Synthesis of Fe-Fe₂B catalysts via solvothermal route for hydrogen generation by hydrolysis of NaBH₄

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ABSTRACT
In this study, iron sulfate (FeSO₄) and sodium borohydride (NaBH₄) were used to synthesize Fe-Fe₂B nanocrystals via the solvothermal route. Synthesis of Fe-Fe₂B nanocrystals was carried out under Argon (Ar) gas atmosphere with aqueous solutions of FeSO₄, 7H₂O and NaBH₄ at various concentrations and reaction time. The phases and microstructures of nanocrystals thus formed were characterized by X-Ray diffraction (XRD) spectroscopy and scanning electron microscopy (SEM). Surface areas of nanocrystals were measured by a surface area and pore-size analyzer using nitrogen adsorption-desorption method together with Brunauer-Emmett-Teller (BET) equation. The vacuum dried nanoparticles were calcined under both Ar and air at 500 °C. Nano-cylindrical structures of Fe-Fe₂B were observed when calcinated under Ar atmosphere; whereas more irregular shaped particles were noticed when calcinated under air. The surface areas of Fe-Fe₂B were determined as 12 m²/g, 5.5 m²/g and 16.5 m²/g, for vacuum dried, Ar-calcined and O₂-calcined products respectively. The catalytic effect of those nano-particles to generate hydrogen was studied by determining reaction rate of decomposition of NaBH₄ in aqueous alkaline solution. The catalytic activity was investigated by systematic variation of three parameters (1) the amount of Fe-Fe₂B, (2) the concentration of NaBH₄ and (3) the concentration of NaOH. The effect of temperature on the catalytic activity was also studied separately for the most effective composition by varying the temperature from 25 to 70 °C. It was noticed that the catalytic activity of vacuum dried nanocrystals was the highest. The catalytic activity was found to increase with the increase in NaBH₄ concentration and decrease with the increase in NaOH concentration. The influence of temperature studied with 0.01 g of Fe-Fe₂B in 1 % w/w NaBH₄ solution showed that the rate of hydrogen generation could be increased almost 5 times more by varying the temperature from 25 °C to 70 °C.

1. Introduction

Besides their characteristic high hardness properties, high melting points, excellent electrical and thermal conductivities, and corrosion and abrasion resistance properties [1-5], metal borides are also used as catalysts for an efficient hydrogen generation in the fuel cell [6-9].

For fuel cell applications, the use of metal borides is particularly important for catalyzing the decomposition of alkaline borohydrides, such as sodium borohydride (NaBH₄) [10-19], lithium boron hydride (LiBH₄) [20-21], potassium borohydride (KBH₄) [22-23] and ammonia borane (NH₃BH₃) [24-28].

Among all borohydrides studied, NaBH₄ is regarded as the most promising and reliable one because of its high H₂ storage capacity per mass (10.8 wt %), for its well-controlled H₂ generation, its good storage and oxidation stability; moreover, it is non-toxic and non-flammable. In the presence of any heterogeneous or homogenous catalyst, aqueous solutions of sodium borohydride (NaBH₄) can undergo hydrolytic decomposition to produce H₂ gas at room temperature. During hydrolysis, H₂ is produced together with the formation of sodium metaborate (NaBO₂) as shown in Eq. 1 [12-13,15,17].

\[
\text{NaBH}_4 + 2\text{H}_2\text{O} \rightarrow \text{NaBO}_2 + 4\text{H}_2 \tag{1}
\]

For catalysis of NaBH₄, the use of finely divided metal catalysts are often emphasized elsewhere, particularly the use of Pd [29-32], Pt [33-36] and Ru [37-41]. However, despite their excellent catalytic efficiencies, the use of those metal catalysts is highly cost prohibitive,
which makes their usage for fuel-cells applications highly uneconomical. For that matter use of suitable metal borides of finer particle sizes, nano-particles for example, are highly desirable.

