Research Article

Carbon Dioxide Dry Reforming of Glycerol for Hydrogen Production using Ni/ZrO₂ and Ni/CaO as Catalysts

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Abstract

Glycerol, byproduct from the biodiesel production can be effectively utilized as the promising source of synthesis gas (syngas) through a dry reforming reaction. Combination of these waste materials with greenhouse gases which is carbon dioxide (CO_2) will help to reduce environmental problem such as global warming. This dry reforming reaction has been carried out in a fixed bed batch reactor at 700 °C under the atmospheric pressure for 3 hours. In this experiment, reforming reaction was carried out using Nickel (Ni) as based catalyst and supported with zirconium (ZrO_2) and calcium (CaO) oxides. The catalysts were prepared by wet impregnation method and characterized using Bruanaer-Emmett-Teller (BET) surface area, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Thermo Gravimetric (TGA), and Temperature Programmed Reduction (TPR) analysis. Reaction studies show that 15% Ni/CaO give the highest hydrogen yield and glycerol conversion that peaked at 24.59% and 30.32%, respectively. This result is verified by XRD analysis where this catalyst shows low crystallinity and fine dispersion of Ni species resulted in high specific surface area which gives 44.93 m²/g that is validated by BET. Copyright © 2016 BCREC GROUP. All rights reserved

1. Introduction

Declining of the fossil fuels and petroleum reserves will drive to energy crisis; so it is imperative to find alternative energy so that it can sustain the world energy requirements.

Syngas is touted as the promising alternative energy due to its high efficiency, clean emission and it helps to reduce the dependency on these non renewable sources [1]. Syngas or synthesis gas is comprised mainly of hydrogen (H_2) and carbon monoxide (CO_2) and it was used as feedstock in several of process like Fischer-Tropsch, methanol, ammonia and synthetic natural gas [2]. Syngas is normally derived from a variety of different materials that contain carbon, such

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as natural gas or biomass [3]. To date, biomass particularly glycerol has become one of the attractive feedstock for the syngas production and it received considerable attentions from the researchers worldwide.

Glycerol is commercially used in pharmaceutical, cosmetics and food industry. It is naturally produced as by-product through the transesterification process of biodiesel. It was estimated that approximate 10% of crude glycerol will be produced from the transesterification process [4-6] and it was expected to grow dramatically in the near future. Rising demand of biodiesel led towards prompt production of glycerol. This surplus has caused the oversupply crisis that rendered the development of biodiesel industry particularly in terms of economic viability [7]. Exploiting glycerol as feedstock for the syngas will help to reduce the refining cost in production biodiesel and it will also added some values towards this waste product and directly resolved the environmental problems. To date there are several types of processes that has been implemented to convert glycerol to syngas like autothermal reforming, partial oxidation, aqueous phase reforming, supercritical reforming and steam reforming [8].

Commercially, syngas is produced through the natural gas steam reforming where steam (H_2O) is use as feedstock and CO_2 is produced as its byproduct. This process is found to contribute to energy-intensive related problem and the releases of greenhouse gases, carbon dioxide (CO_2) that contributed to the global warming problems [1-2]. Besides that, steam reforming produces several side reactions such as carbon formation, methanation and reverse water-gas shift [7, 9-11] that affecting the purity of the reforming product [12] .

Glycerol dry reforming offer a better pathway for the production of hydrogen as it reported to have a greener process where it utilize waste products, glycerol and greenhouse gases (CO_2) as its feedstock. Overall glycerol dry reforming is represented by Equation (1).

$$C_3H_8O_3(g) + CO_2(g) \leftrightarrow 4CO(g) + 3H_2(g) + H_2O(g)$$

(1)
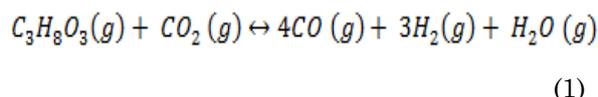
Prior works has been done on the glycerol dry reforming, concentrating on the thermodynamic analysis and effect on different types of support and promoters over Nickel (Ni) based catalyst [1, 13-14]. Wang and co workers [15] has performed the thermodynamic analysis using Gibbs free energy method and found that the maximum quantities of syngas can be

reached at atmospheric pressure where the temperature is set at 1000 K. Lee *et al.* [13] reported on the use of cement clinker as support for the Ni based where the reaction temperature was held at 1023 K. In the experiment, the CO_2 to glycerol ratio (CGR) was manipulated with the pressure of CO_2. The result shows that higher pressure of CO_2 and CGR will favor the side reaction (i.e. hydrogenation, methanation) and it need to be control so that it can achieved least carbon deposition and higher glycerol conversion. Carbon deposition cause the catalyst to lost its effective surface area and it will affect the purity of reforming products [12], therefore suitable catalyst is need to seize this carbon deposition.

