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Experimental studies on renewable hydrogen production by steam reforming of glycerol over zirconia promoted on Ni/Al$_2$O$_3$ catalyst

Abstract: The impact of ZrO$_2$ as a catalytic promoter for nickel-based alumina supported catalysts has been studied for the hydrogen synthesis via glycerol steam reforming. Hydrogen is a promising contender of clean fuel and has a key significance in the quest of an environment-preservation, low emission and more sustainable energy approach. Glycerol is a by-product produced during production of biodiesel by trans-esterification of vegetable oils. The higher hydrogen content in glycerol makes it the potential renewable feedstock for hydrogen production. Steam reforming process is the best method available which is highest in energy efficiency and most importantly most economical. The production of catalysts was based on the wet impregnation and co-precipitation methods. The majority of the bulk and surface properties of different synthesized catalysts were considered and determined by several characterization techniques like X-ray diffraction technique, BET surface area and scanning electron microscopy. The performance of catalyst is based on glycerol conversion and hydrogen yield obtained from the steam reforming process taking place in the fixed bed catalytic reactor. The effect of different operating conditions like contact time, temperature, metal loading, and steam to glycerol ratio were investigated to produce maximum hydrogen and glycerol conversion. The results show that the incorporation of promoter 2 % ZrO$_2$ improved the activity of Ni/Al$_2$O$_3$ catalysts significantly resulting 96 % glycerol conversion, 84 % hydrogen production and greater stability at contact time = 15 kg cat s/mol, temperature = 800 °C, steam to glycerol ratio = 9:1 mol/mol, and pressure = 1 atm.

Keywords: steam reforming; zirconium oxide; nickel; hydrogen; glycerol

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1 Introduction

International organizations such as the European Commission and United Nations Industrial Development Organization and International Energy Agency, predict that the world will alter from a fossil fuel-based economy to a decarbonized hydrogen-oriented economy [1]. To make the following transition, there would be a high demand for the production and the distribution channel of hydrogen, along with the development and deployment of fuel cells and hydrogen systems. Hydrogen as a fuel plays a significant role as a fuel because of its highly promising and advanced characteristics like clean, efficient and carbon free fuel [1]. Hence, it is safe to assume that hydrogen will play a critical part in energy demand in the future [2]. Innovation for new and non-conventional methods and devices that can be utilized in the hydrogen synthesis sector needs to be focused upon for reaching sustainable development goals, high-yield, high-purity hydrogen production and reduction in carbon footprint [3].

Glycerol is one of the best renewable sources of energy which can be converted into hydrogen. This contains high energy content and can be utilized for the electricity production through the fuel cells. As a result, researchers and industries have gained interest in finding new uses of glycerol. The steam reforming process is found to be the most favorable for hydrogen production as it produces 7 mol of hydrogen which requires a mole of glycerol and it is highly endothermic in nature and carried out at atmospheric pressure [4, 5].

Overall desired reaction:

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \qquad \Delta H° = +128\,kJ/mol$$
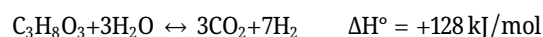
In the steam reforming process for hydrogen production, the catalysts based on nickel over alumina are the best choice as they are easily available for the commercial purpose and widely used in the sector. They possess good carbon resistance and high thermal stability. Nickel is efficient in breaking carbon–carbon, carbon–hydrogen and carbon–oxygen bonds and help in removal of carbon monoxide absorbed on the surface by water gas shift reaction [6]. Zirconia despite having smaller surface areas compared to

Al_2O_3 exhibits higher strength and toughness. To improve the catalyst stability and to reduce the metal particles sintering in the presence of water at very high temperature, the ZrO_2 is added to the alumina [7]. The catalyst performance was analyzed to evaluate various parameters that can affect hydrogen production. The performance of catalyst is completely dependent on the glycerol conversion and hydrogen yield.

2 Experiment

2.1 Preparation of catalyst

In the present study, Ni/Al_2O_3 catalysts doped with ZrO_2 were prepared by the use of methods such as wet impregnation and co-precipitation.

