EXPERIMENTAL STUDY OF PRODUCT DISTRIBUTION: REFORMING OF BIOETHANOL IN FIXED BED CATALYTIC REACTOR FOR H_2 PRODUCTION

P. R. Tayade[1], V. S. Sapkal[2], R. S. Sapkal[3], P. V. Sapkal[4]

[1]Assistant Professor, Department of Chemical Engg.,
Jawaharlal Darda Institute of Engg. & Technology, Yavatmal, M. S.,(India)
[2]Prof & Head, Department of Chemical Technology, Sant Gadge Baba Amravati University,(India)
Former-Vice-Chancellor, Rashtrasant Tukdoji Maharaj Nagpur University, (India)
[3]Head & Associate Prof, Department of Chemical Technology,
Sant Gadge Baba Amravati University, Amravati, M.S., India,
[4]ICT, Mumbai, Maharashtra (India)

ABSTRACT

The environmental pollution, global warming, and energy crises, all resulted by the extensive use of fossil fuels in automobiles and industry. In this situation of need of sustainable energy, hydrogen as a fuel obtained by steam reforming of bio-derived ethanol (bioethanol) substantially can fulfill the requirement of clean energy for the future. By keeping this view, steam reforming of bioethanol for the production of hydrogen using 10 % Co-ZnO catalyst in fixed bed catalytic reactor was studied. For this, a fixed bed tubular SS-316, 15 mm diameter, 28 cm in length reactor was developed. The reforming reactions were carried to observe the product distribution under atmospheric pressure condition in the temperature range of 350 ^{0}C – 550 ^{0}C and bio-ethanol to water feed molar ratio of 1: 8 to 1:12. The Co-ZnO catalyst prepared by co-precipitation method has shown very good catalytic activity in the studied range of molar ratio of feed and reforming temperatures.

Keywords -- Hydrogen, Bioethanol, Reforming, Fixed Bed Reactor, Renewable Energy

I. INTRODUCTION

CO_2 is one of the main constituent of ecosystem on the earth; life on the earth developed in accordance of CO_2 level that was present in the atmosphere at that time. Now, from the mid of 18th century, we are continuously taking out fossil fuels from the stomach of the earth and adding it into environment in more irregular form (increasing enthalpy of universe). The necessary atmospheric conditions required for life on earth are being continuously disturbed by the extensive use of fossil fuels (adding of CO, CO_2, SO_x, NO_x, VOC and other pollutants in the environment). If this is continuously executed, the life of mankind on the earth will be difficult up to the end of this 21st century. Therefore, it is inevitable to generate alternative new source of energy which must be clean with respect of the environment.

To uphold this priority of clean energy source, hydrogen can substantially fulfill the load of clean energy. Though, till the hydrogen could not stand on the basis of economics if we compare with the cost of fossil fuels, (cost of H_2/Kg ≈ 2 x cost of fossil fuel/kg for large scale production of H_2) [1] due to technological hurdles such as hydrogen storage, transportation and its distribution, continuous research efforts can stand the hydrogen in the global economic era of energy sector. For keeping the view of global cycle of clean and sustainable production of energy, new eco-friendly reservoirs of hydrogen are needed and this can be fulfill by the ethanol or bio-derived ethanol (bioethanol). This research work was done to generate hydrogen using Co/Zno catalyst by steam reforming of bioethanol which can maintain the CO_2 neutral cycle of ecosystem.

Hydrogen is the potential source of clean energy and possesses the highest energy content per unit weight (i.e. 120 KJ/g), as compare to other fuels. Although, most of the used technologies to produce hydrogen are based on natural gas steam reforming, the hydrogen production from bio-liquids such as bioethanol is a promising technology for the future, because it appears as the more attractive alternative due to its renewable characteristics (it is a part of CO_2 neutral cycle), high H_2 yield and low CO_2 emissions [2-4]. In addition to this, most of the Indian region is mainly a farming region and produces the biomass that gives bioethanol by fermentation such as Sugarcane molasses, Wheat straw, Cotton stalk, Rice bran etc [5]. Therefore, on the basis of bioethanol as a feedstock for production of H_2, more world reforming technologies may attract towards the Indian region in future.

