



Research Article

Characterization of Ag-promoted Ni/SiO₂ Catalysts for Syngas Production via Carbon Dioxide (CO₂) Dry Reforming of Glycerol

Norazimah Harun¹, Jolius Gim bun^{1,2}, Mohammad Tazli Azizan³,
Sumaiya Zainal Abidin^{1,2*}

¹Faculty of Chemical Engineering & Natural Resources, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

²Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

³Department of Chemical Engineering, Faculty of Engineering, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia

Received: 22nd January 2016; Revised: 22nd February 2016; Accepted: 23rd February 2016

Abstract

The carbon dioxide (CO₂) dry reforming of glycerol for syngas production is one of the promising ways to benefit the oversupply crisis of glycerol worldwide. It is an attractive process as it converts carbon dioxide, a greenhouse gas into a synthesis gas and simultaneously removed from the carbon biosphere cycle. In this study, the glycerol dry reforming was carried out using Silver (Ag) promoted Nickel (Ni) based catalysts supported on silicon oxide (SiO₂), i.e. Ag-Ni/SiO₂. The catalysts were prepared through wet impregnation method and characterized by using Brunauer-Emmett-Teller (BET) surface area, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Thermo Gravimetric (TGA) analysis. The experiment was conducted in a tubular reactor which condition fixed at 973 K and CO₂ to glycerol molar ratio of 1, under atmospheric pressure. It was found that the main gaseous products are H₂, CO and CH₄ with H₂:CO molar ratio < 1.0. From the reaction study, Ag(5)-Ni/SiO₂ results in highest glycerol conversion and hydrogen yield, accounted for 32.6% and 27.4%, respectively. Copyright © 2016 BCREC GROUP. All rights reserved

Keywords: Glycerol; Dry reforming; Syngas; Nickel-based catalysts; Silicon Oxide

How to Cite: Harun, N., Gim bun, J., Azizan, M.T., Abidin, S.Z. (2016). Characterization of Ag-promoted Ni/SiO₂ Catalysts for Syngas Production via Carbon Dioxide (CO₂) Dry Reforming of Glycerol. *Bulletin of Chemical Reaction Engineering & Catalysis*, 11 (2): 220-229 (doi:10.9767/bcrec.11.2.553.220-229)

Permalink/DOI: <http://dx.doi.org/10.9767/bcrec.11.2.553.220-229>

1. Introduction

Fossil fuels such as coal, crude oil and natural gas are formed from the remains of dead plants and animals over million years ago. It has been utilized as energy resources globally

for the past decades. World has relied on this non-renewable energy as the primary fuel source for the electricity, heating and powering vehicles. However, increasing global energy consumption as a result of rising population growth may lead to the depletion of fossil-based resources in the near future. Moreover, the risk of global climate change rises as global consumption rises. It is believed that carbon emissions from fossil fuels are the main factor for

* Corresponding Author.

E-mail: sumaiya@ump.edu.my

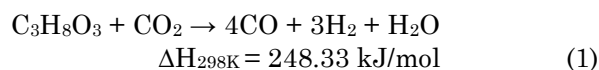
Telp: +6095492890, Fax: +6095492889

the rise in atmospheric concentrations and global temperatures. Today, renewable energy sources especially biomass have been gaining attention as an alternative for fossil fuels consumption [1]. As the most viable alternative fuel, biodiesel is considered as a promising alternative energy. Biodiesel is produced industrially through transesterification of vegetable oil (edible oil) and non-edible oil, where the side product is glycerol. Approximately 10 wt% of crude glycerol constituted from the total product. Therefore increasing demands of biodiesel contribute to a dramatic growth in glycerol production.

The production of synthesis gas (syngas) and hydrogen is a promising way to benefit oversupply of glycerol production. Syngas is a gas mixture constitutes of carbon monoxide, carbon dioxide and hydrogen. It is widely used as intermediates in creating synthetic natural gas and petroleum and for the production of ammonia and methanol [2]. The most common method of producing hydrogen and syngas using is through steam reforming. However, this endothermic process requires high-energy consumption in order to provide optimum condition for reaction to occur. This high reaction temperature, in the other way promotes the formation of carbon which negatively affect the stability of the catalyst.

The glycerol CO₂ dry reforming process is an attractive process as it converts carbon dioxide, a greenhouse gas into a synthesis gas and simultaneously removed from the carbon biosphere cycle. Dry reforming of glycerol is an endothermic reaction in which as the temperature increases, the favourable product formed will also be higher. However, to date, there are limited literatures reported on the glycerol dry reforming.

Equation 1 shows the primary reaction occurred in the dry reforming of glycerol:



Wang *et al.* [3] had performed a thermodynamic analysis of glycerol dry reforming. The possible products formed at the end of the process are hydrogen, carbon monoxide, carbon dioxide, methane, water and carbon (solid deposition). It is found that the synthesis gas reached the maximum production at temperature 1000 K and CO₂: glycerol molar ratio of 1:1. Atmospheric pressure was preferable for the system. Glycerol conversion achieved 100% conversion, while carbon dioxide conversion was increased

with the increase of temperature [3].

Lee *et al.* investigated the glycerol dry reforming over Ni catalyst supported on cement clinker. They found that addition of Ni has significantly improved the surface area of the catalyst even though the cement clinker is a non-porous substance. At 1023 K reaction temperature, hydrogen-to-carbon dioxide ratio is less than 2.0 which is suitable for Fischer-Tropsch synthesis. Unfortunately, side reactions like methanation and hydrogenation of carbon dioxide affected the production of syngas [4].

