

# Ethanol oxidative steam reforming over Ni-based catalysts

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## Abstract

Oxidative steam reforming of ethanol for hydrogen production in order to feed a solid polymer fuel cell (SPFC) has been studied over several catalysts at on board conditions (a molar ratio of H<sub>2</sub>O/EtOH and of O<sub>2</sub>/EtOH equal to 1.6 and 0.68 respectively) and a reforming temperature between 923 and 1073 K. Two Ni (11 and 20 wt.)/Al<sub>2</sub>O<sub>3</sub> catalysts and five bimetallic catalysts, all of them supported on Al<sub>2</sub>O<sub>3</sub>, were tested. The bimetallic catalysts were Ni (approximately 20 wt.%) based catalysts doped with Cr (0.65 wt.%), Fe (0.6 wt.%), Zn (0.7 wt.%) or Cu (0.6 and 3.1 wt.%). The results in terms of H<sub>2</sub> production and CO<sub>2</sub>/CO<sub>x</sub> ratio obtained over Ni-based catalysts supported on Al<sub>2</sub>O<sub>3</sub> are compared with those obtained over Ni–Cu/SiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts reported in our previous works. Tendencies of the product selectivities are analyzed in the light of the reaction network proposed.

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## 1. Introduction

Fuel cells (FC) have the potential to replace the internal combustion engine in vehicles and provide power in stationary and portable power applications because they are energy-efficient, clean, and fuel-flexible. A significant barrier to using these FC in vehicles is hydrogen storage.

Chemical storage of hydrogen in liquid fuels is considered to be one of the most advantageous options for supplying hydrogen to the fuel cells. A variety of liquid fuels, such as alcohols and hydrocarbons are suitable for this purpose. Fuels containing hydrogen generally require a “fuel reformer” that extracts the hydrogen from any hydrocarbon fuel. Hydrogen sources include fossil fuels as methanol, ethanol, natural gas, petroleum distillates, liquid propane and gasified coal and even gas from landfills and wastewater treatment plants.

Methanol steam reforming (SR) has been thoroughly studied in recent years, since methanol is available as an abundant

feedstock and already largely distributed. However, the main drawback of methanol, beside its relatively high toxicity, is that its production is essentially based on reforming of non-renewable fossil fuels (mostly natural gas), and therefore its use as a feedstock for electrical vehicle will release fossil carbon into the atmosphere. Ethanol appears as an attractive alternative to methanol since it is much less toxic, offers a high octane number, a high heat of vaporization and a low photochemical reactivity. Moreover, bio-ethanol can be produced in large quantities from biomass fermentation, therefore as a renewable energy source. This alcohol has also a significant advantage over fossil-fuel based systems: it is CO<sub>2</sub> neutral, since the carbon dioxide that is produced in the process is consumed by biomass growth and a closed carbon cycle is operated.

Polymer electrolyte membrane fuel cells (PEMFC) are particularly suitable for use in passenger vehicles, such as cars and buses due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio. However, PEMFC use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst that

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is extremely sensitive to CO poisoning, limited to 100 ppm [1]. If the hydrogen is derived from an alcohol or hydrocarbon fuel the working catalyst is required to be both very efficient for abstracting hydrogen atoms from the carbon-containing reactant and oxidize the carbon atoms to CO<sub>2</sub> as much as possible. However, the CO content at the reactor outlet makes necessary other processes to reduce the CO concentration within the tolerance limit of the Pt anode catalyst. These processes are high temperature water gas shift (HTS-WGS), low temperature water gas shift (LTS-WGS) reactions, and/or selective oxidation (SELOX). Consequently, the ratio CO<sub>2</sub>/CO<sub>x</sub> at the reformer outlet, CO<sub>x</sub> defined as CO<sub>2</sub> + CO, must be high enough to limit the importance (weight and volume) of the WGS and SELOX steps downstream.

Supported group VIII metals are good catalysts for ethanol SR [2–5]. One serious problem, though, is the catalyst deactivation due to carbon deposition, especially for Ni-based catalysts. Although noble metals suffer less coking than nickel the high cost of noble metals renders their application. Therefore, development of Ni catalysts with little or no coking deactivation and with a high CO<sub>2</sub>/CO<sub>x</sub> ratio at the reformer outlet, is of great interest to automotive application.

This paper presents the oxidative steam reforming of ethanol for hydrogen production in order to feed an SPFC at on-board conditions. The objective of this study was to screen a wide range of commercial and prepared Ni-based catalysts in order to find those that simultaneously offer an increase in the selectivity to hydrogen and in the ratio CO<sub>2</sub>/CO<sub>x</sub> at the reactor outlet.

## 2. Experimental

### 2.1. Catalyst

The active materials selected for ethanol SR were two commercial Ni-based catalysts (11 and 20 wt.%) and five bimetallic catalysts all of them supported on Al<sub>2</sub>O<sub>3</sub>. These bimetallic catalysts were also Ni-based (approximately 20 wt.%) and doped with Cr (0.65 wt.%), Fe (0.6 wt.%), Zn (0.7 wt.%) or Cu (0.6 and 3.1 wt.%). Metals were added by impregnation of the support with an aqueous solution containing the corresponding nitrates as precursors under stirring at room temperature followed by drying (393 K), calcination at 923 K for 15 h and sieving to 0.2–0.3 mm. BET surface area was determined by N<sub>2</sub> adsorption at 77 K using a Micromeritics ASAP2010 apparatus.

