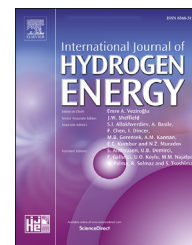




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Enhancing the efficiency of sodium borohydride hydrolysis with a novel CoB-Triton catalyst

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HIGHLIGHTS

- Use of Triton X-100 surfactant during chemical reduction of CoB catalyst.
- 150 μ l Triton X-100 use increases HGR 40.2%.
- Activation energy of the CoB-T150 is 44.21 kJ/mol.
- Triton X-100 is a good alternative with easily implementation.

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ABSTRACT

Hydrogen is increasingly recognized as the most significant alternative solution for reducing global greenhouse gas emissions in maritime transportation. In particular, solid-state sodium borohydride (NaBH_4) with its high hydrogen storage density stands out as the preferred choice due to its higher efficiency and improved safety. In present study, a surfactant-stabilized CoB catalyst was used in order to improve the hydrolysis performance of NaBH_4 . For this reason, the effects of Triton X-100, used as a surfactant in different quantities, on the hydrogen generation rate were tested. To characterize the prepared samples, several analytical techniques were employed, including field emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FT-IR), Mastersizer analysis, X-ray diffraction (XRD), and Brunauer-Emmett-Teller (BET) analysis. According to findings, 40.2% faster hydrogen generation rate is obtained with CoB-Triton 150 contrary to CoB catalyst. The optimum concentrations are found as 5% NaOH and 5% NaBH_4 and activation energy is 44.21 kJ/mol for developed CoB-Triton 150 catalyst. Last of all, fuel cell performances show that the produced hydrogen from hydrolysis reaction through CoB-Triton 150 catalyst has nearly same fuel cell performance compared to industrial pure hydrogen. Consequently, Triton X-100 is a good candidate to improve the hydrolysis performance of NaBH_4 and needs further research.

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Introduction

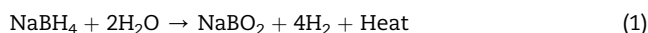
With technological developments and the ever-increasing population, the need for energy throughout the world is increasing day by day [1], and the use of traditional fossil fuels meets a large proportion of this demand. Nevertheless, fossil fuels pose significant threats to the environment and human health by the release of carbon dioxide, carbon monoxide, nitrogen, and sulfur oxides, leading to climate change, acid rain, and global warming. Moreover, since fossil fuels are limited and predicted to be depleted shortly, it is essential to seek different energy sources and reduce foreign energy dependency. Furthermore, ships powered by the combustion of fossil fuels have significantly contributed to emissions of CO₂ and other greenhouse gases (GHGs), as well as pollutants of concern such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and particulate matter, by consuming approximately 298 million tons of fuel in 2015 [2]. In this regard, the International Maritime Organization (IMO) implemented an Initial Strategy in 2015 with the objective of reducing greenhouse gas emissions from international shipping in alignment with the Paris Agreement. Lately, the interest in clean, cheap, and independent energy alternatives has been increasing day by day in order to overcome the global energy crisis [3,4].

Related to the raising tailpipe or life cycle emission regulations, for an alternative energy option, hydrogen is recognized as a considerable candidate to replace fossil fuels thanks to its advantages like theoretic abundance, emission-free structure, high calorific value, production diversity, and compatibility with renewable energy systems. Moreover, it is important to note that hydrogen presents significant potential as an energy carrier. The storage of hydrogen in various forms, such as gases, liquids, or bonded structures, poses a significant challenge that requires further development. In terms of hydrogen storage, the major factors can be listed as safety measures (due to its flammability), efficiency, light-weight, volumetric/gravimetric density, recyclability, environmental impacts, and total cost [5–8].

Recently, in comparison with traditional storage methods such as gas storage in pressurized tanks or liquefaction, solid-state storage, especially chemically bonded forms of hydrogen, stands out as it can provide storage at lower pressures and temperatures. Even though hydrogen is the most abundant element in the universe, instead of being present as H₂, it is available in the form of compounds such as metal or chemical hydrides [9]. Thanks to their stability, maintenance of hydrogen under ambient conditions, recyclability of by-products and lower hydrolysis temperature, chemical hydrides such as borohydrides, aluminohydrides, and amide groups gain importance. In this regard, boron-based chemical hydrides (metal borohydrides M(BH₄)_n, where the M represents metal and n is the valance value), show promise due to their high hydrogen content, and greater hydrogen density [10].

Sodium borohydride (NaBH₄), also known as sodium hydroborate or sodium tetrahydroborate [11], is widely used as a bleaching agent [12] or reducing agent in chemistry [13], as a direct fuel for alkaline direct borohydride fuel cell [14] and as a hydrogen carrier. Moreover, the NaBH₄ is an appropriate

hydrogen sources for proton exchange membrane fuel cells (PEMFCs) with the benefits of non-flammability and absence of toxicity [15]. With its advantages it takes attention as the H₂ storage method for electronic devices [16], road [17] and aerial vehicles [18] or maritime transportation [19]. In particular, its safe structure [20] and high hydrogen storage capacity [21] makes it suitable fuel for maritime transportation for the future. Despite the NaBH₄ can be produced by Brown-Schlesinger and Bayer methods, the high production cost is still a disadvantage [22]. Additionally, the production of other hydrogen carriers like lithium borohydride (LiBH₄), potassium borohydride (KBH₄), and ammonia borane (NH₃BH₃) is carried out through the NaBH₄, and this raises the significance of this compound [23]. Furtherly, the NaBH₄ has a relatively high gravimetric hydrogen content (10.8 wt%) [24]. Dehydrogenation of this hydrogen may be carried out by thermal decomposition (at elevated temperatures), alcoholysis, or hydrolysis [25]. Hydrolysis, which can be defined as chemical separation under an aqueous medium, is preferred because of its mild conditions [26] rather than thermal decomposition, and the availability of water when compared to alcohol. The hydrolysis reaction of the sodium borohydride is given below:



The above reaction has some advantages. With a negative enthalpy change value, the reaction is exothermic and its negative Gibbs value indicates that the reaction is thermodynamically favorable and spontaneous [27,28]. Besides, production of NaBO₂ the above equation is not harmful to the environment [29]. Furthermore, it can be recycled to sodium borohydride again [30–32], but the cost and energy consumption drawbacks still need to be solved [33]. Additionally, storage of the sodium borohydride that reacts with the excess water may be carried out as dry but considering moisture [34], and also may be performed as an alkaline solution that is non-flammable and safe [35]. However, storage in alkaline media to improve stability [36], causes slower reaction rates [37] therefore, needs suitable catalysts to speed up [38] the reaction. Obtaining the active catalyst that releases high-velocity pure hydrogen from the NaBH₄ has been the subject of raising interest, recently. For this purpose, precious noble metals such as platinum (Pt), palladium (Pd), or ruthenium (Ru) are valuable candidates to catalyze the hydrolysis reaction. Nevertheless, depending on their limited resources, the high cost of these materials is a major barrier to their commercial usage. Along with the necessity of searching for different options for catalyzing, this situation has led to an increased interest in the use of non-precious metals as catalysts [39–41].

