





Optimization of hydrogen generation rate with Co/MMT catalyst from NaBH₄ using Box-Behnken method

Box-Behnken metodu kullanılarak NaBH₄'ten Co/MMT katalizörü ile hidrojen üretim hızının optimizasyonu

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Received/Geliş Tarihi: 28.09.2022
Accepted/Kabul Tarihi: 09.03.2023

Revision/Düzeltilme Tarihi: 07.03.2023

doi: 10.5505/pajes.2023.34919
Research Article/Araştırma Makalesi

Abstract

In this study, a Co/MMT catalyst was synthesized by pillaring method using montmorillonite (MMT) as a support material for hydrogen production by hydrolysis reaction from sodium borohydride (NaBH₄) solution. N₂ sorption, XRD, SEM-EDS, and FTIR spectroscopy techniques were used for catalyst characterization. To optimize the amount of hydrogen obtained as a result of the hydrolysis reaction, the NaBH₄ concentration (0.3-0.5 M), the sodium hydroxide (NaOH) concentration (0.3-0.5 M), the amount of catalyst (20-50 mg) and the reaction temperature (30-50 °C) were investigated. The optimal conditions obtained from the Box-Behnken analysis were 50 °C, 0.33 M NaBH₄, 39 mg catalyst, 0.46 M NaOH, and the maximum reaction rate (hydrogen production) was 2328 mL min⁻¹ gcat⁻¹ at standard temperature and pressure (298K, 1atm). According to the analysis of variance, it was found that all parameters had a significant effect on the hydrogen production rate.

Keywords: Hydrogen, Sodium borohydride, Montmorillonite, Box-Behnken.

Öz

Bu çalışmada, destek malzemesi olarak Montmorillonit (MMT) kullanılarak sütunlama yöntemiyle Co/MMT katalizörü, sodyum borhidür (NaBH₄) çözeltisinden hidroliz reaksiyonu ile hidrojen üretimi için sentezlenmiştir. Katalizör karakterizasyonu için N₂ sorpsiyon, XRD, SEM-EDS ve FTIR spektroskopi teknikleri kullanılmıştır. Hidroliz reaksiyonu sonucunda elde edilen hidrojen miktarını optimize etmek amacıyla, NaBH₄ konsantrasyonu (0.3-0.5 M), sodyum hidroksit (NaOH) konsantrasyonu (0.3-0.5 M), katalizör miktarı (20-50 mg) ve reaksiyon sıcaklığı (30-50 °C) gibi parametrelerin etkisi incelenmiştir. Box-Behnken analizinden elde edilen optimal koşullar 50 °C, 0.33M NaBH₄, 39 mg katalizör, 0.46 M NaOH olup, maksimum reaksiyon (hidrojen üretim) hızı standart sıcaklık ve basınç koşullarında (298K, 1atm) (2328 mL dak⁻¹ gcat⁻¹ olarak bulunmuştur. Varyans analizine göre tüm parametrelerin hidrojen üretim hızı üzerinde önemli bir etkisi olduğu belirlenmiştir.

Anahtar kelimeler: Hidrojen, Sodyum borhidür, Montmorillonit, Box-Behnken.

1 Introduction

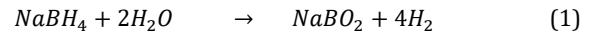
Today most of the energy used in the world is derived from fossil fuel sources. But, the burning of fossil fuels has hazardous effects such as greenhouse gases and acid rain that harm the environment and people. Therefore, it is very important to increase the share of renewable energy in global energy use. [1],[2].

Hydrogen is considered a promising alternative energy because it is non-toxic, environmentally friendly, can be obtained from a variety of sources, and is relatively inexpensive [3]. Solid materials-based hydrogen storage technologies are recognized as one of the best options designed to realize a hydrogen-based energy system [4].

Chemical hydrides are convenient materials that generate hydrogen by using water. They generally have a high gravimetric energy density. Also, chemical hydrides are stable for long terms [5]. The thermodynamics and kinetics of the hydrogenation-dehydrogenation of borohydrides should be applicable at the desired operating temperatures and pressure conditions. In this context, sodium borohydride (NaBH₄) seems

to be a promising candidate due to its high hydrogen (10.8%) content. [4,6].

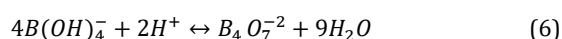
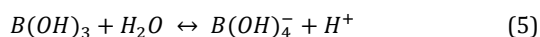
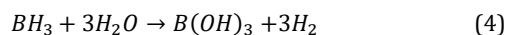
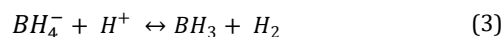
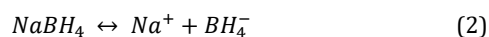
Equation (1) shows the hydrolysis reaction of NaBH₄. According to equation (1), the hydrolysis of 1 mole of NaBH₄ in water releases 4 moles of hydrogen [5].



