



ETHANOL REFORMING FOR HYDROGEN PRODUCTION IN HIGH PRESSURE CONDITION: EFFECT OF DIFFERENT SUPPORT ON COBALT BASED CATALYST

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ABSTRACT

In this study the steam reforming of Ethanol under the Cobalt catalyst with different support was studied, the yield of Hydrogen with respect to different support was measured. Catalysts were prepared on laboratory scale and its properties such as, (TPD), (TPR), XRD, surface area and pore volume were measured. The analysis of liquid and gas products were done by G.C. and found to be varying with different support.

Under the supercritical condition of water the support can affect the catalyst physically as well as chemically. The degree of catalyst reduction can effect the Hydrogen production. The C₂H₄ production is favoured by Cobalt oxide. The comparison of XRD of YSZ and Co₂O₃ over YSZ catalyst, suggests that the Cobalt (III) oxide in the presence of hydrogen reduced to Co^{II} and then to metallic cobalt. The degree of Cobalt reduction affects directly the amount of products.

TPR of catalysts show that Co₂O₃/YSZ and Co₂O₃/ZrO₂ reduce by H₂ below 500 °C in favour of more hydrogen production. The catalyst tendencies for unfavorable product CO are very low. The production of CO₂, CH₄ and especially Hydrogen is increasing with Co₂O₃/YSZ and Co₂O₃/ZrO₂. In the liquid phase the amount of Acetal and Acetone are more than Ethyl ether.

The results of this work suggest that Co/YSZ shows high conversion of Ethanol to Hydrogen as well as a good resistance toward deactivation under high pressure.

Keyword: Ethanol, Steam reforming, hydrogen production, Cobalt catalyst, Catalyst support, supercritical water.

INTRODUCTION

In recent years, the proton exchange membrane fuel cells (PEMFC) with hydrogen as fuel has attracted many attentions due to its potential application in electric vehicles and power station. The use of hydrogen as a fuel offers an important reduction in NO_x and CO_x emissions. Hydrogen is used as a feedstock in the chemical industry as well as in the manufacture of ammonia and methanol, in refinery reprocessing and conversion processes^{1,2}. The increased hydrogen demand especially for fuel cell applications imposes the development of new methods for hydrogen production. The economic future of ethanol production looks even more favorable when one considers the likely increases in the price of petroleum and other fossil fuels as world reserves are depleted.

Methane, methanol and gasoline, all of which are derived from fossil fuels, have been studied as possible liquid feed stocks to produce hydrogen for automotive fuel cell applications³⁻⁵. In contrast, ethanol steam reforming has been studied to a more limited extent. Ethanol has several advantages over fossil-fuel derived hydrocarbons as a source for hydrogen production in fuel cell applications. It represents a renewable and CO₂-neutral source that can readily be obtained from biomass fermentation⁶.

Catalytic steam reforming is a new interest focus as the main pathway to obtain hydrogen from hydrocarbons or alcohols to be supplied to a fuel cell^{7,8}.

Nickel, copper, cobalt, and precious metal (e.g. platinum, palladium, ruthenium, gold and rhodium) or combinations of different metals have been studied for the ethanol steam reforming. The role of the

support has also been studied; examples of support investigated are Al₂O₃, MgO, TiO₂, La₂O₃, Tin, ZrO₂ or SiO₂. Catalysts modification by doping of alkali (e.g. Li, Na, K) has also been reported⁹⁻¹².

There are several alternatives to carry out the reforming process: auto-thermal reforming, and steam reforming, Equation (1), endothermic reaction where reaction heat has to be supplied by an external device. In order to maximize the hydrogen yield, an excess of water is usually fed to carry out the water gas shift reaction.

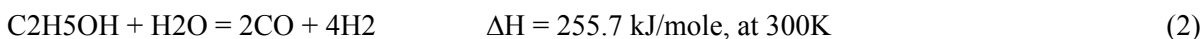


Ethanol steam reforming is a very complex reaction where many reaction pathways are possible. Some of them are favoured depending on the catalyst used¹³⁻¹⁹.

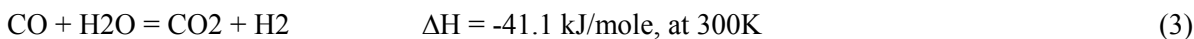
The main reaction mechanisms involve dehydration or dehydrogenation reactions. Dehydration reactions produce intermediate products such as ethylene, which is easily transformed into carbon that is deposited on the active phase producing the catalyst poisoning.

Experimental catalytic studies reported in literature have been performed to investigate the effect of the reaction temperature on the conversion and selectivity toward the main products and by-products obtained. Studies at different temperatures have allowed optimising the experimental conditions in order to maximize hydrogen yield, to limit by-product formation and to propose a reaction scheme¹⁷⁻¹⁹. Several schemes have been proposed for ethanol steam reforming depending on the desired products, operating conditions (e.g. temperature), and catalyst used.

The formation of CO, which is undesirable as it poisons the Pt catalyst of the electrochemical cell, must also be considered under steam reforming conditions:



Furthermore, some steam reforming catalysts can also catalyze the following water gas shift reaction:



which, at high steam concentrations enhances CO₂ production over CO. The formation of other byproducts such CH₄, C₂H₄ and CH₃CHO have also been observed in ethanol reforming processes²⁰⁻²².

