

Controlling of NaBH₄ hydrolysis by synthetic Ni-Co cited and MOFs supported novel catalyst and determination of kinetic parameters

¹Aybüke Ayşe ERTÜRK, ²Tuğba AKKAŞ BOYNUEĞRİ, ¹Metin GÜRÜ

¹* Department of Chemical Engineering, Faculty of Engineering, Gazi University, Ankara, Türkiye

²University of St Andrews, School of Chemistry, Fife, Scotland, UK

*Corresponding Author: erturkaybuke@gmail.com (A.A. Ertürk)

Phone Number: +90 507 738 66 78

ORCID Number: 0000-0001-7278-9301

Tuğba AKKAŞ BOYNUEĞRİ 0000-0003-1047-6267

Metin GÜRÜ 0000-0002-7335-7583

Abstract

This study focuses on establishing the kinetic parameters for the catalytic dehydrogenation process of NaBH₄. This reaction occurs in the presence of a co-catalyst derived from metallic sources of Co and Ni. For this purpose, a heterogeneous catalyst was synthesized using metal-organic frameworks (MOFs) as the supporting material. CoF₂ and NiF₂ for cobalt and nickel were the active metal sources, respectively. Metal organic framework (MOF), MIL-101 (Cr), was chosen because it has a larger specific surface area than other materials (2504 m²g⁻¹). The reaction rate constants and rate order were calculated via the differential method. As a result, zero-order kinetics was proved by using the experimental data. After that, the activation energy was calculated as 51.06 kJ/mol through the slope of the graph of lnk versus 1/T for the hydrolysis reaction. The dehydrogenation index of NaBH₄ was calculated as 2150 mL H₂/g NaBH₄ according to the amount of NaBH₄ in the aqueous solution. There is no doubt MOFs are promising novel materials synthesized for various aims. Here, we tried to indicate its different usage areas in catalytic reactions.

Keywords: Sodium borohydride, metal organic frameworks, catalytic dehydrogenation, activation energy, kinetic parameters.

¹*Corresponding author: erturkaybuke@gmail.com

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¹ Gazi University, Faculty of Engineering, Department of Chemical Engineering, Maltepe, Ankara, Turkey

² University of St Andrews, School of Chemistry, Fife, Scotland, UK

³ Gazi University, Faculty of Engineering, Department of Chemical Engineering, Maltepe, Ankara, Turkey

* E-mail address: erturkaybuke@gmail.com

Orcid id: <https://orcid.org/0000-0001-7278-9301> Aybüke Ayşe Ertürk, 0000-0003-1047-6267 Tuğba Akkas Boynuegri, 0000-0002-7335-7583 Metin Gürü

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1. Introduction

Currently, our primary energy demand is predominantly met through the utilization of fossil fuels. However, the burning of these fossil fuels leads to the emission of undesirable greenhouse gases, mainly CO₂ and SO₂. Predictions suggest that the average global temperature could increase by approximately 1 to 4 °C before 2100 due to the continuous emission of greenhouse gases into the environment. The World Energy Outlook (WEO) 2014 estimates that, in the period following 2040, total energy demand is expected to increase by around 40%. Meanwhile, the contribution of fossil fuels to the overall energy production from various sources has decreased. Nevertheless, fossil fuels retain their role as the dominant energy source, with oil, coal, and natural gas collectively accounting for about a quarter of the world's energy requirements. Simultaneously, it is widely recognized that fossil fuels are one of the primary sources of global environmental pollution [1]. It is intuitive to seek clean energy solutions to combat climate change and reduce greenhouse gas (GHG) emissions. One of the most promising alternative energy sources is hydrogen [2]. Investigation studies to find alternative energy resources and their effective use have boosted research activities about hydrogen for two decades. The entire hydrogen chain - production, storage, distribution, final use, and cost - have still drawbacks to its practical and safe usage. Safety is an inevitable issue among them, so the chemical storage of hydrogen, especially with boron-based hydrides, has become prominent. Metal borohydrides have been a promising candidate as the carrier of hydrogen to solve the energy problem and its unwanted result, global warming. At the same time, hydrogen has been declared the energy resource for the 21st century [3].

In particular, NaBH₄ and its catalytic dehydrogenation to produce H₂ were reported to have high hydrogen storage capacity (10.7% (w/w)). Also, hydrogen and water recovery can occur by choosing the catalytic decomposition way to release H₂ from NaBH₄. Theoretically, hydrogen production from NaBH₄ is performed safely with the catalyst given in Eq.(1).



At the end of the hydrolysis of NaBH₄, the hydrogen carrier compounds provided emergence not only H₂ but also a by-product, hydrated crystalline sodium metaborate (NaBO₂). The catalytic dehydrogenation of NaBH₄ was reported as given in Eq.(2) [4].



Here, coefficient x probably changes depending on the used catalyst type and reaction conditions. There is no doubt the effect of catalysts is crucial for the dehydrogenation reactions of borohydrides [5]. On the other hand, it was stated that there is another option, thermal hydrolysis. However, it has some disadvantages, such as its low yield, 10% (by weight), and high-temperature requirements causing extra cost [6]. As a result, thermal decomposition has been barely used for hydrogen generation.

For decades, catalysts and their preparation have been the most investigated research area in chemical

reactions. Catalysts' properties have a crucial effect on reaction time, activation energy, and other reaction parameters. In addition, they are especially critical elements in allowing us to control reactions.

