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Bio-ethanol steam reforming on Ni/Al_2O_3 catalyst

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Abstract

In this work, the ethanol steam reforming on $Ni/\gamma Al_2O_3$ catalyst at temperatures between 573 and 773 K was studied and an overall reaction scheme as a function of temperature was proposed. It can be concluded that higher water/ethanol ratio (6:1) and higher temperature (773 K) promote hydrogen production (91% selectivity). Over Ni-based catalyst there would not be evidences that water gas shift reaction occurs. The presence of oxygen in the feed produces a favorable effect on carbon deposition; nevertheless the carbon monoxide production is not reduced.

Keywords: Ethanol reforming; Hydrogen production; Fuel cell; Ni-based catalyst

1. Introduction

Fuel cell powered vehicles using hydrogen as a fuel are currently being developed in an effort to mitigate the emissions of green house gases such as CO_2, NO_x and hydrocarbons.

The fast development of fuel cell technologies and particularly of the solid polymer fuel cell (SPFC) [1] involves the storage of a liquid fuel free from sulfur and metals, which would be transformable into hydrogen without polluting emissions. There exist several routes for hydrogen production from the primary fuels. A promising route involves the steam reforming of alcohols, primarily methanol and ethanol. The possibility of using alcohol steam reformer to generate hydrogen for a fuel cell engine has resulted in an increased interest in the study of the alcohol-steam reforming process [2–16].

Ethanol presents several advantages related to natural availability, storage and handling safety, ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agro-industries or forestry residue materials, organic fraction of municipal solid waste, etc. Besides the bio-ethanol-to-hydrogen system has the significant advantage of being nearly CO_2 neutral, since the produced carbon dioxide is consumed for biomass growth, thus offering a nearly closed carbon loop.

In conclusion, among the various process and primary fuels that have been proposed in the production of hydrogen for fuel cell applications, steam reforming of ethanol is very attractive.

Thermodynamic studies [5,6] has shown that the steam reforming of ethanol is feasible for temperature higher than 500 K, being methane, carbon oxides and H_2 the main products.

Iwasa and Takezawa [7] have reported that ethyl acetate, acetic acid and C_4 species are produced at 380–420 K over Cu-based catalysts in the absence of hydrogen as reaction products. They concluded that the dehydrogenation step to acetaldehyde occurs much more rapidly than its decomposition to ethyl acetate and acetic acid, being the acetaldehyde the intermediate product. Cavallaro and Freni [8] have investigated the steam reforming of ethanol over supported oxide catalysts. They have concluded that $CuO/ZnO/Al_2O_3$ exhibit a good activity and CO, CO_2 and H_2 were the main products obtained at temperatures above 630 K.

Mariño et al. [9,10] have studied the effect of different copper loading on catalytic behavior of $Cu/Ni/K/Al_2O_3$ catalyst. They have found an acceptable performance to hydrogen at low temperatures (573 K).

Cavallaro [11] have carried out the steam reforming of ethanol on Rh/Al_2O_3 catalysts at temperatures between 373 and 923 K. The acetaldehyde formed by dehydrogenation of ethanol, was easily decarbonylated by Rh/Al_2O_3 catalyst. At 973 K only C_1 products are obtained in the outlet stream. The coke formation is prevented at high temperatures with sufficiently large amount of Rh and strong excess of water.

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Liguras et al. [14] have found that supported Rh catalysts is acceptably stable under severe conditions (800 °C) and could be used for the production of hydrogen for fuel cell applications.

Aupretre et al. [15] used different supported metal (Rh, Pt, Ni, Cu, Zn, Fe) catalysts; in order to maximize the hydrogen production and to minimize the carbon monoxide formation, the authors propose a catalytic formulation free of any promoter in the water gas shift reaction. Llorca et al. [16] have obtained CO-free hydrogen during ethanol steam reforming using a mixture of 1:13 ethanol/water molar ratio in the temperature range 573–723 K over supported Co/ZnO catalysts.

Spite of the apparent simplicity of the stoichiometry reaction for maximum hydrogen production:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$

the steam reforming of ethanol for hydrogen production involves a complex reaction system, therefore the selectivity to hydrogen is affected by many undesirable side reactions. Then, the yield of hydrogen depends on the process variables such as, temperature, reactants ratio, space time, etc. and obviously, on the catalytic composition. In order to design an effective catalyst for maximizing the yield of hydrogen, it is necessary to know the effect of these variables on product distribution, and from these results it is possible to propose the reactions scheme involved.

