



# Cobalt Nanoparticles Supported Active Carbon from Chitosan Biopolymer Using Thermal Method: Synthesis, Characterization, and Hydrogen Production

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## Abstract

Activated carbon based Cobalt nanoparticles (Co@AC NPs), considered in the context of hydrogen energy, which is a renewable and sustainable energy, were synthesized by the hydrothermal method, and their catalytic activities were tested. For this, hydrogen production tests were carried out with the help of sodium borohydride (NaBH<sub>4</sub>) methanolysis of Co@AC NPs synthesized by the thermal method. Ultraviolet–visible spectroscopy (UV–Vis), Fourier transmission spectroscopy (FTIR), transmission electron microscopy (TEM), and X-ray diffraction (XRD) characterization tests were performed. According to the TEM characterization result, it has been observed that the NPs have a spherical shape and an average size of  $2.52 \pm 0.92$  nm. Then, using the catalytic studies, it was observed that hydrogen production's reusability is found to be 86%. The activation energy ( $E_a$ ), enthalpy ( $\Delta H$ ), and entropy ( $\Delta S$ ) values were found to be  $20.28 \text{ kJ}\cdot\text{mol}^{-1}$ ,  $17.74 \text{ kJ}\cdot\text{mol}^{-1}$ , and  $-125.97 \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$ , respectively. The obtained values have yielded excellent results and guide future sustainable and renewable hydrogen energy studies by reducing costs, ensuring environmental sustainability by avoiding the formation of undesirable by-products, and producing hydrogen from NaBH<sub>4</sub> through its high catalytic properties.

**Keywords** Catalytic studies · Activated carbon based Cobalt nanoparticles · Hydrogen energy · Turner of frequency

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## 1 Introduction

The energy utilized daily to meet humanity's needs is of paramount importance [1]. Fossil fuels used in line with these needs are on the verge of extinction today and at the same time harm the environment to a large extent [2]. Given this impending scarcity, the imperative now is to transition to sustainable energy sources [3]. Hydrogen energy, which is a positive option in terms of both power density and ease of transportation, has been found among alternative energy sources, which can be a solution for this purpose [4, 5].

Hydrogen is very interesting because it is a non-toxic, environmentally friendly, emission-free, sustainable, and renewable energy type [6]. There are various reports on hydrogen energy in the literature [3, 6–9]. Hydrogen energy is an emission-free, environmentally friendly, and efficient alternative energy type compared to fossil fuels [4, 10–12]. There are many hydrogen sources such as amine boranes, phosphoric acid, and borohydrides from which hydrogen energy is obtained [6, 13, 14]. Among these sources, there are derivatives of borohydrides ( $\text{BH}_4$ ) such as sodium borohydride ( $\text{NaBH}_4$ ) [15], potassium borohydride ( $\text{KBH}_4$ ) [16], calcium borohydride ( $\text{Ca}(\text{BH}_4)_2$ ) [17] and magnesium borohydride ( $\text{Mg}(\text{BH}_4)_2$ ) [17] etc. Among these sources, sodium borohydride is a more applicable source in terms of hydrogen content, ease of use, and cost compared to other sources [18]. It is also crucial for sustainable and renewable energy as it is a substrate that can be recycled through the by-products obtained from the methanolysis or hydrolysis of  $\text{NaBH}_4$ . The methanolysis reaction of  $\text{NaBH}_4$  is as in Eq. 1 [6, 9, 18].



Nano-sized catalysts that facilitate the methanolysis of sodium borohydride are very effective and there are various studies reported in the literature on this subject [19–21]. In addition, it is thought the efficiency is directly proportional to increasing the surface areas of nano-structured materials with support materials (Activated carbon, Vulcan carbon, Poly(vinylidene fluoride), etc.) [22–24]. While many nontoxic organic materials can be used in the production of activated carbon, there is also information on the use of chitosan. In a reported study, activated carbon synthesized through chitosan has been shown to have very positive effects in terms of both efficiency and cost, as well as sustainability [25]. In a study reported on  $\text{Co}_3\text{O}_4$  microplates, it was stated that electron-rich and electron-deficient areas facilitate the adsorption of  $\text{BH}_4^-$  and  $\text{H}_2\text{O}$  and are vital in the hydrolysis of  $\text{NaBH}_4$  for rapid hydrogen production [26]. Despite these studies, there are still deficiencies in efficiency and speed studies, as well as deficiencies in the use of high-function support materials such as activated carbon, which is a very

effective method for increasing the surface areas of nanomaterials. It is thought that these deficiencies can be eliminated by developing the synthesis methods of catalysts or by testing various metals.