Nanoparticles of metal borides of various crystallite size and shapes can be produced by self-propagating high-temperature synthesis [42], molten salt method [43], electrolysis method [44], chemical vapor deposition [45], carbothermal method [46], sol-gel [47-48], mechanochemical [49] and solvothermal methods [50]. However, solvothermal methods are preferred over the other methods due to their ability to produce nanoparticles of uniform shapes and sizes. Various studies about the production of metal borides via solvothermal routes are well elaborated in the literatures [51-55]. The solvothermal synthesis of magnetic metal borides and their studies on catalytic activities such as Fe-B, Co-B, and Ni-B and draws special attention in this regard [56-59].

The present work mainly focuses on the study of nano-ironboride catalyst as a cost-effective alternate for the hydrolysis of NaBH₄. To the best of our knowledge, the comparative catalytic activities of vacuum dried versus Ar-calcined and O₂-calcined Fe-Fe₂B nanoparticles were investigated for the first time for the hydrolysis of NaBH₄. This study was pursued by essentially varying three parameters, (a) the amount of catalyst, (2) the concentrations of NaBH₄, and (3) the concentration of NaOH. The effect of temperature on the rate of reaction was also investigated by varying the temperature from 25-70 °C for a fixed concentration of Fe-Fe₂B and NaBH₄.

2. Materials and Methods

2.1. Catalysts preparation and calcination treatment

Iron sulfate (FeSO₄·99%, Aldrich Chem. Corp.) and sodium borohydride (NaBH₄·98%, Aldrich Chem. Corp.) are used as Fe and B sources. Sodium hydroxide (NaOH, 97%, Aldrich Chem. Corp.) is used as a buffer. All experiments were performed in distilled water and under Argon (%99.999) gas atmosphere. Three-necked glass reactor (500 ml) and magnetic stirrer (MTops HSD180) are used in experiments.

The preparation of Fe-Fe₂B catalyst performed by the chemical reduction of different FeSO₄ and NaBH₄ concentration given in Table 1. The first set of experiments were carried out in aqueous medium for 3, 12, 60 and 120 min for determination of the optimum reaction time while second set of experiments were performed for determination of the FeSO₄ and NaBH₄ concentration. Firstly, FeSO₄ was dissolved in cold distilled water and this aqueous water solution was introduced in to three-necked glass reactor. To prevent formation of unwanted phases, experiments were carried out in ice bath at about 4 °C. The main solution was stirred with magnetic stirrer for thermal equilibrium for 10 minutes under Ar gas atmosphere. Secondly, alkaline NaBH₄ was dissolved in 20 mL distilled water and added to main solution drop-by-drop carefully. As soon as NaBH₄ was added to solution, black nanocrystals were obtained. When the reactions were completed, particles were washed with distilled water for several times to remove residual ions. Particles were centrifuged to separate from liquid to solid and dried in vacuum (Memmert VO400) at 20 mbar and 70 °C for 12 h. Then, vacuum dried nanoparticles were calcined at 500 °C under Ar and O₂ for 2 hours with a heating rate of 2 °C/min. respectively.

2.3. Catalyst characterization

Phases of synthesized samples are characterized by X-Ray diffraction spectrophotometer (XRD, Rigaku, D/ MAX-2200 with CuKα, (λ=1.5408 Ǻ) at 40 kV working voltage, 30 mA current, 2-90° 2θ angle interval and 4°/ min scan rate. Microstructure and morphology studies were performed by scanning electron microscopy (SEM, FEI Quanta 200F). Surface area of nanoparticles were performed by a surface area and pore-size analyzer (Quantaochrome, Nova 220E) using nitrogen adsorption-desorption method together with Brunauer- Emmett-Teller (BET) equation.