In syngas technologies, Nickel (Ni), which categorized as a transition metal is predominantly used as a catalyst due to its viability and low cost compared to platinum (Pt), palladium (Pd) and rhodium (Rh) [5, 16-18]. According to Saad *et al.* [19], Ni was chosen as based catalyst in reforming process due to its high catalytic activity and stability. The primary drawback of Ni related to coke formation and sintering of Ni particles where it cause the catalyst to rapidly deactivate due to losses of surface area [8, 20]. Previous research found that introduction of an alkaline earth oxide (MgO and CaO) and rare earth oxides (La_2O_3 and CeO) would help to inhibit the formation of coke [5, 13, 19]. Magnesium Oxide (MgO), Aluminium oxide (Al_2O_3), Titanium dioxide (TiO_2), cement clinker, Zirconium oxide (ZrO_2) and Calcium oxide (CaO) are the example of supports that has been explored in the glycerol reforming process.

According to Chang *et al.* [22], addition of alkaline or alkaline earth oxide improves the anti-carbon properties of Ni based as it helps in reduce the polymerization of the carbon group. This also proved by researches that has been done by Dias & Assaf [23], Ranjbar & Razaei [24], and Quincoces *et al.* [25]. ZrO_2 has shown interesting properties as catalyst modifier for the catalytic reaction [26, 27]. In methanation reaction, addition of ZrO_2 into Ni supported on Al_2O_3 showed high surface area and thermal stability resulting in high catalytic performance in the reforming reaction [28-29].

Therefore, the objective of the present work is to study the performance of the both type of synthesized catalyst (Ni/ZrO_2 and Ni/CaO). Besides that, this work also report on reaction studies of glycerol dry reforming over 5, 10 ,15 % of Ni as based supported over calcium oxide (CaO) and zirconium oxide (ZrO_2).

2. Materials and Methods

2.1. Chemicals

Glycerol (Fisher Scientific, 99.95% purity), nickel(II) nitrate hexahydrate (Acros Organics, 99%), zirconium(VI) oxide (Acros Organics, 98.5%) and calcium oxide (Acros Organics, 99.99%) were employed for this work. Glycerol was used as the feedstock for the dry reforming process. Carbon dioxide was used as reactant and nitrogen gas was used as reforming agent carrier gas for this reaction.

2.2. Catalyst preparation

All the catalysts were prepared via wet impregnation method with 5%, 10%, and 15% nickel (Ni) metal, respectively. Initially, supported oxides were calcined at 1073 K for 6 hours in a carbolite furnace. After that, an accurately weighted calcined oxides was mixed with $Ni(NO_3)_2.6H_2O$ aqueous solution and magnetically-stirred for 3 hours. Then, the slurry was dried overnight in an oven at 383 K for 12 hours to remove excess water. The product was crushed and calcined again for 6 hours at 1073 K. It was then cooled down and sieved to a particle size of 90-200 μm for characterization and reaction studies.

2.3. Catalyst Characterization

The surface structure and morphology of the catalysts were captured by using Scanning Electron Microscopy (SEM) unit JOEL.JSM-7800F model. The analysis was carried out at a condition of 2kX, 5kX, 100X and 500X. Liquid N_2 adsorption analysis was used to determine the BET specific surface area of fresh catalyst using Thermo-Scientific Surfer. In the analysis, liquid N_2 was used as an adsorbate at temperature 77 K. The thermal-programmed calcination (TPC) of the catalyst was carried out using a TGA Q-500 system while the temperature programmed reduction was conducted by using Thermo Finnigan TPDRO. The ramping rate was set at 10K min^{-1} and it was conducted from room temperature to 1173 K. X-Ray Diffraction (XRD) analysis was conducted using Rigaku Miniflex II to obtain crystalline structure of the catalysts. This analysis was carried out using CuKα radiation (λ = 1542 Å) at 15 mA and 30 kV. The scan rate was 1° min^{-1} for values between $2\theta = 10°$ and $80°$. The crystallite size was determined using Scherrer equation (Equation (2)).

$$d = \frac{K\lambda}{\beta \cos\theta}$$

(2)

where d is the crystallite size, K is the shape factor, λ is the X-ray radiation (λ=0.154 nm), β is the full-width at half maximum (FWHM) and θ is half of diffraction angle [12-13].

