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Supercritical Water Ethanol Reforming for Hydrogen Production: (Effect of Different Support on Nickel Based Catalyst in Supercritical Water Condition)

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The aim of this work is to study the behaviour of different supports of nickel based catalyst for hydrogen production by supercritical water reforming of ethanol in high pressure. Catalytic tests have been performed at laboratory scale under high pressure and supercritical water condition. Catalyst characterization was carried out to identify catalytic properties such as, surface area, temperature programmed desorption (TPD) and temperature programmed reduction (TPR). The analyses of liquid and gas were carried out in different G.C. In present condition, the support effects well the physical and chemical properties of catalyst. γ-Alumina and YSZ increase the acid sites. The composition of product and production of hydrogen varies with different support. ZrO_2 and YSZ make easier the reduction of nickel oxide at temperature blow 500 ºC and increase the ethanol conversion and hydrogen production. The product composi-tion depends not only to temperature but also to the degree of nickel oxide reduction over support. In low temperature, nickel oxide favorite production of C_2H_4, C_2H_6 and heavier compounds. ZrO_2 and specially YSZ are the best support to produce hydrogen with less carbon monoxide.

Key Words: Ethanol, Steam reforming, Hydrogen production, Nickel catalyst, Catalyst support, Supercritical water.

INTRODUCTION

It is well known that the hydrogen is commercially produced by gasification, partial oxidation reactions of heavy oil and steam reforming reactions. 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 for fuel cell applications in combination with the global request to reduce the atmospheric pollution and greenhouse gas emission imposes the development of new methods for hydrogen production, especially from renewable sources such as biomass.

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

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fuel cell applications[3-5]. 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. First, it represents a renewable and CO_2-neutral source that can readily be obtained from biomass fermentation[6].

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.

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 Al_2O_3, MgO, TiO_2, La_2O_3, Sn, ZrO_2 or SiO_2. Catalysts modification by doping of alkali (*e.g.* Li, Na, K) has also been reported[9-12].

There are several alternatives to carry out the reforming process: auto-thermal reforming (eqn. 1), a self sustained process fed with fuel, steam and oxygen, where a part of the ethanol is consumed to produce the necessary heat to maintain the reaction and steam reforming (eqn. 2), 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. If it is performed in the same catalytic bed as the reforming, then the net processes proceed according to the following equations.

$$CH_3CH_2OH + 0.5O_2 + 2H_2O \rightleftharpoons 5H_2 + 2CO_2,\ \Delta H^o = -50.3\ kJ\ mol^{-1} \quad (1)$$

$$CH_3CH_2OH + 3H_2O \rightleftharpoons 6H_2 + 2CO_2,\ \Delta H^o = +173.5\ kJ\ mol^{-1} \quad (2)$$

Ethanol steam reforming is a very complex reaction where many reaction pathways are possible. Some of them are favoured depending on the catalyst used[13-19].

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.

The presence of some reaction intermediates decreases the hydrogen production efficiency and can reduce the operation time of the catalyst. Studies about the influence of the steam/carbon (S/C) ratio on the hydrogen yield, the reaction intermediates and the catalyst performance have been reported in the literature[9-16]. These studies demonstrate that the catalyst must operate at high S/C ratios to avoid the carbon deposition problems previously mentioned. 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 optimizing the experimental conditions in order to maximize hydrogen yield, to limit by-product formation and to propose a reaction scheme[17-19].

Ethanol can be split at several bonds, as seen in Fig. 1[20]. Depending on the type of interaction with catalysts, the presence of other molecules and the operating conditions, it is possible to favour certain reactions to obtain desired product(s).

