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Sustainable Hydrogen Production by Catalytic Bio-Ethanol Steam Reforming

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1. Introduction

Energy is an essential input for social development and economic growth. At present, globally the demand for energy is increasing in consonance with socio-economic development, though in developing countries it increases a little bit more quickly than developed countries. Energy consumption in developed countries grows at a rate of approximately 1% per year, and that of developing countries, 5% per year.

The International Energy Agency estimates that world energy demand will increase by half again between now and 2030, with more than two-thirds of this increase coming from developing and emerging countries. Moreover, global population is predicted to further increase by 2050, and global primary energy consumption is projected to considerably increase during the same time period.

Nowadays, our energy requirements are almost fully provided for carbon containing-fossil sources such as oil, coal and natural gas, which have been formed during many millions of years from plant biomass. According to the recently released 1008 BP Statistical Review of World Energy, the world's total proven oil, natural gas and coal reserves are respectively 169 billion tons, 177 trillion cubic meters and 847 billion tons by the end of 2007. With current consumption trends, the reserves to oil lower than of the world proven reserves of natural gas and coal- 42 years versus 60 and 133 years, respectively.

Known petroleum reserves are limited resources and are estimated to be depleted in less than 50 years at the present rate of consumption. The dramatic increase in the price of petroleum, the finite nature of fossil fuels, increasing concerns regarding environmental impact, especially related to climate change from greenhouse gas emissions, and health and safety considerations are forcing the search for renewable energy sources. (Mustafa Balat & Mehmet Balat, 2009).

Hydrogen has many social, economic and environmental benefits to its credit. It has the long-term potential to reduce the dependence on foreign oil and lower the carbon and criteria emissions from the transportation sector. Only in the last decade the idea of a post-fossil fuel hydrogen-based economy started to gain mainstream interest (Ni et al., 2007).

Hydrogen can be used either as a fuel for direct combustion in an internal combustion engine or as the fuel for a polymer electrolyte membrane (PEM) fuel cell (Kotay & Das, 2008). It can be produced through different methods but the steam reforming of hydrocarbons (mainly natural gas) is the most commonly used.

From an environmental point of view, steam reforming is not a sustainable method for hydrogen production due to the use of fossil fuel-based feedstock and the transformation of almost all the carbon of the hydrocarbons into carbon dioxide. Taking these aspects into considerations, bio-mass derived ethanol is suited to substitute the conventional fossil fuels based on petroleum or natural gas and to perform the ethanol steam reforming (ESR) reaction, that is a fuel well-adapted to the production of hydrogen.

Since the 1970s, Brazil has led the way in developing ethanol as a major fuel source. More recently, the USA has become a major producer of ethanol, with production doubling from 8 billion L yr^{-1} (B L yr^{-1}) in 2002 to 15 B L yr^{-1} in 2005 and increasing further by 25% to 20 B L yr^{-1} in 2006 (Institute for Agriculture and Trade Policy, 2006).

The EU has a similarly ambitious plan. Nowadays, the Italian ethanol production has a lower area of application respect to the European context, in particular in comparison with Spain, Germany, France and Poland. However, the communitarian potentialities of bioethanol are higher than the biodiesel ones (Figure 1) and the predicted trend in the ethanol production will probably lead to a considerably reduction in the production costs.

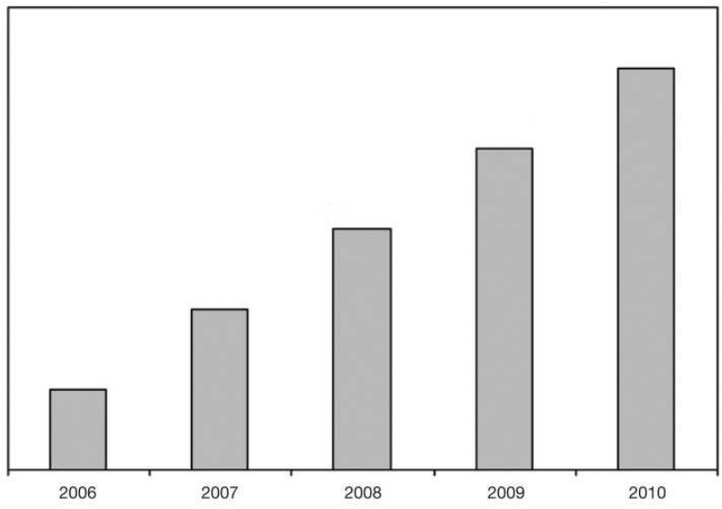


Fig. 1. Trend of ethanol production in application of the 81/06 Law (AssoDistil, Bioetanolo in Italia, BIOFUEL EXPO 2006)

Recently, intensive researches have been devoted to the ESR reaction performed at high temperature. In a catalytic steam reforming process the ethanol is converted in combination with water into a hydrogen rich gas which consist of H_2, CO, CO_2, CH_4 and H_2O. The CO in the reforming product gas will deactivate the anode catalyst of the PEM fuel cell. Therefore a gas cleaning process is necessary: a catalytic high and low temperature water shift reaction (WGS) reduces the CO content of the reforming product gas to about 0.2 vol%. Since this reaction is exothermic, it is favoured at low temperature, then the high temperature-ESR

reaction coupled with the low temperature-WGS reaction whole process could suffer from thermal inefficiencies. When using a low temperature operating range, in order to minimize the CO amount in the outlet gas stream and to reduce the thermal duty, a decrease of the H_2 selectivity and the catalyst deactivation, due to coke formation, are quite unavoidable.

This chapter deals for a great part with the ESR process. For the reformer process, a catalyst screening is carried out. The influence of different parameters on the reforming reaction and catalyst performance is evaluated.

2. Hydrogen production

Hydrogen is the simplest, lightest, most plentiful and most abundant element in the universe. It is colourless, odourless, tasteless and nontoxic gas found in air at concentrations of about 100 ppm (0.01%). It is made up of one proton and one electron revolving around the proton. It has the highest specific energy content per unit weight among the known gaseous conventional fuels (143 GJ ton^{-1}) and is the only carbon-free fuel which ultimately oxidizes to water as a combustion product (some nitrogen oxized are formed at very high combustion temperatures). Therefore burning hydrogen not only has the potential to meet a wide variety of end use applications but also does not contribute to greenhouse emissions, acid rain or ozone depletion. The use of hydrogen will contribute to significant reduction of these energy-linked environmental impacts.

The properties that contribute to hydrogen use as a combustible fuel are reported in Table 1 (Mustafa Balat, 2008).

Characteristic	**Details**
Limits of flammability	Wide range
Ignition energy	Very low (0.02 M)
Detonation limits	Detonable over a wide range of concentrations when confined. Difficult to detonate when unconfined
Ignition temperature	Higher than other fuels
Flame speed	An order of magnitude higher (faster) than that of gasoline
Diffusivity	Very high
Density	Very low

Table 1. Hydrogen properties (Mustafa Balat, 2008)

There are different production technologies, schematically reported in Figure 2.

All methods can, generally, fall into four broad categories (Haryanto et al., 2005):

i. Thermochemical technologies:

they involve thermally assisted chemical reactions that release the hydrogen from hydrocarbons or water. The advantage of the

thermochemical process is that its overall efficiency (thermal to hydrogen) is higher (about 52%) and production cost is lower.

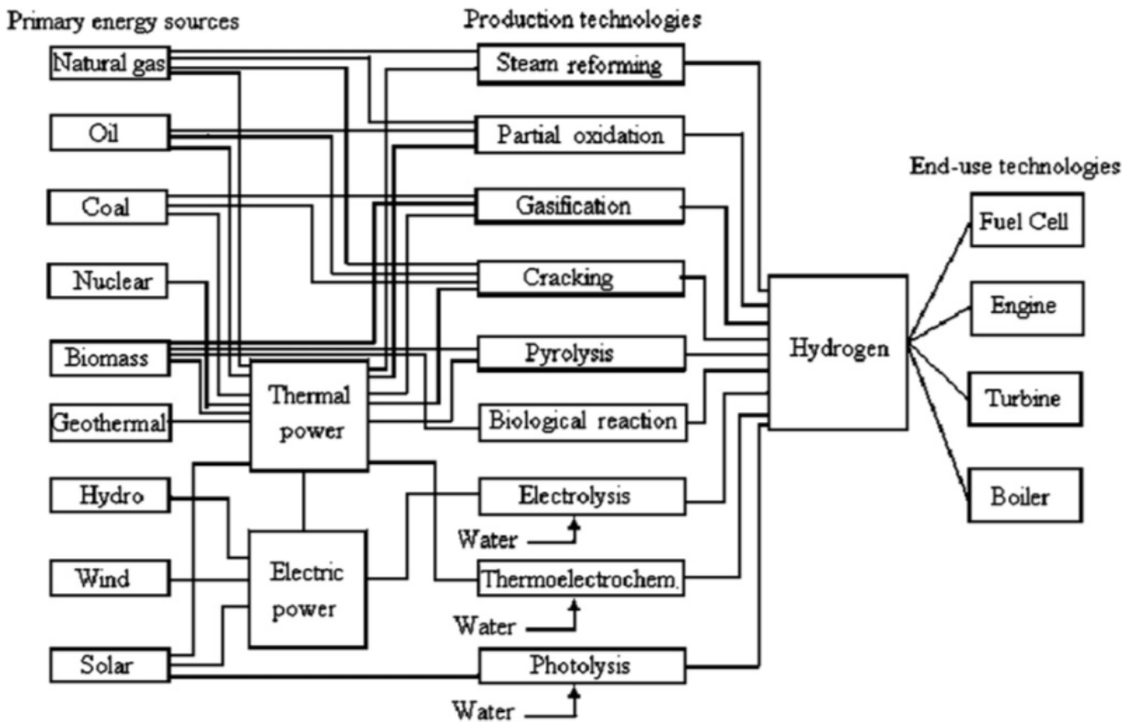


Fig. 2. The main alternative methods of hydrogen production from energy sources (Mustafa Balat et al., 2008)

Thermochemical technologies can be divided into two categories:

a. steam reforming from raw materials such as natural gas (Eq. 1), coal, methanol, ethanol, or even gasoline.

$$CH_4 + 2H_2O = 0.5O_2 \rightarrow CO_2 + 4H_2 \quad (1)$$

b. gasification (Eq 2, carbon gasification), partial oxidation (Eq 3) and pyrolysis from solid or semisolid feedstocks.

$$CH_{1.8} + H_2O = 0.5O_2 \rightarrow CO_2 + 1.9H_2 \quad (2)$$

$$CH_{0.8} + 0.6H_2 + 0.7O_2 \rightarrow CO_2 + H_2 \quad (3)$$

ii. Electrochemical technologies:

by these processes, the hydrogen is produced by electrochemically splitting water molecules into their constituent hydrogen and oxygen through the electrolysis of water (reported in Eq. 4)

$$2H_2O_2 \rightarrow H_2 + O_2 \quad (4)$$

The decomposition of water takes places in a so-called electrolysis cell and consists of two partial reactions that take place at two electrodes. To achieve the desired production capacity, numerous cells are connected in series forming a module: larger systems can be assembled by adding up several modules. It depends on cheap power, which is regionally

dependent on the presence of limited and inexpensive hydroelectric sources of power. This technology would be competitive only if low-cost electricity is available.

iii. Photobiological technologies:

These techniques use natural photosynthetic activity of bacteria and green algae. These processes are still immature and in the experimental stage. There are several types of photobiological processes, mainly:

a. biophotolysis;
b. photofermentation;
c. dark-fermentation.

iv. Photoelectrochemical technologies:

They consist in the production of H_2 in one step, splitting water by illuminating a water-immersed semiconductor with sunlight. They are in the early stage of development; so the pratical applicabilities are unclear. Interest in the production of hydrogen continues unabated because of the additional reason that hydrogen is perceived as the energy of the future. Extensive research is being carried out in many other processes for hydrogen production such as high temperature electrolysis of steam, solar photovoltaic water electrolysis and plasma decomposition of water. At present, approximately 96% of the hydrogen produced coming from fossil fuel-based processes, in particular steam reforming.

3. The steam reforming of hydrocarbons

Reforming separates hydrogen from hydrocarbons by adding heat; the reforming efficiency is obtained through studying of physical-chemical properties of feedstock, thermodynamic conditions (temperature and pressure of reaction, technical configurations of reformer such as dimensions and catalysts), and feedstock and water flows (Mustafa Balat & Mehmet Balat, 2009).

Heavy hydrocarbons are very active and water activation may be the rate determining step in the steam reforming, specially at lower temperatures (400-600°C).

The steam reforming reaction for a generic hydrocarbon is:

$$C_nH_{2n+2} + nH_2O \Leftrightarrow nCO + (2n+1)H_2 \tag{5}$$

For methane, n=1, the above equation becomes:

$$\begin{aligned} &CH_4 + H_2O \Leftrightarrow CO + 3H_2 \\ &\Delta H^0_{298} = +206 KJmol^{-1} \end{aligned} \tag{6}$$

It is typically followed by the water gas shift (WGS) reaction

$$\begin{aligned} &CO + H_2O \Leftrightarrow CO_2 + H_2 \\ &\Delta H^0_{298} = -41 KJmol^{-1} \end{aligned} \tag{7}$$

The methane steam reforming (MSR) reaction is strongly endothermic with an increase of the number of molecules, thus it is favoured at high temperatures and low pressures.

