Renewable hydrogen production by steam reforming of glycerol over Ni/CeO₂ catalyst prepared by precipitation deposition method

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Abstract−Catalytic steam reforming of glycerol for renewable hydrogen generation has been investigated over Ni/CeO₂ catalyst prepared by precipitation-deposition method. The fresh and used catalysts were characterized by surface area and pore size analysis, X-ray diffraction patterns and scanning electron micrographs. Reforming experiments were carried out in a fixed bed tubular reactor at different temperatures (400-700 °C), glycerol concentrations (5-15 wt%) and contact times. (W/F_{Ao}=2-80 g-cat·h/mol of glycerol). The investigation revealed that the Ni/CeO₂ catalyst prepared by the above method is effective to produce high yield of hydrogen up to 5.6 (moles of H₂/moles of glycerol fed). The formation of methane and carbon monoxide was greatly reduced over this catalyst. Significantly low amount of coke deposition was observed on the CeO₂ supported catalyst. From the kinetic analysis, the activation energy for the steam reforming of glycerol was found to be 36.5 kJ/mol.

Key words: Steam Reforming, Glycerol, Catalyst, Ni/CeO₂, Renewable Hydrogen

INTRODUCTION

The generation of renewable fuels from bio oil components is becoming important in this era of diminishing petroleum reserves and increased environmental awareness. Hydrogen can be produced from biomass materials or bio oils via steam reforming and gasification [1-7]. Glycerol is produced as a by-product during bio-diesel production from vegetable oils, and is available at low cost in large supply from renewable raw materials. Glycerol is also produced during sugar fermentation and as a byproduct of ethanol production by lignocelluloses [8]. Efforts are being made to find alternative and optimum ways of utilizing glycerol. Steam reforming is an effective way to utilize the diluted glycerol aqueous solution to produce hydrogen. However, the steam reforming reactions of these bio-oxygenates are often accompanied by the formation of various by-products, which greatly affects the selective production of hydrogen and leads to rapid deactivation of the catalysts due to the severe coke deposition. Steam reforming of glycerol and other oxygenated compounds for hydrogen production has received attention during recent years. Faungnawaki et al. [9,10] and Czernik and co-workers [11,12] studied hydrogen generation via steam reforming of crude glycerol using a commercial nickel based naphtha reforming catalyst. Simonetti et al. [13] conducted experiments to measure the rate of glycerol conversion to H₂/CO gas mixtures under kinetically controlled reaction conditions over carbon-supported platinum and platinum-rhenium catalysts. Dauenhauer et al. [14], Garcia et al. [15] and Byrd et al. [16,17] reported the performance of noble metal catalysts for the reforming of model biomass materials.

Iriondo et al. [18] investigated glycerol steam reforming over Ni catalysts supported on bare CeO₂ and Al₂O₃, and CeO₂ promoted Al₂O₃ to produce H₂. Results revealed that low amount of coke deposition observed on ceria promoted catalyst. Adhikari et al. [19] also studied the nickel-based catalysts with MgO, CeO₂, and TiO₂ supports for glycerol reforming. Ni/CeO₂ showed the highest H₂ selectivity at 550 °C under the reaction conditions investigated. Zhang et al. [20] reported that ceria-supported noble metals are stable and highly active for ethanol reforming. Incorporation of ceria favors the coke gasification and water gas shift reaction, and also improves the redox reversibility of metallic phase. In addition to preventing the metal particles from sintering, ceria also exhibits strong resistance to coke deposition because of its high oxygen storage-release capacity, which facilitates coke gasification under steam reforming of oxygenates [21].

Adhikari et al. [22,23] investigated thermodynamic analysis for hydrogen production by steam reforming of glycerol. Their results revealed that the most suitable conditions for producing hydrogen are at a temperature above 625 °C and a molar ratio of water to glycerol of 9 : 1. Under these conditions methane production can be minimized, and carbon formation is thermodynamically inhibited. Although excess water in the feed increases the hydrogen production, a significant amount of unused water remains in the reactor effluent.

Following reactions can be summarized in general reforming of glycerol for hydrogen production [22].
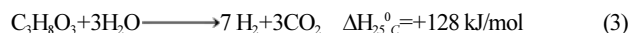
Steam reforming of glycerol:

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2 \qquad \Delta H_{25\,°C}^0 = +250 \text{ kJ/mol} \qquad (1)$$
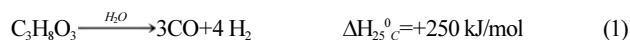
Followed by the water-gas shift reaction:

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H_{25\,°C}^0 = -41 \text{ kJ/mol} \qquad (2)$$

The desired overall reaction is then summarized as:

$$C_3H_8O_3 + 3H_2O \longrightarrow 7H_2 + 3CO_2 \quad \Delta H_{25\,°C}^0 = +128 \text{ kJ/mol} \qquad (3)$$

Some hydrogen is also lost during the methanation reaction:

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$$CO + 3H_2 \longrightarrow CH_4 + H_2O \qquad \Delta H_{25}^0 {}_C = -206 \text{ kJ/mol} \qquad (4)$$