The increase in the yield of H_2 by suppressing the side products such as CO, CO_2, and CH_4 is the prime requirement of ethanol reforming reaction. Also, if these side products are at minimum level on the product side of this reaction, the purification of H_2 will be easy and it will reflect in the improvement of overall process cost of steam reforming of ethanol. Therefore, catalyst is the main crucial part of ethanol steam reforming technology. Lot of researchers has collected the data on number of catalyst [6-14]. Among these catalyst Co/ZnO, ZnO, Rh/CeO_2, and Ni/Al_2O_3 are the best suitable catalysts for reforming of ethanol at atmospheric pressure and temperature range of 300-700 ^{0}C.

The objective of this research work is to verify the feasibility of Co/ZnO supported catalyst in the fixed bed catalytic reactor and to observe the effect of the process parameters such as temperature and bioethanol-to-water feed molar ratio on product distribution of reforming of bioethanol.

II. EXPERIMENTAL METHODS

2.1 Catalysts preparation

Catalyst was prepared by the co precipitation method from $Zn(NO_3)_2$ and $Co(NO_3)_2$ aqueous solutions. In this preparation, catalyst precipitation was accomplished by the addition of a K_2CO_3 solution at 40 ^{0}C. After aging at 40 ^{0}C for 1.5 hr with vigorously stirring on a heating plate and then resulting solution washed with distilled water. After washing, the samples were dried at 90° C overnight. The samples were calcined at 400 °C under air for 12 hrs with a heating rate of 10 °C/min. After calcinations the catalyst sample was reduced under hydrogen for 12 hrs at 400 ^{0}C.

2.2 Catalyst characterization

The characterization of 10% Co-ZnO Catalyst was carried using X-ray Diffraction. in order to identify the component phases present, using the X-ray microdiffractometer Rigaku D-max-RAPID, with a cylindrical imaging plate detector, that with Cu-Kα radiation allows to collect the diffraction data from 0 to 204° (2ϑ) horizontally and from -45 to 45° (2ϑ) vertically. Fig. 1 shows the enlarge view of XRD of catalyst samples before reaction. It is clearly observed from the Fig. 2 i.e. XRD of catalyst samples after reaction, that intensity of peaks gets reduced after reaction. It is clear indication of reforming of ethanol was happened on the 10 % Co-ZnO catalyst.

