

# Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production

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## Abstract

New catalysts for hydrogen production by steam reforming of bio-ethanol have been developed. Catalytic tests have been performed at laboratory scale, with the reaction conditions demanded in a real processor: i.e. ethanol and water feed, without a diluent gas. Catalyst ICP0503 has shown high activity and good resistance to carbon deposition. Reaction results show total conversion, high selectivity to hydrogen (70%), CO<sub>2</sub>, CO and CH<sub>4</sub> being the only by-products obtained. The reaction yields 4.25 mol of hydrogen by mol of ethanol fed, close to the thermodynamic equilibrium prediction. The temperature influence on the catalytic activity for this catalyst has been studied. Conversion reaches 100% at temperature higher than 600 °C. In the light of reaction results obtained, a reaction mechanism for ethanol steam reforming is proposed. Long-term reaction experiments have been performed in order to study the stability of the catalytic activity. The excellent stability of the catalyst ICP0503 indicates that the reformed stream could be fed directly to a high temperature fuel cell (MCFC, SOFC) without a further purification treatment. These facts suggest that ICP0503 is a good candidate to be implemented in a bio-ethanol processor for hydrogen production to feed a fuel cell.

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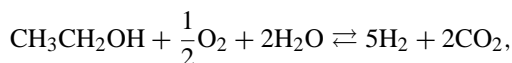
**Keywords:** Bio-ethanol; Steam reforming; Fuel processor; Fuel cell; Hydrogen

## 1. Introduction

Nowadays 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 [1,2]. In comparison with other fuels, 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. In addition, this alcohol can be distributed in a logistic net similar to the conventional gas stations. From this standpoint, ethanol steam reforming is one of the best alternatives to obtain hydrogen. Ethanol can be obtained from biomass by fermentation processes, and the ethanol obtained in this way is named bio-ethanol. Vegetables consume the carbon dioxide produced from the use of ethanol as a fuel; therefore the carbon cycle is closed and these car-

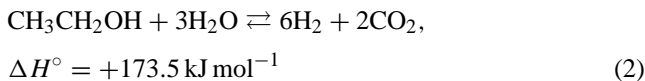
bon dioxide emissions are not considered that contribute to the global warming.

Thermodynamic studies have shown the feasibility of hydrogen production from ethanol steam reforming for fuel cell applications [3–5]. There are several alternatives to carry out the reforming process: auto-thermal reforming, Eq. (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, Eq. (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.



$$\Delta H^\circ = -50.3 \text{ kJ mol}^{-1} \quad (1)$$

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Ethanol steam reforming is a very complex reaction where many reaction pathways are possible [3–16]. Some of them are favoured depending on the catalyst used [8–13,17–21]. 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 [4–9]. These studies demonstrate that the catalyst must operate at high *S/C* ratios to avoid the carbon deposition problems previously mentioned. For high *S/C* ratios the autonomy of the final application, for example, an on-board processor or mobile appliance is limited due to the lower amount of ethanol that it is possible to store.

Experimental catalytic studies reported in literature have been performed to investigate the effect of the reaction temperature on the conversion and selectivity toward the main products and by-products obtained. Studies at different temperatures have allowed optimising the experimental conditions in order to maximize hydrogen yield, to limit by-product formation and to propose a reaction scheme [4–11,13].

The behaviour of the catalysts versus time has been studied [7–8,20–21]. This type of experiment is indispensable to study the catalyst resistance to deactivation prior to its implementation in a final appliance. Deactivation phenomena are the main reason for the lack of commercial catalysts for this reaction.

In the present study, three catalysts prepared in our laboratory have been tested in operation conditions similar to conditions presented in a fuel processor to hydrogen production. Several active phases and promoters have been selected in order to study the reaction pathways of bio-ethanol reforming. Catalyst characterization will be the aim of further papers. The influence of reaction temperature, space velocity on catalytic activity and selectivity has been studied. On the basis of the products distribution obtained at different space velocities, a reaction scheme is proposed. The knowledge of the reaction mechanism will be very important to design a catalyst resistant to carbon poisoning that can be applied to produce high hydrogen purity to achieve the requirements demanded in a PEMFC.

