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Steam reforming of glycerol over Ni/Al_2O_3 catalyst

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Glycerol steam reforming has been investigated in a 10-mm ID fixed-bed reactor containing Ni/Al_2O_3 catalyst using a wide range of the steam-to-carbon ratio ($1.1 \leq STCR \leq 4.0$) at temperatures between 723 K and 823 K. Physicochemical characterization revealed that the catalyst surface was populated by both weak and strong acid and basic sites although the catalyst appeared to have a net surface acidity. H_2, CO_2 and CO were the main gaseous products with H_2:CO_2 ratio at approximately 2.15 while H_2:CO ratio varied between 6.0 and 16.0 depending on the reactant feed composition. The specific glycerol consumption rate exhibited fractional reaction orders with respect to both glycerol (0.48) and steam (0.34) and activation energy of about 60 kJ mol^{-1}. Mechanistic considerations indicated that glycerol and steam underwent associative and dissociative adsorption, respectively on two different sites with the surface reaction being the rate-determining step. Additionally, carbon deposition has a positive dependency on the glycerol partial pressure, but it was inhibited in the presence of steam.

1. Introduction

The use of biomass as potential energy provider has gained more prominence in light of high crude oil price. Current world annual energy consumption derived from biomass (renewable source) only represents 14% with the rest coming from coal, electricity and gases [1]. The conversion of biomass to bio-fuels and other value-added chemicals proceeds via different chemistries including esterification, acid hydrolysis, gasification, thermal pyrolysis and steam reforming to syngas [2–10].

In recent years, a considerable amount of research effort has been invested in the area of aqueous or vapour-reformation of oxygenated hydrocarbons [11–22]. Theoretical consideration alone indicates that the reforming of oxygenated hydrocarbons is less energy-intensive than that of the hydrocarbons of similar carbon number. For example, the steam reforming of propane (C_3H_8) has $\Delta G^{\circ}_{823\,K} = 2.2$ kJ mol^{-1} ($K_{eq} = 0.73$) [23] while the steam reforming of glycerol ($C_3H_8O_3$) has a much lower value, $\Delta G^{\circ}_{823\,K} = -309.3$ kJ mol^{-1} ($K_{eq} = 4.2 \times 10^{19}$). For hydrocarbons, both carbon–oxygen and hydrogen–oxygen bonds have to be formed. In contrast, oxygenated fuels contain these bonds already and tend to react more easily [24].

Glycerol, a non-edible oxygenated hydrocarbon, is a by-product of biodiesel synthesis and currently over-supplied to the world market due to its limited commercial exploitation. As part of green process engineering (the principle of low-pollutant discharge), the conversion of waste glycerol to the high value-added products is a desirable loop closure step in biodiesel processing plants. Dumesic and co-workers have shown that H_2 may be produced from various carbohydrates employing aqueous phase reforming [25,26]. The present work examines the steam reforming of glycerol, thus, the pertinent reaction is:

$$C_3H_8O_3(g) + 3H_2O(g) \leftrightarrow 3CO_2(g) + 7H_2(g) \tag{1}$$

Reaction in Eq. (1) may be viewed as the combination of the glycerol decomposition (cf. Eq. (2)) and water–gas-shift reaction (cf. Eq. (3)):

$$C_3H_8O_3(g) \leftrightarrow 3CO(g) + 4H_2(g) \tag{2}$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \tag{3}$$

These may also be accompanied by other reactions as shown in Eqs. (4)–(10).

$$C_3H_8O_3(g) + 5H_2(g) \leftrightarrow 3CH_4(g) + 3H_2O(g) \tag{4}$$

$$CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g) \tag{5}$$

$$CO_2(g) + 4H_2(g) \leftrightarrow CH_4(g) + 2H_2O(g) \tag{6}$$

$$CO_2(g) + CH_4(g) \leftrightarrow 2CO(g) + 2H_2(g) \tag{7}$$

$$CH_4(g) \leftrightarrow 2H_2(g) + C(s) \tag{8}$$

$$C(s) + H_2O(g) \leftrightarrow CO(g) + H_2(g) \tag{9}$$

$$2CO(g) \leftrightarrow C(s) + CO_2(g) \tag{10}$$

Recent studies have shown that supported Ni catalysts exhibited good glycerol steam reforming activity [27–34]. From a practical standpoint, Ni-based catalyst has a strong appeal since it has been

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widely used in the petroleum and natural gas processing industries [35,36], hence, the rationale for its application to glycerol steam reforming as part of process development initiatives in commercial biosyngas production.

