

KINETICS OF GLYCEROL STEAM REFORMING CATALYZED BY BIMETALLIC Co-Ni/Al₂O₃

Chin-Kui Cheng and A. A Adesina*

Reactor Engineering and Technology Group, School of Chemical Sciences and Engineering
University of New South Wales, Sydney, New South Wales 2052, Australia

Summary

The steam reforming of glycerol (waste from biodiesel synthesis) has been studied over Co-Ni/Al₂O₃ catalyst at atmospheric pressure in the range 773–823 K. H₂, CO₂, CO and CH₄ were the primary products. The kinetics of each product formation has a positive fractional order dependency on both glycerol and steam partial pressure with the exception of CO which has a mild negative order (−0.07) with respect to steam. A dual-site Langmuir-Hinshelwood mechanism adequately captured the rate-reactant composition behaviour. Post-reaction analysis of the used catalyst also revealed significant carbon deposition especially at high glycerol : steam ratios (> 5). Even so, catalyst activity restoration to nearly nascent level was obtained after 2 cycles of TPO (in air) – TPR (in H₂).

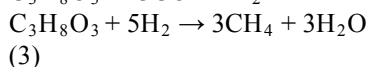
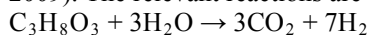
Keywords

Sustainability, Hydrogen production, Alternate energy, Reaction path analysis

Introduction

The use of renewable feedstock is important especially in the context of securing sustainable use of energy and protecting the environment for future generations. Considerable effort has been devoted into applying green catalytic process to convert renewable feedstock such as biomass into commodity chemicals and clean bio-fuels. In particular, glycerol (1,2,3-propanetriol) is produced in excess as by-product during biodiesel synthesis, representing approximately 10wt% of the total product. In an effort to add value to glycerol as precursor for renewable and clean energy production, it was steam reformed to produce H₂, CO and CO₂ which are important intermediates for the manufacture of a variety of industrial chemicals.

There is however, a paucity of information on the kinetics of glycerol reforming. Simonetti et al.¹ showed that CO turnover frequency was fractional order with respect to glycerol (0.1–0.2) with activation energy of 60–90 kJ mol^{−1} over carbon-supported Pt and Pt-Rh catalysts. Adhikari et al.² reported activation energy of 103 kJ mol^{−1} and reaction order of 0.233 over Ni/CeO₂ catalyst. In the current study, the kinetics of glycerol reforming over alumina-supported bimetallic Co-Ni catalyst has been examined. The catalyst has been found effective for alkane reforming (Hardiman et al.³, 2005; Althenayan et al.⁴, 2009). The relevant reactions are



Experimental

Co-Ni/Al₂O₃ was prepared via co-impregnation of cobalt and nickel nitrates on γ -alumina which had been preheated at 873 K for 6 h. BET surface area was obtained from N₂ adsorption on the Quantachrome Autosorb-1 unit. The metal catalyst dispersion and surface area was determined from Micromeritics ASAP 2000. Temperature-programmed (oxidation (TPO) and reduction (TPR)) experiments were performed in a ThermoCahn TG-2121 TGA unit. Reaction runs were conducted in a stainless-steel fixed bed reactor under minimal influence from physical transport limitations.

Results and Discussion

Table 1 shows the comparison between physicochemical properties of calcined Al₂O₃ and impregnated Co-Ni/Al₂O₃. The BET area and pore volume for the fresh catalyst was smaller than the original (but similarly calcined) alumina support due to pore blockage by the metal oxide particles. H₂ chemisorption data revealed a metal dispersion of 0.67% with metal nanoparticles (40 nm).

Table 1 Physicochemical properties of catalyst

Properties	Calcined Al ₂ O ₃	Co-Ni/Al ₂ O ₃
BET surface area (m ² g ^{−1})	210.6	180.5
Pore volume (cm ³ g ^{−1})	0.6876	0.5899
Pore diameter (Å)	130.6	130.7
Dispersion (%)	-	0.67
Metal surface area (m ² g ^{−1})	-	20.01
Metal particle diameter (nm)	-	40.07

NH₃-TPD revealed two distinct acidic sites on Co-Ni/Al₂O₃ catalyst with heat of desorption, ΔE_d of 35.5 kJ mol^{−1} (523–573 K) and 87.3 kJ mol^{−1} (700–750 K)

* To whom all correspondence should be addressed. Tel.: +61-2-9385-5268. Fax: +61-2-9385-5966. E-mail: a.adesina@unsw.edu.au

respectively while CO₂-TPD also showed two different basic sites measuring 29.1 kJ mol⁻¹ (400–420 K) and 52.9 kJ mol⁻¹ (650–840 K).