Nowadays researchers have been focused on transition metals such as cobalt (Co), nickel (Ni), and iron (Fe), especially their metal borides [42], as these materials, are much cheaper than precious metals and can perform high catalytic performance [43]. From the perspective of many researchers thanks to its high catalytic activity, relatively lower cost, applicability, and ease of preparation, the Co becomes a significant option [44]. As an alternative catalyst, cobalt boride (CoB) drew attention [45] due to its cost [46] hardness, oxidation resistance [47], and catalytic activity [48]. The effect of the presence

of boron can be summarized as follows: As a result of this combination, electron transfer occurs from the boron to cobalt, and increase the valence electron density. Thus, this makes the active cobalt sites more stable to oxidation. Despite these materials perform better for catalytic activity, their agglomeration tendency during reduction adversely affects their properties and performances [49]. To enhance their catalytic activity, cheap, commonly used and easily accessible alternatives are needed. For this purpose, various studies have been carried out recently, which focus on improve the NaBH_4 hydrolysis performance of CoB catalyst. Theoretical or statistical methods such as Taguchi and Response Surface Methods can be used to obtain optimum conditions for higher hydrogen generation rates [50]. Hoşgün et al. [51] used halloysite as a support material and optimum conditions was obtained for highest hydrogen generation rate with the help of response surface methodology. Moreover, synthesizing temperature may be crucial for produced catalyst. Pour and Paydar [52] investigated synthesizing temperature effect during chemical reduction to catalytic activity of CoB, NiB and NiCoB catalysts. According to results, reducing synthesis temperature raised catalytic activity thanks to changed particle shape, reduced particle size and increased boron content of the particles. To enhance catalyst performance, different elements have different effects on CoB catalyst performance. Xia et al. [53] performed experiments with CoB catalyst doped with Tin (Sn), Bismuth (Bi), Manganese (Mn), Chromium (Cr) metals and better results were achieved with Cr and Bi thanks to both of the raised specific surface area and electronic interaction between dopants and Co. Balciunaite et al. [54] prepared Co/Cu, CoB/Cu, CoBMo/Cu, CoBMn/Cu, CoBZn/Cu, CoBFe/Cu catalysts using electroless deposition method. Better results obtained with CoBMo/Cu catalyst with the roughness surface area and cauliflower-shaped structures. Jia et al. [55] developed graphene modified CoB–P catalyst (CoB–P/GO) to improve catalytic activity of CoB. With the graphene use that exposed more catalytically active sites and synergistic effect between Co, B and P, raised catalytic performance has been obtained. Furthermore, support materials are attractive for CoB lately. Baydaroğlu et al. [56] investigated tungsten doping and polypyrrole support to CoB catalyst. While tungsten use provides more homogeneous surface and less agglomeration, support of PPy prevents the adhesion of nanoparticles to each other and homogenous dispersion of metal to support. Li et al. [57] developed polyaniline polymer support through polystyrene nanofibers for CoB catalyst. According to results, CoB particles highly dispersed into the polyaniline nanotubes and optimum loading content of CoB was achieved for better hydrogen generation. Peng et al. [58] used bacterial cellulose derived carbon to support CoB. The raised performance attributed to smaller pore size, N and functional groups content of support that increases wettability and causes adsorption of metal ions. İskenderoğlu and Baltacıoğlu [59] developed blast furnace slag (BFS) supported Co–B catalysts and acid treatment and other conditions have been investigated. According to observations, acid treatment has been found as an effective method.

Beside the aforementioned studies, metal free, cheap alternative methods to increase CoB catalyst performance are needed. Surfactants known as surface or interfacial tension

reducing agents, arouse interest recently. Its main and known role is linking the phases with occurred micelle structure that includes hydrophilic and hydrophobic parts [60,61]. In addition to its wide industrial applications, surfactant is also used in catalyst preparation for hydrogen generation through hydrolysis reaction, as reported in previous studies [62–70]. However, as a non-ionic surfactant, Triton X-100 has a catalytic activity improvement potential that is generally ignored and proved by the study carried out by Elçiçek et al. [71] and need to be more studied. Therefore, in this study, Triton X-100 a non-ionic, water-soluble surfactant has been used and a novel CoB-Triton catalyst was developed for alkaline NaBH_4 hydrolysis reaction. CoB, CoB-Triton 25, CoB-Triton 50, CoB-Triton 100, CoB-Triton 150, CoB-Triton 200, and CoB-Triton 250 catalysts have been prepared and catalytic activities have been compared with measuring hydrogen generation rates from alkaline NaBH_4 solution hydrolysis reaction. NaOH, NaBH_4 ratios, reaction temperature and catalyst amount have been studied parametrically for the Triton-added catalyst that gave the best HGR result. FE-SEM, Mastersizer, XRD, FTIR, BET analyses were carried out for pure CoB and CoB-Triton catalysts. Last of all, the fuel cell performance of the developed catalyst was measured to examine the purity of produced hydrogen.

Materials and methods

This section encompasses the preparation of the catalyst, the evaluation of hydrogen generation rate, the characterization process, and the measurement of fuel cell performance.

Test bench and experimental setup

Equipments used in experiments have been showed in Table 1.

The experimental process in this study consists of four main stages, namely catalyst preparation, hydrogen generation determination, characterization, and fuel cell experiments. All sections have been summarized in Fig. 1.

Table 1 – Brand/model of used equipment.

Equipment	Brand/Model
Benchtop pH meter	Orion Star A111
Magnetic stirring (for reduction)	Wisestir MSH-20A
Circulating water bath (for reduction)	Heidolph Rotachill
Magnetic stirring (for HGR tests)	Daihan Scientific MSH-20D
Circulating water bath (for HGR tests)	JSRC-13C
Syringe pump	Chemyx-Fusion 6000
Vacuum oven	Nuve EV 018
Analytical balance	Radwag-AS 220.R2
XRD	Thermo Cu–K alpha
BET	Quantachrome Quadrosorb SI
FTIR	Thermo scientific NICOLET iS10
Mastersizer	Hydro 2000MU
FE-SEM	Thermo Scientific Apreo 2 S LoVac
Fuel cell test system	WonaTech Smart 2