### 2.2. Catalytic tests

Prior to catalytic testing, the catalyst was placed in a fixed bed reactor and reduced under flowing hydrogen (30 ml min<sup>-1</sup>) at 923 K for 8 h with a heating rate of 2 K min<sup>-1</sup>. After reduction the catalyst was cooled down to reaction temperature under helium atmosphere. The runs were performed under on-board conditions with helium in-

stead of nitrogen at atmospheric pressure in a fixed bed reactor (ID = 4 mm and  $H_{\text{bed}} = 7$  mm) where 50 mg of the catalyst are introduced. Catalyst was dispersed with SiC to minimize hot spot effects.

Two parallel reactors and a system of valves allow pre-treating a catalyst while a second one is being tested. There are two lines of gases to the reactors providing an ethanol/water/air-like (79% He and 21% O<sub>2</sub>) mixture from a gaseous He/O<sub>2</sub> mixture and a liquid water/ethanol (H<sub>2</sub>O/EtOH) blend or a gas flow to pre-treat the catalyst with H<sub>2</sub>. The H<sub>2</sub>O/EtOH blend is regulated by an HPLC pump, the liquid is vaporized at 403 K and then mixed with the gas flow before being fed to the fixed bed reactor or being sent to analysis before reaction. Gases are analyzed on line by mass spectrometry and by gas chromatography. Wet gases are analyzed by means of a Hewlett Packard gas chromatograph model 6890, equipped with a TCD detector and an HP-PlotQ column that analyses CO<sub>2</sub>, CO, CH<sub>4</sub> and other hydrocarbons as C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>O as well as ethanol and H<sub>2</sub>O. Helium was used as internal standard and the variation of its concentration measured by gas spectrometry allows the evaluation of the volume correction factor and of the ethanol conversion and selectivities to the reaction products.

Based in our previous works [4,6], the experimental conditions involve a molar ratio of H<sub>2</sub>O/EtOH equal to 1.6, a molar ratio of O<sub>2</sub>/EtOH equal to 0.68 and a contact time close to 0.2 min kg mol<sup>-1</sup> and temperatures from 923 to 1073 K.

### 2.3. Parameter formulae

Since this work was carried out at on-board conditions a volume correction factor (CF) that takes into account the volume change as a result of reactions was considered to calculate conversions and selectivities.

$$\text{CF} = \frac{\text{He}_{\text{in}}}{\text{He}_{\text{out}}} = \frac{V_{\text{out}}}{V_{\text{in}}} \quad (1)$$

where He<sub>in</sub> and He<sub>out</sub> are the helium concentration at the inlet and at the outlet of the reactor respectively. The reactants conversion (ethanol, water or oxygen), denoted  $X_{\text{reactant}}$  is calculated according to Eq. (2) where  $F_{i,\text{in}}$  and  $F_{i,\text{out}}$  represents the molar flow rate of the  $i$  species measured at the inlet and at the outlet of the reactor respectively.

$$X_{\text{reactant}} = \frac{[F_{\text{reactant}}]_{\text{in}} - [F_{\text{reactant}}]_{\text{out}} \text{CF}}{[F_{\text{reactant}}]_{\text{in}}} \quad (2)$$

and selectivities to carbon-containing products ( $C_n$ ) are calculated by the following equation:

$$S_{C_n} = \frac{[F_{C_n}]_{\text{out}} \text{CF}}{n[[F_{\text{EtOH}}]_{\text{in}} - [F_{\text{EtOH}}]_{\text{out}} \text{CF}]} \quad (3)$$

where  $n$  is the number of atoms of carbon in the product ( $n = 1$  for CO, CO<sub>2</sub> and CH<sub>4</sub> and  $n = 2$  for C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>CHO).

Selectivity towards hydrogen is calculated taking into account the variation of ethanol and water concentrations.

$$S_{\text{H}_2} = \frac{[F_{\text{H}_2}]_{\text{out}} \text{CF}}{3[[F_{\text{EtOH}}]_{\text{in}} - [F_{\text{EtOH}}]_{\text{out}} \text{CF}] - [[F_{\text{H}_2\text{O}}]_{\text{in}} - [F_{\text{H}_2\text{O}}]_{\text{out}} \text{CF}]}$$

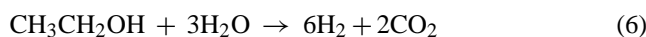
The contact time ( $t_c$ ) is defined as the ratio between the mass of catalyst and the molar flow of the inlet ethanol. Though contact time is usually defined as the ratio between the mass of catalyst and the total inlet flow rate, the present definition focuses on the ethanol contact time for a direct evaluation of the link between the active sites concentration and the number of ethanol moles to convert.

$$t_c = \frac{m_{\text{cata}} \text{ (kg)}}{\text{EtOH} \text{ (mol min}^{-1}\text{)}} \quad (5)$$

#### 2.4. Calculations at thermodynamic equilibrium

Product selectivities were calculated at thermodynamic equilibrium. The results vary in practical situations, nevertheless these calculations provide a valuable indication of the starting point for experimental research.

Despite the apparent simplicity of the stoichiometry of the reaction for maximum hydrogen production,



no exact knowledge of the reactions involved in the oxidative steam reforming of ethanol exists. We have solved this system by minimization of the Gibbs free energy. The operating parameters used were the following: (a) temperature (298–1073 K), (b) H<sub>2</sub>O/ethanol (1.6), and O<sub>2</sub>/ethanol (0.68) molar feed ratios and (c) pressure (1 atm).