Temperature-programmed calcination and H₂ reduction data from TGA unit were analyzed with the Coats-Redfern equation based on the Avrami-Erofeev model. Activation energy for the oxide formation was estimated as 44 kJ mol⁻¹. Indeed, characterization results showed that physicochemical attributes of the bimetallic system appears to be the sum of the metal composition-average of the same property for the constituent monometallic oxide, thus,

$$\lambda_{\text{Ni-Co}} = x_{\text{Ni}}\lambda_{\text{Ni}} + x_{\text{Co}}\lambda_{\text{Co}} \quad (4)$$

where λ_i is an intrinsic physicochemical property, x_i is the mass composition, viz.; 0.333 for Co and 0.667 for Ni.

Steady-state analysis of glycerol steam reforming carried out at reaction temperature of 823 K showed the formation of H₂, CO₂, CO and CH₄ as major products, with CO₂ formation rate being the fastest. The glycerol steam reforming rate was fitted to the power-law expression

$$-r_{i,SR} = k_{rxn} P_{\text{glycerol}}^{\alpha_i} P_{\text{steam}}^{\beta_i} \quad (5)$$

where α_i and β_i are the reaction orders with respect to glycerol and steam, estimated as 0.286 and 0.317 respectively. As Fig. 1 shows, good parity was obtained between predicted and experimental rate data.

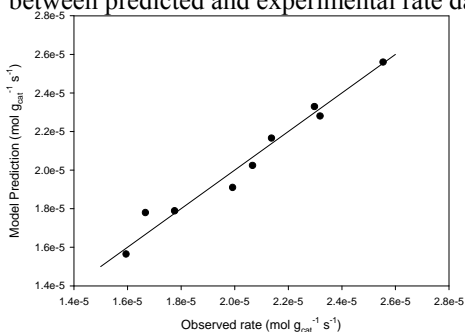


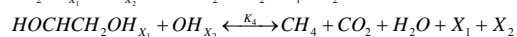
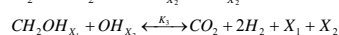
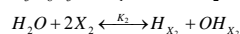
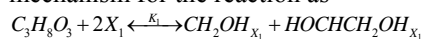
Figure 1
Parity Plot
for
reforming
rate

Nonlinear regression analysis was also performed on the formation rate of products using similar power-law model to glycerol steam reforming rate (cf. Eqn. (5)) where $i = \text{H}_2, \text{CO}_2, \text{CO}$ and CH_4 . The parameter estimates are provided in Table 2.

Table 2 Estimates of parameters for glycerol steam reforming (nonlinear least squares)

Major product	$k (\times 10^6)$ mol g _{cat} ⁻¹ s ⁻¹ kPa ^{-($\alpha+\beta$)}	α	β
H ₂	18.43	0.2563	0.2738
CO ₂	4.84	0.2678	0.4036
CO	10.95	0.3051	-0.0696
CH ₄	0.1587	0.570	0.3884

Additional data in fact show a plausible dual-site mechanism for the reaction as



where X_1 is the site for glycerol adsorption while X_2 is the site for steam adsorption. This leads to

$$r_i = \frac{k_{rxn} \sqrt{P_{\text{C}_3\text{H}_8\text{O}_3} P_{\text{H}_2\text{O}}}}{(1 + \sqrt{K_1 P_{\text{C}_3\text{H}_8\text{O}_3}})(1 + 2\sqrt{K_2 P_{\text{H}_2\text{O}}})}, \quad i = \text{products or reactants} \quad (6)$$

Post-reaction total organic carbon analysis of the used catalyst samples revealed variation in both BET area and TOC content as functions of reaction conditions. Fig. 2 shows the 3D-plot for TOC content from whence it is apparent that regardless of the steam partial pressure, high glycerol content in the feed favoured carbon deposition. Fig. 3, however, suggests that a double cycle TPO-TPR-TPO-TPR regenerative procedure can restore its physicochemical and activity levels close to the nascent state. Detailed analysis and implications for reactor operation are provided in the full manuscript.

Figure 2 TOC concentration (%) as function of partial pressure

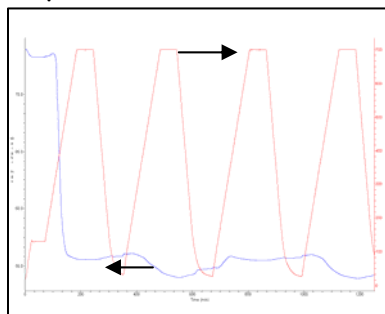


Figure 3 Derivative weight changes of spent catalyst employing TPO-TPR-TPO-TPR cycle

Conclusions

The present study provided analysis of the kinetic behavior of glycerol steam reforming over a bimetallic Co-Ni/Al₂O₃ catalyst. TOC analysis showed that carbon deposition was a strong function of glycerol partial pressure.

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