2.4. Catalytic activity runs

H₂ generation capacity of nanocrystals by the hydrolysis of NaBH₄ were determined in a pyrex glass reactor equipped with an apparatus capable of measuring H₂ evolution by the water-displacement method. H₂ generation system was shown in Figure 1. Typically, 10 mL distilled water and alkaline NaBH₄ solution was poured in a flask and then catalyst was added to solution under magnetic stirring at 700 rpm. Then, the volume of H₂ released was measured by opening the valve.

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>FeSO₄·7H₂O solution</th>
<th>NaBH₄ solution</th>
<th>Addition time (s)</th>
<th>Reaction time (min)</th>
<th>Magnetic stirring (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FeSO₄·7H₂O (g)</td>
<td>H₂O (ml)</td>
<td>NaBH₄ (g)</td>
<td>H₂O (ml)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.795</td>
<td>180</td>
<td>0.332</td>
<td>20</td>
<td>3-12-60-120 300</td>
</tr>
<tr>
<td>2</td>
<td>1.590</td>
<td>180</td>
<td>0.644</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.180</td>
<td>180</td>
<td>1.289</td>
<td>30</td>
<td></td>
</tr>
</tbody>
</table>
In order to investigate the catalytic activity of Fe-Fe$_2$B catalyst for the hydrolysis of NaBH$_4$, five different sets of experiments were performed in the aqueous medium of NaBH$_4$. The parameters used in the H$_2$ generation experiments are shown in Table 2. The effects of calcination, amount of catalyst used, concentrations of NaBH$_4$ and NaOH, and the temperature of reaction were investigated in the hydrogen generation experiments. In the first set of experiments, vacuum dried (0.01 g) and crystalline powders (0.01 g) were used as catalyst for H$_2$ generation by the hydrolysis of NaBH$_4$ (1 % w/w, 0.1 g) in aqueous media (10 mL distilled water). In the second set of experiments, hydrolysis reaction was carried out with various amount of catalysts (0.01, 0.02, 0.05, 0.1 g) at constant NaBH$_4$ concentration (1 % w/w, 0.1 g). In the third set of experiments, the amount of catalyst kept constant as 0.01 g and NaBH$_4$ concentration varied in the range of 1, 2, 5 and 10 % w/w. In the fourth set of experiments, concentration of NaOH was varied from 0.1-2 % w/w while NaBH$_4$ concentration was kept constant at 1 % w/w in the presence of 0.01 g of catalyst. In the fifth set of experiments, hydrolysis reaction were conducted by varying the reaction temperature from 25-70 °C.

3. Results and discussion

3.1. Phases and microstructural characterization of synthesized nanoparticles

The XRD pattern of starting materials of FeSO$_4$ is given in Figure 2. It can be noticed that the starting material, FeSO$_4$, showed the peaks for FeSO$_4$.4H$_2$O (ICDD Card No: 00-016-0699) and FeSO$_4$.7H$_2$O (ICDD Card No: 01-072-1106).

Iron boride catalyst was obtained by reduction of FeSO$_4$ with NaBH$_4$ in aqueous medium under Ar atmosphere. Expected reactions were given in Eq. 2 [60].

$$4\text{FeSO}_4 + 8\text{NaBH}_4 + 18\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{B} + 6\text{B(OH)}_3 + 25\text{H}_2 + 4\text{Na}_2\text{SO}_4 \ (2)$$

Fe$^{2+}$ reacts with NaBH$_4$ quickly to form Fe$_2$B, and H$_2$, Na$_2$SO$_4$ and B(OH)$_3$ as reaction byproducts. Fe-Fe$_2$B nanocrystals were formed by using alkaline NaBH$_4$ solution for the reaction with aqueous FeSO$_4$.7H$_2$O solution. Synthesis of Fe-Fe$_2$B nanocrystals was monitored over a reaction time period 0-120 min in order to determine the effect of reaction time on the final phase structure and particle morphologies of Fe-Fe$_2$B. It was seen that within the first 3 minutes H$_2$ was released.
intensively, and then it slowed down and the reaction continued very slowly. It was noticed that up to 10 min, the black particles in the medium nearly became stable and very low amount of H₂ release was still observed. At the end of the 12th minute the reaction was complete, and H₂ release was not observed. The morphology of the nanoparticles in these experiments was monitored by keeping them over 120 minutes in the reaction mixtures. The nanoparticles with their prolonged stay under such conditions did not show any major changes in their morphology excepting some growth in their grain sizes. That's how the time the period for the synthesis of Fe-Fe₂B nanoparticles was optimized to 12 minutes.