2.4. Dry Reforming Experimental Work

The glycerol dry reforming was carried out in a stainless-steel fixed bed reactor (ID = 0.95 cm; length 40 cm) under a pressure of 1 bar as shown in Figure 1. The reactor was loaded with 0.2 g of catalyst. Molar ratio of CO_2 to glycerol was fixed at 1:1. Glycerol was delivered to the
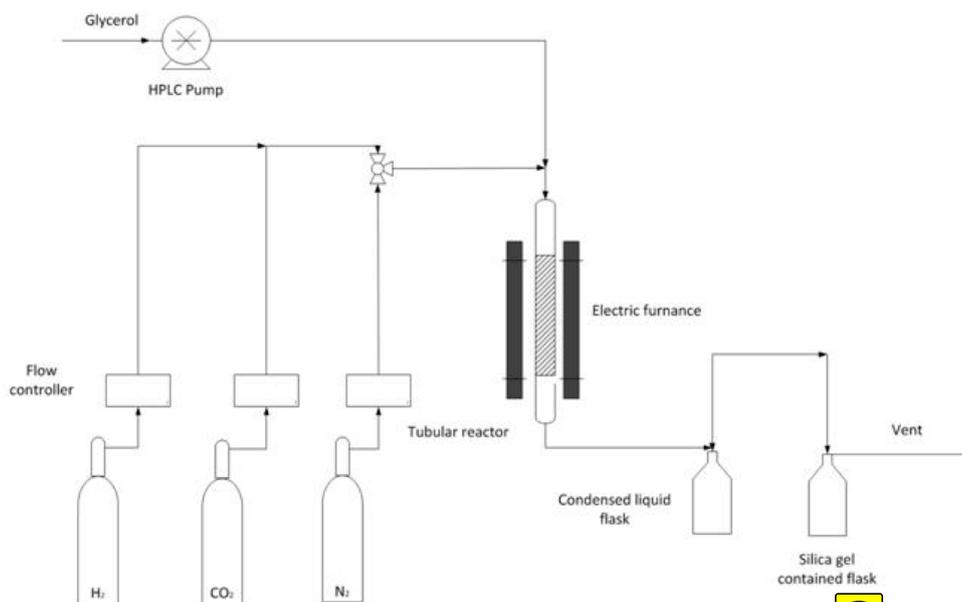

Figure 1. Experimental setup for the glycerol dry reforming

reactor using the high performance liquid chromatography (HPLC) pump via the downward flow motion at 0.03 mL/min. The reaction temperature was fixed at 973 K. Before experiment started, hydrogen was flow into the reactor for catalyst reduction. Flow of nitrogen gas to the reactor was set at 0.1 L/min at 1 bar while flow of carbon dioxide gas to the reactor was set at 9.9 ml/min at 1 bar. The outlet gases were passed through a gas wash bottle which consists of silica gel flask to absorb moisture. The exit gas flowrate was measured using a bubble meter and finally collected into a gas sampling bag. The composition of syngas produced was determined using online Agilent gas chromatography (GC) with TCD capillary columns, HP-MOLSIV (30.0 m × 530 µm × 40.0 µm)

The catalyst performance was evaluated in terms of the glycerol conversion and hydrogen yield. The glycerol conversion to gaseous products was determined based on the atomic H-balance and defined as Equation (3). The yield of hydrogen is expressed as Equation (4), where F_{H_2} and F_{CH_4} represents the molar flow rate of hydrogen and methane product, respectively, while $F_{C_3H_8O_3}$ refers to the molar flow rate of the inlet glycerol.

$$X_G = \frac{2F_{H_2} \times 4F_{CH_4}}{8F_{C_3H_8O_3}} \times 100$$

(3)

$$Y_{H_2} = \frac{2F_{H_2}}{8F_{C_3H_8O_3}} \times 100$$

(4)

