SYNGAS PRODUCTION FROM ETHANOL DRY REFORMING OVER La AND Ce PROMOTED Co/Al_2O_3 CATALYSTS

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I hereby declare that the work in this thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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ABSTRAK

Pembaharuan kering etanol telah muncul sebagai laluan yang berpontesi dalam menukarkan etanol diperbaharui dan gas rumah hijau yang tidak diingini (CO_2) kepada syngas yang diiktiraf oleh industri. Syngas boleh digunakan sebagai bahan mentah bagi pengeluaran metanol hiliran dan sintesis Fischer-Tropsch. Walau bagaimanapun, pemendapan karbon semasa proses EDR menyebabkan penyahaktifan pemangkin. Oleh itu, pemangkin berasaskan Co telah disediakan dengan penggalak La dan Ce menggunakan kaedah pengisitepuan basah dan menyelidik sifat fizikokimia 10%Co/Al_2O_3 serta menilai kesan parameter operasi terhadap aktiviti pemangkin untuk tindak balas pembaharuan kering etanol dalam reaktor kuarza turus tetal. Di samping itu, kesan kandungan ceria yang berlainan (dari 2% hingga 5%) telah dinilai dalam tindak balas pembaharuan kering etanol pada 973 K dan juga pada keadaan stoikiometri. Hasilnya menunjukkan bahawa 3% pemangkin Ce-penggalak menunjukkan aktiviti dan rintangan tertinggi terhadap pemendapan karbon. Pemangkin dengan penggalak 3%Ce dibandingkan dengan pemangkin dengan penggalak 3%La dan pemangkin tanpa penggalak pada nisbah C_2H_5OH:CO_2 berbeza iaitu 2.5:1-1:2.5 dan pada suhu tindak balas 923 hingga 973 K. 3%La terhadap 10%Co/Al_2O_3 telah meningkatkan penyebaran logam yang tinggi (kira-kira 16.6%) dan kadar pengurangan (98.3%). Selain itu, penukaran C_2H_5OH dan CO_2 meningkat sehingga 150.6% dan 55.5%, masing-masing terhadap peningkatan suhu tindak balas dari 923 hingga 973 K disebabkan oleh sifat endotermik tindak balas pembaharuan kering etanol. Di samping itu, penukaran kedua-dua reaktan telah meningkat dengan peningkatan tekanan separa CO_2 daripada 20 hingga 50 kPa untuk semua pemangkin, sementara, penukaran reaktan menurun dengan peningkatan tekanan separa C_2H_5OH. Dalam pembaharuan kering etanol, nisbah H_2/CO selalu lebih tinggi daripada satu disebabkan adanya tindak balas sampingan (penyahhidrogenan etanol). Tanpa mengira keadaan tindak balas, pemangkin dengan penggalak La menjadi pemangkin optimum dari segi penukaran C_2H_5OH dan CO_2. Pertukaran reaktan meningkat dalam susunan; 10%Co/Al_2O_3 < 3%Ce-10%Co/Al_2O_3 < 3%La-10%Co/Al_2O_3 pemangkin pada semua keadaan operasi. Pemangkin 10%Co/Al_2O_3 dan 3%La-10%Co/Al_2O_3 telah diuji untuk ujian lanjutan masa dalam pembaharuan kering etanol dan menunjukkan bahawa pemangkin 3%La-10%Co/Al_2O_3 mempamerkan aktiviti yang tinggi berbanding pemangkin tanpa penggalak pada keadaan stoikiometri untuk 72 h dan 973 K. Tambahan pula, pemangkin dengan penggalak La telah diperbaharui dengan tiga kitaran dan diplot dengan masa pada komposisi suapan stoikiometri selama 90 h dan T = 973 K. Hasilnya mendapati bahawa 3%La mempamerkan prestasi pemangkin tertinggi dari segi aktiviti dan pemendapan karbon berbanding pemangkin yang tanpa penggalak. Sifat heterogen bagi karbon mendap (karbon nanofilament dan grafit) pada permuakaan pemangkin yang telah digunakan adalah jelas. Selain itu, penggalak 3%La mengurangkan pembentukan karbon dari 51.49% kepada 30.06%. Di samping itu, pengiraan undang-undang kuasa mendapati bahawa tenaga pengaktif untuk pemangkin dengan penggalak Ce dan penggalak La (kira-kira 98 kJ mol^{-1} untuk penggalak Ce dan 93 kJ mol^{-1} untuk penggalak La) adalah lebih kecil berbanding 10%Co/Al_2O_3 tanpa penggalak dengan lebih kurang 108 kJ mol^{-1}). Ekspresi kadar Langmuir-Hinshelwood juga mencadangkan bahawa kedua-dua reaktan (C_2H_5OH dan CO_2) dikaitkan secara berserat pada satu tapak pemangkin dengan tenaga pengaktifan sebanyak 106 kJ mol^{-1}. Kajian ini menunjukkan bahawa syngas yang dihasilkan daripada pemangkin berasaskan Co dengan nisbah H_2/CO yang wajar boleh digunakan secara langsung dalam sintesis Fischer-Tropsch tanpa keperluan penyesuaian komposisi bahan.

ABSTRACT

Ethanol dry reforming has been emerged as a promising route for converting the renewable ethanol and undesirable greenhouse gas (CO_2) to industrially recognized syngas. It can also be used as feedstock for downstream methanol production and Fischer-Tropsch synthesis. However, the carbonaceous deposition during ethanol dry reforming process leads to deactivation of the catalyst. Therefore, the Co-based catalysts were prepared with La and Ce promoters using a wet impregnation method and investigated the physicochemical attributes of 10%Co/Al_2O_3 as well as evaluated the effect of operating parameters on the catalytic activity of ethanol dry reforming reaction in a quartz fixed-bed reactor. In addition, the effect of different ceria loading (from 2% to 5%) was evaluated for ethanol dry reforming reaction at 973 K and stoichiometric conditions. The results revealed that the 3% Ce-promoted catalyst showed the highest activity and resistance from coke deposition. The 3%Ce-promoted catalyst was compared with 3%La-promoted and unpromoted catalyst at different C_2H_5OH:CO_2 ratios of 2.5:1-1:2.5 and reaction temperature of 923 to 973 K. The 3%La over bare 10%Co/Al_2O_3 significantly improved the metal dispersion (about 16.6%) and degree of reduction (98.3%). Besides, C_2H_5OH and CO_2 conversions increased up to 150.6% and 55.5%, respectively with growing reaction temperature from 923 to 973 K due to the endothermic character of ethanol dry reforming reaction. In addition, both reactant conversions increased with rising CO_2 partial pressure from 20 to 50 kPa for all catalysts while, the decreasing reactant conversions with increasing C_2H_5OH partial pressure. In ethanol dry reforming runs, H_2/CO ratio was always higher than unity due to the presence of side reaction (ethanol dehydrogenation). Irrespective of reaction conditions, La-promoted catalyst seemed to be the best catalyst in terms of both C_2H_5OH and CO_2 conversions. Reactant conversions of catalysts increased in the order; 10%Co/Al_2O_3 < 3%Ce-10%Co/Al_2O_3 < 3%La-10%Co/Al_2O_3 catalysts for all operating conditions. The 10%Co/Al_2O_3 and 3%La-10%Co/Al_2O_3 catalysts were examined for longevity tests in ethanol dry reforming and showed that the 3%La-10%Co/Al_2O_3 catalyst exhibited the high catalytic activity than that of unpromoted catalyst at stoichiometric condition for 72 h and 973 K. Furthermore, La-promoted catalyst was regenerated with three cycles and plotted with time-on-stream at stoichiometric feed composition for 90 h and T = 973 K. The results found that the 3%La exhibited the highest catalytic performance in terms of activity and carbon deposition compared to the counterpart unpromoted catalyst. The heterogeneous nature of deposited carbons (carbon nanofilament and graphite) on spent catalyst surface was evident spent catalyst characterizations. Additionally, the 3% La promoter reduced the carbon formation from 51.49% to 30.06%. Furthermore, from the power law expression found that the activation energy for Ce- and La-promoted catalysts (about 98 kJ mol^{-1} and La-promoted 93 kJ mol^{-1}, respectively) was smaller compared to unpromoted 10%Co/Al_2O_3 catalyst (about 108 kJ mol^{-1}). The Langmuir-Hinshelwood rate expressions also suggested that both reactants (C_2H_5OH and CO_2) were associatively adsorbed on single-site of catalyst with corresponding activation energy of about 106 kJ mol^{-1}. This study suggests that the syngas produced over Co-based catalysts with desirable H_2/CO ratios could be used directly in Fischer-Tropsch synthesis without the requirement of adjusting feedstock composition.

