AKÜ FEMÜBİD 24 (2024) 051201 (1061-1070)
AKU J. Sci. Eng. 24 (2024) 051201 (1061-1070)

Study of the Sodiumborohydride Hydrolysis Reaction’s Performance via a Kaolin-Supported Co-Cr Bimetallic Catalyst

***Makale Bilgisi / Article Info**
Alındı/Received: 30.11.2023
Kabul/Accepted: 27.06.2024
Yayımlandı/Published: xx.xx.xxxx

Kaolin Destekli Co-Cr Bimetalik Katalizör Yoluyla Sodyum Borhidrür Hidroliz Reaksiyonunun Performansının İncelenmesi

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Abstract

Hydrogen is an attractive source of energy because of its properties, which include superior quality, effectiveness, pureness, dependability, and sustainability. Technologies for producing and storing hydrogen are being developed in parallel with fuel cell development. Chemical storage of hydrogen in a metal hydride containing boron eliminates the problem of hydrogen transportation and storage. Through catalytic reactions, hydrogen stored in solid form in boron hydrides can be recovered. In this study, a nowel developed Co-Cr bimetallic catalyst supported by kaolin, a natural mineral, was synthesized to be used for hydrogen production by hydrolysis of sodium boron hydride. The structural characteristics of the produced Co-Cr@Kaolin catalyst were ascertained by EDX, FT-IR, and SEM analyses. Next, the ideal conditions for the hydrolysis reaction of sodium borohydride ($NaBH_4$) catalyzed by Co-Cr@Kaolin were examined. These included the concentration of the catalyst, the amount of support material (kaolin), the amount of catalyst, and the concentration of $NaBH_4$. The optimal hydrolysis conditions were found to be 2.5 % NaOH concentration, 40 mg of catalyst, and 2% $NaBH_4$ concentration at 303 K. The maximum rate of hydrogen production was determined as 5007 mL g^{-1} min^{-1} under optimal conditions. After conducting hydrolysis operations at different temperatures to elucidate the reaction kinetics, it was found that the catalytic hydrolysis reaction was of the 0th order and that the reaction activation energy was 19.36 kJ mol^{-1}. The hydrogen production rate obtained as a result of the hydrolysis reaction accompanied by a Co-Cr catalyst was determined as 3166 mL g^{-1} min^{-1}. It is therefore established that supporting kaolin to Co-Cr catalyst enhances its efficacy.

***Keywords:** Hydrogen; Kaolin; Sodium borohydride; Co-Cr@Kaolin; Supported Catalyst.*

Öz

Hidrojen, üstün kalite, etkinlik, saflık, güvenilirlik ve sürdürülebilirlik gibi özellikleri nedeniyle cazip bir enerji kaynağıdır. Hidrojenin üretilmesi ve depolanmasına yönelik teknolojiler yakıt hücresi gelişimine paralel olarak geliştirilmektedir. Hidrojenin bor içeren bir metal hidrit içerisinde kimyasal olarak depolanması, hidrojenin taşınması ve depolanması sorununu ortadan kaldırır. Katalitik reaksiyonlar yoluyla bor hidritlerde katı halde depolanan hidrojen geri kazanılabilir. Bu çalışmada, sodyum bor hidrürün hidrolizi ile hidrojen üretiminde kullanılmak üzere doğal bir mineral olan kaolin ile desteklenen yeni geliştirilmiş Co-Cr bimetalik katalizörü sentezlendi. Üretilen Co-Cr@Kaolin katalizörünün yapısal özellikleri EDX, FT-IR ve SEM analizleri ile belirlendi. Daha sonra Co-Cr@Kaolin tarafından katalize edilen sodyum borohidrürün ($NaBH_4$) hidroliz reaksiyonu için ideal koşullar incelendi. Bunlar, katalizörün konsantrasyonunu, destek malzemesinin (kaolin) miktarını, katalizörün miktarını ve $NaBH_4$ konsantrasyonunu içermektedir. Optimum hidroliz koşullarının 303 K'de, % 2.5 NaOH konsantrasyonu, 40 mg katalizör ve % 2 $NaBH_4$ konsantrasyonu olduğu sonucuna varılmıştır. Optimum koşullar altında hidrojenin maksimum üretim hızının 5007 mL g^{-1} dk^{-1} olduğu belirlenmiştir. Reaksiyon kinetiğini aydınlatmak için farklı sıcaklıklarda hidroliz işlemleri yapıldıktan sonra katalitik hidroliz reaksiyonunun 0. mertebeden olduğu ve reaksiyonun aktivasyon enerjisinin 19.36 kJ mol^{-1} olduğu bulunmuştur. Co-Cr katalizörü eşliğinde yapılan hidroliz reaksiyonu sonucunda elde edilen hidrojen üretim hızı ise 3166 mL g^{-1} dk^{-1} olarak belirlenmiştir. Bu nedenle, Co-Cr katalizörünün kaolin ile desteklenmesinin katalizörün etkinliğini arttırdığı tespit edilmiştir.