3. Results and Discussion

3.1. X-Ray Diffraction Characterization (XRD)

Crystalline phase and particle size of the synthesised catalyst was determined using XRD technique and recorded in the 2θ range of 10° to 80°. The crystalline phase correspond to NiO for Ni/CaO were detected at 2θ of 37.1° and 43.3° while for Ni/ZrO$_2$, the NiO phase were detected at 2θ = 41.2°, 41.9° and 44.1° which comparable with findings of Ebshish *et al.* [30] and Siew *et al.* [14]. The presence of CaO and ZrO$_2$ support can be detected at the peak of 2θ as shown in Figure 2. For all loadings of Ni/CaO, the characteristic peak correspond to Ni/CaO$_2$ were found at 2θ = 62.6°. All loadings of Ni/ZrO$_2$ relatively have sharp and intense peaks due to the presence of bigger crystallite size ranging from 0.32 to 0.68 nm. This bigger crystallite size will cause high crystallinity that led to less nickel dispersion within the solid matrix, simultaneously contribute to lower surface area. These finding were also confirmed by Rezaei *et al.* [31] and Zangouei *et al.* [32]. On the other hand, Ni/CaO shows a broader and shorter peak as compared t Ni/ZrO$_2$. The weak appearance of Ca species is
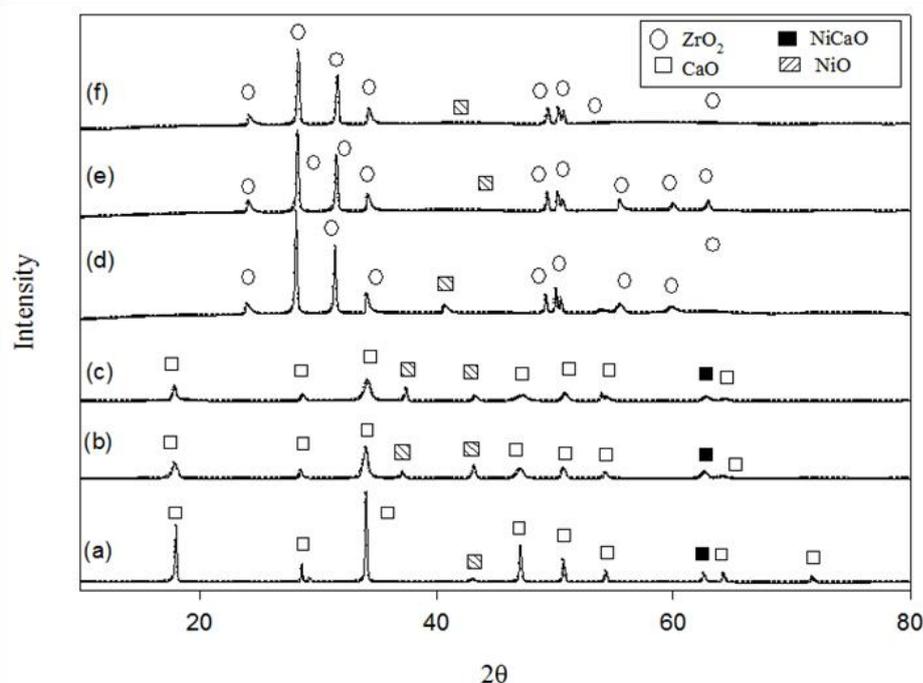
Figure 2. XRD pattern of prepared catalysts with various CaO and ZrO$_2$ loadings (a) 5% Ni/CaO, (b) 10%Ni/CaO, (c) 15% Ni/CaO, (d) 5% Ni/ZrO$_2$, (e) 10% Ni/ZrO$_2$, and (f) 15% Ni/ZrO$_2$

resulted from a very fine dispersion of NiO onto CaO. This fine dispersion of Ca^{2+} ions found to help the catalyst sintering and reduce the carbon deposition on the catalyst [23-24, 33]. Besides that, crystalline size of Ni/CaO is smaller than Ni/ZrO$_2$ ranging from 0.24-0.29 nm which lead to the higher surface area of catalyst.

3.2. Scanning Electron Microscopy (SEM)

Scanning of electron microscopy (SEM) was used to observe the morphology of support on different Ni loading prepared catalyst. Figures 3 and 4 shows the SEM results for all samples and comparison took place at 5000 times magnification. It can be observed that 15% of Ni-CaO has the smoother surface compared to other catalysts. The results significantly show the high interaction between Ni-based and the supports which simultaneously contribute to high dispersion of Ni catalyst onto the support. These results agree with the findings in XRD analysis shown in Figure 2. The 5% and 10% of

N/CaO shows rougher and bulkier surface, indicating the presence of large Ni atoms resulted from the low interaction between Ni metal and CaO. For Ni/ZrO$_2$, all the surface morphology shows large particles surrounded with agglomerated crystallites that lead to lower specific surface area. This contributed to less glycerol conversion and hydrogen yield as less surface area exposed during the reaction.