Glycerol dry reforming over La-promoted Ni/Al₂O₃ catalysts for the production of syngas was conducted by Siew *et al.* [5]. Catalysts were prepared by wet-impregnation method with promoter loading ranging from 1 to 5wt%. The study revealed that 3%La-Ni/Al₂O₃, which possessed the largest surface area exhibited the most stable catalytic activity and achieve the optimum hydrogen production and glycerol conversion. It was found that, although production of hydrogen and glycerol increased by addition of La promoter, the addition of promoter over the optimum level led to the reduction of catalytic activity due to clogging in the pores which cover the active sites of the catalyst and thus reduce the catalyst activity.

Selection of suitable catalyst is crucial in every process. Ni-based catalyst is widely used in reforming activities due to highly abundance and low in cost. Moreover, it can work well towards optimum results with introduction of metal promoter. Noble metals (Ru, Pd, Pt etc.) are often use as the promoter. However, these catalysts are also known to favor the deposition of carbon (coking), which may reduce the performance of the catalyst. Ag is uncommonly used in dry reforming studies. Nevertheless, Ag has been reported possessing the ability to inhibit the formation of coke and thus maintain the stability of the catalyst [6, 7]. Moreover, Ag as the promoter improves the ethanol conversion and hydrogen selectivity in ethanol steam reforming, as reported by Chen *et al* [8]. This paper is focuses on CO₂ dry reforming of glycerol over Ni-based catalyst supported on silicon oxide (SiO₂) promoted with Ag. It is expected that Ni-based catalyst promoted with Ag enhances the conversion of glycerol and yield of desired gaseous products besides contributes to the stability of the catalyst by minimizing the coke formation.

2. Materials and Methods

2.1. Materials

Glycerol (Fisher Scientific, 99.95% purity) was used as feedstock for the dry reforming process. A series of silver promoted nickel-based catalyst supported on silica was prepared using nickel(II) nitrate hexahydrate (Acros Organics, 99% purity), silicon oxide (Acros Organics, 99% purity) and silver nitrate (Acros Organics, 99% purity). Gaseous carbon dioxide is used as the reactant for the dry reforming process. Since the mass flow rate of carbon dioxide gas is low, inert nitrogen gas had been utilized as carrier gas to facilitate the transportation of reactants through the reactor system.

2.2. Catalyst preparation

Silicon oxide was ground and sieved to 250 μm particle sizes beforehand. Prior to wet impregnation method, the oxide support was first calcined at 1073 K for 6 hours, with ramping rate of 5 K min^{-1} to remove the impurities and to avoid the transition of phase when exposed to high temperature in reforming reaction. The calcined oxide support was then impregnated with the aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 to synthesized 15 wt% Ni-based catalysts with 0-5 wt% Ag loadings. The solutions were magnetically stirred for 3 h at ambient temperature for metal impregnation. Then, the slurries were dried in the oven at temperature of 373 K overnight. The catalyst was

manually stirred using the glass rod during the first six hours using glass rod to avoid particle agglomeration. After that, the dried compound was calcined in the furnace at 773 K for 5 h employing heating rate of 5 K min^{-1} . The catalysts were cooled down, ground and sieved using 150 μm sieve size.

2.3. Catalyst characterization

The surface structure and morphology of the catalysts were captured by using Scanning Electron Microscopy (SEM) JOEL.JSM- 7800F model. Brunauer-Emmet-Teller (BET) analysis was carried out using Thermo-Scientific Surfer to determine the specific surface area of the calcined catalysts where liquid N_2 was used as an adsorbate. X-Ray Diffraction (XRD) analysis was conducted using Rigaku Miniflex II to obtain crystalline structure of the catalysts. This analysis was carried out using $\text{CuK}\alpha$ radiation ($\lambda = 1542 \text{ \AA}$) at 15 mA and 30 kV. The scan rate was 1° min^{-1} for values between $2\theta = 10^\circ$ and 80° . The crystallite size was determined using Scherrer equation shown in Equation 2.

$$d = \frac{K\lambda}{\beta \cos \theta} \quad (2)$$

where d is the crystallite size, K is the shape factor, λ is the X-ray radiation ($\lambda=0.154 \text{ nm}$), β is the full-width at half maximum (FWHM) and θ is half of diffraction angle. Thermogravimet-

