

Technical Note

Hydrogen production from glycerin by steam reforming over nickel catalysts

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Abstract

Increasing biodiesel production has resulted in a glut of glycerin that has led to a precipitous drop in market prices. In this study, the use of glycerin as a biorenewable substrate for hydrogen production, using a steam reforming process, has been evaluated. Production of hydrogen from glycerin is environmentally friendly because it adds value to this byproduct generated from biodiesel plants. The study focuses on nickel-based catalysts with MgO, CeO₂, and TiO₂ supports. Catalysts were characterized with thermogravimetric analysis and X-ray diffraction techniques. Maximum hydrogen yield was obtained at 650 °C with MgO supported catalysts, which corresponds to 4 mol of H₂ out of 7 mol of stoichiometric maximum.

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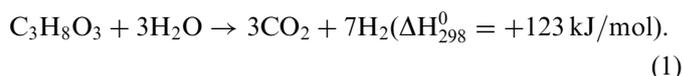
Keywords: Glycerin; Hydrogen; Nickel; Steam reforming

1. Introduction

With its environmental benefits and national energy security, use of biodiesel and its production has gained worldwide momentum [1]. For example, biodiesel production in the United States alone has increased dramatically from 500,000 gallons in 1999 to 75 million in 2005 [2]. In converting vegetable oils into biodiesel, approximately 10% (w/w) of glycerin is produced as a byproduct. With the increased production of biodiesel, an overabundance of glycerin is expected to flood the world market. It is beneficial to find alternative applications for this excess glycerin. Presently, glycerin is used to produce a variety of products, such as 1,3 propanediol, succinic acid, polyesters, lactic acid, and polyglycerols. A detailed review on glycerin utilization can be found elsewhere [3]. One possible option for using glycerin is in hydrogen (H₂) production. Demand for H₂, the simplest and most abundant element, is growing due to the technical advancements in fuel cell industry [4]. Therefore, it is necessary to find a renewable source of raw materials for H₂ production. Currently, almost 95% of the

H₂ is being produced from fossil fuel-based feedstocks [5], which are non-renewable.

A few studies have been carried out on hydrogen production from glycerin [6–11]. Recently, we studied a steam reforming process for hydrogen production derived from glycerin over Al₂O₃ supported noble metal catalysts [12,13]. Overall, the reaction of glycerin steam reforming can be given as follows:



A comparison of MgO, CeO₂, and TiO₂ supported Ni catalysts for glycerin steam reforming has been presented in this study. The impetus behind selecting the aforementioned supports is because MgO [14] and CeO₂ [15] have been reported to retard coke formation, while TiO₂ interacts with metal and promotes catalysis activity [16].

2. Experiment

2.1. Catalyst preparation

Ni catalysts were prepared over three different supports (i) MgO, (ii) CeO₂, and (iii) TiO₂, purchased from

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nanoscale materials (Manhattan, KS). Catalysts were prepared by the wet impregnation method using nickel nitrate hexahydrate $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, purchased from Sigma-Aldrich (St. Louis, MO). Ni loading was 15 wt% in all the catalysts. Catalysts were dried at 110°C for 12 h and calcined at 500°C for 6 h in air. Catalyst samples were sieved and 16–35 mesh fraction was used for the catalytic activity measurement.

2.2. Catalyst characterization

Catalysts were characterized by various techniques. X-ray diffraction (XRD) analysis was done at AMIA Labs (Leesburg, VA). Thermogravimetric analysis (TGA) experiments were performed on a TG/DTA 6300 Perkin-Elmer Instrument (Wellesley, MA). The system is capable of measuring the change in mass of a sample and heat flow as a function of temperature up to 1200°C . The change in mass is related to the changes taking place in the catalyst during calcination. Therefore, the calcination temperatures for different catalysts were based on the TGA analysis. For each sample prepared, nitrogen was flowed through the TGA at 20 ml/min and the temperature was ramped at $10^\circ\text{C}/\text{min}$.

2.3. Catalyst performance testing

All experiments were carried out in a tube furnace that could reach temperatures up to 1100°C . Glycerin and water, mixed at a 1:6 glycerin to water molar ratio, was introduced into the reactor using a HPLC pump (LC-20AT, Shimadzu Scientific Instrument, Columbia, MD). Experiments were carried out at a constant flow rate of 1.0 ml/min and at three different temperatures: 550, 600, and 650°C . Catalyst powder was placed in the core of the reactor supported by quartz wool, and 1.5 g of catalyst was used in all the experiments. Prior to the experiment, all the catalysts were reduced by sending H_2 gas (50 ml/min) for 1 h at 700°C .