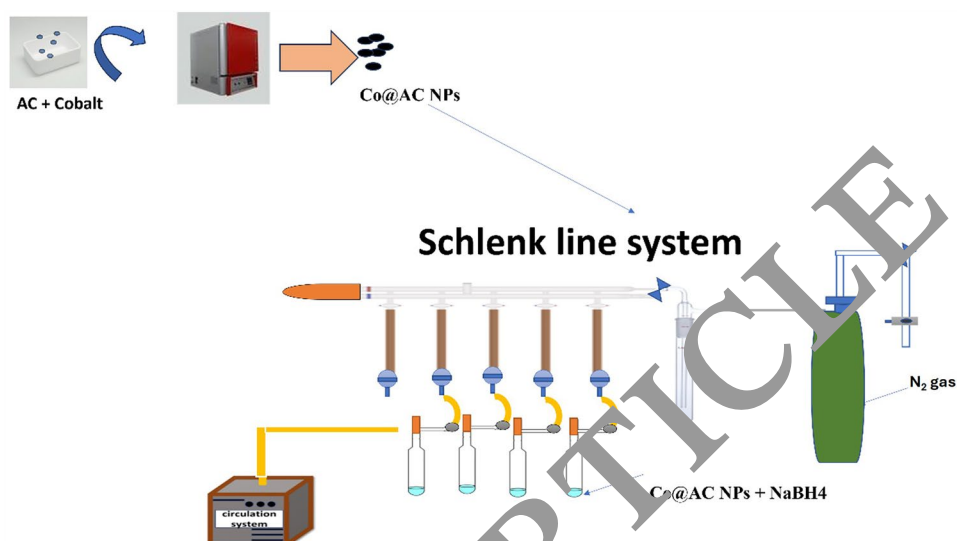
Nanoparticles (NPs) are materials in the size range of 1–100 nm [27–31]. NPs are studied in chemistry [32, 33], catalytic studies [3, 6, 34, 35], sensor studies [36–38], optics [39], and electronics [40]. Studies on the hydrogenation and photocatalytic decomposition of zinc oxide nanoparticles made from coffee oil have been published [8]. Hydrogen catalytic studies and antibacterial measurements of silver-platinum nanoparticles synthesized from propolis have taken their place in the literature [41]. An aptamer-based sensor was developed using mesoporous silica nanoparticles [33].

There are many synthesis derivatives of nanomaterials in the literature [42]. Among these synthesis methods, the hydrothermal synthesis method is a very valid method for the stabilization of particle sizes of nanomaterials [43]. Studies using  $\text{NaBH}_4$  in the reduction of nanomaterials by the hydrothermal method are also available in the literature [44]. However, the hydrothermal synthesis of Co and AC, which is very cost-effective and can provide great functionality in terms of efficiency, and the study and sustainability of hydrogen production from  $\text{NaBH}_4$ , have originality.

This study aims to synthesize Co nanoparticles by hydrothermal route to have well-crystallized nanoparticles with a smaller size and to have a more efficient catalyst for kinetic research. For the first time, cobalt nanoparticles were synthesized by hydrothermal method and also combined with activated carbon as a support, and the obtained nanoparticles were used as a catalyst for hydrogen production by methanolysis at different  $\text{NaBH}_4$  concentrations in the Schlenk system.

Herein, the methanolysis of  $\text{NaBH}_4$  employing activated carbon-supported cobalt nanoparticles ( $\text{Co@AC}$  NPs) as catalysts and the hydrothermal synthesis of activated carbon from chitosan (CTS) are discussed. For this study, the hydrogen production capacity of NPs at different concentrations, substrates, and temperatures was analyzed. Activation energy, enthalpy, entropy, and turnover frequency (TOF) were obtained from the activation parameters of NPs in the methanolysis reaction of  $\text{NaBH}_4$ . To test the sustainability of the nanomaterial obtained in the context of a catalyst in hydrogen energy studies, reusability tests were carried out in 4 cycles and the average reusability data of the nanomaterial was obtained. The synthesized samples were characterized by X-ray diffraction characterization (XRD), transmission electron microscopy (TEM), Fourier transmission infrared spectrophotometer (FTIR), and ultra-violet visible (UV–Vis) analysis. The results were compared with the literature.