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LIST OF SYMBOLS

A	Pre-exponentioal factor
B	The line broadening at half the maximum intensity in radian (FWHM)
b	Inert solids fraction of catalyst bed
c	The adsorbate constant
C_{Ab}	Bulk gas phase concentration of component A
C_{AS}	Concentration of C_2H_5OH on the catalyst surface
C_D	Amorphous carbon percentage
C_p	Specific heat capacity of gases
C_{pg}	Specific heat capacity of feed gas mixture at constant pressure
C_α	Carbon formed via decomposition of hydrocarbon
C_β	Carbon formed via dissociation of CO
C_C	Graphitic carbon
C_γ	Carbides
C_υ	Whisker-like or vermicular carbon
D	Dispersion
D_{eff}	Effective diffusivity
D_g	Diffusivity
d_p	Average particle diameter
E_A	Activation energy
F	Flow rate
h	Heat transfer coefficient
j_D	Colburn’s mass transfer factor
k_c	Mass transfer coefficient
L_a	Size of crystallite

n_m	Number of molecules adsorbed
N	Avogadro’s number
n	Reaction order
M_{ad}	The adsorbed moleculars weight
P	Pressure of gas
Pr	Prandtl number
P_s	Saturation pressure of adsorbed gas
R	Universal gas constant
R_t	Reactor tube radius
r	Rate of production
$r_{\exp}$	Reaction rate
r_p	Actual radius
R_p	Catalyst particle radius
S_A	Total surface area of catalyst
Sc	Schmidt number
T_b	Boiling point
t_{ads}	Adsorbed layer thickness
U	Superficial gas velocity
V_a	Volume of gas adsorbed
W_{cat}	Weight of the catalyst
y	Mole fraction of component gases
λ	Wavelength
θ	Bragg angle
ρ_b	Bulk density of catalyst bed
ρ_c	Catalyst pellet density
ρ_g	The gas mixture density
σ_c	Constraction factor

μ_g	Viscosity of the gas mixture
ω_p	Catalyst pellet porosity
$\tilde{\tau}$	Tortuosity
λ_p	Thermal conductivity of catalyst pellet
ε	Void fraction
ΔH	Heat of reaction
ΔG	Gibbs free energy

LIST OF ABBREVIATIONS

ATR	Autothermal reforming
BET	Brunauer-Emmett-Teller
CNF	carbon nanofilament
EDR	Ethanol dry reforming
EDX	Energy-dispersive x-ray
ESR	Ethanol steam reforming
FTS	Fischer-Tropsch synthesis
MARI	Most abundant reactive species
MDR	Methane dry reforming
MT	Metric ton
GC	Gas chromatography
GHSV	Gas hourly space velocity
GTL	Gas to liquid
O.D.	Outer diameter
OSRE	Oxidative steam reforming of ethanol
POX	Partial oxidation
SEM	Scanning electron microscopy
SR	Steam reforming
TCD	Thermal conductivity detector
TEM	Transmission electron microscopy
TPC	Temperature-programmed calcination
TPD	Temperature-programmed desorption
TPR	Temperature-programmed reduction
TOS	Time-on-stream
TPO	Temperature-programmed oxidation
TGA	Thermogravimetric analysis
WGS	Water-gas shift
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

REFERENCES

Adhikari, S., Fernando, S., & Haryanto, A. (2007). Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts. *Catalysis Today*, 129(3–4), 355–364.

Aditiya, H. B., Chong, W. T., Mahlia, T. M. I., Sebayang, A. H., Berawi, M. A. and Nur, H. (2016). Second generation bioethanol potential from selected Malaysia's biodiversity biomasses: A review. *Waste Management*, 47(1), 46–61.

Akdim, O., Cai, W., Fierro, V., Provendier, H., Veen, A. van, Shen, W. and Mirodatos, C. (2008). Oxidative Steam Reforming of Ethanol over Ni–Cu/SiO_2, Rh/Al_2O_3 and Ir/CeO_2: Effect of Metal and Support on Reaction Mechanism. *Topics in Catalysis*, 51(1–4), 22–38.

Akpan, E., Akande, A., Aboudheir, A., Ibrahim, H. and Idem, R. (2007). Experimental, kinetic and 2-D reactor modeling for simulation of the production of hydrogen by the catalytic reforming of concentrated crude ethanol (CRCCE) over a Ni-based commercial catalyst in a packed-bed tubular reactor. *Chemical Engineering Science* 62(12), 3112–3126.

Ali, S., Asmawati, N. M. Z., & Subbarao, D. (2011). Correlation between Fischer-Tropsch catalytic activity and composition of catalysts. *Chemistry Central Journal*, 5(1), 2–8.

Amghizar, I., Vandewalle, L. A., Geem, K. M. Van, & Marin, G. B. (2017). New Trends in Olefin Production. Engineering, 3(2), 171–178.

Ao, K., Li, D., Yao, Y., Lv, P., Cai, Y. and Wei, Q. (2018). Fe-doped Co_9S_8 nanosheets on carbon fiber cloth as pH-universal freestanding electrocatalysts for efficient hydrogen evolution. *Electrochimica Acta*, 264(2), 157–165.

Argyle, M. D., & Bartholomew, C. H. (2015). Heterogeneous Catalyst Deactivation and Regeneration: *A Review. Catalysis*, 5(2), 145–269.

Arregi, A., Lopez, G., Amutio, M., Artetxe, M., Barbarias, I., Bilbao, J., & Olazar, M. (2018). Role of operating conditions in the catalyst deactivation in the in-line steam reforming of volatiles from biomass fast pyrolysis. *Fuel*, 216(10), 233–244.

Araujo, J. C. S., Zanchet, D., Rinaldi, R., Schuchardt, U., Hori, C. E., Fierro, J. L. G. and Bueno, J. M. C. (2008). The effects of La_2O_3 on the structural properties of La_2O_3-Al_2O_3 prepared by the sol-gel method and on the catalytic performance of Pt/La_2O_3-Al_2O_3 towards steam reforming and partial oxidation of methane. *Applied Catalysis B: Environmental*, 84(3–4), 552–562.

Ayodele, B. V, Khan, M. R., & Cheng, C. K. (2015). Syngas production from CO_2 reforming of methane over ceria supported cobalt catalyst: Effects of reactants partial pressure. *Journal of Natural Gas Science and Engineering*, 27(11), 1016–1023.

Bahari, M. B., Fayaz, F., Ainirazali, N., Phuc, N. H. H., & Vo, D.-V. N. (2016). Evaluation of Co-promoted Ni/Al_2O_3 catalyst for CO_2 reforming of ethanol. *ARPN Journal of Engineering and Applied Sciences*, 11(11), 7249–7253.

Bahari, M. B., Goo, B. C., Pham, T. L. M., Siang, T. J., Danh, H. T., Ainirazali, N., & Vo, D. -V. N. (2016). Hydrogen-rich Syngas Production from Ethanol Dry Reforming on La-doped Ni/Al_2O_3 Catalysts: Effect of Promoter Loading. *Procedia Engineering*, 148, 654–661.

Bahari, M. B., Phuc, N. H. H., Abdullah, B., Alenazey, F., & Vo, D. -V. N. (2016). Ethanol dry reforming for syngas production over Ce-promoted Ni/Al_2O_3 catalyst. *Journal of Environmental Chemical Engineering*, 4(4), 4830–4838.

Bahari, M. B., Phuc, N. H. H., Alenazey, F., Vu, K. B., Ainirazali, N., & Vo, D.-V. N. (2017). Catalytic performance of La-Ni/Al_2O_3 catalyst for CO_2 reforming of ethanol. *Catalysis Today*, 291(8), 67–75.

Bahari, M. B. (2016). Ethanol dry reforming over Lanthanide-promoted Ni/Al_2O_3 catalysts for syngas production. Master Thesis. Universiti Malaysia Pahang, Malaysia.

Bartholomew, C. H. (2001). Mechanisms of catalyst deactivation. *Applied Catalysis A: General*, 212(1-2), 17–60.

Baruah, R., Dixit, M., Basarkar, P., Parikh, D., & Bhargav, A. (2015). Advances in ethanol autothermal reforming. *Renewable and Sustainable Energy Reviews*, 51(8), 1345–1353.

Batista, M. S., Santos, R. K. S., Assaf, E. M., Assaf, J. M., & Ticianelli, E. A. (2003). Characterization of the activity and stability of supported cobalt catalysts for the steam reforming of ethanol. *Journal of Power Sources*, 124(1), 99–103.

Batista, M. S., Santos, R. K. S., Assaf, E. M., Assaf, J. M., & Ticianelli, E. A. (2004). High efficiency steam reforming of ethanol by cobalt-based catalysts. *Journal of Power Sources*, 134(1), 27–32.

Bej, B., Bepari, S., Pradhan, N. C., & Neogi, S. (2017). Production of hydrogen by dry reforming of ethanol over alumina supported nano-NiO/SiO_2 catalyst. *Catalysis Today*, 291(8), 58-66.

Bellido, J. D. A., Tanabe, E. Y., & Assaf, E. M. (2009). Carbon dioxide reforming of ethanol over Ni/Y_2O_3–ZrO_2 catalysts. *Applied Catalysis B: Environmental*, 90(3-4), 485–488.

Benito, M., Sanz, J. L., Isabel, R., Padilla, R., Arjona, R., & Daza, L. (2005). Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production. *Journal of Power Sources*, 151(10), 11–17.

