The activity of ceria supported complex in hydrogen generation

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ABSTRACT

In this study, we studied the ceria supported Ni complex preparation and using it as a catalyst in NaBH₄ hydrolysis for H₂ production. NaBH₄ hydrolysis system was studied in different parameters, as concentration of Ni complex, concentration of NaBH₄, concentration of NaOH, amount of catalyst and temperature. Additionally, catalyst was characterized by several analysis methods. Finally, the kinetic calculation of NaBH₄ hydrolysis reaction was studied at 20 °C-50 °C the activation energy was found to be 27.581 kJmol⁻¹. The aim of this study is to emphasize that ceria support can be used to increase the catalyst surface and to obtain the high hydrogen generation activity through hydrolysis of NaBH₄. The experimental results show that ceria supported Ni complex was an effective catalyst in hydrolysis of NaBH₄.

Keywords: Ni-complex, Sodium borohydride, Hydrogen generation.

1. INTRODUCTION

Hydrogen is a renewable energy sources which deliver sufficient energy that was clean and environmentally friendly. But, two important impediments are present to hydrogen generation and storage for using hydrogen. Due to its H₂ evolution at low temperature, great 10.8 % H₂ content, delivered non-toxic byproducts and stability in alkaline solutions NaBH₄ is commonly used.²

NaBH₄ + 2H₂O → 4H₂ + NaBO₂ (1)

The use of heterogeneous catalysts was considered one of the ways to control the hydrolysis of NaBH₄.³ NaBH₄ hydrolysis reaction is controlled by different noble or non-noble metal (Pt, Ru, Pd Co, Ni, and Cu) catalysts in many forms.⁴-¹¹ To improve of the catalyst different studies have been tried.¹²⁻¹⁵ Between them a different support materials using is started to attract attention and be widely used.¹⁶⁻¹⁷ Typical catalyst supports include TiO₂,¹⁸⁻²⁰ Al₂O₃,²¹⁻²³ MgO²⁴, clays²⁵, SiO₂,²⁶, ²⁷ CeO₂,²⁸ activated carbon²⁹ etc... Though activated carbon is a good support material, the fabrication of activated carbon is expensive since it requires high-temperature values. Ceria support (CeO₂) is important material in hydrogen generation due to its storage performance, reducing activation energy and effect of oxygenation.³⁰⁻³² Herein, the Ni complex (4,4’,-methylenebis-(2,6-diethyl) aniline-3,5-di-tert-butylsalisyaldimine-Ni)³³ was used to supported on ceria and the catalytic effects was
investigated on sodium borohydride hydrolysis for hydrogen production. The catalytic studies were realized by different parameters at 30 °C. The aim of this study is to emphasize that ceria support can be used to increase the catalyst surface and to obtain the high hydrogen generation activity through hydrolysis of NaBH₄. The experimental results show that the ceria supported Ni complex was an effective catalyst in hydrolysis of NaBH₄. Moreover, ceria supported Ni complex catalyst was characterized with BET, FT-IR, XRD and SEM.

2. MATERIALS AND METHODS

2.1. Materials

All solvents: chloroform (CHCl₃), methyl alcohol (CH₃OH), ethyl alcohol (CH₃CH₂OH), and the main chemicals: NiCl₂·6H₂O, 4-4’-methylenebis-(2,6-diethyl) aniline, 3,5-ditertbutylsalisylaldehyde, and cerium oxide, NaBH₄, NaOH were purchased from Merck and they were used without applying any purification.

Infrared spectrum was measured in the range of 4000–400 cm⁻¹ on a PerkinElmer Spectrum 100 FTIR (ATR sampling accessory) spectrophotometer. With using Rigaku X-Ray diffracometer, the XRD patterns were determined. By using Brunauer–Emmett–Teller (BET) surface area measurement the important surface area parameters were identified. SEM results were determined with JEOL JSM 5800.

