

Research Article

Sonochemical Approach to Synthesis of Co-B Catalysts and Hydrolysis of Alkaline NaBH₄ Solutions

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Co-B catalysts are promising candidates for hydrogen evolution via hydrolysis of alkaline sodium borohydride (NaBH₄) solutions. In the present paper, a sonochemical approach was investigated for synthesis of Co-B catalysts and hydrolysis of alkaline NaBH₄ solutions. Sonochemical application on synthesizing process improved the intrinsic and extrinsic properties of Co-B catalysts such as crystal, spectral, surface area, pore volume, pore diameter, and particle size. Co-B catalysts prepared by sonochemical approach possessed smaller particle size, higher surface area, and higher pore volume than the Co-B catalysts prepared by coprecipitation synthesis. The effects of sonochemical process on hydrolysis of alkaline NaBH₄ solutions were investigated by Arrhenius theory. It was clearly demonstrated that the advantages of alkaline NaBH₄ solution sonohydrolysis provide superficial effects on hydrogen evolution kinetic as maximum H₂ generation rate (HGR) and minimum activation energy (E_a).

1. Introduction

NaBH₄ as a solid state hydrogen storage material for on-board hydrogen generation systems has drawn much attention due to its superficial properties as it is non-flammable, nontoxic, selective, environmentally friendly, and also one of the light weight complex hydrides with high hydrogen capacity (11 wt.%) [1–3].

NaBH₄ is self-decomposable in aqueous solutions and can be stabilized by alkalization [2, 4]. Hydrogen generation from NaBH₄ is supplied for fuel cells by means of alkaline solution hydrolysis in contact with certain catalysts. Several researchers have been focused on homogeneous and/or heterogeneous catalysts such as acids, metal complexes, metal salts, metal alloys, and supported catalysts. Non-noble metals, especially, have attracted significant attention in terms of both reactivity and costs. Among different non-noble catalysts such as Co, Ni, Cu, and Fe catalysts could be used for hydrolysis reactions of alkaline NaBH₄ solutions from the view point of low cost, stability, crystallinity, and high activity [4–8].

Between all non-noble metals for hydrogen evolution via hydrolysis of alkaline NaBH₄ solutions, researchers have shown much attention to Co-B catalysts because of their prior properties. Cavaliere et al. stated that Co-B catalyst, a black

solid, could be classified in two categories as cobalt boride (Co_xB) and cobalt-boron alloy (Co-B). Considering this the chemical structure of cobalt borides has been reported unclear and obtained variety of structure as CoB, Co₂B, Co₃B, and Co_xB [9, 10]. Researchers suggested that XRD and XPS techniques can be used to characterize Co-B structure. Furthermore amorphous Co-B catalyst is identified with a broad peak centered at around 45° diffraction angle [11]. Many methods for synthesizing of Co-B catalysts including chemical reduction [12], sol-gel [13, 14], and wet impregnation [15] are reported in the literature.

Sonochemical approach has been performed in a large number of organic reactions. Sonowaves, that is, to say ultrasonic irradiation, are oscillating sound pressure waves with a frequency from about 20 to 100 MHz [16]. This method has been widely used in the preparation of chemical materials such as ceramics [17], alloys [18], composites [19], and polymers [20] due to its cavitation effect on chemical process. Sonowaves enhance the chemical reaction and mass transfer via the physicochemical changes in processed medium [21, 22]. In addition to this, sonowaves are proven as useful technique for inhibiting particle agglomeration in chemical environments [23]. The activity of catalysts can improve by means of using of sonowaves in catalysts preparation step [24].