***Anahtar Kelimeler:** Hidrojen; Kaolin; Sodyum borohidrid; Co-Cr@Kaolin; Destekli katalizör.*

1. Introduction

Besides the gradual depletion of fossil fuels, burning them releases pollutants including unburned hydrocarbons, soot, odor, and carbon monoxide (CO), which are hazardous to human health and disturb the natural equilibrium of the environment (İzgi et al. 2017, Tarasova et al. 2022). In light of the concerning patterns of environmental deterioration and the decrease of fossil fuel reserves, it is crucial to investigate alternatives to fossil fuels in order to promote the sustainable development of human civilization (Abdalla et al. 2018, Chen et al. 1997, Kumar and Das 2023). Scientific research indicates that hydrogen energy, which is becoming more and more popular as a fossil fuel substitute, is a clean and effective energy source. Hydrogen-powered fuel cells are

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receiving a lot of attention as possible power sources for high-power applications and portable devices (such as energy generators) (Sartbaeva et al. 2008, Arzac et al. 2011, Koh et al. 2023). Hydrogen can be used as a fuel by means of systems called proton exchange membrane fuel cells (PEMFCs) (Ekinci 2020). In these cells, hydrogen is introduced into the system as a gas to produce electricity (Linden and Reddy 2001). The main argument in favor of using hydrogen as a fuel is the fact that it can be discovered in many different places. Carbon-based materials can be converted into hydrogen using thermochemical processes. Water can be converted into hydrogen using electrolysis, hydrolysis, and other processes. Solar energy can be converted into hydrogen using photoelectrochemical processes (Onat et al. 2024a, Onat et al. 2024b, Izgi et al. 2024). However, there are several drawbacks to using hydrogen as a fuel source (Acar and Dinçer 2019, Tutar and Eren 2011). These include the high expense of hydrogen fuel technology as well as the storage and gaseous hydrogen transportation. The chemical formation of hydrogen in boron compounds provides practically a whole solution to the transit and storage problem. (Sahiner and Demirci 2017, Lang et al. 2020). Its cost is significantly decreased by synthesizing the catalyst with loading-supported material. One of the most significant chemical hydrides is sodium borohydride ($NaBH_4$) due to its large (10.6 wt %) storage of hydrogen capability. Moreover, to have a high hydrogen storage capability, sodium borohydride also has a high hydrogen yield due to the hydrolysis that occurs when the hydrogen in its structure is separated from the water (Su et al. 2012, Demirci et al. 2010, Wee et al. 2006). Thermolysis or hydrolysis are two methods for dehydrogenating hydrogen contained in sodium borohydride (Sing 2022).

