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Research Article

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 $NaBH_4$ hydrolysis for H_2 production. $NaBH_4$ hydrolysis system was studied in different parameters, as concentration of Ni complex, concentration of $NaBH_4$, concentration of NaOH, amount of catalyst and temperature. Additionally, catalyst was characterized by several analysis methods. Finally, the kinetic calculation of $NaBH_4$ 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 $NaBH_4$. The experimental results show that ceria supported Ni complex was an effective catalyst in hydrolysis of $NaBH_4$.

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

Seryum oksit destekli kompleksin hidrojen üretimindeki aktivitesi

ÖZ

Bu çalışmada, seryum oksit destekli Ni kompleksinin hazırlanışını ve $NaBH_4$ den hidrojen üretiminde katalizör olarak kullanılışını inceledik. seryum oksit destekli Ni kompleks katalizli $NaBH_4$ hidroliz reaksiyonu; $NaBH_4$ ve NaOH konsantrasyonuna, sıcaklığa, katalizör miktarına ve katalizör içersindeki Ni kompleksinin konsantrasyonuna bağlı olarak çalışıldı. Ayrıca sentezlenen katalizör farklı analiz yöntemleriyle karakterize edildi. Son olarak da 20 °C-50 °C sıcaklık aralığında sodyum borhidrürün hidroliz reaksiyonunun kinetik verileri incelendi, reaksiyonun aktivasyon enerjisi 27.581 $kJmol^{-1}$ olarak bulundu. $NaBH_4$ hidrolizinde seria destekli Ni kompleksinin etkin bir katalizör olduğu görüldü.

Anahtar Kelimeler: Ni-kompleks, Sodyum borhidrür, Hidrojen üretimi.

1. INTRODUCTION

Hydrogen is a renewable energy sources which deliver sufficient energy that was clean and environmentally friendly. [1] But, two important impediments are present to hydrogen generation and storage for using hydrogen. Due to its H_2 evolution at low temperature, great 10.8 % H_2 content, delivered non-toxic byproducts and stability in alkaline solutions $NaBH_4$ is commonly used.[2]

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \quad (1)$$

The use of heterogeneous catalysts was considered one of the ways to control the hydrolysis of $NaBH_4$.[3] $NaBH_4$ 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 TiO_2[18-20], Al_3O_2[21-23], MgO[24], clays[25], SiO_2[26, 27], CeO_2[28], activated carbon[29], etc... Though activated carbon is a good support material, the fabrication of activated carbon is expensive since it requires high-temperature values. Ceria support (CeO_2) 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-butylsalisylaldimine-Ni)[33] was used to supported on ceria and the catalytic effects was

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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 $NaBH_4$. The experimental results show that the ceria supported Ni complex was an effective catalyst in hydrolysis of $NaBH_4$. 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 ($CHCl_3$), methyl alcohol (CH_3OH), ethyl alcohol (CH_3CH_2OH), and the main chemicals: $NiCl_2{\cdot}6H_2O$, 4-4'-methylenebis-(2,6-diethyl) aniline, 3,5-ditertbutylsalisylaldehyde, and cerium oxide, $NaBH_4$, 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 diffractometer, 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 Figure1 preparation of ceria supported Ni complex catalyst was shown.

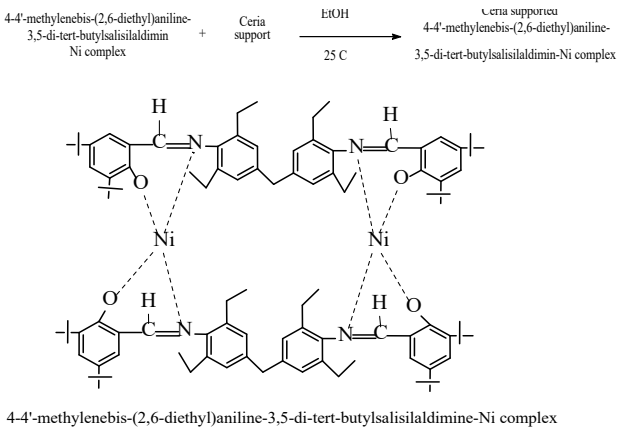

Figure 1. Preparation of Ceria supported Ni complex

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 % $NaBH_4$ 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 H_2 generation, different NaOH concentrations from 0 to 10 % were tried with using ceria supported-Ni complex catalyst, while the concentration of 2 % $NaBH_4$ at 30 °C. The hydrogen generation rates increased as 8193.60; 8343.40; 11550.20; 14123.00;16535.40 mL H_2 $g_{cat}^{-1}{\cdot}min^{-1}$ in order of 0 %, 5 % 7 %, and 10 % NaOH and the reaction times decreased (Figure 2). In this study, H_2 production rates increased with the increasing concentration of NaOH.