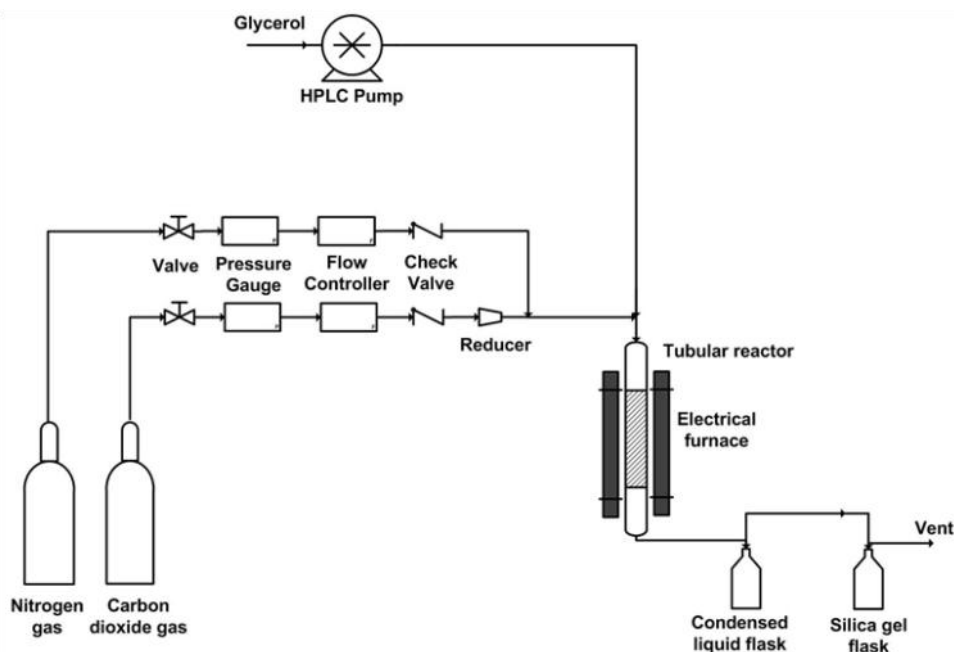


Figure 1. Experimental set-up for glycerol dry reforming

ric analysis was conducted using the Q500-model thermogravimetry analyser, with the ramping rate fixed at 10 K min⁻¹. The temperature-programmed reduction (TPR) profiles of the catalysts under H₂-blanket were carried out using Thermo Finnigan TPDRO. The ramping rate was fixed at 10 K min⁻¹, increasing the temperature from room temperature to 1173 K followed by 1 h holding period.

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) at atmospheric pressure. Figure 1 shows the experimental set-up for glycerol dry reforming. The reaction temperature was fixed at 973 K and CO₂ to glycerol molar ratio of 1:1. The volume flow rate of glycerol was fixed at 0.03 mL/min and 100 mL/min for CO₂. The reactor was loaded with 0.2 g of catalyst. Prior to reaction, the catalyst was reduced in 50 ml/min hydrogen for 1 h at 700 °C. Glycerol was flowed into the reactor using the HPLC pump. The outlet gases were passed through a gas wash bottle which consists of silica gel flask to absorb moisture. The exit gas flow rates was measured using a bubble meter and 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).

2.5. Catalytic reaction performance

The catalyst performance was evaluated based on the glycerol conversion and hydrogen yield. The glycerol conversion to gaseous products was determined based on the atomic H-balance and defined as:

$$X_G = \frac{(2F_{H_2}) \times (4F_{CH_4})}{8F_{C_3H_8O_3}} \times 100 \quad (3)$$

The yield of hydrogen is expressed as:

$$Y_{H_2} = \frac{2F_{H_2}}{8F_{C_3H_8O_3}} \times 100 \quad (4)$$

The yield of C-containing yield is expressed as in Equation (5), where $i = CO, CO_2$ or CH_4 :

$$Y_i = \frac{F_i}{3F_{C_3H_8O_3}} \times 100 \quad (5)$$

where, F_{H_2} and F_{CH_4} represents 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.

3. Results and Discussion

3.1. X-Ray Diffraction characterization (XRD)

Figure 2 shows the crystalline structures of the catalysts depicted by the peaks between 2θ of 10° and 80°. The diffraction peaks at 2θ of 37.3°, 43.3°, 62.9°, 75.4° and 79.4° characterize the NiO phase. SiO₂ peak appeared at 2θ of 21.5° and this peak was shifted to the right as Ag loading increases. Other SiO₂ phases co-exist with NiO peaks at the same diffraction angles and possess near-similarity crystalline structure. The metal particles size of the catalysts show no significant change upon addition of Ag. This finding is also confirmed by Parizotto *et al.* [6]. However, four additional peaks appear at 2θ of 38.2°, 44.4°, 64.5° and 77.5°, which coincide with peaks of Ag. Interestingly, the peaks of AgSi in Ag(1)-Ni/SiO₂ and Ag(2)-Ni/SiO₂ appeared between 2θ of 29.0° to 80.0° are short and unnoticeable, indicates the weak dispersion of Ag with the catalyst support at low Ag loading. The short peaks indicate the formation of small crystalline particles, which might cover the active sites of the catalyst [9].

3.2. Scanning Electron Microscopy (SEM)

The morphology structures of the catalysts at 5000 times magnification are shown in Figure 3. The calcined SiO₂ in Figure 3(a) reveals a smooth surface with few crystallites formed. Upon impregnation with Ni, the surface has become rougher and bulkier, and this finding suggests the formation of NiO crystallites. Larger particles formation are observed on the promoted catalysts (in Figure 3(c) and (d)) which indicates the agglomeration of AgSi and Ag crystallites besides the smaller NiO crystallites. The surface of Ag(5)-Ni/SiO₂ is rougher and bulkier compared to Ag(1)-Ni/SiO₂ due to the higher Ag loading. This results were co-current with the findings from XRD analysis, where it shows the presence of large Ag particles at higher Ag loading and it was represented by the additional peaks appear at 2θ of 38.2°, 44.4°, 64.5° and 77.5°.