$$\mathrm{NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2} \qquad (1)$$

The catalyst can modify the reaction rate specified in Equation 1. This situation offers considerable advantages for employing hydrogen as a form of energy carrier by eliminating transit and storage problems (Özkar and Zahmakıran 2005). $NaBH_4$ undergoes an exothermic, spontaneous reaction known as self-hydrolysis. However, at ambient conditions, only 7-8 % of sodium borohydride produces hydrogen through self-hydrolysis. This value is insufficient for any fuel cell application. Consequently, the hydrolysis reaction can be accelerated by using metal or acid catalysts, particularly for sodium borohydride (Boran et al. 2013, Bai et al. 2006, Huang et al. 2021, Retnamma et al. 2011). Thus, a continuous hydrolysis reaction is possible at low temperature and pressure in the presence of metal catalysts (Kojima et al. 2011). In an alkaline solution, sodium borohydride does not burn. It also has various benefits, such as recycling byproducts. When a catalyst is used to hydrolyze $NaBH_4$, hydrogen is released spontaneously into the water (Su et al. 2012, Şahin et al. 2014a). In addition to releasing hydrogen from its structure, sodium borohydride also enables the recovery of hydrogen from the water structure, as shown in Equation 1. Thus, it becomes even more crucial to use it as a source of hydrogen (Tomasso et al. 2020).

Equation 1 can be used to generalize the hydrogen production from metal hydrides. The fact that this reaction is catalyst-controlled demonstrates how crucial the catalyst is for producing hydrogen (Strmcnik et al. 2016). Usually, valuable metals like Rh, Ru, Pd, and Pt are utilized as catalysts. Because these metals are expensive, metal combinations incorporating Co, Cu, Ni, and Mn are used instead, with increasing efficiency. Supported catalyst synthesis is another crucial technique for creating catalysts (Vesborg et al. 2015, Birry and Lasia 2004, Chen et al. 2013, Vračar and Conway 1990, Durst et al. 2014, Han et al. 2015, Kibsgaard and Jaramillo 2014, Huynh et al. 2013, Fernandes et al. 2009).

One common clay mineral, kaolin, is a significant non-metallic mineral source. After going through procedures including purifying and wroughting, kaolin is ground up and utilized to make pigment items and additives (Hubadillah et al. 2018, He et al. 2023). Kaolin is used widely in cement, ceramics, thermal energy storage materials, and other industrial areas due to its features of stable physical and chemical qualities, superior electrical isolation, high whiteness, a large area of a specific surface, high void proportion, and superior surface activation (Xie et al. 2019, Huang et al. 2017, Li et al. 2019).

This work demonstrates the synthesis of a novel material (Co-Cr@kaolin) that catalyzes the reaction of sodium borohydride hydrolysis. Following an identification of the Co-Cr@Kaolin catalyst's structure using EDX, FT-IR, and SEM investigations, the ideal conditions (kaolin amount, concentration of NaOH solution, catalyst amount, and concentration of $NaBH_4$) for the hydrolysis reaction were investigated. This work aims to produce an effective and dynamic catalyst with an affordable method for hydrogen production.

2. Materials and Method

2.1 Materials

Catalyst synthesis was carried out using an oven, burette, nitrogen tube, vacuum filtering device, and digital precision scale. For hydrolysis, a water bath, a gas measurement instrument, a stopwatch, and a digital precision scale were utilized.

2.2 Synthesis of Co-Cr catalyst

A chemical reduction technique was used to produce the Co-Cr catalyst according to the reference article (Fernandes et al. 2009). $CoCl_2$ and $Cr(NO_3)_3$ were dissolved in water, and $NaBH_4$ was added as a reductant while the mixture was stirred quickly. The reduction of the Co and Cr cations into metal required an excessive number of borohydrides. After filtering and carefully washing with distilled water and ethanol, the black powder reaction result was dried at 323 K with a steady flow of N_2. The [Cr/(Cr + Co)] molar ratio of the final Co-Cr catalyst powder could be changed by varying the molar concentration of $Cr(NO_3)_3$ in the aqueous solution.

2.3 Synthesis of Co-Cr@Kaolin catalyst

The impregnation method was utilized to support the Co-Cr catalyst with kaolin. The synthesis technique involved weighing and mixing the indicated amounts of Co-Cr catalyst for each experiment in a magnetic stirrer at 500 rpm for 30 minutes. Next, kaolin was added at a varied rate (70 %, 80 %, 90 %, and 95 %) in each trial. It was mixed once more for 20 hours at 500 rpm. Following that, it was reduced with sodium borohydride in the prescribed amounts. After the reduction, the catalyst was collected and vacuum-filtered before being dried for six hours at 60°C while surrounded by nitrogen. The catalyst, which was seen to be fully dry, was ground up and used to catalyze hydrolysis reactions of sodium borohydride.