2.1.1 Catalyst preparation by using wet impregnation method: Nickel based catalysts are prepared by using different-different compositions of promoters which are prepared by the use of wet impregnation method which uses a pelletized $\gamma - Al_2O_3$ which is supplied by the (IPCL, India) as basic supportive element and in addition with salts of nitrates which are supplied by (Merck, CDH, Finer and HPLC Grade). The preparation of a hydrated solution of nickel nitrate, zirconyl nitrate, is based on the mixing of a significant amount of chemicals and double distilled water [8]. It is desirable to reduce the size of alumina pellets by crushing below 1 mm before using them for the impregnation process [9]. For the purpose of uniform deposition, the crushed particles were soaked for the time duration of 4 h under continuous stirring in nitrate solutions. Then pellets dried at 110 °C for 12 h in an oven followed by calcination at 500 °C in the presence of air for 4 h in a muffle furnace in order to convert into oxides from nitrates [10]. The reduction is carried out in the presence of hydrogen and nitrogen as an inert gas [11]. The hydrogen to nitrogen gas ratio is maintained is 15/85 % V/V along with the increment in temperature of 10 °C per minute, where the dwelling temperature of the process is maintained at 500 °C for the 2 h of duration [12]. The same method was used for the preparation of different types of catalysts by the method of wet impregnation [13].

2.1.2 Catalyst preparation by using co-precipitation method: The preparation of a hydrated solution of nickel nitrate, zirconyl nitrate is based on the mixing of the significant amount of chemicals and distilled water to which is used to prepare $Ni/ZrO_2/Al_2O_3$ catalysts. The flask containing the solution is maintained at a temperature of 70 °C in a heater. The 1 M Na_2CO_3 solution was added drop by drop in the solution of nitrates to attain the value of pH 10 at room temperature or normal atmospheric conditions [12]. Now the formed precipitates were subjected for 1 h of aging at room temperature along with the stirring. Afterwards the filtration process takes place followed by the washing with distilled water in a repeated manner in order to attain a value of pH 7 at room temperature or normal atmospheric condition [8]. Drying process of washed precipitate was carried out within an oven in which hot air is passed at a temperature of 110 °C for a time duration of 12 h. This fine powder is then sent for calcination with the use of a muffle furnace. The temperature maintained in muffle furnace is 650 °C with increment of 10 °C/min ramp for the total time duration of 4 h [14]. The catalysts of various compositions were prepared by the same procedure [15].

2.1.3 Catalyst characterization: In the current study, catalyst characterization was conducted using various techniques like (BET) area of surface, size of pore and volumetric analysis, X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy (SEM). The Brunauer – Emmett Teller (BET) method is used to measure the specific surface area and pore volume of various types of catalysts. The BET method is based on the nitrogen adsorption at –196 °C. First the samples were degassed at high temperature of 150 °C and in the vacuum condition for the time period of 6 h prior to the nitrogen adsorption-desorption measurements. The X-ray diffraction method is used by X'pert – MPD system to obtain the phase analysis. The X'pert – MPD system is operated at voltage of 40 kV and 30 mA current using CuK_α radiation which has a wave of length of 1.5406 Å. Spectra were recorded with a gap of 0.050 for 2θ in between 20 and 990. The "LEO 44 I (JEOL)" is used to retrieve the morphology and the size of the catalyst. The system is operated at 10 kV. The FTIR 6000 series type A spectrometer is used to measure FTIR spectra. The FTIR 6000 series type A spectrometer collects high resolution spectral data of 4 cm^{-1} with a spectral range of 400–6000 wavenumbers [16]. Ultrahigh pure gases were used for analysis purposes. The main objective of the characterization is to set up an identification as well as classification of synthesized catalysts, developing its physiochemical parameter data along with the study of its structure as well as surface morphology [17].

3 Catalyst performance testing

3.1 Catalytic activity

In an atmospheric fixed bed reactor activity tests of various catalysts were carried out. The illustrative experimental setup diagram has been shown in Figure 1. Using peristaltic pump glycerol and water was pumped to the vaporizer which is maintained at 250 °C [18]. The flow of the simulated gas of for pre-treatment process. The pre-reduction process was regulated with the help of a rotameter. The dimensions of the reactor are: outer diameter (O.D.) 1.905 cm, inner diameter (I.D.) 1.805 cm and length (L) 50 cm. The material of construction of the reactor is stainless steel 316. The reactor is also equipped with flow controllers and a heating system. The reactor had the capacity of 25 cm^3 and it operated at a max pressure of 1 atm and 1000 °C temperature. Condensers and separators were used to collect gases. The temperature of the furnace was measured using 'K' type thermocouple and controlled using a PID controller. The gas chromatography (GC) Shimadzu GC 2010 is used to analyze the gaseous product. The method is equipped with a Shin Carbon 'micro-packed' column, provided by Restek's thermal conductivity detector (TCD). The µTCD is operated at a current of 90 mA.