The particles synthesized over a time period of 12 min were centrifuged and dried under vacuum at 70°C for 12 h. Then, the samples were calcined under Ar and O₂ atmosphere for structural evolutions. XRD spectrum of vacuum dried, Ar-calcined and O₂-calcined Fe₂B nanoparticles obtained are shown in Figure 3.

It is seen from XRD pattern that the phase structures of vacuum dried samples were composed of Fe (ICDD Card No: 01-087-0722) phase before calcination. After drying the particles under vacuum and calcining at 500°C for two hours under Ar and O₂, it appeared that the nano-particles comprised of Fe-Fe₂B and Fe-FeO₂-Fe₃O₄ phases (Figures 3-b, and 3-c). XRD patterns of the vacuum dried particles is shown in Figure 3-a, and it exhibited the peaks of Fe phase around 2θ=44.76°, 65.16° and 82.53°. From Figure 3-b it was clearly seen that after calcination under Ar, the amorphous phases of Fe₂B were changed to crystalline Fe₂B (ICDD Card No: 01-089-1993) phases, and the nanopowder mixtures were composed of Fe and Fe₂B. The diffraction peaks around 2θ=24.61°, 35.09°, 42.51°, 45.07°, 50.47°, 56.93°, 74.16° and 80.69° are assigned to the diffraction of the Fe₂B phase. Unit cell refinements of iron phases were found and schematic representations of unit cells were also drawn in Figure 3. Cubic structure of Fe in Im-3m space group with the lattice parameters of of a=b=c=2.8573 Å and tetragonal structure of Fe₂B in I4/mcm space group with the lattice parameters of a=b=5.1074 Å and c=4.2348 Å and were confirmed with single phase unit cell refinements. For oxide phases, single unit cell refinements confirm the rhombohedral structure of FeO₃ in R-3c space group with the lattice parameters of a=b=5.0324 Å and c=13.7557 Å and cubic structure of Fe₃O₄ in Fd-3m space group with the lattice parameters of a=b=c=8.3414 Å. The lattice parameters of

![Figure 2. XRD pattern of starting materials of FeSO₄.](image)

![Figure 3. XRD pattern and schematic representation of unit cell of a) Vacuum dried, b) Ar-calcined, c) O₂-calcined nanocrystals.](image)
the catalyst were agreed fairly well with previous data [61-64]. In literature, the effect of calcination on the phases was investigated very intensively. Similar results were also reported in the study conducted by Bindai et al. They reported that the amorphous structure was transformed to crystalline structures after calcination process at 500 °C [65]. In another similar study, it is reported that vacuum dried samples structure was amorphous cobalt while the structures at elevated temperatures consisted of cobalt and cobalt boride [66]. By calcination under O$_2$, the phase structure of Fe$_2$B comprised oxides metallic Fe, Fe$_2$O$_3$ (ICDD Card No: 01-072-0469) and Fe$_3$O$_4$ (ICDD Card No01-088-0315) phase. As seen from XRD images given in Figure 2c, exposure of vacuum dried nanoparticles to air resulted in forming yellow-brown powder mixtures comprising Fe, Fe$_2$O$_3$ and Fe$_3$O$_4$. This can probably be best explained by the Eq. 3 given below. The continuous exposure to oxygen environment possibly led the Fe$_2$B to oxidize to form multiple oxide phases of Fe [67].