Benrbaa, R., Löfberg, A., Caballero, G. J., Bordes-richard, E., Rubbens, A., Vannier, R., … Barama, A. (2015). Sol–gel synthesis and characterization of silica supported nickel ferrite catalysts for dry reforming of methane. *Catalysis Communications*, 58(1), 127–131.

Bimbela, F., Abrego, J., Puerta, R., Garcïa, L., & Arauzo, J. (2017). Catalytic steam reforming of the aqueous fraction of bio-oil using Ni-Ce/Mg-Al catalysts. *Applied Catalysis B: Environmental*, 209(7), 346–357.

Bilal, M. and Jackson, S. D. (2013). Steam reforming of ethanol at medium pressure over Ru/Al_2O_3: effect of temperature and catalyst deactivation. *Catal. Sci. Technol*, 3(3), 754–766.

Blanchard, J., Oudghiri-Hassani, H., Abatzoglou, N., Jankhah, S., & Gitzhofer, F. (2008). Synthesis of nanocarbons via ethanol dry reforming over a carbon steel catalyst. *Chemical Engineering Journal*, 143(1-3), 186–194.

BP. (2016). Statistical Review of World Energy 2016 (online). Retrieved from http://www.bp.com/en/global/corporate/energy-economics/statistical-review-of-world-energy.htm on 19 June 2017

Boudart, M. and Djéga-Mariadassou, G. (2014) Kinetics of heterogeneous catalytic reactions. Princeton University Press.

Bobrova, L. N., Bobin, A. S., Mezentseva, N. V., Sadykov, V. A., Thybaut, J. W., & Marin, G. B. (2016). Kinetic assessment of dry reforming of methane on Pt+Ni containing composite of fluorite-like structure. *Applied Catalysis B: Environmental*, 182(3), 513–524.

Bravo-Suárez, J. J., Chaudhari, R. V., & Subramaniam, B. (2013). Design of heterogeneous catalysts for fuels and chemicals processing: An Overview. *In Novel Materials for Catalysis and Fuels Processing*, (6) 3-68.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, 60(2), 309–319.

Budiman, A. W., Song, S.-H., Chang, T.-S., Shin, C.-H., & Choi, M.-J. (2012). Dry reforming of methane over cobalt catalysts: A literature review of catalyst development. *Catal Surv Asia*, 16(4), 183–197.

Budiman, A. W., Song, S. H., Chang, T. S., & Choi, M. J. (2016). Preparation of a high-performance cobalt catalyst for CO_2 reforming of methane. *Advanced Powder Technology*, 27(2), 584–590.

Cabell, K. R., & Valsiner, J. (2014). The catalyzing mind: Beyond models of causality.

Cai, W., Wang, F., Veen, A. C. Van, Provendier, H., Mirodatos, C., & Shen, W. (2008). Autothermal reforming of ethanol for hydrogen production over an Rh/CeO_2 catalyst. *Catalysis Today*, 138(3-4), 152–156.

Campanati, M., Fornasari, G., & Vaccari, A. (2003). Fundamentals in the preparation of heterogeneous catalysts. *Catalysis Today*, 77(4), 299–314.

Cançado, L. G., Takai, K., Enoki, T., Endo, M., Kim, Y. A., Mizusaki, H., Pimenta, M. A., Jorio, A., Coelho, L. N., Magalhães-Paniago, R., & Pimenta, M. A. (2006). General equation for the determination of the crystallite size La of nanographite by Raman spectroscopy. *Applied Physics Letters*, 88(4), 1–3.

Cao, D., Cai, W., Li, Y., Li, C., Yu, H., Zhang, S., & Qu, F. (2017). Syngas production from ethanol dry reforming over Cu/$Ce_{0.8}Zr_{0.2}O_2$ Catalyst. *Catalysis Letters*, 147(12), 2929–2939.

Cao, D., Zeng, F., Zhao, Z., Cai, W., Li, Y., Yu, H., Zhanga, S., & Qu, F. (2018). Cu based catalysts for syngas production from ethanol dry reforming : Effect of oxide supports. *Fuel*, 219(5), 406–416.

Carbajal Ramos, I. A., Montini, T., Lorenzut, B., Troiani, H., Gennari, F. C., Graziani, M., & Fornasiero, P. (2012). Hydrogen production from ethanol steam reforming on M/CeO_2/YSZ (M = Ru, Pd, Ag) nanocomposites. *Catalysis Today*, 180(1), 96–104.

Campos-roldán, C. A., Ramos-sanchez, G., Gonzalez-Huerta, R. D. G., Vargas-garcia, J. R., Balbuena, P. B. and Alonso-vante, N. (2016) Influence of sp-sp carbon nano-domains on metal / support interaction, catalyst durability and catalytic activity for the oxygen reduction reaction, *ACS Applied Materials & Interfaces*, 8(9), 23260–23269

Centi, G., & Santen, R. A. van. (2007). *Catalysis for Renewables: From Feedstock to Energy Production*. Weinheim, Germany: WILEY-VCH.

Chen, L., Zhu, Q., Hao, Z., Zhang, T., & Xie, Z. (2010). Development of a Co-Ni bimetallic aerogel catalyst for hydrogen production via methane oxidative CO_2 reforming in a magnetic assisted fluidized bed. *International Journal of Hydrogen Energy*, 35(16), 8494–8502.

Chen, Q., Cai, W., Liu, Y., Zhang, S., Li, Y., Huang, D., Wang, T. and Li, Y. (2019) Synthesis of Cu-$Ce_{0.8}Zr_{0.2}O_2$ catalyst by ball milling for CO_2 reforming of ethanol. *Journal of Saudi Chemical Society*, 23(1), 111-117

Chen, H., Yu, H., Peng, F., Wang, H., Yang, J. and Pan, M. (2010). Efficient and stable oxidative steam reforming of ethanol for hydrogen production: Effect of in situ dispersion of Ir over Ir/La_2O_3. *Journal of Catalysis*, 269(2), 281–290.

Cheng, C. K., Foo, S. Y., & Adesina, A. A. (2010). H_2-rich synthesis gas production over Co/Al_2O_3 catalyst via glycerol steam reforming. *Catalysis Communications*, 12(4), 292–298.

Cheng, C.K., Foo, S.Y., & Adesina, A.A., (2011). Carbon deposition on bimetallic Co – Ni/ Al_2O_3 catalyst during steam reforming of glycerol. *Catalysis Today*, 164(1), 268–274.

Chiou, J. Y. Z., Wang, W. Y., Yang, S. Y., Lai, C. L., Huang, H. H. and Wang, C. Bin (2013). Ethanol steam reforming to produce hydrogen over Co/ZnO and PtCo/ZnO catalysts. *Catalysis Letters*, 143(5), 501–507.

Chorendorff, I., & Niemantsverdriet, J. W. (2003). *Concepts of modern catalysis and kinetics*. Weinheim, Germany: WILEY-VCH.

Chuah, G. K., Jaenicke, S., & Xu, T. H. (2000). The effect of digestion on the surface area and porosity of alumina. *Microporous and Mesoporous Materials*, 37(3), 345–353.

Cimenti, M., & Hill, J. M. (2009). Thermodynamic analysis of solid oxide fuel cells operated with methanol and ethanol under direct utilization, steam reforming, dry reforming or partial oxidation conditions. *Journal of Power Sources Journal*, 186(2), 377–384.

Comas, J., Marino, F., Laborde, M. and Amadeo, N. (2004). Bio-ethanol steam reforming on Ni/Al_2O_3 catalyst *Chemical Engineering Journal*, 98(1–2), 61–68.

Coleman, L. J. I., Epling, W., Hudgins, R. R., & Croiset, E. (2009). Ni/Mg– Al mixed oxide catalyst for the steam reforming of ethanol. *Applied Catalysis A, General,* 363(1), 52–63.

Cooper, C. G., Nguyen, T. H., Lee, Y. J., Hardiman, K. M., Safinski, T., Lucien, F. P., & Adesina, A. A. (2008). Alumina-supported cobalt-molybdenum catalyst for slurry phase Fischer-Tropsch synthesis. *Catalysis Today,* 131(1–4), 255–261.

Cui, W., Yuan, X., Wu, P., Zheng, B., Zhang, W., & Jia, M. (2015). Catalytic properties of γ-Al_2O_3 supported Pt–FeOx catalysts for complete oxidation of formaldehyde at ambient temperature. *RSC Adv*ances 5(126), 104330-104336.

D.B. Williams, & Carter, C. B. (2009). *Transmission Electron Microscopy: A Textbook for Materials Science,* 2nd ed. New York, USA: Springer US, Inc.

da Silva, A. L. M., Den Breejen, J. P., Mattos, L. V., Bitter, J. H., De Jong, K. P., & Noronha, F. B. (2014). Cobalt particle size effects on catalytic performance for ethanol steam reforming - Smaller is better. *Journal of Catalysis,* 318(10), 67–74.

Da Silva, A. M., de Souza, K. R., Jacobs, G., Graham, U. M., Davis, B. H., Mattos, L. V., & Noronha, F. B. (2011). Steam and CO_2 reforming of ethanol over Rh/CeO_2 catalyst. *Applied Catalysis B: Environmental*, 102(1-2), 94–109.

