Oxidative Steam Reforming of Bioethanol over Rh/CeO$_2$-Al$_2$O$_3$ Catalyst for Hydrogen Production

Anamika Srivastava$^1$ and Pant KK*$^*$

$^1$Department of Applied Sciences and Humanities, Anand Engineering College, Keetham, Agra-282007, India
$^2$Department of Chemical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Abstract

Oxidative steam reforming of ethanol for hydrogen production was studied over 1%Rh/CeO$_2$-Al$_2$O$_3$ catalyst prepared in the laboratory. Support with CeO$_2$ content of 5wt% on γ-Al$_2$O$_3$ was prepared by impregnation with Ce(NO$_3$)$_3$·6H$_2$O solution. The effects of temperature (450°C and 550°C), Water/Ethanol ratio (mol/mol) (3 and 8) and Oxygen/Ethanol molar ratio (0.23 and 0.3) were studied at 1 atmospheric pressure in a down-flow tubular fixed bed reactor. The percentage conversion of ethanol ranged from 90% to 98% and maximum hydrogen selectivity was observed up to 70% at a selected Water/Oxygen/Ethanol molar ratio at 550°C. On increasing Water/Ethanol molar ratios in the feed, the catalytic activity for hydrogen production could be enhanced.

Keywords: Hydrogen; Bioethanol; Oxidative steam reforming; Catalyst

Introduction

The present renewable energy sources like solar, wind, tidal, biomass energy being utilized are site specific, intermittent and thus not stable. Hydrogen has been identified as a potential alternative fuel produced from renewable energy sources. It has the highest energy content per unit weight, 120 KJ/g [1] and is the only carbon-free fuel which ultimately oxidizes to water as a combustion product. Therefore burning hydrogen has the potential to meet a wide variety of applications and also it does not contribute to greenhouse emissions [2]. Hydrogen can be used either as a fuel for direct combustion in an internal combustion engine or as the fuel for a polymer electrolyte membrane (PEM) fuel cell [3,4]. Thus, hydrogen has many social, economic and environmental benefits and has the long-term potential to reduce the dependence on fossil fuel and lower emissions from the transportation sector.

Hydrogen can be produced from variety of feed stocks and among them biomass is being considered as a promising source of hydrogen. Hydrogen can be produced from organic waste and waste water by anaerobic fermentation [5]. Bioethanol is of great interest as a feedstock for hydrogen production due to its renewability and low toxicity. Bio-oil produced from biomass has a complex composition with more than 200 different compounds. These includes mainly acids, alcohols, glycerol, aldehydes, ketones and lignin derived oligomers [6-9]. Biooil can be produced in large amounts from biomass such as agricultural wastes and forestry residues and hence is a renewable resource, as against methanol and gasoline. Ethyl alcohol is preferable as the hydrogen resources since it can be easily produced by degradation and fermentation of biomass. It can be produced relatively from several biomass sources (sugarcane, beet root, corn, etc.) including waste materials from agro industries or forestry residue materials, organic fraction of municipal solid [10]. The ethanol obtained in this way is named bio-ethanol, a mixture of ethanol and water (18-23 wt% ethanol). Hydrogen can be produced through different methods like water electrolysis, gasification, partial oxidation reactions of heavy oil, and steam-reforming reactions. The most effective process for hydrogen production from ethyl alcohol are - the steam reforming reactions, partial oxidation and oxidative steam reforming reactions.

The steam reforming reaction of ethanol is endothermic and produces CO$_2$, a global warming gas, as a byproduct. C$_2$H$_5$OH + 3H$_2$O → 6H$_2$ + 2CO$_2$ $\Delta H_{25}^{\circ}$ = 41.6 kcal/mol (1)

In partial oxidation steam is replaced by oxygen and hydrogen is produced by exothermic reaction. C$_2$H$_5$OH + 3/2O$_2$ → 3H$_2$ + 2CO$_2$ $\Delta H_{25}^{\circ}$ = -132.0 kcal/mol (2)

In oxidative steam reforming ethanol can be reformed by co-feeding steam and oxygen. C$_2$H$_5$OH + (3-2δ) H$_2$O + δ O$_2$ → (6-2δ) H$_2$ + 2CO$_2$ $\Delta H_{25}^{\circ}$ = 0 kcal/mol (3)

This process can be made auto thermal when δ=0.35. This does not require any external heat to be supplied as the thermal energy generated in the partial oxidation of ethanol is used for steam reforming. Thus it is also called Auto thermal steam reforming [11,12].