It was reported that the reaction of hydrogen release from metal borohydrides was efficiently carried out in the presence of the Co-based hydrogel-supported catalyst [7]. It was mentioned that CoCl_2 , NiCl_2 , CuCl_2 , and ZnCl_2 provided satisfactory results when they were used as a catalyst for hydrogen release from NaBH_4 [6, 8-10]. According to the literature, cobalt (Co) and nickel (Ni) are prevalently used metal sources to prepare the catalyst. The first reason is that their price is lower than that of ruthenium (Ru), palladium (Pd), etc. The second reason is that they show high reactivity and can be formed in different formulations [11]. These metal sources have been loaded in any materials such as $\gamma\text{-Al}_2\text{O}_3$, silica, active carbon, surfactants, alumina, zeolites, clays, and polymeric materials. It is known that not only the kinds of support materials but also preparation methods have an impact on their surface properties [9]. Apart from all these, metal-organic frameworks (MOFs) have potential as heterogeneous catalysts because they provide high surface area, tunable porosity, and diversity in metal and functional groups [12].

Metal-organic frameworks (MOFs), which are crystalline porous hybrid materials, consist of organic compounds with carboxylates or N-containing aromatic groups combined with a variety of metal ions such as chromium, zinc, copper, zirconium, aluminum, and other metals. Their most appealing attributes include well-distributed pores of varying sizes and impressive textural characteristics, such as high surface areas and pore volumes [13]. Research studies have intensively proceeded in particular novel MOF synthesis routes and their application areas, such as separation, catalysis, sensing, biomedical, and gas storage, to use MOFs' exceptional properties over the past two decades. MIL-101 has been by far the most used MOFs because of its high hydrothermal/chemical stability for catalysis involving various transition metals such as Cr [14]. Furthermore, MOFs can be produced as excellent supports suitable for constructing of composite or derived materials to improve the number of active sites and catalytic reaction stability [15-17].

Catalyst support materials are just as crucial as metal sources for catalyst preparation. These support materials play a vital role in determining the catalyst's durability, or in other words, its reusability potential. A common challenge is their production cost, making efforts to reduce expenses and enhance longevity particularly significant for these support materials.

This study selected a novel supporter material, MIL-101 (Cr), to form the catalyst. This metal-organic framework was synthesized and analyzed for specific surface area using Brunauer–Emmett–Teller (BET) Analysis. Metal sources were supplied via CoF_2 and NiF_2 . MIL-101 (Cr) supported catalysts were prepared in 3 different formulations involving 10, 20, and 30% Co-Ni co-metal sources, respectively. In this way, the impact of the metal amount in it was investigated in some ways such as forming pellet, durability, etc. After that, all three catalyst pellets were used in the hydrolysis of NaBH_4 to produce H_2 to determine the optimum one. Finally, the prepared and selected heterogeneous catalyst was employed in the NaBH_4 dehydrogenation reactions at five different temperatures for kinetic studies. We aim to identify the behavior of the chosen catalyst and carry out the experiments to obtain kinetic parameters in detail.

2. Material and Methods

2.1 Synthesis of Supporting Material of MOF

Reactants, sodium acetate (CH_3COONa , Anhydrous 99%, Cas No:127-09-3), terephthalic acid (C_6H_4 -1,4- $(\text{CO}_2\text{H})_2$, 98%, Cas No:100-21-0), and chromium (III) nitrate nonahydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99%, Cas No: 7789-02-8) were purchased from Sigma Aldrich to synthesize MIL-101 (Cr), the catalyst's support material. First, aqueous CH_3COONa aqueous solution was prepared at a concentration of 0.05 mol/L. Then, terephthalic acid and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added to this solution, respectively. This solution was stirred at 200 rpm at room temperature for 30 minutes. The mixed solution was poured into the hydrothermal reactor's pot, and its lid was closed neither tightly nor gently. The hydrothermal reactor was put in an oven, setting up to 200 °C, for 12 h. Reaction parameters were determined regarding previous publications in the literature [18]. This naturally cooled sample was divided into four centrifuge tubes, and then the aqueous part of it was drained by using centrifugation at 7,500 r/min. After that, a purification procedure was applied to the obtained green MIL-101 (Cr) powder sample in the synthesis. For this aim, deionized water, N, N-dimethylformamide (DMF, 99% Alfa-aesar, Cas No:68-12-2), and ethanol were used to wash the sample. The sample was washed twice with adequate water and dried at 150 °C for 5 hours. The same procedure was applied using DMF and ethanol to remove unreacted reactants. Finally, purified MIL-101 (Cr) powder was ready to utilize as support material.

2.2 Analysis of MOF

2.2.1 Brunauer–Emmett–Teller (BET) Analysis

Brunauer–Emmett–Teller (BET) analysis was performed via Quantachrome Instruments, Autosorb-1 to determine the specific surface area of the metal-organic framework, MIL-101(Cr). The adsorbate gas was nitrogen in this study.

2.2.2 XRD Analysis of (Cr) MIL-101

Analysis of the synthesized MIL-101 (Cr) sample was performed by XRD for confirmation. X-ray diffraction (XRD) pattern was recorded via RIGAKU X-ray diffractometer with a $\text{Cu K}\alpha$ anode ($\lambda = 0.1542 \text{ nm}$) operating at 40 kV and 30 mA.

2.3 Preparation of Co-Ni co-catalyst

CoF_2 (Sigma-Aldrich, Cas No:10026-17-2), NiF_2 (Sigma-Aldrich, Cas No:10028-18-9), stearic acid, naphthalene, and the synthesized MIL-101 (Cr) were weighted given amounts as seen in Tab.1 and put in Spex (8000-D Mixer Mill) type grinder to make them a homogeneous mixture. These pellets with 10%, 20%, and 30% metal sources were prepared by using the hydraulic press at 11 tons (CrushIR™, PIKE TECHNOLOGIES). Afterward, they were put in the oven to remove binders, stearic acid, and naphthalene

at about 80 °C. Also, preparation of 20% Co-Ni involved co-catalyst pellet was tried using additional epoxy resin to avoid pellet dispersion.