Besides these some additional reactions may also take place

$$C + H_2O \xrightarrow{H_2O} CO + H_2 \qquad \Delta H_{25}^0 {}_C = +131 \text{ kJ/mol} \qquad (5)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \qquad \Delta H_{25}^0 {}_C = -165 \text{ kJ/mol} \qquad (6)$$

$$C + CO_2 \longrightarrow 2CO \qquad \Delta H_{25}^0 {}_C = +172 \text{ kJ/mol} \qquad (7)$$

Thus, the product stream is a mixture of mainly CH_4, CO, CO_2 and H_2. Furthermore, the yield of hydrogen depends on several process variables, such as temperature, space time and water-to-glycerol feed ratio. Limited studies are available on the kinetics of the steam reforming of glycerol. In most of the studies, the glycerol/water/catalyst is loaded in a small steel tube reactor and then sealed and placed in an oven. Typical reaction time varied from minutes to hours. It is reported in literature that high reaction time leads to the secondary reaction of methane formation [16,24,25]. Byrd et al. [26] investigated the hydrogen production from glycerol in supercritical water in a continuous reactor with a short reaction time and at a temperature ranging from 700-800 °C using a commercially available Ru/Al$_2$O$_3$ catalyst. The effects of the process variables such as temperature, contact time, and water-to-glycerol ratio on hydrogen yield are investigated. However, reforming of oxygenated compounds in supercritical water requires a significantly high temperature (>600 °C) and pressure above 220 atm [16,26]. The effective utilization of an oxygenated compound as a hydrogen source depends critically on the discovery of catalysts with high selectivity towards hydrogen and sufficient reaction rate under mild conditions.

The aim of this study is to examine the effectiveness of Ni/Ceria catalyst prepared by precipitation deposition method for hydrogen production from glycerol by catalytic steam reforming in a continuous reactor. Nickel based ceria and alumina supported catalysts were prepared on a lab scale by wet impregnation and precipitation-deposition method and characterized by BET surface area, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. The morphology of the catalyst after the reaction was also analyzed by SEM and thermogravimetric analysis (TGA). Effects of the process variables such as temperature, contact time, and steam-to-glycerol ratio on products yield were investigated to elucidate the reaction mechanism and evaluate the reaction kinetics.

EXPERIMENTAL

1. Catalyst Preparation and Characterization

M/CeO$_2$ (M=15% Ni by weight) catalyst was prepared by the deposition-precipitation method. Commercially available CeO$_2$ (Merck, Germany) was used as support material. The CeO$_2$ support was first suspended into the aqueous solutions containing certain amounts of metal precursor (Ni (NO$_3$)$_2$·6H$_2$O) and heated to 75 °C under constant stirring. 0.25 M Na$_2$CO$_3$ aqueous solution was then gradually added until the pH value of the mixture reached 7.5 and further aged for 1 h, after which the metal hydroxide species were exclusively deposited on the surface of ceria. After filtration and washing with hot water, the obtained solid powder was dried at 110 °C overnight and finally calcined at 500 °C for 5 h in atmospheric condition. This fine catalyst powder was then pelletized (3 mm size
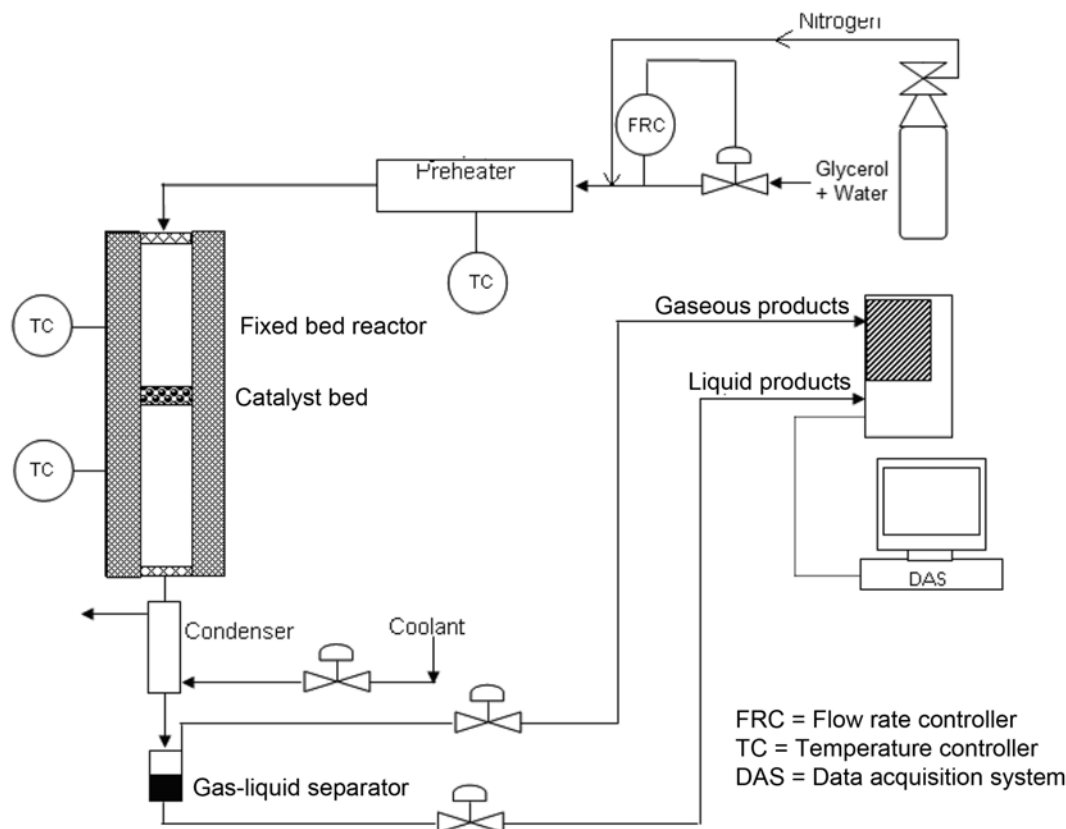