Elliot and coworkers^{23,24} at Pacific Northwest Laboratory pointed out the possibility of hydrogen production in high-pressure water after they demonstrated the gasification of various feedstocks such as p-Cresol and polypropylene glycol into hydrogen and methane in SCW at temperatures between 250 and 350°C and pressures up to 20 MPa. In this subcritical water region, higher feedstock conversions led to higher selectivity toward methane.

Taylor et al.²⁵ studied the reforming of organic compound such as methanol, ethyl glycol and ethanol in supercritical water at 550 – 700°C and 27.6 MPa in a tubular Inconel-625 reactor. They showed that methanol can be completely converted to a gas product rich in hydrogen, carbon dioxide, carbon monoxide and small amount of methane.

An important by-product that must be considered in the design and operation of all reforming catalysts is solid carbon formation. Because of its accumulative nature, carbon formation can lead to catalyst deactivation and in the limit can even result in the plugging of the reforming reactors with potentially catastrophic consequences. Carbon formation is a problem at high temperatures and at low H₂O/C₂H₅OH ratios. Consequently, the discovery and development of new catalytic materials that can efficiently convert ethanol to hydrogen at *low temperatures* and at *low H₂O/C₂H₅OH ratios* is crucial for the practical utilization of fuel cells in the transportation industry.

Water in its supercritical state (SCW) is a very reactive substance^{26,27}, particularly at high temperature. The water dissociation constant and ionic product near its critical point are important properties for

chemical reactions. Comparison of several water properties between ambient water, SCW and superheated steam is presented in Table-1.

Table-1: Summary of physicochemical properties of water (Bröll et al., 1999).

	“Normal” Water	Subcritical Water	Supercritical Water		Superheated Steam
T [°C]	25	250	400	400	400
P [MPa]	0.1	5	25	50	0.1
Density [g cm ⁻³]	0.997	0.8	0.17	0.58	0.0003
Relative dielectric const.	78.5	27.1	5.9	10.5	1
pK _w	14.0	11.2	19.4	11.9	-
Heat capacity [kJ kg ⁻¹ K ⁻¹]	4.22	4.86	13	6.8	2.1
Dynamic viscosity [m Pa s]	0.89	0.11	0.03	0.07	0.02

EXPERIMENTAL

All chemicals needed for this project are provided from Alfa Aesar Company. Catalyst characterization was carried out to identify catalytic properties such as Temperature Programmed Desorption (TPD), Temperature Programmed Reduction (TPR), XRD, surface area, and pore volume, that are shown in Table-2.

Table-2 Characterization techniques

Property	Technique
Surface area and pore volume	Brunauer-Emmett-Teller (BET) Nitrogen physisorption
Phase transformation	Powder X-ray Diffraction (XRD)
Acid and basic site density	Temperature-programmed desorption (TPD) of NH ₃ & CO ₂
Surface topography	Scanning electron microscopy (SEM)

Catalytic ethanol water reforming in SCW was performed in a modified process system that was originally designed for supercritical water oxidation. Figure (1) presents the diagram of the experimental setup.

Water was delivered to a pre-heater at a set flow rate between 1 and 3 g/min by a high-pressure pump. The temperature of the pre-heater was set at 200°C. The water feed was then further heated to the desired reaction temperature in a ¼” coil of 16-ft long (“Main heater” in Figure 1) made of Hastelloy© tube prior to entering the reactor.

Ethanol water mixture with composition of 75% wt. ethanol was injected through a 1/16” 316 SS tubing with 2.6mm ID by a high precision syringe pump, model 260D ISCO™. The reactant fluid flows downward through the reactor and enters the catalyst bed. In this work the flow rate is 1.8 g / min with 5% of ethanol. Figure (2) shows the connection and the position of the main heating coil, cross, thermocouple and reactor inside the furnace.