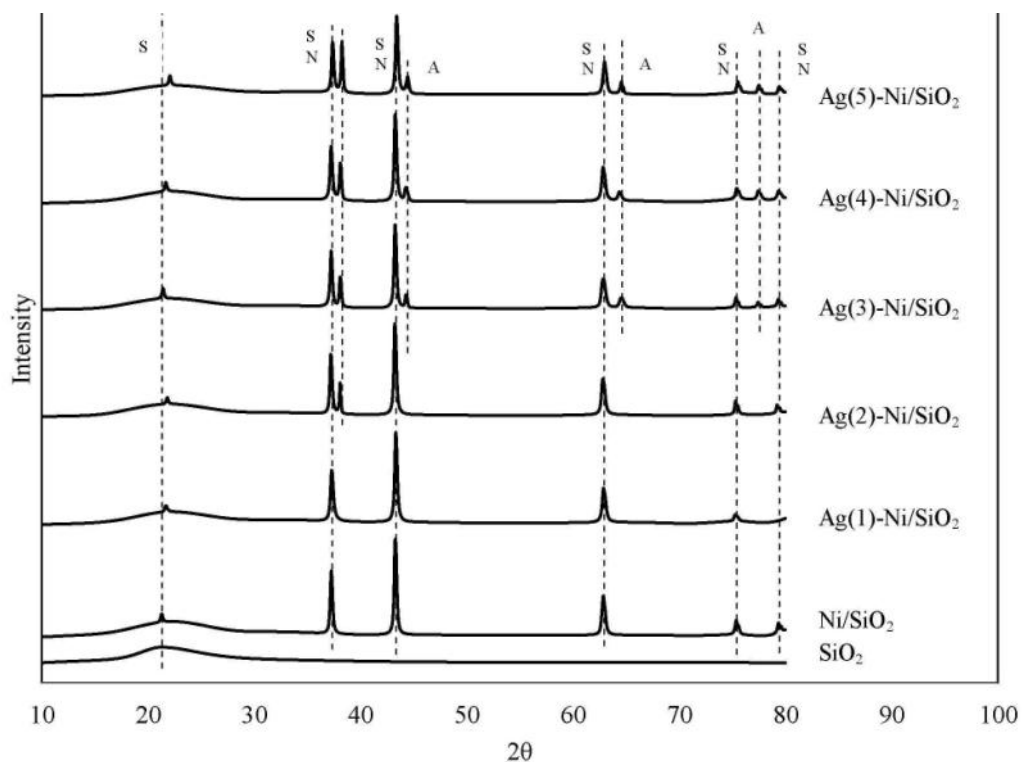


Figure 2. XRD pattern for the prepared catalysts. (S-SiO₂, N-NiO, and A-Ag)

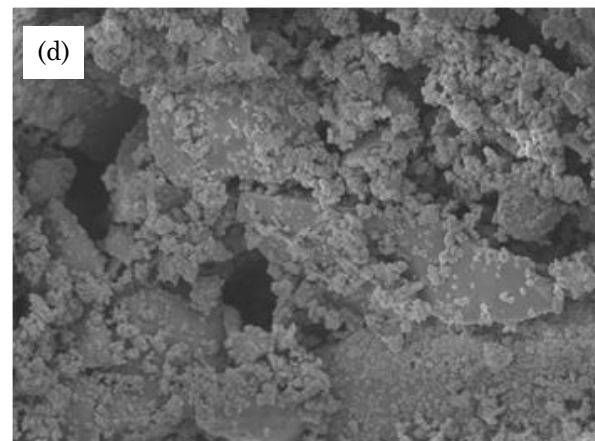
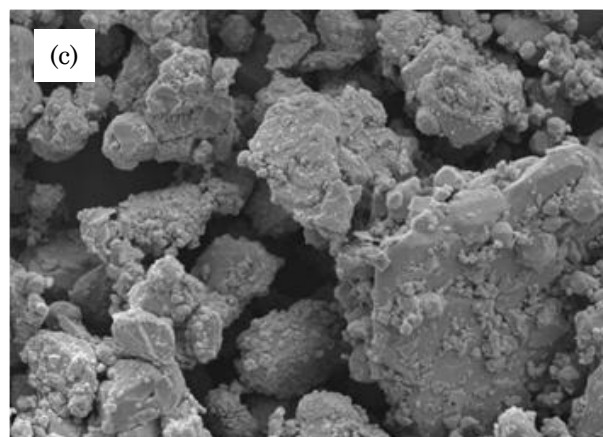
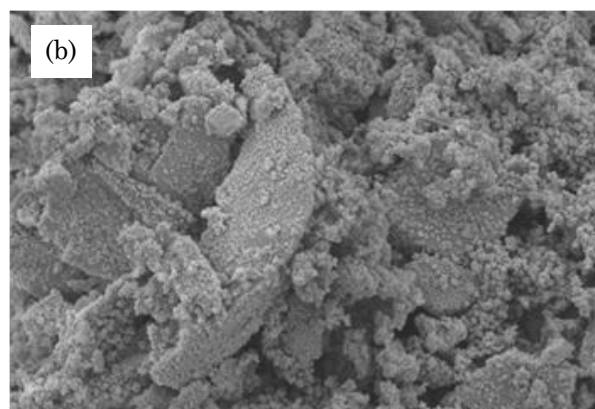
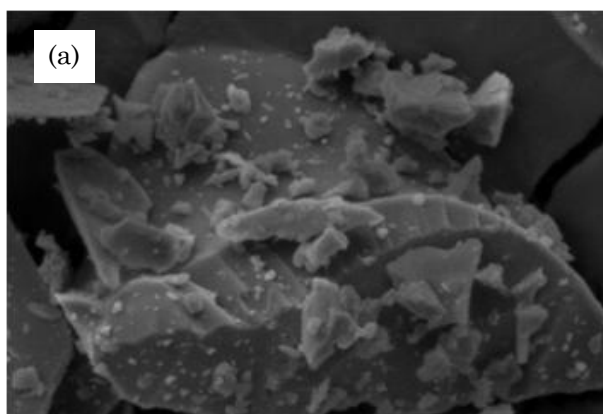