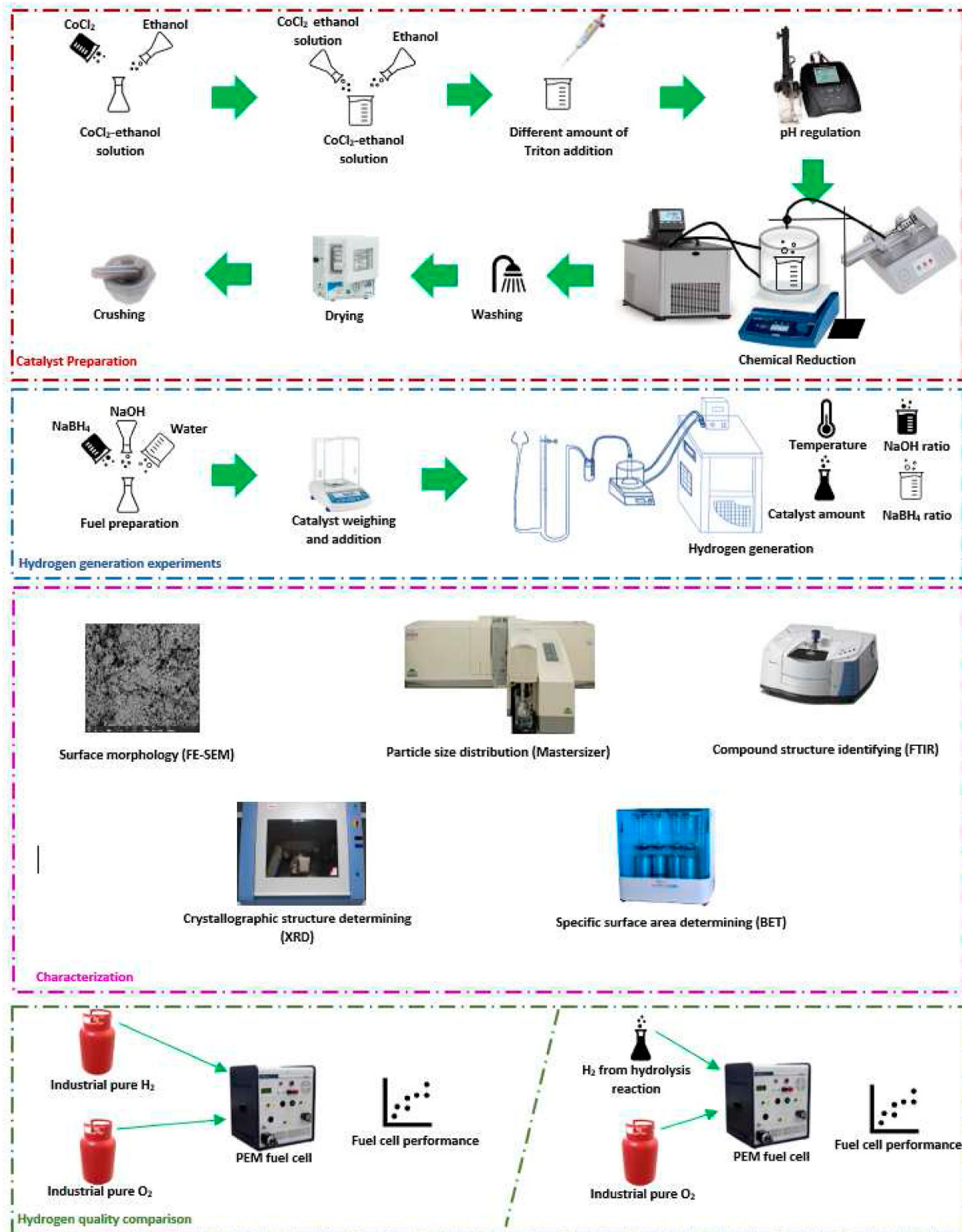


Fig. 1 – Experimental phases.

Catalyst preparation

CoB compounds were successfully synthesized by using chemical reduction method. In the literature, there are different solvents have been used during catalyst synthesis as water, methanol, ethanol and etc. [72–74] and ethanol may give better results [74]. In our preliminary studies, Triton use in water caused foaming and resulted as worse solubility. Moreover, it was observed that instead of water, ethanol used catalysts resulted as better HGR. For this reason, ethanol as a solvent has been used during the catalyst fabrication. Briefly, 0.02 M of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution was prepared with ethanol solution. Then, certain amount of prepared solution, ethanol and various amount Triton X-100 surfactant was mixed to obtain a homogenous suspension by vigorous magnetic stirring. The pH value of obtained mixture was set to 4 for all solution. After that, 10 mL pure NaBH_4 solution as a reducing agent was added dropwise with stirring in a circulating water bath, the temperature of which was kept constant at 6 °C. The obtained black products were washed in sequence more than once with distilled water and ethanol to remove the unwanted ions on the catalyst. Eventually, the final products were dried in a vacuum oven at 110 °C. The abbreviations of the samples prepared using different amounts of Triton X-100 are listed in Table 2.

Hydrogen generation tests

In present study, hydrogen generation rate tests from NaBH_4 hydrolysis of the obtained CoB-Triton catalysts were carried out by water displacement method. A schematic representation of the experimental setup is given in Fig. 2. In a typical reaction, 10 mg of catalyst was dispersed in an aqueous solution containing 2.5% wt. NaBH_4 and 2.5% wt. NaOH . The temperature of the reaction was maintained constant using a thermostatic bath. The volume of hydrogen released was recorded at regular intervals and the HGR value was calculated as $\text{L min}^{-1} \text{g}^{-1}$. To determine the catalyst reaction activation energy, experimental studies were carried out at temperatures of 35–65 °C. Moreover, the effects of sodium hydroxide concentration and sodium borohydride concentration on the rate of hydrogen generation were studied by the hydrolysis reaction of NaBH_4 .

Characterization

As an electron microscope with high resolution, scanning electron microscope (SEM) is effective way to display visualizations of surface structure via focused beam of electrons and

the interactions between the sample and electrons [75]. However, field emission scanning electron microscope (FE-SEM) offers clearer quality and higher resolution [76,77] and it is utilized in different areas for monitoring the nanostructures [78]. In this study, FE-SEM was used to investigate surface morphologies of CoB and CoB-T150 catalysts. Furthermore, particle size and surface area are important parameters to evaluate catalyst performance. For this reason, particle size distribution was obtained with Mastersizer analysis. Hydro 2000MU Mastersizer accessory was used. To determine the specific surface area and porosity of the catalysts, BET analysis was used. In the BET theory, gas (generally N_2) adsorption characteristics of the surface with the changing pressure is utilized [79]. To obtain information regarding molecular fragments, structure environment and functional groups, Fourier transform infrared spectroscopy is an effective tool [80]. Thermo scientific branded NICOLET iS10 FTIR Spectrometer was utilized. Last of all, to identify the crystallographic structure and phase composition of the catalyst, XRD method as a useful technique that compares the sample and reference database X-ray diffractions [81] was used.

Fuel cell performance tests

Purity of released hydrogen is a key parameter [82], especially for fuel cells compared to ICEs [83]. Undesirable impurities may deteriorate performance and lifespan of fuel cell [84]. To understand the interaction between fuel cell and produced hydrogen from hydrolysis reaction, proton exchange membrane fuel cell experiments have been carried out. Cell has been exposed to nitrogen gas before the experiments. Pure hydrogen gas (Linde, 99.99%) from the industrial hydrogen cylinder and released hydrogen from borohydride-water reaction was fed to anode side of the single fuel cell. Test cell is 5 cm^2 and on a catalyst side, 100 $\mu\text{gPt.cm}^{-2}$ with 40% ratio platinum-carbon catalyst was used, and as a membrane, commercial Nafion 212 was used. Cathode side was fed by 500 ccm pure O_2 (Linde, 99.5%) from industrial oxygen cylinder. Voltage-current density curves and thus, power density results were demonstrated.

