Selective Production of Hydrogen via Steam Reforming of Glycerol by Magnesium-based Catalysts

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Abstract--**Production of 100 kg biodiesel generates 10 kg of glycerol as waste which is hazardous to environment. Considering environmental impact it's necessary to convert it into useful product. The steam reforming of glycerol   was carried out to produce the hydrogen using magnesium with different supports. Various catalyst were prepared by wet impregnation method and performance was evaluated in a packed bed reactor over a wide range of operating conditions, and reaction parameters were optimized in order to maximize the hydrogen production with minimum carbon monoxide formation This study focuses on hydrogen production from glycerol via steam reforming in fixed bed catalytic reactor using magnesium catalyst over Al_2O_3, TiO_2, La_2O_3 and ZrO_2 supports for which feed ratio of glycerol to water was fixed which is 1:9 and flowrate 3ml/min leading to temperature range of 600°C to 850°C. 10%Mg loaded on Al_2O_3 shows highest hydrogen yield and glycerol conversion. The various effects ofreaction temperature, H_2O/glycerol molar ratio, and the feed flow rate on the steam reforming of glycerol over were also examined. Various catalyst prepared by the wet-impregnation methodand characterized by X-ray diffraction technique, scanning electronmicroscopy (SEM) analysisand BET surface area analysis**

Keywords: Biodiesel, Steam reforming, Glycerol, Hydrogen, Magnesium Catalyst,

I.   INTRODUCTION

In 21st century to overcome from addiction of fossil fuels is major issue. Biodiesel can be solution because it possess environmental favorable characteristic, which produced by transesterification of vegetable oil in which 10wt% of glycerol produced as major by-product. Due to hike demand of a biodiesel, glycerol stock increases which leads to environmental issues. Reducing glycerol into useful chemical compounds is favorable [1]. Many researchers pays their attention to solve this problem. Conversion of glycerol into hydrogen is most interesting way of reduction of glut stock [2-3]. Various water reforming processes [4] used for conversion of glycerol to hydrogen. Amongst all steam reforming process is more benign over supercritical and liquid water reforming processes [5] which provides 7 hydrogen moles using single glycerol mole, however in practice 5.7 to 6 moles of hydrogen can be produced.Steam reforming of glycerol is largely endothermic and favors atmospheric pressure. The major reaction pictured as follows [6]:
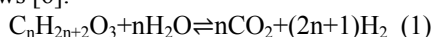
$$C_nH_{2n+2}O_3 + nH_2O \rightleftharpoons nCO_2 + (2n+1)H_2 \quad (1)$$

TABLE I.   METHOD USED IN PRODUCTION OF HYDROGEN FROM GLYCEROL

Sr. No.	Descriptions of Method Used in Hydrogen Production from Glycerol	
	Method	**Energy Requirements**
1	Liquid phase reforming	High pressure, T< 400°C [7]
2	Steam Reforming	Atmospheric pressure,T> 450°C [8-9]
3	Partial oxidation gasification	Highly endothermic,T> 900°C [10]
4	Supercritical water reforming	P>Atmospheric pressure,T>384°C [11]
5	Auto thermal reforming	540°C < T <1000°C [12]

Several study have been done using nickel catalyst in alcohol steam reforming with magnesium, cerium, and lanthanum as promoter [13]. By analyzing the action of impetus metals loaded on oxides (CeO_2, Y_2O_3, SiO_2, MgO), the lineup of catalyst Ru> Ni > Co >Pd was best supported on La_2O_3. Amongst all 3wt.%Rh/Y_2O_3 was found more efficient in conversion of glycerol and hydrogen conversion [14]. Co impetus loaded on economic supports such as La_2O_3, YSZ and

ZrO_2 were figured out for supercritical steam reforming. In which 10wt% cobalt loaded on YSZ showed highest glycerol conversion [15]. Considering above study selection of catalyst and support shows important change in glycerol conversion and yield of hydrogen.

In this research synergistic study of magnesium catalyst loaded on Al_2O_3, TiO_2, La_2O_3 and ZrO_2 have been prepared and analyzed for production of hydrogen from glycerol via steam reforming.