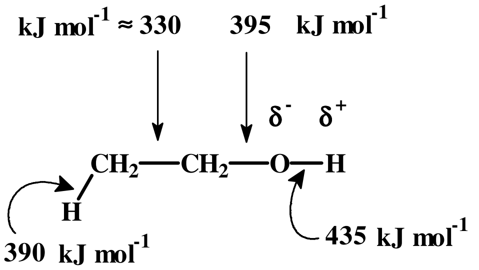

Fig. 1. Approximate bond energies for ethanol (Ref. 20)

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:

$$C_2H_5OH + H_2O = 2CO + 4H_2; \quad \Delta H = 255.7 \text{ kJ/mol at } 300 \text{ K} \qquad (3)$$

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

$$CO + H_2O = CO_2 + H_2; \quad \Delta H = -41.1 \text{ kJ/mol at } 300 \text{ K} \qquad (4)$$

which, at high steam concentrations enhances CO_2 production over CO. The formation of other byproducts such CH_4, C_2H_4 and CH_3CHO have also been observed in ethanol reforming processes[21-23]. 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 H_2O/C_2H_5OH ratios. Consequently, the discovery and development of new catalytic materials can efficiently convert ethanol to hydrogen at low temperatures and at low H_2O/C_2H_5OH ratios is crucial for the practical utilization of fuel cells in the transportation industry.

The literature review focused on atmospheric to moderate pressure conditions. In super critical water (SCW) environment due to the extremely high pressure conditions and the very high water to ethanol ratio, the results regarding catalyst activity, deactivation, and selectivity might be different from atmospheric conditions. Nonetheless, the studies at atmospheric pressure are very important as a starting point and give first insight into screening of the best catalyst.

Water in its supercritical state is a very reactive substance[24,25], 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 PHYSICO-CHEMICAL PROPERTIES OF WATER (Ref. 25)

	Normal water	Subcritical Water	Supercritical water	Superheated steam
Temperature (ºC)	25	250	400	400
Pressure (MPa)	0.1	5	25	0.1
Density (g cm^{-3})	0.997	0.8	0.17	0.0003
Relative dielectric const.	78.5	27.1	5.9	1
pK_w	14.0	11.2	19.4	-
Heat capacity (kJ kg^{-1} K^{-1})	4.22	4.86	13	2.1
Dynamic viscosity [m Pa s)	0.89	0.11	0.03	0.02

Strongly ionized water with formation of H_3O^+ and OH^- ions in sub- and supercritical region creates a corrosive environment. Material selection is critical and often, if not always, specialty alloys are necessary.

Elliot and coworkers[26,27] 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 ºC and pressures up to 20 MPa. In this subcritical water region, higher feedstock conversions led to higher selectivity toward methane.

Taylor *et al.*[28] studied the reforming of organic compound such as methanol, ethyl glycol and ethanol in supercritical water at 550-700 ºC 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.

EXPERIMENTAL

All chemicals needed for this project are provided from Alfa Aesar Company.

The wet impregnation method was used to prepare 10 % wt. of nickel loaded in all different supported catalyst (Ni/γ-Al_2O_3, Ni/α-Al_2O_3, Ni/ZrO_2, Ni/ YSZ).

Catalyst characterization was carried out to identify catalytic properties such as, surface area, pore volume, temperature programmed desorption (TPD) and temperature programmed reduction (TPR).

Catalytic ethanol water reforming in SCW was performed in a modified process system that was originally designed for supercritical water oxidation. Fig. 2 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 ºC. The water feed was then further heated to the desired reaction temperature in a ¼″ coil of 16 ft long (main heater in Fig. 2) 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 2.6 mm 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.