## 2. Experimental

A micro-activity reactor designed and built at the Institute of Catalysis and Petro-chemistry was used to perform the catalytic activity measures. This equipment is implemented

with a software for data acquisition and control: temperature, pressure and mass flows for gases and liquids. This acquisition system allows obtaining detailed information of the catalytic process since all reaction parameters are measured and controlled in real time. The reactor used to perform reaction experiments is a 3/8 inch tubular reactor made of AISI-316 stainless steel, where the catalyst sample constitutes a fixed bed. The reaction temperature is measured by a K-type thermocouple and controlled by a PID temperature controller. To follow the reaction operation, gas chromatography was the analytical technique used. The chromatograph used is an Agilent 6890 equipped with FID and TCD detectors connected in line with the chemical reactor. To separate different compounds a molecular sieve 5 Å and a Porapak Q packed column were used. To identify possible reaction by-products, reaction effluent was analysed with a gas chromatograph with a mass spectrometer detector (Agilent 5973).

Three catalysts with different active phases (Ni, Cu and Co) supported on zirconia labelled as ICP3004, ICP2307 and ICP0503, respectively, have been prepared and tested in the ethanol steam reforming. The catalysts and the catalytic process have been patented [22]. The experimental reaction conditions were atmospheric pressure and gas hourly space velocities (GHSV) 76,000 h<sup>-1</sup>. An ethanol–water solution with a ratio *S/C* = 4.84 without diluents was fed to the reactor, in the same operation conditions that a real processor. Reaction tests at different temperatures (500–700 °C) have been performed.

The influence of space velocity on the product distribution has been studied. Reaction experiments have been carried out at different GHSV from 50,000 to 300,000 h<sup>-1</sup>, at the same *S/C* ratio (4.85) and 700 °C.

In order to study the resistance to catalyst deactivation, endurance tests up to 60 h have been performed.

Ethanol conversion denoted as  $X_{\text{EtOH}}$  and product selectivity denoted as  $S_i$ , are calculated according to Eqs. (3)–(4):

$$X_{\text{EtOH}} = \frac{\text{moles EtOH}_{\text{in}} - \text{moles EtOH}_{\text{out}}}{\text{moles EtOH}_{\text{in}}} \times 100 \quad (3)$$

$$S_i = \frac{\text{moles } P_i}{\sum_{i=1}^n \text{moles } P_i} \quad (4)$$

## 3. Results and discussion

### 3.1. Catalytic tests

Catalytic performance tests have been conducted for three different catalysts in the same reaction conditions, *S/C* = 4.84 and GHSV = 76,000 h<sup>-1</sup>. The reaction temperature inside the catalytic bed was fixed at 700 °C. The ethanol conversion for ICP3004 and ICP0503 catalysts was 100% while for the catalyst ICP2307 decreased to 30% after 10 h under reaction conditions (Fig. 1). In Fig. 2 is represented the molar ratio H<sub>2</sub>/EtOH yielded in the reactor. This parameter gives information of the reaction efficiency; the stoichiometric value

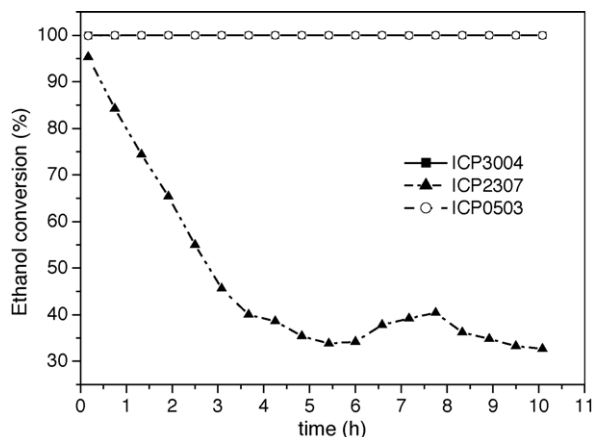


Fig. 1. Ethanol conversion for the catalysts ICP3004, ICP2307 and ICP0503.