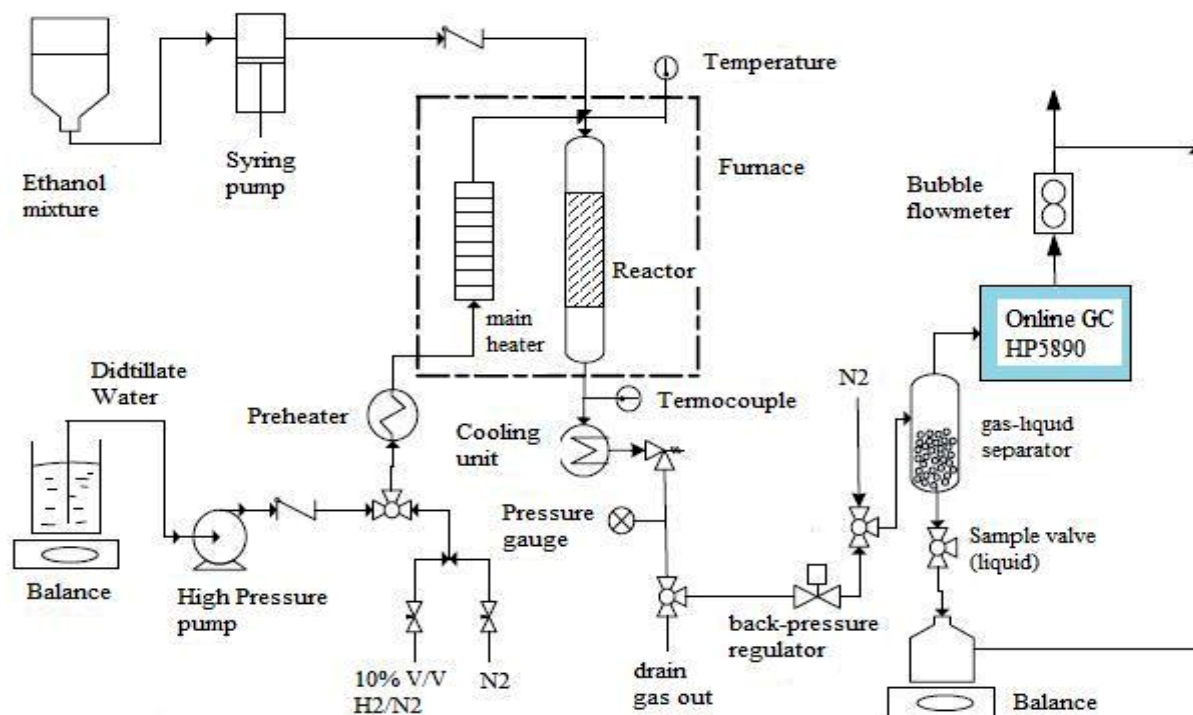


Fig.-1: Supercritical water ethanol reforming experimental setup



Fig.-2: Photograph of the reactor/feeding assembly located inside the furnace.

A special vessel/reactor was designed to carry out experiments for catalytic reactions in a fixed bed reactor. The reactor (Kuentzel closure pressure vessel), made of Inconel-625 was fabricated by Autoclave Engineers. The catalyst was located in the middle of the reactor supported by a 100 mesh 316 SS wire screen. A 10 mm long stainless steel tube with 12.7 mm OD and 2 mm thickness was

placed to support the screen. Figure (3) shows the schematic diagram of the vessel with the catalyst bed.

The product stream exits the reactor and furnace and was cooled down to 10°C through a heat exchanger (Thar Technologies) before entering the backpressure regulator (BPR) where the pressure was decreased from the reaction pressure (typically 25 MPa) down to atmospheric pressure.

The condensable species were separated from the gaseous species in a gas liquid separator. The gaseous product stream exits the separator unit at its top and was directed either to the GC or to a soap bubble flow meter for composition and flow rate analysis, respectively.

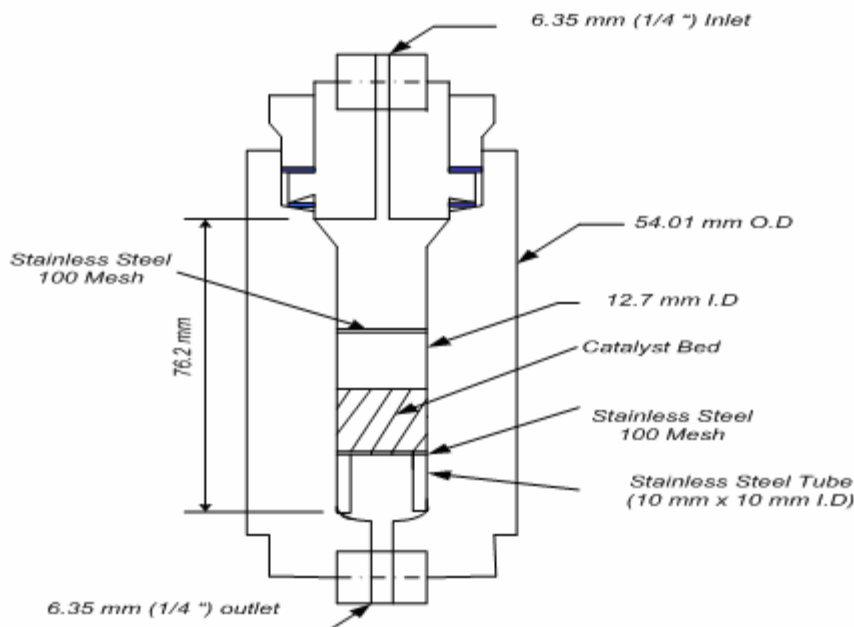


Fig.-3: Schematic diagram of the reactor.

The liquid collected at the bottom of the separator, was periodically sampled for further analysis. The liquid flow rate was measured by a balance and then was recorded in the computer while the GC was doing its analysis. Gas and liquid were analyzed separately using two gas chromatographs (GC-1(TCD) and GC-2(FID)) model HP5890 series II, which are equipped with a thermal conductivity detector (TCD) and a flammable ignition detector (FID), respectively.

Each time the gas sample was automatically injected into GC-1, 2.5 mL of the liquid sample was extracted from the bottom of the separator unit using a syringe and was transferred to a 10 mL sample vial. Then, 1-mL of the liquid sample and 1-mL of 1 vol.%- 1-propanol (internal standard) were immediately poured into a 10-mL volumetric flask and diluted with de-ionized water to fill up the 10-mL flask. Subsequently, 1- μ L of the prepared sample was injected using a 10- μ L Hamilton syringe into GC-2 equipped with FID.

RESULTS AND DISCUSSION

The wet impregnation method was used to prepare 10% wt. of Cobalt loaded in all different supported catalyst ($\text{Co}_2\text{O}_3 / \gamma\text{Al}_2\text{O}_3$, $\text{Co}_2\text{O}_3 / \alpha\text{Al}_2\text{O}_3$, $\text{Co}_2\text{O}_3 / \text{ZrO}_2$, $\text{Co}_2\text{O}_3 / \text{YSZ}$).