In a recent work, Klouz et al. [1], have studied the effect of the reaction temperature and water/ethanol ratio in the reforming process over Ni/Cu catalyst. The tests were carried out under diluted conditions and at temperatures between 573 and 873 K. The study allowed optimizing the experimental conditions in order to maximize hydrogen yield, to limit CO formation and carbon deposition and to propose a kinetic scheme.

In this work we have performed the study of the steam reforming of ethanol over Ni/Al_2O_3 catalyst between 573 and 773 K. The aim is to describe the products distribution obtained for different operating condition in order to propose a reaction scheme. Therefore, the effect of varying: space time, reaction temperature, water/ethanol feed ratio, and water/oxygen/ethanol feed ratio is studied.

2. Experimental

2.1. Catalyst

In all the kinetics experiments, a $Ni/\gamma Al_2O_3$ catalyst developed and provided by Royal Military College of Canada was used. The catalyst has a specific area of 15 m^2/g and a total Ni content of 35% (w/w).

2.2. Catalytic tests

Steam reforming of ethanol was carried out in a conventional fixed bed reactor operated isothermally at atmospheric pressure. The reactor was made with a Pyrex glass tube of 12 mm inner diameter, and it was placed into an electric oven. Ethanol and water were fed by means of a carrier nitrogen stream flowing through a saturator. In a few experiment acetaldehyde or ethylene were used as reactant, instead ethanol, and oxygen was added together with nitrogen. The feed ethanol/water molar ratio was controlled by adjusting both, the saturator temperature and the input nitrogen flow rate. The reaction temperature was measured with a sliding thermocouple placed inside the bed.

The composition of the input and output streams was analyzed by on-line gas chromatography. A Shimadzu GC 8A, equipped with a TCD detector and Porapack Q 2m column were used to analyze the concentration of the ethanol, water, acetaldehyde, acetone, carbon dioxide, and ethylene. Molecular sieve 5A column was used to determine carbon monoxide, methane and hydrogen compositions.

The experiments were performed under the following conditions—catalytic mass: 0.105–0.840 g; temperature: 573–773 K; total feed rate: 210 ml/min; ethanol molar fraction: 0.017; water/ethanol molar ratio: 1–6.

Prior to catalytic tests the catalyst was reduced in situ under flowing hydrogen (10 ml/min) and nitrogen (90 ml/min) at 823 K for 1 h and under flowing hydrogen (10 ml/min) for 0.5 h. After reduction the catalyst was cool down to reaction temperature.

Preliminary catalytic tests were carried out in order to ensure that the kinetic experiments provide meaningful results. Some of them were carried out without catalyst in order to verify the absence of homogeneous reaction. These tests have showed a negligible contribution of homogeneous reforming. The absence of internal and external diffusion limitations, for particle diameters below 0.450 mm and total gas flow equal or greater than 150 ml/min was confirmed. The catalyst bed was diluted (1:10) with glass particles, of the same diameter range, in order to avoid adverse thermal effects.

The reactants conversion (ethanol or water) denoted X_{reactant}, products selectivities (hydrogen, methane, carbon oxides, acetaldehyde, etc.) denoted S_{product} and products yields, denoted Y_{product}, are calculated according to Eqs. (1)–(4). $F_{\mathrm{in\ or\ out}}$, represents the molar flow rate of the i species measured at the inlet or at the outlet of the reactor, respectively, and n is the ratio of the stoichiometric factors between the carbon containing products and ethanol.

Taking into account that total selectivity to compounds containing carbon must be equal or lower than 1, the fraction of reactant converted, which it was not detected in the reactor outlet, was assigned to the formation of carbonaceous deposits adsorbed on the catalyst surface as coke deposit. Therefore, coke selectivity is calculated by Eq. (5).