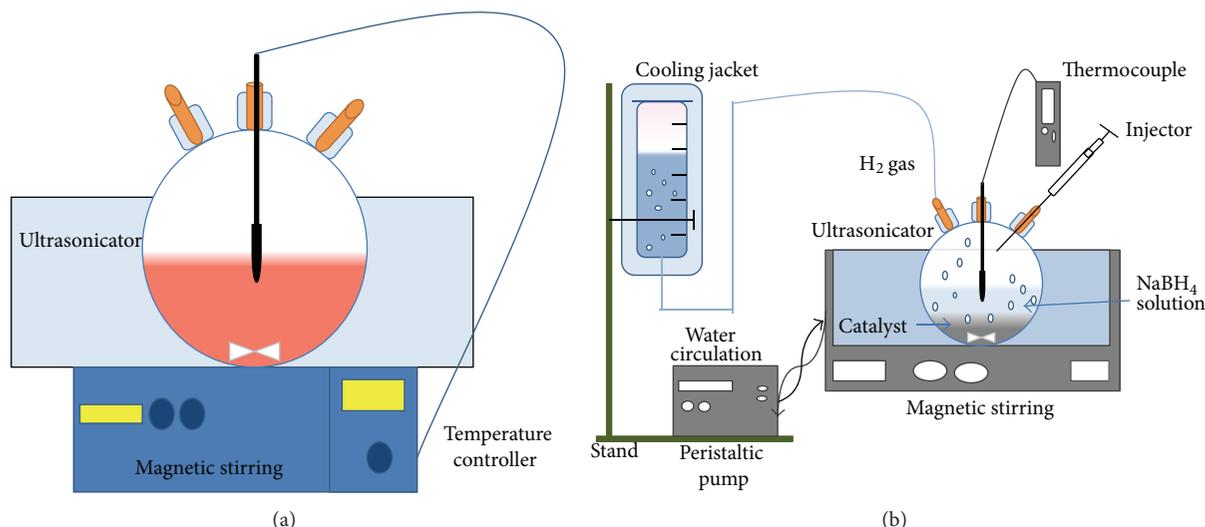


FIGURE 1: Experimental systems. (a) Coprecipitation and sono-coprecipitation synthesis system of Co-B catalyst. (b) Alkaline NaBH₄ sonohydrolysis/hydrolysis system.

It has been reported that uniform spherical Co-B amorphous alloys were prepared by ultrasound assisted (50 W) reduction of $\text{Co}(\text{NH}_3)_6^{2+}$ with BH_4^- in aqueous solution in 30 min. It is also noted that extremely extensive power or very long time is harmful for activity and selectivity due to melting [23]. Vanadium phosphorous oxide catalyst is synthesized using ultrasound irradiation in a relatively short time and its activity improved for hydrocarbon oxidation is tested [22]. Uniform Ni-B amorphous alloy nanoparticles are prepared by ultrasound-assisted reduction of $\text{Ni}(\text{NH}_3)_6^{2+}$ with BH_4^- in aqueous solution and the particle size is controlled by adjusting the ultrasound power. The unique characters of amorphous alloy, morphologic structure, and Ni active sites with higher electron density of this catalyst are crucial for its superior catalytic properties [25]. Ultrasonic hydrolysis of ammonia borane (NH_3BH_3) with sol-gel synthesized Co-B catalyst is firstly investigated and it is noted that hydrogen generation rate has been increased by 37.79% under ultrasonic conditions [26].

The aim of this study was to provide a sonochemical approach and investigation of effects on synthesizing of Co-B catalysts and hydrolysis of alkaline NaBH₄ solutions. For confirming this, Co-B catalysts were synthesized by two methods, as sono-coprecipitation and coprecipitation from cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and boron oxide (B_2O_3), and hydrolysis of alkaline NaBH₄ solutions were performed under sonowaves and magnetic stirring. The intrinsic and extrinsic properties of Co-B catalysts were discussed based on Brunauer-Emmett-Teller surface analysis (BET), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and scanning electron spectroscopy (SEM) characterizations. The hydrolysis of alkaline 0.12 M NaBH₄ solutions were investigated under different reaction temperatures (22°C–60°C) in presence of Co-B catalysts under two different conditions. For identifying the effect of sonochemical approach on hydrolysis kinetics of

alkaline NaBH₄ solutions, Arrhenius theory was used to determine the kinetic parameters.

2. Materials and Methods

B₂O₃ (99% purity) was supplied from Eti Mine Works General Management-Turkey. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ with 97% purity, used as cobalt source, was purchased from Merck. Sodium hydroxide (NaOH) was purchased from Labor Technic, used as stabilizer for NaBH₄ solutions. NaBH₄ with a minimum purity of 96% was supplied by Fluka.

2.1. Sonochemical Approach to Coprecipitation Synthesis of Co-B Catalyst. The system for synthesizing the Co-B catalysts was illustrated in Figure 1(a). In synthesis of Co-B catalysts, two different methods were used. For sonochemical approach, reactor modified with ultrasonicator was used in coprecipitation synthesis of Co-B catalyst. The laboratory type ultrasonicator, that was commonly used for cleaning purpose, was selected. The ultrasonic power of the bath-type ultrasonicator (Bandelin Sonorex Super RK 255H) is 280 W and frequency of irradiation is 35 kHz. Self-certification of sono-co-precipitation synthesis, which was provided by coprecipitation synthesis of Co-B catalyst via reactor modified with magnetic stirring system, was used.