2.4 Hydrolysis experiments

Experiments on hydrolysis were conducted in a jackketed tube with a magnetic stirrer at a speed of 600 rpm, at a temperature of 30 °C. Furthermore, a circulating water bath was employed to regulate the temperature since the system's temperature needed to be maintained consistently. An aqueous $NaBH_4$ solution was added to the reactor first, and then the catalyst was added. The produced hydrogen amount was then measured with a gas burette. The results were evaluated by drawing graphs for each experiment. Figure 1 shows an experimental working system of the hydrolysis reaction.

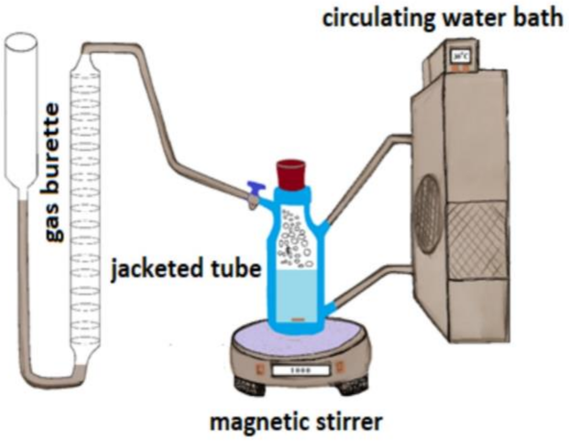

Figure 1. Hydrolysis reaction system

3. Results and Discussion

3.1 Catalyst characterization

Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), and Energy dispersion X-ray spectrometry (EDX) were used to characterize catalysts. SEM images of kaolin, Co-Cr catalysts, and Co-Cr@Kaolin catalysts are displayed in Figure 2.

The SEM picture of kaolin in Figure 2a demonstrates that it has a well-crystallized structure made up of hexagonal particles with varying thicknesses and diameters. According to the Co-Cr catalyst's morphology (Fig. 2(b)), the particles are spherical and small in size. Using NaBH4 as a reducing agent during the catalyst manufacturing results in the fast reduction of Co ions, which prevents the creation of pertinent growth of particles. The Co-Cr@Kaolin catalyst has improved interparticle spacing without aggregation, which raises the catalyst's surface area that is actively catalyzing (Figure 2 (c)).

Identifying the compatibility of the catalyst content with the synthesized values is one of the crucial aspects of catalyst characterization. The catalyst for the Co-Cr system had 96 % Co and 4 % Cr. Figure 3(b) illustrates how these values are maintained in the catalyst content. The Co-Cr catalyst's EDX examination revealed the presence of Co and Cr metals (Figure 3 b). The Al and Si components in the kaolin's structure, which are visible in Figures 3(b) and 3(c), respectively, demonstrate that the kaolin binds to the catalyst (Bektaş et al. 2023, Onat and Ekinci, 2024).

The catalysts' FT-IR spectrum analysis results are displayed in Figure 4. The low-frequency portion of the FT-IR spectrum of Co-Cr reveals the cobalt ion-coordinated librational vibrations of molecules (Netskina et al. 2020). A potential metal-oxygen interaction is thought to be the cause of the band at 630 cm^{-1} (Nakamoto, 1963). While examining a Co(II) combination with pullulan, Miti et al. also discovered these bands (Sotiles et al. 2019). The peak at 1200 cm^{-1} is ascribed to vibrations of chromyl (Cr=O) (Weckhuysen et al. 1996, Trivedi et al. 2015). Cobalt (Co) and chromium (Cr) bands become increasingly prominent in the kaolin-supported catalyst structure, and the absorption bands of kaolin align with the stretching frequencies of OH groups between 3500 and 3750 cm^{-1}.

The peaks belonging to the Si-O, Al-OH, Si-O-Al, and Mg-Al-OH groups, in the structure of kaolin are seen at 1009, 912, 754, and 636 cm^{-1}, respectively, in the Co-Cr@kaolin spectrum (Tironia et al. 2012, Onat 2024). The SEM image in Figure 2 c is supported by this circumstance. Kaolin-supported catalyst surfaces crystallized more successfully and revealed themselves more clearly.