### 3.3. Brunauer-Emmett-Teller (BET) characterization

All the prepared catalyst show same hysteresis that indicating the mesoporous structure. Table 1, reveals the BET specific area and cumulative pore volume of synthesis catalyst that is obtained from the N$_2$ physisorption. The surface area for all catalyst is within the range value of its support. For the synthesis catalyst, 5% of Ni/CaO show the highest surface area while 10% of Ni/ZrO$_2$ has the lowest surface area. It was found that Ni supported with
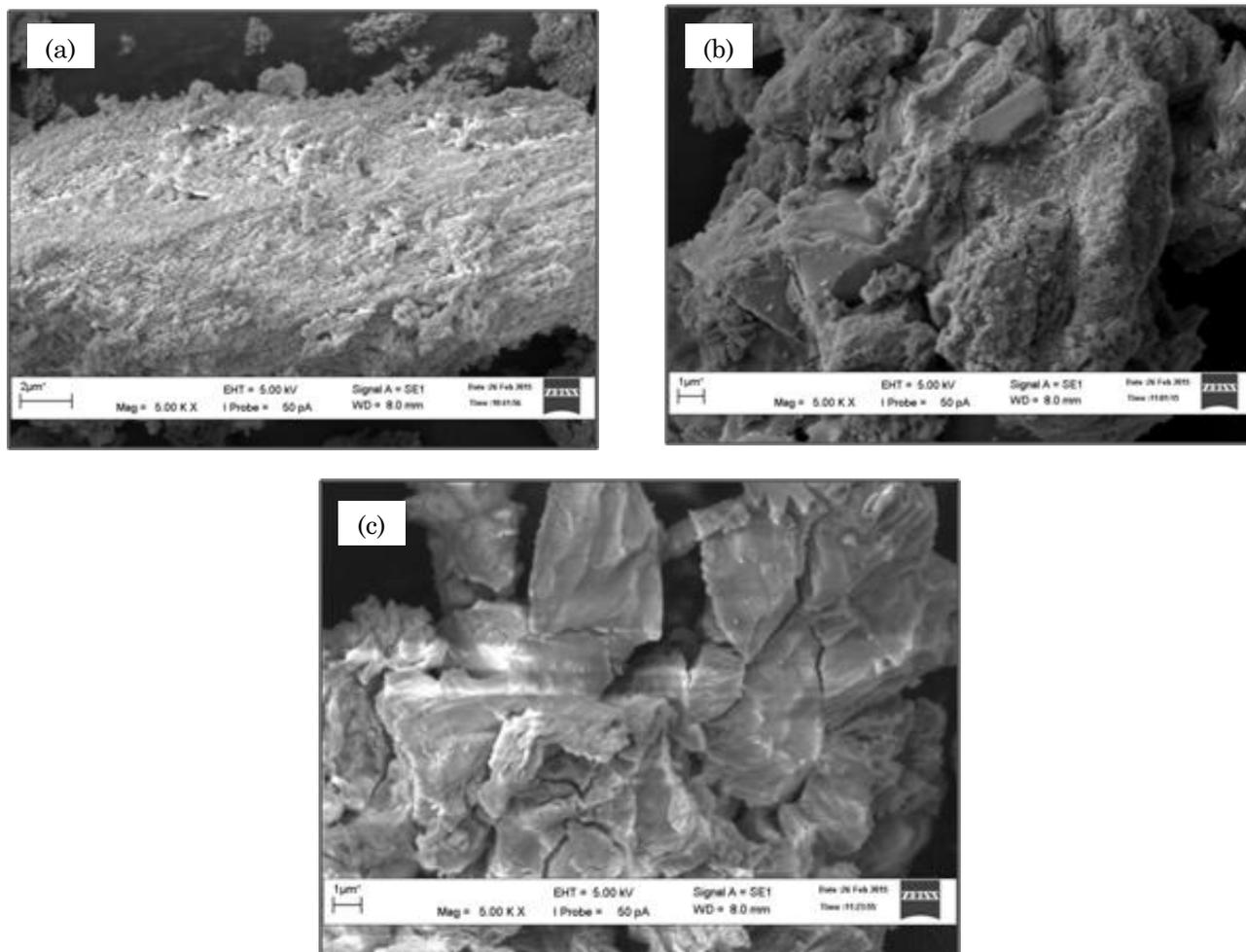
Figure 3. Morphology structure of the calcined: (a) 5% Ni/CaO, (b) 10% Ni/CaO, (c) 15% Ni/CaO was taken at magnification of 5000 times

Table 1. BET specific surface area, density and cumulative pore volume of the catalysts

