

Renewable hydrogen generation via steam reforming of glycerol over Magnesium based catalysts

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Abstract:

The depleting fossil fuels with their ever increasing prices have paved way for alternative fuels. Biodiesel is one of those alternative fuels which have picked up keen interest of the people due to its similar properties of diesel. Use of biodiesel and its production are expected to grow steadily in the future. With the increase in production of biodiesel, there would be a glut of glycerin in the world market. Glycerin is a potential feed stock for hydrogen production because one mole of glycerin can produce 7 moles of hydrogen. The most efficient method for obtaining hydrogen from glycerol is the steam reforming. This study focuses on hydrogen production from steam reforming of glycerol over magnesium based catalyst using various supports Al_2O_3 , La_2O_3 , and ZrO_2 in fixed bed catalytic reactor. Catalysts were prepared by the wet-impregnation method and characterized by X-ray diffraction technique, BET surface analysis, scanning electron microscopy analysis. The performance of the catalyst was evaluated in terms of hydrogen yield, selectivity and glycerol conversion in the range of temperature 600-850 °C. Glycerol conversion and hydrogen yield were obtained maximum at 800°C for magnesium supported on Al_2O_3 .

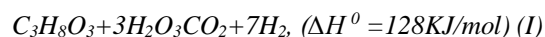
Keywords

Biodiesel, Hydrogen, Steam reforming, Glycerol, Magnesium.

1. Introduction

At present almost 95% of the hydrogen is being produced from fossil fuel based feed stocks and most is used as a chemical ingredient in petrochemical, metallurgical, food, and electronics processing industries. The depleting fossil fuels with their ever increasing prices have paved ways for alternative fuels. Recent years have seen the rapid development of biodiesel as alternative to nonrenewable energy resources, and it is forecasted that biodiesel could make up as much as 20% of all transportation fuel by 2020. Use of biodiesel and its production are expected to grow steadily in future. With the increase in production of biodiesel, there would be a glut of glycerol in the world market [I]. Glycerol is a

potential feed stock for hydrogen production because one mole of glycerol on steam reforming produces 7 moles of hydrogen. Production of hydrogen from glycerol is environmentally friendly because it adds value to glycerol generated from biodiesel plants [II, III]. The various methods used for production of hydrogen from glycerol are steam reforming, liquid phase reforming, partial oxidation, supercritical water reforming, and auto thermal reforming [IV,V]. Steam reforming is the most energy efficient technology available, and it is the most cost-effective. It is strongly endothermic and ideally, it must be carried out at high temperature, low pressure and at high steam to glycerol ratio to achieve higher conversion [VI]. The steam reforming of glycerol proceeds according to the following reaction [VII,VIII].



The effective utilization of glycerol as source of hydrogen depends critically on the invention of new catalysts with high selectivity towards hydrogen, low deactivation and a sufficient reaction rate under mild conditions [IX, X].

In the present study. In this research magnesium catalyst loaded on Al_2O_3 , La_2O_3 and ZrO_2 were prepared for hydrogen production from glycerol. Magnesium is preferred because it has good activity for C-C, O-H, and C-H bond cleavage in the hydrocarbon and it also catalyzes the water gas shift reaction in order to remove adsorbed carbon monoxide from the surface [XI]. The catalysts were characterized by BET surface area, XRD and SEM Techniques.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by incipient wetness impregnation method. Magnesium catalysts were prepared over there different supports (1) γ - Al_2O_3 . (2) La_2O_3 . (3) ZrO_2 Purchased from central drug house private limited, New Delhi. For this purpose aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ (99% Merck) was prepared. γ - Al_2O_3 , La_2O_3 and ZrO_2 were

impregnated with aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$. Magnesium loading was 15 wt% in all the catalysts. Catalysts were dried at $110^\circ C$ for 12 h followed by calcinations at $600^\circ C$ for 6 h in air [XII, XIII]. Catalyst samples were sieved and 35-50 mesh fractions were used for the catalytic activity measurement. During drying and calcinations stages a temperature ramp of $10^\circ C/min$ was employed. Prior to impregnation, $\gamma-Al_2O_3$ was crushed and sieved in order to obtain particles with diameter between $50\ \mu m$ to $125\ \mu m$.

