Fe₃O₄@SA MNCs Synthesis, Characterization, and First-time Use in Hydrogen Production by NaBH₄ Hydrolysis

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Abstract: Hydrogen is a clean energy carrier that will reduce dependence on fossil fuels and contribute to reducing the harmful effects on the environment resulting from using fossil fuels. Hydrogen is produced by the hydrolysis of sodium borohydride (NaBH₄), one of the chemical hydrides, using a catalyst. In this study, Fe₃O₄@Salicylic acid magnetic nano-catalyst (Fe₃O₄@SA MNCs) was synthesized using the co-precipitation technique. The structural, physical, and chemical properties of the produced Fe₃O₄@SA MNCs were characterized by FT-IR, XRD, VSM, SEM, and SEM-EDX methods. At room temperature, the effect on hydrogen production performance was examined in the amounts of Fe₃O₄@SA MNCs (10, 25, 50, 75, and 100 mg), NaOH (0, 10, 20, and 25 mg), and NaBH₄ (25, 50, 100, 150 and 200 mg). The highest hydrogen generation rates (HGR) were obtained using 10 mg Fe₃O₄@SA MNCs, 150 mg NaBH₄ and 0 mg NaOH at room temperature. The obtained HGR value was calculated as 400 mL g⁻¹ cat⁻¹ min⁻¹. Fe₃O₄@SA MNCs were used for hydrogen production for the first time in this study. This study showed that Fe₃O₄@SA MNCs exhibit catalytic properties and are a promising, efficient catalyst in hydrogen production from NaBH₄.

Keywords: Fe₃O₄@SA, hydrogen production, magnetic nano-catalyst, NaBH₄


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1. INTRODUCTION

Population growth and rising living standards of individuals cause an increase in energy consumption. The decrease in fossil fuel reserves makes fossil fuel-based energy unsustainable. At the same time, due to fossil fuels, which are the dominant energy source, the world is facing serious climate change. Although fossil fuel-based energy meets a large part of the global energy demand, it has undesirable negative effects on humanity and the environment, such as greenhouse gas emissions, global warming, acid rain, and poor air quality. In order to prevent these vital negativities, researchers have started to focus on the search for innovative, carbon-free, sustainable alternative energy without environmental negative effects (1,2).

At this critical point, hydrogen energy is referred to as the best possible promising energy alternative that is environmentally friendly, renewable, and sustainable. Considering the cost-effectiveness and reliability of hydrogen energy, it has the potential to solve many environmental problems. When hydrogen is used as a fuel, it is expressed as a zero pollution producer because it gives water as a by-product (no treatment required) along with its excellent efficiency in energy conversion. Hydrogen is the most common and most abundant element in the universe. Hydrogen is found in compounds with other elements, such as carbon and oxygen. With this, it is an excellent clean energy carrier after separation (3).

Hydrogen energy can be produced from a wide variety of primary energy sources using different substrates and technologies and then used as the main energy source. NaBH₄ is used in hydrogen production technologies for its advantages, such as non-flammability, stability, and non-toxicity. Also, the hydrolysis of NaBH₄ can be controlled by suitable catalysts. The hydrolysis of NaBH₄ is shown in Equation 1. The catalyst is used to
control the hydrolysis of NaBH4 and achieve higher reaction rates. The hydrolysis of NaBH4 using inexpensive and environmentally friendly catalysts has recently received more attention (4,5).

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

(1)

Nanotechnology offers effective materials with special structural design and a wide range of potential applications in environmental remediation solutions. The term "Nano" means a particle with at least one size less than 100 nm. Its nanoscale dimensions make its physical, optical, magnetic, chemical, mechanical, electrical, and magnetic properties significantly different from related materials. The application of nanomaterials in catalysis has attracted great interest. Nano-catalysts uniquely have selectivity, reactivity, enormous surface areas, and extended catalytic efficiencies. Homogeneous and heterogeneous catalysis applications are an evolving field. Excellent efficiency, highly selective, and fast catalytic systems are being developed through a green process. Research on environmentally friendly catalysis contributes to alleviating the pollution problem. Researchers continue to seek to obtain the ideal nano-catalyst with excellent stability, selectivity, and activity by green methods (6).