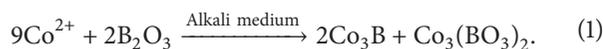
In synthesis of Co-B catalysts, firstly 0.5 M B₂O₃ solution was prepared and then $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were added. 0.1 M NH₄OH was added by drop wise method until pH level of solution reached 6. The solution was mixed for 2 hours at $85 \pm 3^\circ\text{C}$ in reactor to obtain bulk structure. According to the procedure, ultrasonicator or magnetic stirring (500 rpm) was applied during the Co-B catalyst synthesis reaction.

In the synthesis of Co-B catalysts, cobalt precious- CoCl_2 and boron source-B₂O₃ were solved into water. CoCl_2 separates into its anions and cations; by the effect of 0.1 M

TABLE 1: Texture properties of Co-B catalysts.

Code	Synthesis type	Specific surface area (m ² /g)	Pore size (cm ³ /g)	Pore volume (Å)
CoB-1	sono-coprecipitation	3.36 ± 0.16	0.0141	168.67
CoB-2	Coprecipitation	1.98 ± 0.11	0.0066	133.39

NH₄OH addition, the synthesis reaction occurred as (1). The coprecipitation synthesis reaction of Co-B compounds are given as below:



Subsequently, bulk materials were dried at approximately 100°C under the vacuum condition for overnight to eliminate the remaining water molecules. Moreover, forming stable structure, catalysts were calcined at 500°C for 4 hours in air. As a last step, Co-B catalysts were prepared for characterization of the intrinsic and extrinsic properties.

XRD patterns of Co-B catalysts were recorded using Philips Analytical X'Pert-Pro diffractometer with Cu K α radiation in a range of diffraction angles from 5° to 80° with Cu K α radiation ($\lambda = 0.15418$ nm) at operating parameters of 40 mA and 45 kV with 0.02° step size and speed of 1°/min. The morphology and particular size of the Co-B catalysts were observed by using SEM techniques (JEOL JSM 5410 LV). The catalysts were covered with Au and made ready for analysis by fixing to the device's sample holder with the help of a carbon sticky band. Surface properties of Co-B catalysts were determined via using a surface area and porosimetry analyzer (Micromeritics ASAP 2020). Spectral properties were characterized via FT-IR (Perkin Elmer Spectrum One) with ATR accessories in the spectral range of 4000 cm⁻¹–650 cm⁻¹ with a spectral resolution of 4 cm⁻¹ in the transmittance mode.

2.2. Sonochemical Approach to Hydrolysis of Alkaline NaBH₄ Solutions. The hydrolysis reaction of NaBH₄ is as given below. Four mole H₂ is generated during efficient hydrolysis reaction per mole NaBH₄ [1–3]



Figure 1(b) shows the systems; the hydrolysis reactions of alkaline NaBH₄ solutions were carried out. The 15 mL glass reactor was immersed in a system and connected to the water filled inverter burette in order to measure the evolved hydrogen volume. The measured data was used in investigation of hydrolysis kinetic. To compare the results of sonochemical hydrolysis, the system modified with magnetic stirrer and the same procedure was followed for magnetic stirring (500 rpm). According to the procedure, ultrasonicator or magnetic stirring was applied during the hydrolysis of alkaline NaBH₄ solutions.

In the experiments, 10 wt.% NaOH alkaline 0.12 M NaBH₄ was hydrolyzed in presence of 0.5 mg catalysts. The reactions applied in range of 22°C–60°C with temperature controlling system.

The kinetic investigation of sonochemical and magnetic stirring hydrolysis of alkaline NaBH₄ solution was identified

via Arrhenius theory. The characterization of hydrolysis reaction behavior was enlightened by zero-order, first-order, and second-order reaction kinetic models. The activation energies and rate constants were determined via Arrhenius theory [12, 26, 27].