### 3. Results and discussion

#### 3.1. Product selectivities and conversions at thermodynamic equilibrium

Fig. 1 shows the product selectivities calculated at equilibrium for comparison with the experimental ones. The temperature has a significant effect on the equilibrium con-

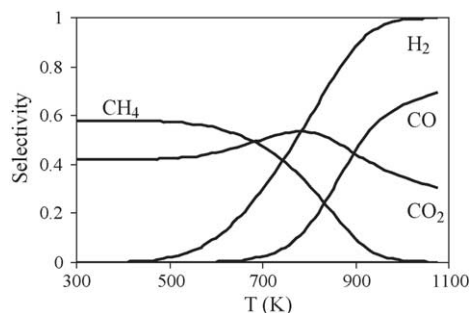


Fig. 1. Effect of reactor temperature on equilibrium selectivities to the reaction products for the oxidative steam reforming of ethanol (O<sub>2</sub>/EtOH = 0.68 and H<sub>2</sub>O/EtOH = 1.6; pressure, 1 atm).

centrations of the products. Ethanol and O<sub>2</sub> are converted completely over the whole temperature range. As the reac-

$$(4)$$

tion temperature increases the selectivity to H<sub>2</sub> increases and reaches a maximum equal to 1 from 1023 K on, which coincides with the total disappearance of methane. CO<sub>2</sub> selectivity is almost constant up to 573 K, has a maximum at around 773 K and decreases steadily at higher temperatures. Methane selectivity decreases with temperature while CO increases. There is no selectivity towards C<sub>2</sub> products since they are not stable thermodynamically.

#### 3.2. Homogeneous reactions

Homogeneous reactions are very important when studying the oxidative steam reforming of ethanol and special attention must be paid to reduce the dead volume to avoid them. Fig. 2 shows the selectivity of ethanol conversion in absence of catalyst at temperatures from 723 to 1073 K, with an H<sub>2</sub>O/EtOH molar ratio of 1.6 and a O<sub>2</sub>/EtOH molar ratio of 0.68. Ethanol decomposes at temperatures higher than 723 K reaching a conversion of 95% at 973 K with a total oxygen conversion from 823 K. The selectivity to the reaction products is nearly constant at temperatures higher than 773 K. There is a high selectivity to CO (≈50%) and the selectivity to hydrogen remains very low (≈30%) due to the high reaction selectivities to hydrogenated products as methane, ethane and ethylene and the production of water by the combustion of ethanol. The selectivity to C<sub>2</sub>H<sub>4</sub> (≈18%) is also rather important, ethylene acts as a very strong promoter of carbon formation and an important quantity of ethanol is converted to coke.

#### 3.3. Product selectivities and conversions at heterogeneous conditions

A wide range of catalysts were tested, changing the Ni content (11 and 20%), the metal added (0.6% Cu, 0.65% Cr, 0.7% Zn and 0.6% Fe) and the percentage of Cu (0.6

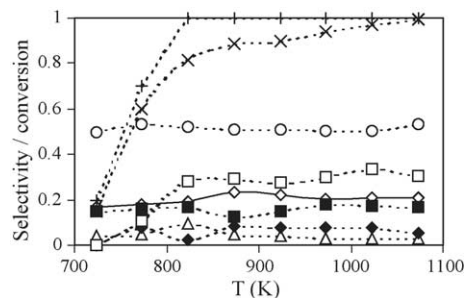


Fig. 2. Conversion of ethanol and oxygen and product selectivity of ethanol reforming reaction vs. temperature at homogenous conditions: (+) O<sub>2</sub>, (x) EtOH, (□) H<sub>2</sub>, (○) CO, (△) CO<sub>2</sub>, (◇) CH<sub>4</sub>, (■) C<sub>2</sub>H<sub>4</sub>, (◆) C<sub>2</sub>H<sub>6</sub> (O<sub>2</sub>/EtOH = 0.68, H<sub>2</sub>O/EtOH = 1.6 and flow rate = 80 cm<sup>3</sup> min<sup>-1</sup>).

and 3.1%). The results obtained in this work, in terms of H<sub>2</sub> selectivity and CO<sub>2</sub>/CO<sub>x</sub>, are compared with those obtained over Ni–Cu/SiO<sub>2</sub> and 5%Rh/Al<sub>2</sub>O<sub>3</sub> in previous works. BET surface area of the 11 and 20% Ni commercial catalysts were 85 and 77 m<sup>2</sup> g<sup>-1</sup>, respectively. BET surface areas of bimetallic catalyst were found equal to 179, 200, 162, 188 and 223 m<sup>2</sup> g<sup>-1</sup> for Ni<sub>19.4</sub>Cu<sub>0.6</sub>Al, Ni<sub>20.4</sub>Cu<sub>3.1</sub>Al, Ni<sub>19.2</sub>Cr<sub>0.65</sub>Al, Ni<sub>20.1</sub>Zn<sub>0.7</sub>Al, Ni<sub>19.6</sub>Fe<sub>0.6</sub>Al, respectively.

### 3.3.1. Ni/Al catalysts

Ethanol reforming over two Ni-based catalysts, 11 and 20 wt.%, supported on Al<sub>2</sub>O<sub>3</sub> was studied on-board conditions optimised in previous works [4–6]. Ethanol was completely converted over the whole studied temperature range for the two catalysts while the water conversion increased with temperature. Results in terms of product selectivities for the two catalysts are shown in Fig. 3. Fig. 3(a) shows the effect of temperature on selectivities to H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> and Fig. 3(b) shows selectivities to C<sub>2</sub> compounds: C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>O. The product selectivities shown by the catalysts are very different depending on the Ni content.

For 20% Ni catalyst, selectivities to H<sub>2</sub> and CO increased while selectivities to CH<sub>4</sub> and CO<sub>2</sub> decreased with increasing temperature. No production of C<sub>2</sub> compounds was detected over the studied temperature range.