The development of optimal catalytic materials for the steam reforming of ethanol is an important issue. Selecting a suitable support and addition of a proper metal to the metallic active phase are two important factors which play a crucial role in enhancing hydrogen production and ethanol conversion.

Rh has been shown to have excellent ability to break C-C bond and increased selectivity of C1 products (CO, CO$_2$, CH$_4$). The main products are CO and CO$_2$ which indicates that all the H atoms of ethanol can participate in hydrogen production giving highest Y$_{H_2}$ [13,14]. This capability is related to its high-lying d-band structure and with empty d states, which lowers the C-C bond dissociation barrier by stabilizing the intermediates [15,16]. Among the noble metals on various supports, Rh was found to be the most active metal (Rh, Pd, and Pt) with alumina as a support in the ethanol steam-reforming reactions [17]. Rh, Ru and
Ir on Al₂O₃ support have been shown to have highest CH₄, CO and CO₂ selectivity and best value of \( Y_H \) compared to other metals [16]. However, the high cost of noble metals is a major limiting factor in their use for hydrogen production via steam reforming.

Al₂O₃ was shown to convert 100% ethanol at temperature of 350°C which was related to its large adsorption capacity [18,19]. But the yield of hydrogen (\( Y_H \)) was very small was attributed to \( C_\text{H}_\text{O} \) dehydration to \( C_\text{H}_\text{₂} \). Al₂O₃ is an active catalyst but it has acidic sites on its surface which promotes coke formation by polymerization of \( C_n \) species. Cavallaro et al. [20] reported that Rh is active metal and it reduces coke formation. Rh/Al₂O₃ was found to be more active than Pt/Al₂O₃, Ni/Al₂O₃ or Pt/Al₂O₃ as reported by Breen et al. [17].

Compared to Al₂O₃ low surface area supports are preferred like ceria, zirconia is better because of their preferred thermal stability during steam reforming. Rh/CeO₂ showed almost 100% activity and produced 5 mol H₂ in oxidative steam reforming at 300-800°C [21]. At high Rh loading, Rh/Al₂O₃ was promising for \( C_\text{H}_\text{O} \) steam reforming. H₂ yield was 5.5 mol [20,22]. Rhodium catalyst derived from a chlorinated metal precursor was found to be effective [23].

Based on literature it can be revealed that ethanol conversion and hydrogen selectivity strongly depends on the type of metal and support chosen as catalyst materials, preparation methods, and operating conditions for reforming reaction such as water/oxygen/ethanol molar ratios, space time and temperature. Incorporation of oxygen in the steam reforming reaction lowers the temperature required for the reforming reaction. However, limited data are available on the choice of a suitable catalyst and reactions for the oxidative steam reforming of ethanol. Therefore this study aims at studying the catalytic oxidative steam-reforming of ethanol for the production of hydrogen using 1%Rh/5%CeO₂Al₂O₃ catalyst along with quantitative determinations of hydrogen and hydrocarbons.

**Experimental Work**

**Catalyst preparation and characterization**

Support with CeO₂ content of 5wt% on γ-Al₂O₃ was prepared by impregnation with Ce(NO₃)₃·6H₂O solution. After impregnation, samples was dried overnight at 110 ± 5°C in oven and subsequently calcined at 550 ± 10°C for 5 h. The supported Rh catalysts with Rh loading of 1wt% were prepared by the incipient impregnation method, using RhCl₃·xH₂O (40%). The catalyst thus prepared was dried overnight at 110 ± 5°C in oven and subsequently calcined at 550 ± 10°C for 5 h. It was further powdered and pelletized (3 mm size) using an automatic pellitizing press (Techno Search AP-15) and subsequently crushed and sieved to an average particle size of 0.6 mm.

The BET surface area, total pore volume and pore size distribution of the catalyst was determined from nitrogen adsorption/desorption isotherms measured at -196°C using Micromeritics ASAP 2010 apparatus.