for reaction steam reforming is 6 and the thermodynamic prediction is 5.4 at 700 °C and  $S/C=4.84$ . The molar ratio  $H_2/EtOH$  increased versus time for the catalysts ICP3004 and ICP0503. This fact suggests that catalyst activity increased to reach the steady state. On the other hand, this parameter decreases sharply for ICP2307 after 2 h in the reaction mixture, in close correlation with its deactivation. Fig. 3 represents hydrogen selectivity versus time for the catalysts studied. While ICP3004 and ICP0503 increase the selectivity to hydrogen with time, to reach values close to 70%, ICP2307 decreases its hydrogen selectivity to 40%. The catalysts ICP3004 and ICP0503 have different performances versus time. The selectivity to CO for ICP3004 (Fig. 4) decreases and selectivity to CO<sub>2</sub> increases versus time. This fact indicates a higher contribution of the water gas shift reaction. In comparison with ICP3004, ICP0503 shows constant selectivity values (Fig. 5). It is noteworthy that there is no evidence of by-products.

Carbon dioxide, carbon monoxide and methane are present in the ICP0503 product distribution. This fact indi-

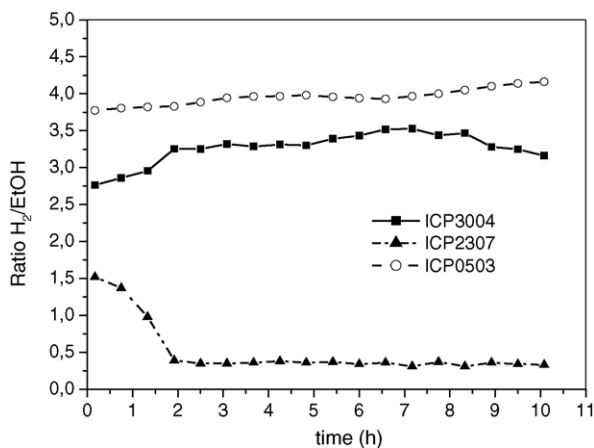


Fig. 2. Hydrogen/ethanol ratio for the catalysts ICP3004, ICP2307 and ICP0503.

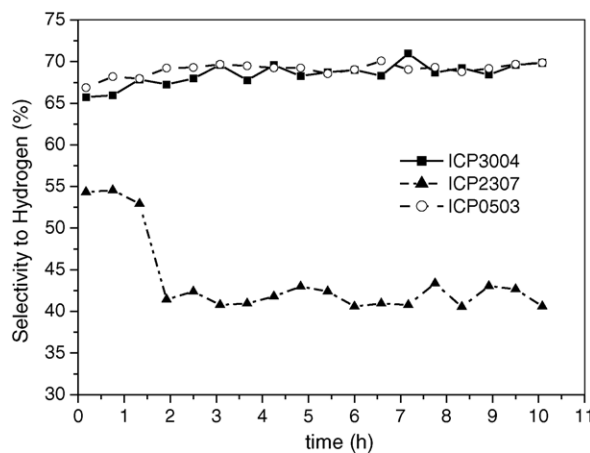


Fig. 3. Hydrogen selectivity for the catalysts ICP3004, ICP2307 and ICP0503.

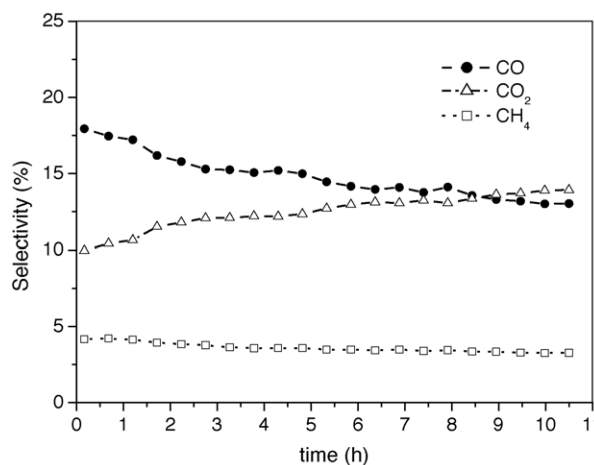


Fig. 4. Selectivity toward by-products and reaction intermediates for ICP3004 catalyst.