The physical properties of the cobalt over various supports are shown in table (3).

Table-3: Physical properties of the Cobalt over various supports

Type of Catalyst	BET surface area (m^2/g)	Packing bulk density (g/cm^3)	Height of the bed for 1 gr. Cat.
$\text{Co}/\alpha \text{Al}_2\text{O}_3$	13.8	0.66	1.2

Co/ γ Al ₂ O ₃	36.1	0.69	1.2
Co/ZrO ₂	13.4	1.62	0.5
Co/YSZ	9.8	1.14	0.7

The G.C. used to analysis gas and liquid products. G.C. peaks were used to evaluate the conversion of Ethanol to product. The catalytic effect of reactor's wall and supports were investigated at 500^oC and summarized in Figure (4). This experiment could not be carried out for alumina catalysts due to low resistance and their powder state.

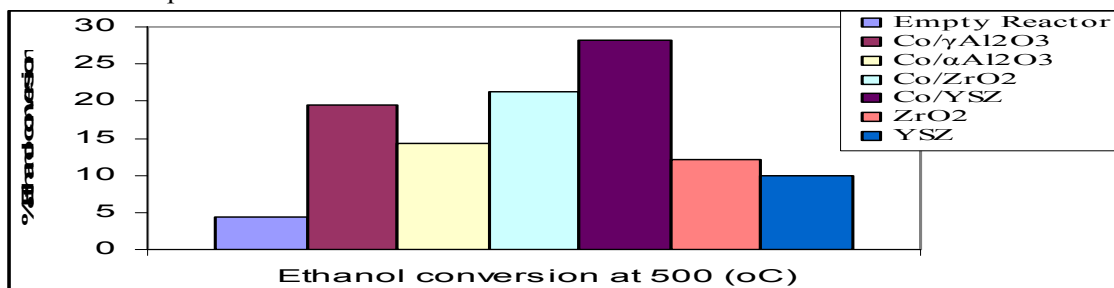


Fig.-4: Ethanol Conversion at 500^oC over Co supported catalysts, supports (except for Al₂O₃) and empty reactor.

As figure (4) shows effect of reactor's wall and supports can't be ignored in low conversion of Ethanol, also ZrO₂ and YSZ, as support, have sufficient catalytic effect on the steam reforming of ethanol in this condition. Due to plugging and low resistance of Cobalt over alumina at high pressure, the experiments for higher temperature (550^oC) were failed and so for comparing the effect of different catalysts in different temperature, the experiments were done at three temperatures 475^oC, 500^oC and 525^oC, and results were listed in Figure (5). It should be noted the conversion of Ethanol using Co₂O₃ / α Al₂O₃ at 525 temperatures failed because of low resistance and plugging.

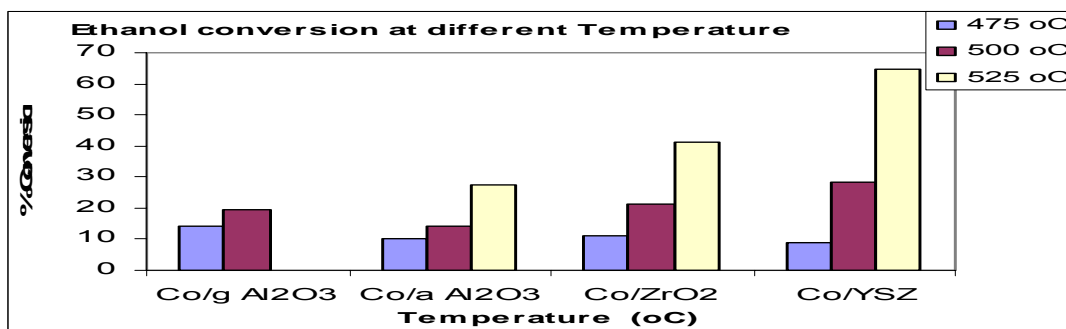
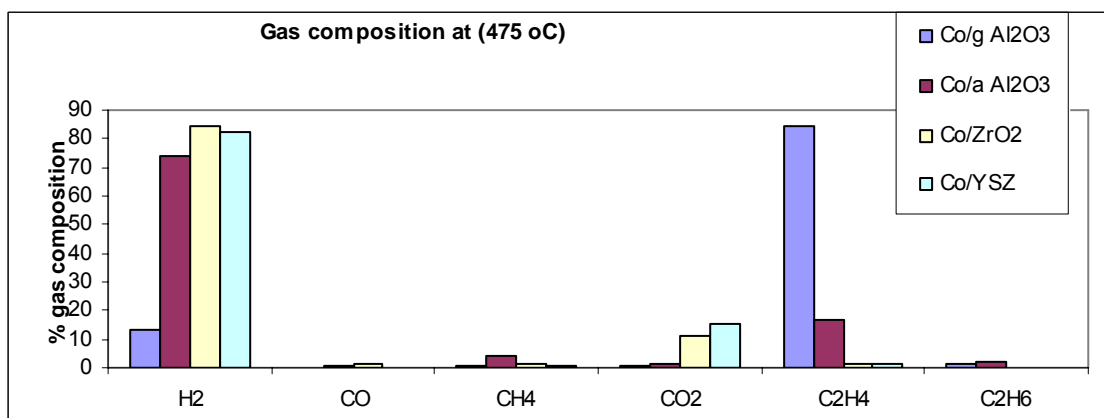