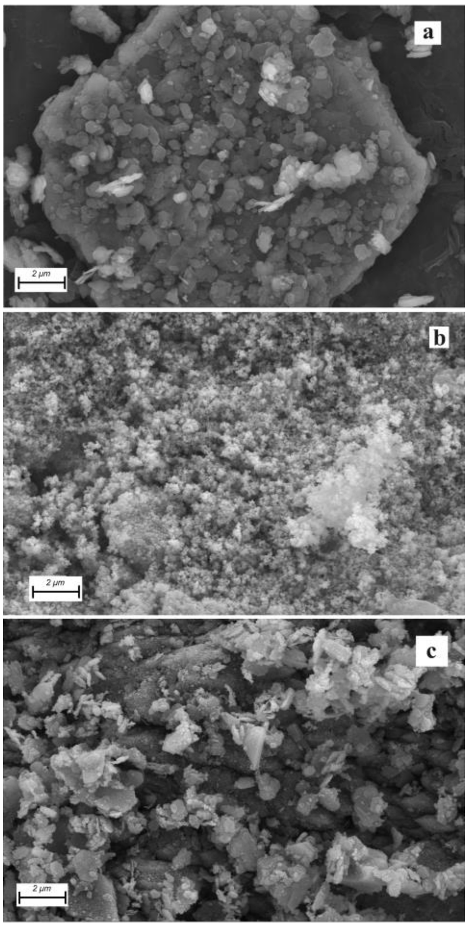

Figure 2. SEM images of a) kaolin b)Co-Cr catalyst c)Co-Cr@Kaolin catalyst.

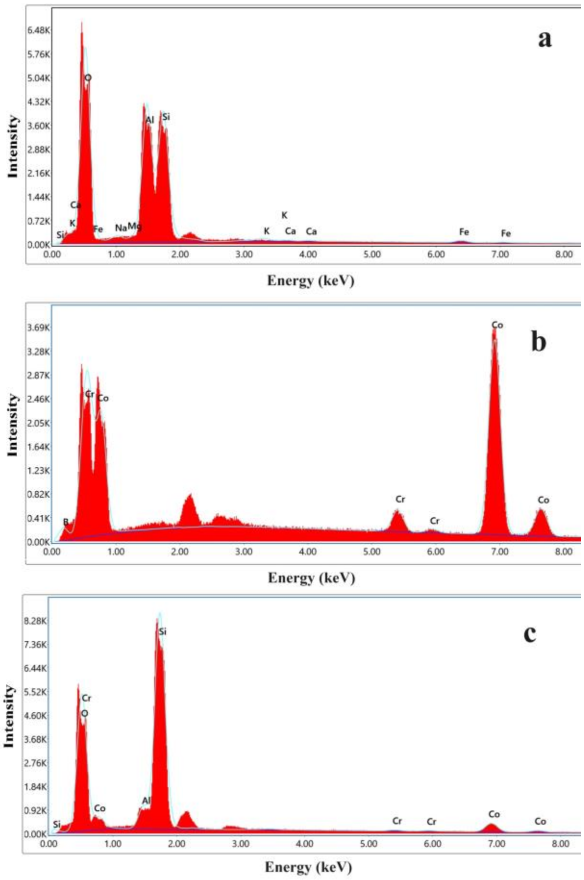

Figure 3. EDX analysis of a)Kaolin b)Co-Cr catalyst c)Co-Cr@Kaolin catalyst.

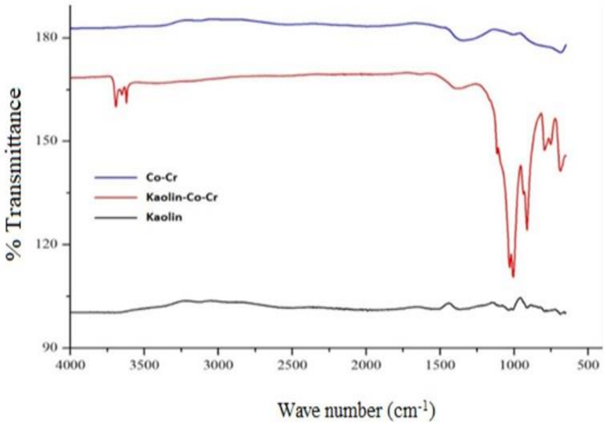

Figure 4. FT-IR analysis of Kaolin, Co-Cr catalyst, and Co-Cr@Kaolin catalyst.