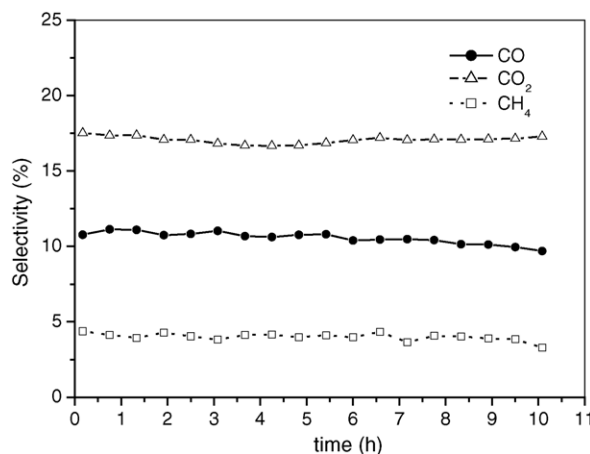


Fig. 5. Selectivity toward by-products and reaction intermediates for ICP0503 catalyst.

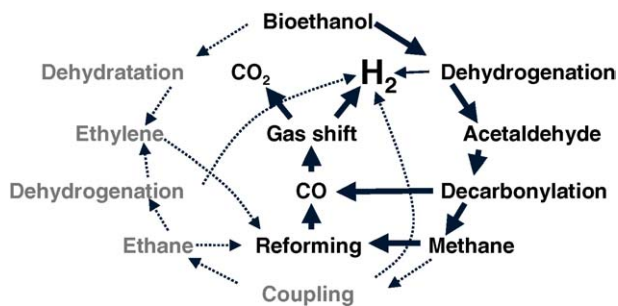
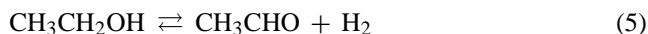


Fig. 6. Reaction scheme proposed.

states that cobalt favours dehydrogenation reactions (Fig. 6). Ethanol dehydrogenation yields hydrogen and acetaldehyde, Eq. (5). Acetaldehyde decomposition leads to methane and carbon monoxide, Eq. (6). Methane is reformed with steam in the next reaction step to obtain hydrogen and carbon monoxide, Eq. (7). The last reaction step in this proposed mechanism is the water gas shift reaction, Eq. (8), that produces hydrogen and carbon dioxide.



The selectivity towards different products obtained for the catalyst ICP2307 is represented in Fig. 7. It is observed that carbon monoxide, carbon dioxide, methane, acetaldehyde, ethylene and acetone are present. At the beginning of the catalytic test, copper favours the ethanol dehydration that leads to ethylene production, Eq. (9). Ethylene is decomposed easily to carbon, Eq. (10), and is deposited on the active phase, poisoning the catalyst.

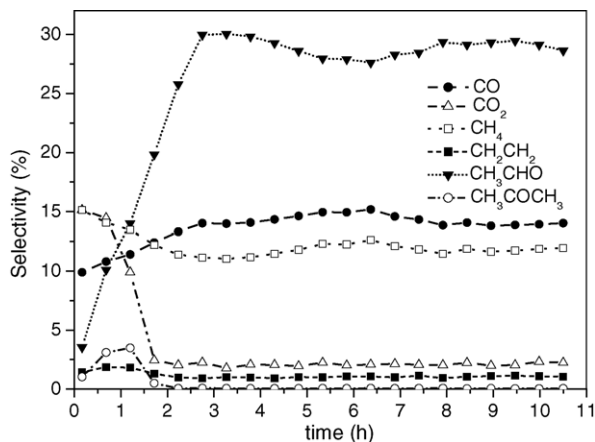
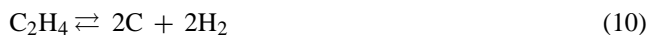
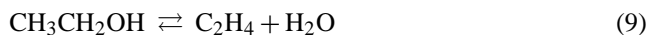


Fig. 7. Selectivity toward by-products and reaction intermediates for ICP2307 catalyst.