**Scheme 1** The synthesis of nanoparticles and the generation of hydrogen using Schlenk method



## 2 Material & Methods

CTS (deacetylated-90%), cobalt (II) chloride (95%,  $\text{CoCl}_2$ ),  $\text{NaBH}_4$ , and all chemicals were obtained from Sigma & Aldrich.

A Perkin Elmer Spectrum Two brand equipment was used to perform FTIR characterization in the band region of  $500\text{--}4000\text{ cm}^{-1}$ . Using a Perkin Elmer Lambda 750 brand equipment, absorbance readings between 250 and 800 nm were obtained for UV–Vis characterization. With the use of a Panalytical Empyrean XRD instrument, the crystalline nano-size of NPs was determined. The TEM characterization was also performed to determine the NPs sizes and to clarify their morphological structure.

$\text{Co@AC NPs}$  have been prepared by hydrothermal method. For this aim, 100 mg of CTS was placed in a ceramic cuvette. Then, the CTS in the ceramic cuvette was burned at  $250^\circ\text{C}$  for 3 h to perform the carbon generation process. Then, C was obtained by ultrasonication under 25 mL of  $\text{HNO}_3$  and 25 mL of  $\text{H}_2\text{SO}_4$  for 10 min [45, 46]. The prepared NPs were made by transferring 4 mL of 0.3 mM  $\text{CoCl}_2$  in an AC-containing teflon autoclave using 1 mL  $\text{NaBH}_4$  and then handling the mixture for 5 h at  $250^\circ\text{C}$  [47]. The resulting black-colored  $\text{Co@AC NPs}$  were stored for the next step to be used in catalytic reactions [18] (Scheme 1).

In catalytic studies for hydrogen production, a Schlenk mechanism connected to a water circulation system that kept the ambient temperature constant was used [3]. Kinetic studies were validated by performing methanolysis reactions to obtain hydrogen from  $\text{NaBH}_4$ . For this reason, first of all,  $\text{NaBH}_4$  methanolysis was investigated at different concentrations (2.25 mM, 4.50 mM, 6.75 mM, and 9.00 mM  $\text{Co@AC NPs}$ ) under fixed parameters ( $25^\circ\text{C}$  and 125 mM  $\text{NaBH}_4$ ).  $\text{NaBH}_4$  substrate activity was then

determined using 2.25 mM  $\text{Co@AC NPs}$  and concentrations of 125 mM, 300 mM, 350 mM, and 400 mM at  $25^\circ\text{C}$ . Finally, the efficiency of methanolysis was determined at different temperatures ( $25^\circ\text{C}$ ,  $30^\circ\text{C}$ ,  $35^\circ\text{C}$  and  $40^\circ\text{C}$ ) using 2.25 mM  $\text{Co@AC NPs}$  and 125 mM  $\text{NaBH}_4$ . The activation parameters of  $\text{Co@AC NPs}$  in the methanolysis reaction of  $\text{NaBH}_4$  were calculated using the data obtained as a result of kinetic studies. In kinetic calculations, enthalpy and entropy were calculated using Arrhenius equations for activation energy and Eyring equations to obtain information about energy changes. To obtain information about the reuse of  $\text{Co@AC NPs}$ , sustainability experiments were carried out for 4 cycles at a concentration of 2.25 mM  $\text{Co@AC NPs}$  at  $25^\circ\text{C}$  in the presence of 125 mM substrate, and the average efficiency was obtained [3, 6].

## 3 Results & Discussion

### 3.1 Characterization

UV–Vis characterization performed to identify AC and  $\text{Co@AC NPs}$  synthesized using the hydrothermal method in terms of organic molecules, ions, or complexes is shown in Fig. 1. According to Fig. 1a, it was observed that cobalt nanoparticles supported activated carbon gave a broad peak at 514 nm [48]. No clear observation of UV–Vis characterization for AC was observed. However, AC peaks at lower wavelengths have been reported in the literature, but a clear peak could not be obtained as shown in Fig. 1b [49]. According to the results of the UV–Vis characterization of  $\text{Co@AC NPs}$ , it was seen that there was no pollution from the chemicals and the environment used and the synthesis was successful. The results obtained are compatible with the literature [45, 47].

