Hydrogen Production by the Steam Reforming of Bio-Ethanol over Nickel-Based Catalysts for Fuel Cell Applications

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Abstract: The bio-ethanol steam reforming over nickel-based catalysts when the temperature is within the range of 700 to 800 K is studied for fuel cell applications. The effect of operating conditions such as the temperature, space time, water-to-ethanol molar ratio, and oxygen-to-ethanol molar ratio on the product distribution is evaluated. The water-gas shift reaction is examined in the reforming process. Adjusting feed ratios to favor carbon removal from the surface is discussed in detail. It is shown that a nickel-supported-on-alumina catalyst completely converts bio-ethanol and high hydrogen yields are obtained. High temperatures and water-to-ethanol ratios can promote hydrogen production. There is no evidence that the water-gas shift reaction occurs over nickel-based catalysts. Carbon formation can be minimized by using high water-to-ethanol ratios. The presence of oxygen in the feed plays a favorable effect on the carbon deposition, but the carbon monoxide production is not reduced. There are several reaction pathways that could occur in the bio-ethanol steam reforming process, and the catalyst produces ethylene and acetaldehyde as intermediate products. The region of carbon formation depends on the temperature as well as the water-to-ethanol and oxygen-to-ethanol molar ratios. Finally, an overall reaction scheme as a function of temperature is proposed. The best catalysts appear to be those that are sufficiently basic to inhibit the dehydration of ethanol to ethylene, which subsequently polymerizes and causes coke formation.

Keywords: Bio-ethanol, Hydrogen Production, Steam Reforming, Fuel Cells, Reaction Scheme, Nickel-Based Catalysts

1. Introduction

Energy is an indispensable element in everyday life. However, most of the energy comes from fossil fuels, which are a non-renewable energy source. Furthermore, dependence on fossil fuels as energy sources has caused serious environmental problems, such as greenhouse gas emissions, air pollutants, and natural resource depletion. The need for renewable alternatives is becoming ever more urgent. Hydrogen has been identified as an ideal energy carrier to support sustainable energy development [1]. Hydrogen can be used in a fuel cell to generate electricity with high efficiency. It is extremely clean as the only by-product is water. In order to support sustainable hydrogen economy, it is crucial to produce hydrogen cleanly and renewably [2].

Fuel cells are electrochemical devices that convert the chemical energy of a fuel and an oxidant directly into electricity and heat on a continuous basis [3]. A fuel cell consists of an electrolyte and two electrodes. A fuel such as hydrogen is continuously oxidized at the negative anode while an oxidant such as oxygen is continuously reduced at the positive cathode. The electrochemical reactions take place at the electrodes to produce a direct electric current. Fuel cells use hydrogen as a fuel which results in the formation of water vapor only and consequently they provide clean energy. Fuel cells offer high conversion efficiency and thus are promising [4].

A variety of hydrogen production routes have been explored [5]. 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 [6]. The steam reforming of ethanol is a promising choice in hydrogen-based energy systems. Producing hydrogen from ethanol steam reforming would not only be environmentally friendly but also would open new
opportunities for utilization of renewable resources, which are globally available. Additionally, ethanol presents a series of advantages, since it is easier to store, handle and transport in a safe way due to its lower toxicity and volatility [7]. Furthermore, this alcohol can be distributed in a logistic net similar to the conventional gas stations [8]. From this standpoint, ethanol steam reforming is one of the best alternatives to obtain hydrogen. Ethanol can be obtained by fermentation processes from biomass [9]. The ethanol obtained in this way is known as bio-ethanol. Ethanol production from lignocellulose would open up the possibility for the utilization of diverse and low-cost biomass, such as agricultural wastes and forestry residues [10]. In this way, food could be produced along with bioethanol from agricultural sources. Vegetables consume the carbon dioxide produced from the use of ethanol as a fuel. Therefore, the carbon cycle is closed and these carbon dioxide emissions are not considered that contribute to the global warming.

Thermodynamic studies have shown the feasibility of hydrogen production from ethanol steam reforming for fuel cell applications [11]. There are several alternatives to carry out the reforming process. Auto-thermal reforming is 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 [12]. Steam reforming is a strongly endothermic reaction and heat must be supplied to the system by an external device [13]. In order to maximize the hydrogen yield, an excess of water is usually fed to carry out the water-gas shift reaction [14]. Steam reforming is a very complex reaction where many reaction pathways are possible [15]. Some of them are favored depending on the catalyst used [16]. The main reaction mechanisms involve dehydration or dehydrogenation reactions [17]. 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 [18].

Hydrogen production through the steam reforming of ethanol has been extensively studied [19]. The presence of reaction intermediates decreases the hydrogen yield and can also induce catalyst deactivation [20]. By increasing the steam-to-ethanol molar ratio of the feed, the formation rate of the carbon is decreased and this improves catalyst stability [21]. For high steam-to-carbon ratios, the autonomy of the final application is limited due to the lower amount of ethanol [22]. The effect of the reaction temperature on the conversion and selectivity toward the main products and by-products obtained has been evaluated [23]. Studies at different temperatures have allowed optimizing the experimental conditions in order to obtain high hydrogen yield and to limit by-product formation [24]. The effect of space time on the behavior of the catalysts has been studied [25]. This type of experiment is indispensable to study the catalyst resistance to deactivation prior to its implementation in a final appliance [26]. The lack of commercial catalysts is due mainly to the catalyst deactivation [27].

As compared to methanol reforming, ethanol reforming is intrinsically more complicated as it involves an additional carbon-carbon bond cleavage, multiplying the possible pathways in the reaction network [28]. Furthermore, the carbon-carbon bond breaking of ethanol requires higher reforming temperatures, and several competing reactions are also thermodynamically favorable [29]. Significant progress has been made in gaining insight into the reaction mechanisms of ethanol reforming [30]. Yet a consensus is still lacking due to the versatility of the ethanol reforming reaction where numerous combinations of catalyst and reaction conditions could be involved. Realistically, side reactions occur with the steam reforming reaction and thus cause byproducts [31]. Acetaldehyde, ethylene, and methane are important byproducts and intermediate species that contain high hydrogen content, while carbon monoxide is found and could poison fuel cell anodes [32]. Apparently, to obtain high hydrogen yields, these species must be further transformed, but their conversions may take different routes [33]. Furthermore, carbon formation on the catalysts surface, although highly undesired, is often encountered [34]. A possible reaction network is mainly composed of these reactions, but is complicated from both mechanistic and thermodynamic points of view. The relative contribution of individual reaction pathway is not constant, but is dependent on the choice of catalysts and reaction conditions [35]. Ultimately, ethanol conversion, the selectivity to hydrogen, and the rate of deactivation are the most relevant issues in practical applications [36]. These all drive extensive studies on catalyst development and process engineering for superior activity and stability toward hydrogen production.