Table 1: Chemical amounts in the catalysts

No	Metal (w/w)	Source	%	MIL-101 Cr (gr)	CoF ₂ (gr)	NiF ₂ (gr)	Stearic acid (gr)	Naphthalene (gr)
1	10%			0.45952	0.07689	0.01359	0.1375	-
2	20%			0.36904	0.15378	0.02718	0.1375	-
2*	20%			0.36904	0.15378	0.02718	-	0.1375
3	30%			0.27856	0.23067	0.04077	0.1375	-

2.4 NaBH₄ Hydrolysis Reaction

NaBH₄ was provided by Sigma-Aldrich (Cas No: 16940-66-2) for dehydrogenation studies. 0.5 g of NaOH was dissolved in 50 mL of deionized water to prepare an alkaline solution at pH 12-13 and room temperature. Briefly, the amounts of used chemicals in the dehydrogenation reaction were given in Tab.2.

Table. 2: Amounts of used chemicals in the dehydrogenation reaction

Name	Amount
Catalyst	0.55 g
NaOH	0.5 g
NaBH ₄	0.1 g
Deionized H ₂ O	50 mL

NaBH₄ was added and dissolved in this solution stabilizing agent to prevent self-hydrolysis of NaBH₄. It is known that the dehydrogenation reaction of NaBH₄ occurs according to Eq.2, previously given.

First, the solution was enclosed into the reactor, and then a prepared catalyst was added to this solution to start the catalytic dehydrogenation reaction. The reactor lid was closed tightly. Hydrogen release was measured via the inverse burette system seen in Fig 1.

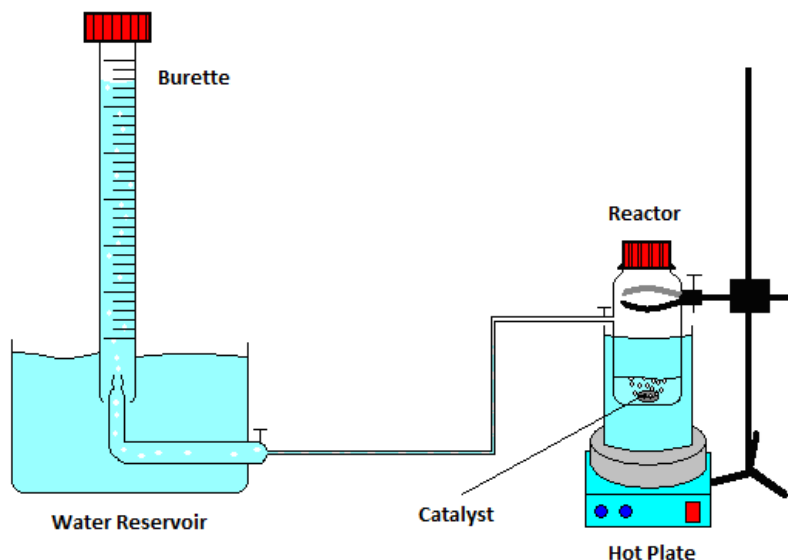


Fig 1. Inverse Burette Apparatus

2.5 Kinetic studies

Dehydrogenation reactions of NaBH_4 were performed to clarify the catalyst's kinetic properties at five different temperatures: 25, 30, 35, 40, and 45 °C. All experiments were carried out for 2 hours at a stirring speed of 250 rpm. All of these experiments occurred to find out the reaction rate order and the activation energy (E_a) of the related hydrolysis reaction by using the Arrhenius Equation as given in Eq. (3). 20% Co-Ni involved MIL-101 (Cr) supported co-catalyst was used in each experiment and releasing hydrogen amount was continuously recorded.

$$k = A \cdot e^{\frac{-E_a}{R.T}} \quad \text{Eq. (3)}$$

3. Results and Discussion

This study aims to create awareness about MOFs' prevalent utility and demonstrate MIL-101(Cr) potential usage applications as a catalyst material, specifically in dehydrogenation reactions. According to the literature, MIL-101 (Cr) is stable after long-term exposure to an aqueous solution. In other words, MIL-101 (Cr) was demonstrated in the thermodynamically stable class among metal-organic frameworks [19].