In the basic hydrolysis reaction described above, the rate of hydrolysis of NaBH₄ in an aqueous medium at room temperature is quite slow. To increase the reaction rate, suitable catalysts must be added to the reaction medium. To this end, it was observed that platinum, ruthenium, and noble metal catalysts with different support forms and loadings significantly increased the hydrolysis rate of NaBH₄. But, the high cost and scarcity of these noble metals limit their use as catalysts. Therefore, it is of great interest to develop catalysts made of non-precious metals that are found in larger quantities on Earth and have comparable efficiency to their counterparts to replace these precious metals [7]. In recent years, catalysts containing cobalt have been synthesized for the hydrolysis reaction of NaBH₄, especially at low costs with high catalytic activity [8].

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In the case studies, the possible main reaction mechanism for NaBH₄ hydrolysis is explained as follows:



The rate of the reaction is generally increased by the use of a catalyst. The hydrolysis of NaBH₄ is negatively affected by the decrease in proton concentration, so that the hydrogen ions in the MMT basic structure are released to the environment as protons, increasing the ability to generate hydrogen from NaBH₄ by hydrolysis [9].

The catalytic activity of heterogeneous solid catalysts decreases due to agglomeration of metals [3]. This is because the surface area of solid catalysts is reduced due to the agglomeration. Metal particle agglomeration can be prevented by loading these metals onto a suitable support material. In this case, the catalytic activity can be increased. For active metals, the support material provides a larger and more suitable surface area. In addition, a more homogeneous distribution of the metals is ensured in porous support materials. Clay minerals, metal oxides, activated carbon, silica, and alumina are the most commonly used support materials. [10]. Clays are composed of two-dimensional layers: tetrahedral (SiO₄) and octahedral (Al₂O₃). MMT clay is also referred to as a subclass of smectites from the soft phyllosilicate group [11]. The basic chemical formula of MMT is [(Na, Ca)_{0.33}(Al, Mg)₂(Si₄O₁₀) (OH)₂-nH₂O] and consists of two-dimensional layers that are electrostatically aligned and have a regular van der Waals cavity. Due to its high durability, hardness, optical clarity, and permeability, MMT clay is preferred over conventional additives and fillers [12].

The hydrolysis reaction of NaBH₄ for hydrogen production is a process in which reaction media such as catalyst activity, reactant concentrations, stabilizer concentration, and reaction temperature all play a significant role. All these limitations affect the practical application of the hydrolysis performance of NaBH₄. Statistical optimization can be used to determine the binary effect of reaction medium and catalyst performance on the hydrogen generation rate and yield of NaBH₄ hydrolysis reaction. The response surface methodology (RSM) technique allows both analysis and modeling of a sample experimental system using mathematical and statistical techniques. With this application of statistical experimental designs, all possible combinations of parameters affecting the system are measured, but still, the number of experiments in these experimental designs is high [6]. Among the advantages of the Box-Behnken design is the fact that they are spherical designs and that the factors only need to be performed on three levels. Also, the designs are rotatable or nearly rotatable. Another advantage of the Box-Behnken design is that it does not include combinations where all factors are at their highest or lowest levels at the same time. Thus, these experimental designs are useful to avoid experiments performed under extreme conditions that could lead to unsatisfactory results [13].

MMT was used as a catalyst support for various reactions such as hydrolysis [9], reduction [14] dehydration [15] and phenon

[16]. In this study, MMT clay was used as a resistance support material to increase the catalytic activity and reusability of the catalyst. The synthesized cobalt catalyst was used for the production of hydrogen from NaBH₄ in an alkaline solution. During hydrogen release from NaBH₄, the effects of NaBH₄ concentration, NaOH concentration, supported catalyst amount, and hydrolysis reaction temperature were studied. The optimal parameters for the hydrolysis reaction of NaBH₄ and their interactions were determined by the Box-Behnken (BB) optimization method. In addition, the synthesized catalyst was characterized by XRD (X-Ray Diffraction), SEM (Scanning Electron Microscopy), and surface area analysis using the BET method, and FTIR (Fourier Transform Infrared Spectroscopy) techniques.

2 Materials and method

2.1 Materials

Cobalt salts (Cobalt (II) chloride hexahydrate (>97%)), sodium hydroxide (>98%), and Montmorillonite K10 clay powder were supplied by Sigma-Aldrich (Taufkirchen, Germany). Sodium borohydride powder (>98%) was purchased from Acros Organics.