The light alcohol ethanol is an important candidate as a chemical carrier of hydrogen, and its production is useful in a range of fuel cell applications. In this study, the steam reforming of bio-ethanol over supported nickel catalysts at the temperature between 600 and 800 K is studied. The effect of operating conditions such as the temperature, space time, water-to-ethanol molar ratio, and oxygen-to-ethanol molar ratio on the product distribution is evaluated. The water-gas shift reaction is examined, as it is an important step in the reforming process. An overall reaction scheme as a function of temperature is proposed. The objective of this study is to describe the product distribution obtained for different operating conditions. Of special interest in this study is to evaluate the effects of reaction temperature, space time, water-to-ethanol feed ratio, and oxygen addition on the product distribution. This study could shed light on a path forward for improving catalyst design.

### 2. Experimental

Bio-ethanol can be obtained from different biomass feedstock such as corn and sugar cane or agricultural residues. The ethanol production processes involve the conversion of biomass into fermentable sugars, which then undergo fermentation. To produce ethanol as a fuel suitable for blending with gasoline, water needs to be removed above the azeotropic levels. Pure ethanol is produced in a multistep distillation, which removes the contaminants and water.
However, steam reforming of ethanol requires that water be added to the process. Therefore, the use of bio-ethanol as the feedstock for hydrogen production could eliminate the need for the energy-intensive distillation steps. This would make the steam reforming process much more attractive from a cost standpoint.

A conventional fixed bed reaction apparatus is used to evaluate the steam reforming of bio-ethanol over nickel-based catalysts. The reaction apparatus consists of a flow system, the reactor unit and the analysis system. Steam reforming of bio-ethanol is carried out for the reactor operated isothermally. All experiments have been performed under atmospheric pressure. This acquisition system allows obtaining detailed information of the catalytic process since all reaction parameters are measured and controlled in real time. The reactor is made with a Pyrex glass tube of 8.0 mm inner diameter, and it is placed into an electric oven. The flow system is equipped with a set of mass-flow controllers (MFCs), which accurately control the flow of the inlet gases, and a set of valves which allow selection of gas feed composition and introduction of the gas mixture to the reactor or to a by-pass stream. A high pressure pump is used for feeding the liquid reagents. Bio-ethanol and water are fed by means of a carrier nitrogen stream flowing through a saturator. Bio-ethanol would react with steam over the catalyst to produce a mixture of hydrogen and other compounds, such as hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and acetaldehyde. In some experiments, acetaldehyde or ethylene are used as a reactant, instead of bio-ethanol, and oxygen is added together with nitrogen. The water-to-ethanol molar ratio is controlled by adjusting both the saturator temperature and the input nitrogen flow rate. Carbon monoxide is poisonous to the noble-metal catalysts, and thus the formation of carbon monoxide is typically reduced by performing the reaction in excess steam. The reaction temperature is measured with a sliding thermocouple placed inside the catalyst bed. Heating of the reactor is provided by an electric furnace, controlled by a proportional-integral-derivative (PID) temperature controller, which is connected with a thermocouple placed in the middle of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed.

The catalyst has an important role in achieving complete ethanol conversion, as it increases the rate of reaction in such a way that the system tends toward thermodynamic equilibrium. However, different catalysts induce different pathways to produce hydrogen. Therefore, the choice of the catalyst has a vital role in the ethanol steam reforming process. Supported nickel catalysts are widely used for catalytic reforming reactions, and the activity can be attributed to their large adsorption capacity toward ethanol [37]. Nickel-based catalysts are apt to sinter under catalytic reforming conditions of high temperatures and in the presence of steam [38]. Severe carbon deposition could also be observed on the catalyst if the surface carbon species adsorbed on metal surface are not removed in time [39]. Carbon deposition over nickel-based catalysts is a fatal problem for the steam reforming of bio-ethanol. Furthermore, the production of hydrogen rich gas with a low concentration of carbon monoxide is a challenge using nickel catalysts, which are not so active in the water-gas shift reaction [40]. Both the nature of the metal and the support significantly affect the product distribution. Significant progress has been made in gaining insight into the reaction mechanisms of ethanol reforming. However, the nature of the metal and its effect on the different reaction pathways are still not well-established. This appears to be mainly due to difficulties in distinguishing between apparent and real effects. In fact, there are numerous factors that can also affect the product distribution: ethanol conversion, metal dispersion, and the nature of the support.

In all the kinetics experiments, a nickel-supported-on-alumina catalyst is prepared using conventional impregnation techniques of commercially available oxides, and then used for hydrogen production through the steam reforming of bio-ethanol. The catalyst has a BET (Brunauer-Emmett-Teller) specific surface area (SSA) of 16 m²/g and a total nickel content of 36% (weight in weight). The nickel content of the used catalyst is determined by the atomic absorption spectroscopy (AAS) Agilent AA Duo. X-ray diffraction (XRD) is conducted using a Rigaku model Miniflex diffractometer. The specific surface area is determined using a Micromeritics TriStar II Plus. Transmission electron microscopy (TEM) is used to analyze pore structure and nickel dispersion of the catalyst using a FEI Themis transmission electron microscope (TEM) platform. A modified Sartorius symmetrical microbalance is used for the determination of the specific surface area and of the pore size distribution. The powder is approximately 80 mg, and is placed in a platinum crucible and introduced in the microbalance. Then the sample is dried at the temperature of 378 K in an electric vacuum drying oven. After the weight is stabilized at the microbalance sensitivity, the sample is cooled at the temperature of 78 K without removing it from the crucible and without air contamination. Nitrogen is introduced step by step in the apparatus until it reaches a maximum relative pressure of 0.998. Adsorption-desorption isotherm is made by recording the increase-decrease of the sample weight at the different relative pressures. The specific surface area is computed using the multipoint BET method. The mesopore size distribution curve is obtained by using the desorption branch of the nitrogen isotherm, according the Orr-Dalla Valle method.