In literature, zero-order reaction is shown as below, model generally defined as reactant independent kinetic model. In the model, C_{NaBH_4} is the concentration, r is the rate of reaction, and k is the reaction rate constant based on the solution volume

$$\frac{dC_{\text{NaBH}_4}}{dt} = -r_{\text{NaBH}_4} = -k(T). \quad (3)$$

Equation (3) is formed as below when the integration is applied:

$$(C_{\text{NaBH}_4} - C_{\text{NaBH}_4}) = -k(T) \cdot t. \quad (4)$$

First-order reaction model is dependent on the reactants' concentration and its basic (5) and integration applied forms (6) are shown below:

$$\frac{dC_{\text{NaBH}_4}}{dt} = -r_{\text{NaBH}_4} = -k(T) \cdot C_{\text{NaBH}_4} \quad (5)$$

$$\ln\left(\frac{C_{\text{NaBH}_4}}{C_{\text{NaBH}_4}}\right) = k(T) \cdot t. \quad (6)$$

The second-order reaction model is also dependent on reactants concentration with second degree and integrated forms are shown below:

$$\frac{dC_{\text{NaBH}_4}}{dt} = -r_{\text{NaBH}_4} = -k(T) \cdot C_{\text{NaBH}_4}^2 \quad (7)$$

$$\left(\frac{1}{C_{\text{NaBH}_4}} - \frac{1}{C_{\text{NaBH}_4}}\right) = -k(T) \cdot t. \quad (8)$$

3. Results and Discussion

3.1. Sonochemical Approach to Coprecipitation Synthesis of Co-B Catalyst. Co-B catalysts were synthesized via two different systems (Figure 1(a)). The CoB-1 catalyst was synthesized with sonochemical approach and CoB-2, which used as control sample, was synthesized by magnetic stirring system. The catalysts were coded according to their synthesis methods (Table 1).

Table 1 shows the textural properties of Co-B catalysts. Comparing the specific surface areas of CoB-1 catalyst with CoB-2 catalyst, the sonochemical approach a considerably increased the surface area of catalyst up to 70%. With this method not only specific surface area increased but also other

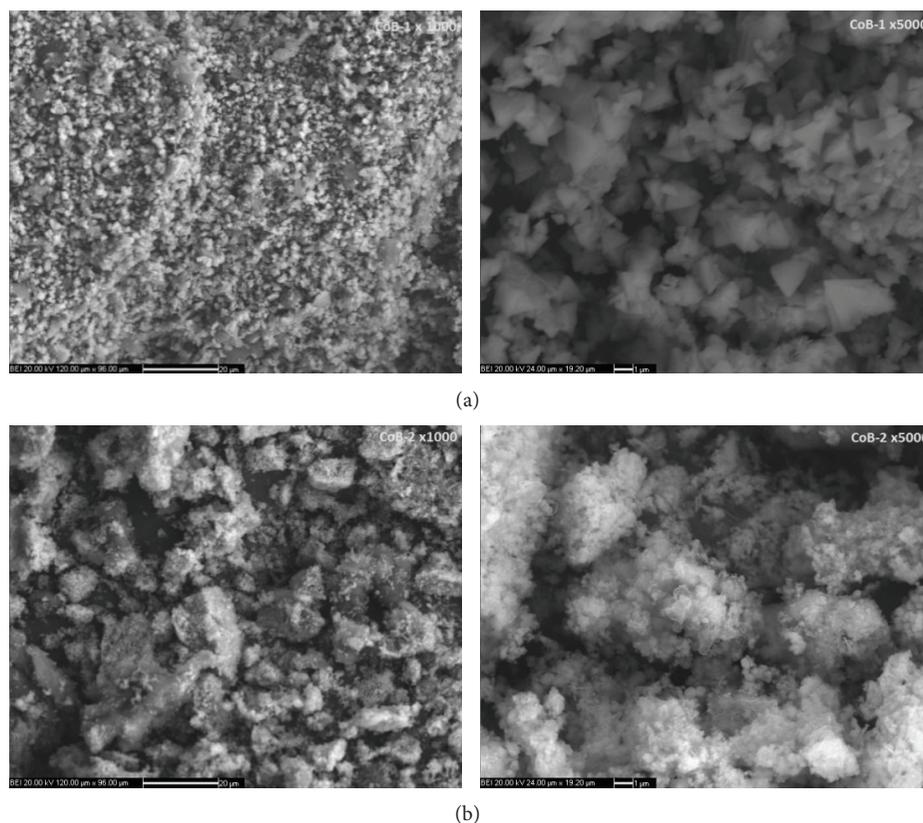


FIGURE 2: The SEM images of Co-B catalysts with $\times 1000$ (left) and $\times 5000$ (right) magnification; (a) CoB-1 catalyst, (b) CoB-2 catalyst.

TABLE 2: Particle size distribution of Co-B catalysts.

Code	Average particle size (μm)	Maximum particle size (μm)	Minimum particle size (μm)
CoB-1	1.25	2.77	0.30
CoB-2	3.00	7.39	0.57

texture properties as pore size and volume of catalysts were improved up to 114% and 26%, respectively.