Catalysts	BET surface area $(m^2 g^{-1})$	Cumulative Pore Volume $(cm^3 g^{-1})$	Density $(g\ cm^{-3})$
CaO	81.54	0.07	3.07
5%Ni/CaO	45.99	0.07	2.25
10% Ni/CaO	41.52	0.05	2.48
15% Ni/CaO	42.98	0.01	2.74
ZrO_2	51.56	0.01	2.37
5%NiZrO$_2$	30.84	0.01	3.42
10%NiZrO$_2$	27.34	0.01	5.84
15%NiZrO$_2$	42.88	0.01	5.83
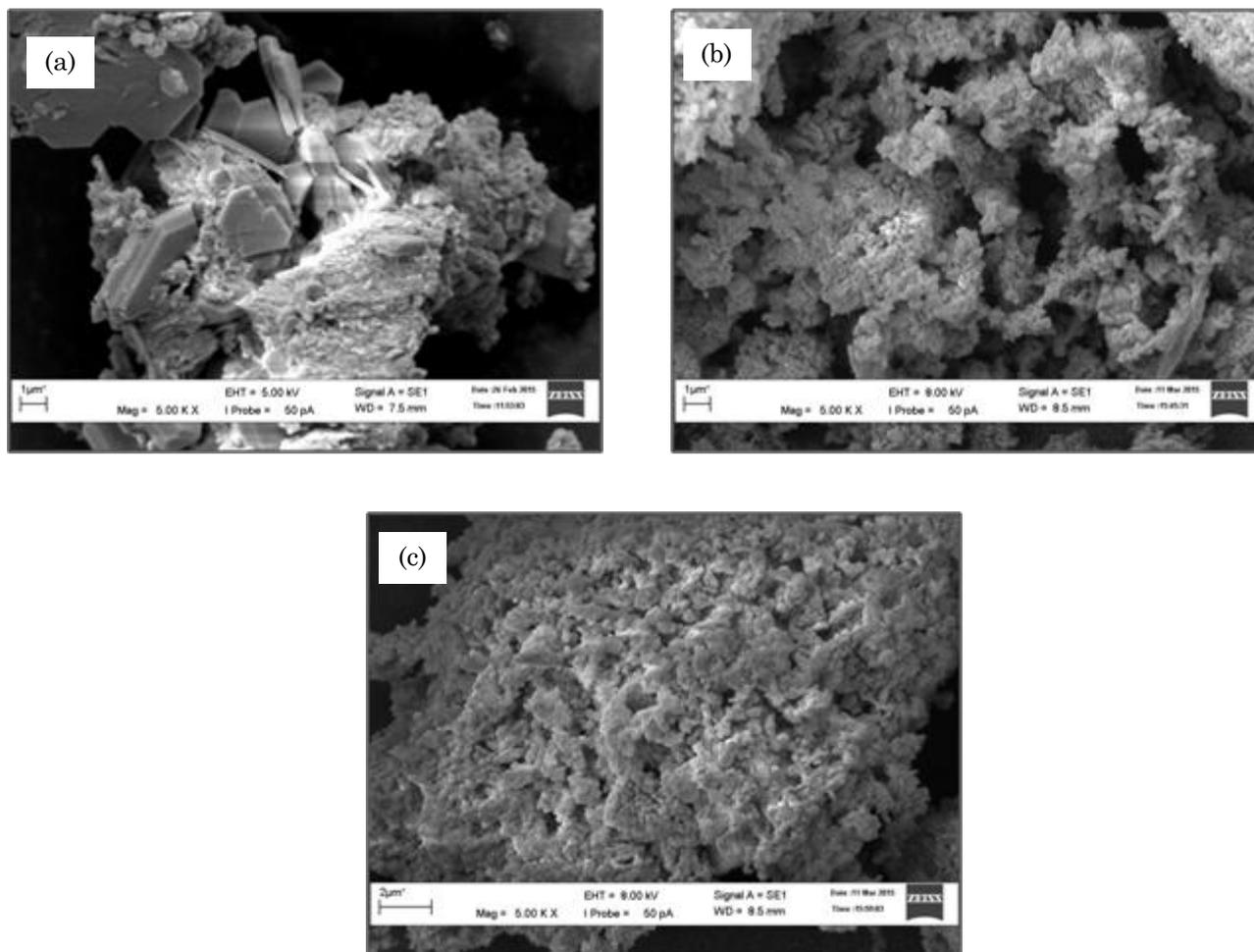
Figure 4. Morphology structure of the calcined: (a) 5% Ni/ZrO$_2$, (b) 10% Ni/ZrO$_2$, (c) 15% Ni/ZrO$_2$ was taken at magnification of 5000 times

ZrO_2 has lower surface area compared to Ni/CaO due to larger nickel species crystallite as evinced in XRD analysis (Section 3.1). Besides that, there was a reduction of surface area for all the synthesized catalysts as compared to the blank support (CaO and ZrO_2). This is due to the blockage created by the metal oxides (NiO) during the catalyst impregnation step.

3.4. Thermogravimetric analysis (TGA) – calcination studies

The temperature-programmed calcination studies of both catalysts, Ni/CaO and Ni/ZrO_2 is presented in Figures 5 and 6. The aim of this analysis is to study the thermal decomposition of the synthesized catalyst. For Ni/CaO, there are peaks that presence before 227 °C. This shows that the water vapour from the catalyst is eliminate [13]. Peak that formed around 300 to 400 °C respectively for all Ni/CaO catalysts shows the transformation of $Ni_3(NO_3)_2.6H_2O$ into NiO [13, 34] which in line with XRD result as shown in Figure 2. Between 400 to 450 °C, Ni/CaO catalysts in ascending orders show a slightly shifted peak location, where higher Ni loading results in larger shifting to higher temperature. This is due to the increase of interaction between metal and the support [24].