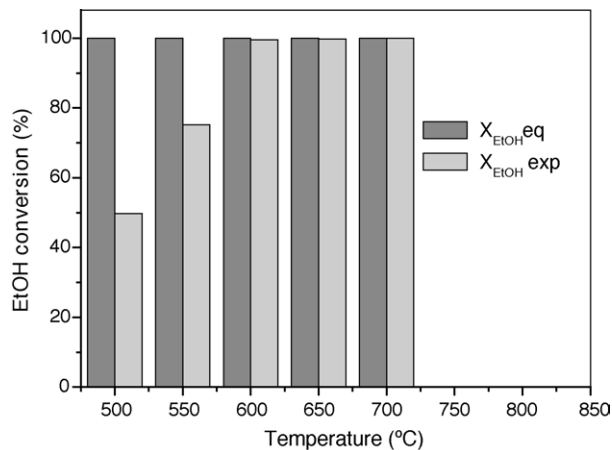


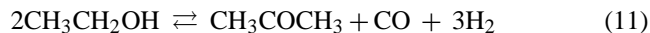
Fig. 8. Effect of reaction temperature on the ethanol conversion for ICP0503 catalyst vs. the thermodynamic equilibrium.

The presence of by-products in the product distribution explains the low selectivity to hydrogen obtained for the catalyst ICP2307 (Fig. 3).

### 3.2. Effect of temperature on conversion and selectivity

To study the influence of reaction temperature, the catalyst ICP0503 was tested from 500 to 700 °C in 50 °C steps. Fig. 8 shows the evolution of the experimental ethanol conversion for the catalyst ICP0503 compared with the thermodynamic equilibrium values. It is observed that ethanol conversion increases when reaction temperature is increased to reach 100% at 600 °C, the value predicted by thermodynamic equilibrium for the temperature range tested. The hydrogen selectivity on a dry basis, reaches a maximum (70%) at 650 °C. It is noteworthy that in the temperature range studied the selectivity to H<sub>2</sub>, CO<sub>2</sub> and CO are very close to the equilibrium predictions (Fig. 9). At lower temperatures, the results obtained are far from equilibrium, this can be explained by the presence of by-products (Fig. 10), such as ethylene, acetaldehyde and acetone. This Figure shows the selectivity on a dry basis to different by-products versus temperature for the catalyst ICP0503.

Thermodynamic equilibrium predicts methane as the only product in the temperature range tested. The temperature increase produces an important drop in acetaldehyde selectivity till its disappearance at 650 °C. At lower temperatures, the catalyst activity is too low to promote decomposition reaction of acetaldehyde. The effect of temperature increase is similar for ethylene and acetone selectivity. Acetone is obtained by the decomposition of ethanol, Eq. (11), a reaction favoured when the catalyst works at lower temperatures.



Methane selectivity remained constant and reached a minimum at 650 °C (Fig. 9). The presence of CH<sub>4</sub> in reaction products diminishes the hydrogen yield.