2.2 Catalyst synthesis

A Montmorillonite (MMT) was used as a support material for the preparation of the cobalt-based supported catalysts by the pillaring method [17]. MMT clay was stirred with water overnight at 25 °C before using for swelling, then solid was obtained by filtrating. 0.05 M of NaOH and CoCl₃ solutions were prepared for loading 10% Co onto the support clay. NaOH solution was added to the Co ion solution drop by drop and the prepared solution was performed in the 90 °C water bath for 24 h. This solution was added to clay dropwise and stirred at 25 °C for 36 h. After mixing obtained solid was filtrated under a vacuum and washed with distilled water several times to remove unpurified materials. The obtained solid was dried at 60 °C then calcinated at 400 °C for 4 hours.

2.3 Catalysts characterization

The structural morphology, crystallinity, and composition of the surface characteristics of catalysts and MMT were analyzed. Tristar 3020 (Micromeritics, Norcross, GA, USA) was used for evaluated N₂ sorption characteristics at 77 K. Initially, degassed conditions were applied at 90 °C for 1h and then at 300 °C for 24h under vacuum before measuring. The Brunauer-Emmett-Teller method (BET) was used for the calculating of surface properties.

X-ray diffraction (XRD) patterns were recorded using the XRD D8 Advance powder diffractometer (Rigaku Ultima II). The samples were scanned in a range of 2θ = 5-80° at a scan rate of 1° min⁻¹. The accelerating voltage was 40 kV and the applied current was 15 mA.

The morphology and surface composition of the catalysts and MMT were analyzed using the SEM -benchtop stage microscope with an accelerating voltage of 15 kV and energy dispersive spectroscopy (EDS) analysis. Doped Co²⁺ ions distribution on the heterogeneous clay surface was recorded with EDS mapping.

FT-IR analyses were performed using the ThermoScientific Nicolet IS10 FT-IR equipped with a universal ATR sampling accessory. ATR-FT-IR Spectra were acquired in the spectral range 4000-650 cm⁻¹ with a resolution of 4 cm⁻¹ for 64 scans.

2.4 The catalytic activity

The practical investigation of the activity of the synthesized catalysts in the reaction for hydrogen production from the hydrolysis of NaBH₄ was performed at different reaction conditions. Initially, a selected amount of the catalyst (20-50 mg) and NaBH₄ (0.3-0.5 g) was added to a 150 mL jacketed reactor. The reactor temperature was controlled with a circulating water bath.

The contents of the reactor at constant temperature were stirred with a magnetic stirrer at 400 rpm. The hydrogen produced during the experimental process was recorded. The water displacement method was used for the determination of the volume of the produced hydrogen. The hydrogen generation rate (HGR) was evaluated from the hydrogen volume as a function of time and the dosage of the catalyst used for the reaction [18].

To optimize reaction parameters for the hydrolysis reaction over NaBH₄ using MMT-supported cobalt catalysts, the effects of catalyst dosage (20-50 mg), initial NaBH₄ concentration (0.3-0.50 M), temperature (30-50 °C), and NaOH concentration (0.3-0.5 M) were investigated using a series of values obtained with Minitab 17 statistical software. All of the experiments were conducted in duplicate under identical conditions and the results are reported as an average value.

2.5 The Box-Behnken experimental design

Reaction conditions for hydrogen generation rate (HGR) were optimized with four independent variables: Hydrolysis reaction temperature, reactant (NaBH₄) concentration, stabilizer (NaOH) concentration, and catalyst amount. For the optimization experiment of HGR parameters with the response surface method, a Box-Behnken experimental design consisting of 4 factors and 27 experimental points was used.

The second-order polynomial model equation recommended for determining the value of the response (Y: HGR) is shown in equation 7.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 \quad (7)$$

Statistical analysis of the data was performed using the ANOVA test with a 95% confidence interval.

The data obtained from the experiments were analyzed using the Box-Behnken design method (BB) to determine the main parameters of the NaBH₄ [19] hydrolysis reaction. The ranges of the variables used are given in Table 1. These levels were chosen from similar studies in literature [9,20,5],

Table 1. Experimental design parameters.

Symbols	Parameters	Levels	-1	0	1
A	Temperature		30	40	50
B	NaBH ₄ concentration		0.3	0.4	0.5
C	Catalyst amount		20	35	50
D	NaOH concentration		0.3	0.4	0.5

3 Results and discussion

3.1 Characterizations

The XRD results of pure MMT clay and Co/MMT catalyst are shown in Figure 1. Characteristic patterns of MMT at (2θ)

around; 9.08° with the chemical formula of SiO₂ indicating the hexagonal zeolite (reference code: 98-008-4802), 12.37° tetragonal zeolite (reference code: 98-004-2211), 26.81° hexagonal quartz (98-007-9711) [9].