The high production of CO, CH<sub>4</sub> and H<sub>2</sub> at 923 K suggests the ethanol decomposition by

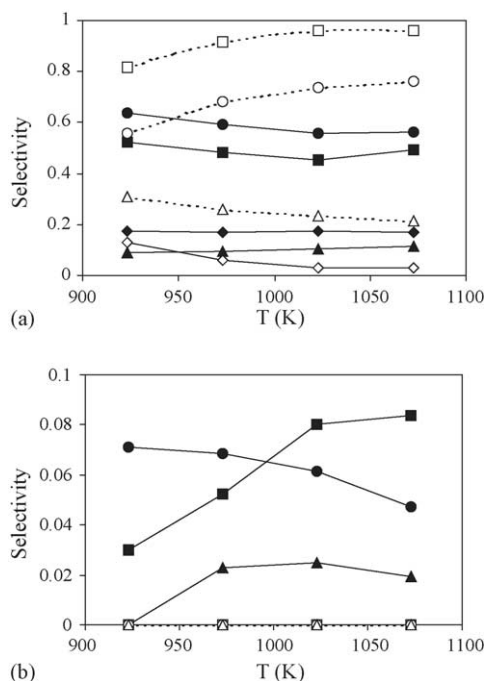
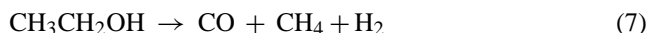
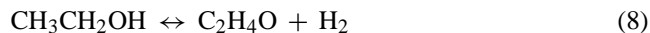
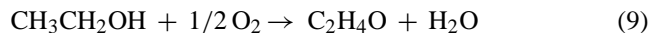


Fig. 3. Product selectivities of oxidative ethanol reforming over 11% Ni (full symbols) and 20% Ni (open symbols) to the reaction products vs. temperature: (a) (■) H<sub>2</sub>, (●) CO, (▲) CO<sub>2</sub>, (◆) CH<sub>4</sub>; (b) (■) C<sub>2</sub>H<sub>4</sub>, (●) C<sub>2</sub>H<sub>6</sub>, (▲) C<sub>2</sub>H<sub>4</sub>O (experimental conditions as in Fig. 2).

or the dehydrogenation of ethanol with concomitant adsorption to give acetaldehyde and hydrogen



as we worked in presence of oxygen it could be also possible



and fast decomposition of acetaldehyde according to



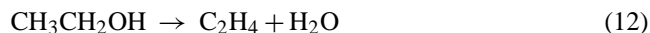
and the higher selectivity to CO compared to methane at 923 K is explained by the SR of methane



The decrease observed in the CH<sub>4</sub> and CO<sub>2</sub> selectivity trends when temperature increases is explained by the thermodynamic equilibria of the SR of methane and by the reverse WGS respectively.

The evolution of the product selectivities with temperature is within experimental errors close to those correspondents to the thermodynamic equilibrium. The lower selectivities to H<sub>2</sub> and CO<sub>2</sub> and higher selectivities to CH<sub>4</sub> and CO indicate that methane SR and WGS have not reached the equilibrium.

Opposite to 20% Ni catalyst, ethanol decomposition over 11% Ni catalysts proceeds also with the formation of ethylene, ethane and acetaldehyde. The 11% Ni catalyst showed a very low selectivity to H<sub>2</sub>, about 50%, due to the selectivity to C<sub>2</sub> products. CO selectivity followed a parallel evolution to H<sub>2</sub> selectivity with a constant decrease from 923 to 1023 K and a slight increase at 1073 K while CH<sub>4</sub> was almost constant over the whole temperature range. Formation of C<sub>2</sub> products are then responsible for the decrease in the selectivity of CO and H<sub>2</sub> at temperatures from 923 to 1023 K. Ethylene is one of the most troublesome byproducts of ethanol SR and partial oxidation since it can deactivate the catalyst by carbon deposition. It is well known that ethanol is dehydrated by the acid sites of the alumina producing ethylene (Eq. (12)), [7] that decomposes to form carbon deposits [8].

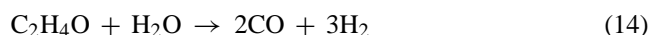


Ethane is most probably, the product of ethylene hydrogenation, which is confirmed by the lower H<sub>2</sub> selectivity compared to CO selectivity,

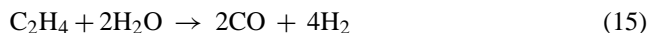


while acetaldehyde is the product of ethanol dehydrogenation (Eq. (8)) or reaction with O<sub>2</sub> (Eq. (9)).

Nickel would favor the ethanol adsorption as acetaldehyde and afterwards the acetaldehyde SR. The selectivity to acetaldehyde is always smaller than 0.025 and a maximum can be observed that could be explained by the existence of two competitive reactions: adsorption or reaction with O<sub>2</sub> and decomposition (Eqs. (8)–(10)) and SR of acetaldehyde,



The change in the tendency of H<sub>2</sub> and CO selectivity at 1073 K is probably originated from acetaldehyde decomposition (Eq. (10)) and acetaldehyde, ethane and ethylene SR.



Although the selectivity to C<sub>2</sub> products decreased with temperature, we found an almost constant selectivity to methane that can be explained by the existence of methanation reactions, according to



Ni/Al<sub>2</sub>O<sub>3</sub> is an effective catalyst for the methanation of CO. Otsuka and coworkers [9] studied the removal of CO by methanation in H<sub>2</sub>-rich gas stream over different metal catalysts. The conversion of CO over a Ni/Al<sub>2</sub>O<sub>3</sub> was of 7.9% at 523 K and increased up to 46.2% at 573 K.