**Catalytic activity measurements**

Before testing, the catalyst was reduced under flowing hydrogen (30 ml min⁻¹) at 550°C for 5 h using \( N₂ \) as carrier gas (30 ml min⁻¹). Reactivity testing was carried out at atmospheric pressure in a packed bed tubular reactor (down flow) for 5 h each. 3 mg catalyst diluted in 1 mg crushed ceramic beads was used for each test. Peristaltic pump was installed as feed pump to supply the feed (mixture of ethanol and de ionized water) from glass storage tank to pre heater. The schematic diagram and other details of the experimental setup are given elsewhere [24]. The capacity of peristaltic pump was maintained in the range of 0.4 ml/min. In order to carry out reaction in vapor phase, the water - ethanol solution was fed to the reactor using peristaltic pump through vaporizer where it was converted into the vapor at 200°C. The catalyst reactivity was tested for different conditions like H₂O/Ethanol (W/E) molar ratio 3 and 8, O₂/Ethanol (O/E) molar ratio 0.3 and 0.23, temperatures 450°C and 550°C.

All the gaseous products \( H₂ \), \( O₂ \), \( N₂ \), CO, CH₄, CO₂ were analyzed using a gas chromatograph (Model Nucon 5700) operated under TCD mode. The unit was equipped with molecular sieve column, and Argon (30 ml/min⁻¹) was used as carrier gas. The column conditions were as follows: Injector Temperature: 110°C, Oven Temperature: 60°C, Detector temperature: 120°C, TCD Current: 117 mA.

The condensate volume was used to approximate the ethanol conversion. The liquid product analysis was done using Nucon 5700 gas chromatograph and operated in FID mode. The column conditions were as follows: Column: SS column (3.2 mm OD × 1.8 m long) packed with carbosphere (80-100 mesh), Carrier gas: Nitrogen (30 ml/ min), Injector temperature: 210°C, Oven temperature: 80°C, Detector temperature: 230°C. The chromatograms were recorded and peak areas were calculated using Winads 6.2 software. The carbon /hydrogen balance for all the runs was checked and runs where mass balance was above 95% were considered for the data analysis. Some runs were also carried out in duplicate for the confirmation of data.

The hydrogen yield and selectivity of species (P=H₂, CO, CO₂, CH₄) were calculated as follows:

\[
Y_H = \frac{\text{moles of hydrogen produced}}{\text{moles of ethanol feed}}
\]

\[
S_P = \frac{\text{moles of gaseous product}}{\text{moles of all gaseous products}} \times 100
\]

Percent Ethanol Conversion = \[
\frac{\text{moles of Ethanol fed} - \text{moles of Ethanol exit}}{\text{moles of Ethanol fed}} \times 100
\]

**Results and Discussion**

The BET surface area, pore volume and pore diameter of 1%Rh/5%CeO₂Al₂O₃ catalyst was 203.7 m²/g, 0.6 cm³/g and 108.5 Å respectively. The decrease in the surface area of catalyst is probably due to the interaction between Al₂O₃ and CeO₂, and a partial blockage of the smaller pores in alumina by oxide additive. Danyanova et al. [25] reported BET surface area and pore volume of Al₂O₃ support as 205 m²/g and 0.5 cm³/g respectively at 500°C. The low ceria loading is also expected to stabilize alumina against surface area loss by preventing the transformation of γ-Al₂O₃ to α-Al₂O₃, which depends on the CeO₂ loading [25-27].

Prior to the experimental analysis, thermodynamic analysis of oxidative ethanol steam reforming was also carried out to understand the viability of reaction-product and to develop relationships between process variables (i.e., temperature, pressure, and feed composition) and the product distribution. Based on these results catalytic performance was investigated at limited set of conditions. The thermodynamic results are briefly presented in figure 1. Results of thermodynamic study revealed that higher water – to – ethanol ratio favours the hydrogen production as it promotes water gas shift reaction activity. However very high water content also increases the reactor loading therefore...
The rate of steam reforming increases as the O/E ratio increases. For example, the selectivity of CO decreases from 55.0% to 65.2% as the O/E ratio increases from 0.23 to 0.3 at 550°C. The improvement in selectivity of CO and CH₄, respectively, is similar to the Ni/Al₂O₃ catalyst supported on CeO₂, ZrO₂, and CeO₂–ZrO₂ [28] and suggests that ethanol decomposition and steam reforming are the main reactions in the reactor, with the O/E ratio increasing from 0.23 to 0.3 at 550°C corresponds to the dramatic increase of CO selectivity from 55.0% to 65.2%.