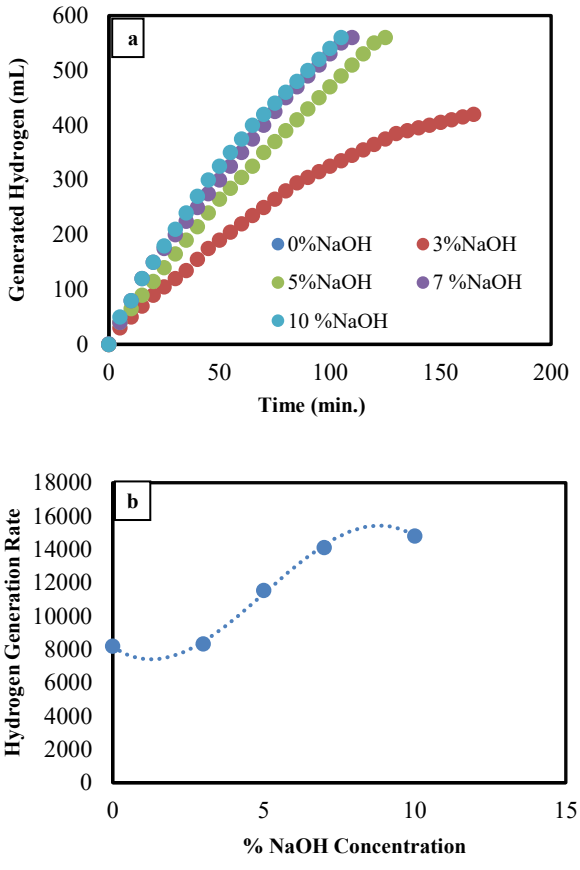

Figure 2. a) Influence of NaOH concentration, b) Graph of % NaOH concentration to hydrogen generation rate (in 2 % $NaBH_4$, 0.01 g catalyst at 30 °C)

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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 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_2 g_{cat}^{-1}·min^{-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_2 g_{cat}^{-1}·min^{-1} with generated 500 mL hydrogen. So that for this study % 5 Ni complex was preferred to use in ceria supported Ni complex catalys

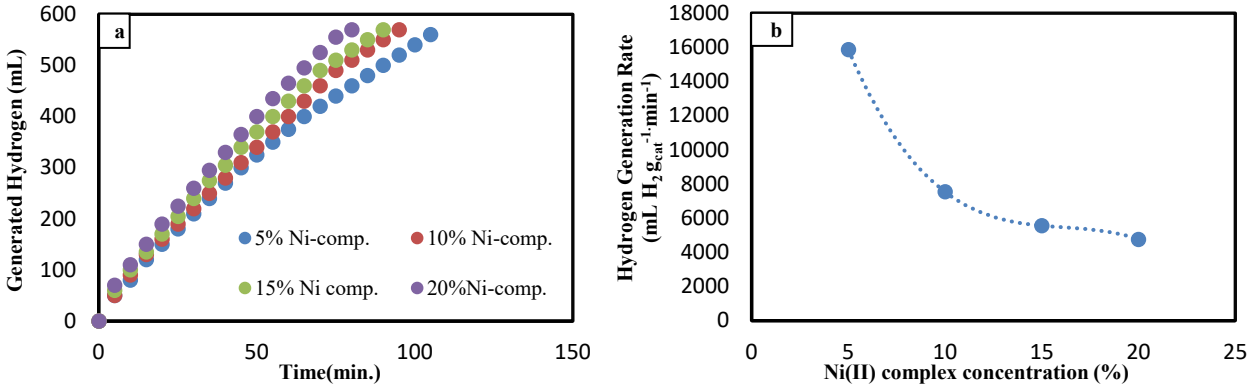

Figure 3. a) Influence of Ni complex concentration in hydrogen generation b) Graph of % Ni concentration to hydrogen generation rate (in 2 % $NaBH_4$, 10 % NaOH, 0.01 g catalyst at 30 °C)

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 % $NaBH_4$ 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_2 generation rates and amounts of catalyst as 20452.00; 16535.40; 6140.00; 3569.00 mL H_2 g_{cat}^{-1}·min^{-1}. So that, H_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).