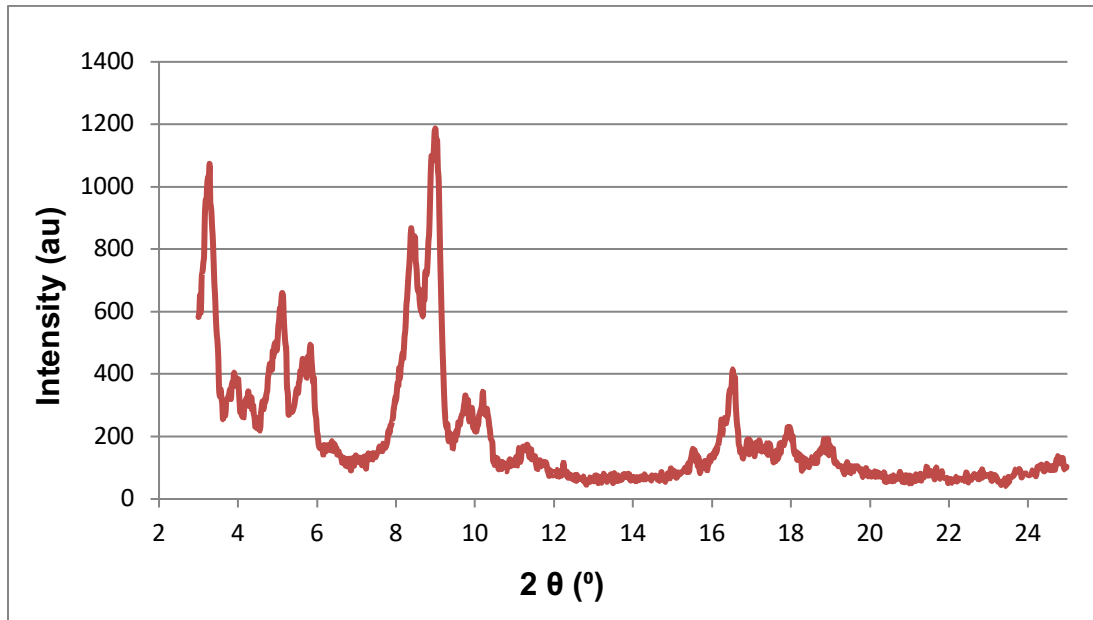


Fig 2. XRD patterns of synthesized MIL-101 Cr (XRD, RIGAKU, Cu (40 kV, 30mA))

In this study, first, the powder of synthesized MIL-101 (Cr) was analyzed by XRD to verify the synthesis. XRD pattern was obtained as given in Fig.2. The synthesized MIL-101 (Cr) was compatible with the MIL-101 (Cr) XRD model shown in the literature [20]. Fig.2 demonstrates the main characteristic diffraction peaks at $2\theta = 4-6^\circ$ and $8-10^\circ$, which belongs to MIL-101 (Cr) consistency with the literature [21]. It is known that MIL-101 (Cr) shows specific peaks between $2\theta: 0-12$ [22]. Then, the synthesized MIL-101 (Cr) specific surface area was measured and found to be $2504 \text{ m}^2\text{g}^{-1}$. This specific surface area is relatively higher than that of the previously reported, such as $2367 \text{ m}^2\text{g}^{-1}$ and $2400 \text{ m}^2\text{g}^{-1}$ [23, 24]. There is no doubt that MIL-101 (Cr) is ideal regarding the high surface area and chemical stability to use as a support material.

It has been reported that metal borohydrides can achieve an accelerated release of stored hydrogen through the use of catalysts, effectively preventing their uncontrolled self-hydrolysis [25].

Here, catalyst pellets, consisting of 10, 20, and 30% bi-metallic sources, were utilized to carry out the dehydrogenation of NaBH_4 . When the reactions were carried out using these catalysts, produced hydrogen volumes were recorded as 34, 104, and 82 mL as seen in Fig.3, respectively.

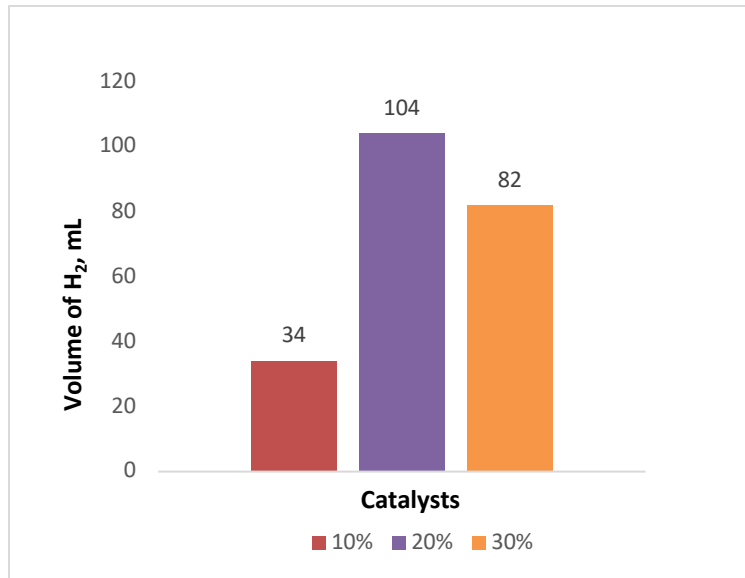


Fig 3. Produced H₂ volumes from NaBH₄ catalytic dehydrogenation

Fig.3 shows that the increase of the metal source amounts in the catalyst pellet affected negatively when it reached a specific point above 20% (w/w). Produced volumes of hydrogen versus time graphs plotted as given in Fig.4.