Figure 2 shows the SEM images of Co-B catalysts at 1000 and 5000 magnification. Particles of Co-B catalyst synthesized by sonochemical approach were homogeneously dispersed and smaller than coprecipitation synthesized Co-B catalyst.

Table 2 shows average, minimum, and maximum particle sizes were measured from SEM images. It was indicated that Co-B prepared with sonochemical coprecipitation synthesis was shown a smaller average size of $1.25 \mu\text{m}$, and particle size of the catalyst was reduced up to 58% (Table 2). BET results were consistent with the SEM results.

Figure 3 shows XRD patterns of synthesized Co-B catalysts. Comparing XRD pattern of synthesized catalysts with the standard diffraction spectrum (JCPDS: 00-012-0443 and 01-073-1540), the synthesized product was crystalline Co_3B and $\text{Co}_3(\text{BO}_3)_2$. The sharpness of XRD reflections clearly

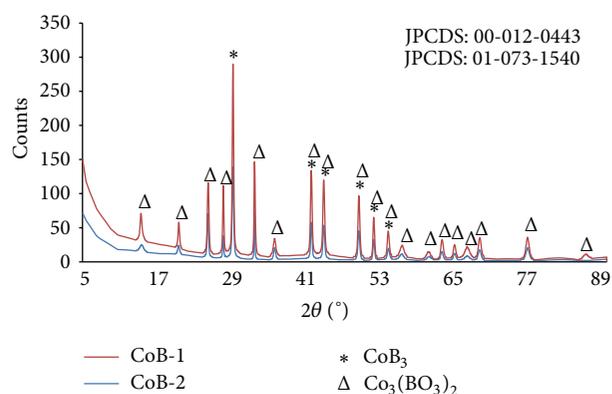


FIGURE 3: The XRD patterns of Co-B catalysts.

shows that the synthesized Co-B catalysts were highly crystalline. The characteristic peaks of phases were indexed in XRD patterns. It was clear that sonochemical treatment does not affect the crystalline phases of Co-B catalysts.

Figure 4 shows FT-IR spectrums of Co-B catalysts. In a direct comparison of the observed FT-IR spectrums of both catalysts, it was clearly seen that B-O band frequencies were detected at the same wave number regions. The bands at 3197 cm^{-1} and 3206 cm^{-1} corresponded to vibration of H-O groups. The bands at 1403 cm^{-1} and $1350\text{--}935 \text{ cm}^{-1}$ were contributed asymmetric stretching of B-O. The bands were

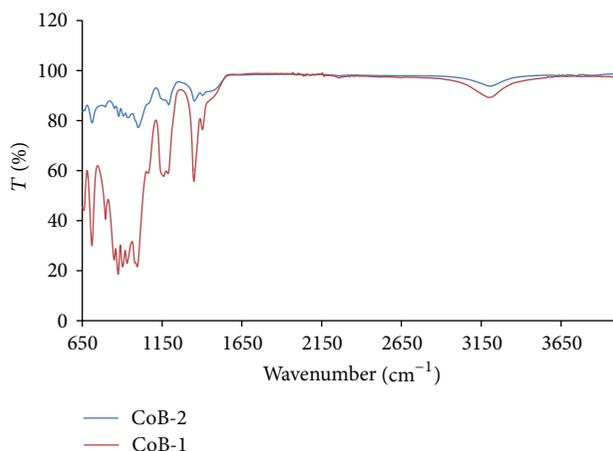
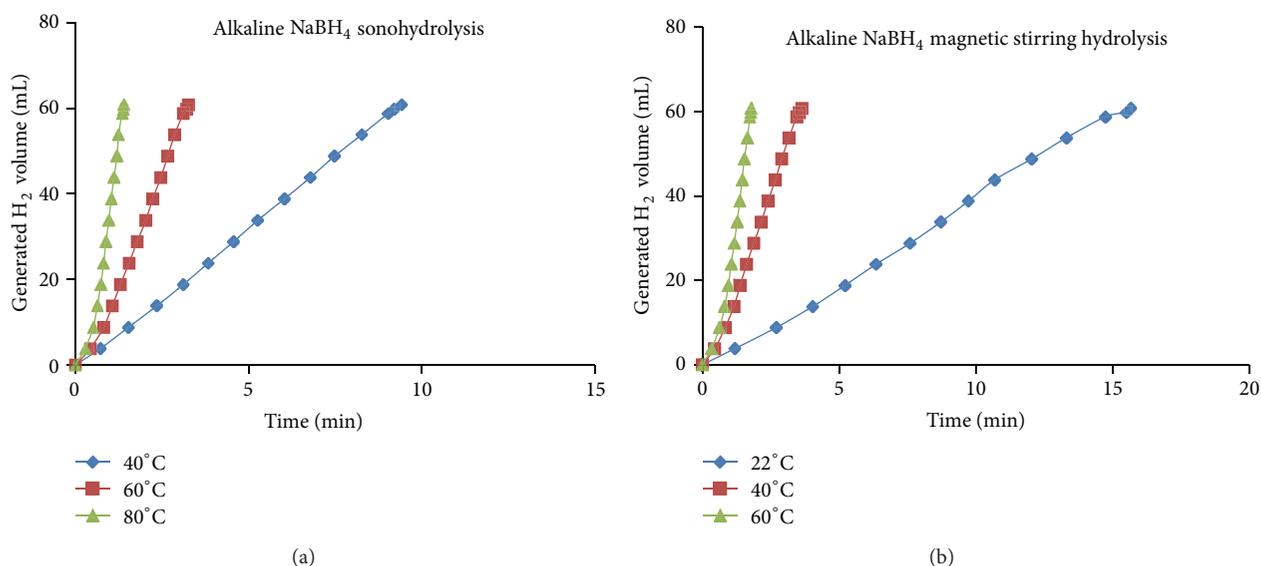