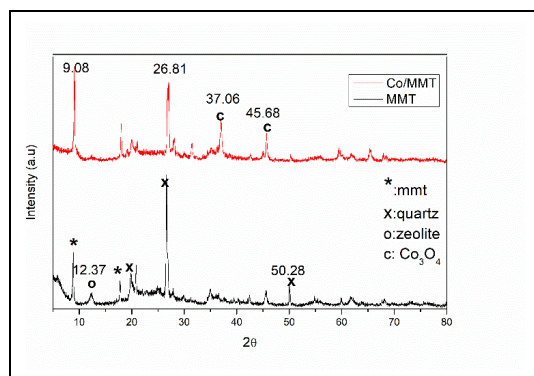


Figure 1. XRD patterns of MMT and Co/MMT catalyst.

The result shows different XRD patterns with the loading of the Co particles onto MMT. It can be seen that the peak at (2θ) around 37.06°, 45.68° with the chemical formula Co₃O₄ cubic cobalt dicobalt(III) oxide (reference code: 98-006-3267) observed after treatment with cobalt impregnation. Peak at 12.37° was disappeared after treatment. In other words, the MMT structure involves an amorphous and crystalline structure formation due to the disruption of the crystal structure, and there are still some peaks after the impregnation of Cobalt onto MMT.

SEM Analysis was performed to gain more insight into the morphological characteristics of MMT clay and Co/MMT catalyst. SEM images of MMT and Co/MMT catalyst are shown in Figure 2. The surface morphology of pure MMT changing. It can be seen significantly after Cobalt loading and it becomes a more homogeneous form. It can also be observed that the MMT surface is nearly covered by the Co particles completely.

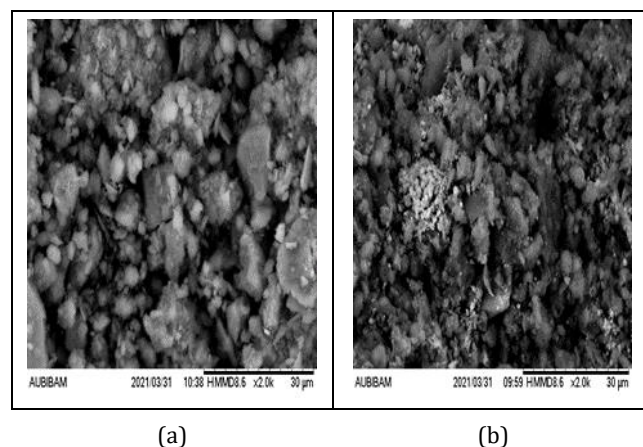


Figure 2(a): SEM analysis of MMT. (b): Co/MMT catalyst.

Energy dispersive spectroscopy (EDS) is most commonly used for qualitative analysis of materials, but can also provide semi-quantitative results.

According to the EDS analysis shown in Table 2, silica and alumina are the major component of MMT and cobalt was successfully loaded to the montmorillonite. Analysis EDS has shown that cristobalite-rich regions where only Si and O peaks are observed contain higher amounts of Co²⁺ than pure montmorillonite.

Table 2. EDS map sum spectrum of MMT and catalyst.

Element	MMT (% wt)	Co/MMT (%wt)
O	56.45	41.17
Al	6.63	4.76
Si	32.87	20.32
Mg	0.93	0.58
K	1.00	0.72
Fe	1.91	1.75
Na	0.21	11.29
Co	-	18.61
Cl	-	0.79
Total	100.00	100.00

Figure 3 shows the BET isotherms of pure MMT and Co/MMT. According to the IUPAC classification, the characteristics of adsorption-desorption isotherms of catalysts correspond to the type IV [21]. Table 3 shows the results in terms of surface area, pore volume and pore size of MMT and Co/MMT catalysts. The values obtained for the pore size ranged from 4.97 to 6.88 nm. According to Thomes et al. 2015, these values indicate that the synthesized catalyst has a mesoporous sample structure [21]. The pore size distributions of the samples were determined from adsorption using the Barrett-Joyner-Halenda (BJH) method, and the pore size distributions of MMT and Co/MMT catalysts are shown in Figure 3(c)-(d). The sharpness of the desorption branches is indicative of the narrow mesopore size distribution. It is common for particles with smaller pores to also have a larger specific surface area, but the surface area of a gram of particle also depends on the number of pores in that particle, i.e., its porosity. A particle can have very small pores, but only a small number of pores and therefore a small specific surface area [22].

Table 3. BET analysis results of the samples.