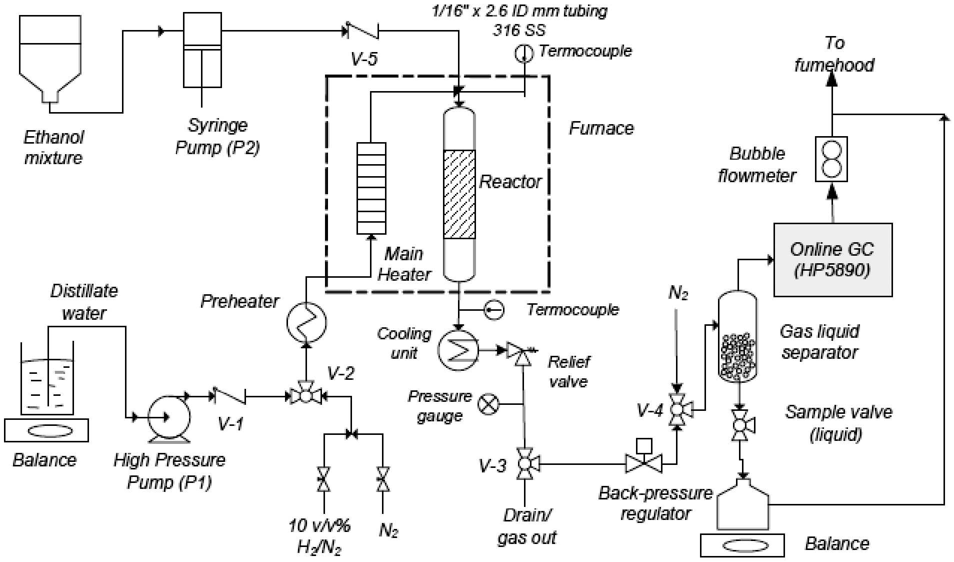

Fig. 2. Supercritical water ethanol reforming experimental setup

Fig. 3 shows the connection and the position of the main heating coil, cross, thermocouple and reactor inside the furnace.

Fig. 3. 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. Fig. 4 shows the schematic diagram of the vessel with the catalyst bed.

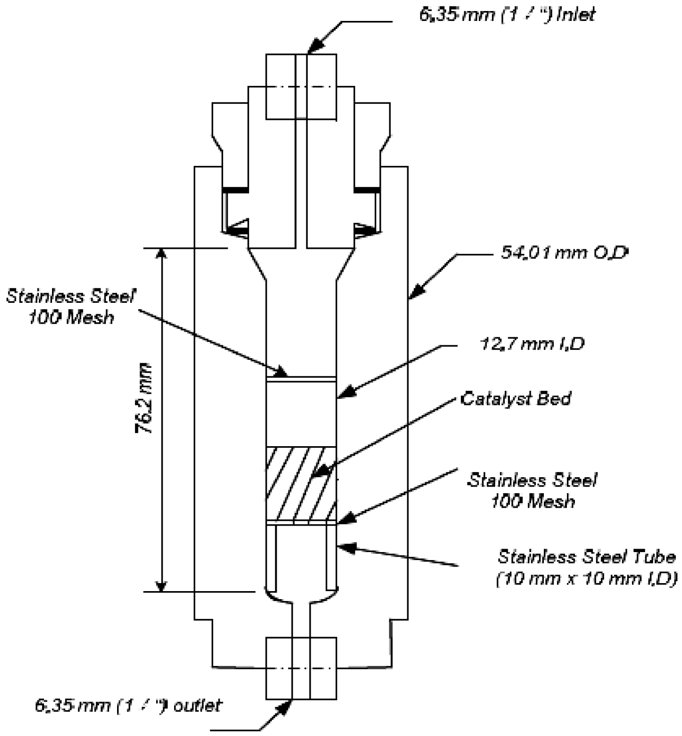

Fig. 4. Schematic diagram of the reactor

The product stream exits the reactor and furnace and was cooled down to 10 ºC through a heat exchanger (Thar Technologies) before entering the back pressure 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 flowmeter for composition and flow rate analysis, respectively.

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 μL of the prepared sample was injected using a 10 μL Hamilton syringe into GC-2 equipped with FID.

RESULTS AND DISCUSSION

The surface of each picks obtained from different gas chromatography is used for calculation of conversion yield and product composition. The physical properties of the nickel over various supports are shown in Table-2.