Fig. 1. Schematic diagram of the experimental setup.

pellets) using an automatic palletizing press (Techno Search AP-15) and subsequently crushed and sieved to an average particle size of 0.6 mm. For the purpose of comparison another batch of catalyst, Ni supported on alumina catalyst, was prepared by wet impregnation technique followed by drying and calcination at 550 °C.

The surface area and pore volume of the catalysts were determined by ASAP 2010 (Micrometrics U.S.A.) micro pore surface area analyzer using adsorption with nitrogen at −196 °C. Powder X-ray diffraction (XRD) patterns were obtained by means of a powder diffractometer using monochromatic Cu-Kα radiation and diffraction angle two theta ranging from 20-80° with a scanning rate of 3°/min. The wavelength of the radiation was 1.5 A°. SEM images were taken at 5,000 X and 25,000 X magnifications. Specimens were mounted and plated with silver to improve the images. Thermogravimetric analysis was done to determine the amount of coke present in the used catalyst. A derivative weight loss curve was used to estimate the temperature at which weight loss is most apparent.

2. Catalytic Steam Reforming

Steam reforming of glycerol was conducted in a continuous flow fixed-bed stainless steel (SS-316) reactor with 19 mm i.d. at atmospheric pressure within the temperature range of 500-700 °C. The schematic diagram of the experimental setup is shown in Fig. 1. Weighed amount of the catalyst ranging from 0.7 to 3.0 g (particle size of 40-60 mesh) was loaded and sandwiched by quartz wool layers at top and bottom. Pure glycerol is hygroscopic, so the glycerol feed was diluted with water and kept covered to prevent absorption of additional water from the atmosphere. Experiments were carried out with different weight percent of glycerol in water ranging from 1-20 weight percent of glycerol. The desired amounts of glycerol and water were injected by a pump (total flow rate 0.5-1.5 ml/min) into a pre-heater where this mixture was heated to 300 °C and mixed with a N_2 stream at flow rate of 30-60 ml/min. The reactor had three temperature zones: one above the catalyst bed, one below the catalyst bed and one at the catalyst bed. Three individual heaters controlled the temperature of all the three zones. A thermocouple was used to measure the actual temperature of the reaction zone. Isothermal conditions were maintained in the central portion of the reactor where the catalyst was placed. The reactor products passed through a condenser where the condensable vapors were condensed back to liquid state using a circulating water chiller. The composition of the outlet product gases was analyzed by gas chromatography in a thermal conductivity detector mode using carbosphere column. H_2, CO, CO_2 were separated by stainless steel column packed with carbosphere and detected by a thermal conductivity detector (TCD) using argon as the carrier gas. Nitrogen was used as an internal standard for the subsequent chromatographic analysis. Knowing the flow rate of nitrogen gas and its area from gas chromatography, flow rates of product gases were calculated. The total organic carbon in the liquid product was determined using a TOC analyzer. At the end of the run the reactor was flushed with nitrogen and then with steam to flush out any hydrocarbon material in the reactor. All measurements were taken at least in triplicate to ensure accuracy, which were further checked by calculating the overall carbon balance for the system. The runs in which carbon balance was more than 96 percent were considered for the data analysis. The performance of the catalyst is reported in terms of % glycerol conversion and hydrogen yield which are defined by the following equations:

Table 1. Surface area and pore volume of the catalysts

Type	Surface area (m^2/g)	Pore volume (cm^3/gm)	Avg. pore diameter (°A)
15% Ni/Al₂O₃	146.3±14.0	0.31±0.01	420.5±34
15% Ni/CeO₂	4.1±0.6	0.05	61.5±5.0

$$\% \text{ Glycerol conversion} = \left[\frac{(\text{glycerol in} - \text{glycerol out})}{\text{glycerol in}} \right] * 100 \quad (8)$$

$$H_2 \text{ Yield} = \frac{H_2 \text{ mole produced}}{\text{moles of glycerol fed}} \quad (9)$$