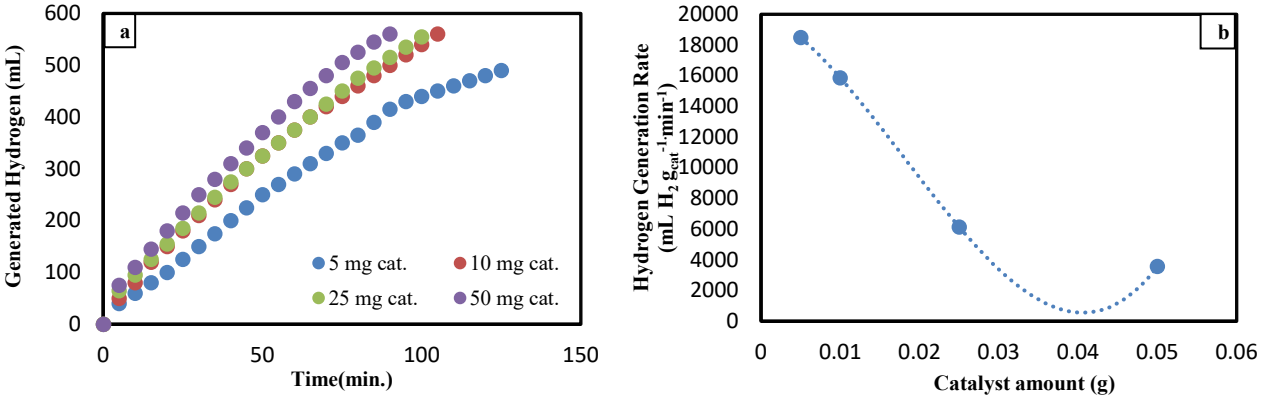

Figure 4. a) Influence of catalyst amount in hydrogen generation b) Graph of catalyst amount to hydrogen generation rate (in 2 % $NaBH_4$, 10 % NaOH at 30 °C)

In order to check the sodium borohydride concentration on H_2 generation rate, the different concentration of $NaBH_4$ 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 $NaBH_4$ percentage as shown in Figure 5. There was any important difference in H_2 generation rates as NaOH concentration increased. It was shown that ceria supported Ni complex catalyzed $NaBH_4$ hydrolysis was not depend on $NaBH_4$ amount.

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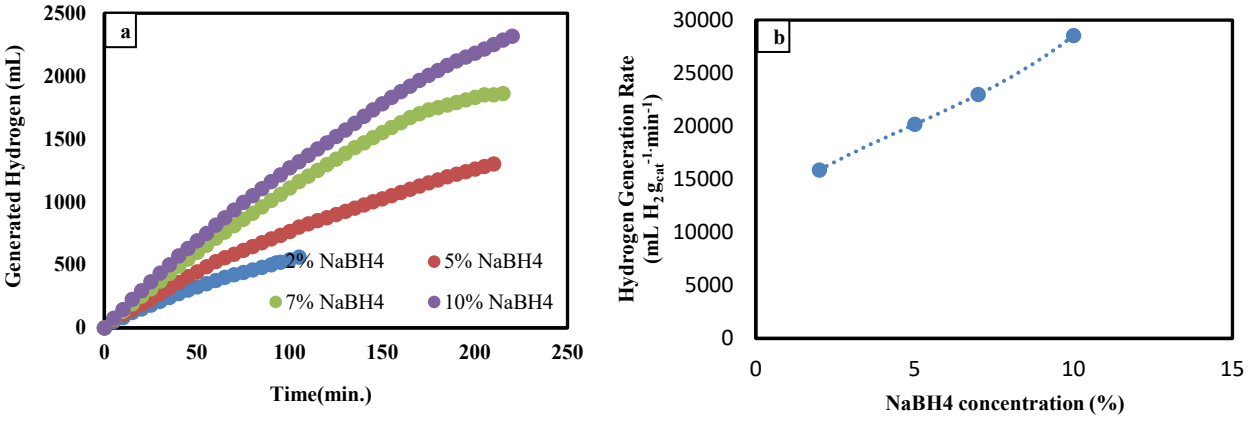

Figure 5. a) Influence of $NaBH_4$ concentration in hydrogen generation b) Graph of % $NaBH_4$ concentration to hydrogen generation rate (in 10 % NaOH, 0.01 g catalyst at 30 °C)

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 % $NaBH_4$ 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 H_2 g_{cat}^{-1}·min^{-1} respectively.