\[
\begin{align*}
\text{Fe}_2\text{B} + 3/4\text{O}_2 & \rightarrow 2\text{Fe} + 1/2\text{B}_2\text{O}_3 \\
\text{Fe}_2\text{B} + \text{O}_2 & \rightarrow \text{Fe}_x\text{O}_{x+1} + \text{B}_2\text{O}_3
\end{align*}
\]

(3)

SEM analyses were carried out for morphological and microstructural observations. SEM images of the nanoparticles obtained with various FeSO$_4$.7H$_2$O/NaBH$_4$ concentrations are shown in Figure 4. As can be seen from this figure, Fe-Fe$_2$B nanoparticles obtained by different FeSO$_4$ initial concentration are clearly in nano-cylinder forms. It is also important to note that the size of the nano-cylinders increased with the increase in initial concentration of FeSO$_4$. The specific surface areas of powders were measured using BET method and surface areas were determined as 12, 12.5 and 15 m$^2$/g with the increased initial concentration of FeSO$_4$. It was also noticed that the nanocylinder structures were of irregular shapes with the sizes varying from 50-500 nm as the concentration of FeSO$_4$ increased.

Furthermore, comparative SEM images of Ar-calcined and O$_2$-calcined nanoparticles were given in Figure 4. It was also observed in Figure 5 that Ar-calcined nanoparticles were in nanocylinder form and particles were mostly agglomerated while O$_2$-calcined particles were composed of irregular shapes, and they were mostly found in aggregated forms with the particle sizes in the range of 40-300 nm. Surface area of nanocylinders of Ar-calcined and O$_2$-calcined were measured as 5.5 m$^2$/g and 16.5 m$^2$/g respectively.

### 3.2. Catalytic activities

Catalytic activities of vacuum dried, Ar-calcined and O$_2$-calcined powders by hydrolysis of NaBH$_4$ were determined in the first set of experiments. The catalytic activities of vacuum dried amorphous nanoparticles, Ar-calcined and O$_2$-calcined nanoparticles were given in Figure 6. The H$_2$ generation rate of vacuum dried amorphous nanoparticles with 0.01 g catalyst and 1 % w/w NaBH$_4$ concentration at room temperature was measured as 570 mL H$_2$.g$^{-1}$.m$^{-1}$. The H$_2$ generation rate of air-calcined Fe-Fe$_2$O$_3$-Fe$_3$O$_4$ and Ar-calcined Fe-Fe$_2$B catalysts were found as 450 mL H$_2$.g$^{-1}$.m$^{-1}$ and 400 mL H$_2$.g$^{-1}$.m$^{-1}$ respectively. These results are in agreement with the studies reported by Patel et al. It is reported that Hydrogen generation rate of heat treated samples was lower than amorphous samples [68]. It was determined that the vacuum dried nanoparticles hydrogen generation rate was the highest for hydro-

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**Figure 4.** SEM images of vacuum dried nanoparticles obtained with FeSO$_4$.7H$_2$O/NaBH$_4$ concentration experiments.
ysis of NaBH$_4$ in this study and so that vacuum dried nanoparticles were used in all subsequent catalytic activity experiments.

In the second set of experiments, the effect of the concentration of catalyst on the catalytic activity was investigated. In the second set the weight of the catalyst was progressively varied from 0.01, 0.02, 0.05 and 0.1g respectively keeping the concentration of NaBH$_4$ constant at 1wt% for the hydrolysis reaction. In all experiments of the second set 10 mL of distilled water was used at room temperature and with magnetic stirrer at 700 rpm. The H$_2$ generation rate of catalyst were given in Figure 7. As seen in Figure 7, as the amount of catalyst increased, the hydrogen generated rate increased. 220 mL H$_2$ was generated in 2700 s with 0.01 g catalyst. The same amount of H$_2$ was generated in 1800, 1080 and 720 s with 0.02, 0.05 and 0.1 g catalyst respectively.