Effect of Water/Ethanol ratio

The product obtained from steam reforming was a gas mixture consisting of H₂, CO, CO₂, and CH₄ with no acetaldehyde or C₂ products. The selectivity of CO and CH₄ decreases with increasing water content in feed as methane reforming reaction is promoted. Instead, CO and CH₄ will follow the water gas shift reaction. Therefore further experiments were carried out only at selected conditions.

Catalytic activity

The product obtained from steam reforming was a gas mixture consisting of H₂, CO, CO₂, and CH₄ with no acetaldehyde or C₂ products. The selectivity of CO and CH₄ decreases with increasing water content in feed as methane reforming reaction is promoted. Instead, CO and CH₄ will follow the water gas shift reaction. Therefore further experiments were carried out only at selected conditions.

The selectivity of CO and CH₄ in reaction (11) and (12) increases from 19.9% to 20.9% as the W/E ratio increases from 3 to 8 at 550°C. The decrease for CO from 9.5% to 7.8% indicates that the rate of H₂O-assisted C-C bond cleavage becomes slower than that of WGS in higher W/E ratios. The variance of S_H₂ decreases with increasing water content in feed as the O/E ratio increases from 0.23 to 0.3 at 550°C corresponds to the dramatic increase of CO selectivity from 55.0% to 65.2%.

Effect of Oxygen/Ethanol (O/E) ratio

The effect of O/E ratios was examined at two different O/E 0.23 and 0.3 on 1% Rh-5%CeO₂Al₂O₃ at a W/E=8 at 550°C. Oxygen, similar to steam, can quickly form atomic O and react with ethanol and its fragments. Thus, the catalytic behavior varies with O/E ratios (Figure 3). S_CO increases as the O/E ratios increases. For example, S_H₂ rises slightly from 65.2% to 65.3% as the O/E ratio increases from 0.23 to 0.3 at 550°C. The improvement in S_CO resulting from a higher O₂ concentration follows different mechanisms than that obtained with higher W/E ratios. At higher O/E ratios, additional H₂ will not be produced from WGS and SRM. Instead, CO and CH₄ will follow the oxidation processes in reactions (13) and (14), respectively.

Thus, the slight improvement in S_CO from 65.2% to 65.3% as the O/E ratio increases from 0.23 to 0.3 at 550°C corresponds to the enhancement of the breaking of the C-C bond of ethanol. Thus all reactions support the experimental observation and this contradiction corresponds to that steam plays an important role in the WGS and the steam reforming of methane (SRM) for CO and CH₄, respectively [16].
increase significantly from 5.8% and 6.1% to 7.1% and 2/ethanol ratio increases.

decreased from 22.0% to 20.9% with implying that O

and S respectively using 3% Rh/MgO and 1% Rh/CeO

bond cleavage and oxidation processes in reactions.

while that of CH 4 decreased from 10.0% to 6.1% with increasing temperature from 450 to 550°C. Meng et al. [29] reported that for Rh supported catalysts methanation reaction occurs at high temperatures. The increase of Y

consumption of CH4 and CO correspond to the rates of ethanol C-C bond cleavage and oxidation processes in reactions.

Thus, the observed increase in S

and S

CH4 + O2 → CO2 + 3 H2O

(14)

This shows the lower oxidation rates of CO and CH4 over the Rh based catalyst.

Effect of temperature

Effect of temperature can be seen by comparing the results of figures 2a and 4. The selectivity of H2 increased from 61.5% to 65.3% while that of CH4 decreased from 10.0% to 6.1% with increasing temperature from 450 to 550°C. Meng et al. [29] reported that for Rh supported catalysts methanation reaction occurs at high temperatures. The increase of Y

directly corresponds to the increase of ethanol conversion which corresponds to kinetic rates [16]. The extent of methanation reaction which also accounts for generation of methane by hydrogenation of CO2 compounds decreases with increasing temperature due to exothermic nature of reaction. Thus selectivity of CO2 decreases from 21.6% to 20.9% while that of CO increases from 6.9% to 7.8% at higher temperatures because water gas shift reaction begins to shift in backward direction as it is an exothermic reaction, especially around 550°C. However, further experiments are in progress at different temperatures to investigate the mechanism.