Since the experiments were performed at diluted conditions (80% N_2), the volume change due to reaction was negligible, in fact the correction factor accounting for this variation was not considered to calculate conversions and selectivities

$$X_{\text{reactant}} = \frac{F_{\text{reactant in}} - F_{\text{reactant out}}}{F_{\text{reactant in}}} \tag{1}$$

$$S_{H_2} = \frac{F_{H_2\,\text{produced}}}{F_{H_2\,\text{consumed}}},$$

$$S_{H_2} = \frac{F_{H_2\,\text{produced}}}{[3(F_{\text{ethanol in}} - F_{\text{ethanol out}}) + (F_{\text{water in}} - F_{\text{water out}})]} \tag{2}$$

$$Y_{\text{product}} = \frac{F_{\text{product out}}}{F_{\text{ethanol in}}} \tag{3}$$

$$S_{i\,\text{carbon-containing product}} = \frac{F_{i\,\text{carbon-containing product}}}{(F_{\text{ethanol in}} - F_{\text{ethanol out}})n} \tag{4}$$

$$S_{\text{carbon}} = 1 - \sum S_{i\,\text{carbon-containing product}} \tag{5}$$

The space time denoted tr is defined as the ratio between mass of catalyst and the total flow rate at the inlet.

3. Results and discussion

3.1. *Influence of the temperature*

Fig. 1 shows the effect of temperature on reactants conversion and products selectivity. According to the stoichiometry of global steam reforming reaction, molar ratio water/ethanol is initially fixed to 3.3 in order to work with an excess of water. Space time was maintained at 1 mg min/ml for all temperatures.

It can be observed that ethanol is completely converted over the whole studied temperature range while the water conversion increases with the temperature. From the analysis of product distribution obtained at 573 K it can be observed that methane selectivity is equal to CO selectivity, suggesting that ethanol decomposition to CO, CH_4 and H_2 (Eq. (6)) is the main reaction at 573 K, while the lower selectivity to CO_2 could be produced either by water gas shift reaction (Eq. (7)) or by ethanol steam reforming (Eq. (8))

$$CH_3CH_2OH \rightarrow CO + CH_4 + H_2 \tag{6}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{7}$$

$$CH_3CH_2OH + H_2O \rightarrow CO_2 + CH_4 + 2H_2 \tag{8}$$

However, thermodynamics estimations lead us to conclude that ethanol steam reforming to CO_2, CH_4 and H_2 (Eq. (8)) is strongly probable. The value of equilibrium constant for Eq. (7) is given by: $\log(K_p) = 1.62$ at $T = 573$ K. On the other hand, it is possible to estimate the mass action ratio (MAR) relative to Eq. (7): $\log(\text{MAR}) = -1.24$. After comparison MAR and K_p values for reaction 7, it can be concluded that Ni/Al_2O_3 is not active to shift reaction at 573 K.

As the temperature increases from 573 to 673 K, CO_2 selectivity and water conversion, which are almost negligible at 573 K, increase strongly, while CO selectivity decreases. This means that at 673 K the ethanol steam reforming (Eq. (8)) instead ethanol decomposition (Eq. (6)) become significant and low quantities of CO are produced by reaction 6.

Finally, when temperature increases from 673 to 773 K methane selectivity decreases, carbon dioxide selectivity

