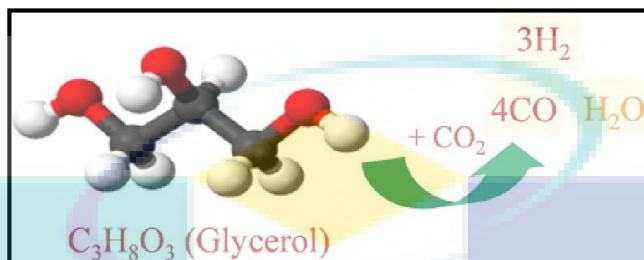**TEMPLATE**
BUKU PROFIL PENYELIDIKAN SKIM GERAN PENYELIDIKAN
FUNDAMENTAL (FRGS) FASA 1/2013 DAN FASA 2/2013

KINETICS AND SPECTROSCOPIC ANALYSES OF SYNGAS PRODUCTION FROM GLYCEROL STEAM REFORMING OVER 15WT%Ni/85WT% ALUMINA CATALYST

CHENG CHIN KUI (Leader)
Md. Maksudur Rahman Khan, Chin Sim Yee, Jolius Gimbun, Vo Nguyen Dai Viet
UMP/ FKKSA
chinkui@ump.edu.my
FRGS Field (Energy Security)

ABSTRACT (120 words)

Part of this project reports on the longevity of glycerol reforming into syngas, specifically the longevity of glycerol reforming over the lanthanum (La) promoted Ni/Al2O3 catalysts. The XRD results showed that the Ni particle was well-dispersed in the presence of La promoter. In addition, via the NH_3-TPD analysis, it was found that the La promoter has reduced the acidity of Ni catalyst which may have explained the mitigation of carbon laydown. It was determined that the 3.0 wt% La-promoted Ni/Al_2O_3 catalyst possessed the largest BET specific surface area of 97 $m^2 \cdot g^{-1}$. Consequently, it yielded the best catalytic longevity performance with conversion attained more than 90%, even after 72 h of reaction duration. Significantly, it can be confirmed that the presence of CO_2 during the glycerol reforming was essential in reducing carbon deposition, most likely via gasification pathway. This has ensured a stability of catalytic activity for a long reaction period (72 h)

1.   INTRODUCTION

Glycerol steam reforming has been touted as a very promising syngas (mixture of H_2 and CO) production route due to the burgeoning use of biodiesel as a liquid transportation fuel. In theory, H_2:CO ratio can be tailored to suit the desired downstream synthesis requirements. Moreover, the kinetics of this reaction is relatively unknown and further research is required.

2. RESEARCH METHODOLOGY

2.1. Catalyst preparation

The alumina support was purchased from Sigma Aldrich and air-calcined at 1073 K for 6 h. Subsequently, it was sieved to the particle size of 140–425 μm. For the catalyst preparation, an accurately weighed calcined alumina was mixed with $Ni(NO_3)_2.6H_2O$ and $La(NO_3)_3.6H_2O$ aqueous solutions and then magnetically-stirred for 3 h. It was later dried at 373 K for 12 h to obtain 3 wt% La-20 wt%Ni/77 wt% Al_2O_3 catalyst. The dried catalyst was then air-calcined at 1073 K for 5 h. Finally, it was ground and sieved to particle range of 140–250 μm for physicochemical characterization and reaction studies. For physicochemical property comparisons, 20 wt%Ni/80 wt% Al_2O_3 was also prepared employing the aforementioned procedures.