Since methane is a very stable molecule, the steam reforming of natural gas should be carried out at high temperatures (around 800-850°C) and it can be expected that methane activation is a critical step of the reaction. In fact, the critical steps having the highest energy barriers on most metals are CH_4 dissociation and CO formation, but the first effect is predominant, specially at high temperature (Wei & Iglesia, 2004). For all metals used as active species of the catalyst, the reaction is of first-order in CH_4 and virtually of zero order in H_2O and CO_2. Moreover, since the turnover frequency of the steam reforming is very close to that of dry reforming, probably neither H_2O activation nor CO_2 activation intervenes in the rate determining steps of methane conversion (Tavazzi et al., 2006, Donazzi et al., 2008 , Maestri et al., 2008).

However, some undesired C-containing intermediates cannot be excluded even though the formation of these compounds would be strongly dependent on the reaction conditions.

Currently, the steam reforming of natural gas comprises almost 60% of the world feedstock for H_2 production; in the United States, about 96% of H_2 is currently produced through steam reforming. It is clear that natural gas is the most commonly used and generally the most economically competitive method for hydrogen production. Natural gas is a kind of fossil fuel, and its usage fails to provide a solution to deal with the huge amount of carbon dioxide emissions during the reforming processes. In addition the use of fossil fuels for secondary energy production is non-sustainable.

As a result, there is a growing interest in the search for effective alternatives to produce renewable hydrogen cleanly and safety.

Hydrogen can be produced from biorenewable feedstocks via thermo-chemical conversion processes such as pyrolysis, gasification, steam gasification, supercritical water gasification of biomass and steam reforming of bio-fuels. The term biofuel is referred to liquid, gas and solid fuels predominantly produced from biomass. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. Biofuels include bioethanol, biomethanol, vegetable oils, biodiesel, biogas, bio-synthetic gas (bio-syngas), bio-oil, bio-char, Fischer-Tropsch liquids, and biohydrogen.

Most traditional biofuels, such as ethanol from corn, wheat, or sugar beets, and biodiesel from oil seeds, are produced from classic agricultural food crops that require high-quality agricultural land for growth.

The biofuel economy will grow rapidly during the 21st century; in the most biomass-intensive scenario, modernized biomass energy contributes by 2050 about one half of total energy demand in developing countries.

Among the various feedstocks, ethanol is a very attractive for hydrogen production from a renewable source thanks to its following features:

- it has a relatively high hydrogen content;
- it is available,
- it is non-toxic;
- it is easy to carry, storage and handle;
- it can be produced renewably by fermentation of biomass;

- it is a clean fuel;
- it doesn't contain sulphur compounds and heavy metals (Demirbas et al. 2008).

Moreover, in the ESR process, ethanol can be used without necessity of water separation, called in this case bio-ethanol.

4. Ethanol steam reforming

The reaction stoichiometry of the steam reforming of a generic alcohol:

$$C_nH_{2n+1}OH + (n-1)H_2O \rightarrow nCO + 2nH_2 \tag{8}$$

Coupled with the WGS reaction, the reaction leads to carbon dioxide and hydrogen:

$$C_nH_{2n+1}OH + (2n-1)H_2O \rightarrow nCO_2 + 3nH_2 \tag{9}$$

The C_1 compound, that in the hydrocarbons steam reforming is methane, is methanol in this case. It is the most reactive alcohol. It decomposes spontaneously at relatively low temperatures with-out water in the reacting gases (n=1). For this reason, methanol is considered as a "liquid" syngas, much easier to transport than the syngas itself.

Comparing the Gibbs free energy of the steam reforming reaction for n=1 and n=4, it is evident that the steam reforming reaction is more facile on alcohols than on corresponding alkanes.

4.1 Thermodynamic analysis

The thermodynamic aspects of the ethanol steam reforming system have received great attention (Freni et al., 1996; Ioannides, 2001; Benito et al., 2005; Vaidya & Rodriguez, 2006; Fatsikostas & Verykios, 2004; Aupretre et al., 2005, 2004; Garcia & Laborde, 1991; Vasudeva et al., 1996; Fishtik et al., 2000; Mas et al., 2006; Rossi et al., 2009; Rabenstein & Hacker, 2008; Alberton et al., 2007; Ni et al., 2007).

The ethanol-steam mixtures can give rise to numerous reactions, even if the desired one is the Eq. 10 with n=1:

$$\begin{aligned} &C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \\ &\Delta H^0_{298} = +173 kJmol^{-1} \end{aligned} \tag{10}$$

However, the reaction pathway is complex: several secondary reactions could occur, among which the ethanol dehydrogenation to acetaldehyde, the ethanol dehydration to ethylene, the ethanol decomposition to acetone, that are by-products, possible precursors of coke formation.

The main reactions are reported as follows:

1. The steam reforming leading to CO and H_2:

$$\begin{aligned} &C_2H_5OH + H_2O \Leftrightarrow 2CO + 4H_2 \\ &\Delta H^0_{298} = +255 kJmol^{-1} \end{aligned} \tag{11}$$

2. The hydrogenolysis to methane

$$C_2H_5OH + 2H_2 \Leftrightarrow 2CH_4 + H_2O$$
$$\Delta H_{298}^0 = -157 kJmol^{-1} \quad (12)$$

3. The ethanol dehydration to ethylene

$$C_2H_5OH \Leftrightarrow C_2H_4 + H_2O$$
$$\Delta H_{298}^0 = +45 kJmol^{-1} \quad (13)$$

4. The dehydrogenation to acetaldehyde

$$C_2H_5OH \Leftrightarrow C_2H_4O + H_2$$
$$\Delta H_{298}^0 = +68 kJmol^{-1} \quad (14)$$

5. The cracking to methane, CO and H_2

$$C_2H_5OH \Leftrightarrow CO + CH_4 + H_2$$
$$\Delta H_{298}^0 = +49 kJmol^{-1} \quad (15)$$

6. The cracking to methane and CO_2

$$C_2H_5OH \Leftrightarrow \frac{1}{2}CO + \frac{3}{2}CH_4$$
$$\Delta H_{298}^0 = -74 kJmol^{-1} \quad (16)$$

7. The cracking to carbon, CO and H_2

$$C_2H_5OH \Leftrightarrow C + CO + 3H_2$$
$$\Delta H_{298}^0 = +124 kJmol^{-1} \quad (17)$$

8. The cracking to carbon, water and H_2

$$C_2H_5OH \Leftrightarrow 2C + H_2O + 2H_2$$
$$\Delta H_{298}^0 = -7 kJmol^{-1} \quad (18)$$

9. The cracking to carbon, methane and water

$$C_2H_5OH \Leftrightarrow 2C + H_2O + 2H_2$$
$$\Delta H_{298}^0 = -7 kJmol^{-1} \quad (19)$$

10. The cracking to carbon, methane and water

$$C_2H_5OH \rightarrow CH_4 + C + H_2O$$
$$\Delta H_{298}^0 = -82 kJmol^{-1} \quad (20)$$

It was found that high temperature (>600°C), high water to ethanol-molar-ratio (in the range 4-10) and low pressure (atmospheric) led to an increase in hydrogen yield and reduced the concentration of by-products (Erdohely et al., 2006; Hernandez & Kafarov et al., 2009; Silveira et al., 2009).

The equilibrium composition of the gases corresponding to the stoichiometric feed ratio, in a low temperature operating range (T=100-600°C), has been calculated.

Eight gaseous species, C_2H_5OH, H_2O, O_2, H_2, CO, CO_2, CH_4, C_2H_4O, C_3H_6O, C_2H_4 and one in solid phase, carbon, have been considered as product. In order to analyze coke formation for a thermodynamic point of view it is assumed that carbon formed is elemental, in the graphitic form, hence, free energy of carbon formation (ΔG_f) is zero and vapour pressure is zero in the range of temperature analyzed, thus the total Gibbs free energy can be considered to be independent of carbon. However the amount of carbon can be included in the elemental mass balance.

The results are reported in terms of ethanol conversion, selectivity to products and hydrogen yield, defined as follows (Eqs. 21 – 30):

$$X_{C_2H_5OH}[\%] = \frac{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}}{n_{in\,C_2H_5OH}} \cdot 100 \tag{21}$$

$$S_{H_2}[\%] = \frac{n_{H_2} / 6}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{22}$$

$$S_{CO}[\%] = \frac{n_{CO} / 2}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{23}$$

$$S_{CO_2}[\%] = \frac{n_{CO_2} / 2}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{24}$$

$$S_{CH_4}[\%] = \frac{n_{CH_4} / 2}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{25}$$

$$S_{C_3H_6O}[\%] = \frac{n_{C_3H_6O} / (2/3)}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{26}$$

$$S_{C_2H_4O}[\%] = \frac{n_{C_2H_4O}}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{27}$$

$$S_{C_2H_4}[\%] = \frac{n_{C_2H_4}}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{28}$$

$$S_C[\%] = \frac{n_C / 2}{n_{in\,C_2H_5OH} - n_{out\,C_2H_5OH}} \cdot 100 \tag{29}$$

$$Y_{H_2}[\%] = \frac{n_{H_2} / 6}{n_{in\,C_2H_5OH}} \cdot 100 \tag{30}$$

In all cases examined ethanol conversion was total in the whole range of temperature, thus hydrogen selectivity and hydrogen yield coincide. At low temperatures, the cracking into methane and carbon dioxide is thermodynamically favoured. Hydrogen and CO contents progressively increase with temperature. Moreover, even if all compounds present in equations are included in the thermodynamic calculations, acetaldehyde and ethylene are never favoured, thus in the following section it has been reported the results as selectivity to major products formed.

The effect of two important parameters, defined as follows, have been calculated:

- Water-to-ethanol molar Feed ratio:

$$r.a. = \frac{molesH_2O}{molesEtOH} \tag{31}$$

- Feed dilution ratio:

$$r.d. = \frac{molesN_2}{molesEtOH + molesH_2O} \tag{32}$$

4.1.1 Effect of water to ethanol molar ratio

Equilibrium selectivity to H_2, CH_4, CO, CO_2, C_2H_4O, C_2H_4, C_3H_6O as a function of temperatures has been investigated. The range of operating conditions used is reported in Table 2.

• Temperature [°C]	• 100 ÷ 1000
• Water to ethanol molar ratio • r.a. H_2O:C_2H_5OH [mol:mol]	• 1:1 ÷ 10:1
• Dilution ratio • r.d. N_2:(H_2O+C_2H_5OH) [mol:mol]	• 4

Table 2. Operating condition for thermodynamic analysis: effect of water-to-ethanol molar ratio

Figure 3 shows the H_2 selectivity as a function of temperature for different values of the S/C (steam-to-carbon) ratio. The results of thermodynamic evaluations indicate that, in the overall temperature range, by increasing the feed ratio, the H_2 selectivity increases. By considering the temperature effect, the behaviour is quite different and in particular it is interesting to note that there is a maximum in the H_2 selectivity in the range 550-700°C, excepted for the S/C ratio lower than 3.

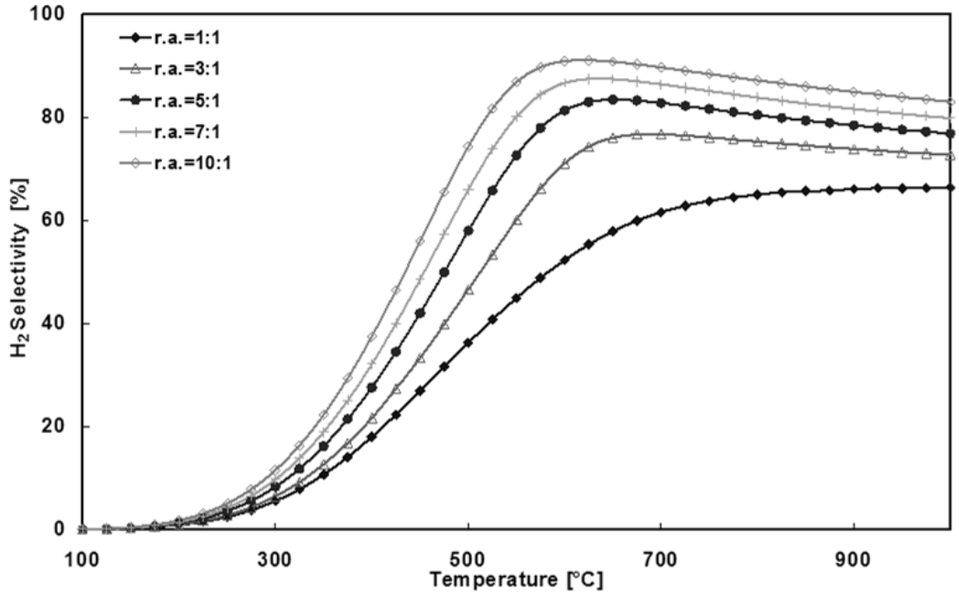


Fig. 3. H_2 selectivity as a function of temperature at different water-to-ethanol molar ratios

CH_4 selectivity has the opposite tendency. It is possible to observe in Figure 4 that the tendency to produce methane decreases by increasing the water content in the feed stream. In particular, at temperatures higher than 750°C, CH_4 selectivity is zero.