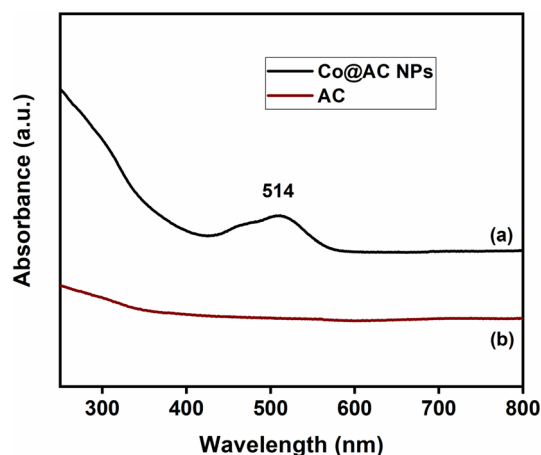


Fig. 1 UV-Vis spectra of (a) Co@AC NPs, (b) AC

Figure 2 shows the result of the FTIR characterization of Co@AC NPs, which was performed for the purpose of molecular bond characterization. According to the FTIR results, the peaks at 3482 and 3412  $\text{cm}^{-1}$  belong to the hydroxyl group of the phenyl groups [50]. The resulting peaks in 2240 and 1592  $\text{cm}^{-1}$  can be attributed to carbonyl groups, amide alcohols, or phenols [50, 51]. The peak of the cobalt metal NPs is responsible for the peak seen at 626  $\text{cm}^{-1}$  [50]. According to the results of FTIR characterization of Co@AC NPs, it was concluded that the nanomaterial obtained was reduced and there was no molecular bond contamination. FTIR characterization results are in good agreement with the previous studies [48, 49].

The XRD characterization performed to understand the crystal lattice structures of Co@AC NPs and to calculate the average particle sizes using the Debye-Scherrer function is shown in Fig. 3. The peaks at 8.4°, 18.4°, and 40.0° theta degrees originating from AC were observed and the corresponding lattices are (002), (002), and (100) planes [52,

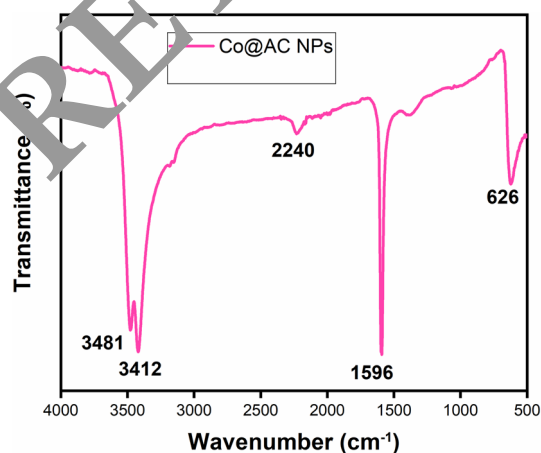


Fig. 2 FTIR spectra of Co@AC NPs

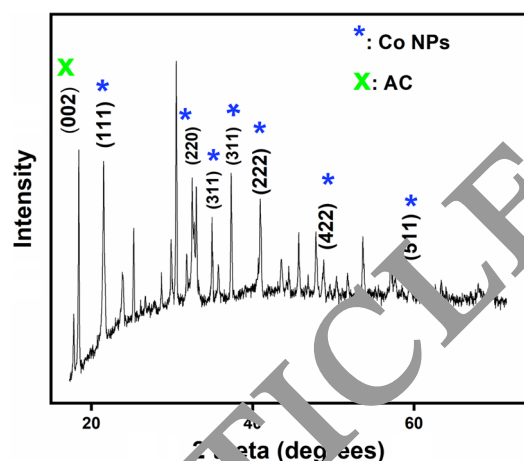


Fig. 3 XRD analysis pattern of Co@AC NPs

[53]. The peaks originating from Co NPs appear at 21.5°, 32.9°, 34.7°, 36.9°, 40.1°, 48.31° and 59.1° theta degrees and corresponding lattice planes (111), (220), (311), (311), (222), (422), and (511) respectively [54–56]. Some peaks that do not belong to Co@AC NPs are predicted to occur due to external conditions in the environment. According to the results of the XRD characterization of Co@AC NPs, it is understood that the nanomaterial obtained is cobalt-doped AC and its crystal lattice structures are face-centered cubic. The average crystalline size of the NPs was determined to be 1.77 nm based on the XRD characterization data. These obtained data are in good agreement with the literature [57, 58].