RESULTS and DISCUSSION

1. Catalyst Characterization

The BET surface area, pore volume and the adsorption average pore radius of the Ni/Al₂O₃ and the Ni/CeO₂ catalyst are given in Table 1. The surface area of catalyst reduced significantly due to the incorporation of Ni. It can be seen from the results that the ceria-supported catalyst has a significantly low surface area as compared with the alumina-supported catalyst. XRD results showed that the diffraction patterns of both NiO and Ni phases were present in the catalyst. Besides these the presence of crystalline CeO₂ phase was also observed. To determine whether the dispersion is regular or scattered, an SEM image at a very high magnification was taken. Fig. 2 shows the SEM images of the freshly prepared Ni/CeO₂ catalyst at a magnification of 25,000X. The nickel particles were present in spherical clusters, whereas ceria was present in form of long chips. The metal particles were well dispersed over the ceria particle, which was further confirmed by hydrogen chemisorptions study. All the catalyst prepared by impregnation method showed lower dispersion as well as higher particle size as compared to the co-precipitated catalyst. For Ni/CeO₂ higher dispersion and smaller crystallite size was also confirmed by XRD analysis.
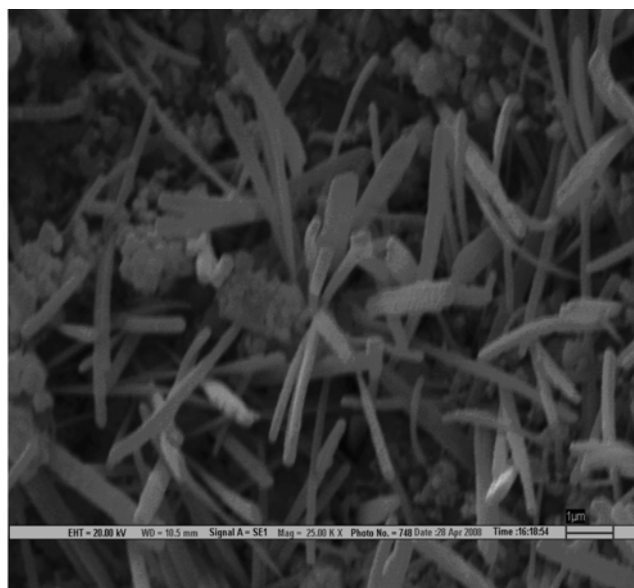

Fig. 2. SEM image of freshly prepared Ni/CeO₂ catalyst.

Temperature programmed reduction (TPR) spectra of the catalyst were recorded to identify the reduction behavior of the catalyst. The two reduction peaks at temperatures 320 °C and 540 °C in the TPR profile of the Ni/CeO₂ catalyst represented the reduction of NiO and ceria support, respectively. Compared to Ni/Al₂O₃ catalyst a lower reduction of Ni^{2+} species was observed in TPR study for Ni/CeO₂ catalyst. The reduction behavior of the catalyst strongly depends on the metal support interaction, which affects the catalyst activity during the reaction. Presence of ceria affects the reduction of Ni^{2+} species, which also depends on the method of catalyst preparation. The changes could be due to changes in Ni support interaction and due to change in nickel dispersion or due to the partial oxidation of ceria [18,27].

2. Glycerol Steam Reforming

The performance of the catalyst was investigated for the steam reforming of glycerol at different temperatures, water-to-glycerol feed ratios, and catalyst residence time in the reactor. Preliminary experiments were carried out at different feed rate and catalyst particle size to eliminate mass transfer and internal diffusion resistances. Plug flow conditions were maintained by avoiding back mixing and to minimize channeling in the reactor. Catalytic steam reforming of glycerol produced a stream rich in H_2 and CO_2 with small amounts of CH_4 and CO. Significantly high conversion was obtained over Ni/CeO₂ catalyst which was prepared by precipitation deposition method compared to Ni/Al₂O₃ catalyst. Investigations carried out at 600 °C revealed that maximum hydrogen yield (moles of hydrogen produced per mol of glycerol reacted) obtained was only 2.5 (mol/mol) over Ni/Al₂O₃ catalyst compared with 4.2 (mol/

mol) over Ni/CeO₂ catalyst. Also the amount of coke on this catalyst was significantly lower compared to wet impregnated catalysts. Thus, Ni/CeO₂ catalyst prepared by precipitation-deposition method has been found more active and selective than Ni/Al₂O₃ for hydrogen production from steam reforming of glycerol and selected for detailed kinetic study.