2.2. Methods

2.2.1. Synthesis of ceria Supported-Ni complex

By using mechanical mixing techniques ceria supported Ni complex catalyst was prepared. With varied amount of Ni complex was dissolved in ethanol (10 mL). Then 0.1 g ceria was added in this solution and stirred 72 h before filtration. In Figure 1 preparation of ceria supported Ni complex catalyst was shown.

\[\text{EtOH} + \text{Ceria support} \rightarrow 
\text{Ceria supported 4-4’-methylenebis-(2,6-diethyl) aniline -} \text{3,5-ditertbutylsalisylaldehyde-Ni complex} \]

Figure 1. Preparation of Ceria supported Ni complex

2.2.2. Catalytic sodium borohydride hydrolysis reaction

Catalytic hydrogen generation system occurred from 0.01 g catalyst that including 5 % Ni complex, with 10 % NaOH in 10 mL 2.0 % NaBH₄ solution at 30 °C. The generated hydrogen amount was measured by using graduated cylinder. The proposed hydrogen volume is 560 mL for Equation 1.

3. RESULTS AND DISCUSSION

3.1. The influence of different parameters on the catalytic activity of ceria Supported-Ni complex in hydrogen generation

To research influence of NaOH concentration on the H₂ generation, different NaOH concentrations from 0 to 10 % were tried with using ceria supported-Ni complex catalyst, while the concentration of 2 % NaBH₄ at 30 °C. The hydrogen generation rates increased as 8193.60; 8343.40; 11550.20; 14123.00;16535.40 mL H₂ gcat⁻¹ min⁻¹ in order of 0 %, 5 %, 7 %, and 10 % NaOH and the reaction times decreased (Figure 2). In this study, H₂ production rates increased with the increasing concentration of NaOH.
To investigate the influence of Ni complex concentration in hydrogen generation, 5%, 10%, 15%, 20% Ni complex concentrations were tried. For ceria supported Ni complex and tried in hydrogen generation reaction (Figure 3).

In Figure 3, it is seen that with increasing Ni complex concentration hydrogen generation rates were started to decrease as 16535.40; 7540.40; 5560.53; 4758.15 mL H\textsubscript{2} g\textsubscript{cat}\textsuperscript{-1}.min\textsuperscript{-1} from 5% to 20% Ni complex concentration. In this study, hydrogen generation rates decreased with the increasing concentration of Ni complex concentration in ceria supported Ni complex catalyst. The lower values from 5% was also investigated with 4% Ni complex concentration, but surprisingly hydrogen generation rate was become to decrease to 16402.50 mL H\textsubscript{2} g\textsubscript{cat}\textsuperscript{-1}.min\textsuperscript{-1} with generated 500 mL hydrogen. So that for this study 5% Ni complex was preferred to use in ceria supported Ni complex catalysis.

The effect of catalyst amount on hydrogen generation rate was investigated with several ceria supported Ni complex catalyst amounts as 0.005, 0.01, 0.025, and 0.05 g including 5% Ni complex in 2% NaBH\textsubscript{4} and 10% NaOH solution at 30°C and the results are seen in Figure 4. As seen from Figure 4, there is an opposite ratio towards the H\textsubscript{2} generation rates and amounts of catalyst as 20452.00; 16535.40; 6140.00; 3569.00 mL H\textsubscript{2} g\textsubscript{cat}\textsuperscript{-1}.min\textsuperscript{-1}. So that, H\textsubscript{2} generation rates decreased with amounts of supported Ni complex increasing due to the catalyst surface saturation. However, 0.005 g catalyst has the best hydrogen generation rate (20452.00), the predicted hydrogen volume is not provided (490 mL). So it was decided that the suitable catalyst amount is 0.01 g for this reaction (560 mL).

In order to check the sodium borohydride concentration on H\textsubscript{2} generation rate, the different concentration of NaBH\textsubscript{4} as 2%, 5%, 7%, 10% was tried in 10% NaOH solution with 0.01 g ceria supported Ni complex at 30°C. Ceria supported Ni complex was highly active catalyst, despite the improving NaBH\textsubscript{4} percentage as shown in Figure 5. There was any important difference in H\textsubscript{2} generation rates as NaOH concentration increased. It was shown that ceria supported Ni complex catalyzed NaBH\textsubscript{4} hydrolysis was not depend on NaBH\textsubscript{4} amount.
To research the effect of temperature on hydrogen generation rates, the studies were carried out at different temperatures as 20, 30, 40, 50 °C with 2 % NaBH₄ and 10 % NaOH solution and 0.01 g ceria supported-Ni complex catalyst. As shown in Figure 6 the hydrogen production rates increased with increasing reaction temperature as 8571.00; 16535.40; 20772.00; 23320.00 mL H₂ g⁻¹ min⁻¹ respectively.