The temperature-programmed calcination analysis for Ni/ZrO_2 which presented in Figure 5 reveals the appearance of few peaks before 100 °C that corresponds to the loss of two water molecules from the decomposition of nickel nitrate hexahydrate. The reduction peaks that formed between 370 to 400 °C indicate the transformation of $Ni_3(NO_3)_2(OH)_4$ to NiO phase that deposited on the zirconia surface [34, 35].
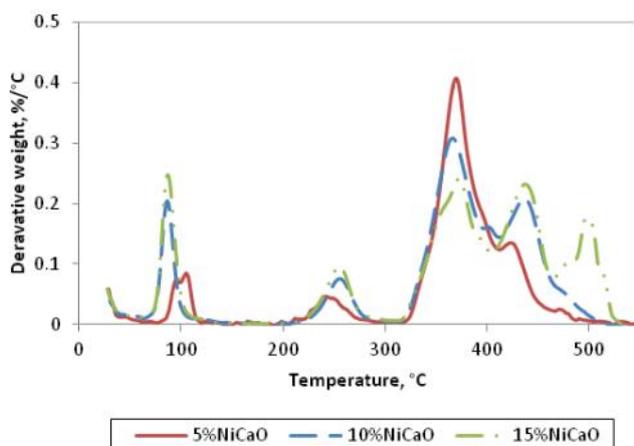
3.5. Temperature Programmed Reduction (TPR)

Temperature programmed reduction is conducted for examined the reducibility of catalyst. From Figures 7 and 8, the pure CaO and ZrO_2 do not show any reduction peak due to its high stability as it is not easily to be reduced [36]. The reduction of NiO can be found at temperature of 347-382 °C and 382-428 °C for 15% Ni/CaO, while for 15% Ni/ZrO_2 it can be seen at 381-429 °C and 429-519 °C [37]. It was found that 15% Ni/CaO was easier to be reduced comparing to 15% Ni/ZrO_2 as it have lower reduction temperature and besides the catalyst have higher oxygen storage capacity which help in preventing the formation of coke deposition [38]. For 15% Ni/CaO, there is reduction peak at 428-614 °C due to reduction of Ni/CaO as in agreement with Lee *et al*. [13].

3.6. Reaction studies

Figures 9 and 10 shows the combination of glycerol conversion and hydrogen yield for the prepared catalyst during the dry reforming reaction at 700 °C. Overall analysis found that the glycerol conversion and hydrogen yield increase in order of 5% Ni/ZrO_2 > 15% Ni/ZrO_2 > 10% Ni/CaO > 5% Ni/ZrO_2 > 10% Ni/ZrO_2 > 15% Ni/CaO. The highest conversion of glycerol, 30.53% was achieved using 15% Ni/CaO at 60 minutes of 700 °C of reaction condition. The same catalyst results in 23.06% of hydrogen yield. This is resulted from the high Ni dispersion that is co-current with the findings from XRD and BET analysis as shown in Figure 2 and Table 1. High specific area and smaller crystallite size contribute to the reduc-
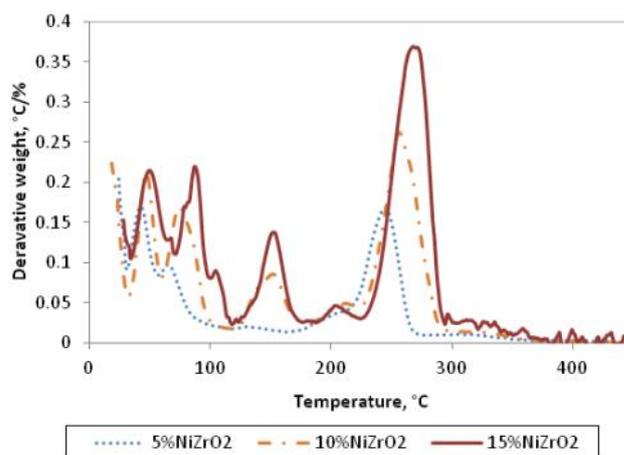

Figure 5. TGA analysis of Ni/CaO catalyst at 10 K min^{-1}

Figure 6. TGA analysis of Ni/ZrO_2 catalyst at 10 K min^{-1}

tion in catalyst sintering and carbon deposition due to strong oxygen storage capacity that is supported by TPR analysis as shown in Figure 7. SEM analysis in Figure 3(a) also shows a smoother morphology structure indicating high dispersion of catalyst on the oxide support. The lowest catalyst performance shows by the 5% of Ni/ZrO$_2$ as it only managed to produce 15% for glycerol conversion and 11.45% for the hydrogen yield. The low yield and conversion obtained by Ni/ZrO$_2$ was influenced by the poor properties of the catalyst, as it found to have low Ni dispersion and higher crystallite, which reduce the interaction between Ni and ZrO$_2$.