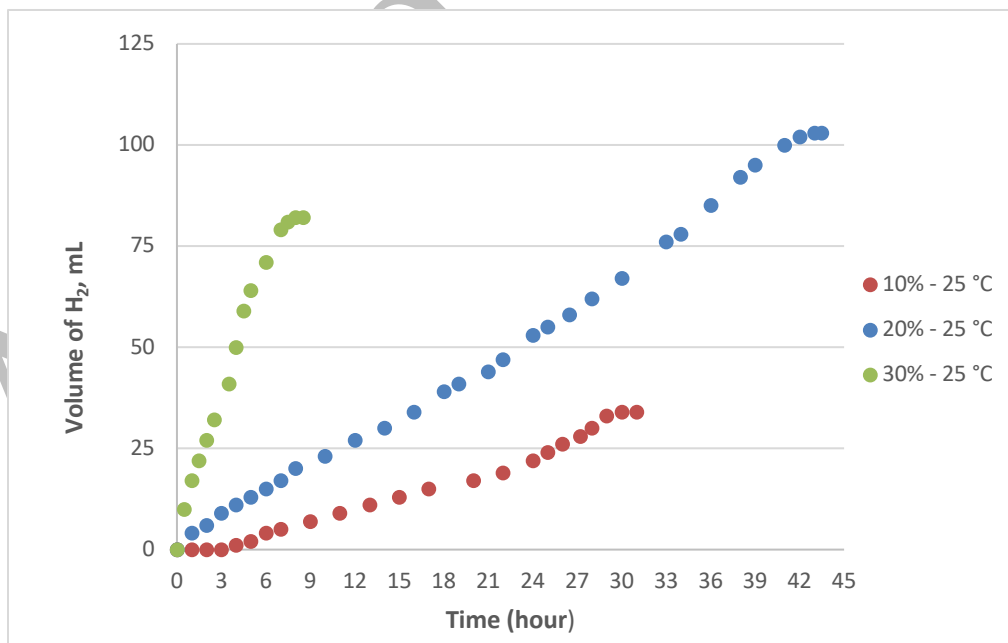


Fig 4. Volume of produce H₂ from NaBH₄ in the presence of catalyst at 25 °C (10%, 20%, 30% Co-Ni involved and bound with stearic acid)

This figure demonstrated that 34 mL, 104 mL, and 82 mL of hydrogen were released when 10%, 20%, and 30% Co-Ni consisting of catalysts were used at 25 °C to perform catalytic dehydrogenation of NaBH₄, respectively. In addition, reaction times were recorded as 30 hours, 42 hours, and 7 hours. These results were collected for the first trial of all catalysts. It was illustrated that reaction time was decreasing according to a study carried out by 30% Co-Ni consisting catalyst compared to others. There was no doubt that it happened due to the dispersion of the catalyst prepared with 30% Co-Ni ingredients and bound with stearic acid. For this reason, the option of the 30% metal source was eliminated not to provide endurance of the catalyst. Also, the selected binder changed with another alternative, such as naphthalene. According to the graphs in Fig.4, the Co-Ni metal amount was selected at 20% (w/w) to prepare the catalyst because the maximum hydrogen production was obtained via this catalyst. However, the theoretically expected volume of hydrogen was 127 mL regarding Eq. (1) if only hydrogen comes from its carrier of NaBH₄.

Dehydrogenation experiments were repeated with the catalyst pellet involving 20% Co-Ni bound with naphthalene and both epoxy resin and naphthalene at the same temperature. The released hydrogen amount versus time was demonstrated in Fig. (5). When NaBH₄ catalytic dehydrogenation reaction occurred in the presence of the catalyst pellet involving 20% Co-Ni metal source and bound via naphthalene, the produced hydrogen increased slightly from 104 to 118 mL.

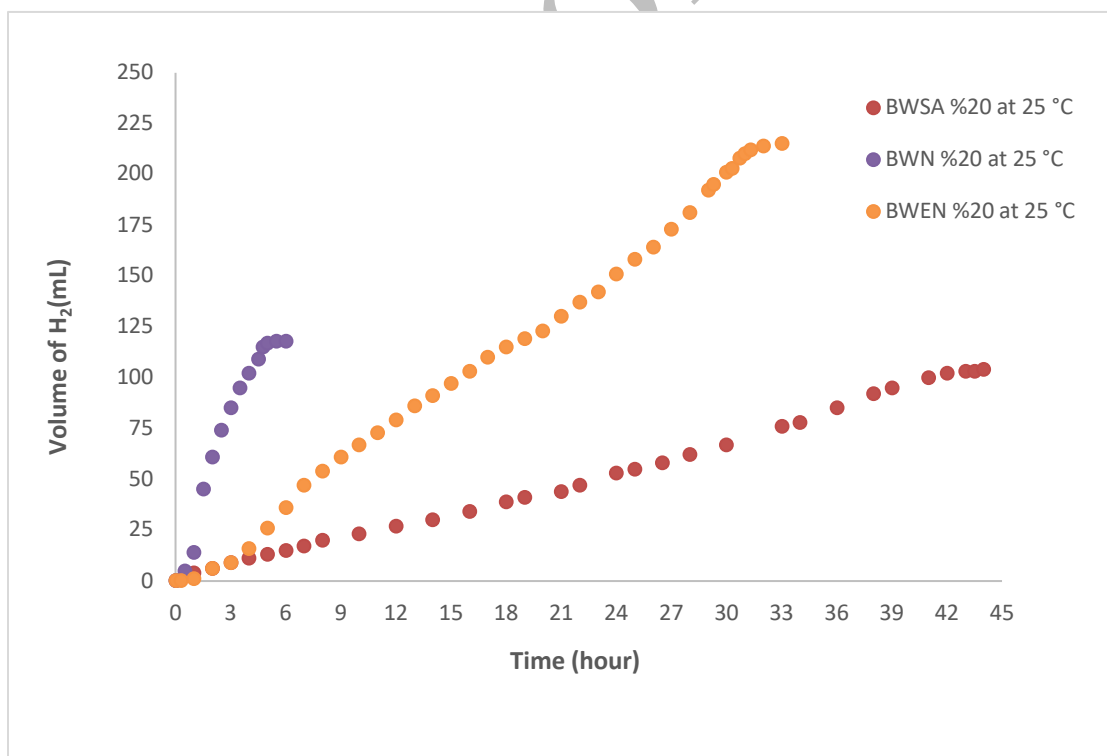


Fig 5. Volume of H₂ vs time, catalyst pellet involving 20% Co-Ni at 25 °C Bound with Stearic Acid (BWSA), Naphthalene (BWN) and Epoxy Resin - Naphthalene (BWEN)

According to our observation, the catalyst's activity increased following structural changes after its initial use. The hydrogen production underwent an approximate difference of 25 mL between the first and fourth cycles when the dehydrogenation reaction was carried out using a catalyst involving 10% metal. Notably, the dehydrogenation reaction time for these experiments, approximately 3 hours, was less than half of the time taken during the first cycle, around 6 hours [26]. The reaction was repeated ten times, and the highest volume of H₂ was measured during the 7th reaction, aligning with the findings in the literature.