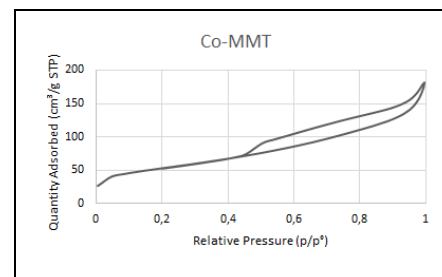
	BET Surface Area (m ² /g)	Pore Volume (m ³ /g)	Average Pore size (nm)
MMT	230.4	0.2863	4.97
Co-MMT	186.6	0.2763	6.88

In Table 3, the BET surface area of pure MMT was reported to be 230.4 m²/g. The surface area of Co/MMT, which is 186.6 m²/g, is lower than that of pure MMT. The result is related to the fact that the interaction of cobalt with the substrate surface blocks the pores of MMT due to the metal loading. Another reason is that the pores in pure MMT are filled with Co and ion impregnation. However, the average pore size of Co/MMT increased significantly with the addition of metal.

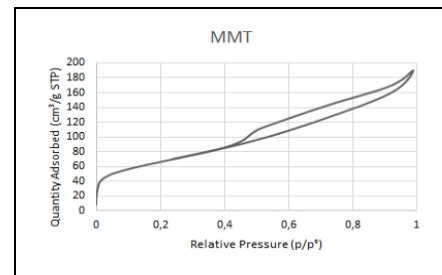
The FTIR spectrum of untreated MMT and Co/MMT samples is shown in Figure 4. The main functional groups such as Si-O and OH⁻ can be seen in the FTIR spectra of both the unmodified clay and the cobalt-loaded clay. The Si-O tensile vibrations of the MMT clay layered silicates were observed at about 1023 cm⁻¹ [23],[24]. After cobalt loading and heat treatment, the density of the band representing OH⁻ bending vibrations at ~910 cm⁻¹ and 885 cm⁻¹ was preserved. The presence of absorption bands around 685 cm⁻¹ is the result of stretching vibrations of the metal oxide in the octahedral (Co-O) group complex of the cobalt phase [25].

3.2 Optimization study

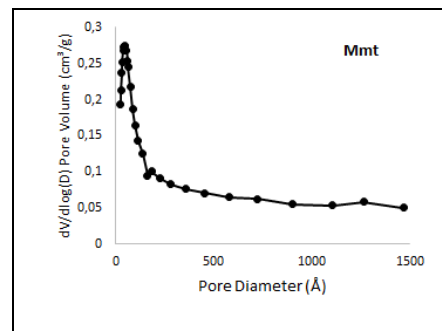
The Box-Behnken (BB) method was used to optimize the experimental parameters. This method was preferred to minimize the energy and chemical costs of the experimental studies.



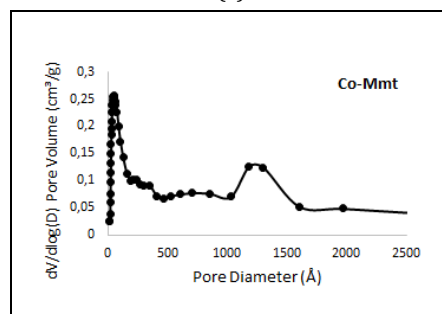
(a)



(b)



(c)



(d)

Figure 3. BET isotherm of MMT. (a): and (b): Co/MMT catalyst. (c): BJH Pore size distribution of MMT. (d): BJH Pore size distribution of MMT catalyst.

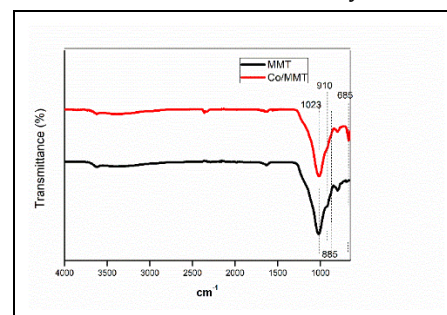


Figure 4. FTIR spectrum of raw MMT and Co/MMT catalyst

Four parameters of the reaction for hydrogen production from NaBH₄ were considered for the optimization, namely the reaction temperature (T), the concentration of the reactant (NaBH₄), the amount of the catalyst, and the concentration of the stabilizer (NaOH). The conditions of the parameters performed and the hydrogen generation rate (HGR) data obtained from the experiments are shown in Table 4. The responses of the experiments performed with four independent parameters to the model were evaluated using the Minitab 17 program. The equation of the hydrogen production rate regression model with the data from BB is as follows:

$$\begin{aligned} \text{HGR} = & -11762 + 88.4 T + 30690 \text{ NaBH}_4 \\ & + 38.0 \text{ Catalyst} + 15026 \text{ NaOH} \\ & - 0.245 T * T - 27324 \text{ NaBH}_4 \\ & * \text{NaBH}_4 - 1.378 \text{ Catalyst} \\ & * \text{Catalyst} - 26085 \text{ NaOH} * \text{NaOH} \\ & - 299.3 T * \text{NaBH}_4 + 1.158 T \\ & * \text{Catalyst} + 209.6 T * \text{NaOH} \\ & + 71.2 \text{ NaBH}_4 \\ & * \text{Catalyst} - 880 \text{ NaBH}_4 * \text{NaOH} \\ & - 25.9 \text{ Catalyst} * \text{NaOH} \end{aligned} \quad (8)$$

Positive signs in front of the parameters indicate that there is a synergistic effect. As you can see in equation. (8), there are significant interactions between the individual parameters. All of the parameters studied in the experiment resulted in an increase in HGR. The statistical significance of the model was examined using analysis of variance (ANOVA). The effects of the input parameters and interactions on the response are presented in Table 5. The p values that are lower than 0.05 indicate that the model and the associated terms are

statistically significant [26]. The F value of the model is 30.72 and P is 0.000, indicating that the model is significant. Temperature, NaBH₄ amount, NaOH concentration and catalyst amount were found to be significant parameters for HGR (Table 5). In addition, NaBH₄*NaBH₄, catalyst*catalyst, NaOH*NaOH, T*NaBH₄, T*catalyst, T*NaOH were significant square and interaction values (P<0.05).

The high R² coefficient indicates a satisfactory fit of the quadratic model to the experimental data. The purpose of the adjusted R² value is to analyze the adequacy and fit of the model. The adjusted R² value fits the R² value to the sample size and to the number of terms in the model. The high value of the adjusted R² (0.9412) indicates a high correlation between the experimental and predicted values [26]. The correlation coefficient (R²) of the developed model BB is 0.9729, which shows that it is a suitable model where the unique difference between R² and Adj and the model is remarkable.

3.3 Effect of reaction parameters on HGR

The maximum HGR yield (2508.71 mL/min gcat) from the experiments was obtained at the highest extraction temperature (50 °C). However, the lowest HGR (320.46 mL/min gcat) was obtained at the lowest reaction temperature (30 °C). When the NaBH₄ concentration was increased from 0.3 to 0.5, the HGR decreased from 850.51 to 757.60 mL/min gcat under the same conditions. Increasing the amount of catalyst from 20 to 50 mg under the same conditions resulted in an increase in HGR from 1485.79 to 2181.82 mL/min gcat. Improving the NaOH concentration from 0.3 to 0.5 also improved the HGR yield from 850.51 to 1065.60 mL/min gcat.

Table 4. Experimental HGR results.

Run Order	T	NaBH ₄	Catalyst	NaOH	HGR (mL/min g cat)
1	40	0.3	35	0.3	850.51
2	40	0.4	35	0.4	1428.57
3	50	0.4	35	0.3	1369.44
4	30	0.5	35	0.4	551.22
5	30	0.3	35	0.4	320.46
6	40	0.3	35	0.5	1065.60
7	30	0.4	50	0.4	371.64
8	30	0.4	35	0.3	436.74
9	30	0.4	35	0.5	371.94
10	40	0.4	50	0.5	1092.65
11	50	0.3	35	0.4	2508.71
12	40	0.5	35	0.5	937.50
13	40	0.5	20	0.4	583.17
14	40	0.4	20	0.5	1040.41
15	50	0.4	35	0.5	2142.86
16	40	0.4	35	0.4	1462.93
17	40	0.3	20	0.4	918.84
18	40	0.4	35	0.4	1439.48
19	30	0.4	20	0.4	370.23
20	40	0.4	20	0.3	744.97
21	40	0.5	35	0.3	757.60
22	50	0.4	20	0.4	1485.79
23	50	0.4	50	0.4	2181.82
24	40	0.3	50	0.4	768.00
25	40	0.5	50	0.4	859.42
26	40	0.4	50	0.3	952.38
27	50	0.5	35	0.4	1542.42

Table 5. Result of analysis variance (ANOVA).