In the present paper, we report results of experimental studies to measure the rates of H_2, CO_2, CO and CH_4 production from glycerol over alumina-supported Ni catalyst. Rate data were collected at various temperatures and different steam-to-carbon ratios (STCR) and used to infer plausible mechanism governing the glycerol steam reforming reaction under typical experimental conditions.

2. Experimental

2.1. Catalysts preparation and characterization

The nickel nitrate for catalyst preparation was obtained from Sigma Aldrich. The support, γ-Al_2O_3, in pellet form was purchased from Saint Gobain NorPro (USA). All solutions for catalyst preparation throughout this study utilized distilled and deionised pure water generated by NANOpure Diamond UV unit (Barnstead International). Glycerol used (99.5% purity) was obtained from Ajax Finechem (Sydney, Australia). The catalyst was prepared via wet impregnation technique on the commercial alumina using $Ni(NO_3)_2{\cdot}6H_2O$ as the Ni precursor. The metal nitrate solution was added to crushed and sieved alumina particles (140–425 μm) which had been previously calcined at 873 K for 6 h. The resulting slurry was left under constant stirring for 3 h at room temperature. Impregnated catalyst was oven-dried at 403 K for 12 h and cooled to room temperature. Subsequently, the dried catalyst was sieved, ground and calcined in flowing dry air at 873 K for 4 h using a heating rate of 5 K min^{-1}. Calcined catalyst (15 wt.% Ni/Al_2O_3) was finally sieved to 90–140 μm particle size for reaction study.

The BET surface area and pore-size distribution of the calcined sample were determined from N_2 physisorption at 77 K in a Quantachrome Autosorb unit. Prior to the analysis, the fresh catalyst was pre-treated under vacuum condition at 573 K for at least 3 h. Powder X-ray diffraction (XRD) pattern of the calcined catalyst was obtained on X'pert Pro Multi-purpose X-ray Diffraction (MPD) system using Cu Kα radiation ($\lambda = 0.154$ nm) operated at 40 mA and 45 kV. The diffractogram was analysed using X'Pert ScorePlus software. Crystallite size was calculated using Scherrer equation, $d = 0.94\lambda/(\beta\cos\theta)$, where d is the crystallite size, λ is the wavelength of the radiation, β is the full-width at half maximum (FWHM) of the diffraction peak and θ is the diffraction half angle.

The metal dispersion and acid–base properties of the catalyst were obtained using Micromeritics 2910 unit (Micromeritics Instrument Corp.). The calcined catalyst was pre-reduced in situ at 873 K using pure H_2 at a ramping of 1 K min^{-1}. For the pulse H_2-chemisorption runs, the system was purged for 30 min with N_2, and then cooled down to room temperature. Subsequently, the temperature was increased at a constant rate of 2 K min^{-1} to 383 K in 40 ml min^{-1} flow of 10% H_2 in N_2 carrier gas, and held there for 30 min to ensure stable background TCD signal. Finally, a series of 1-cm^3 hydrogen doses at periodic intervals of 5 min were injected into the solid catalyst. The composition of hydrogen-containing gas exiting the system was continuously monitored by the TCD detector. The pulse injection was typically stopped after 13 cycles. Data from H_2 chemisorption was used to estimate metal dispersion. The acid–base properties of the catalyst were evaluated from temperature-programmed desorption (TPD) employing NH_3 and CO_2 as probe gases, respectively. NH_3 adsorption was performed at 423 K using 10% NH_3 in N_2 balance, while CO_2 adsorption was carried out using 10% CO_2 in He at 323 K. Adsorption was carried out for 1 h to ensure complete coverage of the catalyst surface with the probe molecules followed by purging at the same adsorption temperature with carrier gas (N_2 or He) for 30 min at 40 ml min^{-1}. The purging step was implemented to ensure removal of any excess or physically bound NH_3 or CO_2 molecules. Temperature-programmed desorption was then commenced at a constant heating rate up to 873 K for NH_3-TPD or 973 K for CO_2-TPD and then maintained at that level for 60 min. During this step, the outlet stream was monitored by a TCD detector and recorded. The sample was then cooled to 423 K for NH_3-TPD or 323 K for CO_2-TPD, and then allowed to equilibrate before re-saturating the surface with NH_3 or CO_2 for 60 min, followed by purging for 60 min. The cycle was then repeated on each occasion with a different heating rate value, The determination of heat of desorption, $-\Delta H_{\text{desorption}}$ from TPD experiments is given by:

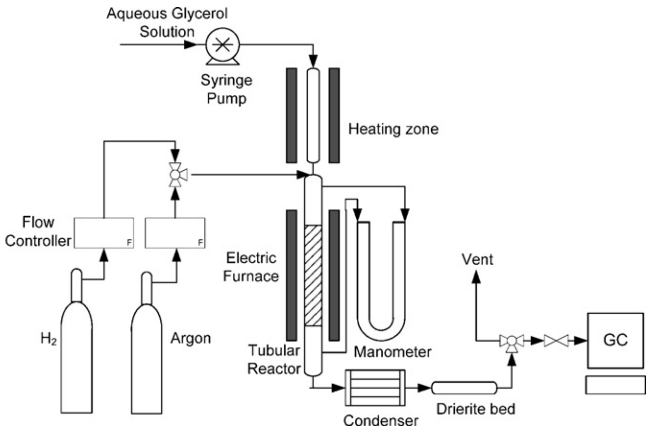

Fig. 1. Schematic diagram of the experimental setup.

$$\ln\frac{\beta}{T_p^2} = \frac{(-\Delta H_{\text{desorption}})}{RT_p} + \ln\frac{(-\Delta H_{\text{desorption}})A_{\text{sat}}}{RC} \qquad (11)$$

where β is the heating rate (K min^{-1}), $-\Delta H_{\text{desorption}}$ is the heat of desorption (kJ mol^{-1}), R is the universal gas constant, T_p is the peak temperature (K), A_{sat} is quantity adsorbed at saturation and C is the constant related to the desorption rate. From Eq. (11), a plot of $\ln\beta/{T_p}^2$ against $1/T_p$ will produce a linear slope $(-\Delta H_{\text{desorption}}/R)$ from which the value of heat of desorption $(-\Delta H_{\text{desorption}})$ of adsorbed gas species may be determined.

Thermogravimetric analysis of the calcination and reduction characteristics of fresh catalyst was performed using a ThermoCahn TG 2121 system. Temperature-programmed calcination was carried out at 873 K, for 5 h, with heating rates of 5, 10 and 20 K min^{-1} using 55 ml min^{-1} high purity air. Temperature programmed reduction (TPR) of the oxide catalyst was performed up to 973 K, for 5 h, at 5 K min^{-1} with 50% H_2/Ar mixture (55 ml min^{-1}).

2.2. Experimental apparatus and catalytic activity evaluation

Glycerol steam reforming reaction experiments were conducted in a stainless-steel fixed bed reactor with 10 mm *i.d.* (cf. Fig. 1) at atmospheric pressure and reaction temperature of 723–823 K. Catalyst bed was supported by quartz wool at the bottom end of the reactor. Glycerol–water mixture with composition 30–60 wt.% glycerol (corresponding to the steam-to-carbon ratio, STCR of 1.1–4.0) was used as feed to ensure stoichiometrically excess steam. The mixture was pumped with a 50 ml motorised syringe (Razel Scientific Instruments, model A-99) directly into the vaporizer upstream of the reactor (at 773 K), and then downwards into the reactor after being mixed with inert Ar to a total flow rate of 5.0×10^4 ml g_{cat}^{-1} h^{-1}. Prior to reaction, the catalyst was reduced in flowing H_2 (50 ml min^{-1} STP) for 2 h. Heating rate was controlled at 10 K min^{-1}. The bed pressure drop was always below 3 kPa as