Dang, M. N., Ung, T. D. T., Phan, H. N., Truong, Q. D., Bui, T. H., Phan, M. N. Tran, P. D. A. (2017). A novel method for preparation of molybdenum disulfide/graphene composite. *Materials Letters*, 194(2), 145–148.

Davis, K. (2010). Material Review: Alumina (Al_2O_3). *European Union Journal*, 109–114.

De Oliveira-Vigier, K., Abatzoglou, N., & Gitzhofer, F. (2005). Dry-reforming of ethanol in the presence of a 316-stainless steel catalyst. *The Canadian Journal of Chemical Engineering,* 83(12), 978–984.

del Río, L., López, I., & Marbán, G. (2014). Stainless steel wire mesh-supported Co_3O_4 catalysts in the steam reforming of ethanol. *Applied Catalysis B: Environmental,* 150–151(3), 370–379.

Deluga, G. A., Salge, J. R., Schmidt, L. D., & Verykios, X. E. (2004). Renewable Hydrogen from Ethanol by Autothermal. *Science*, 303, 993–997.

Deng, X., Sun, J., Yu, S., Xi, J., Zhu, W., & Qiu, X. (2008). Steam reforming of ethanol for hydrogen production over NiO/ZnO/ZrO_2 catalysts. *International Journal of Hydrogen Energy,* 33(4), 1008–1013.

Dissanayake, D., Rosynek, M. P., Kharas, K. C. C., & Lunsford, J. H. (1991). Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/AI_2O_3 catalyst. *Journal of Catalysis*, 132(4), 117–127.

Dixon, A. G. (1997). Heat transfer in fixed beds at very low (< 4) Tube-to-particle diameter ratio. *Ind. Eng. Chem. Res*, 36(7), 3053–3064.

Drif, A., Bion, N., Brahmi, R., Ojala, S., Pirault-Roy, L., Turpeinen, E., Seelam P. K., Keiski R. L., & Epron, F. (2015). Study of the dry reforming of methane and ethanol using Rh catalysts supported on doped alumina. *Applied Catalysis A: General*, 504(1), 576–584.

Dhanala, V., Maity, S. K. and Shee, D. (2015). Roles of supports (g-Al_2O_3, SiO_2, ZrO_2) and performance of metals (Ni, Co, Mo) in steam reforming of isobutanol. *RSC Advances*, 5(65), 52522–52532.

Diagne, C., Idriss, H. and Kinnemann, A. (2002) 'Hydrogen production by ethanol reforming over Rh/CeO_2– ZrO_2 catalysts. *Catalysis Communications*, 3, 565–571.

E Santos, M. A. F., Lôbo, I. P., & Cruz, R. S. da. (2014). Synthesis and characterization of novel ZrO_2-SiO_2 mixed oxides. *Materials Research*, 17(3), 700–707.

Ebert, J. (2011). Syngas. Retrieved September 29, 2016, from: http://syngastek.org/biocomposites/.

F. Frusteri, S. Freni a, L. Spadaro, V. Chiodo, G. Bonura, S. Donato, S. C. (2004). H_2 production for MC fuel cell by steam reforming of ethanol over MgO supported Pd , Rh , Ni and Co catalysts. *Catalysis Communications*, 5(1), 611–615.

Fatsikostas, A. N., & Verykios, X. E. (2004). Reaction network of steam reforming of ethanol over Ni-based catalysts. *Journal of Catalysis*, 225(1), 439–452.

Ferrari, A., & Robertson, J. (2000). Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*, 61(20), 14095–14107.

Firoozi, M., Baghalha, M., & Asadi, M. (2009). The effect of micro and nano particle sizes of H-ZSM-5 on the selectivity of MTP reaction. *Catalysis Communications*, 10(12), 1582–1585.

Fischer, V. F., & Tropsch, H. (1928). Conversion of methane into hydrogen and carbon monoxide. *Brennstoff- Chemie*, 3, 39–46.

Fogler, H. S. (2006). *Elements of Chemical Reaction Engineering*, 4th ed. Upper Saddle River, NJ, USA: Pearson Education, Inc.

Fogler, S. H. (2011). *Essentials of Chemical Reaction Engineering*, Upper Saddle River, NJ, USA: Pearson Education, Inc.

Foo, S. Y. (2012). *Oxidative Dry Reforming of Methane over Alumina-Supported Co-Ni Catalyst Systems*. Ph.D. Thesis. The University of New South Wales, Australia.

Foo, S. Y., Cheng, C. K., Nguyen, T.-H., & Adesina, A. a. (2011a). Kinetic study of methane CO_2 reforming on Co–Ni/Al_2O_3 and Ce–Co–Ni/Al_2O_3 catalysts. *Catalysis Today*, 164(1), 221–226.

Foo, S. Y., Cheng, C. K., Nguyen, T.-H., Kennedy, E. M., Dlugogorski, B. Z., & Adesina, A. A. (2012). Carbon deposition and gasification kinetics of used lanthanide-promoted Co-Ni/Al_2O_3 catalysts from CH_4 dry reforming. *Catalysis Communications*, 26(1), 183–188.

Foo, S. Y., Cheng, C. K., Nguyen, T., & Adesina, A. A. (2010). Oxidative CO_2 Reforming of Methane on Alumina-Supported Co-Ni Catalyst. *Ind. Eng. Chemi. Res*, 49(3), 10450–10458.

Foo, S. Y., Cheng, C. K., Nguyen, T., & Adesina, A. A. (2012). Syngas production from CH_4 dry reforming over Co-Ni/Al_2O_3 catalyst: Coupled reaction-deactivation kinetic analysis and the effect of O_2 co-feeding on H_2:CO ratio. *International Journal of Hydrogen Energy*, 37(22), 17019–17026.

Foo, S. Y., Cheng, C. K., Nguyen, T. H., & Adesina, A. A. (2011b). Evaluation of lanthanide-group promoters on Co-Ni/Al_2O_3 catalysts for CH_4 dry reforming. *Journal of Molecular Catalysis A: Chemical*, 344(1–2), 28–36.

Frusteri, F., Freni, S., Chiodo, V., Donato, S., Bonura, G., & Cavallaro, S. (2006). Steam and auto-thermal reforming of bio-ethanol over MgO and CeO_2 Ni supported catalysts. *International Journal of Hydrogen Energy*, 31(1), 2193–2199.

Frusteri, F., Freni, S., Chiodo, V., Spadaro, L., Bonura, G., & Cavallaro, S. (2004). Potassium improved stability of Ni/MgO in the steam reforming of ethanol for the production of hydrogen for MCFC. *Journal of Power Sources*, 132(1–2), 139–144.

Gallucci, F., Van Sint Annaland, M., & Kuipers, J. A. M. (2010). Pure hydrogen production via autothermal reforming of ethanol in a fluidized bed membrane reactor: A simulation study. *International Journal of Hydrogen Energy*, 35(4), 1659–1668.

Gallego, G. S., Batiot-Dupeyrat, C., Barrault, J. and Mondragon, F. (2008) Dual Active-Site Mechanism for Dry Methane Reforming over Ni/La_2O_3 Produced from LaNiO 3 Perovskite', *Industrial and Engineering Chemistry*, 47(23), 9272–9278.

Ginsburg, J. M., Pin, J., Solh, T. El, & Lasa, H. I. De. (2005). Coke formation over anickel catalyst under methane dry reforming conditions : Thermodynamic and kinetic models. *Ind. Eng. Chem. Res*, 44(1), 4846–4854.

Goyne, K. W., Zimmerman, A. R., Newalkar, B. L., Komarneni, S., Brantley, S. L., & Chorover, J. (2003). Surface charge of variable porosity Al_2O_3 (s) and SiO_2 (s) Adsorbents, 3(1), 243–256.

Gu, W., Liu, J., Hu, M., Wang, F., & Song, Y. (2015). $La_2O_2CO_3$ encapsulated La_2O_3 nanoparticles supported on carbon as superior electrocatalysts for oxygen reduction reaction. *ACS Applied Materials & Interfaces*, 7(48), 26914–26922.

Guo, J., Lou, H., Zhao, H., Chai, D., & Zheng, X. (2004). Dry reforming of methane over nickel catalysts supported on magnesium aluminate spinels. *Applied Catalysis A: General*, 273(1–2), 75–82.

Gutierrez, A., Karinen, R., Airaksinen, S., Kaila, R., & Krause, A. O. I. (2011). Autothermal reforming of ethanol on noble metal catalysts. *International Journal of Hydrogen Energy*, 36(15), 8967–8977.

Guil, J. M., Homs, N., Llorca, J. and de La Piscina, P. R. (2005). Microcalorimetric and infrared studies of ethanol and acetaldehyde adsorption to investigate the ethanol steam reforming on supported cobalt catalysts. *Journal of Physical Chemistry B*, 109(21), 10813–10819.

Hagen, J. (2006). *Industrial Catalysis A Practical Approach*, 2nd ed. Weinheim, Germany: Wiley-VCH.