After activity testing, the catalyst is analyzed by to simultaneous thermal analysis (STA) NETZSCH STA 449 F3 Jupiter.®. The composition of the input and output streams is analyzed by on-line gas chromatography (GC). An Agilent gas chromatography 7890B is equipped with an asymmetric thermal conductivity detector (TCD) and a Porapak Q packed column, which are used to analyze the concentration of the ethanol, water, acetaldehyde, acetone, carbon dioxide, and ethylene in the bio-ethanol steam reforming process. In this case, nitrogen is used as the carrier gas. A flame ionization detector (FID) and a capillary column are used to determine carbon monoxide, methane and hydrogen compositions. In
this case, helium is used as the carrier gas. Determination of the response factors of the thermal conductivity and flame ionization detectors has been achieved with the use of gas streams of known composition such as Scott specialty gas mixtures. Reaction gases are supplied from high-pressure gas cylinders and are of ultrahigh purity.

Prior to catalytic tests the catalyst is reduced in situ under flowing hydrogen (20 ml/min) and nitrogen (80 ml/min) at 800 K for one hour and under flowing hydrogen (80 ml/min) for one hour. Then, it is cleaned for one hour with flowing helium at the same temperature in order to remove adsorbed hydrogen. After reduction and clean, the catalyst is cool down to reaction temperature. Hydrogen adsorption capacity and adsorption strength of the reduced catalyst are measured by hydrogen-thermal desorption spectroscopy (TDS), also known as temperature programmed desorption (TPD), experiments using a BELCA T-B instrument. Finally, the reactant gas mixture is passed through the reactor, and the gaseous products are analyzed by gas chromatography. Preliminary catalytic tests are carried out in order to verify the kinetic experiments. Experiments without catalyst are also carried out in order to verify the absence of homogeneous reaction. A negligible contribution of homogeneous reforming has been found. The absence of internal and external diffusion limitations, for the total gas flow equal or greater than 200 ml/min is confirmed and particle diameters below 0.480 mm. The catalyst bed is diluted with glass particles, of the same diameter range, in order to avoid adverse thermal effects. The experiments are performed under the following conditions - the mass of catalyst: 0.086-0.880 g; temperature: 600-800 K; water-to-ethanol molar ratio: 1.0-6.0; ethanol molar fraction: 0.017; total feed rate: 280 ml/min.

The reactants, ethanol and water, conversion is denoted by $X_{\text{reactant}}$. The selectivity to products such as hydrogen, methane, carbon monoxide, carbon oxide, acetaldehyde, acetaldehyde, acetone, and ethylene is denoted by $S_{\text{product}}$. Products yields are denoted by $Y_{\text{product}}$. They are computed as follows:

$$X_{\text{reactant}} = \frac{F_{\text{hydrogen,produced}}}{F_{\text{hydrogen,consumed}}}$$

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

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

$F_{\text{in or out}}$ 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. A major route to catalyst deactivation is that of carbon formation. Deactivation by coke formation is a challenging problem, especially when a transition metal such as nickel is involved. Taking into account that total selectivity to compounds containing carbon must be equal or lower than one, the fraction of reactant converted, which it is not detected in the reactor outlet, is assigned to the formation of carbonaceous deposits adsorbed on the catalyst surface as coke deposit. Therefore, the selectivity to coke is computed as follows:

$$S_{\text{carbon}} = 1 - \sum S_{\text{carbon-containing product}}$$

Since the experiments are performed at diluted conditions, the change in volume due to reactions is negligible. Furthermore, the correction factor accounting for this variation is not considered to compute conversions and selectivity. The space time is denoted by $\tau_r$ defined as the ratio between mass of catalyst and the total flow rate at the inlet. The variable operating conditions for this study are the temperature, space time, water-to-ethanol molar ratio, and oxygen-to-ethanol molar ratio.

### 3. Results and Discussion

#### 3.1. Effect of Temperature

![Figure 1. Effect of temperature on the reactants conversion and products selectivity.](image)

Figure 1 shows the effect of temperature on the reactants conversion and products selectivity. In order to perform with an excess of water, the water-to-ethanol molar ratio is initially fixed to 3.8 according to the stoichiometry of global steam reforming reaction. Space time is maintained at 0.8 mg·min/ml for all the temperatures. Ethanol is completely converted over the whole range of temperature studied, whereas the water conversion increases with increasing temperature. From the analysis of product distribution
obtained at the temperature of 600K, the selectivity to methane is approximately equal to that to carbon monoxide. This reveals that ethanol decomposition to carbon monoxide, methane, and hydrogen is the main reaction at the temperature of 600K. The overall decomposition reaction of ethanol could be represented as follows:

$$\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CO} + \text{CH}_4 + \text{H}_2 \quad (6)$$

Additionally, the lower selectivity to carbon dioxide could be produced either by ethanol steam reforming or by water-gas shift reaction, which could take place simultaneously in the reactor:

$$\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4 + 2\text{H}_2 \quad (7)$$

$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad (8)$$

However, thermodynamics estimations reveal that ethanol steam reforming to carbon dioxide, methane, and hydrogen is carried out completely. The value of equilibrium constant for the water-gas shift reaction at the temperature of 600 K is given by: \(\log (\text{equilibrium constant}) = 1.68\). On the other hand, the mass-action ratio relative to the water-gas shift reaction is given by: \(\log (\text{mass-action ratio}) = -1.28\). After comparison of equilibrium constant and mass-action ratio values for the water-gas shift reaction, it is found that the nickel/alumina catalyst is not active and the water-gas shift reaction becomes less favorable at the temperature of 600 K. As the temperature increases from 600 to 700 K, the selectivity to carbon dioxide and water conversion, which are almost negligible at the temperature of 600 K, significantly increase, whereas the selectivity to carbon monoxide drops rapidly. This reveals that ethanol steam reforming instead of ethanol decomposition become significant at the temperature of 700 K, and small quantities of carbon monoxide are produced by the ethanol decomposition reaction.