FIGURE 4: The FT-IR spectrum of Co-B catalysts.

FIGURE 5: Hydrogen generation volume versus time for sonohydrolysis and magnetic stirring hydrolysis of alkaline (10 wt.%) 0.12 NaBH₄ solutions in presence of 0.5 mg CoB-1 catalyst.

assigned between 950–870 cm⁻¹ and 710–795 cm⁻¹ and were symmetric stretching band of B-O [28–30].

CoB-1 catalysts, prepared via sonochemical coprecipitation synthesis, show the best intrinsic and extrinsic properties that are contributing factors to the catalytic activity. It was concluded to start sonohydrolysis of alkaline NaBH₄ solutions with CoB-1 catalysts which were prepared via sonochemical coprecipitation synthesis.

3.2. Sonochemical Approach to Hydrolysis of Alkaline NaBH₄ Solutions. In order to investigate the effect of sonochemical approach, hydrolysis of alkaline NaBH₄ solutions in presence of CoB-1 catalyst were carried out with two different procedures. The evaluated H₂ volume versus time during the reactions was given in Figure 5. The H₂ generation started

immediately after catalyst contact with alkaline NaBH₄ solution. As a result of this, CoB-1 catalyst did not have induction period to be active. Effect of increasing in temperature was shown in Figure 5. The H₂ evolution shows direct proportion with temperature in both systems. In sonochemical alkaline NaBH₄ solution hydrolysis, hydrolysis time dropped 1.40 min from 9.41 min by increasing of temperature from 22°C to 60°C. The same tendency was observed in magnetic stirring hydrolysis, and reaction time decreased to 13.88 min.

Figure 6 shows the effects of temperature and sonowaves on hydrogen generation. It was clearly seen that by comparing two different approach, sonowaves developed the hydrolysis characteristics of system via cavitation on surface of catalyst. The ultrasonic approach improved the interaction between the Co-B catalyst and alkaline NaBH₄ solution and made homogeneous distribution in the alkaline NaBH₄

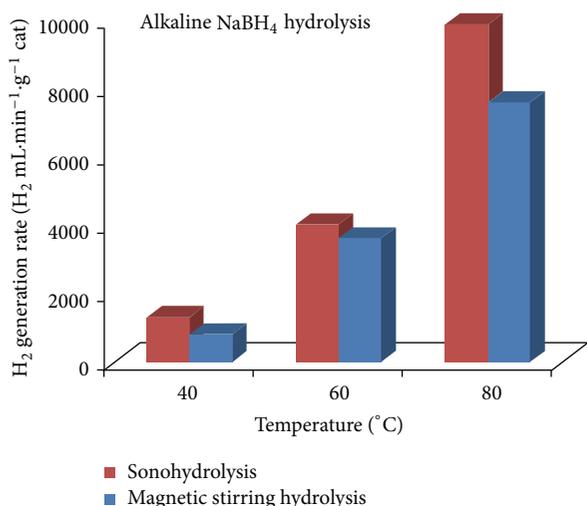


FIGURE 6: Hydrogen generation rate comparison versus temperature for sonohydrolysis and magnetic stirring hydrolysis of alkaline (10 wt.%) 0.12 NaBH₄ solutions in presence of 0.5 mg CoB-1 catalyst.

solution and CoB-1 catalyst. During the sonohydrolysis, cavitation bubbles created high energy effects and this caused continuous acceleration of hydrogen generation rate [19]. As can be seen, ultrasonic treatment during the hydrolysis results in maximum increase in the hydrogen generation from alkaline NaBH₄ solution up to 65% at 40 °C. The authors suggest to use of sonohydrolysis instead of magnetic stirring hydrolysis for improving the hydrogen generation rate of system.