Halabi, M. H., de Croon, M. H. J. M., van der Schaaf, J., Cobden, P. D., & Schouten, J. C. (2011). Reactor modeling of sorption-enhanced autothermal reforming of methane. Part I: Performance study of hydrotalcite and lithium zirconate-based processes. *Chemical Engineering Journal*, 168(2), 872–882.

Haryanto, A., Fernando, S., Murali, N., & Adhikari, S. (2005). Current status of hydrogen production techniques by steam reforming of ethanol: A review. *Energy and Fuels*, 19(11), 2098–2106.

He, S., He, S., Zhang, L., Li, X., Wang, J., He, D., Lu, J. and Luo, Y. (2015). Hydrogen production by ethanol steam reforming over Ni/SBA-15 mesoporous catalysts: Effect of Au addition. *Catalysis Today*, 258(1), 162–168.

Homsi, D., Aouad, S., Gennequin, C., Aboukaı¨s, A., & Abi-Aad, E. (2014). A highly reactive and stable $Ru/Co_{6-x}Mg_xAl_2$ catalyst for hydrogen production via methane steam reforming. *International Journal of Hydrogen Energy*, 39(3), 10101–10107.

Hou, T., Lei, Y., Zhang, S., Zhang, J., & Cai, W. (2015). Ethanol dry reforming for syngas production over Ir/CeO_2 catalyst. *Journal of Rare Earths*, 33(1), 42–45.

Hou, T., Zhang, S., Chen, Y., Wang, D., & Cai, W. (2015). Hydrogen production from ethanol reforming: Catalysts and reaction mechanism. *Renewable and Sustainable Energy Reviews*, 44(1), 132–148.

Hu, X., & Lu, G. (2009). Syngas production by CO_2 reforming of ethanol over Ni/Al_2O_3 catalyst. *Catalysis Communications*, 10(13), 1633–1637.

Hu, Y. H., & Ruckenstein, E. (2004). Catalytic conversion of methane to synthesis gas by partial oxidation and CO_2 reforming. Advances in Catalysis, 48(1), 297–345

Hull, S., & Trawczyński, J. (2014). Steam reforming of ethanol on zinc containing catalysts with spinel structure. *International Journal of Hydrogen Energy*, 39(9), 4259–4265.

Iaquaniello, G., Guarinoni, A., Lainati, A., Salladini, A., Cucchiella, B., Antonetti, E. & Basini, L. (2012). Natural gas catalytic partial oxidation: A way to syngas and bulk chemicals production. *INTECH*, 267-286.

Iyer, M. V, Norcio, L. P., Kugler, E. L. and Dadyburjor, D. B. (2003). Kinetic modeling for methane reforming with carbon dioxide over a mixed-metal carbide catalyst. *Ind. Eng. Chem. Res.*, 42(304), 2712–2721.

Goldstein J., Newbury D.E., Joy D.C., Lyman C.E., Echlin P., Lifshin E., Sawyer L., & J. R. M. (2003). *Scanning Electron Microscopy and X-ray Microanalysis* 3rd ed. New York, USA: Springer US, Inc.

Jabbour, K., El Hassan, N., Casale, S., Estephane, J., & El Zakhem, H. (2014). Promotional effect of Ru on the activity and stability of Co/SBA-15 catalysts in dry reforming of methane. *International Journal of Hydrogen Energy*, 39(15), 7780–7787.

Jaccard, M. (2005). *Sustainable Fossil Fuels*, The Edinburgh Building, Cambridge cb2 2ru, UK.

Jankhah, S., Abatzoglou, N., & Gitzhofer, F. (2008). Thermal and catalytic dry reforming and cracking of ethanol for hydrogen and carbon nanofilaments' production. *International Journal of Hydrogen Energy*, 33(1), 4769–4779.

Jankhah, S., Abatzoglou, N., Gitzhofer, F., Blanchard, J., & Oudghiri-Hassani, H. (2008). Catalytic properties of carbon nano-filaments produced by iron-catalysed reforming of ethanol. *Chemical Engineering Journal*, 139(1), 532–539.

JCPDS Powder Diffraction File (2000), International Centre for Diffraction Data, Swarthmore, PA

Jens R. Rostrup-Nielsen, Jens Sehested, J. K. N. (2002). Hydrogen and synthesis gas by steam- and CO_2 reforming. *Advances in Catalysis*, 47(4), 65–139.

Ji, L., Lin, J. and Zeng, H. C. (2000) 'Metal - Support Interactions in Co/Al_2O_3 Catalysts : A Comparative Study on Reactivity of Support. *Journal of Physical Chemistry B*, 104(1), 1783–1790.

Jin, R., Chen, Y., Li, W., Cui, W., Ji, Y., Yu, C., & Jiang, Y. (2000). Mechanism for catalytic partial oxidation of methane to syngas over a Ni/Al_2O_3 catalyst. *Applied Catalysis A, General*, 201(5), 71–80.

Jin, L., Zhang, Y., Dombrowski, J. P., Chen, C. H., Pravatas, A., Xu, L., Perkins, C. and Suib, S. L. (2011). $ZnO/La_2O_2CO_3$ layered composite: A new heterogeneous catalyst for the efficient ultra-fast microwave biofuel production. *Applied Catalysis B: Environmental*, 103(1–2), 200–205.

Jordi Llorca, Narc´is Homs, J. S., & Piscina, & P. R.de la. (2002). Efficient production of hydrogen over supported cobalt catalysts from ethanol steam reforming. *Journal of Catalysis*, 209(5), 306–317.

Kale, G. R., & Gaikwad, T. M. (2014). Thermodynamic analysis of ethanol dry reforming: effect of combined parameters. *ISRN Thermodynamics*, 3(5), 1–10.

Kale, G. R., & Kulkarni, B. D. (2014). Thermoneutral conditions in dry reforming of ethanol. *Asia-Pacific Journal of Chemical Engineering*, 9(1), 196-204.

Karim, A. M., Su, Y., Sun, J., Yang, C., Strohm, J. J., King, D. L., & Wang, Y. (2010). A comparative study between Co and Rh for steam reforming of ethanol. *Applied Catalysis B: Environmental*, 96(3–4), 441–448.

Kaddouri, A. and Mazzocchia, C. (2004) 'A study of the influence of the synthesis conditions upon the catalytic properties of Co/SiO_2 or Co/Al_2O_3 catalysts used for ethanol steam reforming. *Catalysis Communications*, 5(8), 339–345.

Kambolis, A., Matralis, H., Trovarelli, A. and Papadopoulou, C. (2010). Ni/CeO_2-ZrO_2 catalysts for the dry reforming of methane. *Applied Catalysis A: General*, 377(6), 16–26.

Khila, Z., Hajjaji, N., Pons, M., Renaudin, V., & Houas, A. (2013). A comparative study on energetic and exergetic assessment of hydrogen production from bioethanol via steam reforming, partial oxidation and auto-thermal reforming processes. *Fuel Processing Technology*, 112(1), 19–27.

Kim, Y., Kim, C., Choi, I., Rengaraj, S., & Yi, J. (2004). Arsenic removal using mesoporous alumina prepared via a templating method. *Environ. Sci. Technol.*, 38(3), 924–931.

Krylova, A. Y., Kozyukov, E. A. and Lapidus, A. L. (2008). Ethanol and diesel fuel from plant raw materials: A review. *Solid Fuel Chemistry*, 42(6), 358–364.

Kourtelesis, M., Panagiotopoulou, P., Ladas, S. and Verykios, X. E. (2015). Influence of the support on the reaction network of ethanol steam reforming at low temperatures over Pt catalysts. *Topics in Catalysis*, 58(18), 1202–1217.

Kraleva, E., Sokolov, S., Nasillo, G., Bentrup, U., & Ehrich, H. (2014). Catalytic performance of CoAlZn and NiAlZn mixed oxides in hydrogen production by bio-ethanol partial oxidation. *International Journal of Hydrogen Energy*, 39(1), 209–220.

Kraus, P., & Lindstedt, P. (2017). Microkinetic mechanisms for partial oxidation of methane over platinum and rhodium. *The Journal of Physical Chemistry C*, 121(17), 9442–9453.

Kruk, M., & Jaroniec, M. (2001). Gas adsorption characterization of ordered organic-inorganic nanocomposite materials. *Chem. Mater*., 13(10), 3169–3183.

Kugai, J., Subramani, V., Song, C., Engelhard, M. H., & Chin, Y.-H. (2006). Effects of nanocrystalline CeO_2 supports on the properties and performance of Ni–Rh bimetallic catalyst for oxidative steam reforming. *Journal of Catalysis*, 238(1), 430–440.

Kumar, A., Bhosale, R. R., Malik, S. S., Abusrafa, A. E., Saleh, M. A. H., Ghosh, U. K., Al-Marri M. J., Almomani F. A., Khader M. M., Abu-Reesh, I. M. (2016). Thermodynamic investigation of hydrogen enrichment and carbon suppression using chemical additives in ethanol dry reforming. *International Journal of Hydrogen Energy*, 41(34), 15149–15157.