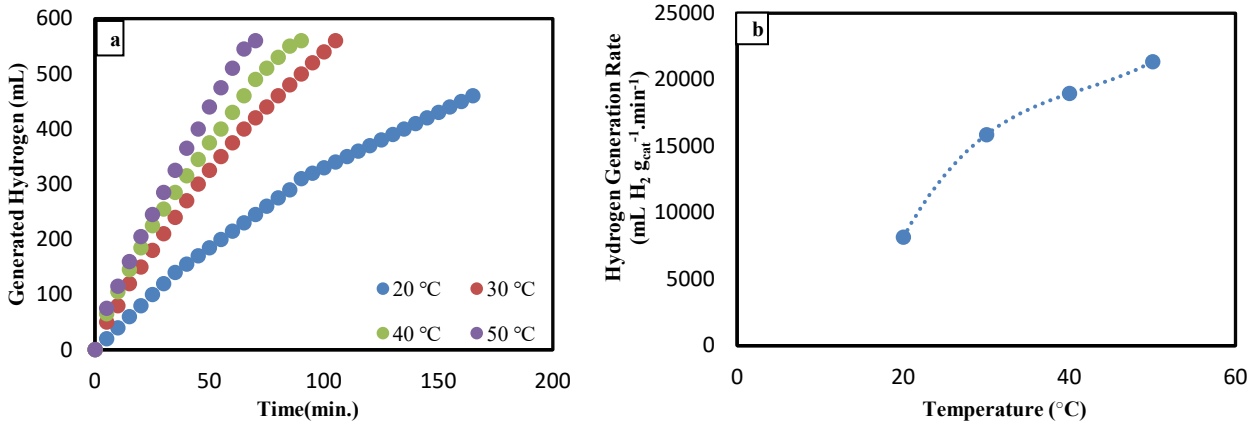

Figure 6. a) Influence of temperature on the hydrogen generation b) Graph of different temperatures to hydrogen generation rate (in 2 % $NaBH_4$, 10 % NaOH, 0.01 g catalyst)

3.2. Kinetic studies of hydrogen generation

Kinetic studies of ceria supported Ni complex catalyzed hydrogen generation reaction are described from n^{th} order reaction equation as;

$$-r_{NaBH4} = -\frac{dC_{NaBH4}}{dt} = k.C_{NaBH4}^{n} \quad (2)$$

Separating and integrating, we obtain:

$$-\int_{C_{NaBH40}}^{C_{NaBH4}} \frac{dC_{NaBH4}}{C_{NaBH4}^{n}} = k\int_{0}^{t} dt \quad (3)$$

$$\frac{1}{(n-1)}\left(\frac{1}{C_{NaBH4}^{n-1}} - \frac{1}{C_{NaBH40}^{n-1}}\right) = kt \quad (4)$$

$$\frac{1}{C_{NaBH4}^{n-1}} = (n-1)k.t + \frac{1}{C_{NaBH40}^{n}} \quad (5)$$

In Equation 5 the reaction rate 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).

$$k = A \cdot \exp(-Ea / RT) \quad (6)$$

The activation energy (Ea.) was recorded as 27.581 kJ mol^{-1}.

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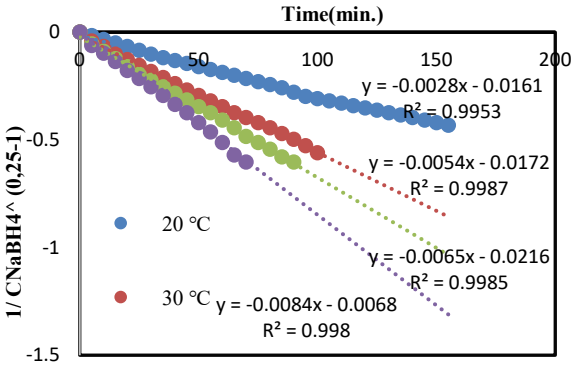

Figure 7. The linear regression based on n[th]-order at 20 °C-50 °C

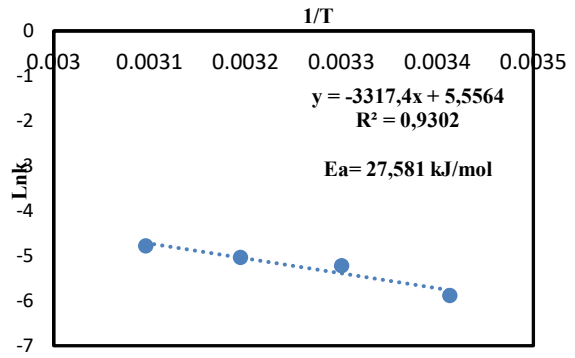

Figure 8. Arrhenius equation according to n[th]-order reaction

3.3. Reusability of Ceria Supported Ni Complex Catalyst

The stability of the ceria supported Ni complex catalyst was tried in the hydrolysis of $NaBH_4$ 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.