The reactor was made of stainless steel tubing with a 1/2 in outer diameter and 0.083 in wall thickness; it was purchased from Swagelok[®] (Pelham, AL). Gas stream from the reactor was cooled using crushed ice and water. Unreacted water, glycerin, and other liquids formed during the reaction were collected and analyzed for determining glycerin conversion. HPLC (Agilent Technologies Incorporated, Palo Alto, CA) was used to analyze glycerin conversion with a Zorbax carbohydrate column ($4.6 \times 150 \text{ mm } 5 \mu\text{m}$) using acetonitrile and water as mobile phases. Outlet gases were sent through a moisture trap before purging into the GC (GC6890-Agilent Technologies Incorporated, Palo Alto, CA). H_2 content in the outlet was analyzed by a thermal conductivity detector (TCD) with an HP Molecular Sieve column. Concentrations of carbon monoxide (CO), methane (CH_4), carbon dioxide (CO_2), ethane (C_2H_6) and ethylene (C_2H_4) were analyzed using a flame ionization detector (FID) with an HP-Plot Q

column. Altogether six gases, including H_2 , were analyzed in this study.

The performance of the catalyst is presented in terms of H_2 , CO_2 , CO, and CH_4 selectivity, glycerin conversion into gaseous products, and glycerin conversion. Performance parameters were calculated based on the following equations:

$$\% \text{H}_2 \text{ selectivity} = \frac{\text{H}_2 \text{ moles produced}}{\text{C atoms produced in gas phase}} \times \frac{1}{\text{RR}} \times 100, \quad (2)$$

where RR is H_2/CO_2 reforming ratio and it is 7/3 in the case of glycerin steam reforming process Eq. (1).

$$\text{H}_2 \text{ yield} = \frac{\text{H}_2 \text{ moles produced}}{\text{Maximum moles of hydrogen (= 7)}} \times 100, \quad (3)$$

$$\% \text{ Selectivity of } i = \frac{\text{C atoms in species } i}{\text{C atoms produced in gas phase}} \times 100, \quad (4)$$

where species $i = \text{CO}, \text{CO}_2$, and CH_4 .

$$\% \text{ Glycerin conversion into gaseous products} = \frac{\text{C atoms in gas products}}{\text{Total C atoms in the feedstock}} \times 100, \quad (5)$$

$$\text{Glycerin conversion} = \frac{\text{Glycerin in} - \text{Glycerin out}}{\text{Glycerin in}} \times 100. \quad (6)$$

3. Results and discussion

Fig. 1 shows the derivative of the mass profile obtained during calcination. The TGA profiles for the Ni catalysts supported on MgO , CeO_2 and TiO_2 were different. Each had two peaks corresponding to the weight loss associated with the decomposition/oxidation of nitrates and precursor materials from the catalyst. In all the catalysts, sharp peaks were observed before 400°C and there was no weight loss after 500°C . Therefore, we used a calcination temperature of 500°C .

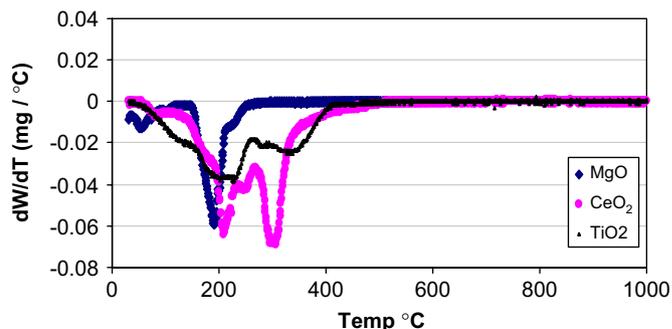


Fig. 1. Weight loss profiles of 15 wt% Ni supported on MgO , CeO_2 , and TiO_2 during calcination under nitrogen

Fig. 2 shows the XRD measurements of Ni/MgO, Ni/TiO₂, and Ni/CeO₂ catalysts calcined at 500 °C. The peaks at 37°, 43°, 62.4°, 74.9°, and 78.8° for 2θ correspond to NiO and MgNiO₂. In the case of Ni/TiO₂, the peaks at 24.1°, 33°, 35.6°, 40.8°, 49.4°, 53.9°, 58°, 62.5°, and 64.1° correspond to Ni(TiO₃). Peaks at 25.3°, 38°, 48°, 55°, and 78.8° are identified for TiO₂. Similarly, in the case of Ni/CeO₂, three peaks at 37.3°, 43.3°, and 62.8° correspond to NiO and other peaks are identified as CeO₂.

Table 1 depicts the hydrogen selectivity and its yield over Ni catalysts at selected temperatures. H₂ selectivity was found to be highest at 650 °C over MgO and TiO₂ supported catalysts. However, Ni/CeO₂ showed the highest H₂ selectivity at 550 °C under the reaction conditions investigated. Similarly, MgO and TiO₂ supported catalysts showed the highest H₂ yield at 650 °C whereas CeO₂ supported catalyst showed the highest H₂ yield at 600 °C. Maximum H₂ yield (56.5%) was obtained at 650 °C with MgO supported catalysts, which corresponds to 4 mol of H₂ out of 7 as given by Eq. (1). Catalysts tested in our lab showed lower performance rates under the conditions investigated compared to other studies. One reason could be the concentration of glycerin in the feed, which was 45 wt% in our study, compared to 10 wt% in the study done elsewhere [17].