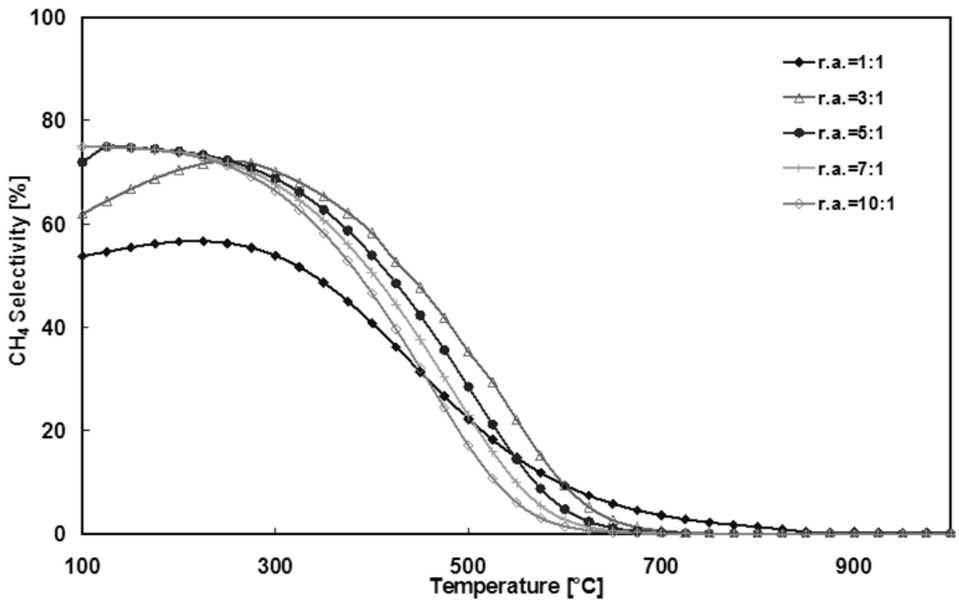


Fig. 4. CH_4 selectivity as a function of temperature at different water to ethanol molar ratios

CO selectivity (Figure 5), at T< 400°C, is not influenced by the presence of water because the CO-WGS reaction is favoured at lower temperatures. With temperature increasing, CO selectivity increase with a more evident tendency for lower water to ethanol molar ratios: at 1000°C, with r.a.= 1, CO selectivity is total, while with r.a.= 10, it results 50%.

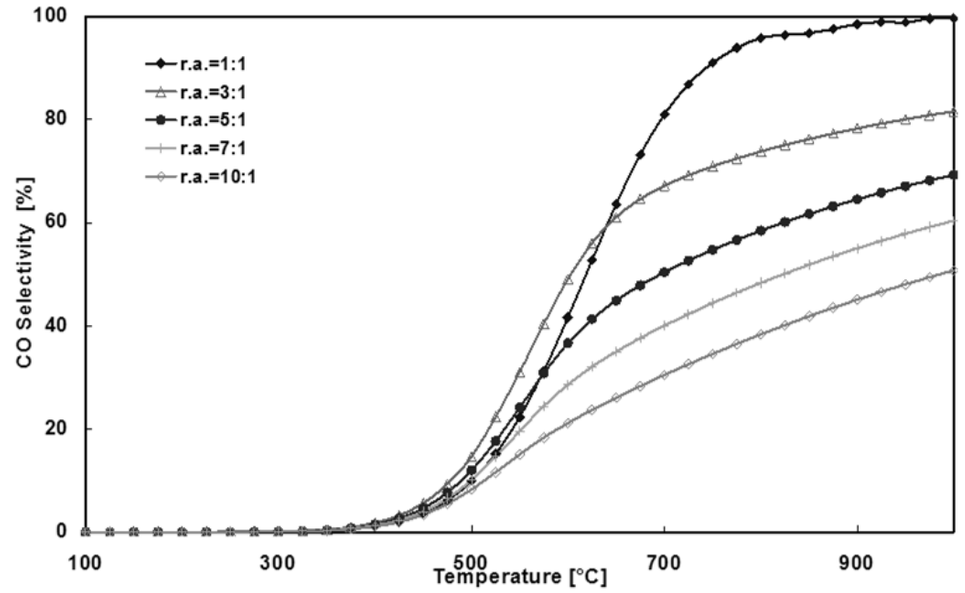


Fig. 5. CO selectivity as a function of temperature at different water to ethanol molar ratios

The data concerning the CO_2 selectivity are reported in Figure 6 as a function of temperature for different r.a. values, showing that S_{CO2} has a maximum in the range 500-700°C and that, by increasing the r.a. value, the CO_2 selectivity increase in the overall temperature range.

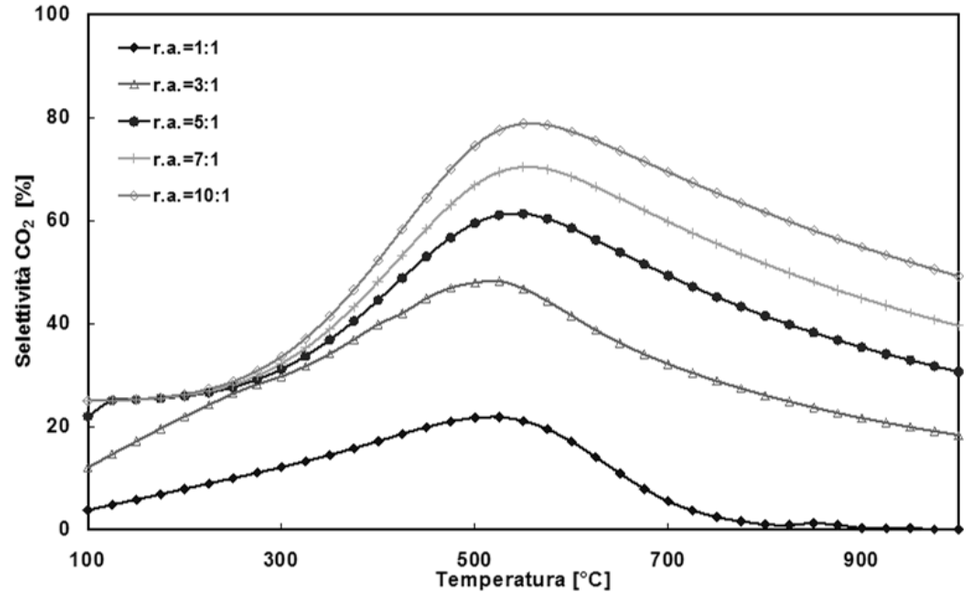


Fig. 6. CO_2 selectivity as a function of temperature at different water to ethanol molar ratios

Coke formation has also been studied at various T and r.a. values (Figure 7). At atmospheric pressure for a fixed temperature, r.a< 4:1 favour coke formation until 900°C. This effect is more obvious lowering temperature below 500 °C, in fact for r.a.= 3, coke formation may

occur only if T< 200 °C. It is worth to note that in the literature is also reported that by increasing the pressure, the S_C is lower, in particular at higher temperature (Hernandez et al. 2009).

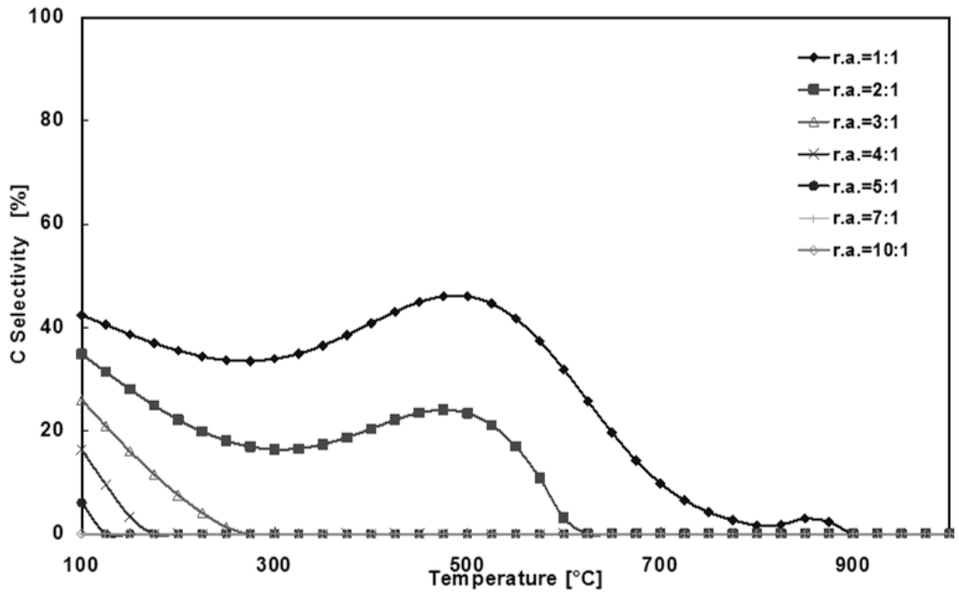


Fig. 7. C selectivity as a function of temperature at different water to ethanol molar ratios.

Since ethanol conversion is complete, H_2 yield and selectivity coincide (Figure 8) and, consequently, the comments are the same of Figure 3.

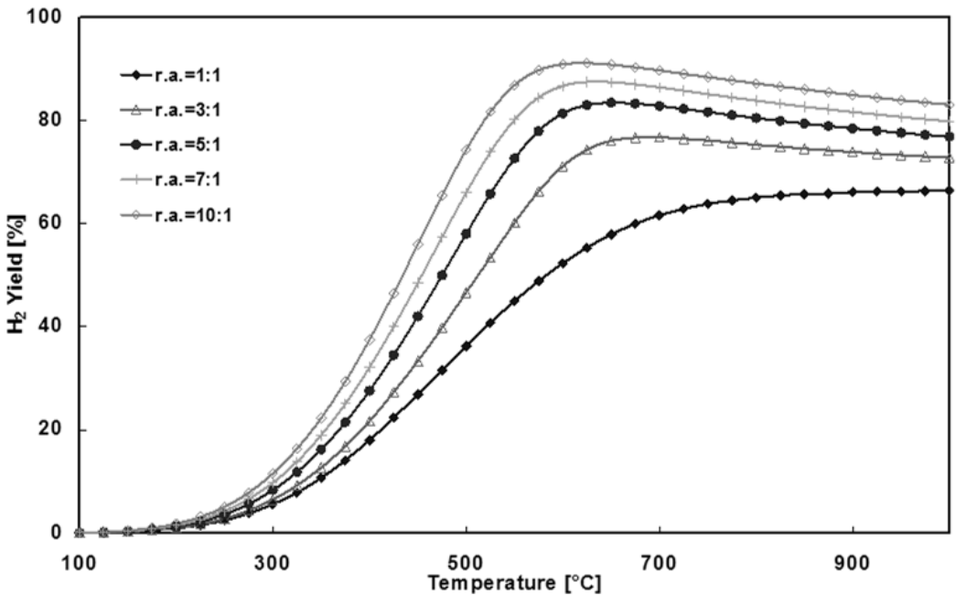


Fig. 8. H_2 yield as a function of temperature at different water to ethanol molar ratios

4.1.2 Effect of dilution ratio

Equilibrium selectivity to H_2, CH_4, CO, CO_2, C_2H_4O, C_2H_4, C_3H_6O as a function of temperature was studied. The range of operating conditions covered for the thermodynamic analysis is reported in Table 3.

Temperature [°C]	100 ÷ 1000
Water to ethanol molar ratio r.a. = H_2O:C_2H_5OH [mol:mol]	3
Dilution ratio r.d. = N_2:(H_2O+C_2H_5OH) [mol:mol]	0 ÷ 49

Table 3. Operating conditions for thermodynamic analysis-effect of dilution ratio

In Figure 9, 10 and 11 are reported results concerning the H2, CH4 and CO selectivity, respectively. Figure 9 shows that , in the range 100-600°C, hydrogen selectivity is favoured when temperature increases, the yield shows a slightly negative trend. Moreover, by increasing the r.d., the selectivity also increases because the reaction takings place with an increase in moles number. The presence of gaseous nitrogen has the same effect of the pressure decreasing (Khedr et al., 2006). Moreover, it is clear that methane selectivity has a complementary behaviour (Figure 9) with respect to CO and H_2, and it decreases when temperature and dilution increase. This result can be explained considering that, by increasing the temperature and the dilution ratio, the methane steam reforming reaction is progressively more favoured and CO and H_2 are produced.