Kunzru, D. (2003). Hydrogen Production from Ethanol for Fuel Cell Applications.1–8). Retrieved from www.aidic.it/CISAP3/webpapers/22Kunzru.pdf%0A.

Levenspiel, O. (1999). *Chemical Reaction Engineering* 3rd ed. Hoboken, New Jersey: John Wiley & Sons, Inc.

Li, D., Zeng, L., Li, X., Wang, X., Ma, H., Assabumrungrat, S., & Gong, J. (2015). Ceria-promoted Ni/SBA-15 catalysts for ethanol steam reforming with enhanced activity and resistance to deactivation. *Applied Catalysis B: Environmental*, 176–177(1), 532–541.

Liguras, D. K., Kondarides, D. I. and Verykios, X. E. (2003). Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. *Applied Catalysis B: Environmental*, 43(4), 345–354.

Liu, L., Ma, X. and Li, J. (2013). Hydrogen production from ethanol steam reforming over Ni/SiO_2 catalysts: A comparative study of traditional preparation and microwave modification methods. *International journal of energy research*, 38(1), 860-874.

Liu, Y. and Lawal, A. (2015). Kinetic study of autothermal reforming of glycerol in a dual layer monolith catalyst. *Chemical Engineering & Processing: Process Intensification.* 95(3), 276–283.

Li, K., Wang, H., Wei, Y., & Yan, D. (2010). Direct conversion of methane to synthesis gas using lattice oxygen of CeO_2–Fe_2O_3 complex oxides. *Chemical Engineering Journal*, 156(5), 512–518.

Li, X., Zhang, Y., & Smith, K. J. (2004). Metal-support interaction effects on the growth of filamentous carbon over Co/SiO_2 catalysts. *Applied Catalysis A: General*, 264(1), 81–91.

Liguras, D. K., Goundani, K., & Verykios, X. E. (2004). Production of hydrogen for fuel cells by catalytic partial oxidation of ethanol over structured Ru catalysts. *International Journal of Hydrogen Energy*, 29(3), 419–427.

Lin, K. H., Wang, C. Bin, & Chien, S. H. (2013). Catalytic performance of steam reforming of ethanol at low temperature over $LaNiO_3$ perovskite. *International Journal of Hydrogen Energy*, 38(8), 3226–3232.

Lin, W.-H., Liu, Y.-C., & Chang, H.-F. (2010). Autothermal reforming of ethanol in a Pd-Ag/Ni composite membrane reactor. *International Journal of Hydrogen Energy*, 35(23), 12961–12969.

Liu, S., Zhang, K., Fang, L., & Li, Y. (2008). Thermodynamic analysis of hydrogen production from oxidative steam reforming of ethanol. *Energy Fuels*, 22(2), 1365–1370.

Liu, L., Ma, X. and Li, J. (2013) Hydrogen production from ethanol steam reforming over Ni/SiO_2 catalysts: A comparative study of traditional preparation and microwave modification methods, *International journal of energy research*, 38(4), 860-874.

Llorca, J., Piscina, P. R. D. La, Sales, J. and Homs, N. (2001) ‘Direct production of hydrogen from ethanolic aqueous solutions over oxide catalysts. *Chemical Communications*, (7), 641–642.

Llorca, J., Piscina, P. R. de la, Dalmonb, J.-A., Sales, J. and Homs, N. (2003). CO-free hydrogen from steam-reforming of bioethanol over ZnO-supported cobalt catalysts Effect of the metallic precursor. *Applied Catalysis A: General*, 43(1), 355–369.

Ma, H., Zhang, R., Huang, S., Chen, W. and Shi, Q. (2012). Ni/Y_2O_3-Al_2O_3 catalysts for hydrogen production from steam reforming of ethanol at low temperature. *Journal of Rare Earths.* 30(7), 683–690.

Maia, T. A., Assaf, J. M., & Assaf, E. M. (2014). Study of Co/CeO_2-γ-Al_2O_3 catalysts for steam and oxidative reforming of ethanol for hydrogen production. *Fuel Processing Technology*, 128(1), 134–145.

Manfro, R. L., Da Costa, A. F., Ribeiro, N. F. P., & Souza, M. M. V. M. (2011). Hydrogen production by aqueous-phase reforming of glycerol over nickel catalysts supported on CeO_2. *Fuel Processing Technology*, 92(3), 330–335.

Mattos, L. V, Jacobs, G., Davis, B. H., & Noronha, B. (2011). Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation. Chemical Reviews, 112(5), 4094–4123.

Mazumder, J., & De Lasa, H. I. (2014). Ni catalysts for steam gasification of biomass: Effect of La_2O_3 loading. *Catalysis Today*, 237(2), 100–110.

Mears, D. E. (1971). Tests for transport limitations in experimental catalytic reactors. *Ind. Eng. Chem. Process Des. Develop*., 10(4), 541–547.

Meille, V. (2006). Review on methods to deposit catalysts on structured surfaces. Applied *Catalysis A: General*, 315(11), 1–17.

Mondal, T., Pant, K. K., & Dalai, A. K. (2015). Catalytic oxidative steam reforming of bio-ethanol for hydrogen production over Rh promoted Ni/CeO_2-ZrO_2 catalyst. International Journal of Hydrogen Energy, 40(6), 2529–2544.

Montini, T., Singh, R., Das, P., Lorenzut, B., Bertero, N., Riello, P., Benedetti, A., Giambastiani, G., Bianchini, C., Zinoviev, S., Miertus, S., Fornasiero, P. (2010). Renewable H_2 from glycerol steam reforming: Effect of La_2O_3 and CeO_2 addition to Pt/Al_2O_3 catalysts. *ChemSusChem*, 3(5), 619–628.

Mokrani, T., & Scurrell, M. (2009). Gas conversion to liquid fuels and chemicals: The methanol route-catalysis and processes development. *Catalysis Reviews*, 51(1), 1–145.

Moraes, T. S., Neto, R. C. R., Ribeiro, M. C., Mattos, L. V, Kourtelesis, M., Verykios, X., & Noronha, F. B. (2015). Effects of ceria morphology on catalytic performance of Ni/CeO_2 catalysts for low temperature steam reforming of ethanol. *Topics in Catalysis*, 58(4–6), 281–294.

Moulijn, J. A., Van Diepen, A. E., & Kapteijn, F. (2001). Catalyst deactivation: Is it predictable? What to do? *Applied Catalysis A: General*, 212(1–2), 3–16.

Nanda, S., Rana, R., Zheng, Y., Kozinski, J. A., & Dalai, A. K. (2017). Insights on pathways for hydrogen generation from ethanol. *Sustainable Energy Fuels*, 1(6), 1232–1245.

Navarro, R. M., Álvarez-Galván, M. C., Sánchez-Sánchez, M. C., Rosa, F. and Fierro, J. L. G. (2005). Production of hydrogen by oxidative reforming of ethanol over Pt catalysts supported on Al_2O_3 modified with Ce and La. *Applied Catalysis B: Environmental*, 55(4), 229–241.

Narula, C. K. (1996). Sol-Gel process from heterometallic alkoxides to incorporate alkaline- and rare earths in alumina for automotive applications. *Materials Research Society*, 431(1), 331–336.

National Biomass Strategy 2020: New wealth creation for Malaysia's biomass industry. Version 2.0, 2013. (online). http://etp.pemandu.gov.my/upload/Biomass_Strategy_2013.pdf

Ni, M., Leung, D. Y. C., & Leung, M. K. H. (2007). A review on reforming bio-ethanol for hydrogen production. *International Journal of Hydrogen Energy*, 32(1), 3238–3247.

Oemar, U., Kathiraser, Y., Mo, L., Ho, X. K. and Kawi, S. (2016). CO_2 reforming of methane over highly active La-promoted Ni supported on SBA-15 catalysts: mechanism and kinetic modelling. *Catalysis Science and Technology*, 6(1), 1173–1186.

Ogo, S., Shimizu, T., Nakazawa, Y., Mukawa, K., Mukai, D., & Sekine, Y. (2015). Steam reforming of ethanol over K promoted Co catalyst. *Applied Catalysis A: General*, 495, 30–38.

Oh, S. H., Baron, K., Sloan, E. M., & Hegedus, L. L. (1979). Effects of Catalyst Particle Size on Multiple Steady States. *Journal of Catalysis*, 59(1), 272–277.

Ortiz, A. L., Samano, R. B. P., Zaragoza, M. J. M., & Collins-Martinez, V. (2015). Thermodynamic analysis and process simulation for the H_2 production by dry reforming of ethanol with $CaCO_3$. *International Journal of Hydrogen Energy*, 40(1), 17172–17179.

Osorio-Vargas, P., Campos, C. H., Navarro, R. M., Fierro, J. L. G., & Reyes, P. (2015a). $Rh/Al_2O_3–La_2O_3$ catalysts promoted with CeO_2 for ethanol steam reforming reaction. *Journal of Molecular Catalysis A: Chemical*, 407(5), 169–181.