### 3.2. Kinetic studies of hydrogen generation

Kinetic studies of ceria supported Ni complex catalyzed hydrogen generation reaction are described from nth order reaction equation as:

\[ -r_{NaBH4} = -\frac{dC_{NaBH4}}{dt} = k \cdot C_{NaBH4}^{n} \] \hspace{1cm} (2)

Separating and integrating, we obtain:

\[ -\int_{C_{NaBH40}}^{C_{NaBH4}} \frac{dC_{NaBH4}}{C_{NaBH4}} = \int_{0}^{t} k \, dt \] \hspace{1cm} (3)

\[ \frac{1}{(n-1)} \left( \frac{1}{C_{NaBH4}} - \frac{1}{C_{NaBH40}} \right) = k \cdot t \] \hspace{1cm} (4)

In Equation 5 the reaction order, \( n \) was recorded as 0.25. From Figure 7 the rate constants, \( k \) was obtained. A linear curve was displayed in Figure 8 with Plotting Ln (k) versus to (1/T).

\[ k = A \cdot \exp \left( -\frac{E_{a}}{RT} \right) \] \hspace{1cm} (6)

The activation energy (Eₐ) was recorded as 27.581 kJ mol⁻¹.
3.3. Reusability of Ceria Supported Ni Complex Catalyst

The stability of the ceria supported Ni complex catalyst was tried in the hydrolysis of NaBH₄ by using in five times. Before reuse the catalyst washed with distilled water to take out the dirtiness on the catalyst. Ceria supported Ni complex exhibited excellent catalytic activity by providing 98 % efficiency even in the 5th cycle as shown in Figure 9.

The experimental results indicate that the ceria supported Ni complex catalyst is highly stable in hydrolysis of NaBH₄.

3.7. Characterization of ceria supported Ni complex

3.7.1. FT-IR Spectrum

The FT-IR measurement was performed to investigate with compare the ceria supported Ni complex and Ni complex [1]. In Table 1 the band that occurred at 2896 cm⁻¹ are due to the free -OH groups or intramolecular OH–N which seen both ceria supported Ni complex and Ni complex. Both ceria supported Ni complex and Ni complex the band that occurred at 2745-2976 cm⁻¹ was corresponding to methyl group. At 1602-1619 cm⁻¹ band for Ni complex, for azomethine (C=N) group was changed as 1607-1623 cm⁻¹ in ceria supported Ni complex. For phenolic –C=O– the bands were occurred at 1692-1733 cm⁻¹ and 1689-1748 cm⁻¹ as ceria supported Ni complex and pure Ni complex respectively.

5 % Ni complex containing ceria supported Ni complex catalyst has the stronger bands in 512 cm⁻¹ that verified the formation of complex on the oxygen atom to metal atom (M–O) and at 421 cm⁻¹ corresponded to vibrations of nitrogen atom and metal atom (M–N), and the same bands are present on pure Ni complex.

Table 1. The results of FT-IR spectrum for Ceria supported Ni complex

| Complex               | cm⁻¹          | δ-O-H (intra molecular) | δ-CH₃ | δ-C=N- | δ-C=O- | δ- M-N | δ- M–O |
|-----------------------|--------------|-------------------------|-------|--------|--------|--------|--------|
| Ni complex            | 2896         | -2745 - 2976            | 1602  | 1689 - 1748 | 421  | 512    |
| Ceria supported Ni complex | 2896         | -2753 - 2977            | 1607  | 1692 - 1733 | 421  | 512    |

3.7.2. X-Ray Diffractograms (XRD)

In Figure 10, the XRD patterns of ceria supported-Ni complex were displayed.

Figure 7. The linear regression based on nth-order at 20 °C-50 °C

Figure 8. Arrhenius equation according to nth-order reaction

Figure 9. The reusability of ceria supported Ni complex catalyst by using five times in the hydrolysis of NaBH₄

Figure 10. XRD results of Ceria supported Ni complex
It was understood that the catalyst has a completely crystal structure. For ceria supported-Ni complex, the major diffraction peaks were observed at 8.62; 9.69; 12.77; 14.92; 20.86; 23.41; 30.79; 43.06 and 44.91 respectively.