II.   EXPERIMENTAL

A. Preparation of Catalyst

Different batches of magnesium catalyst loaded on Al_2O_3, TiO_2, La_2O_3 and ZrO_2 was prepared. Magnesium nitrate hexahydrate $[Mg(NO_3)_2.6H_2O]$ provided by CDH was used as metal precursor for magnesium. Formulation of catalysts were done by wet impregnation method. After loading of catalyst on support overnight drying provided on 110°C followed by calcination at 570°C. Catalysts were sieved in 35-50 mesh screen used in experiments.

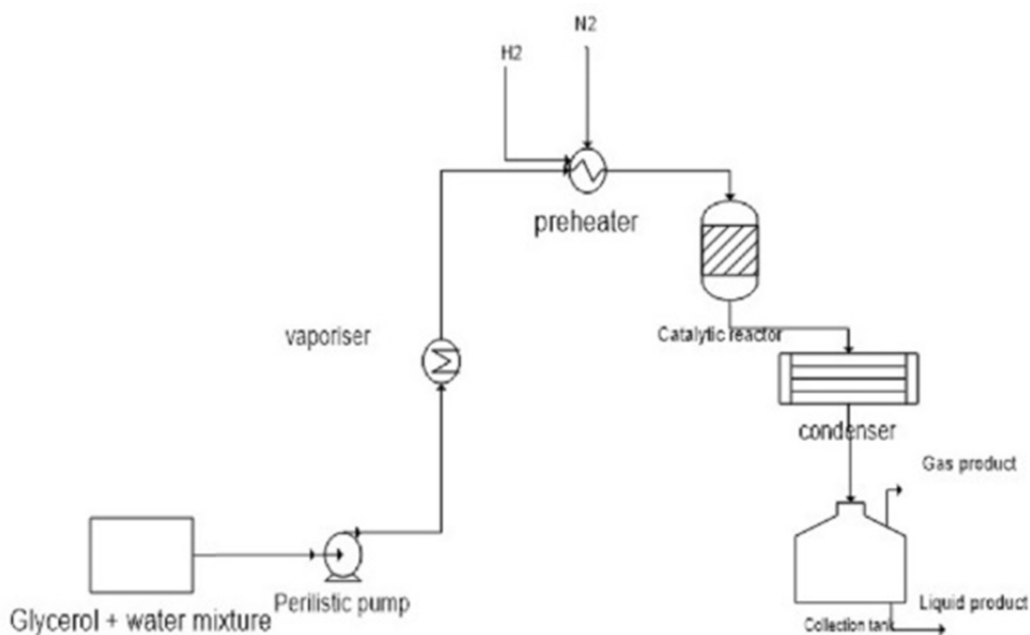### B. Catalyst Characterization

Fig. 1. Schematic of glycerol steam reforming setup [16]

The powder X-ray diffraction (XRD) by using a Philips X'pert MPD system instrument was carried out. For which diffraction angle 2Θ from 20° to 80° was kept employing Copper Kα radiation filtered by graphite, generator setting current of 30 mA and voltage of 40kV. Continuous mode with very minute step interval applied. Thermo Gravimetry Analysis (TGA) for estimation of coke deposition done by using Mettler Toledo (Model No: TGA-180) instrument. 20 mg of catalyst were weighed in alumina crucible with 10°C/min of heating rate and 20 ml/min of nitrogen as carrier gas up to the 900°C. The specific surface area of the impetus was figured out using nitrogen adsorption-desorption isotherms measured at -176°C in ASCP 2011 (Micromeritics) instrument. Samples were first evacuated for 5 h at 200 °C to remove moisture prior to adsorption-desorption experiments. The 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 using the software. The morphology of catalyst samples was obtained with magnification of 10000, 25000, 50000 by a scanning electron microscope (SEM) using a LEO 45 ic (JEOL) instrument operated at 10 kV.