Fig.-5: Ethanol conversion in different Co supported catalyst. (1g Cat. ,1.88g/min feed, 5% wt. ethanol, 250 bar of pressure)



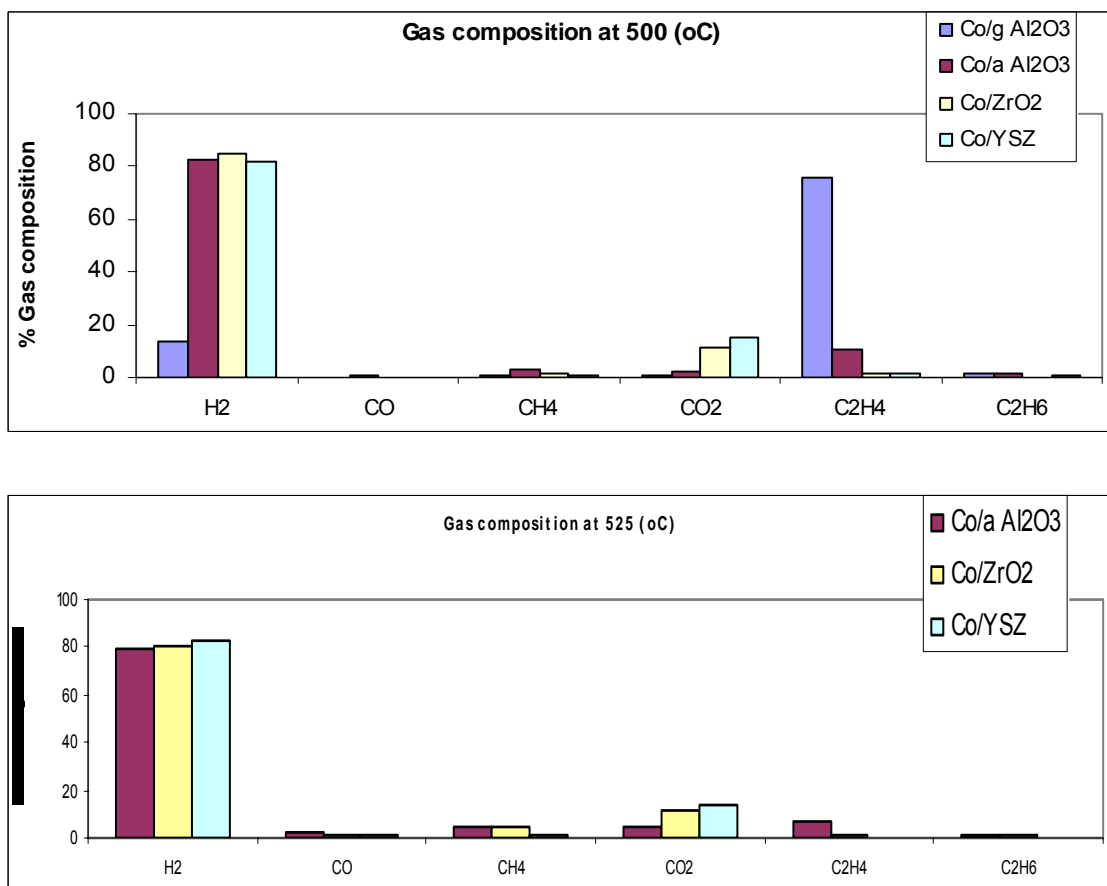


Fig.-6: product composition of Cobalt supported catalyst at different temperature.
 (1g Cat. ,1.88g/min feed, 5% wt. ethanol, 250bar)