Finally, when the temperature increases from 700 to 800 K, the selectivity to methane drops rapidly, the selectivity to carbon dioxide remains constant, and the selectivity to hydrogen and carbon monoxide increases. In this case, carbon monoxide is mainly produced by the steam reforming of methane, which could be represented as follows:

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad (9)$$

At high temperatures, carbon monoxide production is thermodynamically favored, which will poison the electrodes of the proton exchange membrane (PEM) fuel cell. Therefore, further purification steps are required, which increases not only the final cost of the hydrogen produced, but also the size and the weight of the fuel processing system. If the water-gas shift reaction occurs when the temperature is within the range of 700 to 800 K, it should be at equilibrium, and carbon monoxide and carbon dioxide yields should have a consistent behavior with this assertion as the temperature increases. However, carbon dioxide-to-carbon monoxide molar ratios do not correspond with the predictions of thermodynamic equilibrium. Furthermore, the carbon dioxide yield remains constant, whereas the carbon monoxide yield increases in the same range of temperature. On the other hand, the methane yield decreases in the same range of temperature, and at the temperature of 800 K, the relation among carbon dioxide, carbon monoxide, and methane is verified: \(S_{\text{carbon dioxide}} = S_{\text{carbon monoxide}} + S_{\text{methane}}\). Taking into account that ethanol is completely converted, this relation can be analyzed in terms of molar relation. Therefore, the steam reforming of ethanol and the steam reforming of methane, which is at equilibrium, could be determining the product distribution at the temperature of 800 K, and there is no evidence that the water-gas shift reaction occurs.

The proposal that the water-gas shift reaction does not take place over a nickel catalyst may appear to be contradictory according to the results obtained from experimental studies on steam reforming of hydrocarbons. Nevertheless, it is worth noting that this concept is being recently revised. Aupretre et al. [41] have affirmed that nickel is a poor candidate in the water-gas shift reaction using different metallic catalysts. Descorme et al. [42] have found that nickel is poor for the water-gas shift reaction. Jiang et al. [43] have suggested a mechanism where the water-gas shift reaction does not take place using copper catalysts. On the other hand, from the experimental data obtained here, it is found that the best selectivity to hydrogen is obtained at high temperature 800 K, and thus this temperature will be considered for further study.

### 3.2. Effect of Space Time

![Figure 2. Effect of space time on the product distribution.](image)

The effect of varying space time on the product distribution is studied to elucidate the reaction pathway. Experiments are carried out at different space time, keeping constant temperature 800 K and water-to-ethanol molar ratio 3.8. Figure 2 shows the effect of space time on the product distribution. Ethanol is completely converted at all the space times used. For space times higher than 0.8 mg·min/ml, the only products are hydrogen, carbon oxide, and methane. At lower space times, 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. Note that acetaldehyde and ethylene yields have a maximum at lower space times, and theirs yields become null when the space time reaches 0.08 mg min/ml. In contrast, the yields of final products such as hydrogen, carbon monoxide, methane, and carbon dioxide increase, reaching a constant value for space time higher than 0.8 mg·min/ml. Therefore, 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 are fed by means of a carrier nitrogen stream flowing through a saturator. The space time is 0.8 mg·min/ml and the reaction temperature is 800 K. Acetaldehyde and ethylene are intermediates in the ethanol steam reforming, since they react completely over nickel-based catalysts at the temperature of 800 K to form hydrogen, carbon monoxide, carbon dioxide, and methane. It has been reported that different catalyst systems based on cobalt, copper/zinc, copper/zinc/chromium and noble metals supported on different carriers have been studied for the steam reforming of ethanol, indicating that steam reforming of ethanol proceeds through an acetaldehyde intermediate [44]. On the other hand, it is worth noting that ethanol is dehydrated by the acid sites of the alumina producing ethylene [45].

### 3.3. Product Distribution

![Figure 3: Product distribution for acetaldehyde and ethylene steam reforming.](image)

Figure 3 shows the product distribution for acetaldehyde and ethylene steam reforming. The analysis of product distribution at the reactor outlet reveals that the products concentration is computed from the following equation:

\[
\text{Mol number of carbon dioxide} = \text{Mol number of carbon monoxide} + \text{Mol number of methane}
\]  

Therefore, the overall reaction scheme for ethylene steam reforming could be represented as follows:

\[
C_2H_4 + 2H_2O \rightarrow CH_4 + CO_2 + 2H_2, \quad CH_4 + H_2O \leftrightarrow CO + 3H_2
\]

Additionally, acetaldehyde steam reforming may occur through the reactions depicted below:

\[
CH_2CHO + H_2O \rightarrow CH_4 + CO_2 + 2H_2, \quad CH_4 + H_2O \leftrightarrow CO + 3H_2
\]

Methane is detected under these conditions. From a practical point of view, a small concentration of methane in the bio-ethanol steam reforming process may be tolerated since methane present at the exhaust of the fuel cell can be burned, along with unreacted hydrogen, to provide the heat necessary for the highly endothermic reforming reaction. In any event, conversion of methane through reforming with water and carbon dioxide proceeds at higher reaction temperatures, resulting in increased yield of hydrogen production. During the experiment, a considerable carbon imbalance is observed. Moreover, after 8 hours of operation, the reactor is plugged with carbon. Coupling reactions of ethanol or acetaldehyde can also occur and depend on base sites on the catalyst surface. It is worth noting that acetaldehyde and ethylene promotes coke formation. Acetaldehyde and ethylene can undergo further reactions. These reactions may be responsible for coke formation and catalyst deactivation. The main reactions that contribute to coke formation during ethanol conversion reactions are as follows: ethanol dehydration to ethylene, followed by polymerization to coke; the Boudouard carbon deposition reaction; the reverse of carbon gasification; and the decomposition of hydrocarbons such as methane and ethylene. The extent of each reaction depends on both reaction conditions and the catalyst used. While low reaction temperatures favor the formation of carbon through the Boudouard carbon deposition reaction and the reverse of carbon gasification, carbon formation through the decomposition of hydrocarbons are the main routes at higher temperatures [46].
3.4. Effect of Water-to-Ethanol Molar Ratio