Results and discussion

FE-SEM results

The maximum hydrogen generation rate was obtained with CoB-T150 catalyst as seen in Fig. 9 and hence, characterization results are demonstrated for CoB and novel developed CoB-T150. The morphology of the synthesized CoB and CoB-T150 catalysts was investigated by FE-SEM and the images at different magnifications are shown in Fig. 3. Left side images represent the CoB results and the right sides represent the CoB-T150 catalyst surfaces. When Fig. 3a is analyzed using the ImageJ program, it was determined that the average particle size is approximately 0.945 μm , with the largest particle being about 2.3 μm . Similarly, when Fig. 3b is examined, the average particle size is approximately 0.578 μm , and the maximum particle size is approximately 1.168 μm . It was observed that the particles were homogeneously aggregated, resulting the particles appeared

Table 2 – Abbreviations of prepared catalysts.

Amount of Triton X-100, μl	Abbreviation
0	CoB
25	CoB-T25
50	CoB-T50
100	CoB-T100
150	CoB-T150
200	CoB-T200
250	CoB-T250

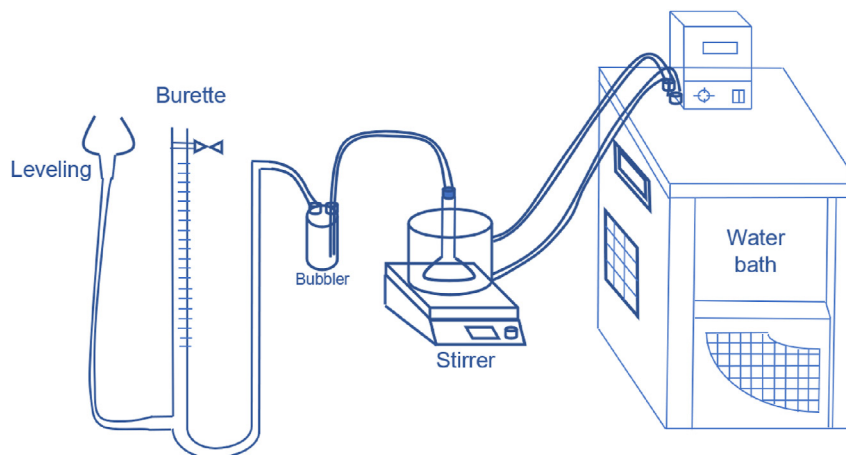


Fig. 2 – Experimental setup of hydrogen generation tests.

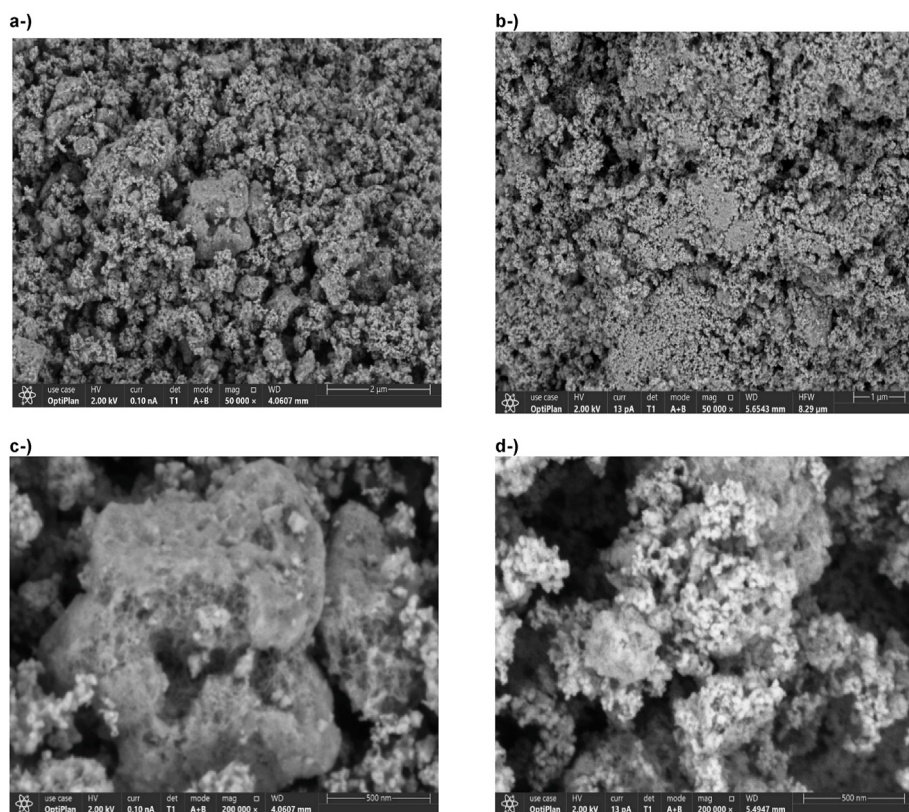


Fig. 3 – FE-SEM images of CoB (a–c) and CoB-T150 (b–d) at different magnifications.

more orderly together. Fig. 3b shows the presence of smaller, more porous particles. These particles aggregate to create a porous structure, while also contributing to the creation of larger particles. It has been observed that the addition of the surfactant Triton X-100 contributes to the reduction in nanoparticle size, consistent with the report by Elçiçek et al. [55].

Mastersizer results

Fig. 4 shows volume-based particle size distribution of the synthesized CoB and CoB-T150 catalysts using Mastersizer

technique. The synthesized catalysts showed particle size distribution of agglomerated particles. According to the results, maximum % volume values have been obtained around 50 μm and above 100 μm for CoB and CoB-T150, respectively. Moreover, according to Fig. 4, particle size distribution of CoB and CoB-T150 were presented unimodal and trimodal size distribution, with aggregate sizes with peaks around 52.48 μm and 120.226 μm , respectively. While CoB catalysts have a more homogeneous particle size distribution, CoB-T150 catalysts show a heterogeneous particle size distribution. CoB-T150 catalysts have a more porous structure due to the coexistence of

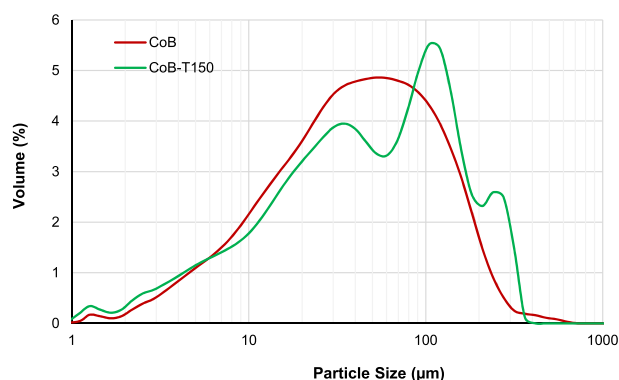


Fig. 4 – Particle size distributions of CoB and CoB-T150.

particles of different sizes and the resulting partial agglomeration. Additionally, agglomeration of catalyst changed the pore size, instead of the micropores, mesopores were dominant, which are believed to be associated with rapid release of large amounts of hydrogen gas.