Figure 3. Morphology structure of (a) SiO₂, (b) Ni/SiO₂, (c) Ag(1)-Ni/SiO₂ and (d) Ag(5)-Ni/SiO₂ at 5000 times magnification

3.3. Brunauer-Emmett-Teller (BET) surface area

The analysis from nitrogen physisorption indicates the presence of mesoporous materials. Table 1 shows the BET surface and pore volume of calcined SiO₂, unpromoted NiSiO₂ and Ag(5)-Ni/SiO₂. The BET surface area of Ni/SiO₂ and Ag promoted catalysts are less than calcined SiO₂ support. Apparently, introduction of Ag promoter decreases the BET surface area. This data is resulted from the pores blockage by the metallic oxide and the promoter. Similar results were also found by Diaz *et al.* and Guo *et al.* [10, 11]. However, increasing of Ag loading significantly increases the BET surface area. Ag(5)-Ni/SiO₂ has the highest surface area among the promoted catalysts.

3.4. Thermogravimetric analysis (TGA)

Calcination profiles of Ni/SiO₂, Ag(1)-Ni/SiO₂, Ag(3)-Ni/SiO₂ and Ag(5)-Ni/SiO₂ pre-

sented in Figure 4 shows three stages of weight loss between 300 K to 650 K. Peaks formation between 300 K to 400 K are due to the removal of water vapour in the catalysts [12]. The second stage of weight loss is between 400 K and 523 K, showing two peaks resulting from the dehydration of hydrated silicon oxide for the final formation of SiO₂, which is correlated to XRD study. The final stage in between 523 K to 650 K reveals the transformation of Ni(NO₃)₂.6H₂O into NiO which is in agreement with the findings reported by Estelle *et al.* [13].

3.5. Temperature-programmed reduction

The TPR profiles of Ni/SiO₂ and Ag(3)-Ni/SiO₂ are depicted in Figure 5. The peak detected at 650 K for both catalysts can be attributed to the reduction of NiO to Ni metal, which is consistent with the findings of Acrotumapathy *et al.* [14]. Both catalysts showed the ability to easily reduce due to the strong oxygen

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

Catalyst	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)
SiO ₂	80.903	0.0113
Ni/SiO ₂	46.345	0.0111
Ag(1)-Ni/SiO ₂	17.265	0.0090
Ag(3)-Ni/SiO ₂	30.283	0.0101
Ag(5)-Ni/SiO ₂	38.848	0.0101

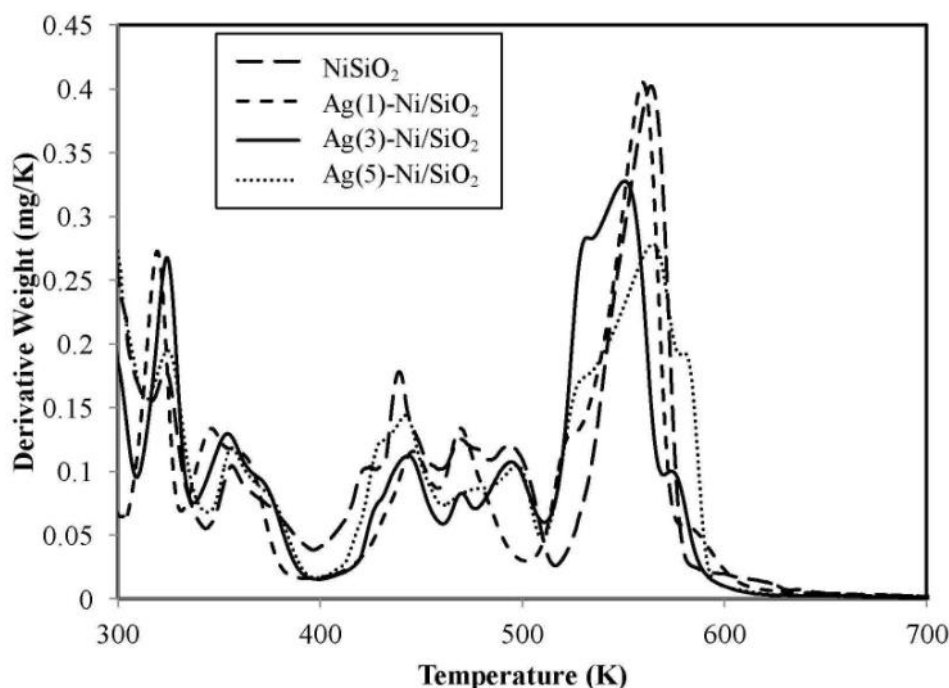


Figure 4. TGA analysis of catalysts at 10 K min⁻¹ ramping rate in N₂/O₂

storage capacity in the catalyst. Because H₂ completely reduced the catalyst at 773 K, this temperature was selected as the reduction temperature for the catalysts during the reaction studies.

3.5. Reaction study

The glycerol dry reforming was conducted at a fixed condition with the reaction temperature of 973K, 3 h reaction time, 1:1 carbon to glycerol ratio and at atmospheric pressure. Through the glycerol dry reforming, glycerol is converted into other gaseous products such as H₂, CH₄, CO, CO₂ and traces of gases.