Osorio-Vargas, P., Flores-González, N. A., Navarro, R. M., Fierro, J. L. G., Campos, C. H., & Reyes, P. (2016). Improved stability of Ni/Al_2O_3 catalysts by effect of promoters (La_2O_3, CeO_2) for ethanol steam-reforming reaction. *Catalysis Today*, 259(3), 27–38.

Palma, V., Ricca, A., & Ciambelli, P. (2013). Structured catalysts for methane auto-thermal reforming in a compact thermal integrated reaction system. *Applied Thermal Engineering*, 61(1), 128–133.

Palmqvist, A. E. C., Wirde, M., Gelius, U., & Muhammed, M. (1999). Surfaces of doped nanophase cerium oxide catalysts. *Nanostructured Materials*, 11(8), 995–1007.

Pakhare, D., Schwartz, V., Abdelsayed, V., Haynes, D., Shekhawat, D., Poston, J. and Spivey, J. (2014). Kinetic and mechanistic study of dry (CO_2) reforming of methane over Rh-substituted $La_2Zr_2O_7$ pyrochlores. *Journal of Catalysis*, 316(2), 78–92.

Papageridis, K. N., Siakavelas, G., Charisiou, N. D., Avraam, D. G., Tzounis, L., Kousi, K. and Goula, M. A. (2016). Comparative study of Ni, Co, Cu supported on γ-alumina catalysts for hydrogen production via the glycerol steam reforming reaction. *Fuel Processing Technology*, 152(1), 156–175.

Palo, D. R., Dagle, R. a, & Holladay, J. D. (2007). Methanol steam reforming for hydrogen production. *Chemical Reviews*, 107(10), 3992–4021.

Papageridis, K. N., Siakavelas, G., Charisiou, N. D., Avraam, D. G., Tzounis, L., Kousi, K., & Goula, M. A. (2016). Comparative study of Ni, Co, Cu supported on γ-alumina catalysts for hydrogen production via the glycerol steam reforming reaction. *Fuel Processing Technology*, 152(1), 156–175.

Patterson, A. L. (1939). The Scherrer Formula for I-Ray Particle Size Determination. *Physical Review*, 56(8), 978–982.

Pechimuthu, N. A., Pant, K. K. and Dhingra, S. C. (2007). Deactivation studies over Ni - K/CeO_2-Al_2O_3 catalyst for dry reforming of methane. *Industrial & Engineering Chemistry*, 1(1), 1731–1736.

Perry, R. H., & Green, D. W. (2008). Perry's Chemical Engineers' Handbook 8th ed. New York, USA: The McGraw-Hill Companies, Inc.

Pino, L., Vita, A., Laganà, M., & Recupero, V. (2014). Hydrogen from biogas: Catalytic tri-reforming process with Ni/LaCeO mixed oxides. *Applied Catalysis B: Environmental*, 148–149, 91–105.

Pichas, C., Pomonis, P., Petrakis, D. and Ladavos, A. (2010). Kinetic study of the catalytic dry reforming of CH_4 with CO_2 over La_2−xSrxNiO_4 perovskite-type oxides. *Applied Catalysis A, General. Elsevier B*, 386(1–2), 116–123.

Profeti, L. P. R., Ticianelli, E. a. and Assaf, E. M. (2009). Production of hydrogen via steam reforming of biofuels on Ni/CeO_2-Al_2O_3 catalysts promoted by noble metals. *International Journal of Hydrogen Energy*, 34(12), 5049–5060.

Roussière, T. L. (2013). Catalytic Reforming of Methane in the Presence of CO_2 and H_2O at High Pressure. PhD Thesis. Zur Erlangung des akademischen Grades eines.

Puigjaner, L. (2011). Syngas from Waste Emerging Technologies. Spain: Springer Netherlands.

Qu, F., Wei, Y., Cai, W., Yu, H., Li, Y., Zhang, S., & Li, C. (2018). Syngas production from carbon dioxide reforming of ethanol over Ir/$Ce_{0.75}Zr_{0.25}O_2$ catalyst: Effect of calcination temperatures. *Energy & Fuels*, 32(2), 2104–2116.

R. M. Navarro, M. A. Pena, and J. L. G. F. (2007). Hydrogen production reactions from carbon feedstocks: Fossil fuels and biomass. *Chem. Rev.*, 107(3), 3952–3991.

Robertson, A. J. B. (1975). The Early History of Catalysis. *Platinum Metals Rev.*, 19(2), 64–69.

Salge, J. R., Deluga, G. A., & Schmidt, L. D. (2005). Catalytic partial oxidation of ethanol over noble metal catalysts. *Journal of Catalysis*, 235(1), 69–78.

Samsudeen, K., Ahmed, A. fatesh, Yahya, M., Ahmed, A., & Anis, F. (2018). Effect of calcination temperature on hydrogen production via ethanol dry reforming over Ni/Al_2O_3 Catalyst. *International Journal of Research in Science*, 4(1), 5–9.

Sahoo, D. R., Vajpai, S., Patel, S. and Pant, K. K. (2007). Kinetic modeling of steam reforming of ethanol for the production of hydrogen over Co/Al_2O_3 catalyst. *Chemical Engineering Journal*, 125(2), 139–147.

Santos, P. S., Santos, H. S. and Toledo, S. P. (2000). Standard transition aluminas. Electron microscopy studies. *Materials Research*, 3(4), 104–114.

Schanke, D., Vada, S., Blekkan, E. A., Hilmen, A. M., Hoff, A., & Holmen, A. (1995). Study of Pt-promoted cobalt CO hydrogenation catalysts. *Journal of Catalysis*, 156(1), 85–95.

Schatten, H. (2013). Scanning Electron Microscopy for the Life Sciences. Cambridge University Press, UK.

Sekine, Y., Nakazawa, Y., Oyama, K., Shimizu, T., & Ogo, S. (2014). General Effect of small amount of Fe addition on ethanol steam reforming over Co/Al_2O_3 catalyst. *Applied Catalysis A, General,* 472(6), 113–122.

Shahirah, M. N. N., Gimbun, J., Ideris, A., Khan, M. R., & Cheng, C. K. (2017). Catalytic pyrolysis of glycerol into syngas over ceria-promoted Ni/A-Al_2O_3 catalyst. *Renewable Energy,* 107(7), 223–234.

Shackelford, J. F. and Doremus, R. H. (2008). Ceramic and glass materials: Structure, properties and processing. 1st ed. New York: Springer.

Shuit, S. H., Tan, K. T., Lee, K. T. and Kamaruddin, A. H. (2009) 'Oil palm biomass as a sustainable energy source: A Malaysian case study. Energy, 34(1), 1225–1235.

Siew, K. W., Lee, H. C., Gimbun, J., & Cheng, C. K. (2014). Production of CO-rich hydrogen gas from glycerol dry reforming over La-promoted Ni/Al_2O_3 catalyst. *International Journal of Hydrogen Energy*, 39(13), 6927–6936.

Singh, P. S. (2008). High surface area nanoporous amorphous silica prepared by dodecanol assisted silica formate sol-gel approach. *Journal of Colloid and Interface Science*, 325(1), 207–214.

Song, H., Zhang, L., Watson, R. B., Braden, D., & Ozkan, U. S. (2007a). Investigation of bio-ethanol steam reforming over cobalt-based catalysts. *Catalysis Today*, 129(1), 346–354.

Song, H. and Ozkan, U. S. (2009). Ethanol steam reforming over Co-based catalysts: Role of oxygen mobility. *Journal of Catalysis*, 261(1), 66–74.

Srisiriwat, N., Therdthianwong, S., & Therdthianwong, A. (2009). Oxidative steam reforming of ethanol over Ni/Al_2O_3 catalysts promoted by CeO_2, ZrO_2 and CeO_2-ZrO_2. *International Journal of Hydrogen Energy*, 34(1), 2224–2234.

Storsæter, S., Tøtdal, B., Walmsley, J. C., Tanem, B. S., & Holmen, A. (2005). Characterization of alumina-, silica-, and titania-supported cobalt Fischer-Tropsch catalysts. *Journal of Catalysis*, 236(1), 139–152.

Sukri, M. F. F., Khavarian, M., & Mohamed, A. R. (2018). Effect of cobalt loading on suppression of carbon formation in carbon dioxide reforming of methane over Co/MgO catalyst. *Research on Chemical Intermediates*, 44(4), 2585–2605.

Takahara, I., Saito, M., Inaba, M., & Murata, K. (2005). Dehydration of ethanol into ethylene over solid acid catalysts. *Catalysis Letters*, 105(3), 249–252.

Tang, C.-W., Wang, C.-B., & Chien, S.-H. (2008). Characterization of cobalt oxides studied by FT-IR, Raman, TPR and TG-MS. *Thermochimica Acta*, 473(1–2), 68–73.

Trueba, M., & Trasatti, S. P. (2005). γ-alumina as a support for catalysts: A review of fundamental aspects. *European Journal of Inorganic Chemistry*, 1(17), 3393–3403.

Tsodikov, M. V, Fedotov, A. S., Antonov, D. O., Uvarov, V. I., Bychkov, V. Y., & Luck, F. C. (2015). Hydrogen and syngas production by dry reforming of fermentation products on porous ceramic membrane-catalytic converters. *International Journal of Hydrogen Energy,* 41(4), 2424–2431.