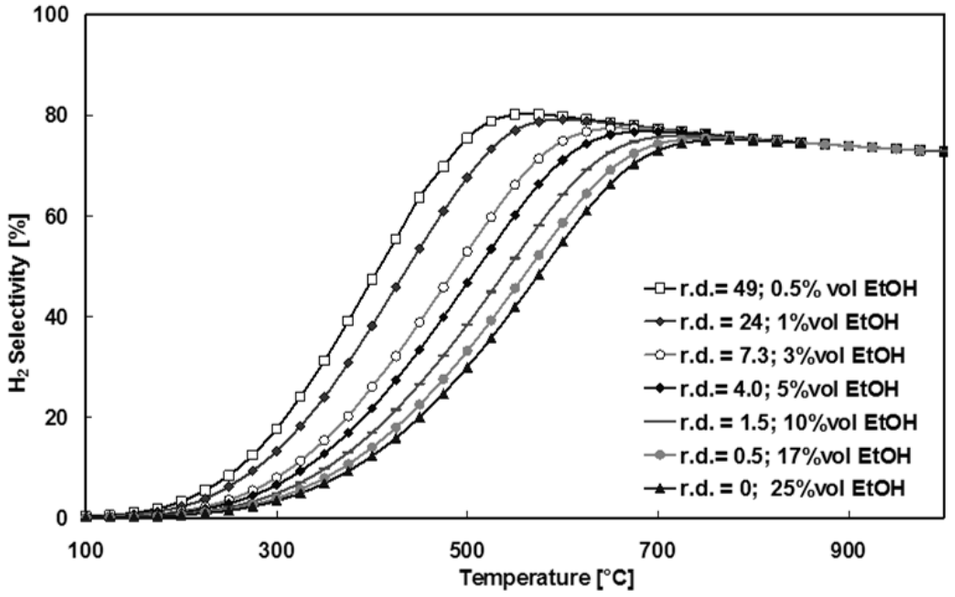


Fig. 9. H_2 selectivity as a function of temperature at different dilution ratios

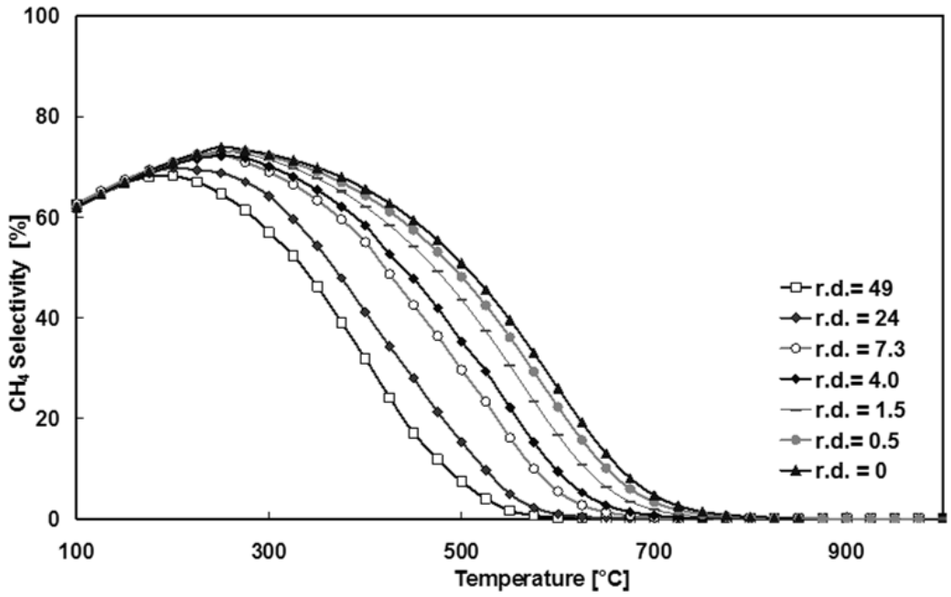


Fig. 10. CH_4 selectivity as a function of temperature at different dilution ratios

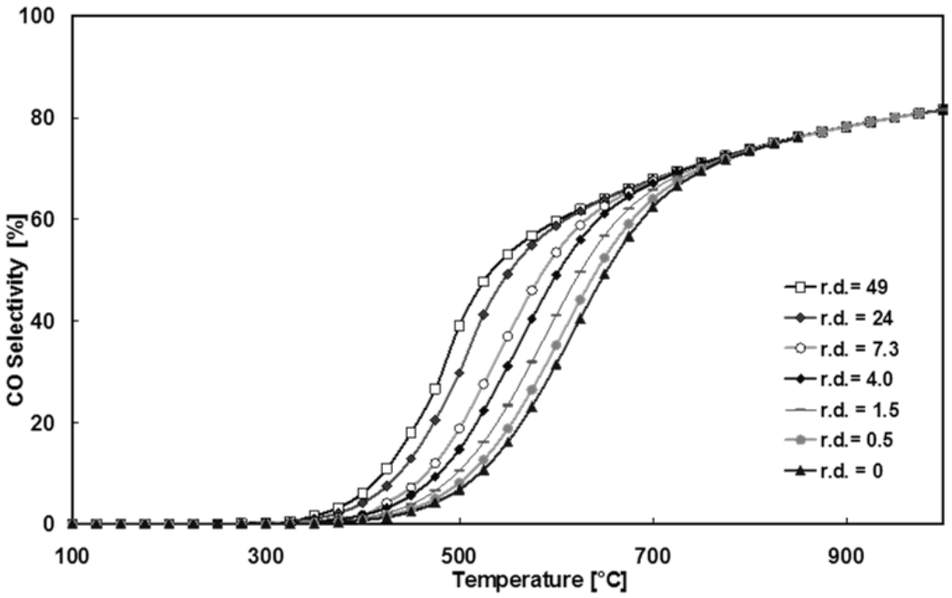


Fig. 11. CO selectivity as a function of temperature at different dilution ratios

The CO_2 selectivity is reported in Figure 12 as a function of temperature at different r.d. values. It is interesting to note that S_{CO2} has a maximum in the range 400-600°C, in agreement with the shoulder observed in the SH_2 profile.

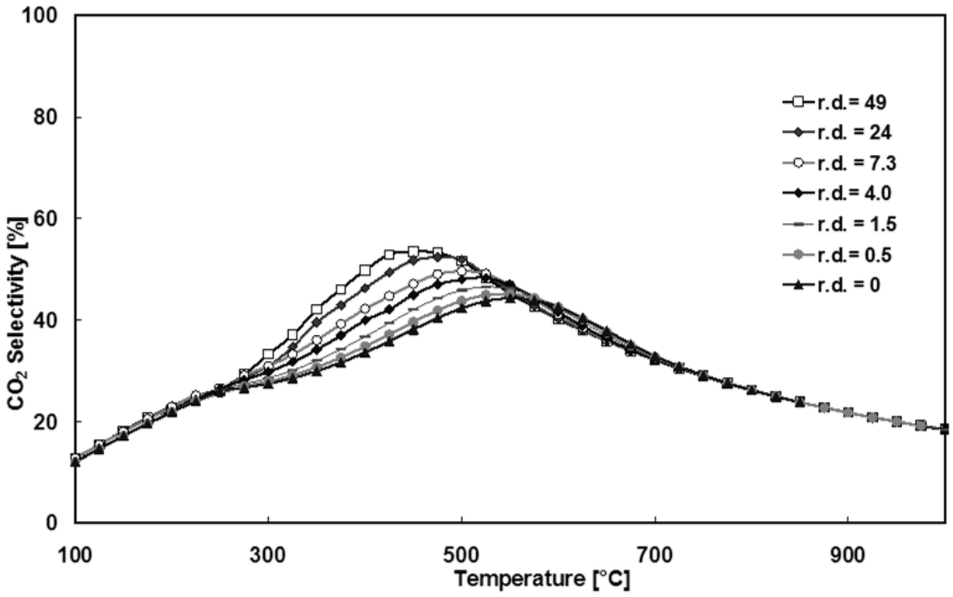


Fig. 12. CO_2 selectivity as a function of temperature at different dilution ratios

About the formation of different HC product, the results showed that, in the operating range considered, there isn't C_3H_6O, C_2H_4O, C_2H_4 formation, at any dilution ratio.

There is, instead, coke formation for temperature lower than 250°C, with a selectivity that decreases from 26% at 100°C, with temperature increasing (Figure 13).

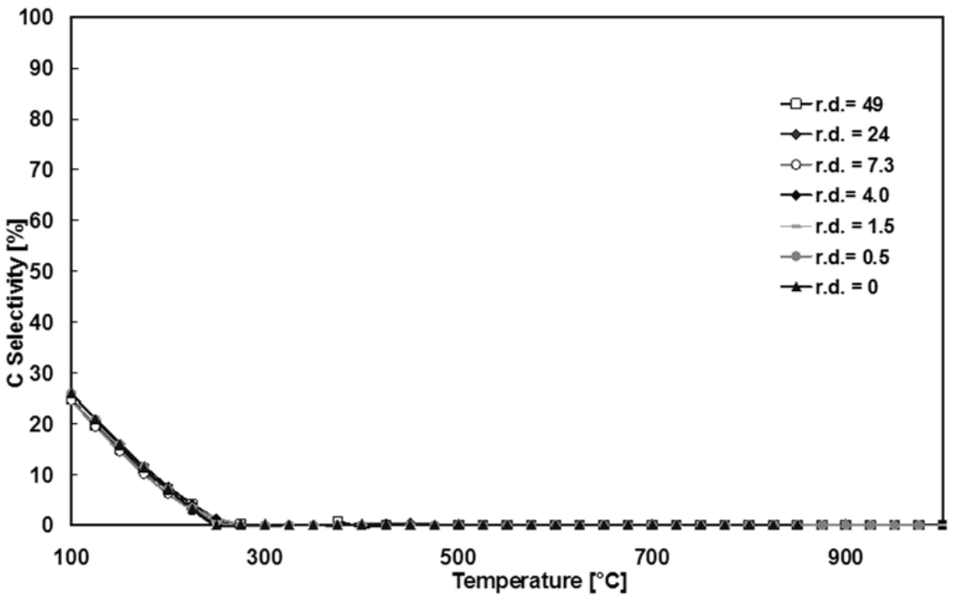


Fig. 13. C selectivity as a function of temperature at different dilution ratios

Since ethanol conversion is complete, hydrogen yield has the same tendency and values of the hydrogen selectivity (Figure 14).

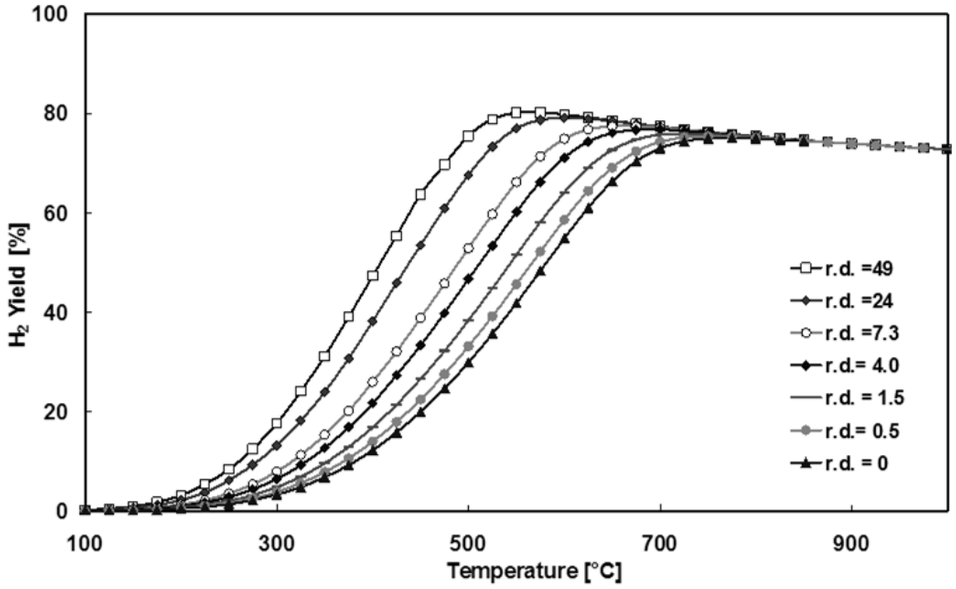


Fig. 14. H_2 yield as a function of temperature at different dilution ratios

4.1.3 ΔH of reaction

Considering the same system, composed of nine species, it has been estimated ΔH of reaction. The effect of temperature and water-to-ethanol molar ratio is shown in Figure 15.

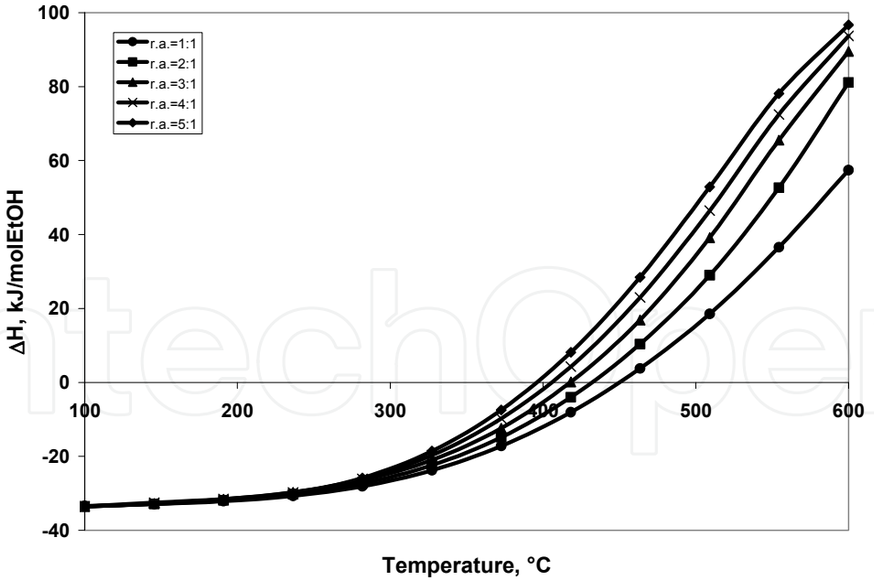


Fig. 15. Effect of temperature and water to ethanol and oxygen to ethanol molar ration on ΔH of reaction

At atmospheric pressure and for a fixed temperature, ΔH increases with water to ethanol molar ratio but it is very interesting to note the effect of temperature: ΔH increases with

temperature for all operating conditions examined but, in the temperature range 400-450°C, the reaction is almost athermic, then in this range the reaction needs a very low thermal duty. This behaviour could better explain the choice of the low temperature operating range.

4.1.4 Selected thermodynamic conditions

From the thermodynamic analysis reported, it may be concluded that hydrogen production through bioethanol steam reforming is favoured at temperatures higher than 600°C, because high H_2 and CO selectivity can be thermodynamically achieved at these high temperatures.