2.2. Catalyst characterization

Liquid N_2 with a cross-sectional area of 0.162 nm^2 was used as an adsorbate for adsorption/desorption cycles performed at 77 K for the determination of surface area and pore volume of solid catalysts. The crystalline structure was obtained via XRD diffraction analysis. The samples were irradiated by Ni-filtered CuK$_\alpha$ with a wavelength (λ) of 1.542 Å at 40 mA and 45 kV, and scanning from 10° to 80° at 4° min^{-1} employing Rigaku Miniflex II XRD instrument. The temperature-programmed reduction (TPR) profiles of freshly-calcined catalysts under H_2-blanket were carried out using IP Thermo Electron TPDRO series 1100. Furthermore, TGA unit (Q500-series model) was utilized to determine the non-isothermal oxide-metal formation from the decomposition of metal nitrate precursor of the uncalcined solid catalyst samples. For each analysis, the catalysts were ramped at 10, 15 and 20 K min^{-1} respectively to 1173 K and held for 1 h under the 50 ml min^{-1} of high purity air. For the used catalysts (collected post-reaction), the temperature-programmed-oxidation (TPO) profiles under O_2 blanket were obtained. TPO analyses were performed with ramping rate fixed at 10 K min^{-1} to reach 1173 K followed by an hour holding period. In addition, the morphology and bulk composition were examined with JEOL/JSM-7800F Thermal FESEM instrument. The accelerating voltage employed for the experiment was in the range of 5–15 kV.

2.3. Catalyst evaluation

All the glycerol dry reforming experiments were conducted in a stainless-steel fixed bed reactor (ID = 0.9525 cm; length = 40 cm) positioned inside a tubular furnace (cf. Fig. 1). Catalyst bed was supported by quartz wool on a stainless steel support welded to the internal wall of reactor tubing. The performance of each catalyst was evaluated from 923 to 1123 K and at 1 atm pressure. Liquid glycerol at a pre-determined flowrate was injected into the vaporizer upstream of the reactor with a HPLC pump (Lab Alliance Series 1). Prior to the testing, catalyst was reduced by H_2 (50 ml min^{-1} STP) for 2 h with heating ramp at 10 K min^{-1}. All the inlet gas flow rates were regulated by the electronic mass flow controller (Alicat Series). The total inlet flow was fixed at a weight-hourly-space-velocity (WHSV) of 3.6 × 10^4 ml g^{-1} h^{-1} STP. Reactor outlet gases were passed through a cold trap for liquid products capture and then over a drierite ($CaSO_4$) bed (8 mesh). The exit gas was collected into a 1-L Tedlar gas sampling bag. The composition of syngas produced was determined using Agilent gas chromatography (GC) with TCD capillary columns, HP-MOLSIV (Model No. Agilent 19095P; 30.0 m × 530 μm × 50.0 μm) and HP-Plot/Q column (Model No. Agilent 19095-Q04; 30.0 m × 530 μm × 40.0 μm). He was used as the carrier gas. Product stream flow rate was measured using a bubble meter. Glycerol consumption was calculated based on the atomic H balance for the

formation of atom H-containing gaseous species, *viz*. H_2 and CH_4. In order to approximate the plug flow conditions and minimize the back-mixing or channelling, the ratio of catalyst bed length to catalyst particle diameter (L/dp) was 80 and the ratio of inner diameter of reactor to particle diameter (dt/dp) was 71.5.

3.   LITERATURE REVIEW

Glycerol steam reforming has been touted as a very promising syngas (mixture of H_2 and CO) production route due to the burgeoning use of biodiesel as a liquid transportation fuel. Nevertheless, the voluminous publications seems to indicate a syngas yield with CO-lean composition [1-6], hence rendering this syngas unsuitable for gasoline production via Fischer-Tropsch synthesis. Most of the earlier studies have ascribed the unsuitable ratio to the water-gas-shift reaction. The use of CO_2, unlike the steam represents a new reforming route with significantly-reduced hydrogen source. Therefore, in theory H_2:CO ratio should be significantly lesser than the steam reforming pathway. Moreover, the kinetics of this reaction is unknown and further research is required.

The alumina supported nickel catalysts have been employed in numerous previous studies for hydrocarbon-based or biomass-based reformation into syngas [7-10]. However, Ni-based catalysts are prone to the carbon deposition. To mitigate carbon laydown, the promoters such as La-metal has been employed [11-15]. In particular, it has been reported before that the La promoted catalysts possessed higher catalytic reactivity and successfully reduced the carbon deposition. Significantly, the increase of anti-coking property has been attributed to the factors such as the size of particle as well as the redox properties of La . Therefore, in the current work, an alumina supported nickel catalyst promoted with 3.0 wt% La was synthesized and employed in glycerol reforming.

