SYNTHESIS GAS PRODUCTION FROM GLYCEROL STEAM REFORMING OVER ALUMINA SUPPORTED BIMETALLIC Co-Ni CATALYST

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ABSTRACT

Glycerol, a carbohydrate substrate, is produced in large quantities by the burgeoning biodiesel industry. The opportunity to produce synthesis gas (H_2/CO mixture) from this bioprocessing residue by steam reforming is a potential advantage in the future integration of biorefineries with current petrochemical plants since syngas may be converted to clean fuels via the Fischer-Tropsch process.

In this work, alumina supported catalysts comprising of bimetallic Co-Ni, alkaline earth oxide (MgO, CaO, SrO, BaO) doped Co-Ni and lanthanide oxide (CeO_2, Pr_2O_3, Sm_2O_3) doped Co-Ni, were synthesized by wetness co-impregnation technique and assessed in a fixed-bed reactor over steam-to-glycerol ratio of $3.0<\mathrm{STGR}\leq 12.0$ and temperatures of 773 to 823 K.

Kinetic examination of glycerol steam reforming over Co-Ni catalyst gave an activation energy of 63.3 kJ mol^{-1}. Mechanistic models were evaluated on the basis of statistical adequacy and thermodynamic consistency. These criteria revealed that the reaction was best characterized by a Langmuir-Hinshelwood (LH) bimolecular model with associative adsorption of glycerol and steam on two different catalytic sites. Carbon deposition during the reaction appeared to be responsible for the loss in surface area and pore volume of the used catalysts. At least two types of carbonaceous species were evidenced on the catalyst – a more reactive atomic carbon species deposited on the metal-support interface while a less reactive carbon of the polymeric nature, was located on the alumina support.

Interestingly, the acidity of doped Co-Ni catalysts decreased with Pauling electronegativity of the dopants. In addition, the metal surface area of all doped catalysts (0.8 to 1.1 $\mathrm{m}^2\ \mathrm{g}_{cat}^{-1}$) was considerably higher than the undoped catalyst (0.7 $\mathrm{m}^2\ \mathrm{g}_{cat}^{-1}$) while lanthanide oxide doped-catalysts also increased the degree of reducibility of Co-Ni catalyst. This study also disclosed that although carbon deposition is inevitable, lanthanide oxide-doped catalysts decreased the carbon laydown (8–20%). The carbon-resilient property of these catalysts was further substantiated through longevity tests.

In the final phase of the work, H_2 and CO_2 were individually added as carbon gasifying agents during the reforming. In particular, CO_2 could be tuned at selected partial pressure and temperature to produce a syngas with more suitable H_2:CO ratio for the Fischer-Tropsch synthesis.

LIST OF PUBLICATIONS

Original research articles:

1. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Steam reforming of glycerol over Ni/Al_2O_3 catalyst", *Catal. Today*, [doi:10.1016/j.cattod.2011.07.011], Article in press (2011).
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3. C.K. Cheng, S.Y. Foo and A.A. Adesina, "H_2-rich synthesis gas production over Co/Al_2O_3 catalyst via glycerol steam reforming", *Catal. Commun.*, **12**(4), pp. 292–298 (2010).
4. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Glycerol steam reforming over bimetallic Co-Ni/Al_2O_3", *Ind. Eng. Chem. Res.*, **49**(21), pp. 10804–10817 (2010).
5. C.K. Cheng and A.A. Adesina, "Evaluation of Co-Ni/Al_2O_3 supported catalysts for glycerol reforming", *Int. J. Chem. Eng.*, **2**(2–3), pp. 235–245 (2009).
6. C.K. Cheng, S.Y. Foo, A.A. Adesina, E.M. Kennedy and B.Z. Dlugogorski, "Glycerol steam reforming over Co-Ni/Al_2O_3: Effect of alkaline earth and lanthanide oxides on catalytic performance", Biomass Bioenergy, Submitted for publication (2011).
7. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Thermodynamic analysis of glycerol steam reforming in the presence of CO_2 and H_2 as carbon gasifying reactants", In preparation (2011).