The results obtained are in agreement with other previous studies (Garcia & Laborde, 1991, Vasudeva et al., 1996). High temperatures and water to ethanol molar ratio favour hydrogen production; the tendency of methane is exactly the opposite of that of hydrogen.

There isn't a remarkable effect of the dilution ratio on products selectivities. Instead, the presence of water in the feed system is in favour of hydrogen yield. A stoichiometric water to ethanol molar ratio (3:1) is the minimum value enough to avoid coke formation in a wide range of temperature, so it has been selected in order to consider the most severe case.

Based on these considerations, ethanol steam reforming has been more widely studied over the high temperature range. Since CO is a poison for the anode of the fuel cells, it is necessary to remove it through the exothermic WGS reaction. For this purpose, it would be necessary to pass the reformate through a bed of low-temperature water-gas shift catalyst in order to generate further hydrogen and eliminate CO. This adversely affects overall system efficiency due to heat losses and increases the capital cost for necessary hardware. As a result, low temperature ethanol steam reforming is an attractive alternative (Roh et al., 2006a; Roh et al., 2006b; Ciambelli et al., 2009; Ciambelli et al., 2010a; Ciambelli et al., 2010b; Palma et al., 2011). This operating range could be useful to obtain a H_2 rich gas stream, also reducing the overall thermal duty. However, at low temperature hydrogen yield is lower and the reaction produces a wide range of undesirable secondary products but the main detrimental effect is related to the catalyst deactivation during ethanol steam reforming at low temperature has been reported to be severe.

Then a proper selection of a suitable catalyst is very important for the low temperature bio-ethanol steam reforming. Catalysts play an important role in the reactivity toward complete conversion of ethanol. However, each catalyst induces different pathways and, therefore, the selection of a suitable catalyst plays a vital role in ethanol steam reforming for hydrogen production. Active catalysts should maximize hydrogen selectivity and inhibit coke formation as well as CO production (Armor, 1999).

The literature surveys presented above reveal that the ethanol conversion and selectivity to hydrogen highly depend on the type of metal catalyst used, type of precursors, preparation methods, type of catalyst support, presence of additives, and operating conditions, i.e. water/ethanol molar ratio and temperature (Ni et al., 2007).

The steam reforming of ethanol over Ni, Co, Cu and noble metal (Au, Pd, Pt, Rh, Ru, Ir), supported on ionic oxides (CeO_2, Al_2O_3, MgO, TiO_2 but also Fe-Cr and Fe-Cu mixed oxides) has been extensively studied. The greatest concern lies in developing an active catalyst that inhibits coke formation and CO production, while there are few studies about low temperature ethanol steam reforming catalysts. In the follow sections it has been taken an overview of the published literature.

4.2 Noble metals-based catalysts

Noble metals on various supports are well-known for their high catalytic activity and have been studied extensively.

The catalytic performance of supported noble metal (Ru, Rh, Pd, Pt, Ir, Au) catalysts for the steam reforming of ethanol has been investigated in the temperature range of 600–850°C with respect to the nature of the active metallic phase, the nature of the support (Al_2O_3, MgO, TiO_2) and the metal loading. Different authors (Breen et al., 2002; Aupretre et al., 2005; Erdohelyi et al., 2006; Frusteri et al., 2004; Men et al., 2007; Diagne et al., 2002; Romero-Sarria et al., 2008; Domok et al., 2010; Basagiannis et al., 2008; Yamazaki et al., 2010) used Rh, Pd, and Pt on different supports such as alumina and ceria/zirconia: the noble metals activity decreased in the order of Pt-loaded catalyst, Rh-loaded catalyst, Pd-loaded catalyst. Dehydration of ethanol to ethylene was noted on alumina-supported noble metal catalysts. The catalyst stability was also monitored with and without the presence of oxygen. It was found that water enhanced the stability of ethoxide surface species formed by the dissociation of ethanol.

4.2.1 Rhodium catalysts

The ethanol steam reforming over Rh/Al_2O_3 catalysts have been investigated. The reaction was carried out at temperatures between 50 and 650°C with a water-to-ethanol molar ratio of 4.2-8.4 with or without O_2 addition for autothermal process, concluding that methane is a primary product whose selectivity decreases with contact time. The mechanism is composed by the following steps:

- ethanol dehydrogenation and/or dehydration
- gasification of acetaldehyde or ethylene formation.

The performance of Rh-based catalysts supported on alumina was compared with other metals: Rh appears as the most active one, but a further performance is obtained when it is doped with Ni or Ru (Breen et al., 2002; Liguras et al., 2003)

Aupetre et al. classified the metal activity in the order:

Ni> Rh>> Pd>Pt>Cu>Ru

A lot of studies suggest that Rh-based catalysts are promising (Freni et al., 2000, Wanat et al., 2004, Diagne et al., 2004).

$Rh/\gamma\text{-}Al_2O_3$ with 5 wt% loading was found to degrade considerably after operation for 100 h. Moreover, it was found that coke formation could be prevented at high temperatures by sufficiently large amounts of Rh and strong excess of water; in particular, at 650°C, only C_1 products were present at the exit of the stream, less coke was formed and the catalyst was more stable in presence of O_2. It is possible to suggest the occurrence of several reactions: acethaldehyde formed by dehydrogenation of ethanol is decomposed to CH_4 and CO (Eq. 33) or undergoes steam reforming (Eq. 34). Then water reforms the C_1 products to hydrogen (Eq. 35, 36). In addition, when O_2 is present, the reactions in Eqs 37-40 occur (Cavallaro et al., 2003).

$$CH_3CHO \Leftrightarrow CH_4 + CO \tag{33}$$

$$CH_3CHO + H_2O \Leftrightarrow 2CO + 3H_2 \quad (34)$$

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (35)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (36)$$

$$CO + 0.5O_2 \Leftrightarrow CO_2 \quad (37)$$

$$C_2H_5OH + 0.5O_2 \Leftrightarrow CH_3CHO + H_2O \quad (38)$$

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O \quad (39)$$

$$C + O_2 \Leftrightarrow CO_2 \quad (40)$$

Rh/γ-Al_2O_3 catalyst was studied to evaluate the complex reaction mechanism, at least at the preliminary stage. When a mixture of ethanol and water is used to supply a heated coil reactor, the reagents are transformed according to the reaction behavior pattern provided by the chemical nature of the catalyst. In the case where a dual function acid-dehydrogenant catalyst is used, it is reasonable to think that the main reactions will be those described in the scheme shown in Figure 16 (Cavallaro, 2000).

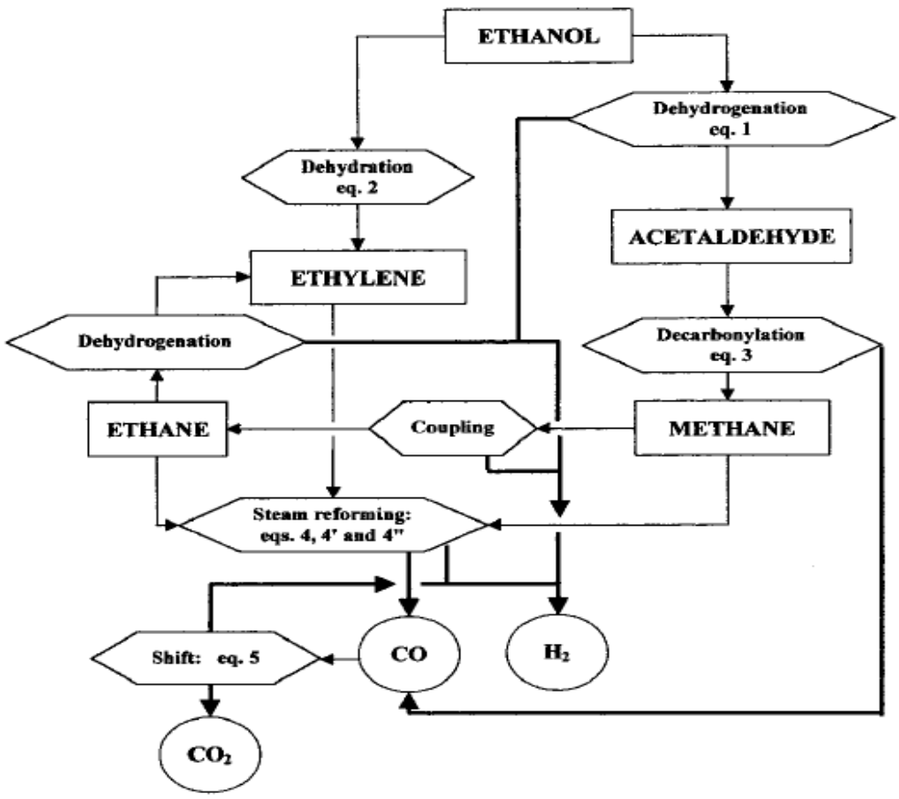


Fig. 16. Pathways for the steam reforming of ethanol over Rh/Al_2O_3 catalysts (Cavallaro, 2000)

In the case of ethanol steam reforming over Rh/Al_2O_3 under pressure (1.1 MPa), the catalysts is highly active, selective and stable in the ethanol at 700°C. Up to 4 g of hydrogen per hour and per gram of catalyst could be produced with a high selectivity towards CO_2 formation. The nature of the metal precursor salt (in terms of metal phase dispersion), metal loading and the reaction conditions influenced the performance of the catalyst (Aupretre et al., 2004).

Depositing Rh on MgAl-based spinel oxide supports (Figure 17) exhibited higher basicity, compared with alumina-supported Rh, whereas the surface acidity was strongly reduced, resulting in improved stability.

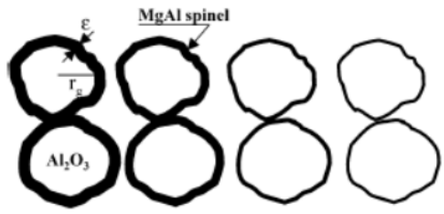


Fig. 17. Schematic picture of the morphology of the $MgAl_2O_4/Al_2O_3$ support (Aupretre et al., 2005)

Rh/ZrO_2 catalysts, in which the catalyst support is decorated with CeO_2, Al_2O_3, La_2O_3 and Li_2O, respectively, were studied for ethanol steam reforming reactiom. The catalyst using ZrO_2 without any decoration as the support exhibits the highest catalytic activity for H_2 production. Moreover it was found that Rh particle size and distribution as well as the surface area of the catalyst are not important factors in determining the catalytic performance.

It was evaluated the catalytic performance of MgO-supported Pd, Rh, Ni, and Co for hydrogen production by ethanol steam reforming. Rh/MgO showed the best ethanol conversion and stability at 650°C, while Ni/MgO exhibited the highest hydrogen selectivity (>95%). The activity of the catalysts reduced in the order Rh> Co> Ni> Pd. Coke formation rate on Rh/MgO was very low as MgO was basic. It was also found that the deactivation was mainly due to metal sintering. It was proposed a reaction mechanism for ethanol steam reforming: ethanol is first dehydrogenated to acetaldehyde which subsequently decomposes to CH_4 and CO. These lead to the formation of H_2 and CO_2 by steam reforming and water gas shift (WGS) reactions. Thus, the exit stream composition is governed by CH_4 steam reforming and WGS reactions (Frusteri et al. 2004).

Some studies (Diagne et al., 2002; Rogatis et al., 2008) deal with the hydrogen production by ethanol steam reforming over Rh catalysts supported on CeO_2, ZrO_2 and various $CeZrO_x$ oxides (Xe/Zr= 4,2, or 1). In the range 300-500°C, with a very Ar-diluted feed stream, with a high water-to-ethanol molar ratio, the H_2 yield resulted not favoured by a high basicity of support. Another paper (Idriss, 2004) outlined the complexity of the ethanol reactions on the surfaces of noble metals/cerium oxide catalysts, suggesting that hydrogen production is directly related to two main steps: the first involves breaking the carbon-carbon bond, and Rh appears the most suitable compound for this reaction at reasonable operating temperatures; the second involves CO oxidation to CO_2. Ethanol reforming on Rh/CeO_2–ZrO_2 does not appear to be sensitive to Rh dispersion. Up to 5.7 mol H_2 can be produced per

mol ethanol at 350-450°C on Rh/CeO_2-ZrO_2 in presence of excess of water (Diagne et al., 2002).

Rh/ZrO_2-CeO_2 catalysts appears to favour ethanol dehydrogenation rather than dehydration during the ethanol steam reforming reaction. They exhibit higher H_2 yield at low temperatures, possibly due to the efficient oxygen transfer from ZrO_2-CeO_2 to Rh. Higher Rh loadings enhance not only the WGS reaction but also CH_4 formation (Roh et al. 2008). Rh/ZrO_2 catalysts, in which the catalyst support is decorated with CeO_2, Al_2O_3, La_2O_3 and Li_2O, respectively, were studied for ethanol steam reforming reaction. The catalyst using ZrO_2 without any decoration as the support exhibits the highest catalytic activity for H_2 production. Moreover it was found that Rh particle size and distribution as well as the surface area of the catalyst are not important factors in determining the catalytic performance.

$CeZrO_x$ is an interesting support for Rh and Ni (Aupretre et al., 2005) since it

- significantly increased the H_2 yield;
- strongly favours the acetaldehyde route to CO_x and H_2 instead of its decomposition into CO and methane, due to the fast oxidation of the CH_3 groups of acetaldehyde, related to the well know oxygen storage capability and mobility of the support;
- favours the direct composition of water into hydrogen and not only into OH groups;
- inhibits the dehydration route to ethylene, that is a coke precursor, and promotes CH_x oxidation and surface cleaning along the steam reforming process. For this reasons, the catalysts stability is improved.