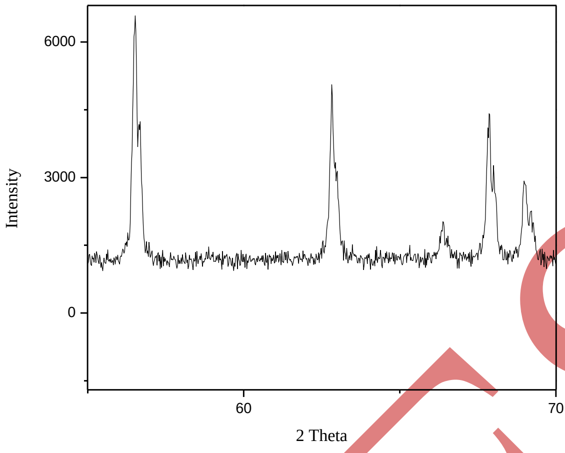

Figure 1Enlarge view of XRD for Co/ZnO catalyst before reaction

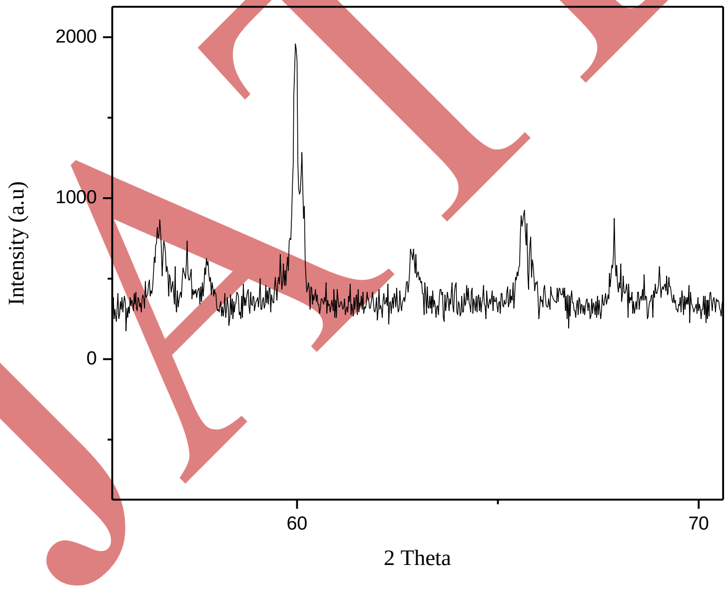

Figure 2Enlarge view of XRD for Co/ZnO catalyst after reaction

2.3. Experimental Setup

A proper experimental setup with requisite instrumentation and accessories was designed for the reforming of bioethanol in presence of 10% of Co/ZnO. Fig. 3 shows the photograph of the actual experimental set-up, whereas Fig. 4 shows the schematic flow diagram for the reforming of bioethanol. All the pipe lines from vaporizer to condenser are SS-316 of 1/4" size; connections are made with ferrule connections and needle valves. The reactor set up consists of following components.

1. Peristaltic feed pump having pumping rate from 1 ml/min – 50 ml/min
2. SS-316 Vaporizer having 8 cm diameter and 12 cm length equipped with two 1000 watt ceramic band heaters and a Pt-100 temperature sensor to read the vaporizer temperature

Feed section

All the gases used in this experimentation with a purity degree of 99.999 %. Nitrogen and argon were fed from cylinders, both gases being the gas carrier for bio-ethanol and water vapors, therefore by changing temperature and N_2 flow rate it is possible to obtain different concentrations in the reaction feed. Also, N_2 was used to clean the reactor and to cool the reactor after completion of experimental run.

Reaction section

A system of three way valves allows feed reactants to the reaction section. In by-pass an independent line is used to send nitrogen to wash the reactor.

Figure 3Photo of Bio-ethanol steam reforming laboratory plant.

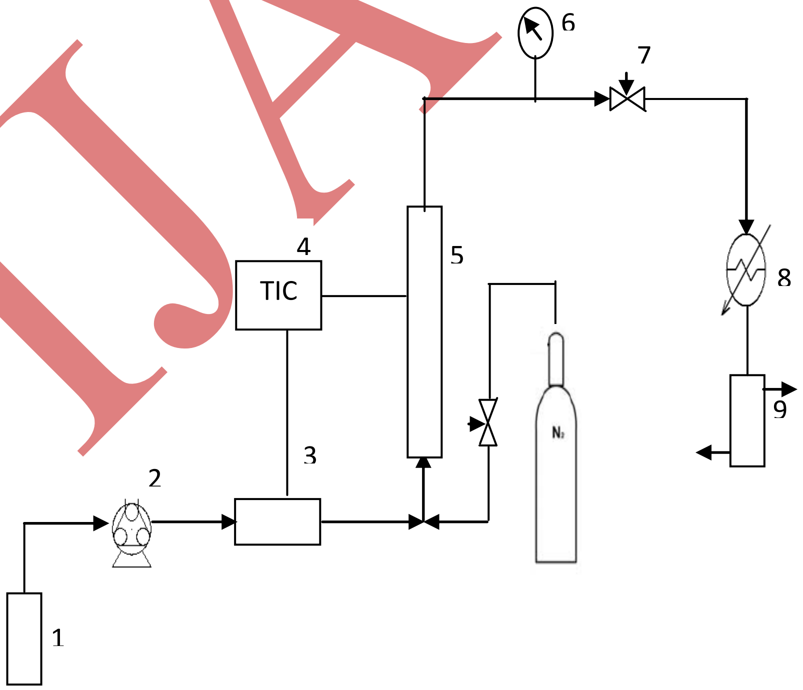

Figure 4 Laboratory flow diagram for Bio-ethanol steam reforming.

The reactor shown in Figure 3 was developed by Smart automation Ltd. Pune; it was made of a SS-316 tube of 30 cm length and internal diameter of 15 mm placed in a two zone electric oven. The thermocouple is located inside the reactor, in an internal quartz tube of internal diameter of 10 mm concentric to the reactor. An isothermal zone of 8 cm, with a temperature variation of ± 1°C, was found at 20 cm from the oven entry (Fig. 5). The catalytic bed is located in the isothermal zone.