The observed ethanol conversion was in the range of 90-98% at all investigated conditions. Breen et al. [17] reported nearly complete conversion of ethanol and approx 70% S

and S

Rh/Al2O3 Catalyst in the Steam Reforming of Ethanol: H2 Production for MC. Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. Haryanto A, Fernando S, Murali N, Adhikari S (2005) Current Status of Hydrogen from Ethanolic Aqueous Solutions over Oxide Catalysts. Chem Commun 641-642.

Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, et al. (2009) Hydrogen production by sorption-enhanced steam reforming of glycerol. Bioreour Technol 100: 3540-3547.

Gao N, Li A, Quan C (2009) A novel reforming method for hydrogen production from biomass steam gasification. Bioreour Technol 100: 4271-4277.

Sahoo DR, Vajpai V, Rode C, Sapkal R (2012) Conventional ethanol reforming technology developments for the production of hydrogen. J Adv Eng Technol 3: 436-450.

Idriss H (2004) Final analysis. Platinum Met Rev 48: 145.

Vaidya PD, Rodrigues AE (2006) Insight into steam reforming of ethanol to produce hydrogen for fuel cells. Chem Eng J 117: 39-49.

Kowal A, Li M, Shao M, Sasaki K, Vukmirovic MB, et al. (2009) Ternary Pt/Rh/ SnO2 electrocatalysts for oxidizing ethanol to CO2. Nat Mater 8: 325-330.

Hung CC, Chen SL, Liao YK, Chen CH, Wang JH (2012) Oxidative steam reforming of ethanol for hydrogen production on M/Al2O3. Int J Hydrogen Energy 37: 4955-4966.

Breen JP, Burch R, Coleman HM (2002) Metal-Catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications. Appl Catal B Env 39: 65-74.

Llorca J, de la Piscina PR, Sales J, Homs N (2001) Direct Production of Hydrogen from Ethanoic Aqueous Solutions over Oxide Catalysts. Chem Commun 641-642.

Haryanto A, Fernando S, Murail N, Adhikari S (2005) Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. Energy Fuels 19: 2098-2106.

Cavallaro S, Chiodo V, Freni S, Mondello N, Frustieri F (2003) Performance of Rh/Al2O3 Catalyst in the Steam Reforming of Ethanol: H2 Production for MC. Appl Catal A 249: 119-128.

Conclusions

1% Rh/CoO2-ZrO2 catalyst was found effective for the oxidative steam reforming of bioethanol. Results revealed that addition of oxygen to the ethanol water stream is crucial in improving the activity and stability of the catalyst system. The maximum H2 yield of 4.2 was obtained out of 6 at 550°C at 1 atm. pressure, molar ratio water to ethanol molar ratio 8:1 and oxygen to ethanol ratio 0.3:1. The H2 yield increases from 2.0 to 4.2 when temperature was increased from 450°C to 550°C. Also ethanol conversion increased from 90 to 98% when water to ethanol ratio of the feed was changed from 8:1 to 3:1.

Acknowledgement

One of the Author, Dr. Anamika, is thankful to the Department of Chemical Engineering, IIT Delhi and the Director, Anand Engineering College, Agra for supporting to attend the ‘Summer Faculty Research Fellow Program’ under Continuing Education.

References

1. Hoogers G (2003) Fuel Cell Technology Handbook. CRC Press.

2. Mustafa B (2008) Potential importance of hydrogen as a future solution to environmental and transportation problems. Int J Hydrogen Energy 33: 4013-4029.

3. Patel S, Pant KK (2007) Hydrogen production by oxidative steam reforming of methanol using ceria promoted copper-alumina catalysts. Fuel Process Technol 88: 825-832.

4. Kotay S M, Das D (2008) Biohydrogen as a renewable energy resource-Prospects and potentials. Int J Hydrogen Energy 33: 258-263.

5. Vasudeva K, Mitra N, Umasankar P, Dhirga SC (1996) Steam-reforming of ethanol for hydrogen production: Thermodynamic Catalysis. Int J Hydrogen Energy 21: 13-18.

6. Mohanty P, Patel M, Pant KK (2012) Hydrogen production from steam reforming of acetic acid over Cu-Zn supported calcium aluminate. Bioresour Technol 123: 558-565.

7. Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, et al. (2009) Hydrogen production by sorption-enhanced steam reforming of glycerol. Bioreour Technol 100: 3540-3547.

8. Gao N, Li A, Quan C (2009) A novel reforming method for hydrogen production from biomass steam gasification. Bioreour Technol 100: 4271-4277.