BET results

The isothermal adsorption–desorption curves of the CoB and CoB-T150 catalysts are given in Fig. 5 the isotherms exhibit a downward concave shape throughout the pressure range, which is indicative of them belonging to the type III isothermal category. The samples exhibit the presence of both macropores and mesopores (indicated by the sharply increasing adsorption isotherm above $P/P_0 = 0.9$ and the presence of the hysteresis loop). A broader hysteresis loop is observed in the relative pressure range of 0.40–0.99 for the CoB-T150 isotherm, indicating that it has a more porous structure. Furthermore, there is a rapid increase in adsorption capacities at high relative pressures, which suggests the presence of a hole filling effect during the adsorption process [85]. The BET results indicate that among the tested catalysts, the CoB-T150 catalyst possesses the highest specific surface area of $42.43 \text{ m}^2 \text{ g}^{-1}$, whereas the specific surface area of the

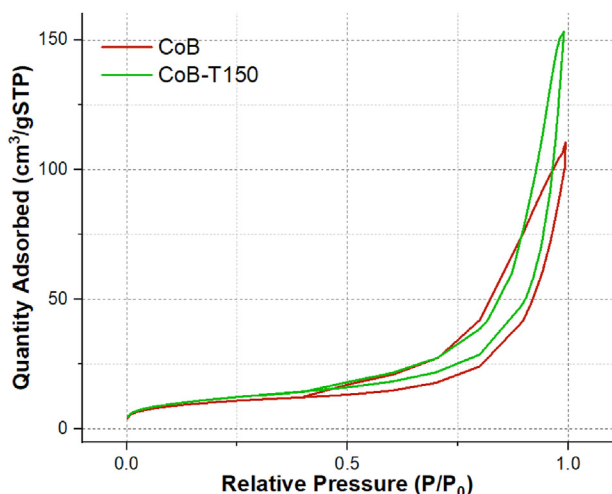


Fig. 5 – Adsorption/Desorption isotherms of CoB and CoB-T150.

Co–B catalyst is $37.72 \text{ m}^2 \text{ g}^{-1}$. As the surface area increased, the particle size of the catalysts decreased with the addition of surfactant during the synthesis, and as a result, a heterogeneous particle size distribution emerged as can be seen in Fig. 4.

During an exothermic reaction, such as a hydrolysis reaction, small particles will have a greater tendency to agglomerate and therefore the porosity of the catalysts will change. The pore size distribution curve (Fig. 6) was calculated by the Barrett–Joyner–Halenda (BJH) method for the desorption branch. The main feature of the curve is that the pore size distribution is unimodal for CoB, while bimodal distribution for CoB-T150.

Particle size distribution and porosity size distribution results confirm each other. As a result of the use of a certain amount of surfactant in the synthesis of catalysts, a more heterogeneous pore distribution has emerged in the catalysts. As it is known, as a result of the increased pore size, it is easier for borohydrides to reach the surface of the catalysts during the hydrolysis reaction and the metabolates, which are released as reaction products, are more easily removed from the catalyst surface.

FTIR results

The prepared catalysts were examined using FTIR and the results are presented in Fig. 7. It was observed that the prepared CoB and CoB-T150 catalysts do not have distinctive functional groups. The peak at 3421 cm^{-1} is indicative of the valence vibrations of O–H groups, suggesting the presence of hydroxyl functional groups. Meanwhile, the peak at 1620 cm^{-1} represents the characteristic deformational vibrations of H–O–H. The bands at 1384 cm^{-1} and 878 cm^{-1} originate from the asymmetric and symmetric vibrations, respectively, of the B (3)–O group. The bands at 1080 cm^{-1} and 738 cm^{-1} arise from the asymmetric and symmetric vibrations of B (4)–O groups, respectively [86]. The absorbance peaks observed at $400\text{--}600 \text{ cm}^{-1}$ in both the CoB and regular CoB-T150 are attributed to the vibration of the CoB alloy [87].

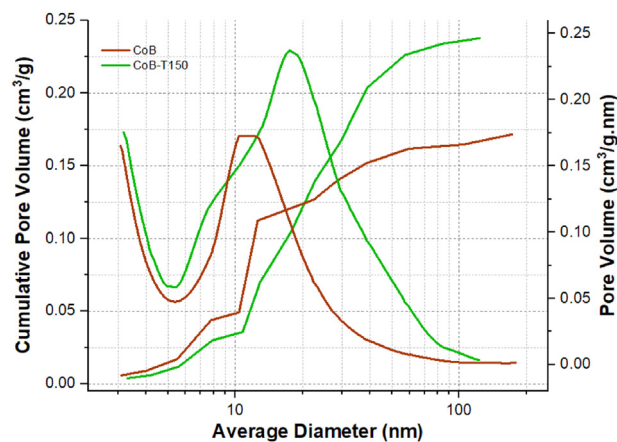


Fig. 6 – Pore size distribution and cumulative pore volume of the samples calculated from desorption branch of the isotherm by the BJH method.

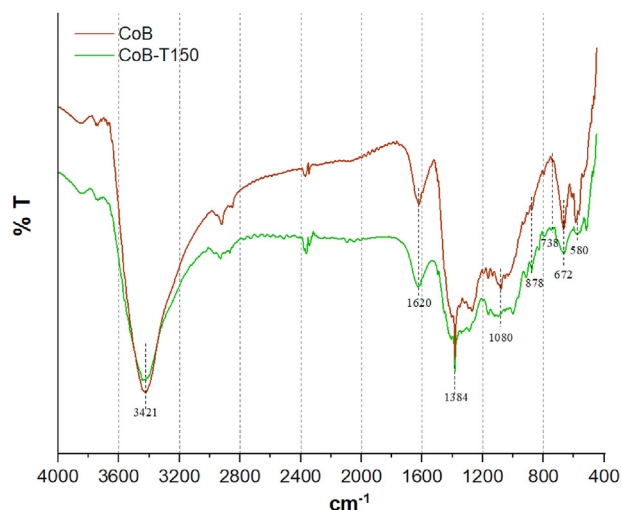


Fig. 7 – FTIR results with CoB and CoB-T150.