Helium is used as the carrier gas at a flow rate of 30 ml/min. The liquid product formed might be of various types from acetic acid, lactic acid, acetaldehyde, acrolein and hydroxy acetone [19]. The performance of catalyst is presented in terms of glycerol conversion and hydrogen yield:

$$\text{Glycerol conversion } \% = \frac{\text{moles } (CO + CO_2 + CH_4) \text{ generated}}{\text{glycerol in feed} \times 3}$$

$$\% \text{ Hydrogen yield} = \frac{\text{moles of Hydrogen generated}}{7 \times \text{moles of glycerol fed}} \times 100$$

4 Results and discussion

4.1 Characteristics of catalyst

Catalyst characterization was based on various technical methods like (BET) area of surface, size of pore and volumetric analysis, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy.

4.1.1 BET analysis

The surface area along with the size of pore and volume of various types of catalysts were estimated by Brunauer–Emmett–Teller (BET) technique are given in Table 1.

The surface morphology & surface area of catalysts can vary as a result of a different method of preparation [20]. The catalyst prepared by wet impregnation had a higher surface area and the surface area along with pore volume decreased by an increase in loading of nickel as the pores on alumina support were partially covered. In the light results of activity, it can be settled that the promoter enhanced the conversion and stability even if the catalyst surface area decreased compared to that of the unprompted catalyst. For

**Table 1:** Physical properties table for calcined catalysts.

Catalytic composition % (w/w)	Catalyst designation	BET surface area (m²/gm)	Volume of pore (cm²/gm)	Diameter of pore (nm)
10 % Ni/90 % Al₂O₃	WNA	176	0.35	6.0
10 % Ni/90 % Al₂O₃	PNA	67	0.23	5.21
10 Ni%/2 % ZrO₂/88 % Al₂O₃	WNZrA	186	0.28	5.56

W denotes wet impregnation and P denotes the co-precipitation method. Similarly, N is used for the nickel catalyst and A is for the alumina support.

the catalysts obtained by the wet impregnation method, optimum loading of nickel and zirconia as a promoter resulted in a higher surface area [21].

4.1.2 Scanning electron microscopy (SEM)

The morphology of surface and size of catalysts were retrieved by "LEO 44 i (JEOL)" operated at 10 kV voltage. The SEM analysis has revealed that the preparation of the morphology of the catalyst is based on the wet impregnation and co-precipitation varied. SEM micrographs of 10 % Ni/90 % Al₂O₃ were larger in size and their surface is rough. The catalyst made by wet impregnation is in the range of 7.8–7.9 mm, while those prepared by co-precipitation were in the range of 5.1–5.2 mm. Agglomeration of particles to a major extent was observed with regular shapes from the SEM micrograph. Small white beads appeared by the addition of zirconia on the alumina base [22]. SEM results of freshly prepared and spent catalysts as shown in Figures 2 and 3 indicate that the particle size of the used catalyst increased as a result of deposition of coking and sintering.
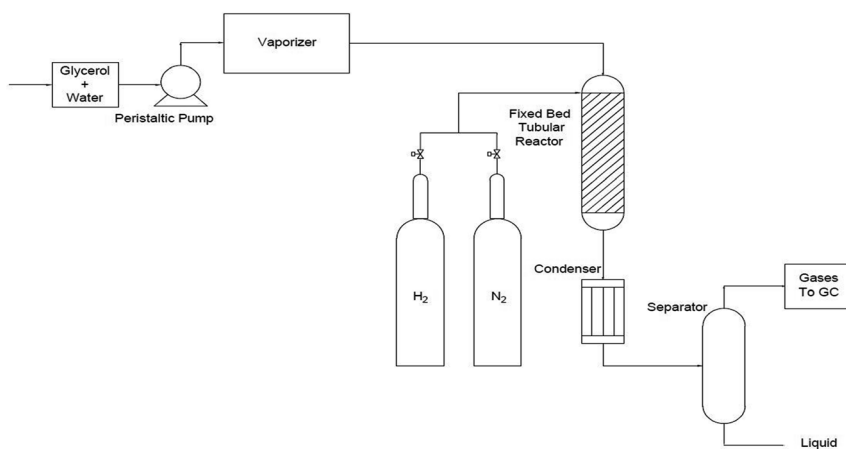