3.2. Effect of kaolin ratio

The efficiency of the pure catalyst (Co-Cr) and the kaolin-supported Co-Cr catalyst (Co-Cr@Kaolin) were compared. 3166 mL g^{-1} min^{-1} was found to be the rate at which hydrogen is produced when a Co-Cr catalyst is present. Figure 5 displays data on hydrogen production during hydrolysis based on different kaolin ratios. Figure 5 illustrates that the maximum rate of production of hydrogen quantity was achieved when 90% kaolin was used. The rate at which hydrogen is produced in the presence of 90% kaolin was determined to be 4084 mL g^{-1} min^{-1}. The following investigations were carried out using 90% kaolin, which was found to be the best value.

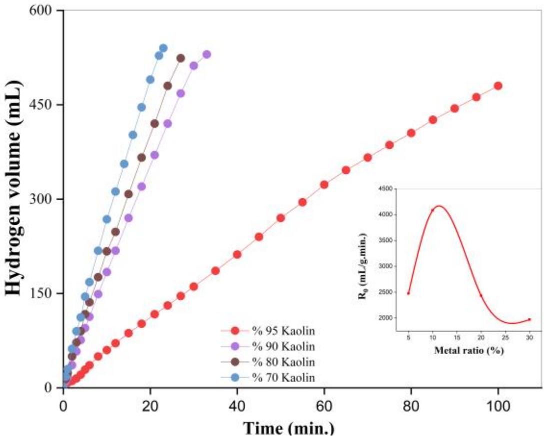

Figure 5. Hydrogen production rate as a function of kaolin ratio (50 mg catalyst, 30 °C, 5% NaOH, 2% $NaBH_4$).

3.3. Effect of NaOH ratio

NaOH concentration has a big impact on the process because the reaction of $NaBH_4$ hydrolysis can be suppressed without a catalyst by altering the pH of the reaction solution. In this study, four different starting NaOH solution concentrations (1%, 2.5%, 5%, and 7.5%) were used to quantify the volume of hydrogen produced by $NaBH_4$ hydrolysis. Figure 6 depicts the graph showcasing these research findings. The greatest rate of generating hydrogen was found at a 2.5% concentration of NaOH, as illustrated in Figure 6. At this NaOH concentration, the rate of hydrogen production was calculated to be 5007 mL g^{-1} min^{-1}. While the catalytic activity of the catalyst increased up to 2.5% NaOH concentration, after this concentration value, the catalyst's efficiency decreased with increasing NaOH concentration (Onat 2024, Izgi et al. 2019).

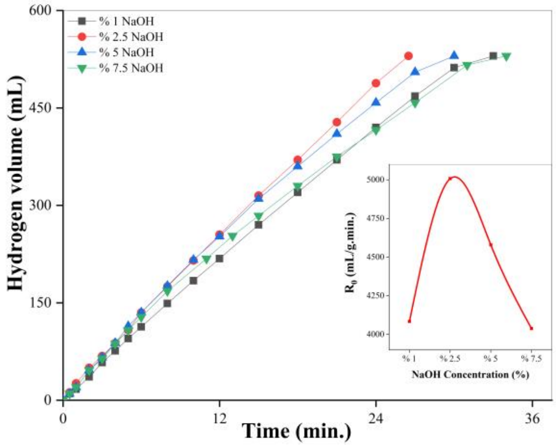

Figure 6. Hydrogen production rate as a function of mass percent of NaOH (50 mg catalyst, 30 °C, 2% $NaBH_4$).