From the glycerol conversion plot shown in Figure 6, an almost similar trend could be ob-

served where the glycerol conversion are increases in the first 30 minute, decrease after 1 hour reaction time and stable along the reaction period. It is probably due to the deposition of carbonaceous species on the catalyst surface upon breakage of C-C bond in glycerol. The highest glycerol conversion obtained over Ag(5)-Ni/SiO₂(32.1%) followed by other catalysts in descending Ag loading, which Ni/SiO₂ possess the least glycerol conversion of 6.5%. This can be attributed to the high distribution of active sites and well dispersion of metallic Ni species on the catalyst surface, as indicated in XRD analysis. Furthermore, according to Jeong and Kang, addition of Ag contributes to higher reforming reactivity compared to unpromoted catalyst by reducing the degree of car-

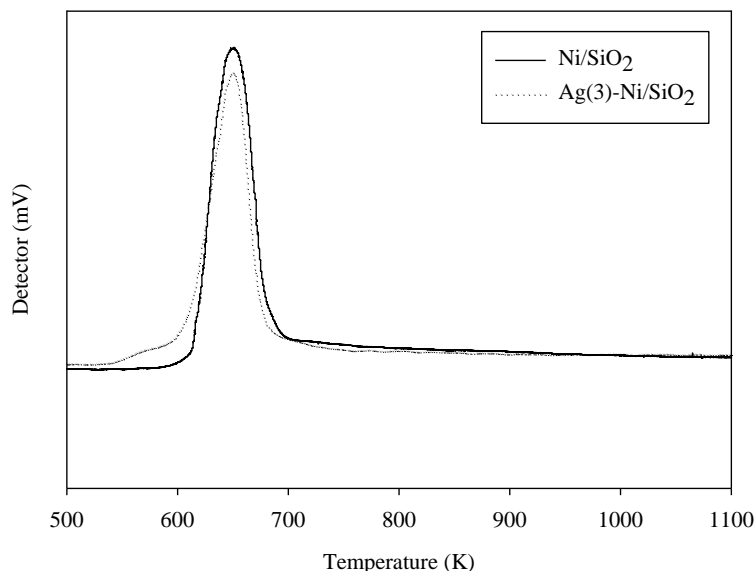


Figure 5. H₂-TPR profile of Ni/SiO₂ and Ag(3)-Ni/SiO₂ catalysts at heating rate of 10 K min⁻¹

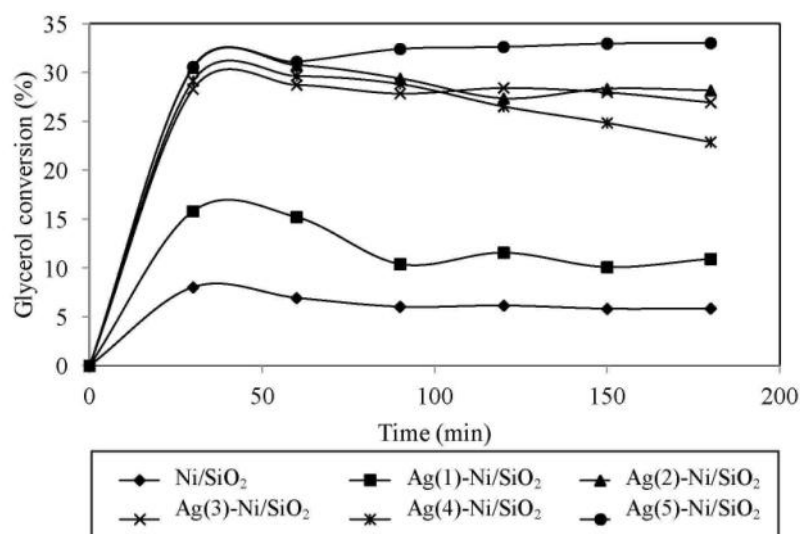


Figure 6. Glycerol conversion over 3 hours reaction time at 973 K, 1 atm and CO₂: Glycerol of 1:1

bon deposition and improves hydrogen yield [15].

Figure 7 shows the products yield for different Ag loading at minute 90. The Ag(5)-Ni/SiO₂ gives the highest hydrogen yield of 27.4% whereas Ni/SiO₂ produced the least yield of hydrogen accounted for 4.8%. Methane yield is apparently lower than yield of hydrogen and carbon monoxide in the consecutive run. Methane is formed via dehydrogenation of glycerol, which also leads to the deposition of carbonaceous species [16]. Carbon monoxide yield is

high for all the catalysts, circa 3 times the yield of hydrogen. High carbon monoxide content contributes to low hydrogen-to-carbon monoxide ratio as shown in Figure 8. Upon promotion with Ag, the ratio is increased which 5% Ag loading possess the highest ratio accounted for 4.0. This ratio is preferable for some synthesis such as production of aldehydes [3].

3.6. Characterization of used catalyst

There are several side reactions that may occur in the dry reforming of glycerol and affect