In nano-catalyst research, Fe3O4 with magnetic properties attracts great attention due to its attractive properties, such as low cost, easy preparation, easy modification, superparamagnetism, and non-toxicity (7). Fe3O4 consists of a magnetic core and has a good surface area/volume ratio. Fe3O4 has a high affinity, and a surfactant is often needed to both cause internal steric repulsion and modify its surface. Extensive studies have been carried out in various engineering applications with Fe3O4, whose surface is functionalized with appropriate functional groups (due to its optical, magnetic, electrical, catalytic, etc. properties) (8). Zero-valent metal nanoparticles supported on the bare surface of magnetite show reduced catalytic activity from incorporating iron in redox processes. Therefore, Fe3O4 needs to be coated with materials such as polymer, carbon, silica, etc. to support metal nanoparticles. Magnetically supported catalysts are considered promising materials with high activity and reusability due to their easy separation by an external magnetic field (9,10). Salicylic acid, which has phenolic, benzoic, carboxylic, and hydroxyl characters as functional groups, adds a very high potential to catalytic activity due to its intramolecular H-H bond structures (11). Because salicylic acid is o-hydroxybenzoic acid, it has n electrons that belong to aromatic compounds and are produced by orbital overlap. Thus, salicylic acid is used in catalysis studies (12).

In this study, Fe3O4@SA MNCs were produced for hydrogen production from NaBH4. Fe3O4@SA MNCs were used for hydrogen production for the first time in this study. The catalytic activity of the synthesized magnetic nano-catalyst regarding hydrogen production by NaBH4 was investigated. Hydrogen production from hydrolysis of NaBH4 of Fe3O4@SA MNCs with different parameters in experimental sets was investigated. SEM-EDX, XRD, VSM, and FT-IR analyses were performed to determine the morphological and structural characterization of Fe3O4@SA MNCs.

2. EXPERIMENTAL

2.1. Chemicals and Solutions
All chemicals and solvents used in the reactions are of analytical purity. Iron (III) chloride hexahydrate (FeCl3.6H2O, 99.9%) and salicylic acid (C7H6O3, 99%) were purchased from MERCK Chemical. Iron (II) chloride tetrahydrate (FeCl2.4H2O, 98%) was purchased from Alfa Aesar Chemical Company. In addition, Ammonia (NH3, 28.0%) and ethanol (CH3CH2OH, 99.9%) were purchased from ISOLAB.

2.2. Fe3O4@SA MNCs Synthesis
FeCl3.6H2O (12 mmol) and FeCl2.4H2O (6 mmol) were mixed in 200 mL of pure water in a two-neck flask at room temperature for 30 minutes. The temperature of the system was increased to 70 °C. For co-precipitation, 50 mL of 8 M NH3 was added to the solution (The solution was orange at first but turned black with the addition of NH3). The resulting black magnetite (Fe3O4) nanoparticles were stirred for another 30 minutes. Salicylic acid (0.6 mmol) was then added to the reaction system, and the reaction was continued for 30 minutes at system temperature. After the mixture in the balloon was cooled, Fe3O4@SA MNCs were isolated from the environment with the help of a magnet. Fe3O4@SA MNCs were washed and dried (13,14). The MNCs synthesis scheme is shown in Figure 1.
Figure 1. The synthesis scheme of Fe₃O₄@SA MNCs.

2.3. Characterization
It was done using Fourier transform infrared spectroscopy (FTIR) (Bruker Vertex 70, 4000-400 cm⁻¹) for identification of bonds in Fe₃O₄@SA MNCs structure, Vibrating Sample Magnetometer (VSM) for magnetization ability (Lake Shore 7407, -20000 – 20000 Oe), Scanning Electron Microscopy (SEM-EDX) (JEOL 6510) and X-ray Diffractometer (XRD) (Rigaku Smartlab).

2.4. Use of NaOH in Hydrogen Production
NaOH is generally used to inhibit the self-hydrolysis of NaBH₄. In this study, NaOH in amounts ranging from 0 to 25 mg was used to determine the effect of the amount of NaOH on hydrogen production.

2.5. Use of the Catalyst in Hydrogen Production
Fe₃O₄@SA MNCs in amounts ranging from 10 to 100 mg were used to determine the effect of catalyst amount on hydrogen production.