XRD results

Fig. 8 shows the XRD patterns of the CoB and CoB-T150 catalysts. The XRD diffraction patterns of CoB and CoB-T150 catalysts were observed to have noise, which could be attributed to the existence of amorphous phases within the catalysts. This led to weak diffraction peaks. Moreover, the CoB and CoB-T150 catalysts displayed noise in their diffraction peaks, which was probably due to their low crystallinity. Furthermore, the presence of the magnetic element Co in the catalysts caused an increase in fluorescence intensity during the XRD test, leading to an increase in the background noise of the diffraction peaks [88]. The diffraction peaks observed at approximately 45° in the CoB and CoB-T150 catalysts were found to overlap with the peaks of Co_2B , Co_3B_2 compounds [89,90]. The results indicate that the broadening of the peak observed in the CoB-T150 catalyst is due to a decrease in particle size. Additionally, the changes in crystal structure may contribute to an improvement in catalytic performance.

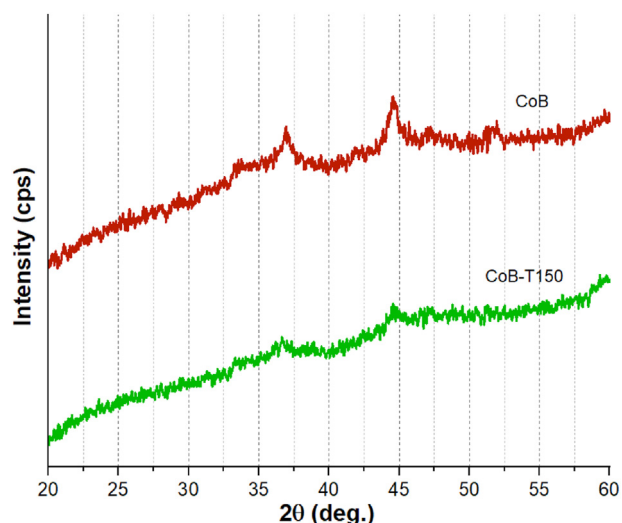


Fig. 8 – XRD results of CoB and CoB-T150.

Surfactant effects on HGR

Fig. 9 illustrates both the final hydrogen generation rates for the various catalysts and Fig. 10 presents the cumulative hydrogen production as a function of time, using 5% NaOH and 5% NaBH_4 concentrations. Hydrogen generation rates (HGR) are presented as L_{H_2} per $\text{g}_{\text{cat}}\cdot\text{min}$. HGR of the CoB is found as $12.61 \text{ Lmin}^{-1} \text{ g}^{-1}$. Triton X-100 addition firstly decreases and furthermore increases the hydrolysis reaction performance. Maximum hydrogen generation rate belongs to CoB-T150 catalyst with $17.69 \text{ L}_{\text{H}_2} \cdot \text{g}^{-1} \cdot \text{min}^{-1}$. The increase from the value of the CoB catalyst was 40.2%. Surfactants are used to control the catalyst surface morphology [65]. As will be seen in the surface and particle characterization, the agglomeration as a result of the exothermic reaction is prevented [67], particle dispersibility and surface area of the catalyst increases [66]. Triton X-100 is a proven surfactant, it increases active sites and releasing hydrogen amount is increasing for the same time [71]. Fig. 10 shows the releasing hydrogen amount versus time. Whereas the CoB-Triton 150 catalyst releases the high amount hydrogen in a short time, CoB-T50 catalyst releases the small amount of hydrogen in above 1200 s. As compared to slow reaction of CoB catalyst performance, CoB-T150 results correspond with the FE-SEM images as seen in Fig. 3. It is concluded that the addition of Triton X-100 into the CoB catalyst has led to an increase in the number of catalytically active sites and porosity, ultimately resulting in an improvement of the hydrogen generation rate. Moreover, 9.4% higher specific surface area of the CoB-T150 catalyst have been obtained in Mastersizer results that will be discussed later. Since the CoB-T150 is the advantageous catalyst with faster hydrogen release, further research like NaOH/ NaBH_4 optimization, temperature and catalyst amount effect, fuel cell performances will be carried out with CoB-T150 catalyst.

Kinetic analysis results

Effect of NaOH

CoB-Triton 150 catalyst has yielded the most favorable hydrogen generation rate results. Therefore, the present section investigates the effects of NaOH and NaBH_4 ratios, temperature, and catalyst amount on CoB-T150. Fig. 11 indicates HGR results with respect to change of NaOH percentage in the solution for CoB-T150 catalyst, with constant catalyst amount as 10 mg, constant sodium borohydride ratio as 5%, and constant reaction temperature as 65°C . Actually, stabilization of NaBH_4 solution depends on pH and temperature [42]. It is difficult to ensure complete stabilization but, self hydrolysis may be slowed down by increasing the pH [33]. Hence, NaOH is added to NaBH_4 -water solution to retard self hydrolysis. In this study, NaOH percentages in fuel have been selected as 2.5%, 5%, 7.5%, 10%, 25%. Results indicate that rising NaOH ratio from 2.5% to 5% increases HGR and peak value is obtained with 5% NaOH ratio. Certain amount of OH^- stimulates the hydrogen releasing since it exists in BH_4 hydrolysis mechanism [91], induces $\text{BH}_n\text{OH}_{4-n}$ species and thus H_2 generation [92]. However, more increase of NaOH ratio from 5% deteriorates hydrogen generation rate. Raising NaOH concentration augments solution viscosity that inhibits NaBO_2

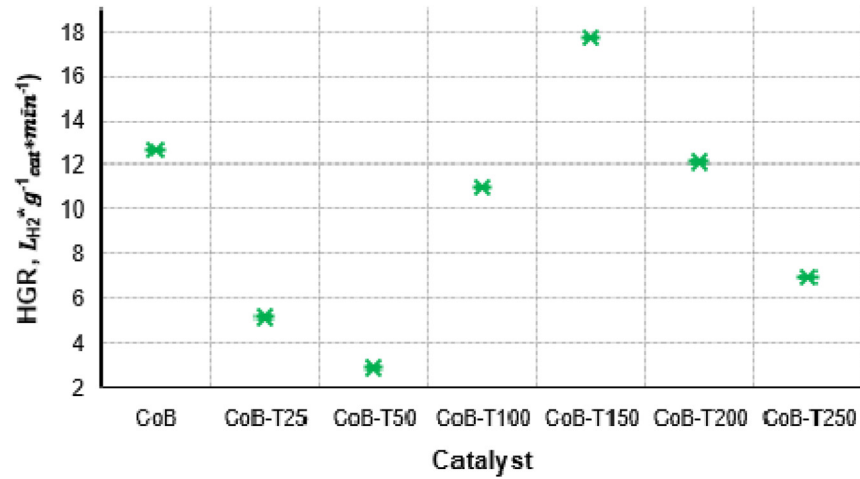


Fig. 9 – HGR results of different catalysts.