TABLE-2
PHYSICAL PROPERTIES OF THE NICKEL OVER VARIOUS SUPPORTS

Type of catalyst	BET surface area (m^2/g)	Packing bulk density (g/cm^2)	Height of the bed for 1 g Cat.
Ni/αAl_2O_3	25.7	0.66	1.2
Ni/γAl_2O_3	55.8	0.69	1.2
Ni/ZrO_2	15.3	1.66	0.5
Ni/YSZ	11.2	1.12	0.7

In the first step to observe the catalytic effect of reactor's wall and different supports, one experiment has done in 500 °C that is shown in Fig. 5. Because of powder state of alumina and mal resistance to high pressure, in present experimental condition, this experiment didn't do for them.

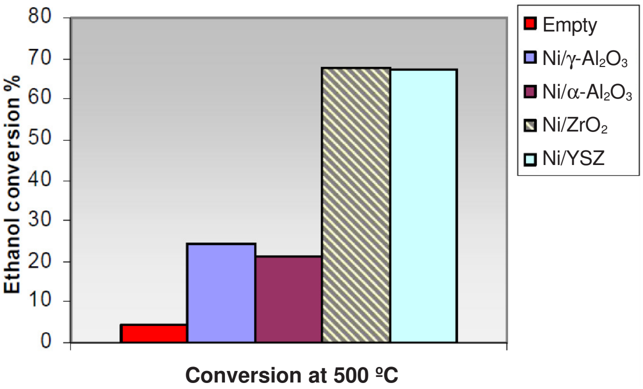

Fig. 5. Ethanol conversion at 500 °C over Ni supported catalyst and empty reactor

It shows that in low conversion the effect of reactor's wall can't be negligible and the support effect the catalytic characteristic of metal supported.

Fig. 6 shows the ethanol conversion at different temperature (475, 500, 525 and 550 °C). Because of mal resistance of nickel over γ-alumina at 525 and 550 °C in high pressure of present experiment condition (250 bar), these results failed.

In high temperature (550 °C) for all catalyst there is total conversion of ethanol and for comparing the effect of different supports, the low temperatures are chosen.

This figure shows that for conversion of methanol in low temperature, the effect of ZrO_2 and YSZ supports are more important than γ- and α-alumina.

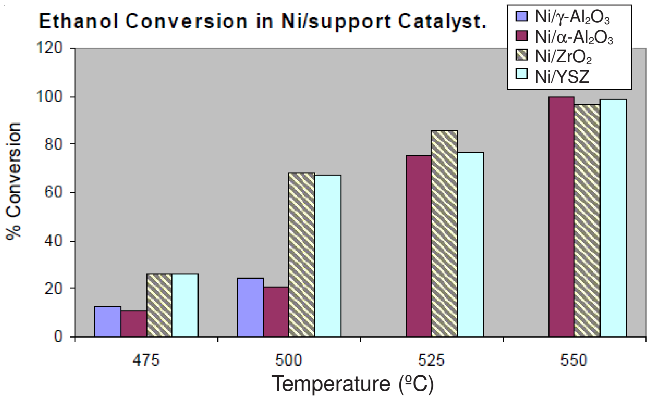

Fig. 6. Ethanol conversion in different Ni supported catalysts. (1 g Cat. ,1.88 g/min feed, 5 % wt. ethanol, 250 bar)

The gas composition and yield of conversion for nickel supported catalyst at 475, 500 and 525 ºC are presented in Fig. 7. Because of mal resistance of nickel over γ alumina at 525 °C in high pressure applied in present experiment condition (250 bar), its result failed. As one can see nickel supported on γ- and α-alumina in low temperature have fewer tendencies to produce light gas products and favourite the production of C_2H_4. On contrast nickel supported over ZrO_2 and YSZ favourite the production of light gases especially H_2 and CH_4.

For better observing the product composition, the mol distribution of all products per mol of ethanol consumed is shown in Table-3 and Fig. 8.

Fig. 9 shows the temperature programmed reduction (TPR) with hydrogen of nickel supported catalysts. It can be seen that the ZrO_2 and YSZ make easier the reduction of nickel oxide to convert it to metal form at temperature less than 500 ºC, that favorite the hydrogen production. On contrast the reduction of nickel oxide on γ-alumina is done mostly after 500 ºC and at temperature less than 500 ºC nickel over γ-alumina is mostly in oxide form.