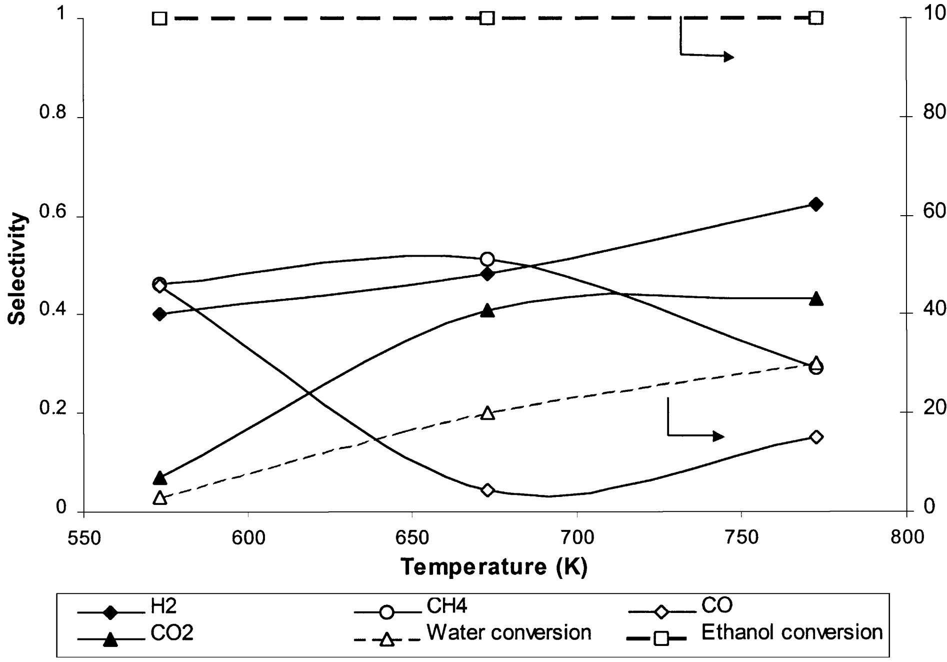

Fig. 1. Effect of temperature on reactants conversion and products selectivity. Space time is 1 mg min/ml, water/ethanol molar ratio is 3.3 and temperature is 773 K.

remains constant while hydrogen and carbon monoxide selectivities increase. Then it can be postulated that CO is mainly produced from the steam reforming of methane by:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{9}$$

If WGSR occurs at 673 and 773 K, it must be at equilibrium and CO_2 and CO yields should have a consistent behavior with this assertion when temperature increases. However, our experimental results show that CO_2/CO molar ratios do not correspond with the thermodynamic equilibrium predictions. The results in Fig. 1 show that CO_2 yield remains constant, while CO yield increases in the same range of temperature. On the other hand, CH_4 yield decreases in the same range of temperatures, and at 773 K the following relation is verified: $S_{CO_2} = S_{CO} + S_{CH_4}$. Taking into account that ethanol is totally converted, this relation can be analyzed in terms of molar relation. Then, it is possible to suggest that at 773 K the steam reforming of ethanol and the steam reforming of methane (Eq. (9)) (the latter reaction is at equilibrium) could be determining the product distribution, and there would not be evidences that WGSR occurs.

The proposal that WGSR does not occur on a nickel catalyst can look like contradictory according to the results obtained by other authors working on steam reforming of hydrocarbons. Nevertheless, it must be noted that this concept is being recently revised. Aupretre et al. [15], working on steam reforming of ethanol at 873 and 973 K, and using different metallic catalysts, affirm that Ni is a poor candidate in the WGSR. The authors performed the reaction at 873 and 973 K and they based this assessment on the comparison of their experimental results and the equilibrium data. Descorme et al. [17] used Ni catalysts for the WGSR and they concluded that this catalyst is poor for this reaction. Jiang et al. [18,19] working on the steam reforming of methanol and using copper catalysts suggested a mechanism where WGSR does not take place.

On the other hand, from our experimental results, we can conclude that the best selectivity to hydrogen is obtained at high temperature (773 K), so this temperature will be considered for furthering.

3.2. *Effect of space time*

In order to dilucidate the reaction pathway the influence of varying space time on products distribution was studied. Experiments at different space time, keeping constant temperature (773 K) and water/ethanol molar feed ratio (3.3) are shown in Fig. 2a and b. Ethanol is completely converted at all the space times used. For space times higher than 0.5 mg min/ml the only products are methane, carbon oxides and hydrogen. At lower space time ethylene and acetaldehyde appears between the reaction products. The yields of these products as a function of space time have a typical behavior of intermediate product. It can be noted in Fig. 2a that acetaldehyde and ethylene yields have a maximum and theirs yields become null when space time reaches 0.1 mg min/ml. On the contrary, the yields of final products (CO, CO_2, CH_4 and H_2) increase reaching a constant value for space time higher than 0.5 mg min/ml. From these results it is possible to consider that ethylene and acetaldehyde are intermediate products, which react completely to form final products.