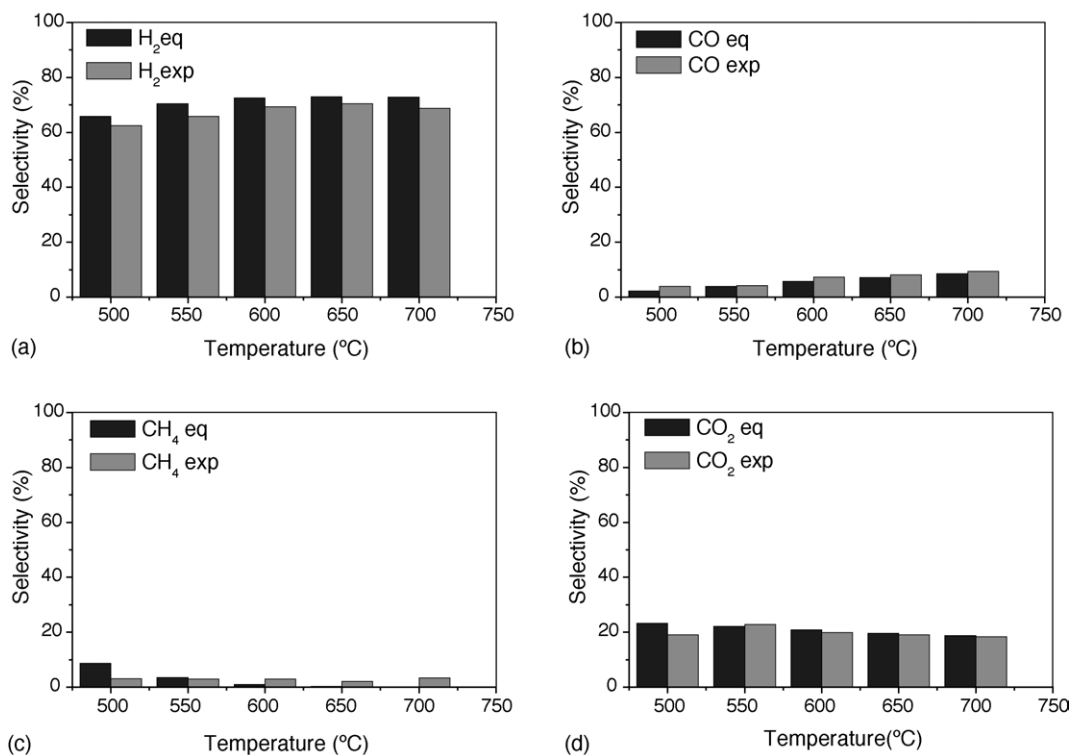


Fig. 9. Effect of reaction temperature on the product selectivity for ICP0503 catalyst vs. the thermodynamic equilibrium.

Fig. 11 shows the evolution of the H<sub>2</sub>/CO and CO<sub>2</sub>/CO ratios with temperature. The cobalt favours the dehydrogenation reaction. From the reaction scheme proposed, in the steam reforming process four consecutive reactions take part. In the temperature range tested, the effluent gas composition was controlled by methane steam reforming Eq. (7) and water gas shift Eq. (8). This fact explains the H<sub>2</sub>/CO and CO<sub>2</sub>/CO ratio decrease with the temperature raise. The temperature increase produces a lower contribution of the water gas shift

reaction, which provokes a decrease in the CO<sub>2</sub>/CO ratio. The reason for the lower contribution of the gas shift reaction is because this reaction is thermodynamically disfavoured at high temperature.

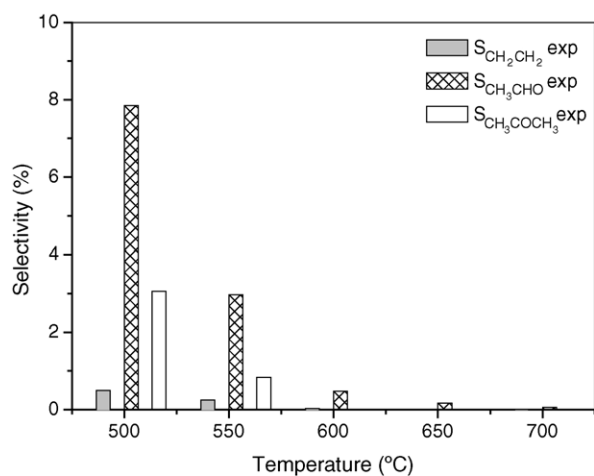


Fig. 10. Effect of reaction temperature on the selectivity toward by-products for ICP0503 catalyst vs. the thermodynamic equilibrium.