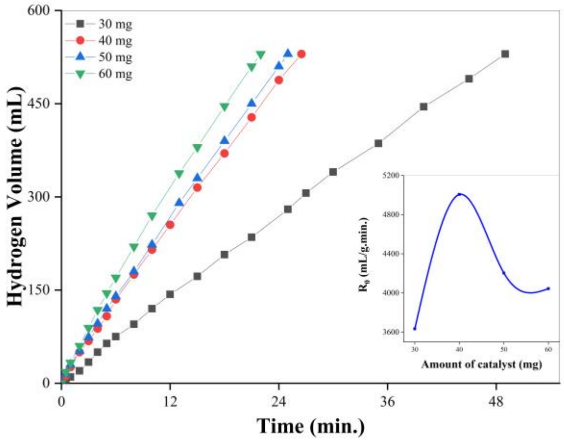

Figure 7. Hydrogen production rate as a function of catalyst amount (30 °C, 2.5% NaOH, 2% $NaBH_4$).

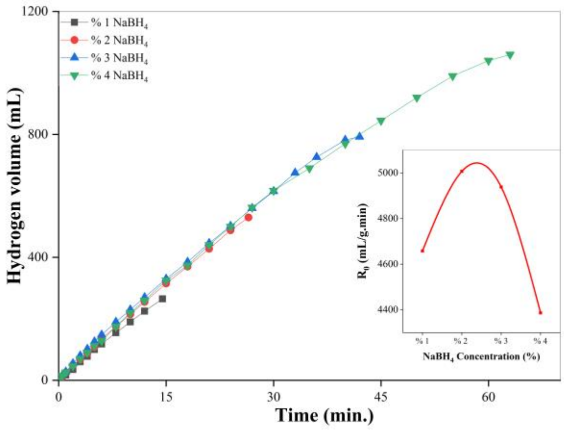

Figure 8. Hydrogen production volume as a function of $NaBH_4$ concentration (40 mg catalyst, 30 °C, 2.5% NaOH).

3.4. Effect of catalyst amount

To investigate the impact of catalyst amount on the rate of hydrogen production, experiments were conducted. Figure 7 shows the graph illustrating this impact. Even though the rate of hydrogen production increased when the catalyst dose was increased, the greatest rate of hydrogen generation was reached when 40 mg of catalyst was used. This demonstrates that using 40 mg of catalyst maintains the catalyst's surface area in contact with the substrate (Tian 2010, Onat and Izgi 2021).

3.5. Effect of Concentration of Sodium Borohydride

Several tests with constant catalyst and NaOH concentrations were conducted to determine the effects of varying $NaBH_4$ concentrations (1%, 2%, 3%, and 4% by mass) on the rate of hydrogen production. The effect of different $NaBH_4$ concentrations on the rate of hydrogen production is shown in Figure 8. As can be observed in Figure 8, the maximum rate of hydrogen generation was achieved when 2% by mass of $NaBH_4$ was used (Izgi et al. 2023). At this $NaBH_4$ concentration, the rate of hydrogen production was calculated to be 5007 mL g^{-1} min^{-1}.

3.6. Effect of reaction temperature

Catalytic hydrolysis reactions of $NaBH_4$ with Co-Cr@Kaolin catalyst were conducted at 30, 40, 50, and 60 ^{o}C temperatures to examine the impact of temperature on the sodiumborohydride hydrolysis. Figure 9 depicts the hydrogen production rate as a function of time and various reaction temperatures. The Active Collision theory can be used to explain this circumstance. In other words, when the temperature rises, more interaction occurs between the particles (Patel and Miotello 2015). At 30 ^{o}C, the rate of hydrogen production is 5007 mL $g^{-1}min^{-1}$. However, at 60 ^{o}C, the rate rises to 30325 mL g^{-1} min^{-1}. This implies that when the temperature rises, the rate of reaction increases rapidly (Zhang et al. 2020).

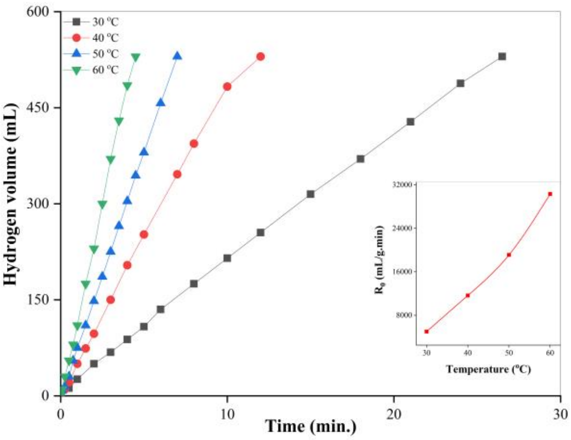

Figure 9. Hydrogen production rate as a function of temperature (40 mg cat., 2.5% NaOH, 2% $NaBH_4$).