The TEM characterization performed to understand the morphological structure of Co@AC NPs and to calculate the particle size obtained as a result of synthesis at the nanoscale is included in Fig. 4. The average value was obtained by counting 100 nanoparticles in the obtained TEM images using the *ImageJ* application. It was observed that the synthesis of Co@AC NPs synthesized with the TEM analysis result was successful. According to Fig. 4a, Co@AC NPs are narrow in size and have a spherical structure [59]. The average size of nanoparticles was computed to be  $2.52 \pm 0.92$  nm (Fig. 4b). It was concluded that the characterization results obtained from XRD and TEM support each other. The size of nanoparticles is similar to previous studies [60, 61].

### 3.2 Catalytic Studies

The catalytic effect of the synthesized Co@AC NPs on the  $\text{NaBH}_4$  substrate methanolysis reaction is as in Fig. 5.

According to Fig. 5a, the effect of hydrogen production was examined under fixed parameters (125 mM  $\text{NaBH}_4$  and 25 °C) with NPs concentrations of 2.25, 4.50, 6.75, and 9.00 mM (Fig. 5a). According to Fig. 5a, the concentration

of 2.25 mM of Co@AC NPs catalyst generates 40 mL of  $H_2$  volume in the time of 60 second, and the concentration of 9.00 mM of catalyst generates 116 mL of  $H_2$  volume in 60 second which mean when the amount of hydrogen generated increase with the increase of the catalyst's concentration. Increasing the catalyst concentration can promote greater hydrogen production by increasing the number of active sites, improving reaction kinetics, promoting interaction between reactants, and reducing

diffusion effects [26]. A 2.9-fold difference in hydrogen volume was reported between the experiments with the lowest and highest catalyst concentrations. The linear sections of the graphs presented in Fig. 5b were used to calculate the hydrogen generated. These results show that the  $NaBH_4$  methanolysis reaction is first order dependent on the catalyst concentration ( $R^2$ : 0.995).

The effect of  $NaBH_4$  substrate at different concentrations in catalytic activity experiments is given in Fig. 6. The

**Fig. 4** TEM analysis of **a** Co@AC NPs image **b** Co@AC NPs size histogram

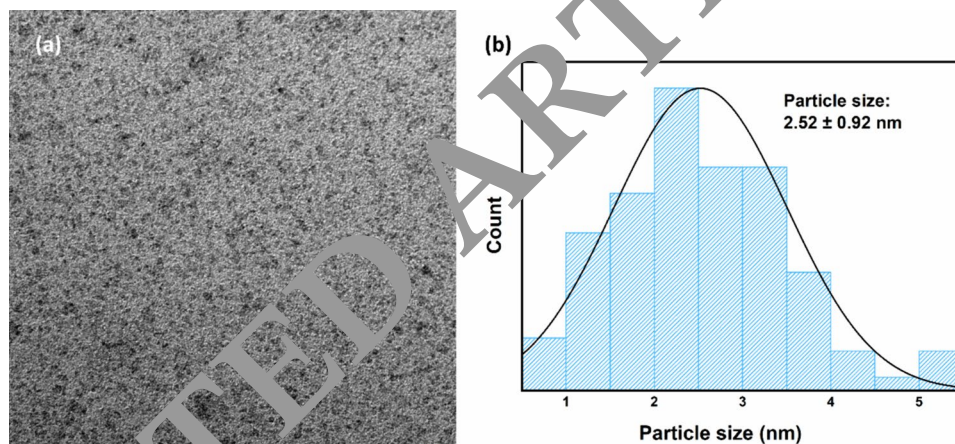


**Fig. 5** **a** Methanolysis of  $NaBH_4$  at various catalyst concentrations ( $NaBH_4$  concentration = 125 mM, 25 °C); **b** Relationship between logarithmic rate of hydrogen release and logarithmic Co@AC NPs concentration. (Experiment repeated at least 3 times)