C. Experimental preocedure

The weighted amount of catalyst loaded in center of reactor supported by ceramic wool reduced by ramping the temperature of reactor by 10°C up to 450°C by flowrate 50 ml/min of hydrogen and 280 ml/min nitrogen as carrier gas. Glycerol and water in 1:9 mol ratio respectively fed by peristaltic pump at constant flowrate 3 ml/min, followed by vaporizer at 250°C, which again followed by pre-heater at 400°C causing conversion of liquid into fully vaporized form. Different temperature was set of a reactor for steam reforming ranging from 450°C to

850°C. After completion of reaction product sent to condenser followed by gas liquid separator from which product sent to analysis. The actual experimental flow path shown in fig.1

D. Product analysis

The gaseous product separated at gas liquid separator was analyzed in Gas Chromatograph (Shimazdu GC-10) equipped with thermal conductivity detector (TCD) using Chincarbon 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 said gases. Activity of catalyst measured in terms of glycerol conversion, hydrogen yield and selectivity using following equations [17-20]:

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

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

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

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

III.   RESULTS

A. Effect of temperature on glycerol conversion:

As the temperature increases glycerol conversion also increases and highest seen in 10% Magnesium loaded on aluminum oxide. Also the activity of catalyst for glycerol conversion in order of 10%Mg/Al$_2$O$_3$>> 15%Mg/Al$_2$O$_3$> 15%Mg/La$_2$O$_3$> 10%Mg/TiO$_2$> 15%Mg/ZrO$_2$ was seen from all experiments according to temperature effect.
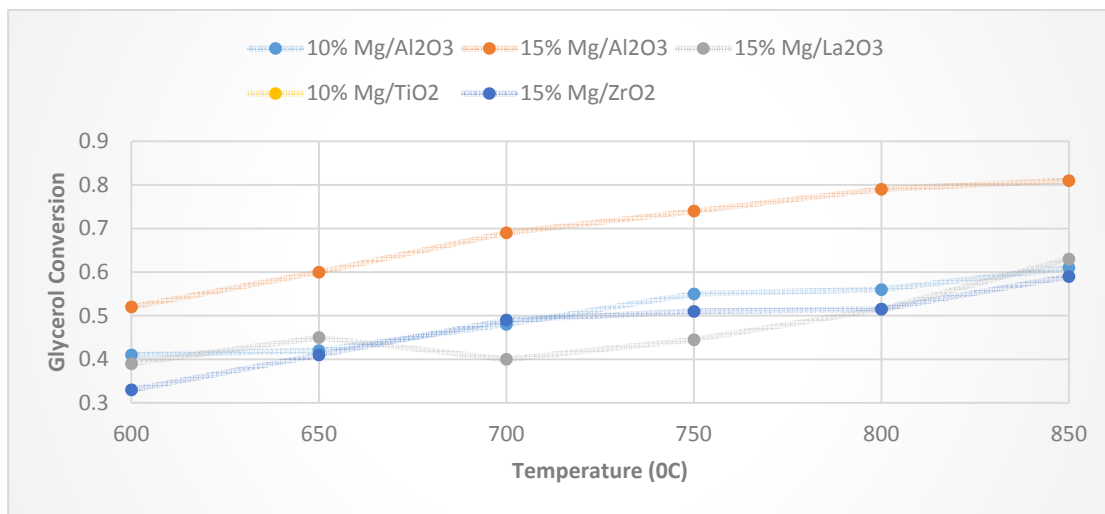