Comparing with other supports, γ-alumina is a porous material and has more micro pore sites with great surface area. The reduction of nickel oxide over micro pore sites needs more energy than surface sites.

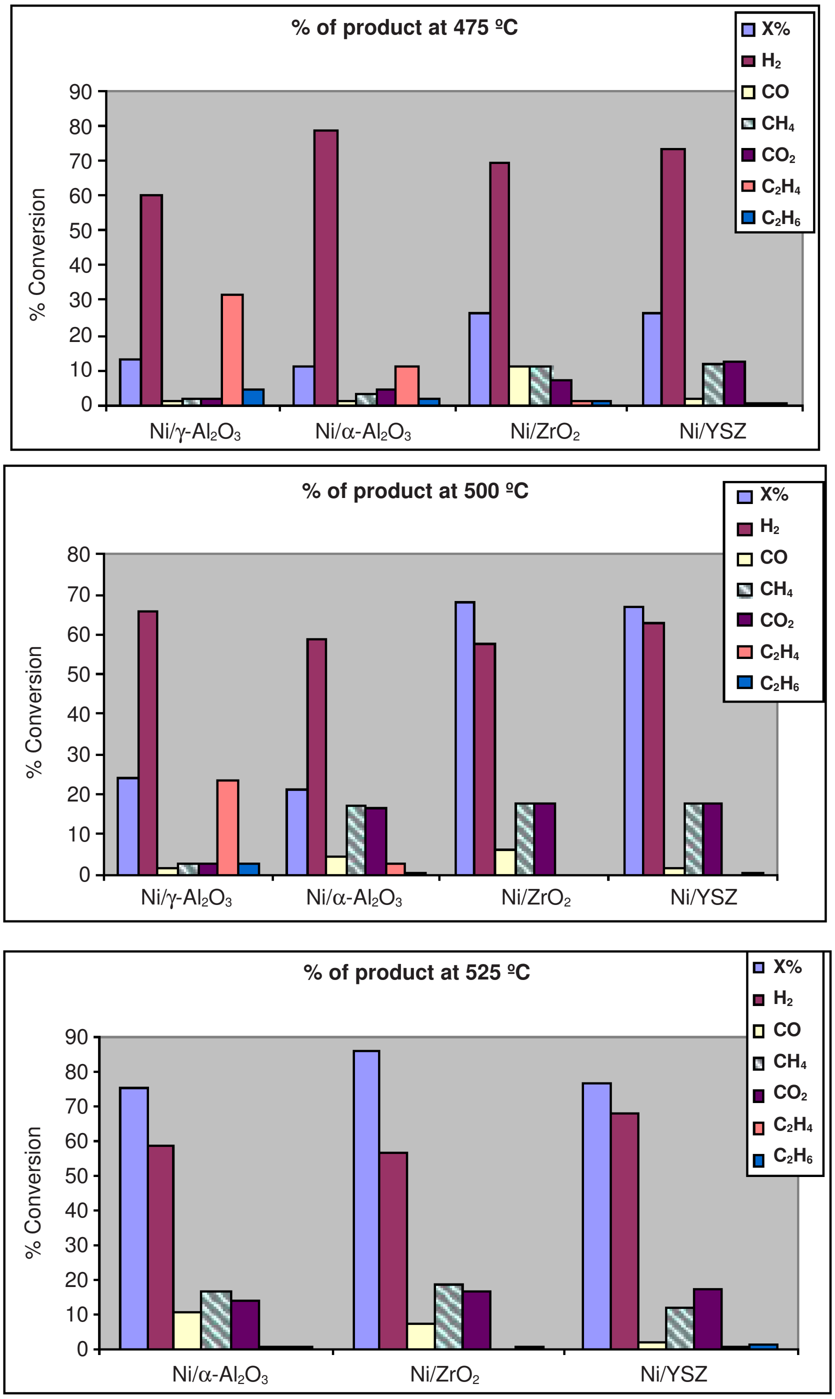

Fig. 7. Gas product composition and % conversion of nickel supported catalyst at 475, 500 and 525 °C. (1 g Cat. ,1.88 g/min feed, 5 % wt. ethanol, 250 bar)