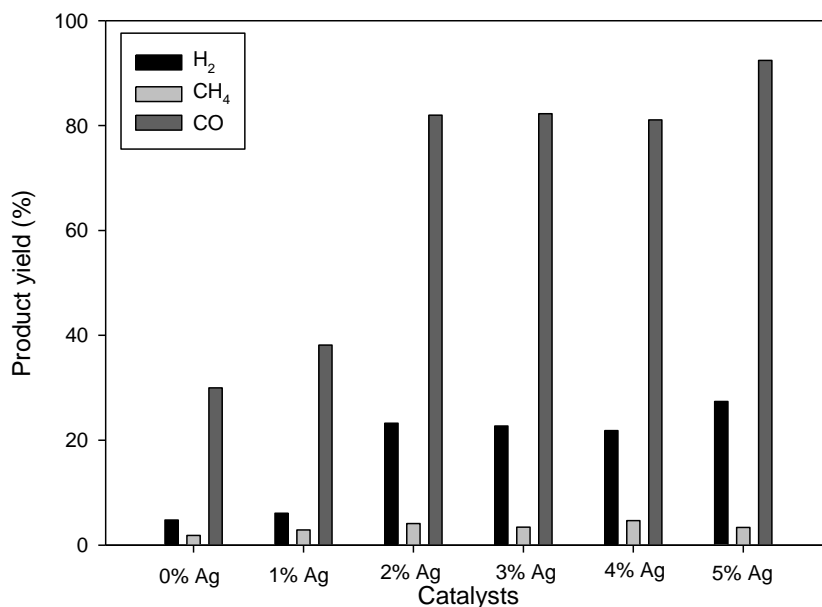


Figure 7. Hydrogen, methane and carbon monoxide yield for different Ag loading at 973 K, 1 atm and CO₂:Glycerol of 1:1

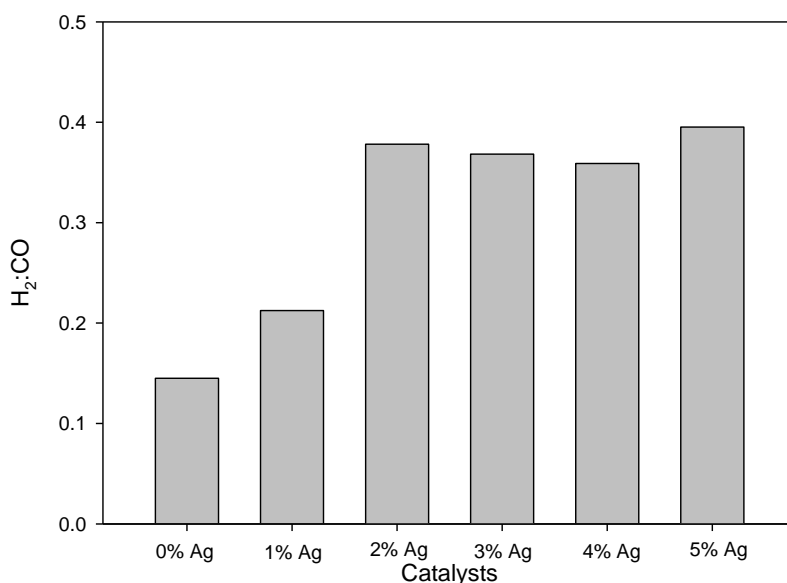


Figure 8. H₂:CO products ratio as function of promoter loadings loading at 973 K, 1 atm and CO₂:Glycerol of 1:1

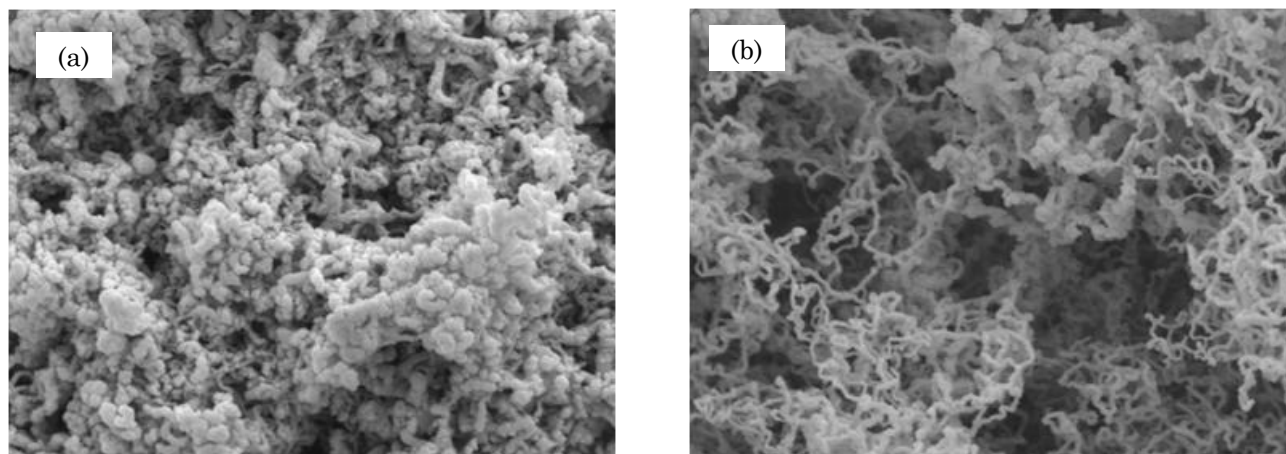


Figure 9. SEM image of the spent catalyst at 30,000X magnification

the catalyst performance. The carbon deposition phenomenon could be observed upon subjected the spent catalyst to SEM study. As shown in Figure 9, there are two types of carbon deposits. The first type is solid carbon deposited on the catalyst surface which covers the active sites of the catalyst as in Figure 9 (a). Another type is shown in Figure 9 (b), the filamentous-type (whisker-like) carbon deposition.