Figure 1: Illustrative diagram of fixed-bed tubular reactor system.
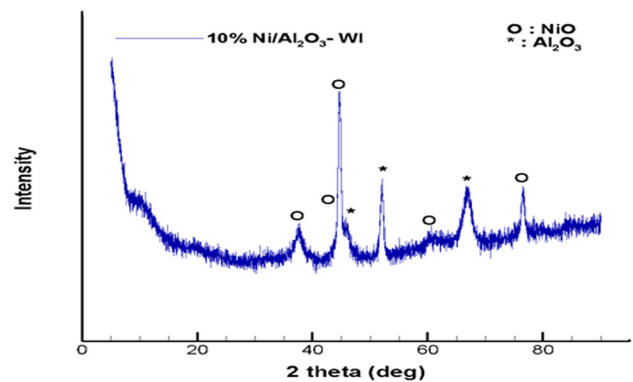
4.1.3 X-ray diffraction

The X-ray Diffraction was carried out by using X'pert – MPD system (Philips) with the help of copper radiation with wavelength, λ = 1.5406 Å to determine the phase analysis of catalysts. From the XRD spectra, the catalyst crystal size was calculated using Scherrer equation XRD analysis of 10 % Ni/90 % Al_2O_3.

In Figure 4 the XRD pattern of 10 % Ni/90 % Al_2O_3 prepared by wet impregnation method shows intense diffraction of NiO (2θ = 37°, 44°, 45°, 60°, 76°), Al_2O_3 (2θ = 46°, 52°, 67°). In this catalyst, five crystalline phases of nickel, three phases of gamma-alumina were found. There was an increase observed in the ratio of NiO intensity to Al_2O_3 intensity as nickel loading was increased. There was an average size of 8 nm recorded for nickel crystallites which is a result of stronger interactions between alumina support and nickel.
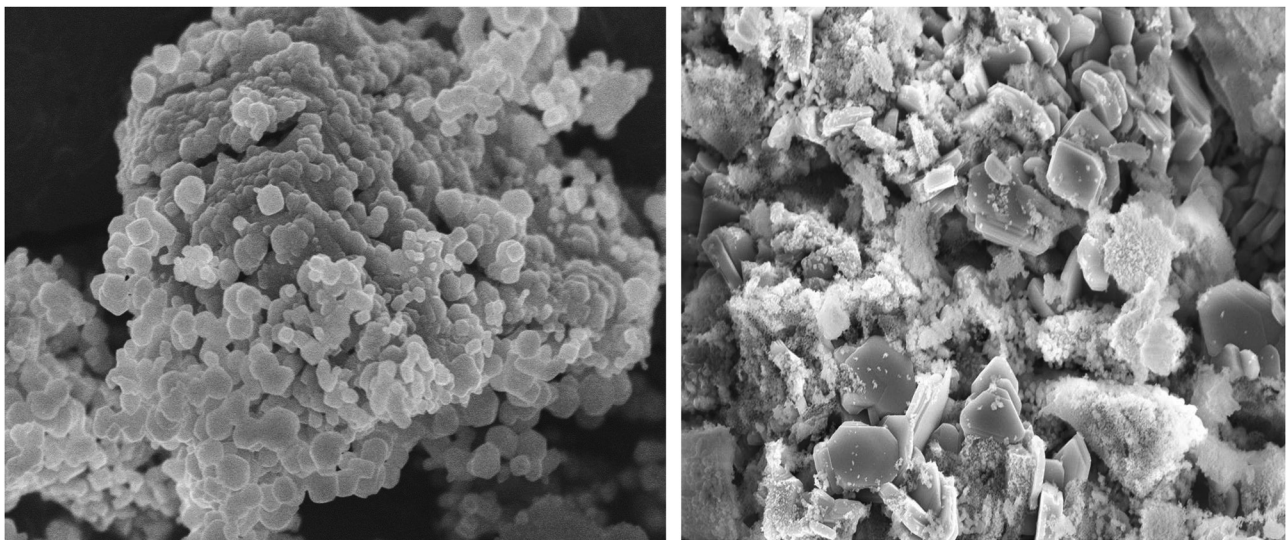
In Figure 5. The XRD pattern of 10 % Ni/2 % ZrO_2/88 % Al_2O_3 prepared by wet impregnation reduced and used catalyst is displayed. Intense diffraction line of Ni (2θ = 28°, 57°), NiO (2θ = 47°, 65°, 76°), Al_2O_3 (2θ = 40°, 50°), a small peak of Ni Al_2O_4 (2θ = 59°) and ZrO_2 (2θ = 35°) is observed in XRD pattern for reduced used catalyst. The relatively small amount of nickel oxide reacts or combines with alumina to form a nickel aluminate composite layer which in turn reduces the deposition of carbon as it indicates the stronger interactions between alumina and nickel which originates from small crystallites of nickel. In the XRD pattern of reduced catalyst, it is seen that most NiO is converted into Ni. Nickel oxide crystals are distinguished in the nickel catalyst due to enhancement in the crystallinity of
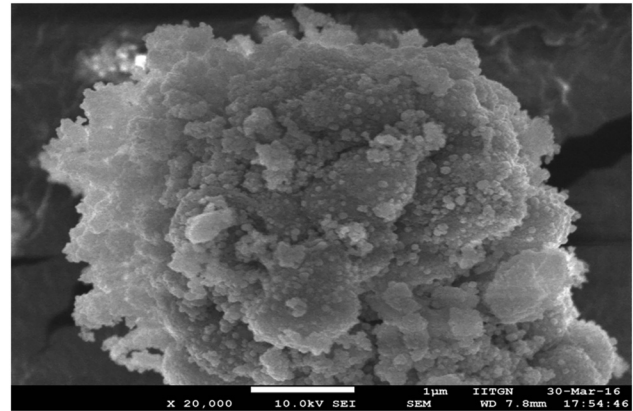
Figure 3: SEM micrograph of 10 % Ni/2 % ZrO_2/88 % Al_2O_3 calcined at 600 °C obtained by wet impregnation method.