Fig. 2.Effect of temperature on glycerol conversion

B. Effect of temperature on hydrogen yield:

As the temperature increases hydrogen yield also increases and highest seen in 10% Magnesium loaded on aluminum oxide. Also the activity of catalyst for hydrogen yield in order of 10%Mg/Al$_2$O$_3$>> 15%Mg/Al$_2$O$_3$> 15%Mg/La$_2$O$_3$> 10%Mg/TiO$_2$> 15%Mg/ZrO$_2$ was seen from all experiments according to temperature effect.
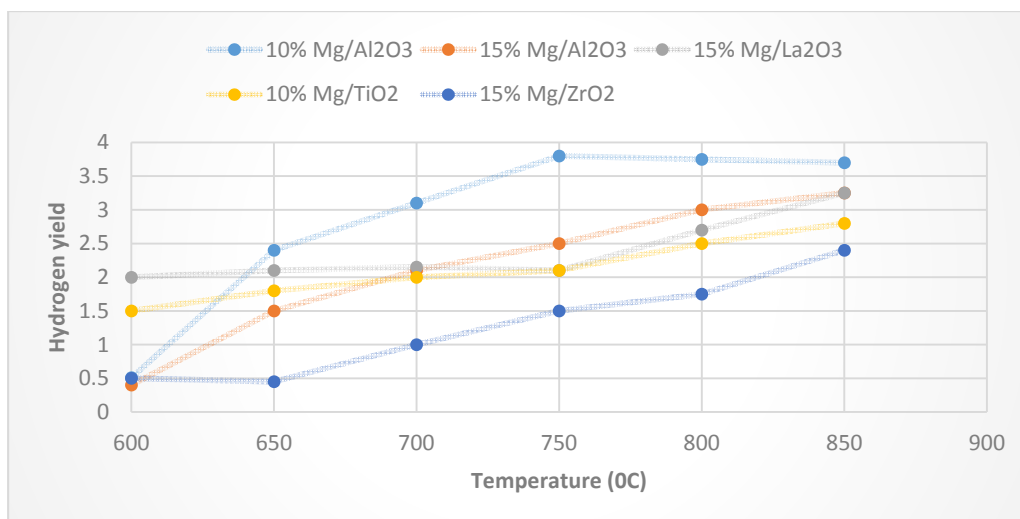
Fig. 3. Effect of temperature on hydrogen yield

C. Characterization result:

For all the runs of experiments it was seen that glycerol conversion and hydrogen yield is highest in 10%Mg/Al_2O_3. So for same catalyst X-ray diffraction(XRD) by JCPDS card no. 98-062-1716 and thermogravitometric 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.
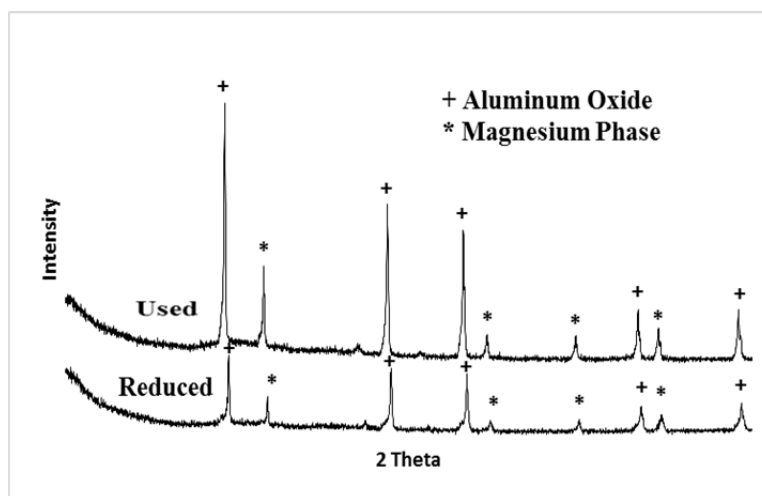

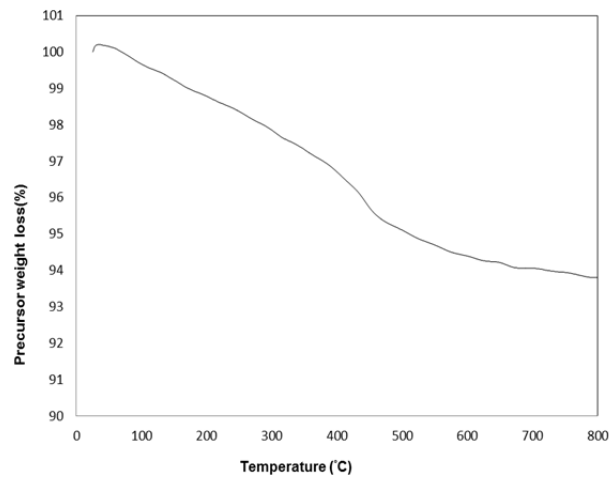Fig. 4. XRD graph for 10%Mg loaded on aluminum oxide