Catalytic tests under different water-to-ethanol molar ratios are performed in order to evaluate the effect of the redox atmosphere on the carbon deposits and the deactivation phenomenon. Figure 4 shows the effect of water-to-ethanol molar ratio on the ethanol conversion and products selectivity. Whatever the amount of water initially introduced, ethanol is completely converted, which is essential for the process to be economical. Additionally, no intermediate products such as ethylene and acetaldehyde are observed. The selectivity to hydrogen increases with increasing water-to-ethanol molar ratio. The formation of coke is accumulated on the catalyst surface, which can in turn induce catalyst deactivation. Carbon formation may take place in several ways. However, the lowest values of Gibbs free energy corresponds to the Boudouard carbon deposition reaction. Another possible route for the formation of carbon over the catalyst is through ethylene produced by dehydration of ethanol on the acidic alumina support. The catalyst exhibits severe deactivation, which is more pronounced at lower water-to-ethanol molar ratios. The loss of stability observed with decreasing water-to-ethanol molar ratio in the feed is in accordance with thermodynamic predictions regarding the formation of coke. However, the coke formation can be minimized by the gasification with steam. As the water-to-ethanol molar ratio increases from low values, the selectivity to carbon decreases, and then remains constant at sufficiently high water-to-ethanol molar ratios. Therefore, carbon formation is minimized in the range of moderate to high water-to-ethanol molar ratios. In addition, an elemental analysis performed on spent catalysts reveals significant amounts of carbon for a used sample with a low water-to-ethanol ratio and after 38 hours of operation. As the water-to-ethanol molar ratio increases from low to moderate values, the selectivity to methane slightly decreases, whereas the selectivity to hydrogen significantly increases. This reveals that methane steam reforming is promoted for high water-to-ethanol molar ratios. It is also worth noting that the selectivity to hydrogen is very high for high water-to-ethanol molar ratios. By increasing the water-to-ethanol molar ratio of the feed, the formation rate of the carbon is decreased and this improves catalyst stability. In this case, methane production is minimized and carbon formation is thermodynamically inhibited. This is essential, since currently the greatest challenge in developing new catalysts is improvement in catalyst stability. This challenging problem arises as a result of carbon-carbon bond scission in the ethanol molecule, whereas this is not encountered with methanol. The approach used here to reduce carbon formation is based on the rapid conversion of carbon to gaseous products for ease of removal. However, an excess of water results in higher operating costs due to a less energy-efficient plant as a result of increased utility costs for producing the steam. Furthermore, the effectiveness of this strategy depends on the rate of the gasification reaction ultimately achieved by the catalyst.

3.5. Effect of Oxygen

With the aim of reducing carbon formation and carbon monoxide concentration, the oxygen-to-ethanol ratio must be low in order to avoid hydrogen combustion [47]. In contrast, another strategy adopted has been the addition of oxygen to the feed as has been employed for oxidative steam reforming [48]. It has also been used for partial oxidation [49]. Oxygen from the feed enhances the gasification rate of the carbon deposits formed, and this improves catalyst stability [50]. Figure 5 shows the effect of oxygen on the product distribution in the steam reforming of ethanol.

As the water-to-ethanol molar ratio increases from low to moderate values, the selectivity to methane slightly decreases, whereas the selectivity to hydrogen significantly increases. This reveals that methane steam reforming is promoted for high water-to-ethanol molar ratios. By increasing the water-to-ethanol molar ratio of the feed, the formation rate of the carbon is decreased and this improves catalyst stability. In this case, methane production is minimized and carbon formation is thermodynamically inhibited. This is essential, since currently the greatest challenge in developing new catalysts is improvement in catalyst stability. This challenging problem arises as a result of carbon-carbon bond scission in the ethanol molecule, whereas this is not encountered with methanol. The approach used here to reduce carbon formation is based on the rapid conversion of carbon to gaseous products for ease of removal. However, an excess of water results in higher operating costs due to a less energy-efficient plant as a result of increased utility costs for producing the steam. Furthermore, the effectiveness of this strategy depends on the rate of the gasification reaction ultimately achieved by the catalyst.
The methane and hydrogen yields remain constant for low oxygen-to-ethanol ratios. For high oxygen-to-ethanol molar ratios, the hydrogen yield slightly increases, whereas the methane yield slightly decreases. This reveals that carbon deposited on the catalyst can be gasified by oxygen for low oxygen-to-ethanol molar ratios, and methane could be oxidized in presence of oxygen for high oxygen-to-ethanol molar ratios. Unfortunately, within the range of feed composition studied, the presence of oxygen does not reduce the production of carbon monoxide. Nevertheless, a favorable effect on carbon deposition is observed when oxygen is added in the feed. Furthermore, as the oxygen-to-ethanol molar ratio increases, the yield of carbon deposited is diminished gradually.

### 3.6. Reaction Scheme

Designing an optimum catalyst for hydrogen production from ethanol requires additional insight into the reaction mechanism. A variety of different approaches have been undertaken to shed light on the surface mechanisms involved in the ethanol steam reforming process [51, 52]. Several studies aimed at identifying the reaction pathways taking place in ethanol conversion reactions are based on a detailed analysis of the intermediates obtained during catalytic testing [53, 54]. While the steam reforming of ethanol provides high hydrogen yields, it is a highly endothermic reaction and thus high operation temperatures are necessary. However, many other reactions can occur simultaneously with hydrogen production reactions [55, 56]. Some of these result in the formation of undesirable products. The relative importance of each of these reaction pathways depends on both the reaction conditions selected and the choice of catalyst [57, 58]. Most of the ethanol reaction mechanisms proposed have relied on infrared spectroscopy (IR) data measured under vacuum in order to determine the adsorbed species present on the catalyst surface, and thus not under realistic reaction conditions.