9. Sillm M, Kendall K, Malton C, Andrews J (2008) Steam reforming of biodiesel by-product to make renewable hydrogen. Bioreour Technol 99: 5851-5858.

10. Sahoo DR, Vajpai V, Patel S, Pant KK (2007) Kinetic modeling of steam reforming of ethanol for the production of hydrogen over Co/Al2O3 catalyst. Chem Eng J 125: 139-147.

11. Nageswarapr PR, Kunzru, D (2011) Oxidative steam reforming of ethanol over Rh based catalysts in a micro-channel reactor. Int J Hydrogen Energy 36: 3364-3369.

12. Tayade P, Sapkal V, Rode C, Sapkal R (2012) Conventional ethanol reforming technology developments for the production of hydrogen. J Adv Eng Technol 3: 436-450.

13. Idriess H (2004) Final analysis. Platinum Met Rev 48: 145.

14. Vaidya PD, Rodrigues AE (2006) Insight into steam reforming of ethanol to produce hydrogen for fuel cells. Chem Eng J 117: 39-49.

15. Kowal A, Li M, Shao M, Sasaki K, Vukmirovic MB, et al. (2009) Ternary Pt/Rh/SnO2 electrocatalysts for oxidizing ethanol to CO2. Nat Mater 8: 325-330.

16. Hung CC, Chen SL, Liao YK, Chen CH, Wang JH (2012) Oxidative steam reforming of ethanol for hydrogen production on M/Al2O3. Int J Hydrogen Energy 37: 4955-4966.

17. Breen JP, Burch R, Coleman HM (2002) Metal-Catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications. Appl Catal B Env 39: 65-74.

18. Llorca J, de la Piscina PR, Sales J, Homs N (2001) Direct Production of Hydrogen from Ethanoic Aqueous Solutions over Oxide Catalysts. Chem Commun 641-642.

19. Haryanto A, Fernando S, Murail N, Adhikari S (2005) Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review. Energy Fuels 19: 2098-2106.

20. Cavallaro S, Chiodo V, Freni S, Mondello N, Frustieri F (2003) Performance of Rh/Al2O3 Catalyst in the Steam Reforming of Ethanol: H2 Production for MC. Appl Catal A 249: 119-128.
21. Deluga GA, Salge J R, Schmidt LD, VerykiosXE (2004) Renewable Hydrogen from Ethanol by Autothermal Reforming Science 303: 993-997.

22. Cavallaro S, Chiodo V, Vita A, Freni S (2003) Hydrogen Production by Autothermal Reforming of Ethanol on Rh/Al2O3 Catalyst. J Power Sources 123: 10-16.

23. Aupretre F, Descorme C, Duprez D (2004) Hydrogen Production for Fuel Cell from the Catalytic Ethanol Steam Reforming. Top Catal 30-31.

24. Goyal N, Pant KK, Gupta R (2013) Hydrogen production by steam reforming of model bio-oil using structured Ni/Al2O3 catalysts. Int J Hydrogen Energy 38: 921-933.

25. Damyanova S, Perez CA, Schmal M, Bueno JMC (2002) Characterization of ceria-coated alumina carrier. Applied Catalysis A: Gen 234: 271-282.

26. Ozawa O, Kimura M (1990) J Mater Sci Lett 9: 291.

27. Blom R, Dahl IM, Slagter A, Sortland B, Spjelkavik A, et al. (1994) Catal Today 21: 535.

28. Srisiriwat N, Therdthianwong S, Therdthianwong A (2009) Oxidative steam reforming of ethanol over Ni/Al2O3 catalysts promoted by CeO2-ZrO2 and CeO2-ZrO2. Int J Hydrogen Energy 34: 2224-2234.

29. Ni M, Leung DYC, Leung MKH (2007) A review on reforming bio-ethanol for hydrogen production. Int J Hydrogen Energy 32: 3238-3247.

30. Frusteri F, Freni S, Spadaro L, Chiodo V, Bonura G, et al. (2004) H2 production for MC fuel cell by steam reforming of ethanol over MgO supported Pd, Rh, Ni and Co catalysts. Catal Commun 5: 611-615.

31. Erdohelyi A, Rasko J, Kecskes T, Toth M, Domok M, et al. (2006) Hydrogen formation in ethanol reforming on supported noble metal catalysts. Catal. Today 116: 367-376.