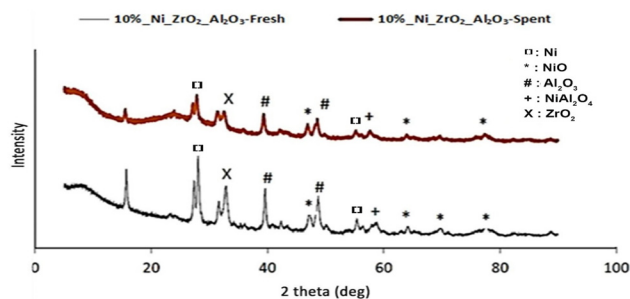**Figure 4:** X-ray diffraction pattern of 10 % Ni/90 % Al_2O_3 prepared by wet impregnation method.

a

b

Figure 2: SEM microgram of 10 % Ni/90 % Al_2O_3 prepared by (a) wet impregnation and (b) co-precipitation methods respectively and calcined at 550 °C.

Figure 5: X-ray diffraction pattern of 10 % Ni/2 % ZrO$_2$/88 % Al$_2$O$_3$ prepared by wet impregnation method of reduced fresh and used catalyst.

the structure caused by the addition of the ZrO$_2$ promoter. The sharp edges of crystals act as anchoring sites for the nickel–metal and it also helps to improve the metal dispersion over the alumina [23].

4.1.4 Fourier transform infrared spectroscopy

The measurement of FTIR spectra were carried out by FT/IR 6000 series type A spectrometer which collected high-resolution spectral data of 4 cm^{-1} over a spectral range of 400–6000 wavenumbers. The composition of the catalyst under FTIR observation i.e., was 10/2/88 and the preparation took place with the help of wet impregnation method. As shown in Figure 6, peak numbers 1, 2 and 3 i.e., at positions 482.117, 563.112 and 829.241 are related to Ni–O stretching vibration mode [24]. The Y – AlO$_4$ vibrations is achieved by the wavelength of 829.241 cm^{-1}. Peak numbers 4 and 5 at 1060.66 and 1153.22 cm^{-1} are aligned with the type of bending vibrations of the group of O–H molecules, bound to the zirconia [25]. Peak numbers 7 and 8 at 1542.77 and

1886.04 cm^{-1} are related to the type of bending vibration for H–O–H.

4.2 Evaluation of catalyst performance

4.2.1 Catalytic activity comparison and stability factor of steam reforming process of glycerol

The various catalysts that were developed by wet impregnation, as well as co-precipitation methods were compared for their use in the process steam reforming of glycerol. The different properties such as contact time W/F as 15 (kg catalyst/molar flow rate), temperature range maintained in between the range of 600 and 800 °C, and the Steam/Glycerol ratio = 9:1 mol/mol [26]. Glycerol degradation occurs at a higher temperature, producing more hydrogen. The overall process of glycerol steam reforming is endothermic due to which increasing the temperature can result in more glycerol conversion and increment in yield of hydrogen [27]. Decomposition of glycerol and water gas shift reaction favors the formation of carbon monoxide at high temperatures. The moles of methane also increase due to the conversion of carbon monoxide to methane by the methanation process [28].