![Figure 5](image1.png)

**Figure 5.** SEM images of Ar and O$_2$-calcined nanoparticles.

![Figure 6](image2.png)

**Figure 6.** Catalytic activity of the vacuum dried, Ar-calcined and air-calcined powders, fixed NaBH$_4$ concentration of 1 w/w % and catalyst amount of 0.01 g.
tively. The similar results were observed with studies conducted by Sahiner et. al. as well. [69]. They reported that the increase in the amount of catalyst increases the rate of hydrogen production almost linearly for all the reactions performed under the same conditions.

In the third set of experiments, the effect of the NaBH₄ concentration of the medium, on the catalytic activity was investigated. The H₂ generation rates were given in Figure 8. In experiments with 0.01 g of vacuum dried nanoparticles in solution with 1 % w/w NaBH₄ concentration (0.1 g NaBH₄ + 10 mL H₂O), the hydrogen generation rate was measured as 570 mL H₂.g⁻¹.min⁻¹. By increasing the NaBH₄ concentration to 2, 5 and 10 % w/w, the H₂ generation rate was found as 1966, 4300 and 7700 mL H₂.g⁻¹.min⁻¹, respectively. It is noticed that the reaction rate was increased too fast with increasing of NaBH₄ concentration. The same results for up to % w/w 10 NaBH₄ concentration was found by Baydaroglu et al. They reported that the hydrogen generation rate increased as the NaBH₄ concentration was increased. Furthermore, it was claimed that high concentration of NaBH₄ more than % w/w 15 concentration leaded to increase in the viscosity and alkalinity of the reaction solution and the rate of hydrogen generation decreased probably due to solubility limitation of both NaBH₄ and NaBO₂ [10].

In the fourth set of experiments, the effect of different NaOH concentrations for H₂ generation performance of catalyst (0.01 g catalyst, 0.1 g NaBH₄ in 10 mL DDI) were investigated. The H₂ generation rate is given in Figure 9. It is known that NaBH₄ tend to the hydrolyze immediately. Therefore, NaOH is added to control the pH. An obvious decrease for NaBH₄ hydrolysis rate was observed with increasing NaOH concentration. It is known that NaBH₄ releases negligible amount of H₂ when it is contact with water. To avoid this release, the aqueous medium environment was controlled with NaOH concentration. Therefore, the effect of NaOH concentration on the catalytic activity was determined with various amount of NaOH concentrations. The H₂

Figure 7. Influence of catalyst amount on the hydrogen generation rate at 25 °C, fixed NaBH₄ concentration of 1 w/w %.

Figure 8. Influence of NaBH₄ concentration on the the hydrogen generation rate at 25 °C, fixed catalyst amount of 0.01 g.
production rate of 0.01 g of catalyst in the concentration of 0.1 % w/w NaBH₄ solution (0.1g NaBH₄ + 10 mL H₂O) at room temperature without addition of NaOH solution was measured as 570 mL H₂ g⁻¹.m⁻¹. It was found that catalytic activity rate was decreased when the NaOH was added to solution. H₂ generation rate of % w/w 0.1 NaOH concentration was 140 mL H₂ g⁻¹.m⁻¹ while no measurable catalytic activity was detected for the first 20 minutes with 0.5 % w/w NaOH concentration. It was determined that after the 20 th minute, the catalytic activity started and H₂ generation rate was 230 mL H₂ g⁻¹.m⁻¹. No catalytic activity was observed for the first 24 min with 1 % w/w NaOH solution. Catalytic activity was started after 24 min and H₂ generation was found as 238 mL H₂ g⁻¹.m⁻¹. With experiments of 2 % w/w NaOH concentration, no catalytic activity was measured similarly in the first 72 min and catalytic activity was started from 72 min and H₂ generation rate was about 120 mL H₂ g⁻¹.m⁻¹. Similar results were also reported by studies conducted by Amendola et al. They claimed that at higher NaOH concentrations, water activity was reduced by the inhibiting effect of hydroxide ions. They thought that it occurred because of the ions, especially OH⁻, strongly complex water, thus decreasing the available free water needed for sodium borohydride hydrolysis. In another study, Liang et al. reported that increasing the NaOH concentration resulted in negative effect on hydrogen generation rate [70-71].