The names were given for catalysts depending on the use of binder, such as stearic acid and naphthalene (BWSA and BWN, respectively). For example, the catalyst was called as BWEN because epoxy resin and naphthalene were used together as binders. The volumes of hydrogen were measured as 118 mL and 215 mL in the use of 20% Co-Ni involved catalysts, BWN and BWEN, at about 6 hours and 32 hours, respectively, as shown in Fig. (5). The optimum way to prepare a catalyst pellet was determined via these experimental studies. In other words, when the catalyst pellet was formed using only naphthalene binder, it did not preserve its shape integrity. However, when both epoxy resin and naphthalene were added as ingredients of the pellet, the previously mentioned dispersion of the pellet was prevented during the reaction. If 0.1 g NaBH₄ is used as a reactant for the catalytic dehydrogenation reaction, 255 mL hydrogen can be produced theoretically at 25 °C and atmospheric pressure according to the ideal hydrolysis reaction. Hence, the reaction yield was calculated by 85% when the experimental and theoretical data were compared in terms of amounts of produced H₂. However, an experimental error, nearly 5%, emerges because of the change in pressure when NaBH₄ is weighted at the inert atmosphere provided by GLOVE-BOX as mentioned in the literature [5]. Briefly, this reaction yield could be taken by 90%. It is possible that if the reaction temperature increases or any acidic compound is added to the reaction solution, the reaction time decrease and the yield can rise as stated in the literature [27].

When the produced hydrogen amount (No:4) compared with the results of 0.1 g NaBH₄ dehydrogenation reactions given in the literature, the measured small gap between them was changed from 15 to 35 mL, as shown in Table 3.

Table 3: Comparison of released H₂ from 0.1 g NaBH₄

No	Amount	Released H ₂ (mL)	Dehydrogenation Parameters
1	92 mg Co / g catalyst	≈250	5% NaOH, 30°C [28]
2	128 mg Co / g catalyst	247	5% NaOH, 30°C [29]
3	135.8 mg Co / g catalyst	230	1% NaOH, 35°C [5]
4	200 mg Co-Ni / g catalyst	215	1% NaOH, 25°C
5	218.5 mg Co / g catalyst	248	5% NaOH, 30°C [30]

Specifically, MOFs have attracted great interest because of their relatively large hydrogen and methane adsorption capacities in theory. However, hydrogen adsorption requires specific pore size and pressure at room temperature [31]. For this reason, hydrogen uptake of the prepared MOFs supported catalyst pellets seems impossible under the selected conditions. In other words, their characteristics can cause an ignorable amount of hydrogen retention in this study.

20% Co-Ni-loaded catalysts showed the maximum hydrogen production. Thus, the dehydrogenation reaction was performed with this in the following parts. Although preliminary trials proceeded over a long period to determine the proper catalyst, all experimental studies were carried out in two hours for kinetic calculations. To determine the kinetic parameters, dehydrogenation reactions of NaBH_4 occurred at 25, 30, 35, 40, and 45 °C for 2 hours and at a stirring speed of 250 rpm. Released H_2 volumes at these five temperatures were demonstrated clearly in Fig.6. Also, the graph, C_A versus time, was plotted using kinetic study results, as given in Fig.7.

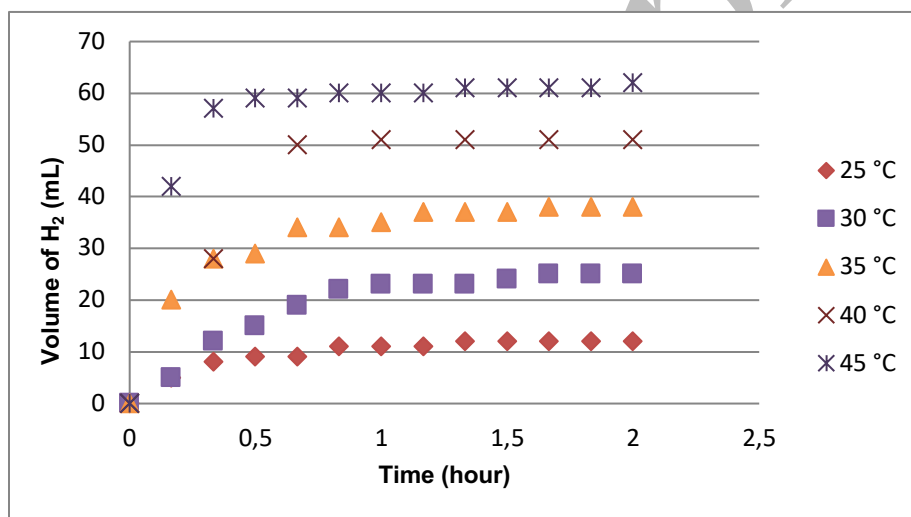


Fig 6. Volume of produce H_2 from NaBH_4 in the presence of catalyst at 25, 30, 35, 40 and 45 °C