4.   FINDINGS

A 3 wt% La-promoted Ni/Al_2O_3 catalyst was prepared via wet co-impregnation technique and physicochemically-characterized. Lanthanum was responsible for better metal dispersion; hence higher BET specific surface area (96.0 $m^2 g^{-1}$) as compared to the unpromoted Ni/Al_2O_3 catalyst (85.0 $m^2 g^{-1}$). In addition, the La-promoted catalyst possessed finer crystallite size (9.1 nm) whilst the unpromoted catalyst measured 12.8 nm. Subsequently, glycerol dry reforming was performed at atmospheric pressure and temperatures ranging from 923 to 1123 K employing CO_2-to-glycerol ratio from zero to five. Significantly, the reaction results have yielded syngas as main gaseous products with H_2:CO ratios always below than 2.0 with concomitant maximum 96% glycerol conversion obtained at the CO_2-to-glycerol ratio of 1.67. In addition, the glycerol consumption rate can be adequately captured using power law modelling with the order of reactions equal 0.72 and 0.14 with respect to glycerol and CO_2 whilst the activation energy was 35.0 kJ mol^{-1}. A 72 h longevity run moreover revealed that the catalyst gave a stable catalytic performance.

5.   CONCLUSION

The results from glycerol dry reforming reaction over the 3 wt% La-promoted alumina supported Ni catalyst showed that copious amounts of H_2 and CO were produced with the attendant H_2:CO ratios which were always lower than 2.0. The syngas was primarily

from glycerol decomposition pathway. At reaction temperature of 1023 K, H_2:CO ratios were in between 2.0 and 0.7 at CO_2-to-glycerol ratio of zero to five. The increasing CO formation rate with concomitant decrease in H_2 formation rate with CO_2-to-glycerol ratio seems to suggest that the CO_2 has also taken part in other reaction pathways, *viz.* the reverse-water-gas shift and carbon gasification. Significantly, the longevity study has revealed a stable reaction even after 72 h of continuous reaction at 1023 K. Moreover, the high glycerol conversions ($X_g = 90\%$) and a stable H_2:CO (1.2–1.7) product ratio over the extended reaction duration have supported the proposition that syngas product from the current work is more suitable for Fischer-Tropsch synthesis compared to the glycerol steam reforming pathway.

ACHIEVEMENT

i) Name of articles/ manuscripts/ books published
   Journal of Energy Chemistry, 24(2015)366–373. Q2
   Renewable Energy, 74(2015)441-447. Q1

ii) Title of Paper presentations (international/ local)
   Nil

iii) *1 Masters graduated (Siew Kah Weng), 1 PhD on-going (Nor Shahirah Bt Mohd Nasir)*

iv) Awards/ Others

v) Others

REFERENCES

[1] Catal Today, 164 (2011), pp. 268–274

[2] J Anal Appl Pyrol, 91 (2011), pp. 316–322

[3] Fuel Process Technol, 91 (2010), pp. 520–530

[4] Catal Ind, 3 (2) (2011), pp. 189–191

[5] Catal Commun, 26 (2012), pp. 183–188

[6] Korean J Chem Eng, 28 (9) (2011), pp. 1859–1866

[7] Maejo Int J Sci Tech, 2 (1) (2008), pp. 140–149

[8] Catal Commun, 12 (2010), pp. 292–298

[9] J Catal, 223 (2004), pp. 432–443

[10] Catal Lett, 52 (1998), pp. 43–47

[11] J Nat Gas Chem, 12 (2003), pp. 183–188

[12] J Catal, 234 (2005), pp. 496–508

[13] Int J Hydrog Energy, 34 (9) (2009), pp. 5409–5416

[14] Int J Hydrog Energy, 36 (2011), pp. 14435–14446

[15] Appl Catal A Gen, 333 (1) (2007), pp. 90–95

APPENDIXES