1. Ethanol and Water feed reservoir
2. Peristaltic Pump
3. Water ethanol feed vaporizer
4. On/off temperature controller
5. Fixed bed tubular reactor (Reformer)
6. Pressure gauge
7. Needle valve
8. Condenser
9. Gas liquid separator
10. Nitrogen cylinder

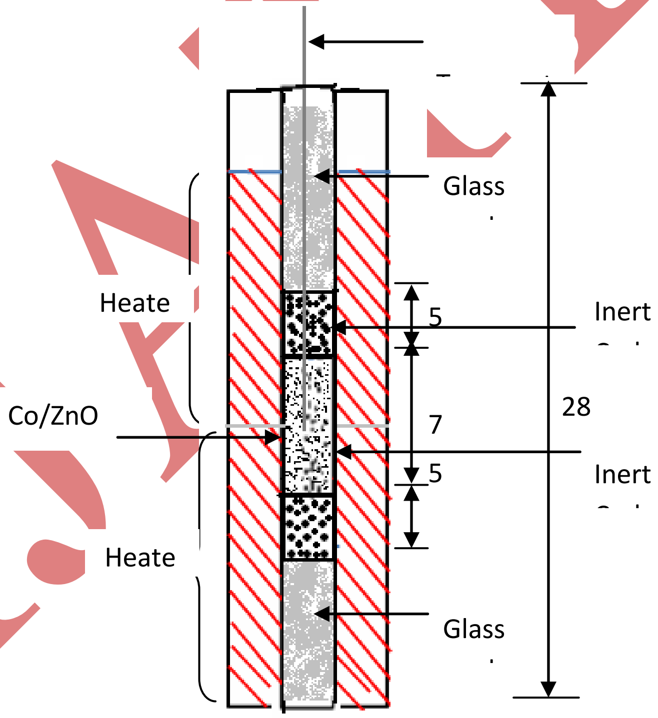

Figure 5. Schematics of Fixed Bed Tubular Reactor. (Reformer)

III. RESULT AND DISCUSSION

The results reported are based on reactant selectivity to hydrogen and other carbon-containing products. Selectivity to products is defined as follows:

$$S_i(\%) = \frac{n_{i\ prod}}{\nu_i n_{C_2H_5OH}\ reacted} \times 100 \tag{2}$$

where ν_i is the ratio of stoichiometric reaction coefficients.

3.1 Effect of Temperature

In the reforming of bioethanol the effect of temperature was studied to observe the selectivity behavior of H_2 with respect to other reforming bi-products such as CO, CO_2 and methane. The temperature effect reactions were carried at atmospheric pressure on 1 gm of 10 % Co-ZnO catalyst with ethanol water molar ratio of 1:12 and feed flow rate of 2 ml/min for 5 hrs by varying the temperature from 350 ^{0}C to 550 ^{0}C. It was observed that selectivity of H_2 goes on increasing progressively with increase in temperature as shown in Fig. 6 and simultaneously CO_2 also increase up to 500 ^{0}C and then it becomes steady. The temperature effect on the selectivity of CO and other gases shows good reverse effect of decreasing selectivity (15% to 5%) with increase in temperature from 350 to 550 ^{0}C. Whereas, many of the catalysts have been reported as low temperature reforming catalyst [15 16], in that selectivity of CO and other gases increases with increase in temperature. This, high-reforming temperatures favor the formation the CO, which poisons the anode. As a result, downstream CO reduction processes such as water gas shift are required. The low temperature ethanol steam reforming faces challenges of formation of undesirable reaction byproducts such as CH_4 and carbon. These are thermodynamically favored at low temperatures [17 18], leading to reduced H_2 selectivity and poor catalyst life. Thus, kinetic rather than thermodynamic control of the reaction is required.