Peer-reviewed conference proceedings:

8. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Thermodynamic analysis of glyceol steam reforming in the presence of CO_2 and H_2 as carbon gasifying agents", 8th European Congress of Chemical Engineering (ECCE), September 25–29 2011, Berlin Germany.
9. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Unsteady-state kinetic analysis of glycerol steam reforming over alumina-supported nickel catalyst", 8th European Congress of Chemical Engineering (ECCE), September 25–29 2011, Berlin Germany.

10. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Deactivation behaviour of modified Co-Ni/Al_2O_3 catalysts for glycerol steam reforming", 22nd North American Catalysis Society Meeting (NAM), June 5–10 2011, Detroit MI USA.
11. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Application of Co/Al_2O_3 catalyst in steam reforming of glycerol", CHEMECA 2010, Sept. 26–29 2010, Adelaide Australia.
12. M.S. Johari, C.K. Cheng and A.A. Adesina, "Steam reforming of glycerol over alkali-promoted Co-Ni/Al_2O_3 catalysts", CHEMECA 2010, Sept. 26–29 2010, Adelaide Australia.
13. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Promotional effect of alkaline earth metal and lanthanide in alumina supported Co-Ni catalyst for glycerol steam reforming", 6th International Conference on Environmental Catalysis (ICEC 2010), Sept. 12–15 2010, Beijing China.
14. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Carbon deposition kinetics during glycerol steam reforming over Co-Ni/Al_2O_3 catalyst", 6th Tokyo Conference on Advanced Catalytic Science and technology & 5th Asia Pacific Congress on Catalysis (TOCAT6/APCAT5), July 18–23 2010, Sapporo Japan.
15. C.K. Cheng, S.Y. Foo and A.A. Adesina, "Kinetics of glycerol steam reforming catalyzed by bimetallic Co-Ni/Al_2O_3", 21st International Symposium on Chemical Reaction Engineering (ISCRE 21), June 13–16 2010, Philadelphia PA USA.
16. C.K. Cheng and A.A. Adesina, "Evaluation of Ni-Co/Al_2O_3 supported catalysts for glycerol steam reforming: Solid-state kinetic analysis", CHEMECA 2009, Sept. 27–29 2009, Perth Australia.
17. C.K. Cheng and A.A. Adesina, "Thermodynamic analysis of glycerol steam reforming for H_2 production", CHEMECA 2009, Sept. 27–29 2009, Perth Australia.

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NOMENCLATURE

A = pre-exponential factor (mol m^{-2} s^{-1} kPa$^{-(\beta+\gamma)}$)

AEO = alkaline earth oxide

C = concentration of acid and basic sites (μmol m^{-2})

$d_{crystallite}$ = crystallite size (nm)

d_p = particle size (μm)

d_t = diameter of reactor (m)

E_A = activation energy

K_G = glycerol adsorption constant (kPa^{-1})

K_W = steam adsorption constant (kPa^{-1})

k_{rxn} = reaction rate constant (mol m^{-2} s^{-1} kPa$^{-(\beta+\gamma)}$)

L = catalyst bed length (m)

LO = lanthanide oxide

MARI = most abundant reactive intermediates

P_i = partial pressure

PR = product ratio

R = universal gas constant (8.314 J mol^{-1} K)

$\hat{r}$ = specific reaction rate (mol m^{-2} s^{-1})

S_i = selectivity of product

STGR = steam to glycerol ratio

T = absolute temperature (K)

TOC = total organic carbon (%)

TPO = temperature-programmed oxidation

TPR = temperature-programmed reduction

w = instantaneous weight (g)

w_f = final weight (g)

w_i = initial weight (g)

Y_i = yield of product

Greek

α = transient solid conversion

β = order of reaction

ΔH = enthalpy changes (kJ mol^{-1})

ΔS = adsorption entropy (J mol^{-1} K^{-1})

γ = order of reaction

λ = wavelength (nm)

φ = full-width at half maximum of diffractogram

θ = diffraction angle

ψ = heating rate (K min^{-1})

These descriptions are valid unless otherwise stated in the text