2.6. Hydrogen Production by NaBH₄ Hydrolysis
A round bottom reaction flask with a volume of 100 mL was utilized to introduce 150 mg of NaBH₄ and 10 mg of Fe₃O₄@SA MNCs. Following the addition of NaBH₄ and Fe₃O₄@SA MNCs, per the prescribed parameters, to the reaction flask at 25 °C, a volume of 20 mL of water was introduced. The solution was stirred at 500 rpm. The volume of hydrogen released was measured depending on time using the water-gas displacement method through an inverted gas cylinder filled with water. In this study, the effects of NaBH₄ (25, 50, 100, 150 and 200 mg), NaOH (0, 10, 20, and 25 mg), and Fe₃O₄@SA MNCs (10, 25, 50, 75, and 100 mg) on hydrogen production were investigated. The HGR value was determined using the following formula (15,16).

\[ HGR = \frac{mL H_2}{\text{gram of catalyst} \times \text{time}} \]  

In this formula, mL H₂, the volume of hydrogen produced, the amount of catalyst used and the time (min) was the reaction time were listed.

3. RESULTS AND DISCUSSION

3.1. Fe₃O₄@SA MNCs Characterization
In the FTIR spectrum of Fe₃O₄@SA MNCs, the peak at 545 cm⁻¹ is the characteristic peak of the stretching of the Fe-O bond. The peak at 1610 cm⁻¹ belongs to the C-O stretching vibration. The peak around 3000 cm⁻¹ belongs to =C-H stretching vibrations. The peak around 3500 cm⁻¹ belongs to the stretching of the O-H bond (Figure 2). The obtained peaks indicate that the synthesis of Fe₃O₄@SA MNCs has occurred successfully. The results obtained are compatible with the literature (17).
Fe₃O₄@SA MNCs XRD patterns are given in Figure 3. Characteristic peaks at 2θ = 18.16°, 30.12°, 35.54°, 37.62°, 45.52°, 53.66°, 57.02°, 62.78° of Fe₃O₄@SA MNCs correspond to the crystal planes (111), (220), (311), (222), (400), (422), (511) and (440), respectively (Figure 3). The results show that Fe₃O₄@SA MNCs have a highly crystalline cubic spinel structure. The results obtained are compatible with the literature (18).

The magnetic property of Fe₃O₄@SA MNCs is given in the VSM plot in Figure 4. Since hysteresis is not observed in the graph, it is understood that the sample is superparamagnetic. Saturation magnetic moment of Fe₃O₄@SA MNCs was found to be 52.8 emu/g (Figure 4). The high of this value indicates that Fe oxidation is either low or absent. The results obtained are compatible with the literature (19).
Fe₃O₄@SA MNCs are given SEM images in Figure 5-A, SEM-EDS graph in Figure 5-B, and SEM-EDS-map graph in Figure 5-C. Figure 5-A shows that the morphology of Fe₃O₄@SA MNCs is spherical, spheres ranging in size from about 20 to 60 nm are adjacent to each other, and agglomeration is present. Its surface is rough. Figure 5-B shows that Fe₃O₄@SA MNCs, Fe (48.8%), O (33.1%), and C (18.1%) are formed. The obtained values show that the synthesis was successful. Figure 5-C demonstrates that the elemental distribution of Fe₃O₄@SA MNCs is very good. The results obtained are in accordance with the literature (18).
3.2. NaBH₄ catalytic hydrolysis

3.2.1. Effect on hydrogen production of NaOH amount

To determine the appropriate amount of NaOH in the reaction solution, hydrogen productions were investigated using 50 mg Fe₃O₄@SA MNCs, 100 mg NaBH₄, and different amounts of NaOH (0, 10, 20, and 25 mg) at 25 °C. The resulting graph is shown in Figure 6. This graph illustrates a notable drop in the volume of hydrogen produced, from 84 mL to 12 mL, as the quantity of NaOH is augmented from 0 mg to 25 mg. The Fe₃O₄@SA MNCs exhibited optimal catalytic efficiency when NaOH was excluded from the solution. The best catalytic performance for the Fe₃O₄@SA MNCs used was achieved by not using NaOH in the solution, and the HGR value was 88 mL H₂ gcat⁻¹·min⁻¹ was measured. It has been reported in the literature (20) that an increase in the amount of NaOH reduces the rate of hydrolysis. Using 10, 20, and 25 mg of NaOH, the HGR values were measured as 48, 16, and 12 mL H₂ gcat⁻¹·min⁻¹, respectively. The decrease in the HGR value is related to blocking the active sites on the Fe₃O₄@SA MNCs of the NaOH increase.