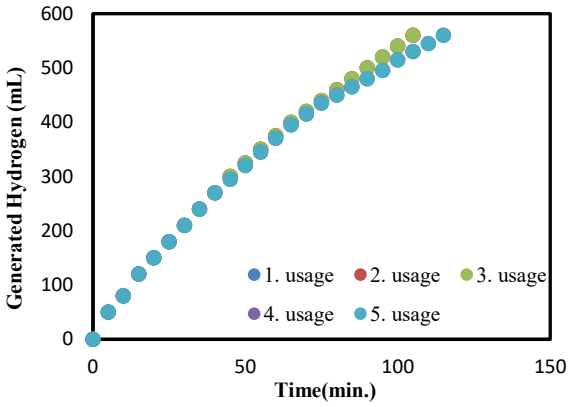

Figure 9. The reusability of ceria supported Ni complex catalyst by using five times in the hydrolysis of $NaBH_4$

The experimental results indicate that the ceria supported Ni complex catalyst is highly stabile in hydrolysis of $NaBH_4$.

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}					
	$\bar{\upsilon}$-O-H (intra molecular)	δ -CH_3	$\bar{\upsilon}$ -C=N-	$\bar{\upsilon}$ -C=O-	$\bar{\upsilon}$-M-N	$\bar{\upsilon}$-M–O
Ni complex	2896	2745 - 2976	1602 - 1619	1689 - 1748	421	512
Ceria supported Ni complex	2896	2753 - 2977	1607 - 1623	1692 - 1733	421	512

3.7.2. X-Ray Diffractograms (XRD)

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

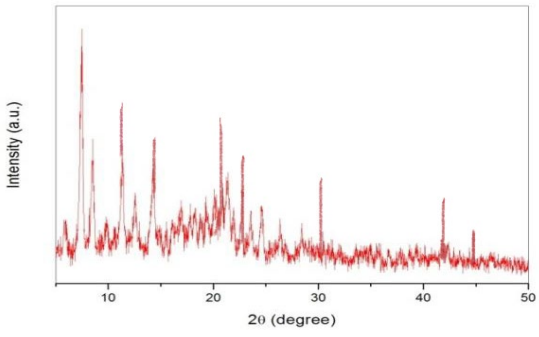

Figure 10. XRD results of Ceria supported Ni complex

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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 m^2g^{-1} and for ceria supported Ni complex, it was 64.377 m^2g^{-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 (cm^3g^{-1})	S BET ($m^2 g^{-1}$)
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.

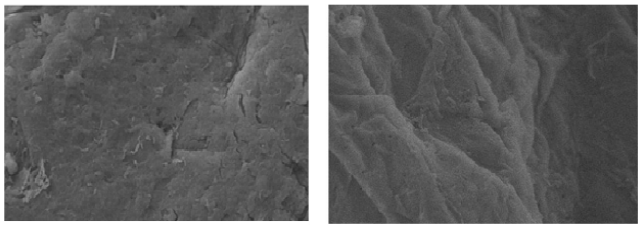

Figure 11. SEM images of Ceria supported Ni complex

generation. ceria supported Ni complex catalyst catalysts was characterized with using the SEM, BET, XRD and FTIR. The highest hydrogen generation rate was 16535.40 mL H_2 $g_{cat}^{-1}.min^{-1}$ and 23320.00 mL H_2 $g_{cat}^{-1}.min^{-1}$ 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 $NaBH_4$ 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 $NaBH_4$ hydrolysis reaction

Catalyst	Hydrogen Generation Rate (mL H_2 $g_{cat}^{-1}.min^{-1}$)	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
$NiCo_2O_4$	1000.00	38

4. CONCLUSIONS

In present study, ceria supported Ni complex was prepared for $NaBH_4$ hydrolysis reaction to hydrogen generation. ceria supported Ni complex catalyst catalysts was characterized with using the SEM, BET, XRD and FTIR. The highest hydrogen generation rate was 16535.40 mL H_2 $g_{cat}^{-1}.min^{-1}$ and 23320.00 mL H_2 $g_{cat}^{-1}.min^{-1}$ 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 $NaBH_4$ 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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