4. Conclusions

Ni supported on CaO and ZrO$_2$ has been successfully synthesized via wet impregnation method and syngas was successfully produced through the dry reforming reaction. From the reactions studies, 15% Ni/CaO results in the highest glycerol conversion and hydrogen yield where it shows higher interaction between Ni and CaO species. This was supported by the XRD analysis, where it shows higher metal dispersion and smaller crystallite size of NiO species formed. This was also significantly proved by BET analysis where 15% Ni/CaO show the highest surface area compared to the other synthesized catalyst. There is also significant reduction of surface area between pure CaO and Ni/CaO due to the blocking the pores of the support.
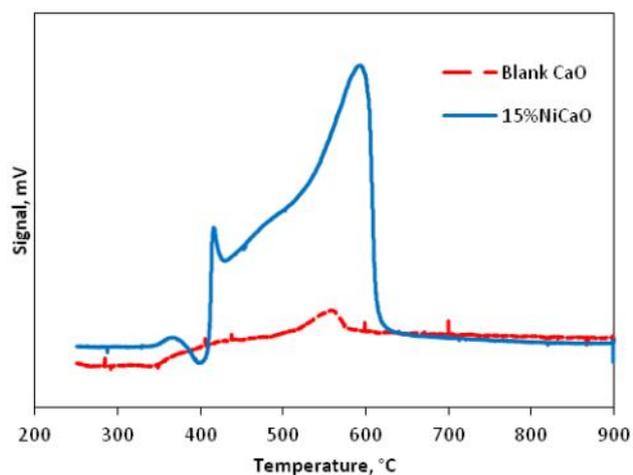

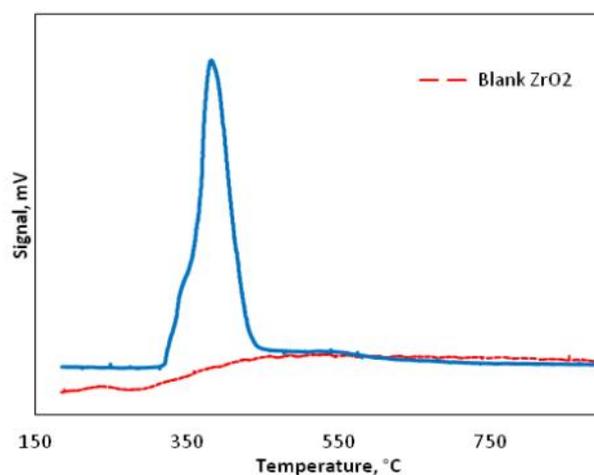**Figure 7**. Temperature programmed reduction for blank CaO and 15% Ni/CaO

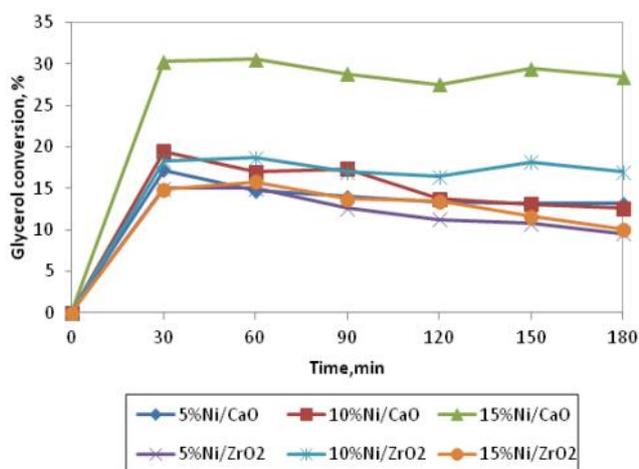**Figure 8**. Temperature programmed reduction for blank ZrO$_2$ and 15% Ni/ZrO$_2$

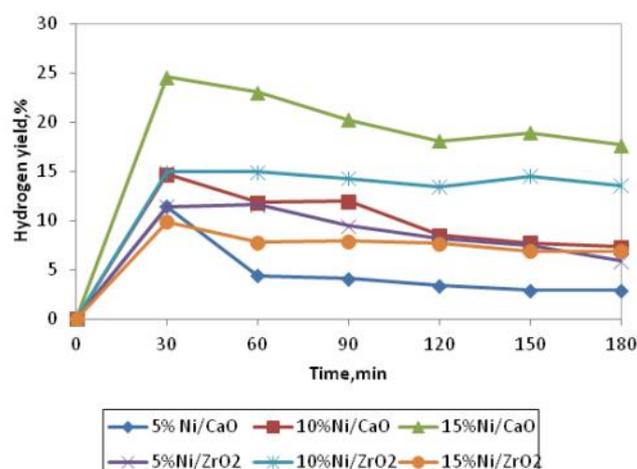**Figure 9**. Glycerol conversion as function of time at 700 °C

Figure 10. Hydrogen yield of Ni/CaO and Ni/ZrO$_2$ versus time at 700 °C

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