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# Catalytic reforming of glycerol in supercritical water with nickel-based catalysts

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## ABSTRACT

The catalytic performance of nickel catalysts supported on La<sub>2</sub>O<sub>3</sub>, α-Al<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and YSZ for supercritical water reforming of glycerol was investigated. Experiments were conducted in a tubular reactor made of Inconel-625 with the temperature range of 723–848 K under a pressure of 25 MPa. Carbon formation causing operation failure was observed for α-Al<sub>2</sub>O<sub>3</sub>, γ-Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> at temperatures higher than 748, 798 and 823 K, respectively. Ni/La<sub>2</sub>O<sub>3</sub> exhibited the highest H<sub>2</sub> yield where almost complete conversion was obtained at 798 K. Moderate space velocities (WHSV = 6.45 h<sup>-1</sup>) and glycerol feed concentration (5wt.%) favor high hydrogen selectivity and yield. Methanation is favored at a low WHSV or high glycerol feed concentration, resulting in a lower H<sub>2</sub> yield. Increasing Ni loading on the Ni/La<sub>2</sub>O<sub>3</sub> catalyst strongly promoted the reforming, water–gas shift, and methanation reactions, which contributed significantly to the product species distribution. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Glycerol, a major by-product of typical ester biodiesel production, is presently produced in large excess due to a significant increase in biodiesel production [1–3]. Since glycerol can be considered as a form of hydrogen chemical storage, a number of research studies have focused on hydrogen production from glycerol via steam reforming [4–9], autothermal

reforming or oxidative steam reforming [10–12], aqueous-phase reforming [13] and supercritical water reforming (SCWR) [14–17]. In recent years, SCWR has attracted more and more interest due to its high reaction efficiency and H<sub>2</sub> selectivity [18–23]. This is because of unique properties of supercritical water offering higher space-time yield, reduced mass transfer limitations, and favorable endothermic reforming reaction conditions. Moreover, hydrogen is

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produced at high pressure, which can be stored directly without large energy penalty from compression [15,21].

May et al. (2010) investigated catalytic glycerol reforming in supercritical water with 1%Ru/CaO-stabilized ZrO<sub>2</sub>. The conditions were 783–823 K, 35 MPa, and 5 wt.% feed glycerol concentration, in a continuous isothermal fixed bed reactor [14]. Hydrogen and carbon monoxide were the main gases with small amounts of methane and ethylene. Ru/ZrO<sub>2</sub> promoted the formation of acetic acid, gasification of glycerol, but inhibited the formation of acrolein. However, complete gasification could not be achieved by using this catalyst because the primary products, including acetaldehyde and acetic acid could not convert to gaseous products while carbon deposition led to lower H<sub>2</sub> yield. The previous work [24] conducted glycerol reforming in supercritical water in a continuous flow tubular Hastelloy C276 reactor at 718–873 K, 25 MPa. H<sub>2</sub> yield of 3.47 could be obtained with an empty reactor at 873 K. With 0.1 wt.% NaOH catalyst, a H<sub>2</sub> yield of 4.93 could be obtained at lower temperature (799 K).

Crude glycerol was employed as a raw feedstock for H<sub>2</sub> production as available low-cost material. Czernik et al. (2002) investigated steam reforming of crude glycerol by using a commercial nickel-based naphtha reforming catalyst (C11-NK), and H<sub>2</sub> yield of ca.5.39 (77% of the stoichiometric potential) could be obtained [25]. Douette et al. (2007) performed crude glycerol reforming using Ni-based catalyst. Maximum H<sub>2</sub> yield of 4.6 could be obtained, but catalyst deactivation and coking was found. Contaminants in crude glycerol, e.g., sodium and chloride ions, were possible causes for the reduction of the reaction performance [26].

In our previous studies, glycerol conversion of 0.91 and H<sub>2</sub> yield of 2.86 were obtained from empty Inconel 625 at 798 K [27]. Cobalt based catalyst supported on commercial supports including La<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and YSZ were evaluated for glycerol supercritical steam reforming in an Inconel 625 reactor. 10wt.%Co/YSZ showed the highest H<sub>2</sub> yield of 3.72 at temperature of 773 K [28]. It is clear that H<sub>2</sub> could be produced in an empty reactor where the reactor's wall is catalytically active. However, an appropriate catalyst is essential to obtain a reasonable H<sub>2</sub> yield.