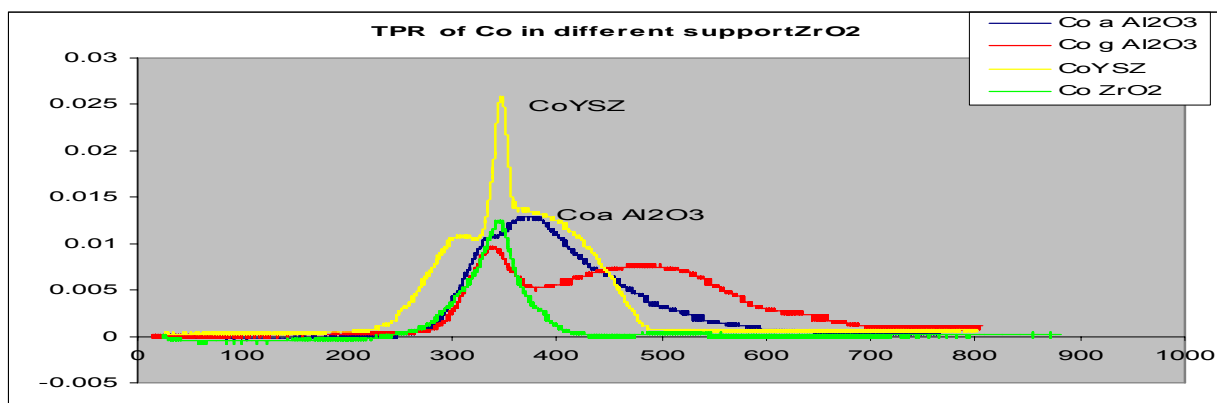


Fig.-7: TPR for Cobalt oxide on different support

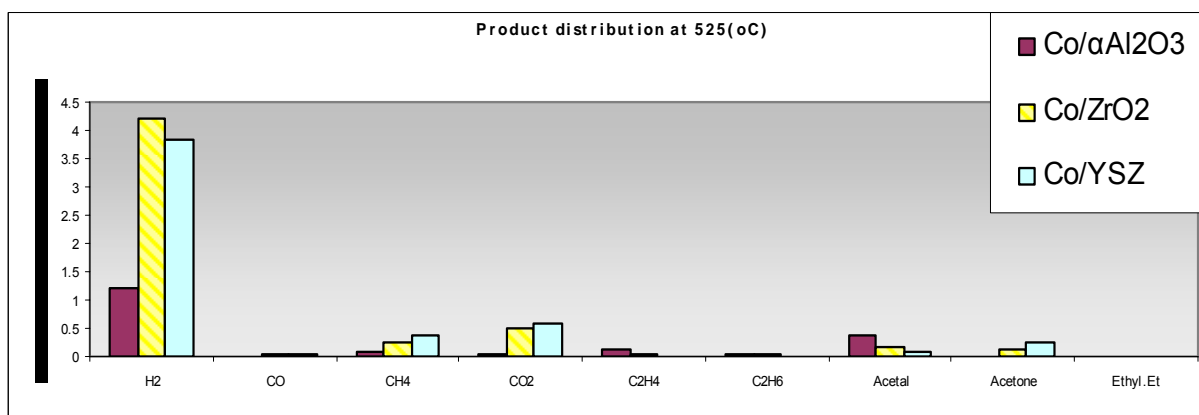
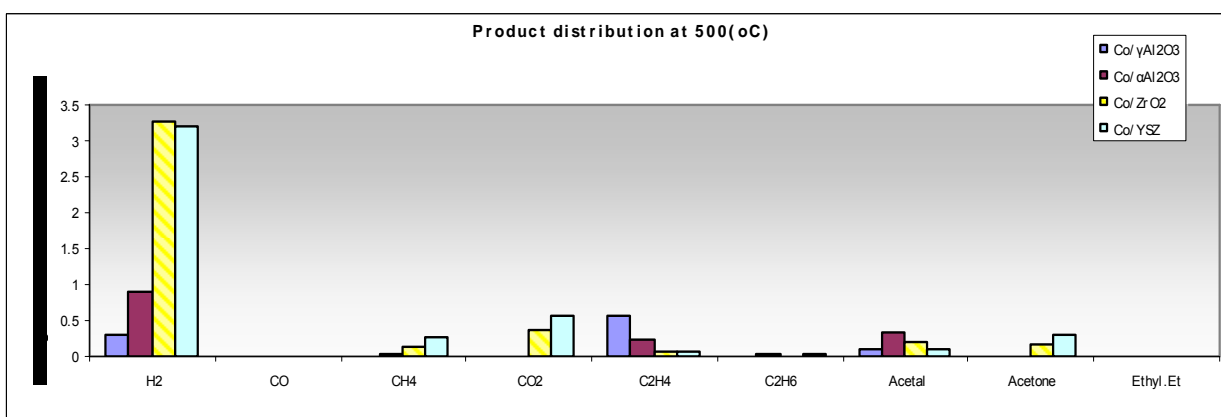
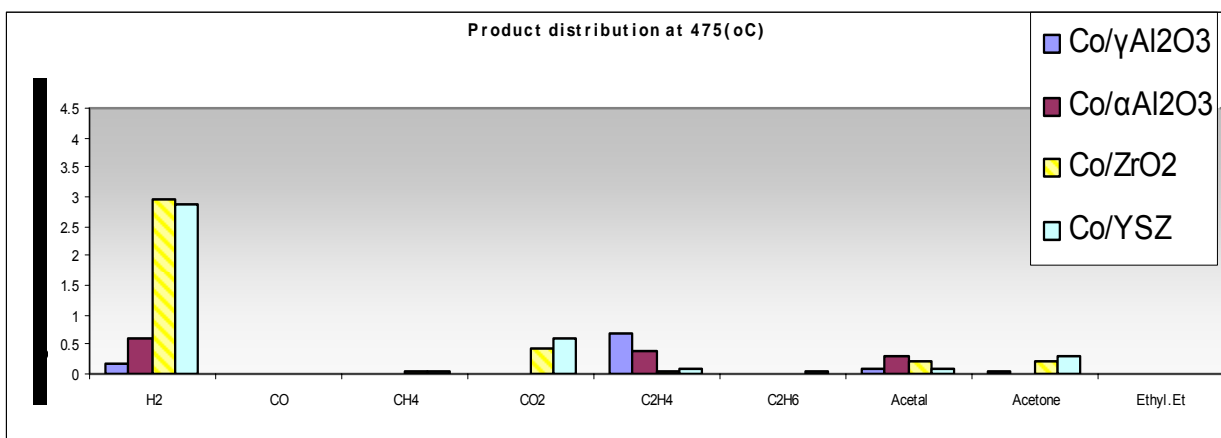