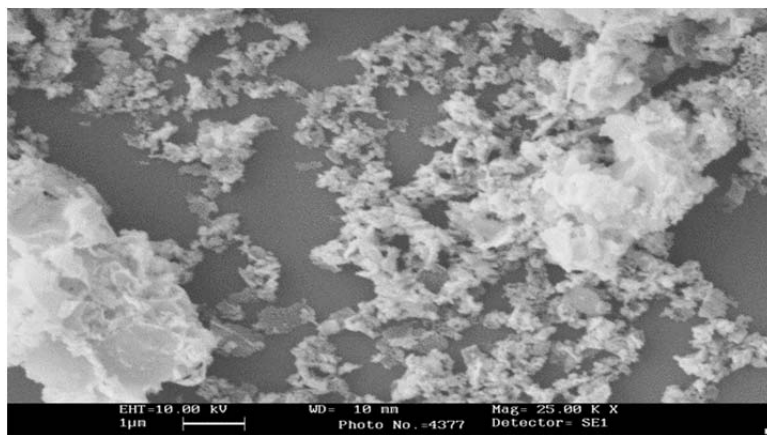Fig. 5. TGA graph for 10%Mg loaded on aluminum oxide1

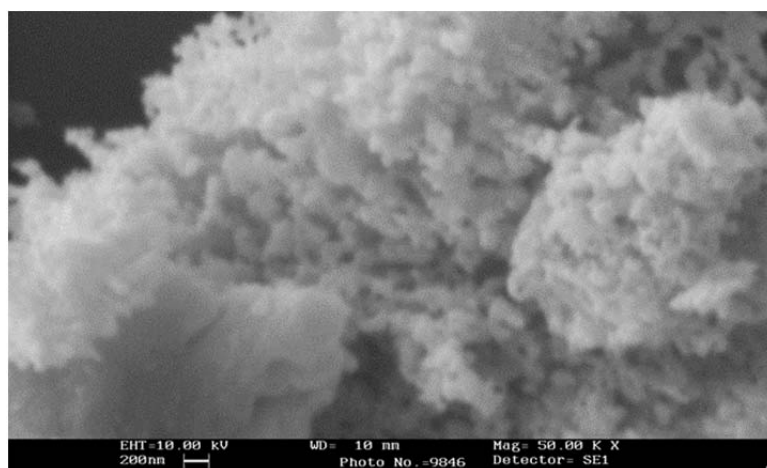Fig. 6. SEM image for calcined 10%Mg loaded on aluminum oxide catalyst

Fig. 7. SEM image for used 10%Mg loaded on aluminum oxide catalyst

TABLE II.   BET ANALYSIS

Catalyst	Calcination temperature and duration	Crystallite size dXRD (nm)	BET(m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
10% Mg/Al$_2$O$_3$	600°C, 5h	33.68	13.44	10.53	0.0354
15% Mg/ Al$_2$O$_3$	600°C, 5h	42.09	8.78	9.77	0.0215
15% Mg/La$_2$O$_3$	900°C, 5h	42.13	5.5	6.75	0.0092
10% Mg/TiO$_2$	750°C, 5h	42.09	3.04	11.29	0.0086
15% Mg/ZrO$_2$	550°C, 5h	31.24	3.91	8.32	0.0081

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 10%Mg loaded on aluminum oxide. The SEM micrograph of 10%Mg loaded on aluminum oxide used catalyst sample is presneted in Fig. 5,6 shows that the particles had a porous and uniform struture. Table II show BET anlaysis data.

IV Conclusion:

Steam reforming of glycerol yielding in hydrogen is one of the most attractive way of hydrogen production. Hydrogen produced from steam reforming yields 4 to 5 moles comparing to 7 moles as stoichiometric conversion. Also from all the support used aluminum oxide with magnesium was best combination which provide 4 moles of hydrogen at 850°C with 3ml/min of feed in proportion of 1:9 of glycerol to hydrogen. Glycerol can be converted in clean energy hydrogen by steam reforming effectively.

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