Rh/TiO_2 catalysts were also studied (Rasko at al., 2004): it was found that ethanol dissociation forms ethoxides at ambient temperature. Dehydrogenation leads to acetaldehyde.

4.2.2 Platinum

There is a scarse information in literature on Pt-based catalysts for low temperature ethanol steam reforming. It was studied oxidative steam reforming of ethanol over a Pt/Al_2O_3 catalyst modified by Ce and La. The presence of Ce as an additive was found to be beneficial for hydrogen production. The presence of La however did not promote ethanol conversion. When both Ce and La were present on the support, poorer catalyst behaviour was observed due to lower Pt-Ce interaction with respect to La-free ceria-alumina support (Navarro et al., 2005).

The reaction of ethanol and water has been investigated over K doped 1% Pt/Al_2O_3 catalysts. The presence of K resulted at room temperature in upward shift of the IR band of CO formed in the ethanol adsorption. At higher temperature the presence of surface acetate species was also detected which, according to the TPD results decomposed above 300°C to form CH_4 and CO_2. The K destabilized these forms. In the catalytic reaction the H_2 selectivities were similar and much higher over all promoted Pt/Al_2O_3 than on the pure catalyst. It was proved that the K had a destabilizing effect onto the surface acetate groups and thus improved the steam reforming activity of 1% Pt/Al_2O_3. The potassium caused significant changes in the product distribution of the steam reforming reactions (Figure 18): over K containing catalysts, higher selectivity of H_2, CO_2, and CH_4 was obtained in the steady state than over pure 1% Pt/Al_2O_3, and the potassium also suppressed the formation of ethylene.

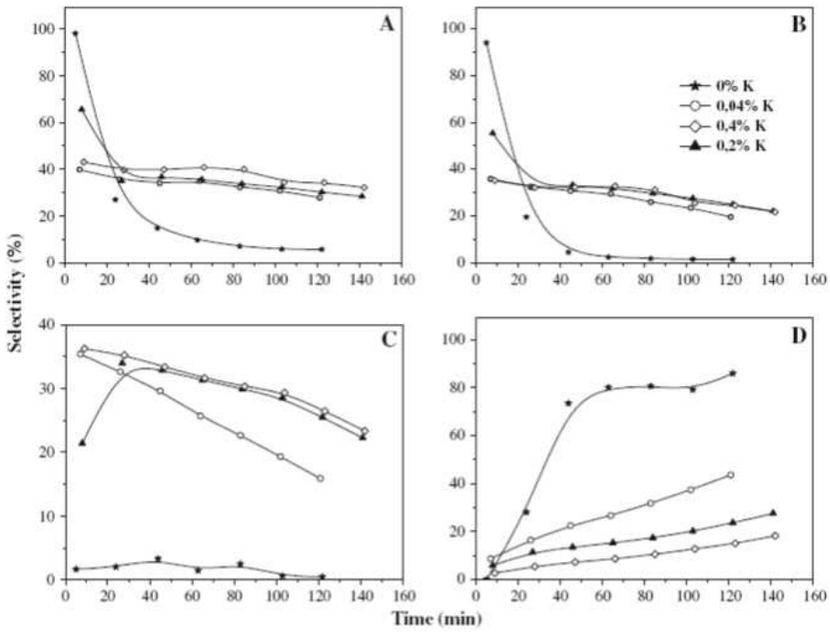


Fig. 18. The selectivity of H_2 (A), CO_2 (B), CH_4 (C), and C_2H_4 (D) formation in the ethanol steam reforming reaction at 450°C on Pt/Al_2O_3 catalysts with different K loading (Domok et al., 2008)

The effect of the support nature and metal dispersion on the performance of Pt catalysts during steam reforming of ethanol was studied (de Lima et al., 2008). H_2 and CO production was facilitated over Pt/CeO_2 and $Pt/CeZrO_2$, whereas the acetaldehyde and ethane formation was favoured on Pt/ZrO_2. According to the reaction mechanism, some reaction pathways are favoured depending on the support nature, which can explain the differences observed on the resulting product distribution. At high temperature, the forward acetate decomposition is promoted by both steam and Pt and is favoured over the CeO_2-based catalyst. These results are likely due to the higher Pt dispersion on Pt/CeO_2 catalyst.

The steam reforming reactions for bio-ethanol and reagent ethanol over several Pt/ZrO_2 catalysts with 1–5 wt% Pt loadings were examined. For the reaction with reagent ethanol, the main products were H_2, CO_2, CO, and CH_4; production of acetone, acetaldehyde, and ethylene at 400°C was very low. The partial ethanol steam reforming reaction and the ethanol decomposition reaction occur competitively in the catalytic system. The activities of the catalysts with larger Pt loadings were higher and more stable. The H_2 yield on the Pt/ZrO_2 catalyst reached 29% at 400°C, but at 500°C the activity of H_2 formation rapidly decreased with time-on-stream. The activity for the ethanol steam reforming reaction decreased more rapidly than that for the ethanol decomposition reaction (Yamazaki et al., 2010).

The effects of the support (alumina or ceria) on the activity, selectivity and stability of 1 wt% Pt catalyst for low temperature ethanol steam reforming have been investigated. Experimental results in the range 300-450°C showed a better performance of ceria supported catalyst, especially with reference to deactivation rate. Moreover, Pt/CeO_2 catalyst performance increase by increasing the Pt load in the range 1-5 wt% (Figure 19). The best catalytic formulation (5 wt% Pt on CeO_2) was selected for further studies. It is worthwhile

that this catalyst is also active for the water gas shift conversion of CO to CO_2, resulting in the absence of CO in the reformate product. (Ciambelli et al., 2010a).

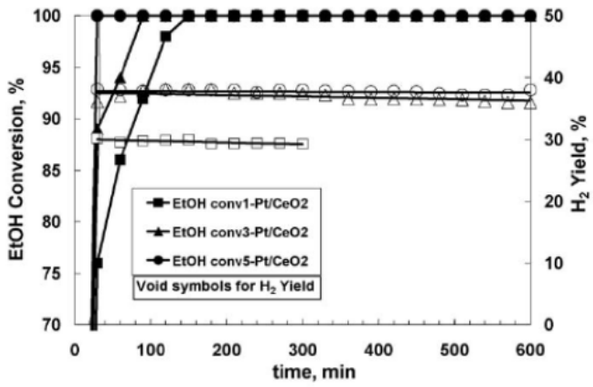


Fig. 19. Effect of Pt load on ethanol conversion and H_2 yield versus time on stream for Pt/CeO_2 catalysts. Experimental conditions: T = 300°C; C_2H_5OH = 0.5 vol%; $C_2H_5OH:H_2O:N_2$ = 0.5:1.5:98; Q_{Tot} = 1000 (stp)cm^3/min; GHSV: 15,000 h^{-1} (Ciambelli et al., 2010a)

Some preliminary results of a kinetic investigation of SR of ethanol on the selected Pt/CeO_2 catalyst and a proposed reaction mechanism are also reported (Ciambelli et al., 2010b). The main promoted reactions are ethanol decomposition, ethanol steam reforming and CO water gas shift, and the apparent reaction orders are 0.5 and 0 for ethanol and steam respectively, with an apparent activation energy of 18 kJ mol^{-1} evaluated in the range 300–450°C. Kinetic evaluations and temperature programmed desorption experiments suggest a surface reaction mechanism reported in Figure 20 and involving the following steps:

i. ethanol dissociative adsorption on catalyst surface to form acetaldehyde intermediate;
ii. decarbonylation to produce mainly H_2, CH_4 and CO;
iii. WGS reaction of CO adsorbed on Pt sites to produce H_2 and CO_2.

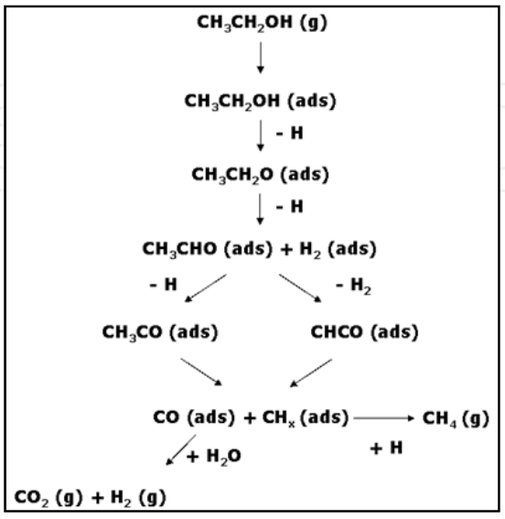


Fig. 20. Scheme of the surface reaction mechanism proposed (Ciambelli et al., 2010b)

4.2.3 Palladium

Few studies on Pd catalyzed steam reforming of ethanol have also been reported earlier. In another such study on Pd/Al_2O_3, these researchers reported that CO concentration was minimum at 450°C and the amount of coke formed was negligible even at stoichiometric water-to-ethanol ratios (Goula et al., 2004).

Pd catalysts supported on a porous carbonaceous material in presence of steam in the range of temperatures 330-360°C was found to have high activity and stability (Galvita et al., 2002). However, it was observed that a Pd/MgO catalyst drastically deactivated during reaction due to metal sintering at 650°C. Coke formation on Pd/MgO occurred at higher rate than on MgO-supported Rh, Ni and Co catalysts (Frusteri et al., 2004).

Unlike Rh, co-deposition of Pd and Zn on ZnO support led to formation of PdZn alloy, which favored dehydrogenation and hydrogen production (Casanovas et al., 2006).

4.2.4 Ruthenium

The catalytic performance of supported Ru-based catalysts for the steam reforming (SR) of ethanol has been studied. The catalytic performance is significantly improved with increasing metal loading; in particular, although inactive at low loading, Ru showed comparable catalytic activity with Rh at high loading. There was a marked increase in conversion of ethanol and selectivity to H_2 over Ru/Al_2O_3 with an increase in the Ru content (Figure 21). The Ru/Al_2O_3 with 5 wt% loading could completely convert ethanol into syngas with hydrogen selectivity above 95%, the only byproduct being methane (Figure22).

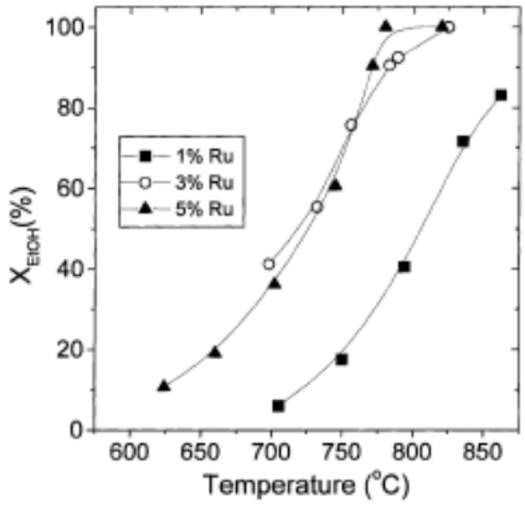


Fig. 21. Effect of reaction temperature on the conversion obtained over Ru/Al_2O_3 catalysts of variable metal content (1-5%) (Liguras et al., 2003)

High dispersion of catalyst atom at the support surface was found to enhance the activity of catalysts. The catalyst was stable and had activity and selectivity higher than Ru/MgO and Ru/TiO_2. The selection of support played an important role in long-term catalytic operation. Acidic supports, such as γ-Al_2O_3, induced ethanol dehydration to produce ethylene, which

was a source of coke formation. Dehydration can be depressed by adding K to neutralize the acidic support or by using basic supports, i.e. La_2O_3 and MgO. About 15% degradation in ethanol conversion was detected for Ru/Al_2O_3 with 5 wt% after operation for 100 h (Liguras et al., 2003).

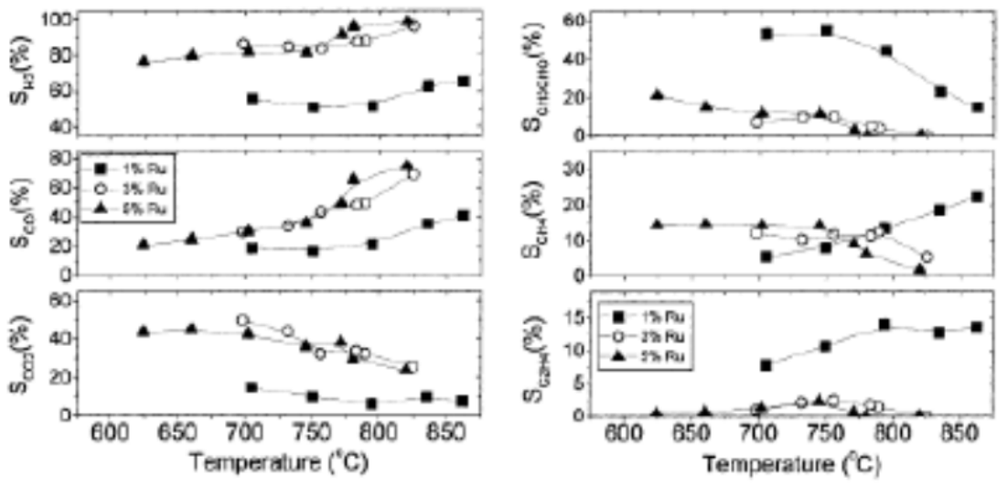


Fig. 22. Effect of reaction temperature on the selectivity toward reaction products over Ru/Al_2O_3 catalysts of variable metal content (1-5%) (Liguras et al., 2003)

4.2.5 Iridium

Steam reforming of ethanol over an Ir/CeO_2 catalyst has been studied with regard to the reaction mechanism and the stability of the catalyst. It was found that ethanol dehydrogenation to acetaldehyde was the primary reaction, and acetaldehyde was then decomposed to methane and CO and/or converted to acetone at low temperatures. Methane was further reformed to H_2 and CO, and acetone was directly converted into H_2 and CO. Addition of CO, CO_2, and CH_4 to the water/ethanol mixture proved that steam reforming of methane and the water gas shift were the major reactions at high temperatures (Figure 23). The Ir/CeO_2 catalyst displayed rather stable performance in the steam reforming of ethanol at 650°C even with a stoichiometric feed composition of water/ethanol, and the effluent gas composition remained constant for 300 h on-stream. Significant deactivation was detected at 450°C. The CeO_2 in the catalyst prevented the highly dispersed Ir particles from sintering and facilitated coke gasification through strong Ir–CeO_2 interaction (Zhang et al., 2008).