Fig.-8: Distribution of product yield over Co catalyst at different temperature

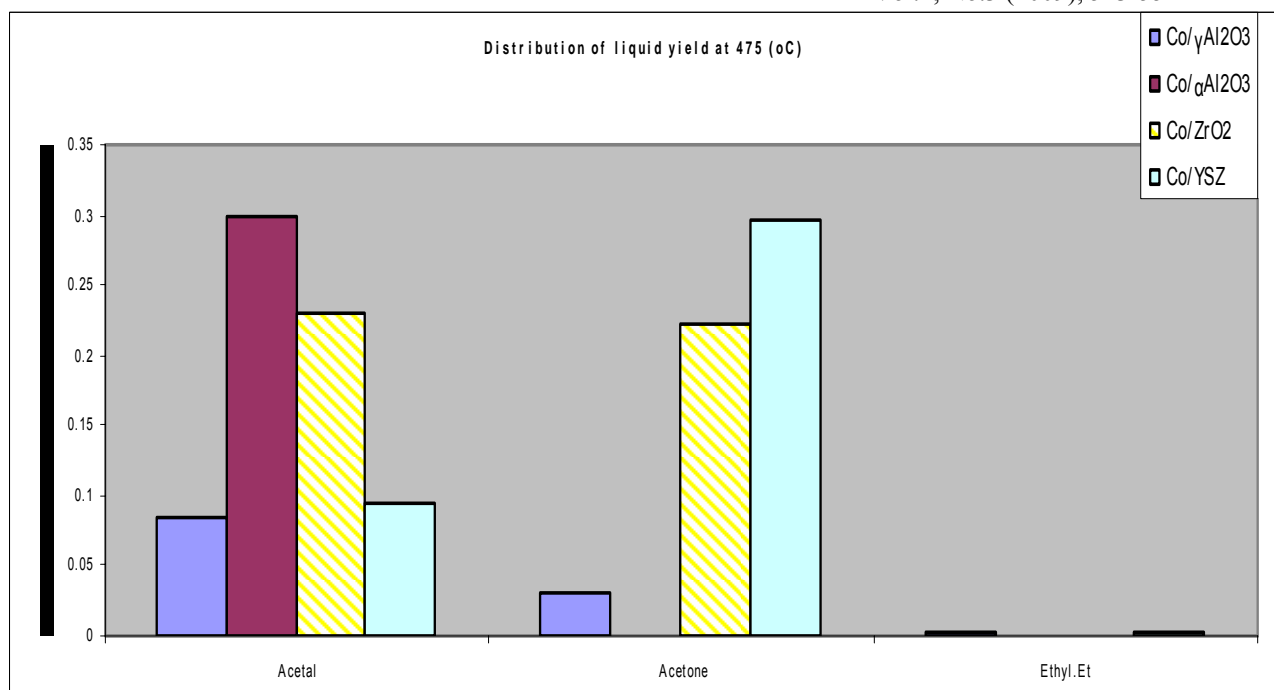


Fig.-9: Distribution of liquid product over Co catalyst at different temperature

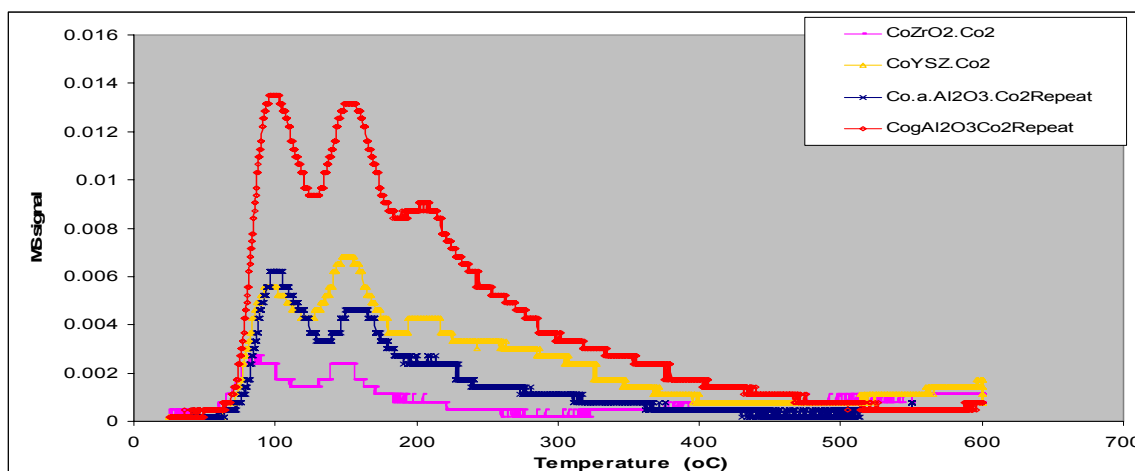


Fig.-10: TPD (CO₂) of Cobalt supported catalyst.

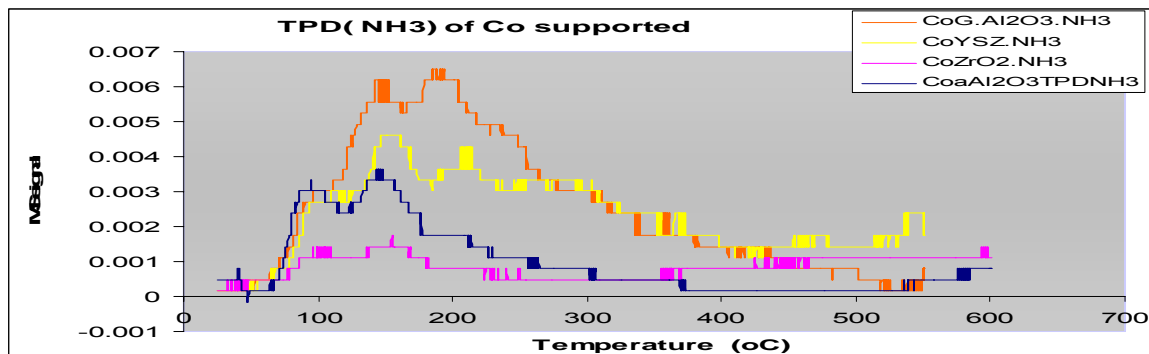


Fig.-11: TPD_(NH₃) of Cobalt supported catalyst.