3.7. Reaction Kinetics

Table 1 lists the kinetic values that were calculated using information on hydrogen production from hydrolysis experiments conducted at different temperatures. As a result, it has been proven that the reaction is of the 0th order, meaning that the catalyst affects the reaction's efficiency.

Table 1. Temperature-dependent kinetic data of $NaBH_4$ hydrolysis catalyzed by Co-Cr@Kaolin catalyst.

Temperature (°C)	Reac. Rate degree	Reac. Cons. (k)	HGR (mLg^{-1}min^{-1})	R^2
30	0. degree	0.019	5007	0.9992
40	0. degree	0.0427	11641	0.9939
50	0. degree	0.0638	19112	0.9998
60	0. degree	0.1052	30325	0.9985

In order to determine the reaction kinetics, the data of hydrogen production rates measured at different temperatures were evaluated in the Arrhenius equation (Equation 2).

$$\ln k \; = \ln A - \frac{E_a}{RT} \qquad (2)$$

Here;

R is the universal gas constant (8.314 kJ $K^{-1}mol^{-1}$), k is the rate constant (min^{-1}), A is a constant known as the Arrhenius factor, and T is the absolute temperature (K). According to the Arrhenius equation, the plot of ln k versus 1/T was drawn (Figure 10). The activation energy (E_a) of the reaction was calculated from the slope of this graph as 19.36 kJ mol^{-1} (Şahin et al. 2014b, Onat et al. 2021).

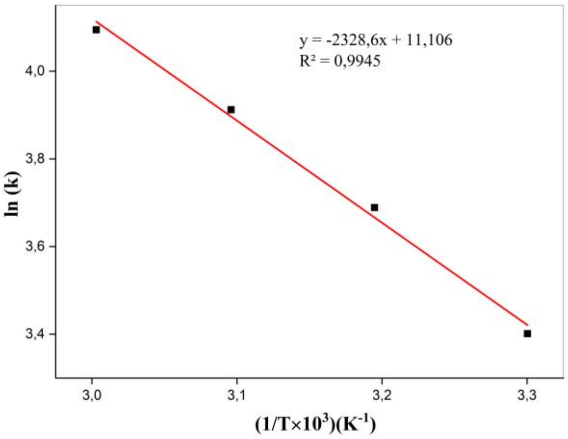

Figure 10. Arrhenius equation graph of hydrolysis reaction in the presence of Co-Cr@Kaolin catalyst.

4. Conclusion

This work investigated the catalytic activity of Co-Cr@kaolin in the hydrolysis of NaBH4 to produce hydrogen. The ideal conditions for the maximum rate of hydrogen production were determined to be 40 mg of catalyst, 2,5% NaOH, and 2% $NaBH_4$ by mass. With the Co-Cr@kaolin catalyst and the pure (Co-Cr) catalyst, the rates of hydrogen production via hydrolysis under these circumstances were found to be 5007 mL g^{-1} min^{-1} and 3166 mL g^{-1} min^{-1}, respectively. Thus, adding kaolin to the pure catalyst enhanced its efficiency. A temperature-dependent increase in the rate of hydrogen generation was observed. Hydrogen production rates at 30 °C, 40 °C, 50 °C, and 60 °C were determined as 5007, 11641, 19112, and 30325 mL g^{-1} min^{-1}, respectively. Investigations on characterization showed that kaolin improved the catalyst's effective surface without changing the catalyst's composition. Moreover, the Co-Cr@kaolin catalyst catalyzed the process at a low activation energy and produced a high amount of hydrogen.

Declaration of Ethical Standards

The authors declare that they comply with all ethical standards.

Credit Authorship Contribution Statement

Author-1: Conception, research, experimental analysis and reporting.
Author-2: Research, characterization, methodology and report.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

All data generated or analyzed during this study are included in this published article.

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