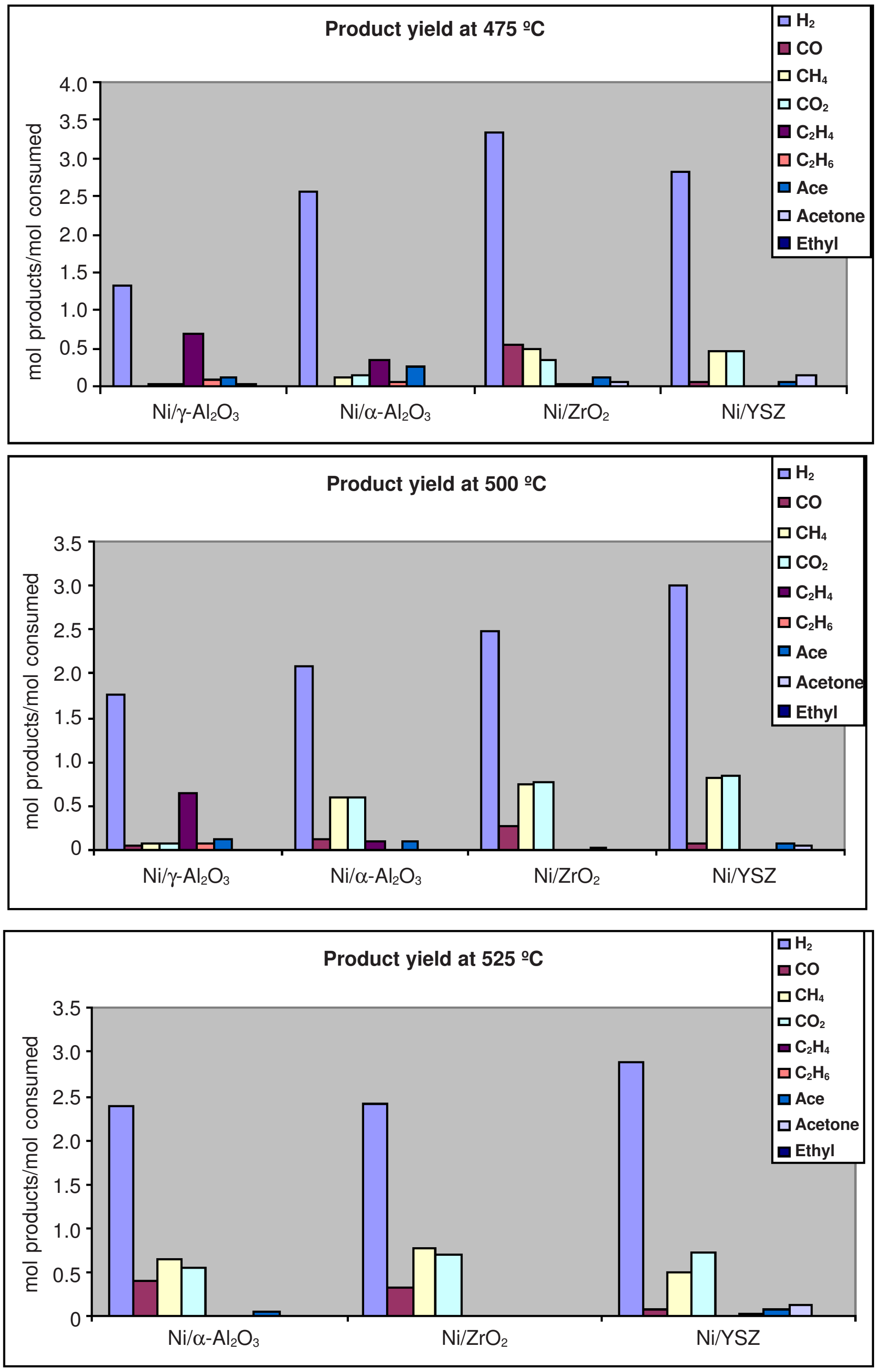

Fig. 8. Distribution of product yield for one mol ethanol consumed at different temperature