In order to confirm that acetaldehyde and ethylene are intermediates of ethanol steam reforming, two different mixtures containing water/acetaldehyde and water/ethylene were fed by means of a carrier nitrogen stream flowing through a saturator. The reaction temperature was 773 K and space time was 1 mg min/ml. The feed composition was that corresponding to typical run during ethanol steam reforming. It is possible to affirm that acetaldehyde and ethylene are intermediates in the ethanol steam reforming since they react completely over Ni-based catalyst at 773 K to form methane, carbon monoxide, carbon dioxide and hydrogen. Joensen and Rostrup-Nielsen [20] reported that different catalyst systems based on Co, Cu/Zn, Cu/Zn/Cr and noble metals supported on different carriers were studied for the steam reforming of ethanol. These studies indicated that steam reforming of ethanol proceeds via an acetaldehyde intermediate [7,8,21]. On the other hand, it is known that ethanol is dehydrated by the acid sites of the alumina producing ethylene [22].

The analysis of product distribution at the reactor outlet (Fig. 3) proves that products concentration obey the following equation:

$$\text{Mol number of } CO_2 = \text{mol number of CO} \\ + \text{mol number of } CH_4$$

So the following reaction scheme for ethylene steam reforming could be postulated:

$$\begin{aligned} &C_2H_4 + 2H_2O \rightarrow CH_4 + CO_2 + 2H_2, \\ &CH_4 + H_2O \leftrightarrow CO + 3H_2 \end{aligned} \tag{10}$$

and for acetaldehyde steam reforming:

$$\begin{aligned} &CH_3CHO + H_2O \rightarrow CH_4 + CO_2 + H_2, \\ &CH_4 + H_2O \leftrightarrow CO + 3H_2 \end{aligned} \tag{11}$$

During these runs a considerable carbon imbalance was detected. Moreover, after 6 h operation, the reactor was plugged with carbon. It can be pointed out that acetaldehyde and ethylene promotes coke formation, as other authors have reported [22].

3.3. *Effect of water/ethanol molar ratio*

The effect of the water/ethanol molar ratio on reforming performance at 723 K and at space time equal to 1 mg min/ml is reported in Fig. 4.

Whatever the amount of water initially introduced, ethanol is completely converted, and no intermediate products (acetaldehyde and ethylene) were detected. Hydrogen selectivity increases with water/ethanol feed ratio.