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	14	8497267	606948	30.72	0.000
Linear	4	6881536	1720384	87.07	0.000
T	1	6466268	6466268	327.27	0.000
NaBH ₄	1	120160	120160	6.08	0.030
Catalyst	1	97650	97650	4.94	0.046
NaOH	1	197457	197457	9.99	0.008
Square	4	909294	227323	11.51	0.000
T*T	1	3207	3207	0.16	0.694
NaBH ₄ *NaBH ₄	1	398198	398198	20.15	0.001
Catalyst*Catalyst	1	512573	512573	25.94	0.000
NaOH*NaOH	1	362895	362895	18.37	0.001
2-Way Interaction	6	706437	117740	5.96	0.004
T*NaBH ₄	1	358231	358231	18.13	0.001
T*Catalyst	1	120625	120625	6.11	0.029
T*NaOH	1	175653	175653	8.89	0.011
NaBH ₄ *Catalyst	1	45600	45600	2.31	0.155
NaBH ₄ *NaOH	1	310	310	0.02	0.902
Catalyst*NaOH	1	6019	6019	0.30	0.591
Error	12	237098	19758		
Lack-of-Fit	10	236481	23648	76.73	0.013
Pure Error	2	616	308		
Total	26	8734365			
Model Summary					
	R-sq	R-sq(adj)	R-sq(pred)		
	140.564	97.29%	94.12%	84.39%	

The main effects diagram (Figure 5) shows the average response of a curve for each parameter level. The main factors are the reaction temperature, the concentration of the reactant (NaBH₄), the amount of catalyst, and stabilizer (NaOH) concentration for the HGR reaction shown in Figure 5. HGR showed significant differences at different reaction temperatures and NaBH₄ concentrations, as well as the amount of catalyst and NaOH concentration had a significant effect on HGR. In Figure 5, a significant increase in HGR was observed when the reaction temperature was increased from 30 °C to 50 °C. There was also a significant increase when the NaBH₄ concentration was increased from 0.3 M to 0.5 M.

The selected model also illustrates the combined effect of operating parameters on HGR. The effects of the various process parameters are explained by three-dimensional diagrams of the box core, as shown in Figure 5(a)-(d). The synergistic effect on HGR between catalyst and NaOH is shown in Figure 5(a). It was observed that HGR increased when NaBH₄ concentration was increased at 30 °C. According to Figure 5(b), HGR increased with NaOH concentration. However, HGR increased with increasing NaBH₄ concentration from 0.3 to 0.4M, but further increase in NaBH₄ concentration resulted in a decrease in HGR value at 30 mg catalyst amount, HGR was maximized, but increase in catalyst amount resulted in a decrease in HGR values Figure 5(c). The HGR increased linearly with increasing temperature Figure 5(d).

The optimum HGR value was calculated using the model with 2434 mL min.⁻¹ g cat.⁻¹, while the experimental conditions for the optimum value were 50 °C reaction temperature, 0.46 M NaOH concentration, 0.33 M NaBH₄ concentration, and 39 mg catalyst amount. Experimental hydrogen production was carried out under these conditions and a value of 2328 mL min.⁻¹ g cat.⁻¹ was found, which is close to the optimum value.

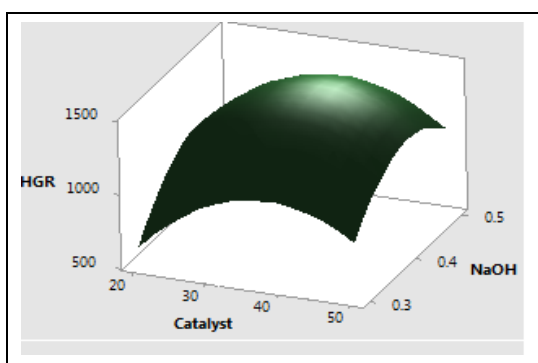
3.4 Reusability

To estimate the reusability of the catalyst in the hydrolysis reaction of NaBH₄, the catalyst was tested under optimal reaction conditions (50 °C temperature, 0.46 M NaOH, 0.33 M NaBH₄, and 39 mg Co/MMT catalyst). After the hydrolysis reaction, the catalyst was recovered from the reaction medium by vacuum filtration, washed with distilled water, and dried overnight in an oven at 105 °C. The catalyst removed from the oven was used for the second time under the same conditions, and the same procedures were repeated for the 3rd and 4th reactions. The hydrogen production rates are shown in Figure 6. After the fourth cycle, the reaction rate decreased from 2328 to 1984 (mL/min g cat). Inactivation of the catalyst surface and active sites by the byproducts formed during the reaction affected the catalytic activity. Also, the surface of the reused catalyst may become smoother and the active cobalt metal on the surface may decrease after reuse [27]. After the catalyst is reused, hydrated macrostructures based on metaborates are formed, causing increased viscosity of the reaction solution [28] and the increasing viscosity of the reaction medium also negatively affected the hydrogen generation performance of NaBH₄ [9]. Another reason for.