4. Conclusions

A series of silica-supported Ni based catalysts with different Ag promotion were prepared via wet impregnation method. Reaction studies at 1 atm, 973 K and CO₂:glycerol of 1:1 showed that glycerol dry reforming successfully produced syngas with H₂:CO molar ratio less than 1. Physicochemical characterization revealed that Ag promotion can enhance the formation of Ag phase crystallites and promotes the dispersion of NiO particles. Significantly, the Ag(5)-Ni/SiO₂ catalyst, which possessed the highest Ag loading gave optimum glycerol conversion and hydrogen yield, accounted for 32.1% and 27.4%, respectively. Through XRD analysis, it was found that Ag(5)NiSiO₂ has the smaller particles which indicates the fine dispersion of NiO particles. Moreover, data from BET surface area reveals that the highest surface area of Ag(5)-Ni/SiO₂ among the Ag-promoted catalysts. SEM analysis showed the rougher surface indicates the formation of Ag particles and NiO.

Acknowledgement

Authors would like to thank MOE for awarding the FRGS research grant vote RDU130108 and Universiti Malaysia Pahang for financial support.

References

- [1] Adhikari, S., Fernando, S., Gwaltney, S., Filipto, S., Markbricka, R., Steele, P. and Haryanto, A. (2007). A thermodynamic analysis of hydrogen production by steam reforming of glycerol. *International Journal of Hydrogen Energy*, 32(14): 2875-2880.
- [2] Lin, Y.C. (2013). Catalytic valorization of glycerol to hydrogen and syngas. *International Journal of Hydrogen Energy*, 38(6): 2678-2700.
- [3] Wang, X., Li, M., Wang, M., Wang, H., Li, S., Wang, S. and Ma, X. (2009). Thermodynamic analysis of glycerol dry reforming for hydrogen and synthesis gas production. *Fuel*, 88(11): 2148-2153.
- [4] Lee, H. C., Siew, K. W., Gim bun, J. and Cheng, C. K. (2013). Application of Cement Clinker as Ni-Catalyst Support for Glycerol Dry Reforming. *Bulletin of Chemical Reaction Engineering & Catalysis*, 8(2): 137-144.
- [5] Siew, K.W., Lee, H.C., Gim bun, J. and Cheng, C. K. (2014). Characterization of La-promoted Ni/Al₂O₃ catalysts for hydrogen production from glycerol dry reforming. *Journal of Energy Chemistry*, 23(1): 15-21.
- [6] Parizotto, N.V., Rocha, K.O., Damyanova, S., Passos, F.B., Zanchet, D., Marques, C.M.P. and Bueno, J.M.C. (2007). Alumina-supported Ni catalysts modified with silver for the steam reforming of methane: Effect of Ag on the control of coke formation. *Applied Catalysis A: General*, 330:12-22
- [7] Yu, M., Zhu, Y., Lu, Y., Tong, G., Zhu, K. and Zhou, X. (2015). The promoting role of Ag in Ni-CeO₂ catalyzed CH₄-CO₂ dry reforming reaction. *Applied Catalysis B: Environmental*, 165 (2015): 43-56.

- [8] Chen, M., Zhang, D., Thompson, L.T. and Ma, Z. (2011). Catalytic properties of Ag promoted ZnO/Al₂O₃ catalysts for hydrogen production by steam reforming of ethanol. *International Journal of Hydrogen Energy*, 36: 7516-7522.
- [9] Siew, K.W., Lee, H.C., Gimbin, J. and Cheng, C.K. (2013). Hydrogen production via glycerol dry reforming over La-Ni/Al₂O₃ catalyst. *Bulletin of Chemical Reaction Engineering & Catalysis*, 8(2): 160-166.
- [10] Diaz, G.C., Tapanes, N.C.O., Camara, L.D.T and Aranda, D.A.G. (2014). Glycerol conversion in the experimental study of catalytic hydrolysis of triglycerides for fatty acids production using Ni or Pd on Al₂O₃ or SiO₂. *Renewable Energy*, 64: 113-122
- [11] Guo, J., Hou, Z., Gao, J. and Zheng, X. (2008). Syngas production via combined oxy-CO₂ reforming of methane over Gd₂O₃-modified Ni/SiO₂ catalysts in a fluidized-bed reactor. *Fuel*, 87(7): 1348-1354.
- [12] Alhassan, F.H., Rashid, U., Al-Qubaisi, M.S., Rasedee, A. and Taufiq-Yap, Y.H. (2014). The effect of sulfate contents on the surface properties of iron-manganese doped sulfated zirconia catalysts. *Powder Technology*. 253: 809-813
- [13] Estellé, J., Salagre, P., Cesteros, Y., Serra, M., Medina, F., & Sueiras, J.E. (2003). Comparative study of the morphology and surface properties of nickel oxide prepared from different precursors. *Solid State Ionics*, 156: 233-243.
- [14] Acrotumapathy, V., Dai-Viet, N. V., Chesterfield, D., Cao, T. Tin, Siahvashi, A., Lucien, F.P., and Adesina, A.A. (2014). Catalyst design for methane steam reforming. *Applied Catalysis A: General*. 479: 87-102.
- [15] Jeong, H and Kang, M. (2010). Hydrogen production from butane steam reforming over Ni/Ag loaded MgAl₂O₄ catalyst. *Applied Catalysis B: Environmental*, 95(3-4): 446-455.
- [16] Siew, K.W., Lee, H.C., Gimbin, J. and Cheng, C. K. (2014). Production of CO-rich hydrogen gas from glycerol dry reforming over La-promoted Ni/Al₂O₃ catalyst. *International Journal of Hydrogen Energy*, 39: 6927-6936.

Selected and Revised Papers from The International Conference on Fluids and Chemical Engineering (FluidsChE 2015) (<http://fluidsche.ump.edu.my/index.php/en/>) (Malaysia, 25-27 November 2015) after Peer-reviewed by Scientific Committee of FluidsChE 2015 and Reviewers of BCREC