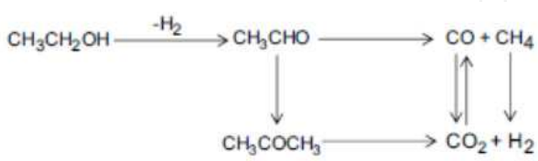


Fig. 23. Proposed reaction scheme of ethanol steam reforming on the Ir/CeO_2 catalyst (Zhang et al., 2008)

Figure 24 shows the concentrations of H_2, CO_2, CH_4, and CO in the outlet gas as a function of time-on-stream (TOS) (Zhang et al., 2008).

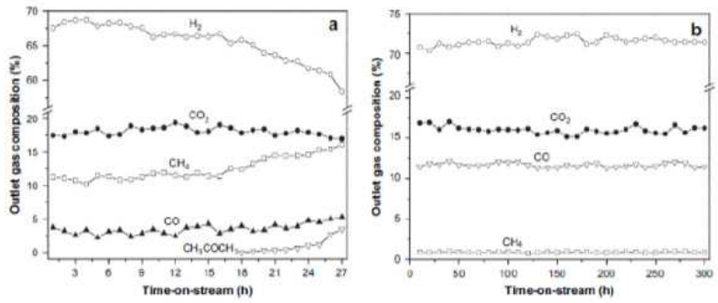


Fig. 24. Long-term stability test of the Ir/CeO_2 catalyst (Zhang et al., 2008)

La_2O_3-supported Ir catalyst was tested for the oxidative steam reforming of ethanol (OSRE). La_2O_3 would transform into hexagonal $La_2O_2CO_3$ during OSRE, which suppress coking. Reduced Ir metal can interplay with $La_2O_2CO_3$ to form Ir-doped $La_2O_2CO_3$. It dynamically forms and decomposes to release active Ir nanoparticles, thereby preventing the catalyst from sintering and affording high dispersion of Ir/La_2O_3 catalysts at elevated temperatures. By introducing ultrasonic-assisted impregnation method during the preparation of a catalyst, the surface Ir concentration was significantly improved, while the in situ dispersion effect inhibited Ir from sintering. The Ir/La_2O_3 catalyst prepared by the ultrasonic-assisted impregnation method is highly active and stable for the OSRE reaction, in which the Ir crystallite size was maintained at 3.2 nm after 100 h on stream at 650°C and metal loading was high up to 9 wt%.

Catalytic activity of a ceria-supported Iridium catalyst was investigated for steam reforming of ethanol within a temperature range of 300–500°C. The results indicated that only less sintering influences the catalytic activities for high temperature reduction. The ethanol conversion approached completion around 450°C via reduction pretreatment for Ir/CeO_2 samples under $H_2O/EtOH$ molar ratio of 13 and 22,000 h^{-1} GHSV. Not only was a high dispersion of both catalysts present but also no impurities (e.g., boron) interfered with the catalytic activities. The hydrogen yield (H_2 mole/EtOH mole) exceeds 5.0 with less content of CO and CH_4 (<2%) (Siang et al., 2010).

4.3 Non noble metals

However, the high cost of noble metals is a major limiting factor in their use for hydrogen production via steam reforming. Some selected studies on ethanol steam reforming over non-noble metal catalysts are reported.

4.3.1 Nickel catalysts

Because of its high performances, its low cost and its high activity, nickel is one of the most studied metals for ethanol steam reforming for catalysts on different supports (Table 4).

The reforming reaction was carried out using various catalysts with Ni on La_2O_3, Al_2O_3, yttria-stabilised zirconia (YSZ), and MgO (Fatsikostas et al., 2002). According to their observations, from among the different catalytic systems selected, Ni/La_2O_3 catalyst exhibited the highest activity in hydrogen production. The ESR activities of three nano-size nickel catalysts, Ni/Y_2O_3, Ni/La_2O_3, and Ni/Al_2O_3, using nickel oxalate as precursor in the

impregnation-decomposition – reduction method, were investigated (Sun et al., 2005). It was found that the Ni/Y_2O_3 and Ni/La_2O_3 catalysts exhibited relatively high activity in ethanol steam-reforming at 250°C. An increase in the reaction temperature to 320 °C resulted in increased conversion as well as selectivity. In their study, Ni/Al_2O_3 exhibited comparatively lower activity in ethanol steam-reforming and hydrogen selectivity.

However, all three catalysts exhibited long-term stability in the ethanol steam-reforming reaction.

Studies on the steam-reforming of ethanol on Ni/B_2O_4 (B = Al, Fe, Mn) focusing on the influence of the B site metal and crystallinity on the catalytic performance of spinel-type oxide catalysts were carried out (Muroyama et al., 2010). All the spinel-type oxides promoted ethanol steam-reforming regardless of the reduction treatment, indicating that the nickel species were gradually reduced during the reaction.

The Ni/Al_2O_4 catalyst exhibited stable ethanol conversion, H_2 yield, and C_1 selectivity. The decrease in the activity of Ni/Fe_2O_4 and Ni/Mn_2O_4 catalysts was found to be due to carbon deposition.

Ni/MgO catalyst has been studied in steam reforming of ethanol (Freni et al., 2002), showing high activity and selectivity to H_2. Frusteri et al. (2004) reported high H_2 selectivity (> 95 %) at a space velocity 40000 h^{-1} over Ni/MgO at MCFC operating conditions (650°C). The performance of alkali-doped Ni/MgO catalysts on bio-ethanol steam reforming was also studied. The addition of Li and K enhanced the catalyst stability mainly by depressing Ni sintering. It was found that, because of the presence of the MgO support, there was a reduction in the amount of carbon decomposition on the catalyst. At higher temperatures (above 600°C), nickel-based catalysts became more effective in ethanol steam-reforming giving H_2, CO, CO_2, and CH_4 as the main reaction products (Fatsikostas & Verykios, 2004; Fatsikostas et al., 2002; Benito et al., 2007).

The steam-reforming of ethanol was investigated on alumina supported nickel catalysts modified with Ce, Mg, Zr, and La (Sanchez-Sanchez et al., 2009). They found that the addition of these promoters directly affected the acidity, structure, and morphology of Ni particles. The presence of Mg decreased the surface acidity of Al_2O_3 and modified the degree of interaction between Ni and Al_2O_3. The addition of Zr to the Al_2O_3 support resulted in a decrease in surface acidity as well as a decrease in the dispersion of Ni phases in the catalyst as compared with that achieved on Al_2O_3 alone; in addition, strong Ni – ZrO_2 interactions were observed in these systems. The addition of Ce to the Al_2O_3 support led to a moderate decrease in the surface acidity of Al_2O_3 and resulted in nickel phases with a better dispersion.

The ethanol steam reforming was also studied over Ni/Al_2O_3 in the range of temperatures 300-500 °C (Comas et al., 2004): it was not find any evidence of the water gas shift reaction occurring over Ni. They proposed a reaction scheme for ethanol reforming on Ni-based catalyst at 500°C. In this scheme acetaldehyde and ethylene formed as intermediates during reaction produces CO, CO_2, CH_4 and H_2 as the final products by steam reforming while the effluent composition is determined by methane steam reforming.

Ni/La_2O_3 exhibited high activity and stability in steam reforming of ethanol to hydrogen. This was attributed to the formation of lanthanum oxycarbonate species ($La_2O_2CO_3$), which

reacts with the surface carbon deposited during reaction and prevents deactivation (Fatsikostas et al., 2001; Fatsikostas et al., 2002).

Ethanol reforming was studied over Ni catalysts supported on γ -Al_2O_3, La_2O_3 and La_2O_3/γ-Al_2O_3 (Fatsikostas and Verykios, 2004). The impregnation of Al_2O_3 with La_2O_3 reduced carbon deposition. The presence of La_2O_3 on the catalyst, high water to ethanol ratios and high temperatures offered high resistance to carbon deposition.

The influence of the support nature (TiO_2, ZnO, Al_2O_3 and Al_2O_3–Fe_2O_3) of nickel catalysts on their activity, selectivity and coking phenomenon in the steam reforming of ethanol in the range of 300–600°C was investigated (Denis et al., 2008). An improvement of the selectivity of the process to hydrogen generation and diminishing of the formation of undesirable products (especially of hydrocarbons, including ethylene, and carbonaceous deposit) may be obtained by promoting nickel catalysts with sodium. On the basis of both ethanol conversions and hydrogen selectivities one may get the following order of hydrogen productivity in the steam reforming of ethanol: Ni/Zn > Ni/ Ti > Ni/Al–Fe > Ni/Al (Figure 25).

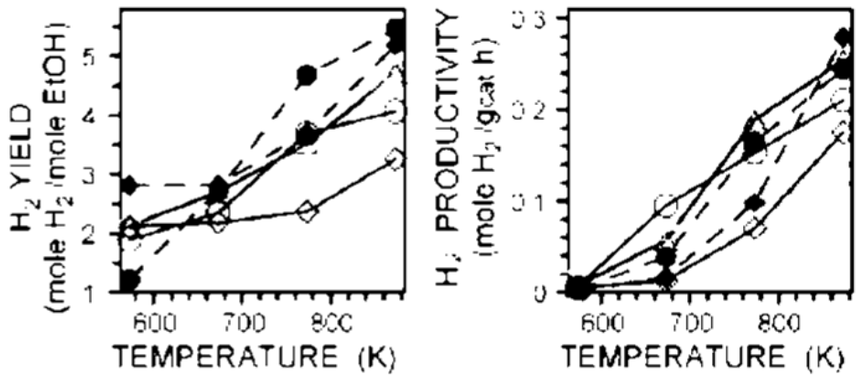


Fig. 25. Effect of nickel catalyst support and sodium promoter on the yield and productivity of hydrogen formation in the steam reforming of ethanol: (◊) Ni/Al; (Δ) Ni/Ti; (○) Ni/Zn; (□) Ni/Al–Fe; (♦) Ni/Al + Na; (● Ni/Zn + Na (Denis et al., 2008)

Perovskite-type oxide supported nickel catalysts, namely NiO/$LaFe_yNi_{1-y}O_3$ are promising candidate for the steam reforming of ethanol. The NiO/$LaFe_yNi_{1-y}O_3$ catalysts show high activity, selectivity as well as very good stability both in terms of anti-sintering of active species of nickel and anti-carbon deposition (Chen et al., 2009; Zhang et al., 2009; de Lima et al., 2010). Ni/ITQ-2 delaminated zeolite was found to be active in the ethanol steam reforming reaction. Deposition of coke occurs; however deactivation was not detected during the experimental time (72 h) (Chica & Sayas, 2009).

The Ni-based spinel-type oxides, NiB_2O_4 (B=Al, Fe, Mn), were investigated for their catalysis of the ethanol steam reforming reaction. Ethanol conversion over spinel-type oxides without reduction treatment was comparable to that over γ-alumina supported Ni catalyst reduction. The spinel oxide of $NiAl_2O_4$ showed extremely stable performance for 48 h, while the activity of $NiFe_2O_4$ and $NiMn_2O4$ catalysts was reduced by carbon deposition. Catalyst stability for reforming reaction was closely related to the stability of the nickel metal dispersed on the catalyst surface and the spinel structure. Differences in crystallinity and

surface area among the catalysts were not crucial factors for determining ethanol conversion for $NiAl_2O_4$ calcined between 800°C and 1100°C. the catalyst calcined at 900°C exhibited the highest activity for the reforming reaction (Muroyama et al., 2010).

Al_2O_3, MgO, SiO_2 and ZnO supported nickel catalysts were prepared and evaluated in the steam reforming for hydrogen production. Comparing the conversion of ethanol and selectivity to hydrogen over nickel-based catalysts, at a reaction temperature of 400°C, the result was: Ni/SiO_2>>Ni/Al_2O_3>Ni/ZnO>Ni/MgO. The highest conversion over Ni/SiO_2, could indicate that there is a greater amount of active sites available for this catalyst. However, selectivity to hydrogen was affected by the support used and occurred in the following order: Ni/SiO_2 ~ Ni/MgO>Ni/ZnO>>Ni/Al_2O_3. The low H_2 selectivity presented by Ni/Al_2O_3 could be due to the great C_2H_4 formation promoted by this catalyst. In addition, according to the results, it is possible to conclude that at 400°C only Ni/SiO_2 was active for ethanol steam reforming and at 500°C of reaction temperature, Ni/SiO_2 and Ni/MgO showed activity for ethanol steam reforming (Fajardo et al., 2010).