2.2. Catalytic activity test

The activity tests were performed in fixed bed reactor (provided by Chemito Technologies Pvt. Ltd, Pune) in which 1g of catalyst is loaded and supported by ceramic wool. Prior to the activity test, the catalysts were reduced in situ by ramping the temperature of reactor by $10^\circ C$ up to $450^\circ C$ by flow rate 50 ml/min of hydrogen and 280 ml/min nitrogen as carrier gas. Glycerol and water in 1:9 mol ratio were mixed in a container and fed by peristaltic pump at constant flow rate 3 ml/min, followed by vaporizer at $250^\circ C$, which again followed by preheater at $400^\circ C$ causing conversion of liquid into fully vaporized form. Different temperature was set of a reactor for steam reforming ranging from $500^\circ C$ to $850^\circ C$. After completion of reaction product sent to condenser followed by gas liquid separator from which gaseous products were collected and analyzed by Gas chromatography (GC 2010, Shimadzu) using shin carbon ST 100/120 micro packed column with TCD detector. Fig.1 shows the schematic flow diagram of glycerin steam reforming process [XIV].

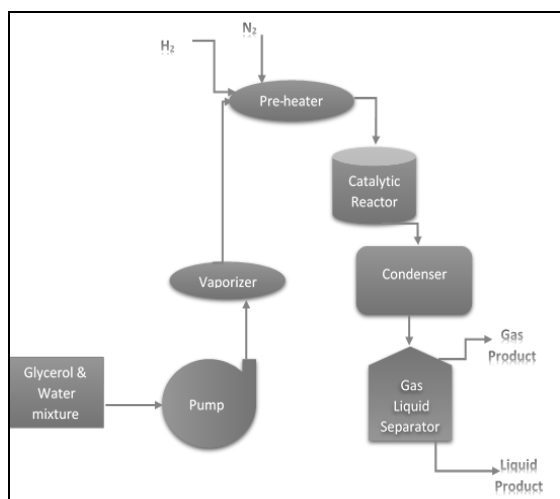


Fig. 1. Schematic diagram of steam reforming process

2.2. Catalyst Characterization

X-ray diffraction powder diffraction (XRD) patterns were obtained by using a Philips X'pert MPD system instrument. For which diffraction angle 2θ from 20° to 80° was kept employing Copper $K\alpha$ radiation filtered by graphite, generator setting current of 30 mA and voltage of 40kV. Continuous mode with very minute step interval applied. Metal crystallites average diameters were estimated from XRD patterns applying Scherer equation [XIV, XV].

The BET specific surface area and the pore average volume and diameter of calcinated catalysts were calculated from N_2 physisorption isotherms using BET volumetric method. The N_2 adsorption-desorption isotherms were obtained at $-176^\circ C$ using ASCP 2011 (Micromeritics) instrument. Before measurements, the samples were degassed at $200^\circ C$ for 5 h. Pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) formula. Pore volume and average diameter were also obtained from the pore size distribution curves [XVI]. Scanning electron microscopic (SEM) images of catalysts were taken using a LEO 45 IC (JEOL) instrument operated at 10 KV to observe the dispersion of the metals on the supports.

2.3. Product analysis

The gaseous product separated at gas liquid separator was analyzed in Gas Chromatograph (Shimadzu GC-10) equipped with thermal conductivity detector (TCD) using shin carbon CT100/120 micro packed column having dimension 3m length and 1.2mm inner diameter. For detection of CO_2 , CO , H_2 , CH_4 gas chromatograph calibrated before doing all the experiments by using pure samples of gases. Activity of catalyst measured in terms of glycerol conversion, hydrogen yield and selectivity using following equations [XVII-XX].

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

$$\% H_2 \text{ yield} = \frac{\text{moles of } H_2 \text{ generated}}{7 \times \text{moles of glycerol fed}} \times 100$$

$$\% H_2 \text{ selectivity} = \frac{\text{moles of } H_2 \text{ generated}}{C \text{ atoms in gas product}} \times \frac{3}{7} \times 100$$

$$\% \text{ selectivity of } i = \frac{i_{out}}{(CO+CO_2+CH_4)_{out}} \times 100$$

3. Results and Discussion

3.1. Effect of temperature on glycerol conversion:

As the temperature increases glycerol conversion also increases and highest seen in 15% Magnesium loaded on aluminum oxide at 850 °C. As the metal loading increases from 10% to 15% more number of active sites were available for the reactions that resulted in higher conversion.