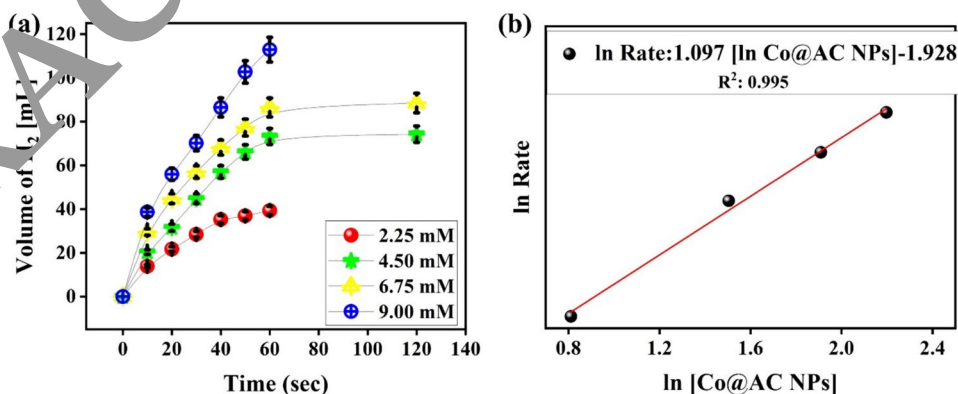
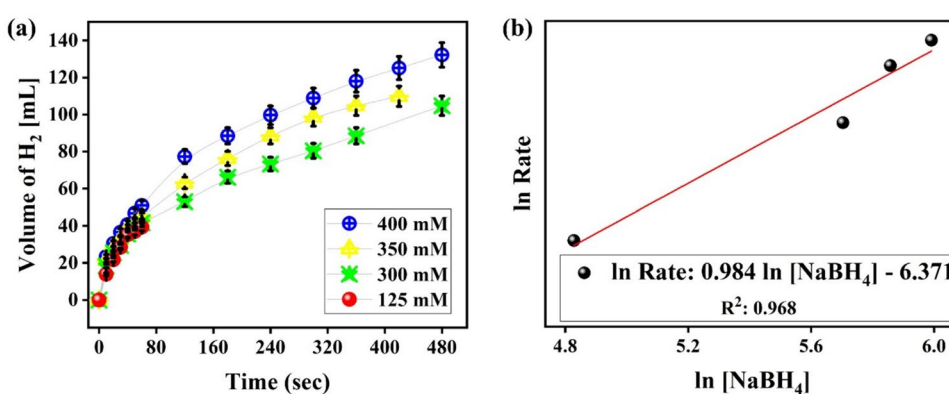


**Fig. 6** Plots of **a** hydrogen volume in various  $NaBH_4$  concentrations (2.25 mM Co@AC NPs, 25 °C), and **b** In the base of the logarithm, the hydrogen release rate is correlated with the  $NaBH_4$  concentration. (Experiment repeated at least 3 times)



catalytic results at different 125, 300, 350, and 400 mM  $\text{NaBH}_4$  constant parameters (25 °C and 2.25 mM Co@AC NPs) are as shown in Fig. 6a. These findings show that hydrogen generation increases as substrate concentration rises and that the difference in hydrogen volume between the lowest and highest substrates is 3.9 times. The hydrogen release rate was calculated using the related linear areas. The logarithmic linear graph has a slope of 0.984 ( $R^2$ : 0.968) (Fig. 6b). Finally, the reaction was seen as first-order substrate dependent.

The rate law equation (Eq. 2) for the computation of activation parameters as a result of  $\text{NaBH}_4$  methanolysis is demonstrated in the order that follows [43]:

$$\text{Rate} = k \cdot [\text{NaBH}_4]^{0.984} \cdot [\text{Co@AC NPs}]^{1.097} \quad (2)$$

After the substrate and catalyst hydrogen production experiments, the effect of hydrogen production at different

temperatures was examined (Fig. 7). Hydrogen production efficiency was tested under 2.25 mM Co@AC NPs and 125 mM substrate under 25, 30, 35, and 40 °C temperatures (Fig. 7a). In order to create the activation parameters, rate constants ( $k$ ) were utilized. Activation parameters were also calculated using Arrhenius and Eyring plots. According to calculations,  $E_a$ ,  $\Delta H$ , and  $\Delta S$  values are 20.28 kJ/mol, 17.74 kJ/mol, and  $-125.97 \text{ J/mol}\cdot\text{K}$  respectively. The TOF, which is the most important determining measurement of catalytic studies, was determined to be  $397.68 \text{ s}^{-1}$ . When hydrogen is generated by  $\text{NaBH}_4$  methanolysis, the resulting  $E_a$  value is much lower than the value of typical catalysts (Table 1). These results show that the production of hydrogen from  $\text{NaBH}_4$  methanolysis utilizing Co@AC NPs results in considerable catalytic activation.