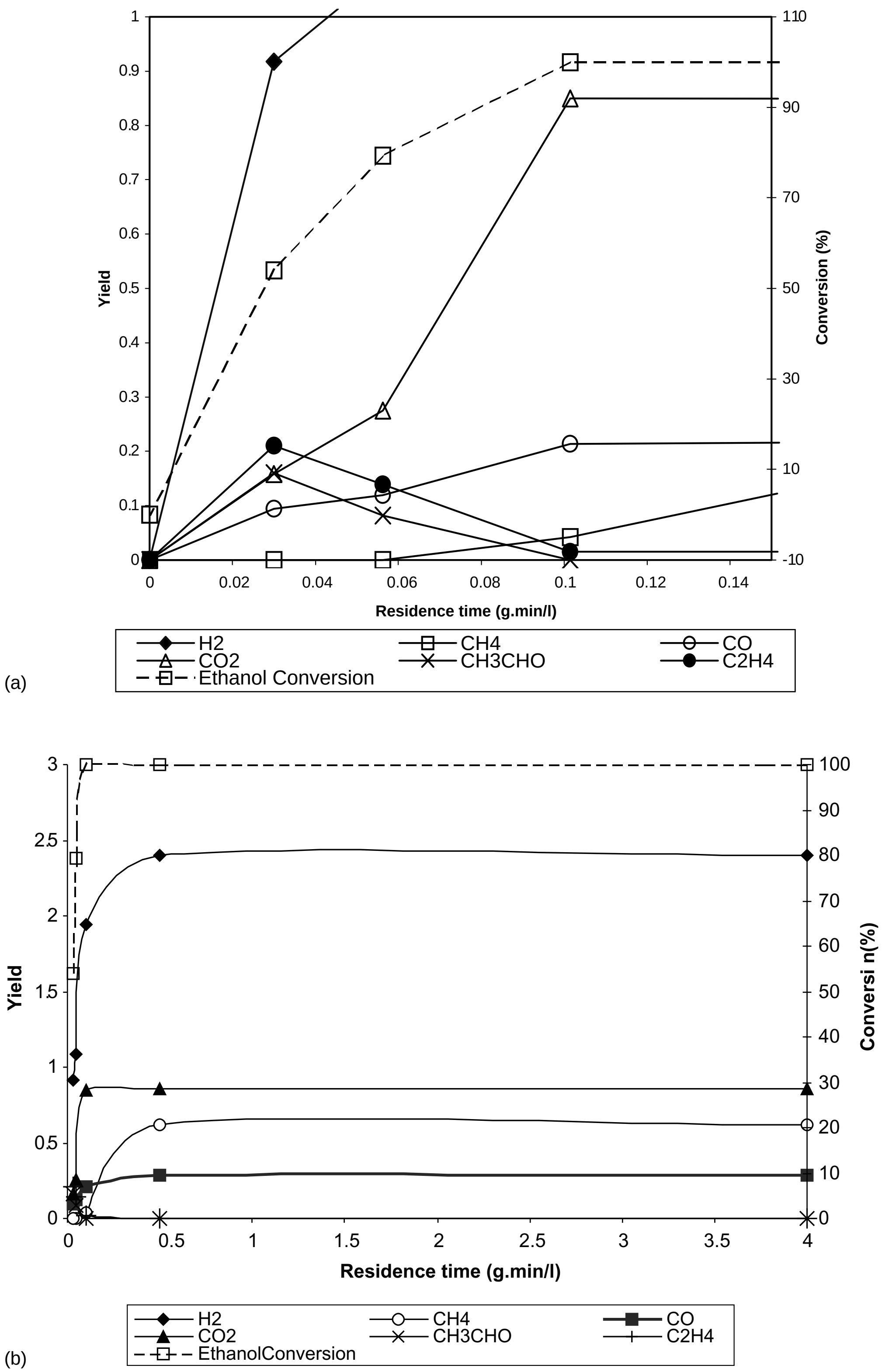

Fig. 2. (a, b) Effect of space time on products distribution. Temperature is 773 K and water/ethanol molar ratio is 3.3.

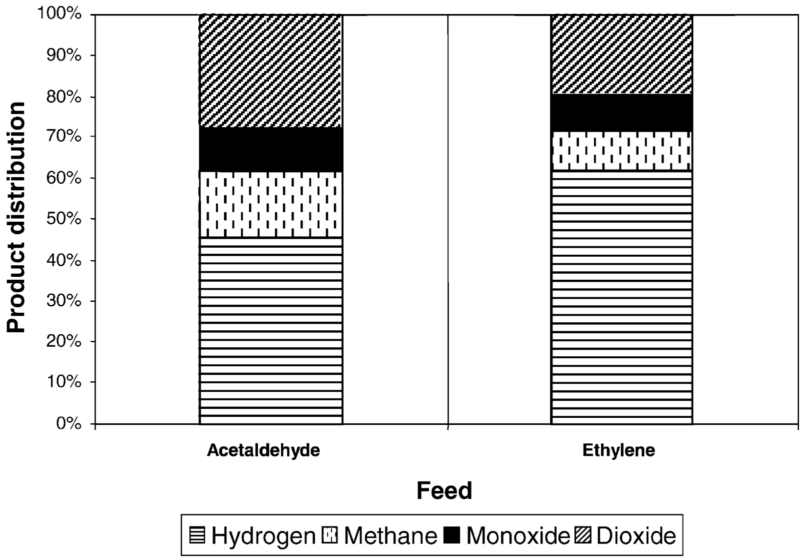

Fig. 3. Product distribution for acetaldehyde and ethylene steam reforming. Temperature is 773 K, water/ethanol molar ratio is 3.3 and space time is 1 mg min/ml.

It is known that coking can be minimized by gasification with steam. By increasing water/ethanol molar feed ratio from 1 to 3.3, the selectivity to carbon decreases, and above 3.3 molar ratios, carbon selectivity remains constant. Therefore, carbon formation is minimized by water/ethanol molar ratio equal or higher than 3.3. In addition, an elemental analysis performed on spent catalysts revealed significant amounts of carbon (38%, w/w) for a used sample submitted to water/ethanol ratio = 1 and after 20 h of operation.

By increasing water/ethanol molar ratio from 3.3 to 6, methane selectivity slightly decreases (from 0.29 to 0.25) while hydrogen selectivity is strongly improved. This means that molar ratio higher than 3.3 methane reforming is promoted. It must be also noted that hydrogen selectivity is 91% for water/ethanol molar ratio about 6.