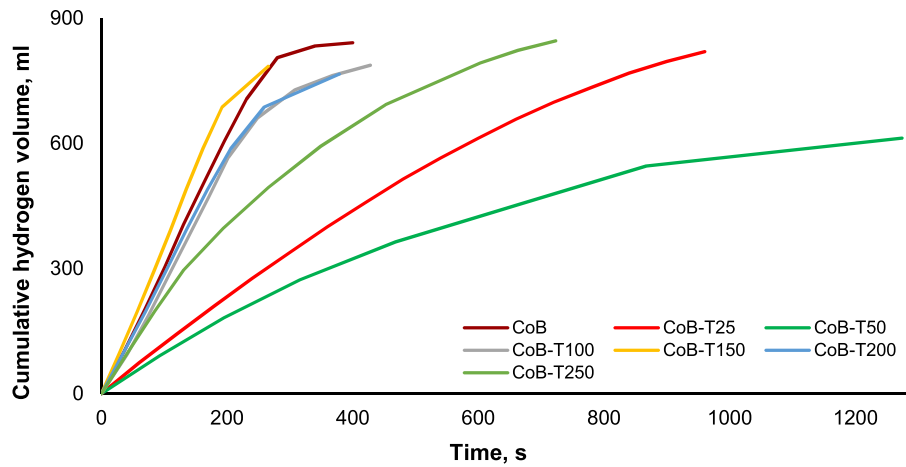
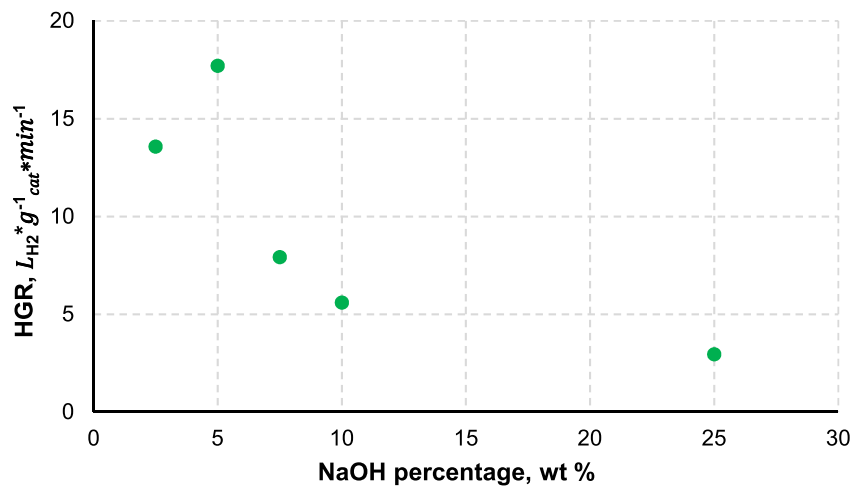
Fig. 10 – Released H₂ volume vs. time.

Fig. 11 – The relation between HGR and NaOH percentage in fuel by weight.

diffusion from catalyst to solution [93], decreasing solubility of NaBO_2 causes deposit on catalyst [94]. Moreover, OH^- ions locate on catalyst surface instead of reactants [37], water activity is reduced [95] and interaction of BH_4^- and catalyst is interrupted [96].

Effect of NaBH_4

NaBH_4 is basis of hydrolysis reaction and is needed. However, its amount that will give best HGR result should be determined. For this reason, Fig. 12 shows HGR results of CoB-T150 with changing NaBH_4 percentages in fuel by weight, in the presence of 5% NaOH and 10 mg catalyst, at constant 65 °C reaction temperature. NaBH_4 percentages were chosen as 2.5%, 5%, 7.5%, 10% and 15%. According to results, whereas maximum HGR belongs to 5% NaBH_4 ratio, more increase causes sharp (5%–7.5%) and slight (7.5%–10% and 15%) decreases. More NaBH_4 produces more H_2 and NaBO_2 , as well. Raised viscosity, reduced solubility of NaBO_2 and lowered mass transfer [97] result as accumulation, blockage [35], catalyst contamination [98] and hence lower hydrogen generation rates.

Effect of temperature

Temperature is another factor on hydrogen generation rate. Arrhenius equation is useful tool that defines the relation between hydrogen generation rate and temperature:

$$k = A e^{-E_a/RT} \quad (2)$$

Above equation, k is rate constant ($\text{L}_{\text{H}_2}\text{g}^{-1}\text{cat}\cdot\text{min}^{-1}$), A is frequency factor, E_a is activation energy (kJmol^{-1}), R is universal gas constant $8.314 \times 10^{-3} \text{ kJmol}^{-1}\text{K}^{-1}$ and T is temperature (K). To obtain HGR changes with temperature, hydrogen releasing experiments have been carried out at 308 K, 318 K, 328 K, 338 K for CoB-T150 and CoB catalysts. As mentioned before, 5% NaBH_4 and 5% NaOH ratios as the optimum HGR results obtained conditions have been used for these experiments. The HGR results were evaluated, and a graph illustrating the relationship between the natural logarithm of HGR and temperature⁻¹ has been presented in Fig. 13. Slope of results refer that temperature has positive effect on hydrogen

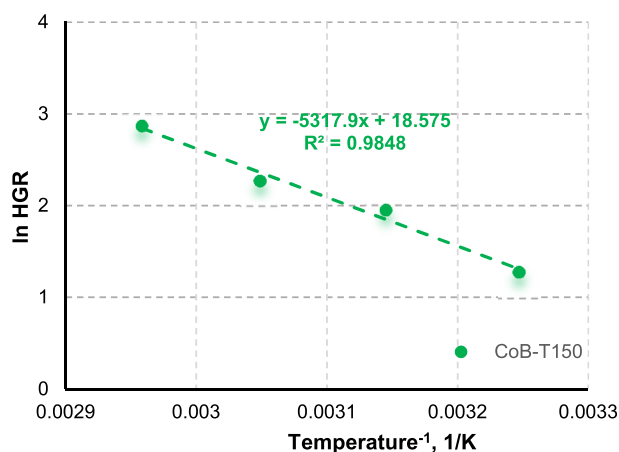


Fig. 13 – Temperature effect on HGR of CoB-T150.

generation rate [35]. In addition to this, activation energy may be obtained from above equation with known temperature and HGR values. This energy may be lowered by suitable catalysts. Activation energy has been obtained as 44.21 kJ/mol for CoB-T150 catalyst. Activation energy is an important indicator for reactions that indicates required barrier energy for reaction. To compare activation energies of CoB-T150 and previous developed cobalt boride catalysts in the literature, Table 3 is given. Activation energies of developed cobalt boride catalysts have been ordered from smallest to largest. It may be concluded that CoB-T150 has relatively smaller value according to literature.

Effect of catalyst amount

Fig. 14 shows CoB-T150 catalyst amount effect on hydrogen generation rate in the presence of 5% NaOH and 5% NaBH_4 . 5 mg, 10 mg and 15 mg catalysts were used during 65 °C reaction temperature. As shown in the figure below, the slope is nearly direct proportional to the catalyst amount. Faster reaction occurs via surface interaction [117] and more catalyst provides more interactive area [15].