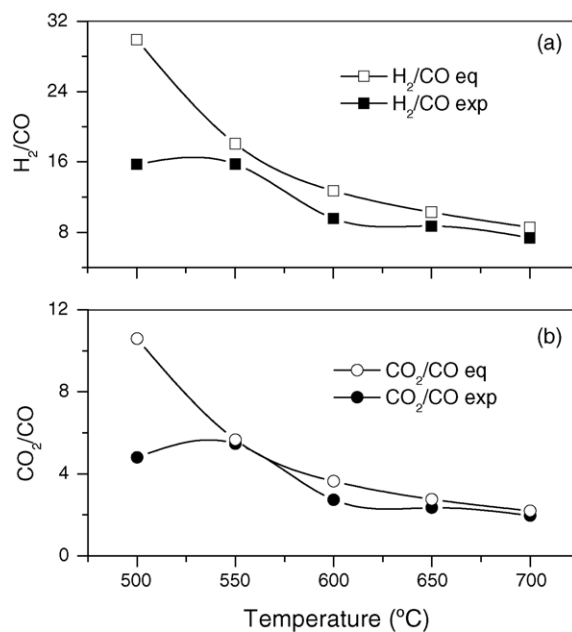


Fig. 11. Effect of reaction temperature on the molar ratios vs. the thermodynamic equilibrium: (a) H<sub>2</sub>/CO and (b) CO<sub>2</sub>/CO, for ICP0503 catalyst.



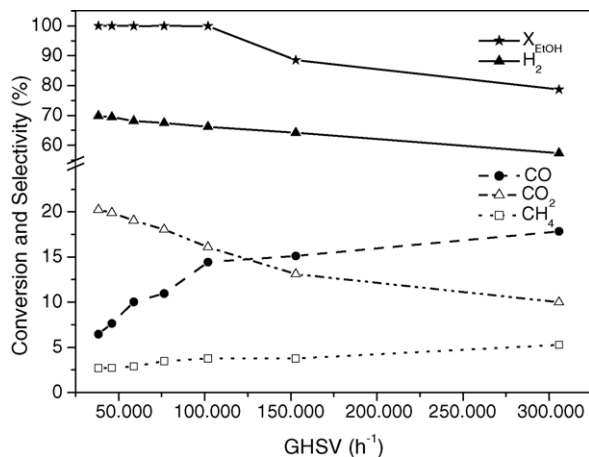


Fig. 12. Effect of GHSV on the ethanol conversion and selectivity toward products for ICP0503.

### 3.3. Influence of space velocity

In Figs. 12 and 13 are represented, for the catalyst ICP0503, the evolution of ethanol conversion, main products, and by-products with space velocity, respectively. It is possible to observe that by increasing space velocity diminishes the ethanol conversion and the selectivity toward H<sub>2</sub> and CO<sub>2</sub>, while the selectivity to CH<sub>4</sub> and CO increases (Fig. 12). By increasing space velocity a selectivity enhancement is produced toward acetaldehyde while the selectivity to ethylene remains constant (Fig. 13). The results obtained for by-products confirm that the reaction mechanism proceeds via ethanol dehydrogenation (Fig. 6) to obtain acetaldehyde on account of the selectivity increase toward ethylene (dehydration product) is negligible (Fig. 13). This fact suggests that acetaldehyde is an intermediate product in the reaction pathway. At lower space velocities, acetaldehyde is transformed by a decarbonylation reaction to CH<sub>4</sub>. A higher space ve-