3.4. *Effect of oxygen in ethanol steam reforming*

The aim of this experiment is to reduce carbon formation and CO concentration. In this process oxygen/ethanol ratio must be low in order to avoid hydrogen combustion [23].

The effect of oxygen addition to the feed for a given water/ethanol molar ratio at 773 K, is examined in Fig. 5. It can be seen that the presence of oxygen in the range O_2/ethanol molar ratio from 0 to 0.6 reduces carbon deposition. On the other hand, CO and CO_2 yields slightly increase in all

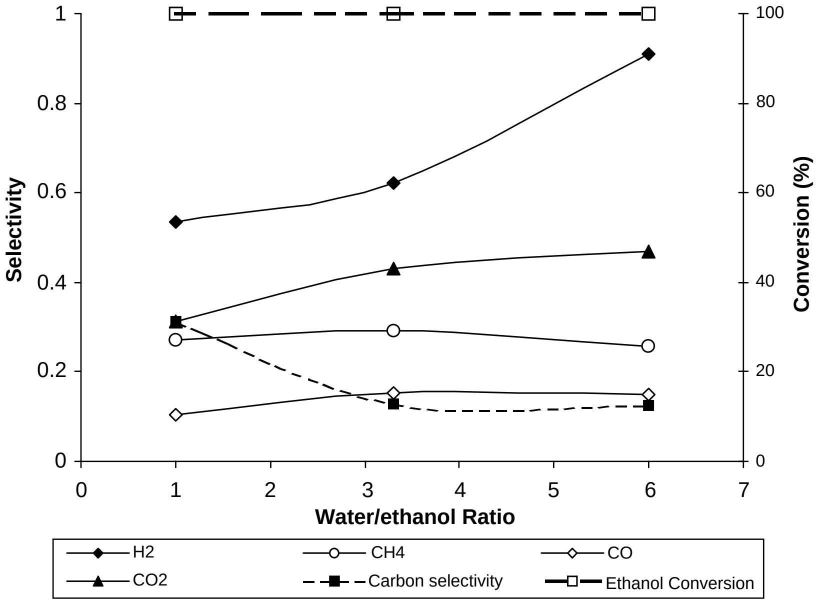

Fig. 4. Effect of water/ethanol molar ratio on ethanol conversion and products selectivity. Temperature is 723 K and space time is 1 mg min/ml.

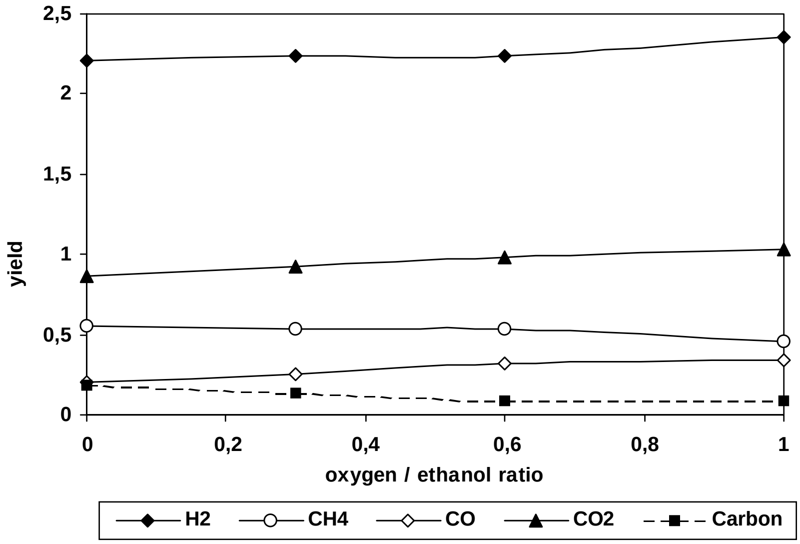

Fig. 5. Effect of oxygen in the steam reforming of ethanol. Temperature is 773 K, water/ethanol feed ratio is 3.3 and space time is 1 mg min/ml.