In the work reported here, we have expanded our previous studies to elucidate the reaction of glycerol reforming in supercritical water (SCW) over Ni catalyst. Nickel is a well-known metal which has been employed in glycerol reforming processes [29–31]. The long term stability for Ni compared with Co and in some cases also higher activity have been reported [32]. Nickel has been substituted for noble metal since nickel is considerably cheaper, while being highly active toward the hydrogen rich gas [33]. Ability of nickel toward C–C bond rupture has been reported as excellent [33,34]. Recently, reforming of glycerol in supercritical water was performed over a bimetallic Pt–Ni supported  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst [35]. Complete conversion of glycerol was achievable at a relatively low temperature (723 K) with high gasification efficiency. However, the gasification efficiency decreases steadily from 99% to 46% with increasing the glycerol feed concentration from 2.6 to 20 wt.%.

Hence, the aim of this work is to investigate the support (i.e. La<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and YSZ) effects on glycerol reforming in SCW over Ni catalyst. The key

operating parameters e.g. operating temperature, weight hourly space velocities and glycerol feed concentration were examined.

## Materials and methods

### Materials

Glycerol (Fisher scientific, USP/FCC) was mixed with deionized water (DI water) at the required concentration as an organic feedstock. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Alfa Aesar, 99.9985%) was used as a precursor for nickel loading. Commercial supports including YSZ (TOSOH, TZ-8Y, powder), La<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.99%, powder), ZrO<sub>2</sub> (Aldrich, 99%, powder),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.97%, powder),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Alfa Aesar, 99.98%, powder) were employed in this work. Acetaldehyde (Sigma–Aldrich,  $\geq$ 99.5%), propionaldehyde (Sigma–Aldrich, 97%), acetone (Sigma–Aldrich, 99.9%), acrolein (Sigma–Aldrich, 90%), methanol (Caledon,  $\geq$ 99.8%), ethanol (Sigma–Aldrich, HPLC grade), isopropanol (Sigma–Aldrich, 99.9%), 1-propanol (Baker analyzed reagent, 99%), allyl alcohol (Aldrich, 99%), acetol (Aldrich, 90%), acetic acid (Sigma–Aldrich, 99.7%), acrylic acid (Aldrich, 99%) and ethylene glycol (Acros Organics, 99.5%) were used as standards for identifying concentrations in the liquid product solution. 1-4 butanediol (Sigma–Aldrich, 99%) was employed as an internal standard. Mixed gas (Praxair, 30% CO, 30% CO<sub>2</sub>, 25% CH<sub>4</sub>, 10% C<sub>2</sub>H<sub>4</sub>, and 5% C<sub>2</sub>H<sub>6</sub>), hydrogen (Praxair, 99.999%), and nitrogen (Praxair, 99.999%) were mixed and filled in Kynar gas sampling bags (Cole-Parmer, 6" × 6") at different concentrations for the calibration in gas analysis. Screens (Sigma–Aldrich, 40, 60 mesh) were used as filters on the top and bottom of the reactor.

### Catalyst preparation

The catalysts were prepared by wet impregnation method similar to our previous work [26]. Briefly, 250 mL of DI water in a beaker was stirred and heated at 363 K. The commercial support (15 g) was immersed in DI water, followed by slight addition of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O precursor (e.g. 3.9114 g of precursor for 5 wt.% loading). The solution was vaporized to obtain paste-like product. The paste product was dried overnight at 383 K and then calcined at 973 K for 5 h. The product was crushed and sieved to collect a particle size between 1.4 and 2 mm for using as a catalyst.

### Method

The reaction was performed in an Inconel-625 reactor and schematic diagram of the supercritical water reforming process is shown elsewhere [28]. The reaction performance was investigated under various operating temperatures (723–848 K). Other operating parameters, such as weight hourly space velocities (WHSV = 3.15, 6.45, and 10.8 h<sup>-1</sup>), glycerol feed concentration (2.5, 5, 7.5, and 10 wt.%) and percent of metal loading (0, 2.5, 5, 10, and 15 wt.%) were also investigated. Glycerol conversion,  $X_{\text{Glycerol}}$  (Eq. (1)), concentration in the gas phase (Eq. (2)), H<sub>2</sub> yield (Eq. (3)), and yield of carbon containing species *i* (Eq. (4)) are defined as follows.

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