![Figure 6. Potential reaction pathways taking place in the steam reforming of ethanol.](image)

Although significant progress has been made in gaining insight into the reaction mechanisms of ethanol conversion, and infrared spectroscopy has been a powerful tool in achieving this goal. However, the main drawback is that the progress is not carried out under reaction conditions, which would involve flowing the reaction mixture at different temperatures. Furthermore, the nature of the intermediate species formed on the surface may be strongly affected by the reaction conditions. Figure 6 shows the potential reaction pathways taking place in the steam reforming of ethanol. Based on the experimental data, a reaction scheme for ethanol steam reforming over nickel-based catalysts at the temperature of 800 K is proposed. There is no evidence that the water-gas shift reaction occurs. However, there are several reaction pathways that could occur in the ethanol steam reforming process. Ethylene and acetaldehyde are intermediate products formed from ethanol dehydration and dehydrogenation, respectively. The direct conversion of ethanol to ethylene can occur at high temperatures. Ethanol dehydrogenation to ethylene and water could be represented as follows:

$$\text{C}_2\text{H}_4\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}, \quad \Delta H_m^\theta = 45.64 \text{ kJ/mol} \quad (13)$$

Ethylene can undergo further reactions such as cracking, aromatization, or oligomerization, producing benzene, toluene, or xylene (BTX). At low temperatures, the reaction is highly selective toward acetaldehyde, which is formed by dehydrogenation of ethanol:

$$\text{C}_2\text{H}_4\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2, \quad \Delta H_m^\theta = 68.75 \text{ kJ/mol} \quad (14)$$

Increasing temperature results in a progressive decrease of the selectivity toward acetaldehyde. No ethylene is detected under these conditions, indicating that no dehydration of ethanol is taking place, as might be expected. Carbon dioxide, methane, hydrogen, and carbon monoxide are final products obtained through acetaldehyde steam reforming and ethylene steam reforming, which could be represented as follows:

$$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{CH}_4 + \text{H}_2, \quad \Delta H_m^\theta = -55.87 \text{ kJ/mol} \quad (15)$$

$$\text{C}_2\text{H}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + \text{CH}_4 + \text{H}_2, \quad \Delta H_m^\theta = -36.90 \text{ kJ/mol} \quad (16)$$

Consequently, ethanol, acetaldehyde and ethylene are completely converted into carbon dioxide, methane, and hydrogen, which can be found in the exit gas mixture. Comparing the equilibrium constant value obtained for methane steam reforming at the temperature of 800 K: log (equilibrium constant) = -2.87, with the mass-action ratio estimation on nickel/alumina catalysts: log (mass-action ratio) = -2.16, the effluent gas composition at the temperature of 800 K may be determined by the thermodynamic equilibrium of methane steam reforming. Therefore, the thermodynamic equilibrium of the methane steam reforming reaction explains the trend observed when the water-to-ethanol molar feed ratio is varied:

$$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \quad \Delta H_m^\theta = 205.88 \text{ kJ/mol} \quad (17)$$
The intent of the reforming process is to make as much hydrogen and carbon dioxide as possible by cracking ethanol in the presence of steam over a catalyst. However, from the reaction network, it is clear that the overall reaction is very complex and involves many potential products. A wide range of undesirable byproducts such as oxygenated compounds and hydrocarbons are formed in the bio-ethanol steam reforming process. Therefore, it is important to reduce the production of undesirable intermediate compounds and byproducts.

4. Conclusions

In this study, the steam reforming of bio-ethanol over nickel-based catalysts is studied for fuel cell applications. The effect of operating conditions such as the temperature, space time, water-to-ethanol molar ratio, and oxygen-to-ethanol molar ratio on the product distribution is evaluated. Adjusting feed ratios to favor carbon removal from the surface is discussed in detail. An overall reaction scheme as a function of the temperature is proposed. The results show that a nickel-supported-on-alumina catalyst completely converts ethanol and high hydrogen yields are obtained. At the temperature of 600 K, ethanol completely reacts to form methane, carbon monoxide and hydrogen, through acetaldehyde and ethylene. When the temperature is within the range of 700 to 800 K, the steam reforming reaction of ethanol becomes significant. At the temperature of 800 K, the effluent composition is determined by the thermodynamic equilibrium of methane steam reforming. The evidence that the water-gas shift reaction occurs is not found. The catalyst produces ethylene and acetaldehyde as intermediate products. Acetaldehyde and ethylene can be observed in the effluent only at short contact times. These contact times decrease with increasing temperature. The region of carbon formation depends on the temperature as well as the water-to-ethanol and oxygen-to-ethanol molar ratios. Carbon formation can be controlled by controlling water-to-ethanol ratios in the feed. It can also be minimized by using high water-to-ethanol ratios. For very low water-to-ethanol molar ratios, carbon is formed at any temperature. Furthermore, 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 for high oxygen-to-ethanol ratios. Finally, high temperatures and water-to-ethanol molar ratios not only improve hydrogen yield and selectivity, but also enhance methane steam reforming and reduce carbon deposition. Nevertheless, the carbon monoxide concentration obtained remains much higher than the tolerance threshold of the fuel cell. Nickel/alumina catalysts could be a promissory alternative to be improved, without temperature restriction represented by the water-gas shift reaction thermodynamic equilibrium over carbon monoxide production. Finally, there are several reaction pathways that could occur in the bio-ethanol steam reforming process. The best catalysts appear to be those that are sufficiently basic to inhibit the dehydration of ethanol to ethylene, which subsequently polymerizes and causes coke formation. Overall, the hope is to make the commercial use of bioethanol as a chemical carrier for hydrogen a reality.

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References

[1] M. Ni, D. Y. C. Leung, M. K. H. Leung, and K. Sumathy. An overview of hydrogen production from biomass. Fuel Processing Technology, Volume 87, Issue 5, 2006, Pages 461-472.
[2] M. Ni, D. Y. C. Leung, and M. K. H. Leung. A review on reforming bio-ethanol for hydrogen production. International Journal of Hydrogen Energy, Volume 32, Issue 15, 2007, Pages 3238-3247.
[3] C. Song. Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century. Catalysis Today, Volume 77, Issues 1-2, 2002, Pages 17-49.
[4] S. Ahmed and M. Krumpelt. Hydrogen from hydrocarbon fuels for fuel cells. International Journal of Hydrogen Energy, Volume 26, Issue 4, 2001, Pages 291-301.
[5] J. D. Holladay, J. Hu, D. L. King, and Y. Wang. An overview of hydrogen production technologies. Catalysis Today, Volume 139, Issue 4, 2009, Pages 244-260.
[6] A. Haryanto, S. Fernando, N. Murali, and S. Adhikari. Current status of hydrogen production techniques by steam reforming of ethanol: A review. Energy & Fuels, Volume 19, Issue 5, 2005, Pages 2098-2106.
[7] Y. C. Sharma, A. Kumar, R. Prasad, and S. N. Upadhyay. Ethanol steam reforming for hydrogen production: Latest and effective catalyst modification strategies to minimize carbonaceous deactivation. Renewable and Sustainable Energy Reviews, Volume 74, 2017, Pages 89-103.
[8] G. A. Deluga, J. R. Salge, L. D. Schmidt, and X. E. Verykios. Renewable hydrogen from ethanol by autothermal reforming. Science, Volume 303, Issue 5660, 2004, Pages 993-997.
[9] M. Balat and H. Balat. Recent trends in global production and utilization of bio-ethanol fuel. Applied Energy, Volume 86, Issue 11, 2009, Pages 2273-2282.
[10] B. Hahn-Hagerdal, M. Galbe, M. F. Gorwa-Grauslund, G. Liden, and G. Zacchi. Bio-ethanol - the fuel of tomorrow from the residues of today. Trends in Biotechnology, Volume 24, Issue 12, 2006, Pages 549-556.
[11] T. Ioannides. Thermodynamic analysis of ethanol processors for fuel cell applications. Journal of Power Sources, Volume 92, Issues 1-2, 2001, Pages 17-25.
[12] R. Baruah, M. Dixit, P. Basarkar, D. Parikh, and A. Bhargav. Advances in ethanol autothermal reforming. Renewable and Sustainable Energy Reviews, Volume 51, 2015, Pages 1345-1353.
[13] S. Cavallaro. Ethanol steam reforming on Rh/Al₂O₃ catalysts. Energy & Fuels, Volume 14, Issue 6, 2000, Pages 1195-1199.
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[14] J. D. Holladay and Y. Wang. A review of recent advances in numerical simulations of microscale fuel processor for hydrogen production. *Journal of Power Sources*, Volume 282, 2015, Pages 602-621.