![Figure 6: Effect on hydrogen volume in NaBH₄ hydrolysis of NaOH (Reaction conditions: 50 mg Fe₃O₄@SA MNCs, 100 mg NaBH₄, 0, 10, 20 and 25 mg NaOH and 25 °C).](image)

3.2.2. Effect on hydrogen production of NaBH₄ amount

The effect on the hydrogen production of NaBH₄ was investigated by using 25, 50, 100, 150, and 200 mg NaBH₄ at 25°C, keeping the amount of Fe₃O₄@SA MNCs (50 mg) constant. Figure 7 shows that when NaBH₄ is increased from 25 mg to 200 mg, the hydrogen produced increases significantly from 50 mL to 314 mL. The best catalytic performance for the Fe₃O₄@SA MNCs used was achieved by using 200 mg of NaBH₄, and the HGR value was 157 mL H₂ gcat⁻¹·min⁻¹ was measured. As the amount of NaBH₄ used increases, the hydrogen volume and HGR value increase depending on time. It was determined that as the amount of NaBH₄ increased, the hydrogen volume increased depending on time. The results obtained are compatible with the literature (21-23).

3.2.3. Effect on hydrogen production of catalyst amount

The effect on hydrogen production of Fe₃O₄@SA MNCs amount (10, 25, 50, 75, and 100 mg) in 150 mg NaBH₄ hydrolysis at 25 °C was investigated. The obtained graph is shown in Figure 8. When the amount of Fe₃O₄@SA MNCs increased from 10 mg to 75 mg, the hydrogen produced increased significantly from 106 to 128 mL. When the amount of catalyst increased from 75 mg to 100 mg, a significant decrease was observed in the volume of hydrogen produced. The reason for this decrease is that the catalyst’s active sites are filled in the reaction and cannot provide enough active sites for the substrate. The results obtained are compatible with the literature (24).
The best hydrogen production volume was achieved with 75 mg Fe₃O₄@SA MNCs, and the HGR value was measured as 85.33 mL H₂ g cat⁻¹·min⁻¹. The HGR values of 10, 25, 50, and 100 mg Fe₃O₄@SA MNCs were determined as 400, 160, 112, and 34 mL H₂ g cat⁻¹·min⁻¹, respectively. The highest HGR value was reached using a 10 mg catalyst. The HGR value increased until the optimum amount of Fe₃O₄@SA MNCs and then decreased. This is due to equation (2) used to calculate the HGR value.

Compared with Table 1, it was determined that the hydrolysis of NaBH₄ catalyzed by the Fe₃O₄@SA MNCs showed a lower HGR value than some catalysts, although it was comparable to other catalysts in the literature (Table 1). The reason for this can be said that the Fe₃O₄-supported structures in the literature have a more stable structure than the salicylic acid support material. Thus, higher HGR values can be obtained by coating the Fe₃O₄ structure with a more stable material and binding different metals to this nano-catalyst.

3.2.4. Reusability of the Fe₃O₄@SA MNCs

The percentage yield results obtained from NaBH₄ catalyzed after five reusability cycles of Fe₃O₄@SA MNCs at 25 °C are shown in Figure 9. It shows the yield results (percentage comparison with cycle 1) obtained from NaBH₄ catalyzed by Fe₃O₄@SA MNCs after five reusability cycles (75 mg catalyst, 150 mg NaBH₄, and 20 mL pure water) at 25 °C. As shown in Fig. 9, the catalytic activity of Fe₃O₄@SA MNCs was found to decrease slightly. It can be said that this situation is due to the accumulation of sodium metaborate, which cannot be removed by washing the catalyst. The results obtained are compatible with the literature (28). Thus, Fe₃O₄@SA MNCs were found to be an effective catalyst for the hydrolysis of NaBH₄.
Table 1. Comparison of Fe₃O₄@SA MNCs with various catalysts used for hydrogen production by NaBH₄ hydrolysis.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>HGR (mL H₂ gcat⁻¹·min⁻¹)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/Fe₃O₄@C</td>
<td>25</td>
<td>1403</td>
<td>(9).</td>
</tr>
<tr>
<td>Oxidized Fe₂O₃</td>
<td>25</td>
<td>264</td>
<td>(25).</td>
</tr>
<tr>
<td>α-Fe₂O₃@N-C NSs</td>
<td>25</td>
<td>637</td>
<td>(25).</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂–Pt</td>
<td>25</td>
<td>800</td>
<td>(26).</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂–Pt/Ni</td>
<td>25</td>
<td>2500</td>
<td>(26).</td>
</tr>
<tr>
<td>Fe₃O₄@SiO₂–Pt@TiO₂</td>
<td>25</td>
<td>1500</td>
<td>(26).</td>
</tr>
<tr>
<td>Fe-B</td>
<td>25</td>
<td>618</td>
<td>(27).</td>
</tr>
<tr>
<td>Fe₃O₄@SA</td>
<td>25</td>
<td>400</td>
<td>This work</td>
</tr>
</tbody>
</table>