Figure 7 shows the kinetic investigation of sonochemical and magnetic stirring hydrolysis in presence of CoB-1 catalyst. The characterization of hydrolysis reaction behavior was identified by zero-order, first-order, and second-order reaction kinetic models and Arrhenius theory. As seen from Figure 7, in both hydrolysis conditions the hydrolyses of alkaline NaBH₄ solutions were in compliance with zero-order reaction kinetic model and this indicated that hydrogen generation rate was independent from concentration of NaBH₄. Depending on Arrhenius theory, activation energy of sonohydrolysis of alkaline NaBH₄ solution was 46.15 kJ·mol⁻¹ and its Arrhenius rate constant was 19.89 min⁻¹. For hydrolysis of alkaline NaBH₄ solution, which was carried out in magnetic stirring systems, the kinetic values were determined as 51.68 kJ·mol⁻¹ activation energy and 15.16 min⁻¹ Arrhenius rate constant.

In literature, Co containing catalysts activation energies were determined and summarized in Table 3. The activation energies of Co containing catalysts show variety; for example, Copowder (75.00 kJ·mol⁻¹), Co-Raney form (53.70 kJ·mol⁻¹), and active carbon supported Co-B (57.80 kJ·mol⁻¹) were relatively higher than our results, while Co nanoparticle (35.00 kJ·mol⁻¹) was lower. The hydrolysis of alkaline NaBH₄ solution was carried out with sonochemical approach, the reaction kinetic was improved and value of them was decreased up to 12%.

TABLE 3: Activation energies in presence of various Co-based catalysts.

Catalyst	Activation energy (kJ·mol ⁻¹)	References
Co powder	75.00	[31]
Co nanoparticle	35.00	[13]
Co (α-Al ₂ O ₃ support)	32.63	[32]
Co (Raney form)	53.70	[33]
Co-B (active carbon support)	57.80	[34]
Co-B powder	64.87	[12]
Co-B (clay support)	56.32	[35]
Co-B	52.73	[36]
CoB-1 (sonohydrolysis)	46.15	At this work
CoB-1 (magnetic stirring hydrolysis)	51.68	At this work

4. Conclusion

In the present study, sonochemical approach to coprecipitation synthesis of Co-B catalyst and hydrolysis of alkaline NaBH₄ solutions was introduced. The following points result from this study.

The sono-co-precipitation of CoCl₂·6H₂O and B₂O₃ in aqueous solution at pH 6 was proven to be a promising procedure in order to obtain Co-B crystalline catalyst with uniform 1.25 μm particle size, improved surface area, and texture properties. On the other hand, it was found that sonochemical approach did not affect the crystalline structure and spectral properties of Co-B catalyst yet.

The improving effect of sonochemical process on hydrolysis of alkaline NaBH₄ solutions was approved when it was compared with magnetic stirring system kinetic results. Hydrogen generation rate of alkaline NaBH₄ solutions via sonohydrolysis method in presence of CoB-1 catalyst has shown enhanced influence at all temperatures. Activation energy as 46.15 kJ·mol⁻¹ of sonochemical coprecipitation synthesized Co-B catalyst has compatible value compared with literature (32–75 kJ·mol⁻¹). Rate law was formulized as given below:

$$r_{\text{NaBH}_4} = 19.89 \cdot e^{-46.15/RT} \quad (9)$$

As a result of this study, the ultrasonic waves improved the intrinsic and extrinsic properties of Co-B catalyst properties as specific surface area increased up to 70%, particle size decreased up to 58%, and hydrogen generation rate increased up to 64%. As can be seen, sonochemical coprecipitation and sonohydrolysis proved to be promising techniques for synthesis of Co-B catalyst and hydrolysis.