Reusability testing was performed using fixed parameters (125 mM  $\text{NaBH}_4$ , 2.25 mM Co@AC NPs, 25 °C) (Fig. 8). The HGP amounts calculated based on the volumetric

**Fig. 7** **a** The effect of temperature for the  $\text{NaBH}_4$  methanolysis to produce hydrogen (125 mM  $\text{NaBH}_4$ , 2.25 mM Co@AC NPs, 25 °C), and **b** the Arrhenius plot. (Experiment repeated at least 3 times)

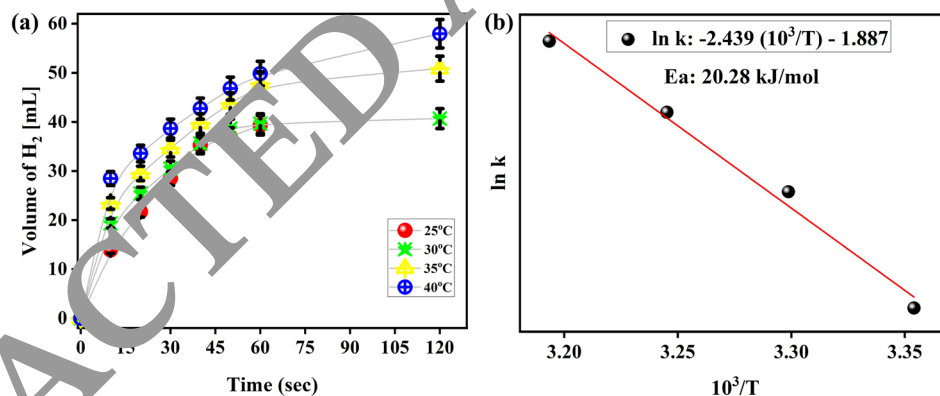
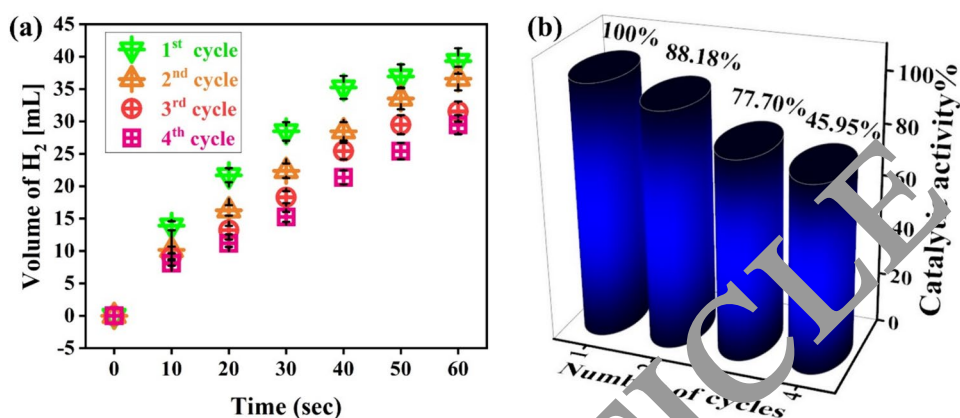