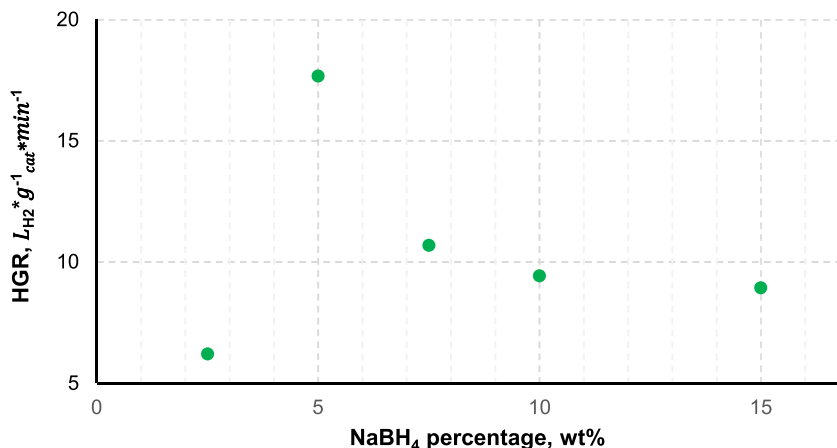
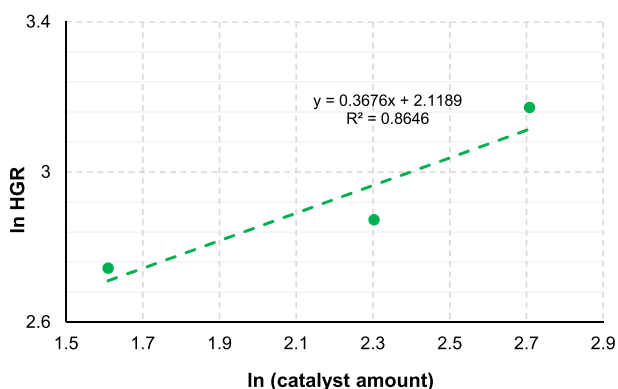


Fig. 12 – The relation between HGR and NaBH_4 percentage in fuel by weight.

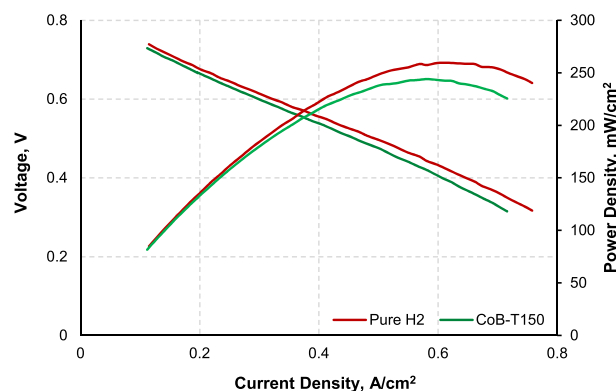
Table 3 – A comparison of the activation energy results of CoB catalysts in the literature (The result of this study is shown in bold type).

Reference	Catalyst	Ea, kJ/mol
Wang et al. [99]	CoB–O	26.85
Dai et al. [100]	Co–W–B/Ni foam	29
Guo et al. [101]	Ni–CoB	33.1
Zou et al. [102]	Co–Ce–B/Chi-C	33.1
Zhao et al. [90]	Co–Mo–Pd–B	36.36
Gupta et al. [103]	CoB–P123 CoB-CTAB	40 44
Huang et al. [104]	CoB/MWCNT	40.4
Ke et al. [105]	Co–Mo–B	43.7
This study	CoB-Triton 150	44.21
Chen and Jin [92]	Co–Cr–B	44.51
Lee et al. [44]	CoB/Ni foam	45
Shen et al. [106]	W–CoB/Ag–TiO ₂	47
Özdemir [107]	Co–B/G	51.3
	(Impregnation–reduction)	
	Co–B/GC	49.5
	(Impregnation–reduction)	
	Co–B/G	48.7
	(Reduction–precipitation)	
	Co–B/GC	47.3
	(Reduction–precipitation)	
Wang et al. [108]	Co–Ru–Mo–B	48.8
Baydaroglu et al. [56]	Co–W–B/Ppy	49.18
Saka et al. [109]	CH ₃ COOH-kaolin-CoB	49.41
Aydin et al. [15]	Co–Ti–B	49.88
Lu et al. [110]	CoB/TiO ₂	51
	CoB/Al ₂ O ₃	56.8
	CoB/CeO ₂	55.3
Wang et al. [111]	Co–Cu–B	52
Yuan et al. [112]	Co–Mn–B	52.1
Aydin et al. [113]	CoB-Graphene	52.45
Loghmani and Shojaei [89]	Co–La–Zr–B	53
Kıpçak and Kalpazan [114]	CoB/bentonite	55.76
	CoB/Na-bentonite	56.61
Tian et al. [115]	CoB/Attapulgit clay	56.32
Zhao et al. [116]	CoB/C	57.8

**Fig. 14 – Catalyst amount effect on HGR of CoB-T150.**

Fuel cell performance

To understand quality of produced hydrogen, Fig. 15 shows single proton exchange membrane fuel cell results of

**Fig. 15 – PEMFC results of pure H₂ and released hydrogen from NaBH₄ with CoB-T150.**

industrial pure hydrogen as 99,99% purity and hydrogen released from NaBH₄ reaction by CoB-T150 catalyst. According to the results, pure hydrogen gives better performance results. Whereas industrial pure hydrogen has maximum power density as 259.53 mW/cm², maximum power density of CoB-T150 is 244.02 mW/cm². Difference is 5.97% compared to industrial pure H₂. Oxidation reaction is taking place at the anode side and purity of hydrogen determines anode potential and hence power. Disadvantage of borohydride reaction is impurities in the H₂ [118]. However, obtained 5.97% maximum difference in this study indicates that the performance is almost same for industrial H₂ and H₂ of hydrolysis reaction.

Conclusion

The effect on hydrolysis performance of the different CoB catalysts formed via Triton X-100 surfactant addition in different amounts has been investigated. The optimum surfactant amount during catalyst preparation have been identified and for the best catalyst, NaOH and NaBH₄ concentrations in the fuel, catalyst amount and temperature effects have been investigated via hydrogen generation rate experiments. Moreover, to determine purity of H₂, fuel cell performance experiments have been carried out. Among the prepared catalysts, 17.69 L_{H₂}*g⁻¹*cat*min⁻¹ hydrogen generation rate has been obtained with CoB-Triton 150 (CoB-T150) catalyst, whereas the result of the standard catalyst (CoB) is 12.61 L_{H₂}*g⁻¹*cat*min⁻¹. According to fuel cell experiments, the developed CoB-T150 catalyst and hydrolysis reaction provides almost same degree of hydrogen quality with industrial hydrogen. Besides, low activation energy was measured as 44.21 kJ/mol with developed CoB-Triton 150 catalyst. Results indicates that, Triton X 100 can be a good promoter for CoB catalysts, with its easily implementation and good results compared to metal alternatives. The findings obtained from the study will significantly contribute to the hydrolysis performance of NaBH₄ and enhance awareness regarding alternative hydrogen energy that can be used to reduce harmful emissions caused by maritime transportation.

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.

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