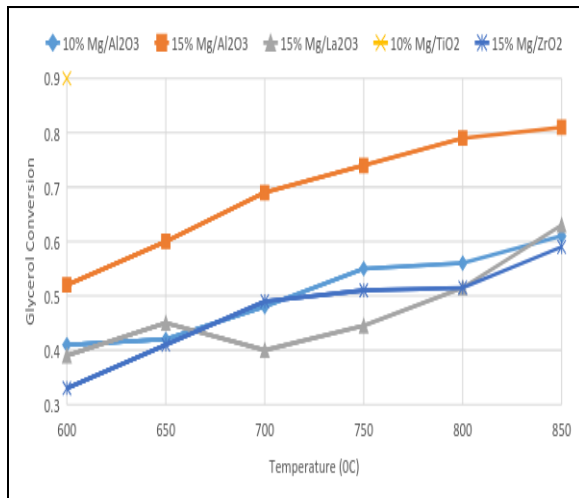


Fig. 2. Effect of temperature on glycerol conversion

3.2. Effect of temperature on hydrogen yield: As the temperature increases hydrogen yield also increases and highest seen in 10% magnesium loaded on alumina and maximum yield is obtained at 750 °C. Beyond this temperature the rate of glycerol decomposition increases and the selectivity of CO and CH₄ increase.

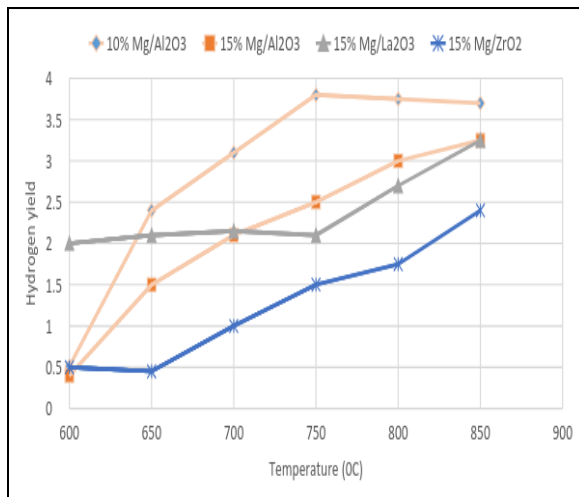


Fig. 2. Effect of temperature on hydrogen yield

3.3. Characterization of catalysts

For all the runs of experiments it was seen that glycerol conversion and hydrogen yield is highest in Mg/Al₂O₃. For 15% Mg/Al₂O₃ X-ray diffraction (XRD) along with BET and SEM investigation was done. From XRD it was concluded that pure phases of magnesium and aluminum oxide formed in catalyst and from TGA we can say that after heating catalyst at 900°C it can be reused. Figure 4, 5 shows the XRD and TGA analysis respectively.