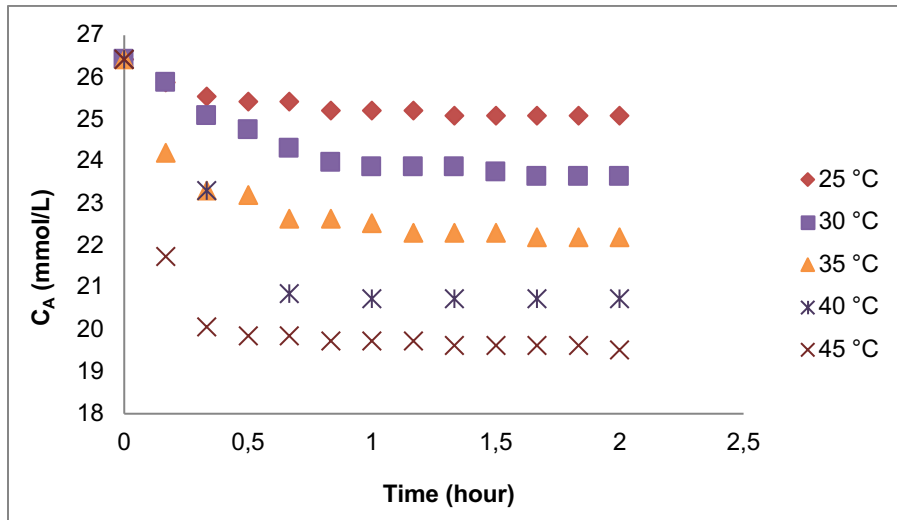


Fig 7. The effect of temperature on dehydrogenation reaction of NaBH₄ concentration

Literature has proved that H₂ production linearly increases depending on the initial concentration of NaBH₄ [7, 28]. In other words, the hydrogen production rate is independent of the initial concentration of NaBH₄. Briefly, the reaction depends on the catalyst rather than the concentration of NaBH₄. As a result, the catalytic dehydrogenation reaction order was assumed to be zero-order concerning the initial concentration of NaBH₄. Here, the reaction rate constant was calculated with the assumption of zero-order kinetics. As seen in Fig.8, the lnk versus 1/T graph was drawn to calculate the activation energy of the catalytic dehydrogenation reaction of NaBH₄.

In Eq.(4), n denotes the reaction order, and this equation was rewritten (Eq.(5)) to conform to zero-order kinetics. Integral method calculations also supported the rate order acceptance.

$$\frac{dC_A}{dt} = kC_A^n \quad \text{Eq. (4)}$$

$$(C_{A0} - C_A) = kt \quad (n=0) \quad \text{Eq. (5)}$$

The observed reaction rate constants were calculated by using Eq. (5). The graph, lnk versus 1/T was plotted as seen in Fig.8.

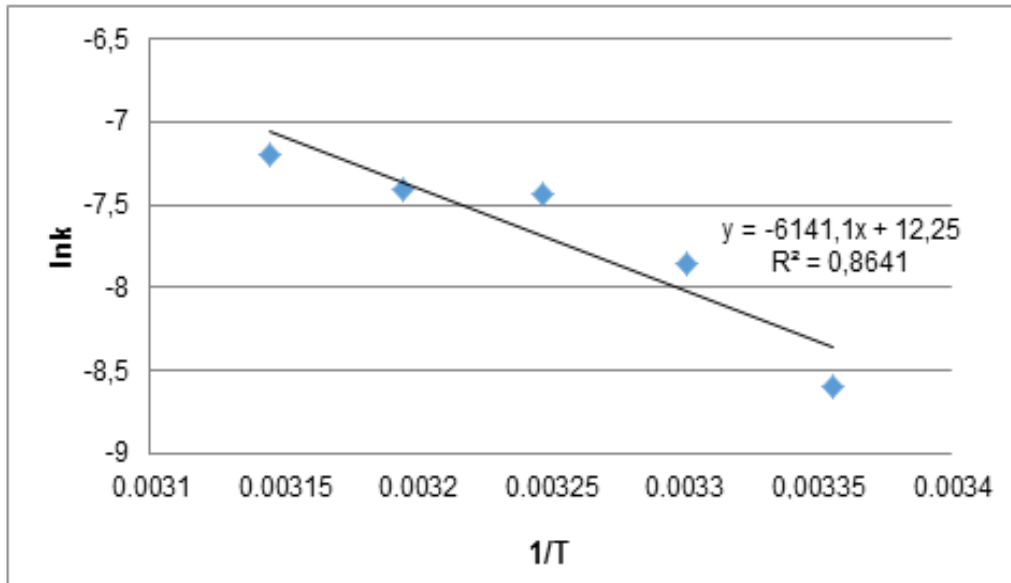


Fig 8. $\ln k - 1/T$ graph for the NaBH_4 dehydrogenation reaction

When Eq.(3) was arranged, the expression formed as seen in Eq.(6)

$$\ln k = \ln A - \frac{E_a}{R.T}$$

The activation energy was calculated via the slope of this graph shown in Fig.8. Thus, the observed activation energy was determined as 51.06 kJ/mol. This value is relatively lower than previously reported ones in the literature [5, 10]. However, the lowest activation energy was reported, 28.6 kJ/mol, for hydrogen generation from NaBH_4 while using different types of catalysts involving Co-Co metal sources [32].

When the Arrhenius Equation was arranged by using the E_a value, its formula transformed the given equation, as seen below. A constant could be calculated by using this expression.

$$k = A \cdot e^{\frac{-E_a}{R.T}} \quad \text{Eq. (6)}$$

In this equation, E_a and constant A were calculated as 51.06 kJ/mol and 16.6×10^{-4} at 25 °C, respectively. E_a value was relatively lower than previously reported ones in literature [5, 9].

4. Conclusions

This paper aims to achieve the optimal production of hydrogen from NaBH_4 and enhance the catalyst's durability during the dehydrogenation reaction by using a catalyst pellet containing 20% CoF_2 and NiF_2 as co-metal suppliers, along with a binder comprising both naphthalene and epoxy resin. This stable material holds promise as a potential candidate for a catalyst support material, ensuring longevity.