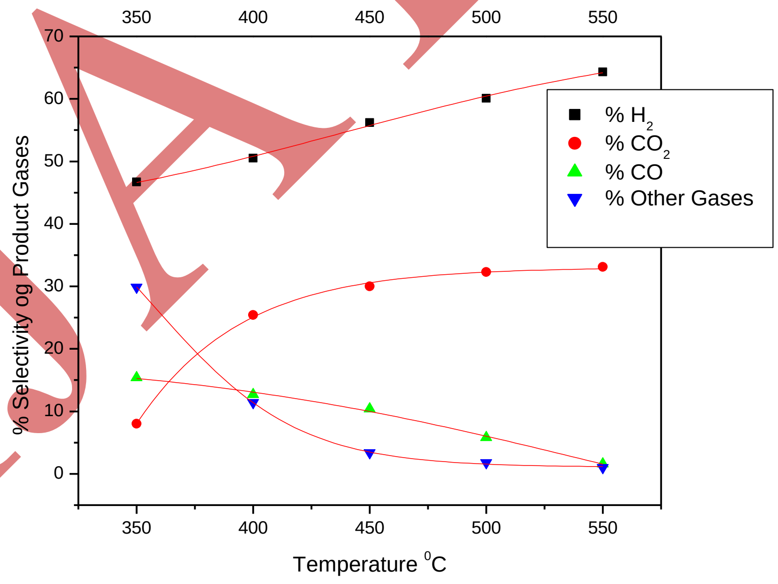

Figure 6: Effect of temperature on selectivity of H_2, CO_2, CO and other gases formed in the reforming of bioethanol : feed flow rate 2 ml/min, water: ethanol ratio-12:1, Pressure-atmospheric, Weight of catalyst- 1 gm, Catalyst particle size- 1mm.

3.2 Effect of Water-Ethanol Mole Ratio

The water-bioethanol molar ratio plays an important role in product selectivity. The effect of water-ethanol ratio was studied for reforming of bioethanol in the molar ratio range of 8:1 to 12:1 at atmospheric pressure and 500

^{0}C for 1 gm of catalyst and 5 hrs times with flow rate of feed solution of 2 ml/min. The water-ethanol mole ratio shows the similar pattern of effect as temperature given shown in Fig. 7. It is observed that increase in amount of water in feed solution of reforming reaction leads in the increase of H_2 and CO_2 formation, H_2 reaching from 52% to near about 60 % by increasing ratio from 1:8 to 1: 12, and CO_2 increases from 15% to 25%. The result of this effect is the decrease in the CO formation and it goes down from 10% to 2%. Also, the conversion of ethanol is increases; the main reason of this increase in H_2 selectivity and ethanol conversion is low coke formation due to increase in water content in the feed (increase in water ethanol mole ratio). The large excess of water in the feed solution of reforming reaction favors the water gas shift reaction given by the following equation 1

$$\mathbf{CO} + H_2O \longrightarrow H_2 + CO_2 \qquad (1)$$

In this reaction CO gets converted into H_2 and CO_2**,** and if more water is available more amount of CO gets converted into H_2 and CO_2.

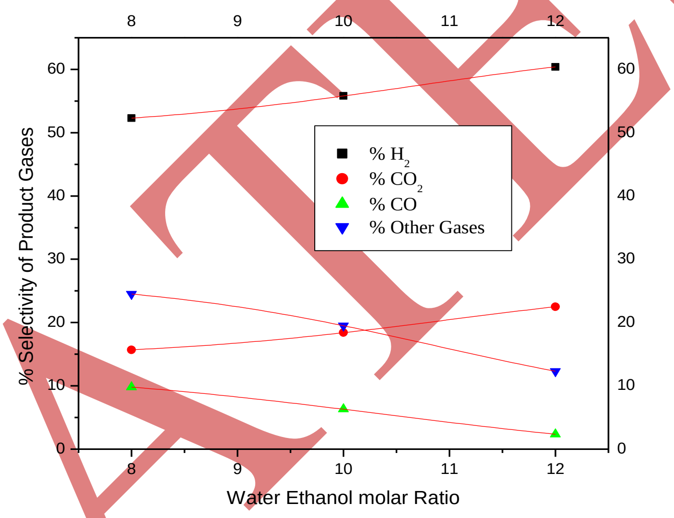

Figure 7:Effect of feed molar ratio on selectivity of H_2, CO_2, CO and other gases formed in the reforming of bioethanol: Temp – 500 ^{0}C, feed flow rate 2 ml/min, Pressure-atmospheric, Weight of catalyst- 1 gm, Catalyst particle size- 1mm.

IV. CONCLUSION

Bio-ethanol is a renewable source of energy, and hydrogen for fuel cell can be efficiently produced from bio-ethanol by the steam reforming reaction. The catalytic performance of 10% Co-ZnO catalyst in the steam reforming of bio-ethanol to produce hydrogen for fuel cell applications was investigated by operating the reactor at different reactor operating conditions. The 10% Co-ZnO catalyst has shown the good effectiveness for the reforming of bioethanol over the given period of experimentation. The product distribution of bio-ethanol reforming reaction over Co-ZnO catalyst was found out, H_2, CO_2 and CO as the main products of reaction along with many side products in minute quantity.