3.7.3. Brunauer-Emmett-Teller surface area analysis (BET)

Ceria supported Ni complex has a big surface area and that provide to increase the catalytic activity. For pure Ni (II) complex the surface area was recorded as 33.284 m²g⁻¹ and for ceria supported Ni complex, it was 64.377 m²g⁻¹ as indicated in Table 2. For ceria supported Ni complex the pore volumes increased almost more than 2 times than pure Ni complex.

Table 2. BET analysis results of catalyst

| Catalyst                  | Average Pore Ratio (nm) | Pore Volume (cm³g⁻¹) | S BET (m²g⁻¹) |
|---------------------------|-------------------------|-----------------------|---------------|
| Ni Complex                | 10.569                  | 0.132                 | 33.284        |
| Ceria supported Ni Complex| 14.245                  | 0.235                 | 64.377        |

3.7.4. Scanning electron microscopy analysis (SEM)

For ceria supported Ni complex the SEM images were displayed in Figure 11. It was clearly seen that ceria supported Ni complex catalyst display completely homogeneous structure. According to SEM results the surface of ceria supported Ni complex catalyst was fully coated by Ni complex as shown in Figure 11.

Figure 11. SEM images of Ceria supported Ni complex

generation. ceria supported Ni complex catalysts was characterized with using the SEM, BET, XRD and FTIR. The highest hydrogen generation rate was 16535.40 mL H₂ g⁻¹cat⁻¹.min⁻¹ and 23320.00 mL H₂ g⁻¹cat⁻¹.min⁻¹ at 30 °C and 50 °C respectively by using 0.01 g ceria supported-Ni complex catalyst. In summary, ceria supported Ni complex catalyst exhibited greater activity in hydrogen generation. The activation energy (Ea.) was recorded as 27.581 kJ/mol. The reusability tests showed the catalyst retained 98 % of its activities after fifth cycles. The hydrogen generation performance the comparison of ceria supported Ni complex and various Ni based catalysts in NaBH₄ hydrolysis reaction is shown in Table 3. Consequently, the prepared ceria supported Ni complex catalyst can be used as highly active, practical and low-cost materials for hydrogen generation in sodium borohydride hydrolysis.

Table 3. The hydrogen generation performance comparison of ceria supported Ni complex catalyst and various Ni catalysts in NaBH₄ hydrolysis reaction

| Catalyst                  | Hydrogen Generation Rate (mL H₂ g⁻¹cat⁻¹.min⁻¹) | References |
|---------------------------|-----------------------------------------------|------------|
| Ceria / Ni-complex        | 16535.40                                      | In This Study |
| Ni-Co/r-GO                | 1280.00                                       | 34         |
| CoB/Ni-foam               | 1930.00                                       | 35         |
| Co-Ni-Mo-P/g-Al2O3        | 10125.00                                      | 36         |
| Ni(II)-complex            | 2240.00                                       | 37         |
| NiCo₃O₄                  | 1000.00                                       | 38         |

4. CONCLUSIONS

In present study, ceria supported Ni complex was prepared for NaBH₄ hydrolysis reaction to hydrogen generation. ceria supported Ni complex catalysts was characterized with using the SEM, BET, XRD and FTIR. The highest hydrogen generation rate was 16535.40 mL H₂ g⁻¹cat⁻¹.min⁻¹ and 23320.00 mL H₂ g⁻¹cat⁻¹.min⁻¹ at 30 °C and 50 °C respectively by using 0.01 g ceria supported-Ni complex catalyst. In summary, ceria supported Ni complex catalyst exhibited greater activity in hydrogen generation. The activation energy (Ea.) was recorded as 27.581 kJ/mol. The reusability tests showed the catalyst retained 98 % of its activities after fifth cycles. The hydrogen generation performance the comparison of ceria supported Ni complex and various Ni based catalysts in NaBH₄ hydrolysis reaction is shown in Table 3. Consequently, the prepared ceria supported Ni complex catalyst can be used as highly active, practical and low-cost materials for hydrogen generation in sodium borohydride hydrolysis.

Conflict of interests

Authors declare that there is no a conflict of interest with any person, institute, company, etc.
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