TABLE-3
MOL DISTRIBUTION OF ALL PRODUCTS PER MOL OF ETHANOL CONSUMED

Catalyst	Temp. (ºC)	H_2	CO	CH_4	CO_2	C_2H_4	C_2H_6	Acetal	Acetone	Ethyl ether
Ni/γAl_2O_3	475	1.340	0.017	0.033	0.029	0.7070	0.0980	0.111	0.0400	t
	500	1.764	0.046	0.078	0.074	0.6300	0.0820	0.140	t	t
	525	-	-	-	-	-	-	-	-	-
Ni/αAl_2O_3	475	2.581	0.026	0.111	0.141	0.3590	0.0600	0.254	0.0180	0.00340
	500	2.104	0.146	0.610	0.605	0.1120	0.0180	0.110	0.0060	0.00020
	525	2.391	0.408	0.664	0.563	0.0160	0.0190	0.069	0.0055	0.00004
Ni/ZrO_2	475	3.338	0.544	0.516	0.348	0.0440	0.0420	0.101	0.0730	T
	500	2.490	0.276	0.753	0.771	0.0020	0.0080	0.038	0.0067	t
	525	2.416	0.318	0.786	0.705	0.0040	0.0226	0.021	0.0057	t
Ni/YSZ	475	2.808	0.072	0.451	0.478	0.0170	0.0190	0.075	0.1570	0.00040
	500	3.024	0.071	0.837	0.851	0.0039	0.0110	0.070	0.0480	0.00010
	525	2.899	0.085	0.499	0.722	0.0120	0.0340	0.100	0.1200	0.00003

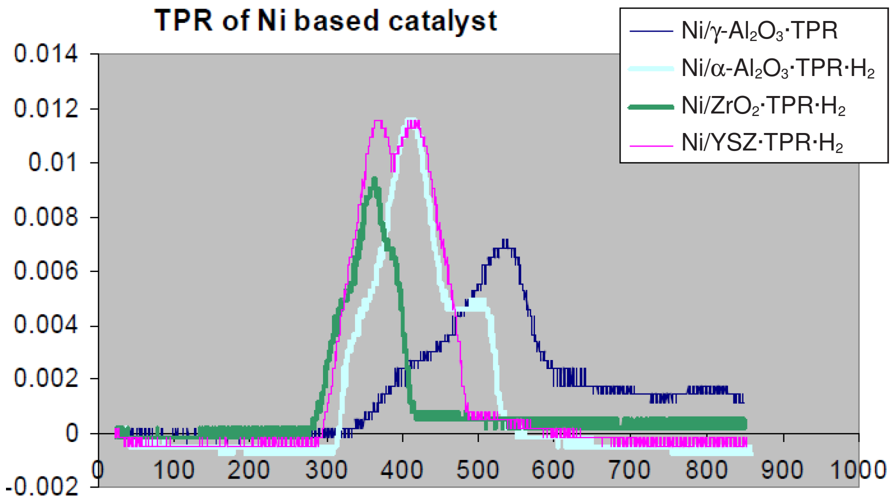

Fig. 9. Temperature programmed reduction for nickel oxide on different support

Figs. 8 and 9 show that the ethanol conversion is more important with ZrO_2 and YSZ supports than alumina especially in low temperature. In present experimental condition ZrO_2 and YSZ supports favorite the production of hydrogen. It seem that the oxide form of nickel favorite the production of C_2H_4. These figures show that in 500 ºC and over, the nickel oxide supported on YSZ and ZrO_2 and also most of nickel oxide over α alumina is reduced to metal form, which favorite the production of hydrogen, methane and CO_2. But under this temperature more of nickel oxide over γ alumina didn't reduced to metal form that favourite the production of heavier hydrocarbons such as C_2H_4 and C_2H_6.