CO<sub>2</sub> increased with temperature from 923 to 1073 K, which could be explained by WGS. Some controversy exists on the viability of WGS on Ni catalysts during SR of ethanol. Duprez and coworkers [10,11] and more recently Laborde and coworkers [12] affirmed that WGS does not take place on Ni catalyst. Although the production of CO<sub>2</sub> is less favorable when increasing temperature the high amount of CO produced by C<sub>2</sub> SR at 1073 K would result in an increase of the selectivity to CO<sub>2</sub>. In fact, the CO and CO<sub>2</sub> concentrations are closer to those correspondents to the thermodynamic equilibrium.

Similar results to those reported in this work were found with increasing metal content in Co based catalysts [13]. Ethylene formation occurred only on the Co/Al<sub>2</sub>O<sub>3</sub> catalyst with small Co contents (≤8%) and no with higher contents (18%). Likewise, pure nickel causes bond breaking of ethanol in the order O–H > –CH<sub>2</sub> > C–C > –CH<sub>3</sub> [14,15], increasing quantities of Ni in the catalyst would privilege the dehydration route to acetaldehyde and the WGS reactions. We think that the less Ni charged catalyst has stronger acidic sites available, from Al<sub>2</sub>O<sub>3</sub>, and so the contribution of the carrier would be predominant and would privilege the dehydration route. These conclusions agree well with the reaction network of ethanol SR over Ni-based catalysts recently proposed by Fatsikostas and Verykios [16] who concluded that Al<sub>2</sub>O<sub>3</sub> promotes dehydration and cracking and the presence of Ni promotes SR of ethanol and acetaldehyde as well as the WGS and methanation reactions.

### 3.3.2. Bimetallic Ni-based catalysts

Once observed that ethanol reforming over a 20% Ni-based catalyst produced high selectivities to H<sub>2</sub> with no production of C<sub>2</sub> compounds, we tested four Ni-based catalysts doped with approximately 0.7% of Cr, Fe, Zn or Cu and supported on Al<sub>2</sub>O<sub>3</sub>. Our aim was to add little quantities on metals, that are well known to promote WGS

[17,18], in order to increase the CO<sub>2</sub>/CO<sub>x</sub> ratio at the reactor outlet.

Fig. 4 shows conversion to ethanol (Fig. 4(a)) and selectivities to H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub>, ethylene, ethane, and acetaldehyde (Fig. 4(b)–(h) respectively) for the four bimetallic catalyst tested in this work. As it is shown in Fig. 4(a), the ethanol conversion is complete over all the whole temperature range for catalysts with Cu and Fe additions while over Ni–Zn and Cr–Ni catalysts the ethanol conversion is not complete up to 1023 and 1073 K respectively. Fig. 4(b)–(h) shows two tendencies of the product selectivities over the temperature range. On the one hand, ethanol reforming over catalyst containing Cu resulted in high and parallel selectivities to H<sub>2</sub> and CO, low selectivities to CH<sub>4</sub>, that decreased as temperature increased up to 1023 K, and no selectivity to C<sub>2</sub> compounds. On the other hand, Ni–Cr, Ni–Fe and Ni–Zn showed low selectivities to H<sub>2</sub> at 923 K, of 0.40, 0.44 and 0.55 for Cr, Fe and Zn respectively, that increased almost linearly with temperature up to 0.98 at 1073 K for the three catalysts.

The Ni–Cu catalyst showed higher selectivities to H<sub>2</sub> than the 20% Ni catalyst over the whole temperature range but especially at 923 K, 0.82 and 0.93 for 20% Ni and Ni–Cu catalyst respectively. The lower H<sub>2</sub> selectivity was due to the lower SR of CH<sub>4</sub> because C<sub>2</sub> products were not produced over 20% Ni catalyst as seen above. Therefore, the alloy Ni–Cu seems to favor the SR of methane produced by ethanol decomposition. At present there is a number of works devoted to the studies of Ni–Cu alloy catalysts for several reactions [19] and more specifically for SR of methane [20] and ethanol [4]. In those works, Cu plays a significant role in decreasing the rate of carbon formation. Based on this study, Cu seems also to promote the SR of methane.

The low selectivities to H<sub>2</sub> exhibited by Ni–Cr, Ni–Fe and Ni–Zn catalysts at 923 K are a consequence of the very high selectivities to C<sub>2</sub> products but also to methane, if they are compared with Ni–Cu selectivities. At 923 K, the SR reactions (Eqs. (10), (13)–(15)) and the decomposition of acetaldehyde (Eq. (9)) are slow, and so acetaldehyde, ethylene and ethane, produced by Eqs. (8), (11) and (12) respectively, are present at the reactor outlet. The Ni–Cr, Ni–Fe and Ni–Zn catalysts exhibited lower selectivities to methane and C<sub>2</sub> products and higher selectivities to CO and H<sub>2</sub> as reforming temperature increased. This tendency was due to the increase in the reaction rates of the acetaldehyde decomposition and the SR of methane and C<sub>2</sub> products. CO<sub>2</sub> increased with temperature from 923 to 1073 K. As seen above, the high amount of CO produced by hydrocarbon SR increases the selectivity to CO<sub>2</sub> by WGS even if this reaction is less favorable when increasing temperature. At 1073 K, the selectivities to H<sub>2</sub> and CO<sub>2</sub> the reaction products over Ni–Cr, Ni–Fe and Ni–Zn catalysts are higher than those over Ni–Cu catalyst. No C<sub>2</sub> production was detected and the selectivity to methane was lower than over the Ni–Cu catalyst.