3. Effect of Temperature on Glycerol Conversion and Hydrogen Yield

Effect of temperature on glycerol conversion and hydrogen yield was studied using 10 wt% glycerol feed at a W/F_{AO} of 9.5 g-cat·hr/mol. The temperature was varied from 550-700 °C. At 750 °C there was significantly high coke in the reactor and hydrogen generation drastically reduced. Therefore, most of the experiments were carried out up to 700 °C only. Fig. 3(a), (b) shows the effect of temperature on glycerol conversion and hydrogen yield. The glycerol conversion increased from 60% to 80% as the temperature was increased from 600 °C to 700 °C The hydrogen yield also increased from 4 to 5 (moles of H_2/mol glycerol fed) as the reactor temperature was raised and reached to a maximum (Fig. 3(b)). The maximum hydrogen yield of approximately 5.6 was obtained at temperature of 680 °C compared to the thermodynamic value of 7. Thermodynamic results also revealed that product gas yield increases with increas-
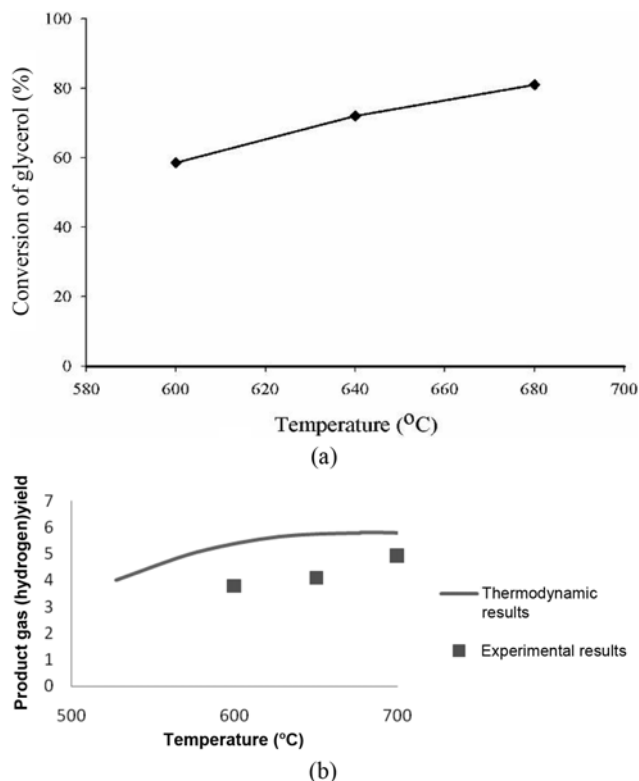
Fig. 3. Effect of temperature on (a) Glycerol conversion and (b) Hydrogen Yield (P, 1 atm; Glycerol concentration, 10 wt%, flow rate 1 ml/min; 0.7 g, Ni/CeO₂ catalyst).
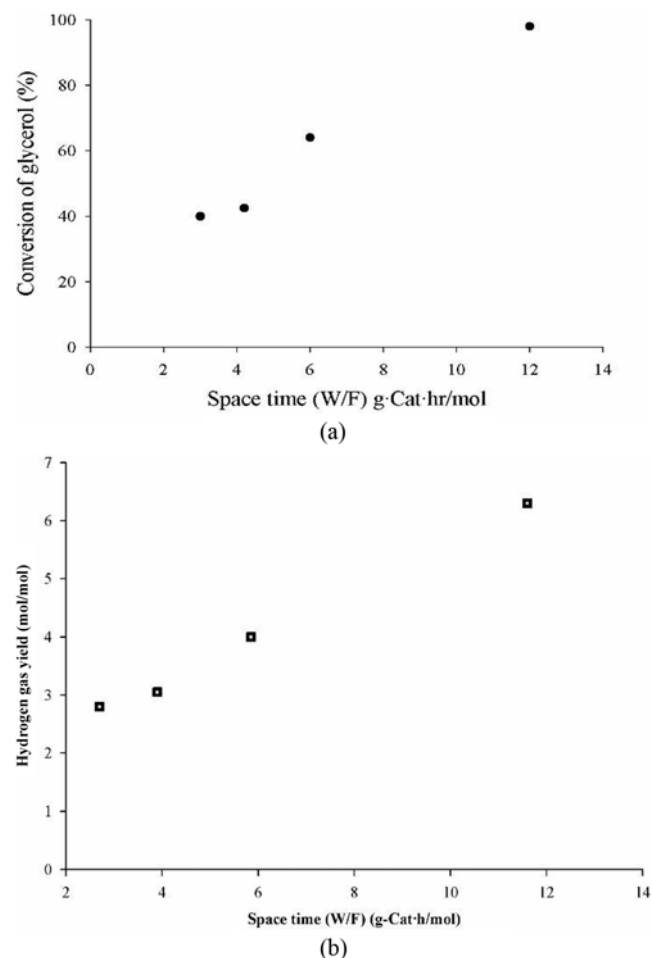
Fig. 4. Effect of space time on (a) glycerol conversion and (b) hydrogen yield (P, 1 atm; Temperature, 640 °C; glycerol concentration, 15 wt%).

ing temperature. Glycerol conversion increases at higher temperature due to the endothermic nature of the reaction which breaks C-H bond present in glycerol and other intermediates that are also formed as a result of cracking leading to higher conversion [2,27]. These results are in agreement with the published literature, where the maximum conversion for model bio-oils is found to be around 85-90% at 700 °C [18,28]. During steam reforming of bio oils and oxygenated compounds, complete conversion of glycerol has been reported; however, undesired methane also forms because of CO$_2$ hydrogenation that consumes hydrogen. Thus at higher temperature the yield of hydrogen decreases and methane formation increases. Ni/Ceria catalyst prepared by precipitation-deposition method had a significantly low methane formation even at high temperature, indicating that ceria also suppresses the methane formation reaction.

4. Effect of Space Time (W/F) and Glycerol Feed Concentration

The contact time (W/F$_{AO}$) was varied from 4.8 to 9.5 g-cat·h/mol by changing the mass of the catalyst at a glycerol feed rate of 0.06 mol/hr. Fig. 4(a), (b) shows the effect of space time (W/F$_{AO}$) on glycerol conversion and hydrogen yield. As expected, glycerol conversion increased as contact time was increased. The corresponding hydrogen yield also increased from 2.8 to 5.6 as glycerol conversion increased from 40% to 90% at 15 wt% glycerol feed. In the range of the experiments the reforming reaction was always below the thermodynamic equilibrium limit, hence hydrogen consumption was minimal due to the unwanted methanation reaction.