Here, dehydrogenation reactions of NaBH_4 were carried out at five different temperatures to investigate of

kinetic parameters. MIL-101 (Cr) supported heterogeneous catalyst was prepared using $\text{CoF}_2\text{-NiF}_2$ metal sources and was used to figure out the hydrogen release characteristic of NaBH_4 in this study. The dehydrogenation index of NaBH_4 was calculated as 2150 mL $\text{H}_2/\text{g NaBH}_4$ according to the amount of NaBH_4 in the aqueous solution. In addition, the reaction rate order was accepted and proved to be zero, and the activation energy was calculated as 51.06 kJ/mol. To sum up, this novel catalyst has great potential, especially for the generation of hydrogen from metal borohydrides. Here, we tried to indicate MOFs' different usage areas in catalytic reactions.

In brief, metal borohydrides have been considered leading contenders for hydrogen storage in energy generation. Currently, practical application in vehicle transportation has been hindered by certain drawbacks such as cost, distribution, and by-product recovery. Nonetheless, in the short term, they will likely find utility in portable devices requiring continuous, relatively modest energy.

Conflict of interest

The authors declare that they have no conflict of interest in this work.

5. References

- [1] A. Hassan. S. Z. Ilyas. A. Jalil, Z. Ullah, *Environmental Science and Pollution Research* 28 (2021) 21204.
- [2] F. Mneimneh. H. Ghazzawi. M. Abu Hejjeh. M. Manganelli, S. Ramakrishna, *Energies* 16 (2023) 1368.
- [3] B. Johnston. M. C. Mayo, A. Khare, *Technovation* 25 (2005) 569.
- [4] U. B. Demirci, P. Miele, *Comptes Rendus Chimie* 12 (2009) 943.
- [5] T. Akkaş, G. Metin, *Isı Bilimi ve Tekniği Dergisi* 41 (2021) 1.
- [6] T. A. Boynuegri. A. F. Karabulut, M. Guru, *Journal of Electronic Materials* 45 (2016) 3949.
- [7] T. A. Boynuegri, M. Gürü, *International Journal of Hydrogen Energy* 42 (2017) 17869.
- [8] Ç. Çakanyıldırım, M. Gürü, *Renewable Energy* 34 (2009) 2362.
- [9] Ç. Çakanyıldırım, M. Gürü, *Renewable Energy* 35 (2010a) 839.
- [10] Ç. Çakanyıldırım, M. Gürü, *Renewable Energy* 35 (2010b) 1895.
- [11] S. Sagbas, N. Sahiner, *International Journal of Hydrogen Energy* 37 (2012) 18944.
- [12] A. Corma. S. Zones, J. Cejka, *Zeolites and catalysis: synthesis, reactions and applications*, John Wiley & Sons 2010.
- [13] S. Bhattacharjee. C. Chen, W.-S. Ahn, *Rsc Advances* 4 (2014) 52500.
- [14] E. Niknam. F. Panahi. F. Daneshgar. F. Bahrami, A. Khalafi-Nezhad, *ACS omega* 3 (2018) 17135.
- [15] Y. Qin. J. Guo, M. Zhao, *Transactions of Tianjin University* 27 (2021) 434.
- [16] C. Wang. J. Kim. J. Tang. M. Kim. H. Lim. V. Malgras. J. You. Q. Xu. J. Li, Y. Yamauchi, *Chem* 6 (2020) 19.
- [17] H. Konnerth. B. M. Matsagar. S. S. Chen. M. H. Pechtl. F.-K. Shieh, K. C.-W. Wu, *Coordination Chemistry Reviews* 416 (2020) 213319.
- [18] H. Zhao. Q. Li. Z. Wang. T. Wu, M. Zhang, *Microporous and Mesoporous Materials* 297 (2020) 110044.

- [19] N. C. Burtch. H. Jasuja, K. S. Walton, Chemical reviews 114 (2014) 10575.
- [20] Z. Liu. B. Zhao. L. Zhu. F. Lou, J. Yan, Materials 13 (2020) 195.
- [21] F. Liu. S. Song. G. Cheng. W. Xiong. L. Shi, Y. Zhang, Adsorption Science & Technology 36 (2018) 1550.
- [22] D. Y. Hong. Y. K. Hwang. C. Serre. G. Ferey, J. S. Chang, Advanced Functional Materials 19 (2009) 1537.
- [23] E. K. Ekinci, Gazi University Journal of Science Part C: Design and Technology 5 (2017) 178.
- [24] A. Henschel. K. Gedrich. R. Kraehnert, S. Kaskel, Chemical Communications (2008) 4192.
- [25] H. N. Abdelhamid, International Journal of Hydrogen Energy 46 (2021) 726.
- [26] İ. Ar. Ö. U. Güler, M. Gürü, International Journal of Hydrogen Energy 43 (2018) 20214.
- [27] A. Balbay, Ö. Şahin, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 36 (2014) 1166.
- [28] N. Sahiner. S. Butun, T. Turhan, Chemical Engineering Science 82 (2012) 114.
- [29] N. Sahiner. O. Ozay. E. Inger, N. Aktas, Applied Catalysis B: Environmental 102 (2011) 201.
- [30] F. Seven, N. Sahiner, Journal of Applied Polymer Science 131 (2014).
- [31] O. M. Yaghi. M. J. Kalmutzki, C. S. Diercks, Introduction to reticular chemistry: metal-organic frameworks and covalent organic frameworks, John Wiley & Sons 2019.
- [32] D. D. Tuan. E. Kwon. J.-Y. Lin. X. Duan. Y.-F. Lin, K.-Y. A. Lin, Chemical Papers 75 (2021) 779.