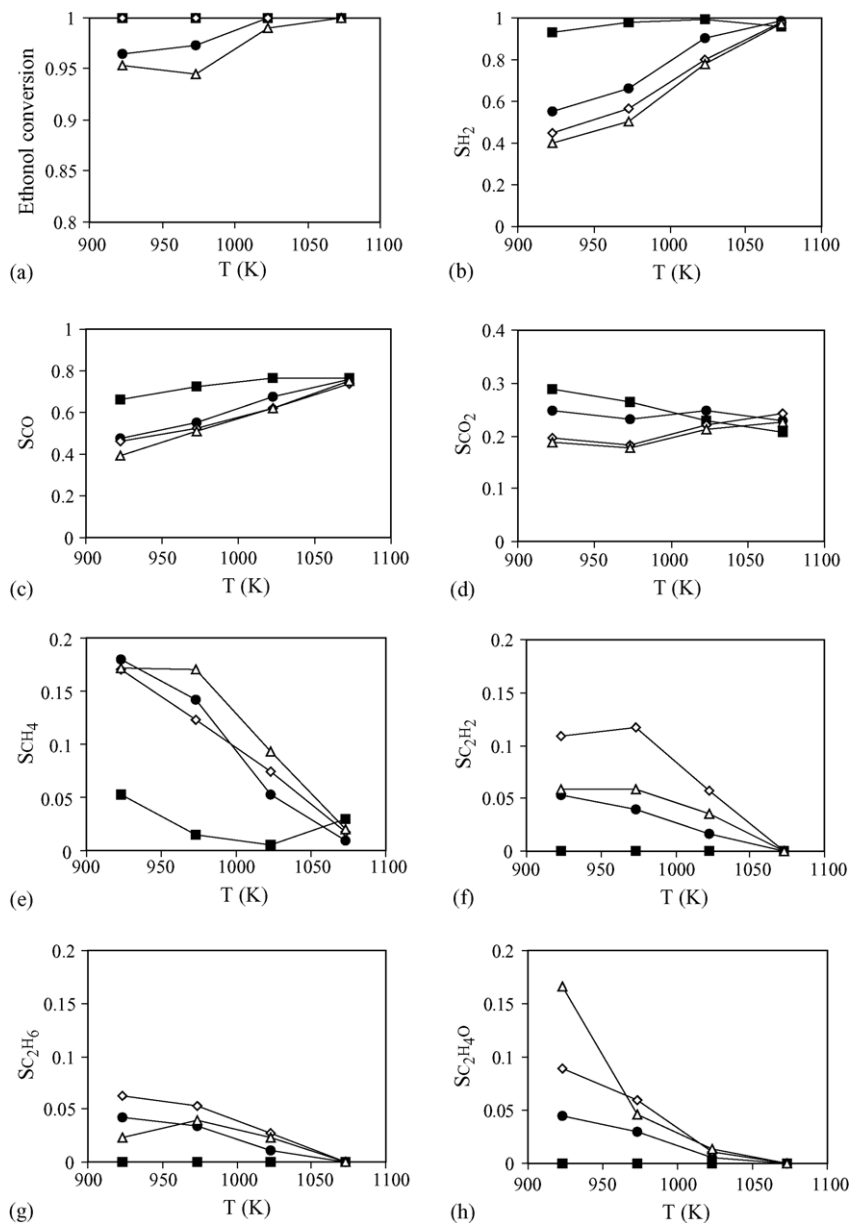


Fig. 4. Ethanol conversion (a) and product selectivities of oxidative ethanol reforming to  $H_2$ , CO,  $CO_2$ ,  $CH_4$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $C_2H_4O$  ((b)–(h) respectively) over the bimetallic Ni-based catalysts [(■)  $Ni_{19.4}Cu_{0.6}Al$ , ( $\Delta$ )  $Ni_{19.2}Cr_{0.65}Al$ , (●)  $Ni_{20.1}Zn_{0.7}Al$ , ( $\diamond$ )  $Ni_{19.6}Fe_{0.6}Al$ ; experimental conditions as in Fig. 2].

There are some references in the literature about the effect of the addition of Cr, Fe and Co to Ni-based catalyst supported on  $Al_2O_3$  for the SR of hydrocarbons [21–24]. The addition of the second metal to Ni seems to have a beneficial effect in the stability of the catalysis, inhibits the encapsulation of Ni catalyst or reduces coking. For example, Ni–Cr/ $Al_2O_3$  catalysts were used in the SR of naphthalene at 1073 K [21]. It appears that nickel was active in aromatic ring opening, while chromium inhibited the encapsulation of the nickel crystallites by inactive carbon filaments. We have not studied the beneficial effect of the addition of Cr, Fe and Co to Ni inhibiting coke formation. However, we can conclude that these three catalysts were only interesting for the oxidative steam reforming of ethanol at 1073 K.

### 3.3.3. Increase of Cu content in Ni–Cu/ $Al_2O_3$ catalysts

Rostrup-Nielsen and co-workers [25] stated that small amounts of Cu alloying in Ni–Cu/ $SiO_2$  catalysts promotes while larger amounts ( $Cu:Ni \geq 10\%$ ) inhibits carbon formation and changes the morphology of the filaments. Above, we have shown that the addition of 0.6% increased  $H_2$  selectivity by encouraging SR of methane and, based on literature, probably with a concomitant reduction of coke deposition.