Fig. 10 shows the TPD(CO_2) for basic properties and TPD(NH_3) for acidic properties of Ni supported catalyst. On considering that the desorption before 100 ºC concern to physico-sorption, one can observed that the acidic site for nickel supported on YSZ and γ-Al_2O_3 are more important than basic sites and the basic compounds can be adsorbed more strongly on these catalysts. For Ni/ZrO_2 and Ni/aAl_2O_3 both acidic and basic sites are week.

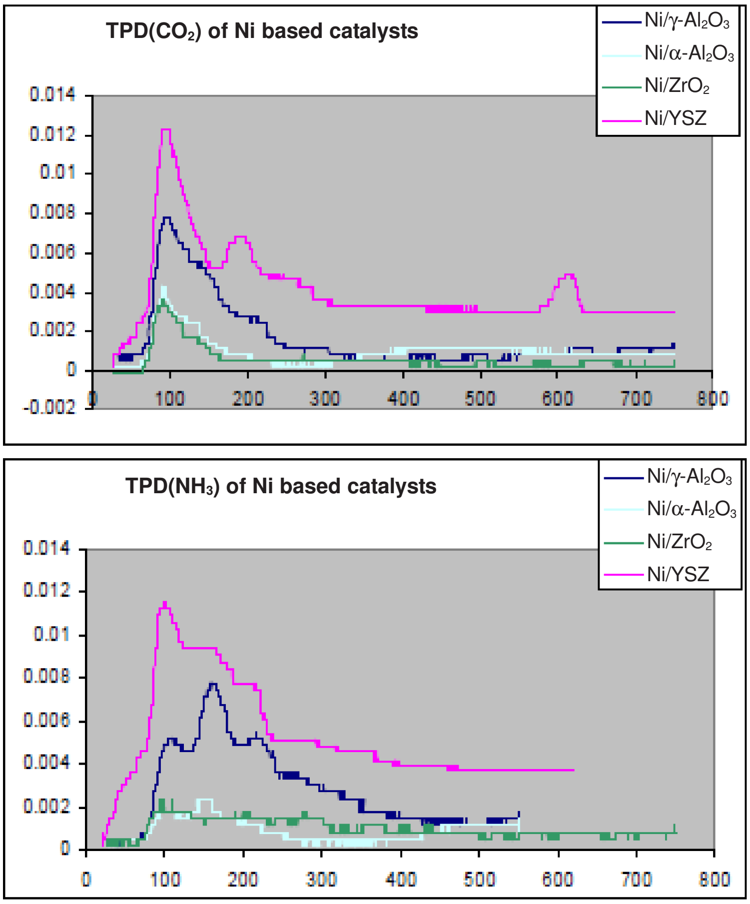

Fig. 10. TPD($_{(CO_2)}$) and TPD($_{(NH_3)}$) of nickel supported catalyst

Conclusion

By observing the results of present work in the supercritical water condition and 250 bar pressure, it can be observed that the support effect well the physical and chemical properties of catalyst. γ-Alumina and YSZ increase the acid sites and tendency to adsorb the basic species on the catalyst. ZrO_2 and YSZ make easier the reduction of nickel oxide over these support at temperature blow 500 ºC and increase the ethanol conversion and hydrogen production.

The product composition depend not only on temperature but also to the degree of nickel oxide reduction over support and in low temperature with less nickel oxide reduction, the production of C_2H_4, C_2H_6 and heavier compounds are favourite. These compounds decrease by increasing of temperature and nickel oxide reduction.

Nickel supported on γ- and α-alumina at low temperature have fewer tendencies to produce light gas products and favourite the production of C_2H_4. On contrast nickel supported over ZrO_2 and YSZ favorite the production of light gases especially H_2 and CH_4.

In present experimental condition for high ethanol conversion and hydrogen production with less carbon monoxide, which is undesirable as it poisons the Pt catalyst of the electrochemical cell, ZrO_2 and specially YSZ are the best support. These supports resist well to high pressure without deactivation for more than 6-7 h.

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