![Figure 9: The reusability of Fe₃O₄@SA MNCs for hydrolysis of NaBH₄ at 25 °C.]

3.3. Optimization of the Catalysis Process
In this study, optimum catalysis process conditions are given in Figure 9. The decrease in the amount of NaOH increased hydrogen production. The study with 0 mg NaOH produced 84 mL of hydrogen in 40 minutes, with other parameters remaining constant (Figure 9.A). Increasing the amount of NaBH₄ increased the hydrogen production. The study with 200 mg of NaBH₄ produced 314 mL of hydrogen in 40 minutes, with other parameters remaining constant (Figure 9.B). Increasing the amount of Fe₃O₄@SA MNCs increased hydrogen production. The study with 75 mg Fe₃O₄@SA produced 128 mL of hydrogen in 40 minutes, with other parameters remaining constant (Figure 9.C).
3.4. A possible Mechanism of NaBH₄ Hydrolysis Catalyzed by Fe₃O₄@SA MNCs

The reaction mechanism of the catalyzed hydrolysis of NaBH₄ is assumed to occur by following the steps of the reaction mechanism, as shown in Figure 10. NaBH₄, catalyst, and water molecules are initially in the same environment. BH₄⁻ ions and water molecules are chemically adsorbed on the catalyst. Second, the H⁺ ion is transferred from the BH₄⁻ ion to the catalyst. Third, hydrogen in hydric form (H⁺) and BH₃⁻ ions react with a water molecule to form H₂ and BH₃(OH)⁻ ions. Hydrogen in each hydric form is transferred from the BH₃(OH)⁻ ion to the catalyst. Finally, each cycle is repeated until 4 moles of H₂ are released, forming the B(OH)₄⁻ form from the BH₃(OH)⁻ ion. The proposed possible mechanism for NaBH₄ hydrolysis catalyzed by Fe₃O₄@SA MNCs is consistent with the literature (29,30). Since the reaction end product, B(OH)₄⁻ is not supported by the catalyst, it reduces the rate of the hydrolysis reaction. It can be said that H₂ is produced more easily with the electrons coming from the BH₄⁻ ions from the hydrogen ion excess in the environment. Thus, it reflects positively on hydrogen production volume and HGR value.
4. CONCLUSION

The use of Fe$_3$O$_4$@SA MNCs as a catalyst in hydrogen production was carried out for the first time in this study. Fe$_3$O$_4$@SA MNCs were produced by a simple, reliable, and inexpensive process. Characterizations with FT-IR, XRD, VSM, SEM, and SEM-EDX methods showed that Fe$_3$O$_4$@SA MNCs were successfully synthesized. To determine the effect of Fe$_3$O$_4$@SA MNCs on HGR, the amounts of NaBH$_4$, NaOH, and catalyst were examined. For Fe$_3$O$_4$@SA MNCs, the highest HGR value was obtained using 150 mg of NaBH$_4$, 10 mg of catalyst, 20 ml of distilled water, and no NaOH in the reaction. The obtained maximum HGR value is found as 400 mL H$_2$ gcat$^{-1}$·min$^{-1}$. HGR values are comparable to values reported in the literature. The economic and large-scale production of Fe$_3$O$_4$-based magnetic nano-catalysts for hydrogen production by NaBH$_4$ hydrolysis offers a much simpler and more commercial process to make hydrogen the main fuel source.

5. CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

6. REFERENCES


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