To study the effect of feed concentration, the glycerol concentration in water was varied from 10-20 wt%. Fig. 5(a), (b) shows that increasing the glycerol concentration or decreasing water to glycerol feed rates (WGFR) results in decrease in the yield of hydrogen. Thermodynamic study also revealed that high steam-to-carbon ratio favors the hydrogen formation (Fig. 5(b)). These results show that the product gas yield increases with increasing steam-to-carbon ratio. At about steam to carbon (S/C)=6 (mol/mol), the gas yield passed through a maximum. Thus, it can be inferred that the best WGFR to obtain the maximum yield is approximately 6 (mol/mol), which is necessary to optimize the S/C ratio as high steam usage makes the process less efficient. As the reaction temperature and the water-to-glycerol feed ratio (WGFR) increased, methane formation decreased. On the other hand, moles of CO produced also increased with increase in temperature and at lower water-to-glycerol ratio in feed. However, the number of moles of CO$_2$ increased with increasing temperature and passed through maxima, and decreased thereafter at higher temperature. This behavior may be attributed to the reformation of CH$_4$ with CO$_2$.

$$CH_4(g)+CO_2(g) \leftrightarrow 2CO(g)+2H_2(g). \tag{10}$$
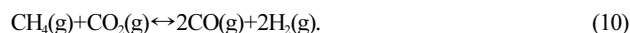
At higher water-to-glycerol feed ratios (WGFRs) and higher temperatures (>670 °C), the formation CH$_4$ is almost inhibited. At higher temperature, due to the contribution of steam methane reforming reaction, moles of water and CH$_4$ decreased, whereas yields of CO, CO$_2$, and H$_2$ increased. Thermodynamic study revealed that at higher temperature, the methanation reaction is significant, which suppresses the hydrogen formation reaction. Due to low reaction severity, thermodynamic equilibrium is not reached in the present study. At low water concentrations, CO is less likely to participate in the water-gas shift reaction; instead, it consumes hydrogen and produces methane. Thus, the product gas has higher mole fraction of hydrogen at
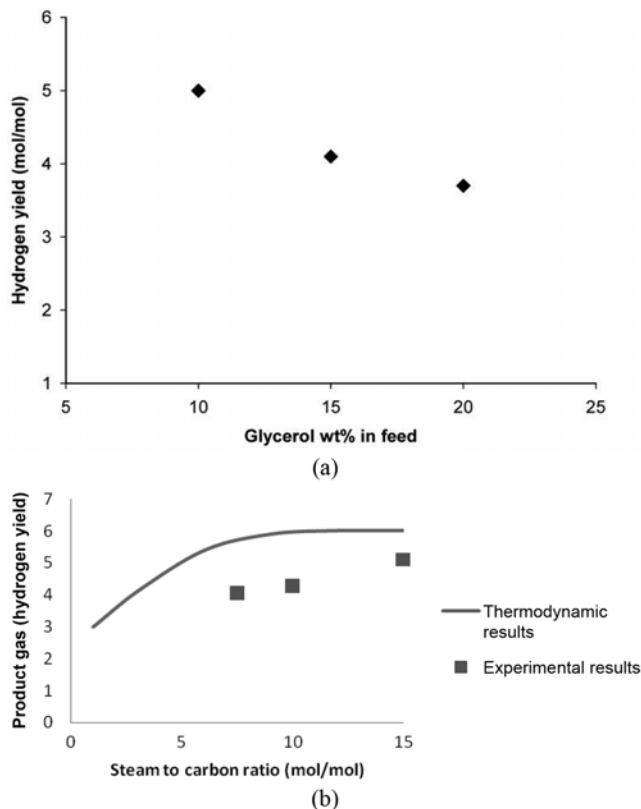

Fig. 5. Effect of glycerol wt% on hydrogen yield and (b) Effect of steam to glycerol ratio on hydrogen yield (P, 1 atm; T, 640 °C; flow rate, 1 ml/min; 0.7 g of Ni/CeO$_2$ catalyst).
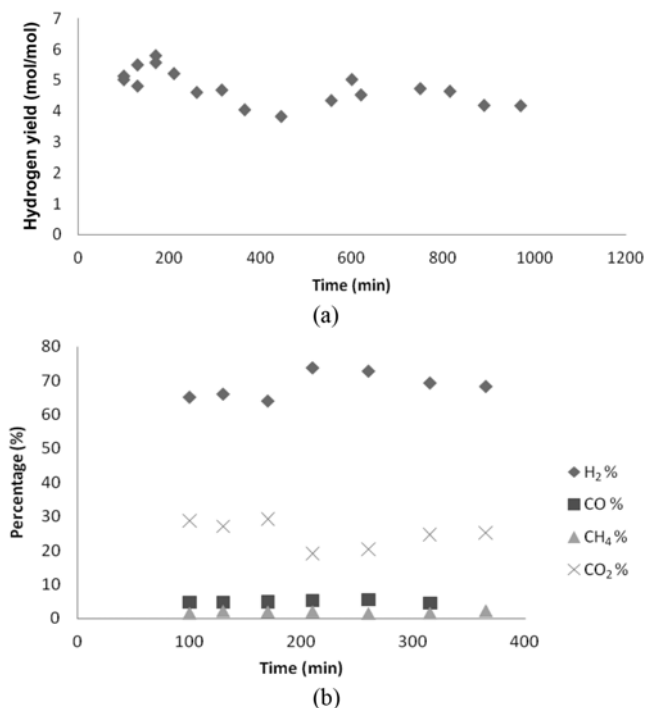