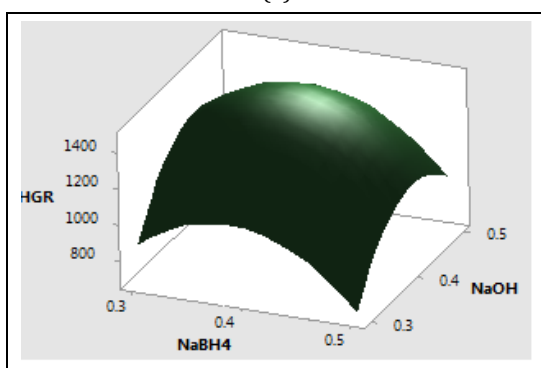
4 Conclusions

MMT clay as a support material with cobalt was used to obtain hydrogen from NaBH₄. The effect of reaction temperature, NaOH and NaBH₄ concentrations, and catalyst amount on hydrogen production by hydrolysis of NaBH₄ was investigated in batch tests, and optimization of the hydrolysis process was performed by using the Box-Behnken method.

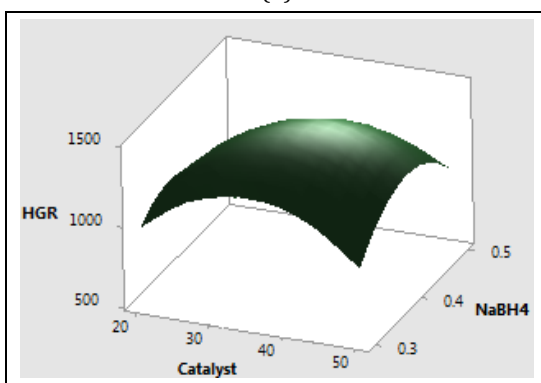
The temperatures, initial NaOH and NaBH₄ concentrations and catalyst amount had an impact on hydrogen production both individually and in interaction.



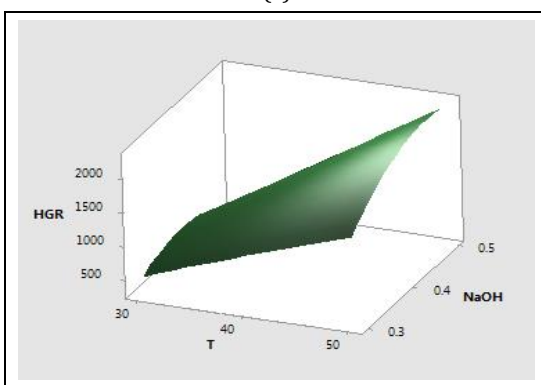
(a)



(b)



(c)



(d)

Figure 5. 3D response surface graph for HGR versus. (a): Catalyst and NaOH. (b): NaBH₄ and NaOH. (c): Catalyst and NaBH₄.(d): Temperature and NaOH for Hydrogen production from NaBH₄.

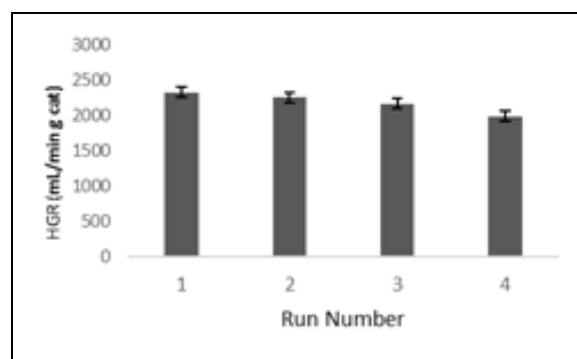


Figure 6. Reusability for NaBH₄ hydrolysis reaction with Co/MMT.

The maximum hydrogen generation rate for the Co/MMT catalyst $2434 \text{ mL min}^{-1} \text{g}_{\text{cat}}^{-1}$ was calculated at a temperature of $50 \text{ }^\circ\text{C}$, an initial NaOH concentration of 0.46 M , and a NaBH₄ concentration of 0.33 M at a catalyst amount of 39 mg . The experimental results at these optimum conditions were $2328 \text{ mL min}^{-1} \text{g}_{\text{cat}}^{-1}$. The synthesized cobalt catalyst on montmorillonite support is suitable for both hydrogen generation performance from NaBH₄ and reusability. These results suggested that have an advantageous for hydrogen generation with low material and energy consumption."

5 Author contribution statement

Seda HOŞGÜN Creation of the idea, literature review, preparation of the article, writing the article, performing the experiments. Emir Zafer HOŞGÜN Catalyst synthesis and characterization, analysis of experimental data, article writing.

6 Ethics committee approval and conflict of interest statement

"There is no need for an ethics committee approval in the prepared article".

"There is no conflict of interest with any person/institution in the prepared article".

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