The effect of temperature on the catalytic activity is revealed with fifth set of experiments given in Figure 10. The increase in temperature has caused a significant increase in catalytic activity. In experiments with 0.01 g of Fe-Fe₂B vacuum dried nanoparticles at 25 °C in solution with 1 % w/w NaBH₄ concentration, the hydrogen production rate was 570 mL of H₂ g⁻¹.m⁻¹, while it reached to 1230 at 50 °C and 2700 mL H₂ g⁻¹.m⁻¹ at 70 °C. As expected, increasing temperature increased H₂ production substantially and these results show that temperature is an important parameter for catalytic activity. As the temperature increased from 25 to 70 °C, the hydrogen generation rate increased from 570 to 2700 mL H₂ g⁻¹.m⁻¹. Many studies can be seen in the literature, about the increased hydrogen production rate of metal catalysts by increasing the temperature [13-16]. The hydrogen generation rate was increased with increasing temperature as expected. An important parameter of reaction kinetics, the activation energy (Eₐ) was determined by using the H₂ generation rates at varied temperature of solution in the range of 20-70 °C. The H₂ generation rate constant at various temperature was determined with the slope of fitting lines. The activation energy was calculated by the Arrhenius equation [4].

\[ k = k_0 \cdot e^{-\frac{E_a}{RT}} \]  (4)

Where k represents the reaction rate (mL.min⁻¹.g⁻¹), k₀ – the reaction constant (mL.min⁻¹.g⁻¹), E_a – the activation energy for the reaction (kJ.mol⁻¹), R – the gas constant (8.314 kJ.mol⁻¹ K⁻¹) and T – the reaction temperature (K). The Arrhenius plot of lnk against to temperature (1/T) is given in Figure b. The Activation Energy was calculated as 38 kJ.mol⁻¹ from the slope of straight line for the Fe-Fe₂B catalyst. It is known that the activation of chemical reaction was influenced by different parameters such as particle size, reaction temperature and the method of synthesis. Similar results were reported by Dinç et al. study. They reported that the activation energy of iron nanocluster for ammonia borane was calculated as 37 kJ.mol⁻¹ [72].

![Figure 9. Influence of NaOH concentration on the the hydrogen generation rate at 25 °C, fixed NaBH₄ concentration of 1 w/w % and catalyst amount of 0.01 g.](image-url)
4. Conclusion

Fe-Fe$_2$B nanocylinder/nanocrystals were synthesized with various FeSO$_4$·7H$_2$O and alkaline NaBH$_4$ concentration in an aqueous medium. It is seen that vacuum dried nanoparticles were composed of Fe phase before calcination. After drying the particles under vacuum and then calcine at 500 °C for 2 hours in Ar and O$_2$, phase structures were comprised of Fe-Fe$_2$B and Fe-Fe$_2$O$_3$-Fe$_3$O$_4$ phases, respectively. It was found that increasing FeSO$_4$·7H$_2$O concentration the nanocylinders formed by calcination under Ar were of diameters between 50-500 nm. Whereas, the nanoparticles formed by calcination under O$_2$ were of irregular shapes and morphology. Surface areas were measured as 12 m$^2$/g, 5.5 m$^2$/g and 16.5 m$^2$/g for the vacuum dried, Ar-calcined and O$_2$-calcined nanoparticles, respectively. The maximum H$_2$ generation rate was obtained as 2700 mL H$_2$.g$^{-1}$.m$^{-1}$ at 70 °C by using amorphous Fe-Fe$_2$B with 1 % w/w of initial NaBH$_4$ concentration. Increasing the amount of catalysts and NaBH$_4$ concentration increased the H$_2$ production rate while increasing NaOH concentration dramatically decreased H$_2$ production rate.

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