The 10 % Ni/90 % Al$_2$O$_3$ catalyst prepared by wet impregnation method gave only 45 % glycerol conversion which is due to the quick deactivation of the catalyst at temperature above 800 °C. The nature of the catalyst affects the deactivation process. The reason behind that is the carbonaceous deposits take place on the surface of the catalyst. The 10 % Ni/2 % ZrO$_2$/88 % Al$_2$O$_3$ prepared by wet impregnation method gave 96 % glycerol conversion and
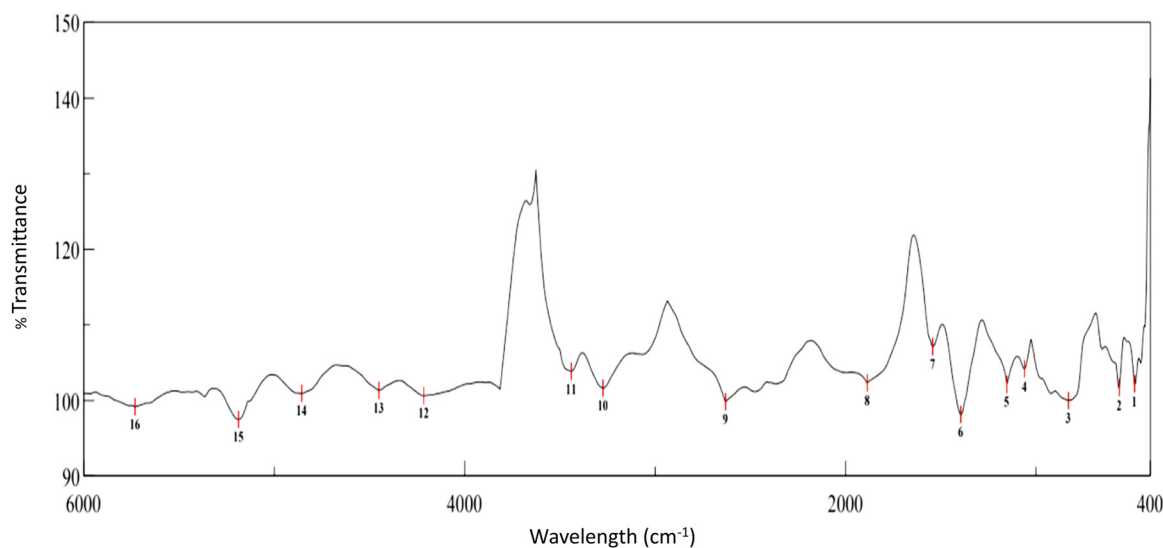
Figure 6: FTIR spectra of 10 % Ni/2 % ZrO$_2$/88 % Al$_2$O$_3$ catalyst.
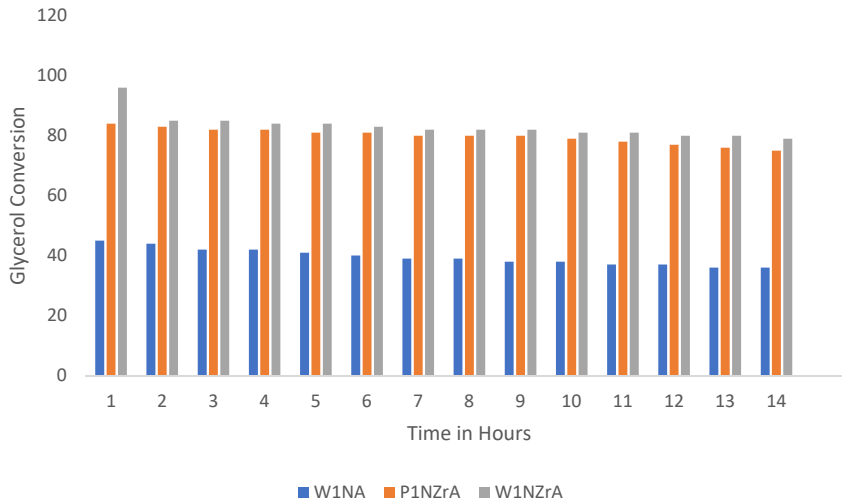
Figure 7: Stream stability test time of catalysts for steam reforming of glycerol.

84 % hydrogen conversion. The use of ZrO_2 as a promoter can help in improving the performance of the glycerol steam reforming process by increasing the hydrogen yield. This also favors the catalyst capacity intermediate products reformation, which is necessary to suppress the secondary reactions taking place due to enhancement of water activation [28]. These improvements are in association only because of the formations of ZrO_2 and Al_2O_3 species. This facilitates the reduction of Ni^{+2} ions formations. ZrO_2 also helps in the sintering of the metallic active sites or particles in the presence of water at very high temperature. The catalysts synthesized by the co-precipitation technique resulted in less enhanced activity due to the increased loading of nickel. The 10 % Ni/2 % ZrO_2 /88 % Al_2O_3 prepared by co-precipitation method gave 84 % glycerol conversion and 68 % hydrogen conversion [29].