the range analyzed. CH_4 and H_2 yields remain constant for O_2/ethanol ratio from 0 to 0.6. For O_2/ethanol ratio from 0.6 to 1, H_2 yield slightly increases while CH_4 yield slightly decreases. It means that carbon deposited on the catalyst could be gasified by O_2 for O_2/ethanol molar ratio from 0 to 0.6, and methane could be oxidized in presence of O_2 for O_2/ethanol molar ratio higher than 0.6. Unfortunately, in the range studied the presence of oxygen does not reduce carbon monoxide production. Nevertheless, a favorable effect on carbon deposition is observed as soon as oxygen is added in the feed. Therefore, adding O_2 to the feed corresponding to an O_2/ethanol molar ratio equal or higher than 0.6, the yield of carbon deposited is diminished by a factor about 2.

3.5. Reaction scheme

From the above results it is possible to propose a reaction scheme for ethanol steam reforming on Ni-based catalyst at 773 K.

Ethylene and acetaldehyde are intermediate products formed from ethanol dehydration and dehydrogenation, respectively

$$C_2H_5OH \rightarrow C_2H_4 + H_2O, \quad \Delta H = 45.64\,\text{kJ/mol}$$

$$C_2H_5OH \rightarrow CH_3CHO + H_2, \quad \Delta H = 68.75\,\text{kJ/mol}$$

Methane, carbon monoxide, carbon dioxide and hydrogen are finals products obtained according to the following reactions: acetaldehyde steam reforming and ethylene steam reforming

$$CH_3CHO + H_2O \rightarrow CO_2 + CH_4 + H_2,$$
$$\Delta H = -55.87\,\text{kJ/mol}$$

$$C_2H_4 + 2H_2O \rightarrow CO_2 + CH_4 + 2H_2,$$
$$\Delta H = -36.9\,\text{kJ/mol}$$

The results showed that ethanol, acetaldehyde and ethylene are completely converted into C_1, so that, carbon oxides, methane and hydrogen can be found in the exit gas mixture. Comparing the K_p value obtained for methane steam reforming at 773 K: $\log K_p = -2.74$, with the MAR estimation on $Ni/\gamma Al_2O_3$ catalyst: $\log(\text{MAR}) = -2.07$, it is possible to conclude that the effluent gas composition at 773 K is determined by methane steam reforming equilibrium. Thus, the thermodynamic equilibrium of the later reaction explains the trend observed when water/ethanol molar feed ratio is changed:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2, \quad \Delta H = 205.82\,\text{kJ/mol}$$

4. Conclusions

This study has allowed proposing an overall reaction scheme as a function of the temperature for steam reforming of ethanol on based Ni catalyst.

- At 573 K, ethanol completely reacts to form methane, carbon monoxide and hydrogen, via acetaldehyde and ethylene:

  $$C_2H_5OH \rightarrow CH_4 + CO + H_2$$

- At 673 and 773 K, ethanol steam reforming reaction becomes significant:

  $$C_2H_5OH + H_2O \rightarrow CH_4 + CO_2 + 2H_2$$

- At 773 K, the effluent composition is determined by the thermodynamic equilibrium of methane steam reforming:

  $$CH_4 + H_2O \leftrightarrow CO + 3H_2$$

- Evidences that WGS reaction occur were not found, in agreement with other authors [15,17–19].

- Only at short contact times, acetaldehyde and ethylene, both intermediates and carbon precursors, can be seen in the effluent. These contact times decrease when the temperature increases.
- The presence of oxygen in the feed reduces carbon formation since carbon is oxidized under oxygen stream. In the same way methane could be oxidized by oxygen, according with the results obtained for O_2/ethanol ratio higher than 0.6.

Finally, it can be concluded that high temperatures (above 773 K), higher water/ethanol molar ratios (about 6:1) promote, on Ni/γAl_2O_3 catalyst, high hydrogen yield (5.2) and selectivity (91%) while enhances methane steam reforming and limits carbon deposition. Nevertheless, the carbon monoxide concentration obtained remains much higher than the tolerance threshold of the fuel cell. Further studies in order to reduce the CO concentration as much as possible considering the low tolerance to CO of the fuel cell anode must be performed. Ni/γAl_2O_3 catalyst could be a promissory alternative to be improved, without temperature restriction represented by WGS thermodynamic equilibrium over CO production.

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