Performance of the catalysts can be measured in terms of gas flow rate, however, this would be only qualitative. As depicted in Fig. 3, gas flow rate decreased over time on Ni/CeO₂, whereas it remained constant with Ni/MgO and Ni/TiO₂. This can be attributed to the higher carbon deposition rate on Ni/CeO₂ as reported elsewhere [18].

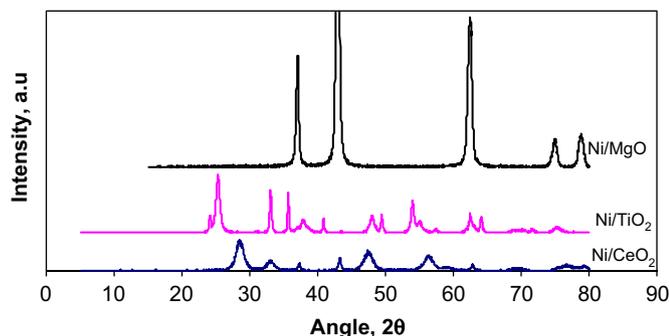


Fig. 2. XRD measurements of the selected catalysts calcined at 500 °C.

CO₂ selectivity was found to be the highest with MgO supported catalyst followed by TiO₂ and CeO₂. As expected, CH₄ selectivity decreased with the increase in temperature. CO selectivity was found to be greater at higher temperatures with MgO and CeO₂ supported catalysts; whereas it was different with TiO₂ supported catalysts, although, thermodynamics favor CO at higher temperatures [19]. C₂H₄ and C₂H₆ were present at low concentrations and the concentrations of both gases were less than 5000 ppm. However, no C₂H₄ was detected with the Ni/MgO catalyst.

Table 2 shows the glycerin conversion and glycerin conversion into gaseous products. As can be seen from Table 2, although the glycerin conversion was high with all the catalysts except for CeO₂ at 550 °C, glycerin conversion to the gaseous products never reached above 90%. This could be attributed to possible conversion of glycerin into other organic compounds, such as ethylene glycol, methanol, hydroxypropane and ethanol [6], which were not analyzed in this study.

4. Conclusion

Glycerin steam reforming for hydrogen production was conducted over Ni-based catalysts. Ni/MgO was found to be the best catalyst compared to Ni/TiO₂ and Ni/CeO₂ under the experimental conditions investigated. Maximum H₂ yield (56.5%) was obtained at 650 °C with MgO supported catalysts, which corresponds to 4 mol of H₂ out of 7 stoichiometric maximum.

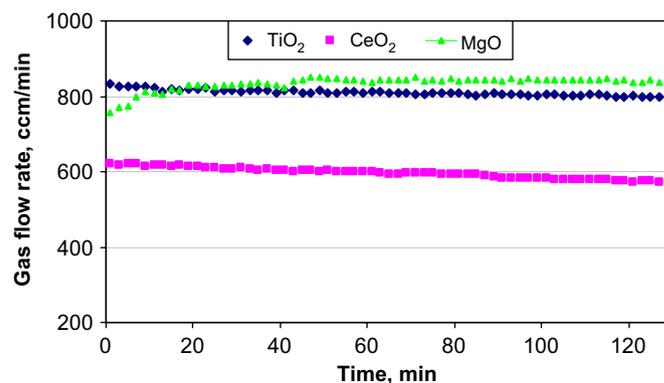


Fig. 3. Gas flow rate over Ni supported catalysts at 650 °C and flow rate of 1 ml/min.

Table 1
H₂ selectivity and yield over Ni supported catalysts

Temperature (°C)	Ni/MgO		Ni/CeO ₂		Ni/TiO ₂	
	Selectivity, %	H ₂ yield, %	Selectivity, %	H ₂ yield, %	Selectivity, %	H ₂ yield, %
650	65.64	56.51	53.88	33.44	62.20	46.99
600	61.08	43.16	63.29	43.62	49.24	41.31
550	62.61	44.32	66.69	30.78	44.39	31.13

Table 2
Glycerin conversion and conversion into gaseous products over Ni supported catalysts

Temperature (°C)	Ni/MgO		Ni/CeO ₂		Ni/TiO ₂	
	Glycerin conversion	Conversion to gases	Glycerin conversion	Conversion to gases	Glycerin conversion	Conversion to gases
650	100.00	86.62	93.06	62.05	98.02	75.81
600	100.00	70.75	97.66	68.89	96.26	84.43
550	100.00	70.78	72.27	46.16	97.87	69.94

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