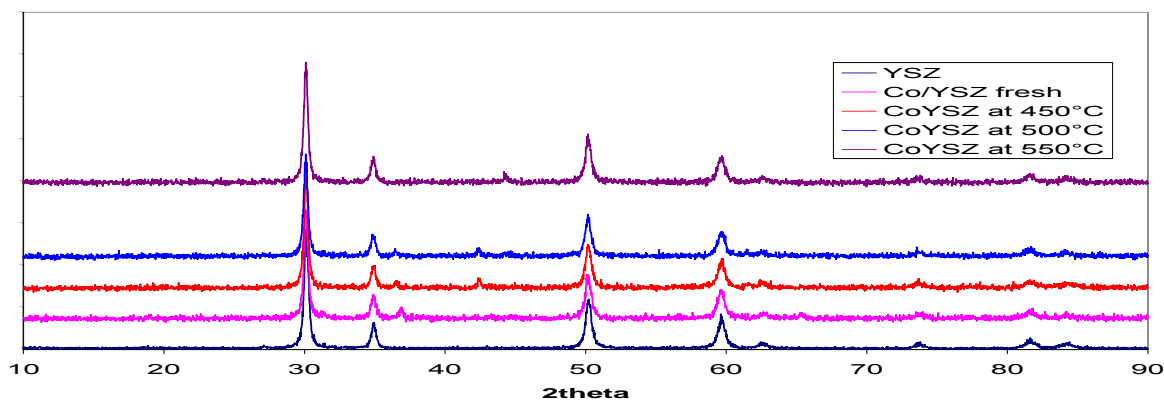


Fig.-12: Comparison of XRD for Co/YSZ at different temperature

The figure (5) indicates that by raising the temperature, the conversion of Ethanol increase over different support with the exception of YSZ which is more significant. The composition of gas mixtures and their yield at these different temperatures were given in figure 6. As this figure shows while the yield of C₂H₄ is conversely proportional with the temperature, for γ Al₂O₃ support the production of hydrogen is more significant for other supports. The yield of other gases are not important and for CO₂ it is about 10% – 15% for Co/ZrO₂ and Co/YSZ.

TPR were done to investigate the behavior of catalyst and the results were given in figure (7). As it can be seen, the reduction of cobalt (III) oxide over YSZ and ZrO₂ at less than 500^oC is much easier compared with other supports which are accompanied by increase in production of hydrogen. It should be emphasis that for Co₂O₃/ γ Al₂O₃ the reduction is mainly occur after 500^oC. The reduction of Cobalt oxide over YSZ was done in two steps because of two different supports. Comparing with other supports, gamma alumina is a porous material and has more micro pore sites with great surface area. The reduction of Cobalt oxide over micro pore sites is more difficult than surface sites.

Figure 8 shows the distribution of all product yields for one mol Ethanol consumed at different temperature and Figure 9 shows the yield of liquid product.

The TPD_(CO₂) for basic properties and TPD_(NH₃) for acidic properties of Co supported catalyst were given in figures (10) and (11). These figures show that peaks below 100^oC can be related to physico-

sorption. Also the basic sites for Cobalt supported on γ Al₂O₃ at low temperature are much more than the acidic sites. In temperature above 300 °C the TPD for both acid and basic sites show weak peaks. For observing the change in catalyst structure in reforming process, the XRD data for Cobalt supported on YSZ were used, and the results were shown in figure (12). Comparing XRD peaks around 35 – 40 , suggest by increasing temperature the Co₂O₃ formed on the support reduced to Co^{II} and to metal cobalt (as temperature increase the peak related to oxide fade away).

CONCLUSION

The investigation of steam reforming of Ethanol obtained in 250 bar of pressure, suggest that the support effect greatly the physical and chemical properties of Cobalt oxide. TPR of catalysts show that Co₂O₃/YSZ and Co₂O₃/ZrO₂ reduce by H₂ below of 500 °C and favours hydrogen production. Co₂O₃ over alpha and especially gamma alumina favours the production of C₂H₄. The Ethanol conversion is more significant in high temperature with ZrO₂ and YSZ support than alumina support. All catalyst has fewer tendencies to produce CO which is undesirable as it poisons the Pt catalyst of the electrochemical cell. The production of CO₂ , CH₄ and especially Hydrogen is more with Co₂O₃/YSZ and Co₂O₃/ZrO₂.

In the liquid phase Acetal and Acetone produced more than Ethyl ether. Alpha alumina have more tendencies to produce acetal and especially at higher temperature. On the contrary, this tendency with temperature decreases for Co₂O₃/YSZ and Co₂O₃/ZrO₂.

The product composition depends on temperature and also to the degree of Cobalt oxide reduction over support. In our experimental condition for high Ethanol conversion and Hydrogen production Co₂O₃/YSZ and Co₂O₃/ZrO₂ are the best supports.

These catalysts resist well to high pressure without deactivation for more than 6-7 hours.

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