[15] L. V. Mattos, G. Jacobs, B. H. Davis, and F. B. Noronha. Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation. *Chemical Reviews*, Volume 112, Issue 7, 2012, Pages 4094-4123.

[16] J. L. Contreras, J. Salmones, J. A. Colín-Luna, L. Nuno, B. Quintana, I. Cordova, B. Zeifert, C. Tapia, and G. A. Fuentes. Catalysts for H₂ production using the ethanol steam reforming (a review). *International Journal of Hydrogen Energy*, Volume 39, Issue 33, 2014, Pages 18835-18853.

[17] P. D. Vaidya and A. E. Rodrigues. Insight into steam reforming of ethanol to produce hydrogen for fuel cells. *Chemical Engineering Journal*, Volume 117, Issue 1, 2006, Pages 39-49.

[18] M. Benito, J. L. Sanz, R. Isabel, R. Padilla, R. Arjona, and L. Daza. Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production. *Journal of Power Sources*, Volume 151, 2005, Pages 11-17.

[19] P. D. Vaidya and A. E. Rodrigues. Kinetics of steam reforming of ethanol over a Ru/Al₂O₃ catalyst. *Industrial & Engineering Chemistry Research*, Volume 45, Issue 19, 2006, Pages 6614-6618.

[20] A. N. Fatsikostas and X. E. Verykios. Reaction network of steam reforming of ethanol over Ni-based catalysts. *Journal of Catalysis*, Volume 225, Issue 2, 2004, Pages 439-452.

[21] D. Zanchet, J. B. O. Santos, S. Damyanova, J. M. R. Gallo, and J. M. C. Bueno. Toward understanding metal-catalyzed ethanol reforming. *ACS Catalysis*, Volume 5, Issue 6, 2015, Pages 3841-3863.

[22] C. A. Cardona and O. J. Sanchez. Fuel ethanol production: Process design trends and integration opportunities. *Bioresource Technology*, Volume 98, Issue 12, 2007, Pages 2415-2457.

[23] J. Sun, X. Qiu, F. Wu, W. Zhu, W. Wang, and S. Hao. Hydrogen from steam reforming of ethanol in low and middle temperature range for fuel cell application. *International Journal of Hydrogen Energy*, Volume 29, Issue 10, 2004, Pages 1075-1081.

[24] I. Fishtik, A. Alexander, R. Datta, and D. Geana. A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reactions. *International Journal of Hydrogen Energy*, Volume 25, Issue 1, 2000, Pages 31-45.

[25] M. A. Goula, S. K. Kontou, and P. E. Tsikalas. Hydrogen production by ethanol steam reforming over a commercial Pd/γ-Al₂O₃ catalyst. *Applied Catalysis B:Environmental*, Volume 49, Issue 2, 2004, Pages 135-144.

[26] D. K. Liguras, D. I. Kondarides, and X. E. Verykios. Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. *Applied Catalysis B:Environmental*, Volume 43, Issue 4, 2003, Pages 345-354.

[27] F. Frusteri, S. Freni, V. Chiodo, L. Spadaro, O. Di Blasi, G. Bonura, and S. Cavallaro. Steam reforming of bio-ethanol on alkali-doped Ni/MgO catalysts: hydrogen production for MC fuel cell. *Applied Catalysis A: General*, Volume 270, Issues 1-2, 2004, Pages 1-7.

[28] D. Li, X. Li, and J. Gong. Catalytic reforming of oxygenates: State of the art and future prospects. *Chemical Reviews*, Volume 116, Issue 19, 2016, Pages 11529-11653.

[29] W. Wang and Y. Q. Wang. Thermodynamic analysis of steam reforming of ethanol for hydrogen generation. *International Journal of Energy Research*, Volume 32, Issue 15, 2008, Pages 1432-1443.

[30] T. Hou, S. Zhang, Y. Chen, D. Wang, and W. Cai. Hydrogen production from ethanol reforming: Catalysts and reaction mechanism. *Renewable and Sustainable Energy Reviews*, Volume 44, 2015, Pages 132-148.

[31] C. Choong, Z. Zhong, L. Huang, A. Borgna, L. Hong, L. Chen, and J. Lin. Infrared evidence of a formate-intermediate mechanism over ca-modified supports in low-temperature ethanol steam reforming. *ACS Catalysis*, Volume 4, Issue 7, 2014, Pages 2359-2363.

[32] Z. Ferencz, A. Erdohelyi, K. Baan, A. Oszko, L. Ovary, Z. Konya, C. Papp, H.-P. Steinruck, and J. Kiss. Effects of support and Rh additive on Co-based catalysts in the ethanol steam reforming reaction. *ACS Catalysis*, Volume 4, Issue 4, 2014, Pages 1205-1218.

[33] J. Zhang, Z. Zhong, X.-M. Cao, P. Hu, M. B. Sullivan, and L. Chen. Ethanol steam reforming on Rh catalysts: theoretical and experimental understanding. *ACS Catalysis*, Volume 4, Issue 2, 2014, Pages 448-456.