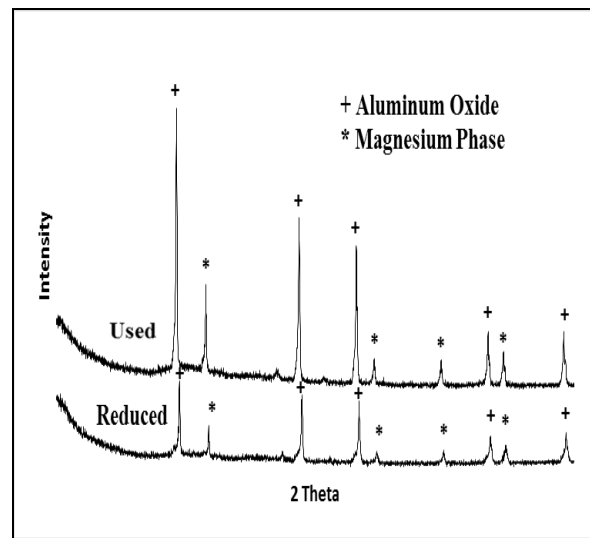


Fig.4. X – ray graph

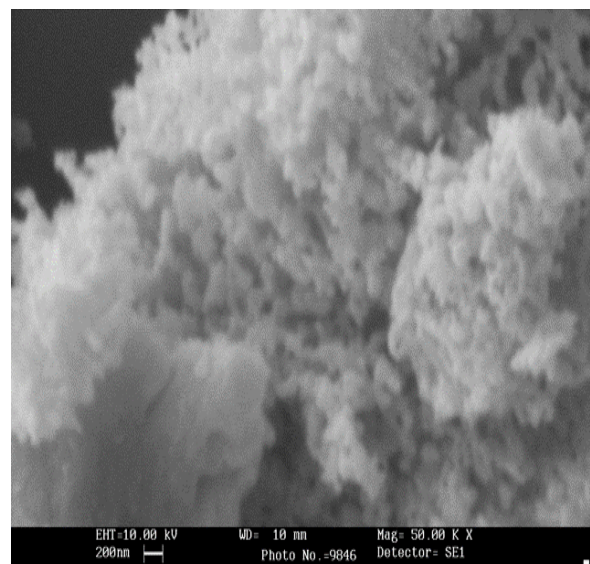


Fig. 5. SEM image for used 15%Mg loaded on aluminium oxide catalyst

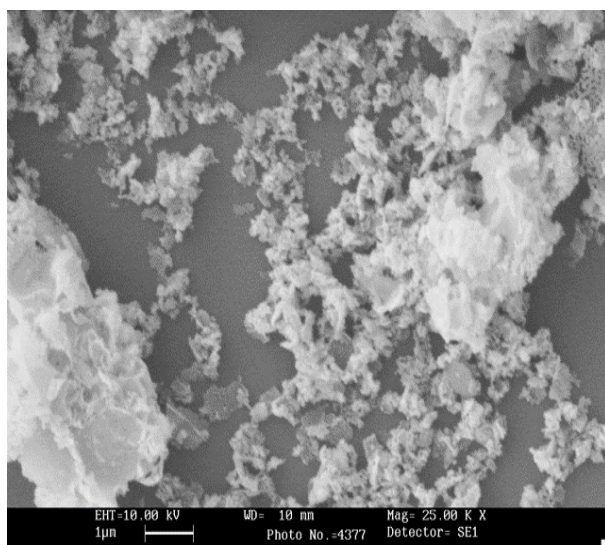


Fig.6. SEM image for calcined 15% Mg loaded on aluminium catalyst

Table.1. BET Analysis

Catalyst	Calcination temperature and duration	Crystallite size dXRD (nm)	BET(m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)
15% Mg/Al ₂ O ₃	600 °C, 6 h	42.0	87.8	9.7	0.021
15% Mg/La ₂ O ₃	700 °C, 6 h	42.1	55.0	6.7	0.009
15% Mg/ZrO ₂	650 °C, 6 h	31.3	39.1	8.3	0.008

The morphology of the catalyst samples was investigated by scanning electron microscopy (SEM). SEM result shows that wet impregnation method was capable of producing more uniform particle having the size close to 150 nm in case of catalyst 15%Mg loaded on aluminium oxide. The SEM micrograph of 15%Mg loaded on aluminium oxide used catalyst sample is presented in Fig. 5,6 shows that the particles had a porous and uniform structure. Table I show BET analysis data.

4. Conclusions

Glycerol steam reforming for hydrogen production using magnesium catalyst over Al₂O₃, La₂O₃ and ZrO₂ was studied under similar conditions. Comparison of Mg/ Al₂O₃, Mg/La₂O₃, Mg/ZrO₂ under similar conditions reveals that Mg/Al₂O₃ catalyst results in maximum glycerol conversion and higher hydrogen yield was observed .4 moles of hydrogen was obtained at 850°C with 3ml/min of feed with glycerol water ratio 1:9. High temperature, higher space time, and lower glycerol feed concentration favour the increase of hydrogen yield and glycerol conversion. Alumina support is proved to be best support for magnesium in steam reforming of glycerol because it possesses all the necessary features: high surface area, high stability in the reaction conditions, strong interactions with the metal phase. Mg/ Al₂O₃ catalyst seems to be very promising and its performance can be improved even further by properly tuning the operational conditions.

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