Fig. 6. Effect of run time on (a) hydrogen yield and (b) product distribution.

high WGFRs, mainly due to the enhanced water-gas shift reaction activity. At high WGFR, coke formation was also inhibited in the range of experiments carried out in this study. Although excess water allows higher selectivity to hydrogen, large amount of water in reaction products is not beneficial as it gives extra loading to the reactor and creates purification problems [29,30].

5. Effect of Run Time on Hydrogen Yield and Coke Deposition

To study the effect of run time on hydrogen yield and coke deposition, experiments were done for 20 hours at 700 °C. Effect of run time on hydrogen yield and product composition is shown in Fig. 6(a), (b). Compared to Ni/Al$_2$O$_3$ catalyst, the product composition was negligibly affected during this period over Ni/Ceria catalyst. TGA analysis of the spent catalyst was done to estimate the total amount of coke deposited on the catalyst surface during the experiment. There was approximately 2% coke on the catalyst after 20 h of run over Ni/Ceria catalyst. Significantly high amount of coke (4.8%) was observed over a Ni/Al$_2$O$_3$ catalyst under identical conditions. Although carbon conversion to CO and CO$_2$ decreased slightly with reaction time, the main impact on the decrease of H$_2$ and CO$_2$ yields is linked to the effectiveness of the Ni/CeO$_2$ catalyst to enhance the water-gas shift reaction. This could be attributed to the higher basic characteristics of Ni/ceria catalyst that inhibited the rearrangement of condensation reactions, which lead to intermediate compounds in the coke formation [21,22,29]. Moreover ceria has a dual oxidation state (+4/+3); therefore, it releases oxygen which reacts with the deposited carbon and thus reduces coke formation [2,18,26].

$$2CeO_2 \rightarrow Ce_2O_3 + [O] \quad (11)$$

Fig. 7 shows the SEM micrograph of the 15% Ni/CeO$_2$ catalyst after a run time of 20 hours at 700 °C. This high magnification image confirms that the particle morphology has completely changed. Results indicated that particle morphology changed after the reaction as the ceria particles were not in fibrous forms as were in the SEM micrographs of the fresh catalyst. Compared to Ni/Al$_2$O$_3$ catalyst,
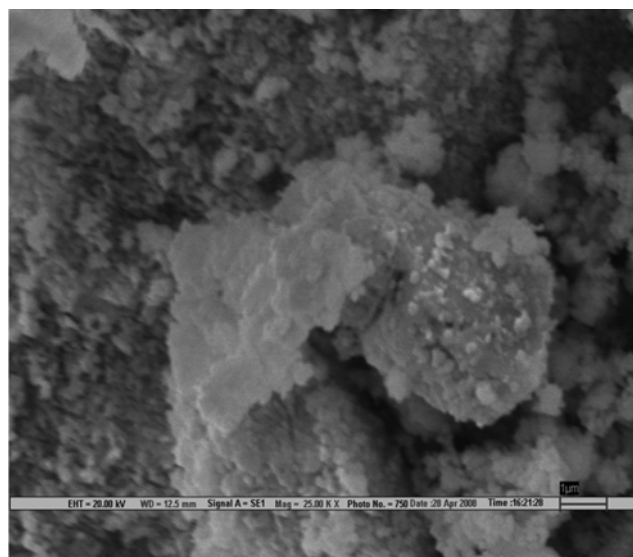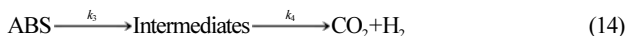

Fig. 7. SEM image of the used catalyst.

Ni/CeO$_2$ catalyst prepared by precipitation-deposition method has improved metallic dispersion, lower sintering, improved thermal stability and high oxygen storage capacity.