In order to study the effect of adding larger amounts of Cu to Ni/ $Al_2O_3$  catalysts, we prepared a catalyst with a higher Cu content (3%) and an approximate Ni content (20%). Results in terms of product selectivities for the two catalysts are shown in Fig. 5. Fig. 5(a) shows the effect of temperature on selectivities to  $H_2$ , CO,  $CO_2$  and  $CH_4$  and

Table 1

H<sub>2</sub> production (l kg<sup>-1</sup> catalyst min<sup>-1</sup>) by oxidative steam reforming of ethanol over Ni and noble metals based catalysts (O<sub>2</sub>/EtOH = 0.68, H<sub>2</sub>O/EtOH = 1.6 and flow rate = 80 cm<sup>3</sup> min<sup>-1</sup>)

T (K)	Ni <sub>20</sub> Al	Ni <sub>19.4</sub> Cu <sub>0.6</sub> Al	Ni <sub>19.2</sub> Cr <sub>0.65</sub> Al	Ni <sub>20.1</sub> Zn <sub>0.7</sub> Al	Ni <sub>19.6</sub> Fe <sub>0.6</sub> Al	Ni <sub>20.4</sub> Cu <sub>3.1</sub> Al	Ni <sub>16.7</sub> Cu <sub>2.1</sub> Si	Rh <sub>5</sub> Al
923	0.81	0.86	0.35	0.49	0.37	0.30	0.78	0.90
973	0.95	0.90	0.45	0.61	0.49	0.27	0.88	0.97
1023	0.99	0.91	0.74	0.89	0.76	0.43	0.97	1.03
1073	0.99	0.87	1.00	1.00	1.00	0.87	1.00	1.04

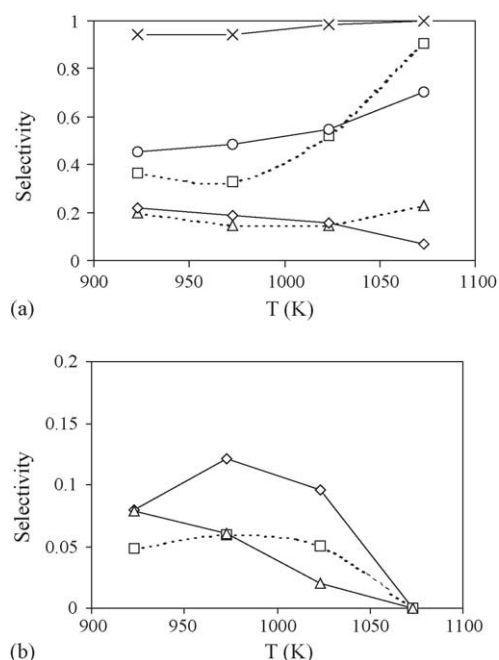


Fig. 5. Ethanol conversion and product selectivities of oxidative ethanol reforming over Ni<sub>19</sub>Cu<sub>3</sub>Al: (a) (x) EtOH, (□) H<sub>2</sub>, (○) CO, (△) CO<sub>2</sub>, (◇) CH<sub>4</sub>; (b) (□) C<sub>2</sub>H<sub>4</sub>, (◇) C<sub>2</sub>H<sub>6</sub>, (△) C<sub>2</sub>H<sub>4</sub>O (experimental conditions as in Fig. 2).

Fig. 5(b) shows selectivities to C<sub>2</sub> products, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>O.

The increase of Cu content up to 3% in the catalyst reduces considerably the good performances to H<sub>2</sub> selectivity of Ni<sub>19.4</sub>Cu<sub>0.6</sub>Al catalyst and has a similar effect to the addition of 0.6% of Cr (see Fig. 4). The ethanol conversion was not complete up to 1073 K and showed low selectivities to H<sub>2</sub> at 973 K, of approximately 0.35%, that increased almost linearly with temperature up to 0.91 at 1073 K. The selectivity to H<sub>2</sub> at 1073 K was the lowest of the bimetallic catalysts tested due to the selectivity to methane.

Table 2

CO<sub>2</sub>/CO<sub>x</sub> ratio at the reactor outlet in oxidative steam reforming of ethanol over Ni, noble metals based catalysts and at the equilibrium (O<sub>2</sub>/EtOH = 0.68, H<sub>2</sub>O/EtOH = 1.6 and flow rate = 80 cm<sup>3</sup> min<sup>-1</sup>)

T (K)	Ni <sub>20</sub> Al	Ni <sub>19.4</sub> Cu <sub>0.6</sub> Al	Ni <sub>19.2</sub> Cr <sub>0.65</sub> Al	Ni <sub>20.1</sub> Zn <sub>0.7</sub> Al	Ni <sub>19.6</sub> Fe <sub>0.6</sub> Al	Ni <sub>20.4</sub> Cu <sub>3.1</sub> Al	Ni <sub>16.7</sub> Cu <sub>2.1</sub> Si	Rh <sub>5</sub> Al	Equilibrium
923	0.36	0.30	0.32	0.34	0.30	0.30	0.44	0.42	0.43
973	0.27	0.27	0.26	0.29	0.26	0.23	0.35	0.32	0.37
1023	0.24	0.23	0.26	0.27	0.26	0.21	0.28	0.27	0.34
1073	0.22	0.21	0.23	0.23	0.25	0.25	0.24	0.25	0.31

Similar results were found for SR of ethanol [26] or more recently during CO<sub>2</sub> reforming of methane [27]. The 1 wt.% Cu addition to the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst enhanced the stability and the activity of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, but CuNi/Al<sub>2</sub>O<sub>3</sub> catalysts added over 5% Cu were deactivated more rapidly. A detailed characterization of these catalysts are necessary to give fundamentals that explain this behavior but it could be due to a lower copper dispersion when increasing copper loading [26] on Ni/Al<sub>2</sub>O<sub>3</sub> catalysts.