Acknowledgement

This research was supported by membrane separation group of Chemical Technology Department of SGBAU, Amravati headed by Dr. V. S. Sapkal, Prof & Head, Chemical Technology Department, SGBAU, Amravati.

REFERENCES

[1] H. Antonia, T. Marika, Hydrogen Future? An Economic and Environmental Assessment of Hydrogen Production Pathways, Natural Resources Defense Council issue paper 2005.

[2] J. Comas, M. Marino, N. Laborde, Amadeo. Bio-ethanol steam reforming on Ni/Al2O3 catalyst. *Chemical Engineering Journal* 98, 2004, 61-68.

[3] Athanasio, N. F., and Verykios, E. 2004. Reaction network of steam reforming of ethanol over Ni-based catalysts. *Journal of Catalysis* 225: 439-452.

[4] Cavallaro, S. and Freni, S. 1996. Ethanol steam reforming in a molten carbonate fuel cell. A preliminary kinetic investigation. *International Journal of Hydrogen Energy* 21: 465-469.

[5] Yun, Y, Xia, L. and Hongwei, W. 2008. Some Recent Advances in Hydrolysis of Biomass in Hot-Compressed Water and Its Comparisons with Other Hydrolysis Methods, *Energy &Fuels* 22, 46–60.

[6] Pilar, R. P., Homs, N. Joaquim, S., Fierro and L. 2004. Effect of sodium addition on performance of Co-ZnO based catalysts for hydrogen production from bioethanol. *Journal of catalysis* 222: 470-480.

[7] Pilar, R. P., Llorca, J. Homs, N. Joaquim, S. and Dalmon, J. 2003. CO-free hydrogen from steam reforming of bioethanol over ZnO-supported cobalt catalysts: Effect of the Mettalic precursor. *Applied catalysis B: Environmental* 43: 355-369.

[8] Benito, M., Padilla, R., Rodriguez, L., Sanz, J., and Daza, L. 2007. Zirconia supported catalyst for bioethanol steam reforming: Effect of Active Phase and Zirconia Structure. *Journal of Power sciences* 169: 167-176.

[9] Homs, N., Llorca, J. and Pilar, R. 2006. Low temperature steam-reforming of ethanol over ZnO-supported catalyst: The effect of nickel and copper addition to ZnO supported cobalt-based catalyst. *Catalysis Today* 116: 361-366.

[10] Vargas, J. C., Libs, S., Roger, A. and Kiennemann, A. 2005. Study of Ce-Zr-Co fluoritetype oxide as catalyst for hydrogen production by steam reforming of bioethanol. *Catalysis Today* 107-108: 417-425.

[11] Chang, Y. U., Lee, W., Park, S. and Lee, Y. 2009. Study on catalytic membrane reactor for hydrogen production from ethanol steam reforming. *International Journal of Hydrogen Energy* 34: 2947-2954.

[12] Kugai, J., Velu, S. and Song, C. 2003. Novel CeO_2 supported Ni-Rh bimetallic catalysts for reforming of bio-ethanol to produce hydrogen for fuel cells. *Preprint Papers -American Chemical Society, Division of Fuel* Chemistry 48: 754-755.

[13] Marino, F., Boveri, M., Baronetti, G. and Laborde, M. 2001. Hydrogen production from steam reforming of bioethanol using Cu/Ni/K/γ-Al2O3 catalyst. Effect of Ni. International Journal of Hydrogen Energy, 26: 665-668.

[14] Carlo, R., Cavallarob, S., Frusteric, F., Frenic, S. and Guido, B. 2007 Initial steps in the Production of H_2 from Ethanol: A FT-IR Study of Adsorbed Species on Ni/MgO Catalyst surface. *React. Kinet. Catal. Lett.* 90: 117−126.

[15] Das, N. K., Dalai, A. and Ranganathan, R. 2007. Hydrogen Yield from Low Temperature Steam Reforming of Ethanol, *The Canadian Journal of Chemical Engineering*, 85:

[16] Kugai, J., Velu, S. and Song, C. 2005. Low-temperature reforming of ethanol over CeO2-supported Ni-Rh bimetallic catalysts for hydrogen production, *Catalysis Letters*, 101: 3–4.

[17] Fishtik, I., Alexander, A., Datta, R. and Geana D. 2000. *Int. J. Hydrogen Energy*, 25- 31,

[18] Tsiakaras, P. and Demin, A. 2001. *J.*