6. Kinetics of Glycerol Reforming

During the steam reforming of an oxygenated compound, methane steam reforming with water and water gas shift reactions also take place simultaneously [22,25,30,31]. Besides these reactions undesired reactions such as methanation reaction and Boudard reaction also occur. Thus, the overall reforming of an oxygenated hydrocarbon entails a complex network of reactions. Adsorption and decomposition of oxygenated compounds containing hydroxyl groups such as methanol has been studied extensively on noble metal surfaces. Oxygenated compounds containing hydroxyl groups have been shown to adsorb on the catalytic Ni surface predominantly through one or more oxygen atoms. First, the reactant undergoes dehydrogenation on the catalyst surface, followed by subsequent cleavage of C-C or C-O bonds. Cleavage of C-C bonds leads to synthesis gas, which is subjected to the water-gas shift reaction and possible methanation, while cleavage of C-O bonds gives organic acids and alcohols. Meanwhile, water gas shift reaction and methanation reaction are favored by low temperatures. Nickel catalysts have strong capacity for breaking the C-C bonds of glycerol that form CO and hydrogen. The concentration of methane over the Ni/CeO$_2$ catalysts decreased significantly at higher temperature, suggesting that the steam reforming of methane was enhanced at higher temperatures over ceria-supported catalyst. As a result, most of the produced methane was almost completely converted into hydrogen. Meanwhile, the concentration of CO$_2$ in the product gas gradually increased, whereas the concentrations of CO decreased with temperature, indicating that the conversion of CO to CO$_2$ took place through the water gas shift reaction. Results suggest that the Ni/CeO$_2$ catalyst catalyzed the reactions of methane reforming and water gas shift and was very selective for hydrogen production from steam reforming of glycerol [22-24,32]. Moreover, the yield of hydrogen is strongly dependent on the nature of the active metal as well as its interaction with ceria [22-25]. Results indicate that high temperature and high water-glycerol feed ratio (WGFR) favor the hydrogen production. Thermodynamic study also revealed that the best conditions for producing hydrogen are at a temperature above 600 °C and a molar ratio of water to glycerol of 6 : 1 [22,32]. Under these conditions methane production is minimized and carbon formation is thermodynamically inhibited. In the present investigation the upper limit of the moles of hydrogen produced per mole of glycerol is 5.6 compared to the stoichiometric limit of 7. Our result indicates that as the reaction temperature increases, the contribution of the glycerol-steam reforming is higher than the glycerol decomposition reaction. Similarly, a decrease in methane yield could be explained by the lower contribution of the methanation reaction at higher temperature. It is reported that 550 °C is the minimum temperature required to initiate the reaction for hydrogen selectivity [19,29]. Nickel catalyst has high activity for C-C bond scission; therefore, it can be assumed that most of the liquid intermediates formed get converted to gaseous products. Hence, the following kinetic model is proposed for the reforming of glycerol based on the literature and product distribution observed [26].

$$A + S \xrightleftharpoons[k_{-1}]{k_1} AS \quad (12)$$

$$AS+B \xrightarrow{k_2} ABS \tag{13}$$

$$ABS \xrightarrow{k_3} Intermediates \xrightarrow{k_4} CO_2+H_2 \tag{14}$$

Where, A and B represent glycerol and water, respectively, and S represents an active site on the catalyst surface. Values of $k_{i,s}$ represent the rate constant for the reaction in Eqs. (12) to (14). Eq. (12) describes the reversible adsorption of glycerol on the catalyst, and Eq. (13) represents the reaction of the adsorbed glycerol with water to form an adsorbed complex molecule, ABS. Assuming steady state of adsorbed intermediates and that decomposition of ABS to form intermediate products is the rate-limiting step, the dependence of rate (r) on partial pressures (p) can be expressed as:

$$r = \frac{k_1 k_2 p_A p_B}{k_{-1} + k_1 P_A + k_2 p_B + (k_1 k_2 p_A p_B / k_3)} \tag{15}$$

Considering that water is in excess, Eq. (15) may be simplified to:

$$r = \frac{k_R p_A}{1 + b p_A} \tag{16}$$

Where k_R and b are lumped parameters defined as:

$$k_R = \frac{k_1 k_2 p_{Bo}}{k_{-1} + b p_{Bo}} \tag{17}$$

and

$$b = \frac{k_1 + (k_1 k_2 p_{Bo} / k_3)}{k_{-1} + k_2 p_{Bo}} \tag{18}$$

The above rate Eq. (16) was solved using a nonlinear regression technique for the rate of hydrogen production at different temperatures and partial pressures of glycerol. The overall activation energy E_a for the steam reforming of glycerol thus calculated from these data was 36.5±4.2 kJ/mol.

CONCLUSIONS

Ni/CeO$_2$ catalyst prepared by precipitation deposition method has been found active and selective for hydrogen production with minimum methane and carbon monoxide formation during the steam reforming of glycerol. Glycerol conversion and hydrogen yield increased with increasing temperature and contact time and reached to maxima at 700 °C. Compared to Ni/Al$_2$O$_3$ catalyst, significantly high conversion of glycerol and hydrogen yield was achieved over ceria-supported catalyst in which the yield of hydrogen reached up to 6. High temperature and high steam-to-glycerol feed ratio favor the hydrogen production. No appreciable deactivation of the Ni/CeO$_2$ catalyst was observed up to a run time of 20 hours. Thus Ni/CeO$_2$ catalyst prepared in this investigation showed higher conversion and hydrogen yield, lower coke formation and higher stability compared to Ni/Al$_2$O$_3$ catalyst. The kinetic experiments revealed that the activation energy for the glycerol steam reforming reaction was 36.5±4.2 kJ/mol.

NOMENCLATURE

b   : lumped parameter used in Eq. (16) and (18)
F_{A0} : molar feed rate of glycerol
$H_{25^{\circ}C}^{0}$: standard heat of reaction

$k_{i,s}$: rate constant for the reaction in Eqs. (12) to (14)
k_R : lumped parameter used in Eq. (17)
p_i : partial pressure of species i
r   : rate of reaction
W   : mass of the catalyst

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