**Table 1** A comparison of the performance of catalysts in hydrogen production

| Entry | Catalysts                              | TOF (Turnover frequency)                                      | Activation energy (kJ/mol) | Enthalpy ( $\Delta H$ ) | Entropy ( $\Delta S$ )               | Ref        |
|-------|----------------------------------------|---------------------------------------------------------------|----------------------------|-------------------------|--------------------------------------|------------|
| 1     | Co-Cu-B                                | $3554.2 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$     | 52                         | —                       | —                                    | [62]       |
| 2     | Co/MWCNTs                              | $409 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$        | 51.3                       | —                       | —                                    | [63]       |
| 3     | Pt                                     | $4028 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$       | —                          | —                       | —                                    | [64]       |
| 4     | Pd/ $\text{Co}_3\text{O}_4$            | $2109 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$       | 65.82                      | —                       | —                                    | [65]       |
| 5     | G-Co-Pt                                | $107 \text{ min}^{-1}$                                        | 16                         | —                       | —                                    | [66]       |
| 6     | $\text{PtCo}_{\text{fiber}}/\text{Cu}$ | $18 \text{ L}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$          | 62.6                       | —                       | —                                    | [67]       |
| 7     | CoPt-PEDOT:PSS/MWCNT                   | $6.9 \text{ L}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$         | 47.3                       | —                       | —                                    | [68]       |
| 8     | Pt/ $\text{LiCo}_2$                    | $3100 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$       | —                          | —                       | —                                    | [69]       |
| 9     | Pt/ $\text{Co}_3\text{O}_4$            | $4713 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$       | 43.52                      | —                       | —                                    | [65]       |
| 10    | Pd/C                                   | $2.8 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$        | —                          | —                       | —                                    | [70]       |
| 11    | NiCoPd                                 | $680 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$        | 58.5                       | —                       | —                                    | [71]       |
| 12    | Au NPs/CTS/AC                          | $202 \text{ h}^{-1}$                                          | —                          | —                       | —                                    | [72]       |
| 13    | ZnO@AC/CTS                             | $1257.69 \text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$    | 42.52                      | 39.98                   | $-181.42$                            | [9]        |
| 14    | Co@AC NPs                              | $397.68 \text{ s}^{-1}$<br>$546.17 \text{ mL/s}\cdot\text{g}$ | 20.28 kJ/mol               | 17.74 kJ/mol            | $-125.97 \text{ J/mol}\cdot\text{K}$ | This study |

**Fig. 8** **a** Reusability test graph and **b** related bar chart of the Co@AC NPs (2.25 mM) catalyst in the methanolysis of  $\text{NaBH}_4$  (125 mM) at 25 °C. (Experiment repeated at least 3 times)



hydrogen amounts obtained as a result of 4 cycles were expressed as a percentage by proportion to the amount of hydrogen obtained under optimum conditions, and it was revealed to what extent the nanomaterial maintained its catalytic activity through the average of 4 cycles. The HGRs were obtained as 546.1 mL/s·g, 508.5 mL/s·g, 430.5 mL/s·g, 402.7 mL/s·g, respectively. These processes were repeated 4 times by washing after each use (Fig. 8a). In the fourth investigation, it was discovered that the Co@AC NPs catalyst maintained 86% of its initial efficiency and showed high reusability (Fig. 8b). As a result of the 4-cycle repeatability experiment carried out to understand the sustainability of NPs, it was concluded that NPs were sustainable by maintaining 89% efficiency.

## 4 Conclusion

In this work, the hydrothermal synthesis of Co@AC NP and the  $\text{NaBH}_4$  methanolysis process were used to investigate the catalytic activity for hydrogen generation. Samples characterization analysis using FTIR, UV–Vis, XRD, and TEM were performed to be able to clarify the structure and morphology of the prepared nanomaterials. XRD and TEM analysis of Co@AC of NPs were performed for determination of their crystal lattice and morphological structure and particle size. As a result of XRD, the average crystalline size of Co@AC NPs with a face-centered cubic crystal lattice structure was 1.77 nm, while as a result of TEM characterization, the average nano size of Co@AC NPs was determined to be  $2.52 \text{ nm} \pm 0.92 \text{ nm}$ . Considering the characterization of Co@AC NPs, it was seen that the results are in good agreement with each other. The catalytic activity and kinetic study of Co@AC NPs were determined, for methanolysis studies using  $\text{NaBH}_4$ , it was determined that the first-order reaction was dependent on temperature, substrate, and catalyst amount. In terms of the sustainability of Co@AC NPs, reusability experiments

were carried out for 4 cycles by determining optimum conditions, and as a result, it was shown that the hydrogen production efficiency was 86%. As a result of kinetic studies of the methanolysis reaction of  $\text{NaBH}_4$  in the presence of Co@AC NPs, Ea,  $\Delta H$ , and  $\Delta S$  values were measured as  $20.28 \text{ kJ} \cdot \text{mol}^{-1}$ ,  $17.74 \text{ kJ} \cdot \text{mol}^{-1}$  and  $-125.97 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ , respectively. According to these results, it has been observed that hydrogen production is achieved perfectly and has a potential important industrial application.

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**Data availability** Data will be made available on request.

## Declarations

**Conflict of interest** There is no conflict of interest between the authors.

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