Torres, J. A., Llorca, J., Casanovas, A., Domínguez, M., Salvadó, J. and Montané, D. (2007). Steam reforming of ethanol at moderate temperature: Multifactorial design analysis of Ni/La_2O_3-Al_2O_3, and Fe- and Mn-promoted Co/ZnO catalysts. *Journal of Power Sources*, 169(1), 158–166.

Umar, M. S., Jennings, P., & Urmee, T. (2014). Generating renewable energy from oil palm biomass in Malaysia: The feed-in tariff policy framework. *Biomass and Bioenergy,* 62(1), 37–46.

Unnikrishnan, P., & Srinivas, D. (2016). Heterogeneous catalysis. In industrial catalytic processes for fine and specialty chemicals, 41–111.

Upadhyay, P. N. D. and S. N. (1977). Particle-fluid mass transfer in fixed and fluidized beds. *Ind. Eng. Chem., Process Des. Develop*., 16(2), 157–165.

Usman, M., Wan Daud, W. M. a., & Abbas, H. F. (2015). Dry reforming of methane: Influence of process parameters-A review. *Renewable and Sustainable Energy Reviews*, 45(4), 710–744.

Vargas, O. A. G., Heredia, J. A. de L. R. H., Wang, J. A., Chen, L. F., Castellanos, A. M., & Llanos, M. E. (2013). Hydrogen production over Rh/Ce-MCM-41 catalysts via ethanol steam reforming. *International Journal of Hydrogen Energy*, 38(3), 13914–13925.

Vannice, M. A., Hyun, S. H., Kalpakci, B. and Liauh, W. C. (1979). Entropies of adsorption in heterogeneous catalytic reactions. *Journal of Catalysis*, 56(3), 358–362.

Vasiliadou, E. S. and Lemonidou, A. A. (2013). Kinetic study of liquid-phase glycerol hydrogenolysis over Cu/SiO_2 catalyst. *Chemical Engineering Journal*, 231(5), 103–112.

Velu, S., Satoh, N., Gopinath, C. S., & Suzuki, K. (2002). Oxidative reforming of bio-ethanol over CuNiZnAl mixed oxide catalysts for hydrogen production. *Catalysis Letters*, 82(1–2), 145–152.

Vicente, J., Montero, C., Ereña, J., Azkoiti, M. J., Bilbao, J., & Gayubo, A. G. (2014). Coke deactivation of Ni and Co catalysts in ethanol steam reforming at mild temperatures in a fluidized bed reactor. *International Journal of Hydrogen Energy*, 39(1), 12586–12596.

Vizcaíno, A. J., Arena, P., Baronetti, G., Carrero, A., Calles, J. A., Laborde, M. A., & Amadeo, N. (2008). Ethanol steam reforming on Ni/Al_2O_3 catalysts: Effect of Mg addition. *International Journal of Hydrogen Energy*, 33(13), 3489–3492.

Vo, D.-V. N., & Adesina, A. A. (2012). A potassium-promoted Mo carbide catalyst system for hydrocarbon synthesis. *Catalysis Science & Technology,* 2(10), 2066–2076.

Wang, H., Ye, J. L., Liu, Y., Li, Y. D., & Qin, Y. N. (2007). Steam reforming of ethanol over Co_3O_4/CeO_2 catalysts prepared by different methods. *Catalysis Today*, 129(3–4), 305–312.

Wang, N., Shen, K., Huang, L., Yu, X., Qian, W., & Chu, W. (2013). Facile route for synthesizing ordered mesoporous Ni-Ce-Al oxide materials and their catalytic performance for methane dry reforming to hydrogen and syngas. *ACS Catalysis*, 3(7), 1638–1651.

Wang, W. (2011). Hydrogen production via dry reforming of butanol: Thermodynamic analysis. *Fuel*, 90(4), 1681–1688.

Wang, W., & Wang, Y. (2009). Dry reforming of ethanol for hydrogen production: Thermodynamic investigation. *International Journal of Hydrogen Energy*, 34(13), 5382–5389.

Wang, X., Cao, R., Zhang, S., Hou, P., Han, R., Shao, M., & Xu, X. (2012). Hierarchical flowerlike metal/metal oxide nanostructures derived from layered double hydroxides for catalysis and gas sensing. *Journal of Materials Chemistry A*, 5(1), 23999–24010.

Wang, Y. H., Wang, H., Li, Y., Zhu, Q. M., & Xu, B. Q. (2005). Performance of Ni/MgO-AN catalyst in high pressure CO_2 reforming of methane. *Topics in Catalysis*, 32(3–4), 109–116.

Wilhelm, D. J., Simbeck, D. R., Karp, A. D., & Dickenson, R. L. (2001). Syngas production for gas-to-liquids applications: Technologies, issues and outlook. *Fuel Processing Technology*, 71(1–3), 139–148.

Wood, D. A., Nwaoha, C., & Towler, B. F. (2012). Gas-to-liquids (GTL): A review of an industry offering several routes for monetizing natural gas. *Journal of Natural Gas Science and Engineering*, 9(1), 196–208.

Wu, X., & Kawi, S. (2009). Rh/Ce-SBA-15: Active and stable catalyst for CO_2 reforming of ethanol to hydrogen. *Catalysis Today*, 148(3–4), 251–259.

Wu, Z. Y., Chen, P., Wu, Q. S., Yang, L. F., Pan, Z., & Wang, Q. (2014). Co/Co_3O_4/C-N, a novel nanostructure and excellent catalytic system for the oxygen reduction reaction. *Nano Energy*, 8(5), 118–125.

Xiong, H., Motchelaho, M. A. M., Moyo, M., Jewell, L. L., & Coville, N. J. (2011). Correlating the preparation and performance of cobalt catalysts supported on carbon nanotubes and carbon spheres in the Fischer–Tropsch synthesis. *Journal of Catalysis*, 278(1), 26–40.

Yahia, L., & Mireles, L. K. (2017). X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF SIMS). *Characterization of polymeric biomaterials*, 83–97.

Yamamoto, T., Hatsui, T., Matsuyama, T., Tanaka, T., & Funabiki, T. (2003). Structures and acid-base properties of La/Al_2O_3 – role of La addition to enhance thermal stability of γ-Al_2O_3. *Chemistry of Materials*, 15(25), 4830–4840.

Yang, J., Ma, W., Chen, D., Holmen, A., & Davis, B. H. (2014). Fischer-Tropsch synthesis: A review of the effect of CO conversion on methane selectivity. *Applied Catalysis A: General*, 470(1), 250-260.

Yang, R., Xing, C., Lv, C., Shi, L., & Tsubaki, N. (2010). Promotional effect of La_2O_3 and CeO_2 on Ni/γ-Al_2O_3 catalysts for CO_2 reforming of CH_4. *Applied Catalysis A: General*, 385(1), 92–100.

Young, J. A. (2003). Aluminum Oxide, Al_2O_3. *Journal of Chemical Education*, 80(3), 258.

Zawadzki, A., Bellido, J. D. A., Lucrédio, A. F., & Assaf, E. M. (2014). Dry reforming of ethanol over supported Ni catalysts prepared by impregnation with methanolic solution. *Fuel Processing Technology,* 128(1), 432–440.

Zhang, B., Tang, X., Li, Y., Cai, W., Xu, Y., & Shen, W. (2006). Steam reforming of bio-ethanol for the production of hydrogen over ceria-supported Co, Ir and Ni catalysts. *Catalysis Communications*, 7(6), 367–372.

Zhang, G., Sun, S., Yang, D., Dodelet, J. P., & Sacher, E. (2008). The surface analytical characterization of carbon fibers functionalized by H_2SO_4/HNO_3 treatment. *Carbon*, 46(2), 196–205.

Zhang, W., Burckle, E. C., & Smirniotis, P. G. (1999). Characterization of the acidity of ultrastable Y, mordenite, and ZSM-12 via NH_3-stepwise temperature programmed desorption and Fourier transform infrared spectroscopy. *Microporous and Mesoporous Materials*, 33(1–3), 173–185.

Zhang, Z., Hicks, R. W., Pauly, T. R., & Pinnavaia, T. J. (2002). Mesostructured forms of γ-Al_2O_3. *Journal of the American Chemical Society*, 124(8), 1592–1593.

Zhao, S., Cai, W., Li, Y., Yu, H., Zhang, S., & Cui, L. (2018). Syngas production from ethanol dry reforming over Rh/CeO_2 catalyst. *Journal of Saudi Chemical Society*, 22(1), 58–65.

Zhang, Z., AU, C.T., & Tsai, K.R. (1990). Methane oxidative coupling to C_2 hydrocarbons over lanthanum promoted barium catalysts. *Applied Catalysis letter*, 62(1), 29–33.

Zhi, G., Guo, X., Guo, X., Wang, Y., & Jin, G. (2011). Effect of La_2O_3 modification on the catalytic performance of Ni/SiC for methanation of carbon dioxide. *Catalysis Communications*, 16(1), 56–59.