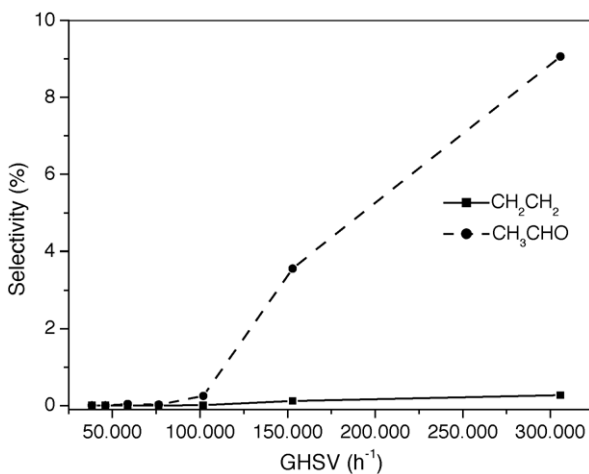


Fig. 13. Effect of GHSV on the selectivity toward by-products and reaction intermediates for ICP0503.

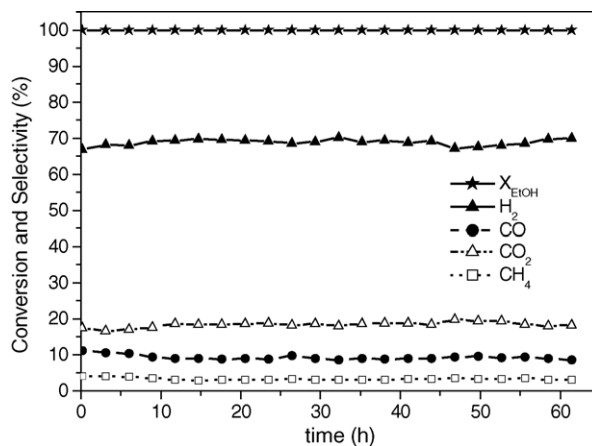


Fig. 14. Long-term stability test of the ICP0503 catalyst: conversion of ethanol and selectivity toward products.

locity makes difficult the CH<sub>4</sub> reforming while the water gas shift reaction is not favoured at high temperatures. These facts explain the increase of selectivity toward CO and CH<sub>4</sub>.

### 3.4. Long-term stability test

In order to study the ICP0503 catalyst behaviour, a long-term reaction test was performed (Fig. 14). It is noteworthy the stability of reaction products after 60 h in reaction conditions at 700 °C. Ethanol conversion remains constant at 100% and the selectivity obtained to different products is very close to thermodynamic equilibrium calculations. The selectivity to hydrogen was very high, close to 70%, even increasing smoothly with time. Carbon dioxide shows a selectivity of 20% and the selectivity to carbon monoxide and methane were 9 and 3%, respectively, showing a process shift to the final products. Conversion and selectivity to different products remains constant versus time, and do not show deactivation signs. These results and the absence of ethylene at high space velocities confirm that the catalyst design has solved the known problems associated with the carbon deposition on the active phase.

## 4. Conclusions

Three catalysts have been synthesized and tested for ethanol steam reforming. Among them ICP3004 and ICP0503 are very active, with 100% ethanol conversion and high selectivity to hydrogen (70%) at 700 °C. In particular, catalyst ICP0503, working in the temperature range 650–700 °C, shows excellent stability after 60 h in operation conditions, CO and CH<sub>4</sub> being the only by-products and hydrogen production close to that predicted by thermodynamic equilibrium.

In the light of space velocity experiments a reaction scheme is proposed where ethanol steam reforming proceeds via a dehydrogenation reaction to obtain acetaldehyde which

is decomposed to produce carbon monoxide and methane. The water gas shift reaction and methane steam reforming control the products distribution in the temperature range studied.

It is noteworthy that the stream obtained by steam reforming with catalyst ICP0503 could be fed directly to a high temperature fuel cell (MCFC, SOFC), without previous treatment. To feed a low temperature fuel cell (PEMFC), a further CO purification treatment (WGS-COPROX, PSA) is necessary in order to decrease the CO concentration to level lower than 50 ppm demanded in a PEMFC.

The present study demonstrates that the process to obtain hydrogen from bio-ethanol is technically feasible and opens an opportunity to the use of a renewable energy source for hydrogen production, a remarkable fact for fuel cell development and implantation.

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