4.2.2 Time on steam performance (stability)

The properties desirable of a commercial catalyst for the steam reforming process are improved stability, low cost, high activity and resistance to deactivation as shown in Figure 7, for the catalyst 10 % Ni/2 % ZrO_2/88 % Al_2O_3 prepared by wet impregnation and 10 % Ni/2 % ZrO_2/88 % Al_2O_3 prepared by co-precipitation method. The glycerol conversion is decreased marginally for first 9 h and then it became almost constant for the next 5 h. This is due to formation of stable monodentate carbonate species resulting slight reduction in the glycerol conversion over a period due to deactivation of catalyst. The coke deposition takes place due to dehydration, cracking reactions taking place on acidic sites of alumina at high temperature resulting coke formation.

4.2.3 Effect of contact time

The range of the feed stream contact time is maintained in between 7 and 15 kg cat h/mol. Figure 8 illustrates the impact of contact time on the conversion of glycerol along with the product yield. An increment in the glycerol conversion has been found with an increment in contact time at a variety of temperatures which makes it proportional to the influence of contact time. Since the contact time increases, the passing time of the gases in the bed also increases due to which catalytic activity/performability is increased and this is why the conversion increases. Once the contact time increases, more active sites are available for the reactants to increase the glycerol conversion [30].

4.2.4 Effect of metal loading

As the nickel loading increases from 5 % to 10 % glycerol conversion and hydrogen yield increases and decreases as it increases from 10 % to 15 %. The 5 % nickel loading has low activity due to lesser metal active sites available while the 10 % has high glycerol conversion and hydrogen yield compared to 15 % nickel loading because as the nickel loading increases, reduction in support's surface is found since it blocks the pores of the support [31]. Hence 10 % nickel loading is the optimum one and it also leads to energy saving if it is operated at lower temperatures. The optimum percentage of ZrO_2 used in the present studies is 2 %. From various studies gradual increment in the percentage of ZrO_2 content on Al_2O_3 can reduce the BET area and 2 % ZrO_2 seemed to be optimum to reduce the interaction between support and Ni^{+2} resulting more nickel active sites [32].
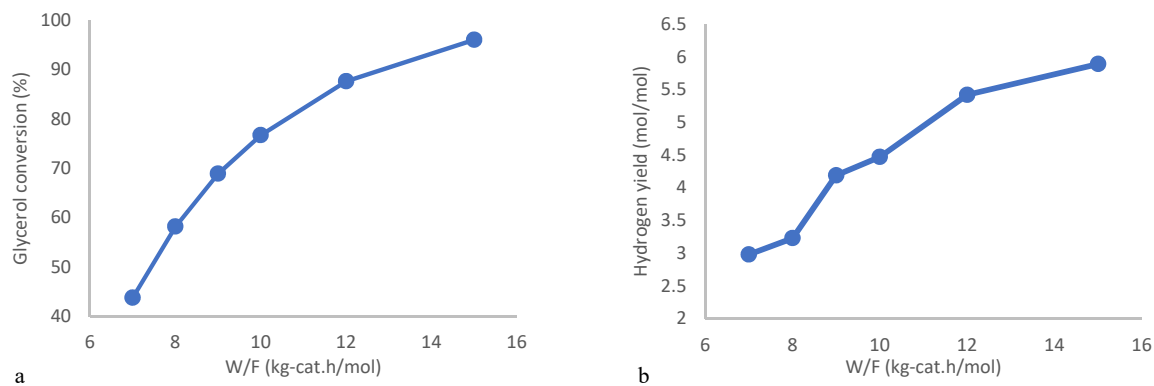
Figure 8: Influence of contact time on (a) glycerol conversion (b) hydrogen yield.