[34] G. Zeng, Q. Liu, R. Gu, L. Zhang, and Y. Li. Synergy effect of MgO and ZnO in a Ni/Mg-Zn-Al catalyst during ethanol steam reforming for H₂-rich gas production. *Catalysis Today*, Volume 178, Issue 1, 2011, Pages 206-213.

[35] J. P. Breen, R. Burch, and H. M. Coleman. Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications. *Applied Catalysis B: Environmental*, Volume 39, Issue 1, 2002, Pages 65-74.

[36] O. Gorke, P. Pfeifer, and K. Schubert. Kinetic study of ethanol reforming in a microreactor. *Applied Catalysis A: General*, Volume 360, Issue 2, 2009, Pages 232-241.

[37] S. Li and J. Gong. Strategies for improving the performance and stability of Ni-based catalysts for reforming reactions. *Chemical Society Reviews*, Volume 43, Issue 21, 2014, Pages 7245-7256.

[38] J. Sehested, J. A. P. Gelten, and S. Helvæg. Sintering of nickel catalysts: Effects of time, atmosphere, temperature, nickel-carrier interactions, and dopants. *Applied Catalysis A: General*, Volume 309, Issue 2, 2006, Pages 237-246.

[39] K. O. Christensen, D. Chen, R. Ledeng, and A. Holmen. Effect of supports and Ni crystal size on carbon formation and sintering during steam methane reforming. *Applied Catalysis A: General*, Volume 314, Issue 1, 2006, Pages 9-22.

[40] J. Sun and Y. Wang. Recent Advances in catalytic conversion of ethanol to chemicals. *ACS Catalysis*, Volume 4, Issue 4, 2014, Pages 1078-1090.

[41] F. Aupretre, C. Descorme, and D. Duprez. Bio-ethanol catalytic steam reforming over supported metal catalysts. *Catalysis Communications*, Volume 3, Issue 6, 2002, Pages 263-267.

[42] C. Descorme, Y. Madier, D. Duprez, and T. Bircham. Surface mobility of oxygen species on mixed-oxides supported metals. *Studies in Surface Science and Catalysis*, Volume 130, 2000, Pages 347-352.
[43] C. J. Jiang, D. L. Trimm, M. S. Wainwright, and N. W. Cant. Kinetic study of steam reforming of methanol over copper-based catalysts. *Applied Catalysis A: General*, Volume 93, Issue 2, 1993, Pages 245-255.

[44] F. Joensen and J. R. Rostrup-Nielsen. Conversion of hydrocarbons and alcohols for fuel cells. *Journal of Power Sources*, Volume 105, Issue 2, 2002, Pages 195-201.

[45] J. Comas, F. Marino, M. Laborde, and N. Amadeo. Bio-ethanol steam reforming on Ni/Al$_2$O$_3$ catalyst. *Chemical Engineering Journal*, Volume 98, Issues 1-2, 2004, Pages 61-68.

[46] D. L. Trimm. Catalysts for the control of coking during steam reforming. *Catalysis Today*, Volume 49, Issues 1-3, 1999, Pages 3-10.

[47] T. Ioannides and S. Neophytides. Efficiency of a solid polymer fuel cell operating on ethanol. *Journal of Power Sources*, Volume 91, Issue 2, 2000, Pages 150-156.

[48] V. Fierro, O. Akdim, and C. Mirodatos. On-board hydrogen production in a hybrid electric vehicle by bio-ethanol oxidative steam reforming over Ni and noble metal based catalysts. *Green Chemistry*, Volume 5, Issue 1, 2003, Pages 20-24.

[49] L. V. Mattos and F. B. Noronha. Hydrogen production for fuel cell applications by ethanol partial oxidation on Pt/CeO$_2$ catalysts: the effect of the reaction conditions and reaction mechanism. *Catalysis Today*, Volume 233, Issue 2, 2005, Pages 453-463.

[50] N. Laosiripojana, S. Assabumrungrat, and S. Charojrochkul. Steam reforming of ethanol with co-fed oxygen and hydrogen over Ni on high surface area ceria support. *Applied Catalysis A: General*, Volume 327, Issue 2, 2007, Pages 180-188.

[51] P. R. de la Piscina and N. Homs. Use of biofuels to produce hydrogen (reformation processes). *Chemical Society Reviews*, Volume 37, Issue 11, 2008, Pages 2459-2467.

[52] J. Xuan, M. K. H. Leung, D. Y. C. Leung, and M. Ni. A review of biomass-derived fuel processors for fuel cell systems. *Renewable and Sustainable Energy Reviews*, Volume 13, Issues 6-7, 2009, Pages 1301-1313.

[53] F. Frusteri and S. Freni. Bio-ethanol, a suitable fuel to produce hydrogen for a molten carbonate fuel cell. *Journal of Power Sources*, Volume 173, Issue 1, 2007, Pages 200-209.

[54] R. M. Navarro, M. A. Peña, and J. L. G. Fierro. Hydrogen production reactions from carbon feedstocks: Fossil fuels and biomass. *Chemical Reviews*, Volume 107, Issue 10, 2007, Pages 3952-3991.

[55] V. Mas, R. Kipreos, N. Amadeo, and M. Laborde. Thermodynamic analysis of ethanol/water system with the stoichiometric method. *International Journal of Hydrogen Energy*, Volume 31, Issue 1, 2006, Pages 21-28.

[56] G. Rabenstein and V. Hacker. Hydrogen for fuel cells from ethanol by steam-reforming, partial-oxidation and combined auto-thermal reforming: A thermodynamic analysis. *Journal of Power Sources*, Volume 185, Issue 2, 2008, Pages 1293-1304.

[57] M. Compagnoni, A. Tripodi, and I. Rossetti. Parametric study and kinetic testing for ethanol steam reforming. *Applied Catalysis B: Environmental*, Volume 203, 2017, Pages 899-909.

[58] S. Turczyniak, M. Greluk, G. Słowiński, W. Gac, S. Zafeiratos, and A. Machocki. Surface state and catalytic performance of ceria-supported cobalt catalysts in the steam reforming of ethanol. *ChemCatChem*, Volume 9, Issue 5, 2017, Pages 782-797.