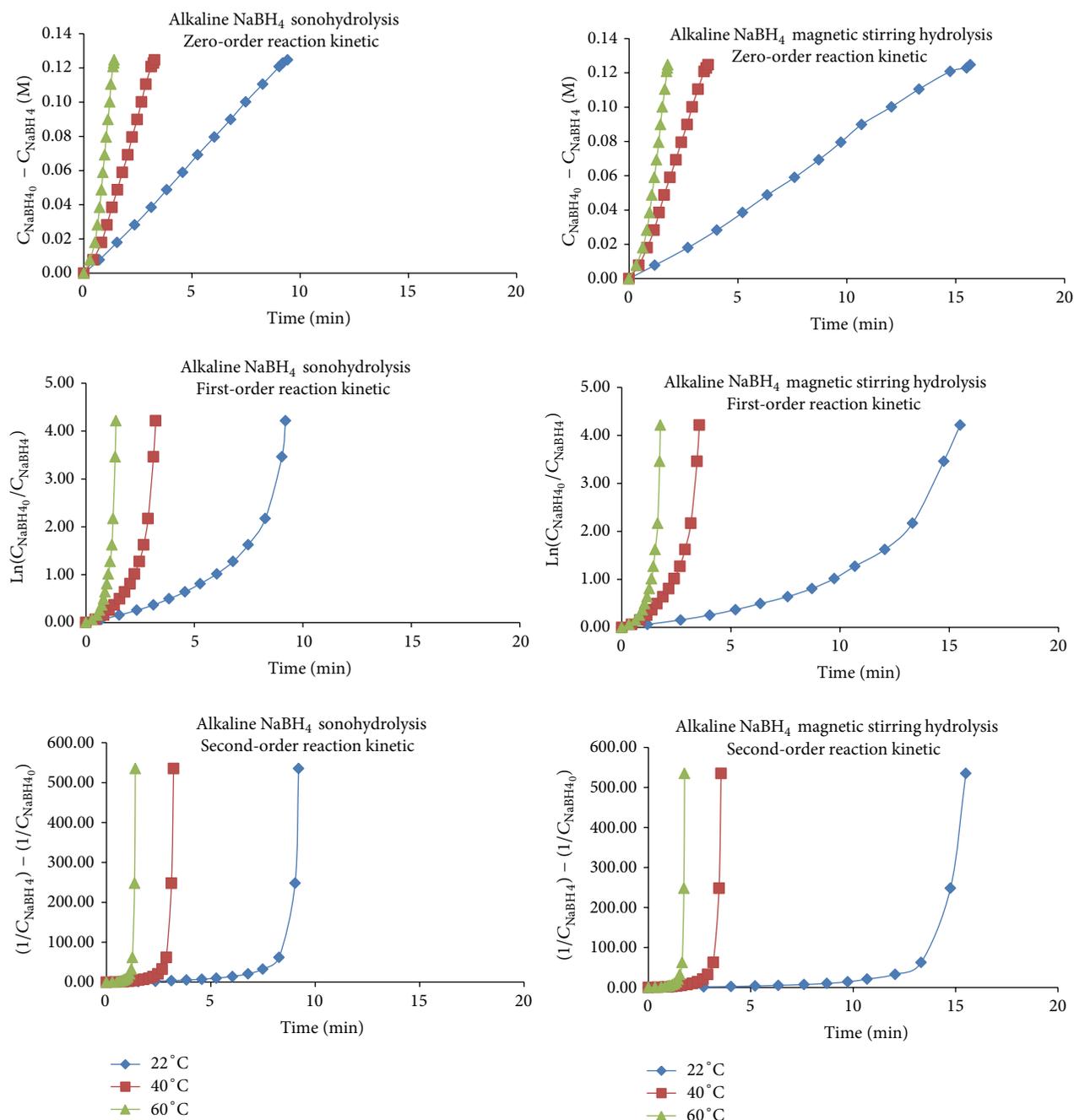


FIGURE 7: The kinetic investigation: the zero, first, and second reaction kinetic models for sonohydrolysis and magnetic stirring hydrolysis of alkaline (10 wt.%) 0.12 M NaBH_4 solutions.

Symbols Used

- r : [$\text{H}_2 \text{ mol} \cdot \text{min}^{-1} \cdot \text{g}^{-1} \text{ cat}$] H_2 generation rate
 E_a : [$\text{kJ} \cdot \text{mol}^{-1}$] Activation energy
 R : [$\text{kJ} \cdot \text{mol}^{-1} \cdot ^\circ\text{C}^{-1}$] Gas constant
 T : [$^\circ\text{C}$] Temperature.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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