Increasing copper content has a very different effect in Ni/Al<sub>2</sub>O<sub>3</sub> or Ni/SiO<sub>2</sub>, Cu:Ni ≤ 10% in Ni–Cu/SiO<sub>2</sub> catalysts promotes while in Ni–Cu/Al<sub>2</sub>O<sub>3</sub> inhibits coke formation.

Therefore, the interaction of the alloy Ni–Cu and the support seems to play an important role in the complex reaction network taking place during the SR of ethanol. The interaction of the metal with the support has been studied during ethanol reforming over Co catalysts on different supports [13,28]. There is no accord on the role played by the catalysts but, as in our work, it is shown that there is a difference on the product selectivity.

### 3.3.4. Comparison of the performances obtained by Ni and the noble metal based catalysts

Tables 1 and 2 show the H<sub>2</sub> production and the CO<sub>2</sub>/CO<sub>x</sub> ratio by oxidative steam reforming of ethanol over different catalysts as a function of temperature. The catalysts selected were the seven Ni/Al<sub>2</sub>O<sub>3</sub> catalysts tested in this work, the Ni–Cu/SiO<sub>2</sub> and the 5% Rh/Al<sub>2</sub>O<sub>3</sub>, chosen between the noble metals studied in a previous work [4] because it presented the best performances.

The objective of this study was to screen a wide range of Ni-based catalysts in order to find those that offer similar performances to noble metal catalysts: high selectivities to hydrogen and high CO<sub>2</sub>/CO<sub>x</sub> ratio at the reactor outlet. The data presented in Tables 1 and 2 show that Rh<sub>0.5</sub>Al is still the best catalyst over the while temperature range. It offers a high H<sub>2</sub> production from 0.91 kg<sup>-1</sup> min<sup>-1</sup> at 923 K to 1.041 kg<sup>-1</sup> min<sup>-1</sup> at 1073 K

and  $\text{CO}_2/\text{CO}_x$  ratios high and close to those found at the thermodynamic equilibrium.  $\text{Ni}_{20}\text{Al}$ ,  $\text{Ni}_{19.4}\text{Cu}_{0.6}\text{Al}$  and  $\text{Ni}_{16.7}\text{Cu}_{2.1}\text{Si}$  also offer high production of  $\text{H}_2$  over the whole temperature range and the performances are in the order  $\text{Ni}_{20}\text{Al} > \text{Ni}_{16.7}\text{Cu}_{2.1}\text{Si} > \text{Ni}_{19.4}\text{Cu}_{0.6}\text{Al}$ . Although catalyst performance is initially reduced by Cu addition, we have shown [4] that it considerably increases the life time of the catalyst for the oxidative steam reforming of ethanol at on-board conditions. Furthermore, copper allows total conversion of ethanol and constant selectivity towards hydrogen.

The rest of the bimetallic catalysts showed a linear tendency in the production of hydrogen with increasing temperature ( $\text{Ni-Zn} > \text{Ni-Fe} > \text{Ni-Cr} > \text{Ni}_{20.4}\text{Cu}_{3.1}$ ) and much lower hydrogen production than the 20%  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst up to 1073 K. At 1073 K, Ni-Zn, Ni-Fe and Ni-Cr catalysts showed a hydrogen production of  $1.01 \text{ kg}^{-1} \text{ min}^{-1}$  close to that produced over 5% Rh catalyst ( $1.04 \text{ kg}^{-1} \text{ min}^{-1}$ ). However, the  $\text{CO}_2/\text{CO}_x$  ratio was somewhat lower except for the Ni-Fe catalyst that reached the same  $\text{CO}_2/\text{CO}_x$  ratio than 5% Rh catalyst.

#### 4. Conclusions

Twenty percentage of Ni-based catalyst supported on  $\text{Al}_2\text{O}_3$  provided very good activity and selectivity for ethanol partial oxidation reaction with high selectivities to  $\text{H}_2$  and good performance over the whole temperature range from 923 to 1073 K. The ethanol decomposition over 11% Ni catalysts proceeded with lower selectivities to hydrogen due to the production of ethylene, ethane and acetaldehyde. Results here reported clearly indicated that Ni promotes SR and WGS reactions while  $\text{Al}_2\text{O}_3$  promotes dehydration.

Taking the 20% Ni catalyst as a reference the addition of 0.6% Cu produced a slight increase in ethanol selectivity to  $\text{H}_2$  at 923 K due to an increase in the SR of methane. The addition of Cr, Zn and Fe produced a decrease of  $\text{H}_2$  production when compared to the reference Ni catalyst at temperatures between 973 and 1023 K. The addition of low quantities of Cr, Zn and Fe to Ni supported on  $\text{Al}_2\text{O}_3$  is useful only at 1073 K and the order in  $\text{H}_2$  production was  $\text{Ni-Zn} > \text{Ni-Fe} > \text{Ni-Cr} > \text{Ni} > \text{Ni-Cu}$  at 1073 K. Moreover, when the addition of Cu increased up to 3.1% the  $\text{H}_2$  production decreased considerably in the temperature range from 923 to 1023 K. The very different results obtained over catalysts supported on  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  with a similar Cu content show that Ni-Cu interaction with the support plays an important role in the reaction network.

Comparing these results with our previous works, the best performances in hydrogen production were obtained over the 5% Rhodium based catalyst followed by the 20% Ni supported on  $\text{Al}_2\text{O}_3$  in the whole temperature range from 923 to 1073 K.

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