4.2.5 Effect of temperature

The steam reforming process favors higher temperatures because it is endothermic in nature. The conversion of glycerol increases with an increase in temperature and as a result production of hydrogen also increases as it is produced by direct glycerol decomposition along with the help of water–gas shift reaction [32]. 10 % Ni/2 % ZrO_2/88 % Al_2O_3 catalyst which is prepared by the method of wet impregnation with contact time of 15 kg cat h/mol resulted in 96 % conversion of glycerol along with the 84 % hydrogen yield at a temperature of 800 °C (Figure 9). If the temperature increases beyond the limit of 800 °C then direct decomposition of glycerol takes place and it produces the carbon monoxide.
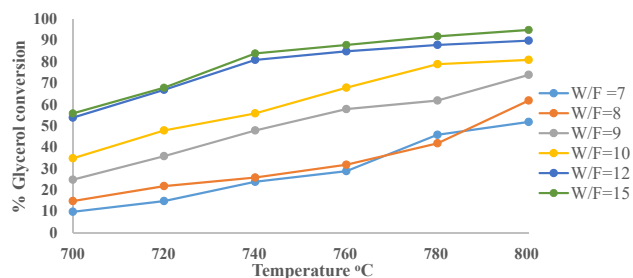
4.2.6 Effect of steam to glycerol ratio

The effect and the influence of the steam to glycerol ratio for the production of hydrogen has been shown in Figure 10. The glycerol conversion increases initially as the steam/glycerol ratio increases and remains constant from the steam to glycerol ratio (S/G) 9:1. Hence the optimum ratio of S/G was 9:1. To reduce glycerol decomposition and catalyst deactivation excess steam can be used. Since the cost of
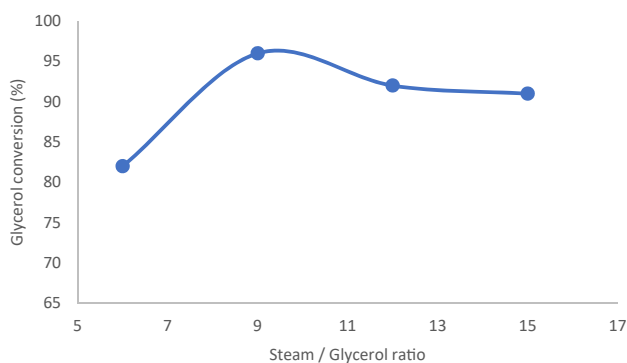
Figure 10: Effect of steam to glycerol ratio for 10 % Ni/2 % Zr/88 % Al_2O_3 (S/G = 9:1 mol/mol, P = 1 atm).

vaporization is high at an industrial scale the amount of water used should not be high [33]. If the steam to glycerol ratio is on a higher level than the excess water consumption takes place which can help in shifting the equilibrium towards right which favors the more hydrogen production according to the Lechleiter's principle. The optimum ratio of S/G is 9:1 and if this is increased to a certain level then it has negligible effect on the carbon monoxide formation but it dilutes the product stream and increases the load on the reactor. The amount of water should be optimum and should not be excess as it will affect the vaporization cost at industrial scale.

5 Conclusions

The impact of promoter addition 2 % ZrO_2 was found to have an improving effect on the performance as well as physicochemical properties of the Ni/Al_2O_3 catalyst systems for the steam reforming process of glycerol. Incorporation of the zirconia by using wet impregnation method was found to have the largest BET surface area amongst

Figure 9: Effect of temperature on glycerol conversion for 10 % Ni/2 % ZrO_2/88 % Al_2O_3 (steam to glycerol ratio = 9:1 mol/mol, P = 1 atm).

exhibiting the presentive effect of higher active sites for catalysis over the Ni/Al_2O_3 catalysts. The method of catalyst preparation also affected the catalytic activity. It has been observed that by increasing reaction temperature the conversion of glycerol and hydrogen increases as steam reforming of glycerol is an endothermic process in nature. The effect of process variables such as contact time, metal loading, temperature, steam to glycerol ratio, and stability test were investigated. The addition of 2 % ZrO_2 helps the catalyst to stay active without getting deactivated, increase the stability of catalyst and inhibit sintering of metallic active sites in the presence of water at high temperature. 10 % Ni/2 % ZrO_2/88 % Al_2O_3 prepared by wet impregnation method exhibited 96 % conversion of glycerol with hydrogen yield 84 % (5.9 mol out of 7 mol theoretically) at contact time = 15 kg cat s mol^{-1}, T = 800 °C, S/G = 9:1 mol/mol, P = 1 atm.

Research ethics: The research ethics and research integrity has been followed by all the authors.

Author contributions: All authors have accepted responsibility for the entire content of this manuscript and approved its submission. Narasimha Reddy Ravuru: conceptualization, methodology, investigation, data collection and analysis, writing original draft and revisions, proof reading and editing of final version. Sanjay Patel: intellectual content, interpretation of data, validation, supervision. Amit Kumar: formal analysis, review and editing.

Competing interests: There are no conflicts of interest.

Research funding: None declared.

Data availability: Data will be made available on request.

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