The reforming of crude ethanol was studied over Ni/Al_2O_3 catalysts (Akande et al. 2005a; Akande, 2005b) suggesting a power law model in the range of temperatures 320 ÷ 520°C. Thus the rate could be expressed as in Eq. 41:

$$-r_A = k_0 e^{-\frac{E}{RT}} C_A^n \tag{41}$$

where "$-r_A$" is in kmol $kgcat^{-1}s^{-1}$, "k_0" is in $kmol^{0.57}(m^3)^{0.43}kg_{cat}^{-1}s^{-1}$, "$C_A$" is crude ethanol concentration in kmol m^{-3}, "n" denotes order with respect to ethanol. The order with respect to ethanol was found to be 0.43 while the energy of activation "E" was found to be 4.41 kJ mol^{-1}. The Eley Rideal type kinetic model was also reported for catalytic reforming of crude ethanol over Ni/Al_2O_3 for temperatures in the range 320 - 520°C (Aboudheir et al., 2006), assuming dissociation of adsorbed crude ethanol as the rate-determining step (Eq. 42):

$$-r_A = \frac{k_0 e^{-\frac{E}{RT}} (C_A - C_C^2 C_D^6 / K_P C_B^3)}{(1 + K_A C_A)^2} \tag{42}$$

where "$-r_A$" is the rate of disappearance of crude ethanol in kmol $kgcat^{-1}s^{-1}$, "k_0" is in m^3 $kgcat^{-1}s^{-1}$, "A" = ethanol, "B" = water, "C" = CO_2, "D" = H_2, "C_i" denotes concentration of species "i" in kmol m^{-3}, "K_P" denotes the overall equilibrium constant in $(kmol\ m^{-3})^4$, "K_A" denotes the absorption constant of A in m^3 $kmol^{-1}$. A kinetic study of ethanol steam reforming to produce hydrogen within the region of kinetic rate control was carried out. A Ni(II)–Al(III) lamellar double hydroxide as catalyst precursor was used. The catalyst, working in steady state, does not produce acetaldehyde or ethylene; H_2, CO, CO_2 and CH_4 were obtained as products. Using the Langmuir–Hinshelwood (L–H) approach, two kinetic models were proposed. The first was a general model including four reactions, two of them corresponding to ethanol steam reforming and the other two to methane steam reforming. When high temperatures and/or high water/ethanol feed ratios were used, the system could be reduced to two irreversible ethanol steam reforming reactions (Mas et al., 2008).

Ni content (wt.%)	Support	r.a.	T (°C)	X_{EtOH} (%)	S_{H2} (%)
10	γ-Al_2O_3	4	600	100	75
10		8	650	100	78.2
15		6	750	100	87
17		3	750	100	93
16.1		3	250	76	44
20		3	700	77	87
20		3	800	100	96
35		6	500	100	91
10	La_2O_3	8	650	100	89.3
15.3		3	250	80.7	49.5
17		3	600	93	87
17		3	700	100	95
17		3	750	100	90
20		3	800	35	70
20		3	500	100	95
15	La_2O_3-Al_2O_3	6	600	100	87
10	TiO_2	4	600	100	86
10	$Ce_{0.5}Ti_{0.5}O_2$	3	600	100	58
30	$Ce_{0.74}Ti_{0.26}O_2$	8	600	98	88
30	$Ce_{0.74}Ti_{0.26}O_2$	8	650	100	93
10	ZnO	4	600	95	80
10		8	650	100	89.1
10	MgO	8	650	100	82.2
17		3	750	100	79
17	YSZ	3	750	100	92
20.6	Y_2O_3	3	250	81.9	43.1

Table 4. Ethanol conversion and initial selectivity to hydrogen obtained on various nickel supported catalysts and different reaction conditions (temperature, water-to-ethanol molar ratio r.a.), at atmospheric pressure

4.3.2 Cobalt

Cobalt (Co) is another non-noble metal catalyst under extensive investigation (Table 5) as supported Co could break C–C bond. Earlier, Co-based catalysts were deemed as appropriate system for steam reforming of ethanol. The use of ZnO-supported cobalt-based catalysts has been proposed for the steam reforming of ethanol (Llorca et al., 2002, 2003, 2004). The use of $Co(CO)_8$ as precursor produced a highly stable catalyst that enabled of the production of CO-free H_2 at low temperatures (350°C). They concluded that the method of catalyst preparation affected its performance and structural characteristics.

The catalytic properties of Co among other metals was also studied (Haga et al., 1998): it was found that selectivity to H_2 was in the order Co>Ni>Rh>Pt, Ru, Cu. In another study found that the supports vastly influenced the properties of Co catalysts (Haga et al., 1997). The formation of H_2 decreased in the order: Co/Al_2O_3>Co/ZrO_2>Co/MgO>Co/SiO_2>Co/C. The Co/Al_2O_3 catalyst exhibited the highest selectivity to H_2 (67% at 400°C) by suppressing

methanation of CO and decomposition of ethanol. Similarly, it was found that Co/MgO is more resistant to coke formation than Co/Al_2O_3 at 650°C (Cavallaro et al., 2001).

It was reported high catalytic activity of Co/SiO_2 and Co/Al_2O_3 for steam reforming of ethanol (Kaddouri & Mazzocchia, 2004), concluding that the product distribution was dependent on both the nature of the support and the method of catalyst preparation, thereby suggesting metal-support interaction. The ethanol steam reforming over Co/Al_2O_3 and Co/SiO_2 was studied (Batista et al., 2004), the catalysts showed average conversion higher than 70 % at 400°C. The metal loading influenced ethanol conversion and product distribution.

The catalytic activity for the ethanol steam reforming of Co_3O_4 oxidized, reduced and supported on MgO, and of CoO in MgO solid solution was investigated. Only samples containing metallic cobalt are found to be active for reforming reaction. It appears that samples containing metallic cobalt are active for the steam reforming of ethanol, whereas Co^{+2} stabilized in MgO solid solution, is able for ethanol dehydrogenation. It has been evidenced that coke deposition is always present in spite of different kinetic conditions and of low ethanol concentration (Tuti & Pepe, 2008).

An excellent ethanol reforming catalysts was performed with cobalt oxides at atmospheric pressure. Apparently, the dehydrogenation of ethanol to acetaldehyde is the first step with cobalt oxides.

$$2C_2H_5OH \rightarrow CH_3CHO_{(ads)} + H_2 \tag{43}$$

The acetaldehyde can be transformed in different pathways: decomposes to methane and carbon monoxide or on the surface of cobalt oxide it can be oxidized to acetate and follow decomposes into methyl group and CO_2.

$$CH_3CHO_{(a)} \rightarrow CH_4 + CO \tag{44}$$

$$CH_3CHO_{(a)} \rightarrow CH_3COO_{(asd)} \tag{45}$$

$$CH_3CHO_{(a)} \rightarrow CH_{3(asd)} + CO_2 \tag{46}$$

In addition, the methyl group can further react with surface OH species or water to form carbon monoxide and hydrogen

$$CH_{3(asd)} + OH_{(asd)} \rightarrow 2H_2 + CO \tag{47}$$

$$2CH_{3(asd)} + 2H_2O \rightarrow 5H_2 + 2CO \tag{48}$$

In the presence of water, the side-reactions of water gas shift (WGS) and methane steam reforming may also occur

$$CO + H_2O \rightarrow H_2 + CO_2 \tag{49}$$

$$CH_4 + H_2O \rightarrow 3H_2 + CO \tag{50}$$

CoO_x catalysts at low temperature possessed high activity. The best sample approached the H_2 yield theoretical value around 375°C. At a molar feed ratio EtOH/H_2O of 1/13 and 22,000 h^{-1}GHSV, the H_2 yield reached 5.72 and only low CO (<2%) and CH_4 (<0.8%) concentrations were detected (Wang et al., 2009).

Also Co/CeO_2-ZrO_2 catalysts were characterized and tested for ESR reaction. It was found that the catalyst reducibility was influenced by the preparation methods; at 450°C, the impregnated catalyst gives a hydrogen production rate of 147.3 mmol/g-s at a WHSV of 6.3 h^{-1} (ethanol) and a steam-to-carbon ratio of 6.5 (Lin et al., 2009).

The ethanol steam reforming was studied at 500 and 600°C on CoZnAl catalysts with different Co loading (9 and 25 wt%) and a Zn:Al atomic ratio nearly constant (about 0.6). the catalysts were active in the ethanol steam reforming at atmospheric pressure in the temperature range studied, but with significant differences in their performance. High hydrogen selectivities, better than 80%, were obtained on catalyst with high Co loading (25 wt%). CO, CO_2 and minor amount of CH_4 were the only carbon produced at 600°C. The catalysts without a previous reduction were very active in the steam reforming of ethanol, with 100% of ethanol conversion at 500 and 600°C. the increase in Co loading decreased the formation of intermediates compounds and improved the H_2 selectivity. At 600°C, the hydrogen selectivity increases from 31 to 86% when Co loading increases from 9 to 25%. This improved behavior was related to the presence of Co_3O_4 on CoZA25 which was mostly reduced to Co^0 and CoO under reforming conditions (Barroso et al., 2009).

Co/ZnO catalyst was applied for ethanol steam reforming, showing high activity with an ethanol conversion of 97% and a H_2 concentration of 73% at a gas hourly space velocity of 40,000 h^{-1} and a moderately low temperature of 450°C. Results on product concentrations at low temperature of 450°C confirm a good and stable performance of Co/ZnO catalyst with H_2, CO_2, CO and CH_4 of 72, 22-25, 2-3, and 1%, respectively (Lee et al., 2010).

Studies using temperature-programmed reaction and isotopic labeling techniques have shown that the reaction network involved in ethanol steam reforming is complex (Song et al., 2010), with many competing reactions taking place depending on the temperature range used, probably in the order reported in Figure 26.

The effect of oxygen mobility on the bio-ethanol steam reforming of ZrO_2- and CeO_2-supported cobalt catalysts was investigated. The catalyst undergoes deactivation; this was due mostly to deposition of various types of carbon on the surface although cobalt sintering could also be contributing to the deactivation. The addition of ceria was found to improve the catalytic stability as well as activity, primarily due to the higher oxygen mobility of ceria. Its use allows gasification/oxidation of deposited carbon as soon as it forms. Although Co sintering is also observed, especially over the ZrO_2-supported catalysts, it does not appear to be the main mode of deactivation. The high oxygen mobility of the catalyst not only suppresses carbon deposition and helps maintain the active surface area, but it also allows delivery of oxygen to close proximity of ethoxy species, promoting complete oxidation of carbon to CO_2, resulting in higher hydrogen yields (Song et al., 2009).

Catalysts based on Co supported on pure silica ITQ-2 delaminated zeolite have been prepared and tested in the bioethanol steam reforming; it exhibited the highest hydrogen selectivity and the lowest CO selectivity. Deposition of coke occurs; however deactivation was not detected during the experimental time (72 h) (Chica & Sayas, 2009).

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \quad (1)$$
$$CH_3CH_2OH \rightarrow CH_4 + CO + H_2 \quad (2)$$
$$CH_3CH_2OH \rightarrow C_2H_4 + H_2O \quad (3)$$
$$CH_3CHO \rightarrow CH_4 + CO \quad (4)$$
$$2CH_3CHO \rightarrow CH_3COCH_3 + CO + H_2 \quad (5)$$
$$CH_3CHO + 3H_2O \rightarrow 2CO_2 + 5H_2 \quad (6)$$
$$CH_3CH_2OH + H_2O \rightarrow 2CO + 4H_2 \quad (7)$$
$$CH_3CH_2OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \quad (8)$$
$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (9)$$
$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \quad (10)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \quad (11)$$
$$CO_2 + H_2 \rightarrow CO + H_2O \quad (12)$$
$$C_2H_4 \rightarrow \text{coke} \quad (13)$$
$$CH_4 \rightarrow C + 2H_2 \quad (14)$$
$$2CO \rightarrow CO_2 + C \quad (15)$$

Fig. 26. Reactions Involved in Ethanol Steam Reforming over Co-Based Catalysts (Song et al., 2010)

Co content (wt.%)	Support	r.a.	T (°C)	X_{EtOH} (%)	S_{H2} (%)
8	Al_2O_3	13	400	74	60-70
18		13	400	99	63-70
8	SiO_2	3	400	89	62-70
18		3	400	97	69-72
10	ZnO	4	350	100	73.4
10 (with Na 0.06 wt% addition)		13	400	100	72.1
10 (with Na 0.23 wt% addition)		13	400	100	73.4
10 (with Na 0.78 wt% addition)	YSZ	13	400	100	74.2

Table 5. Ethanol conversion and hydrogen selectivity obtained on various cobalt supported catalysts and different reaction conditions (temperature, water-to-ethanol molar ratio r.a., in the presence or not of inert gas), at atmospheric pressure

4.3.3 Copper

Cu-based catalyst have received particular attention. The methanol reforming system for industrial H_2 production uses $Cu/ZnO/Al_2O_3$ catalyst (Cavallaro & Freni, 1996): the catalyst exhibited good activity with CO, CO_2 and H_2 as the main product above 357°C.

The steam reforming of ethanol over CuO/CeO_2 to produce acetone and hydrogen has also been studied (Oguchi et al., 2005). The amount of hydrogen produced was not large over CuO, CuO/SiO_2 and CuO/Al_2O_3, indicating that water is not effectively utilized in the reaction. Figure 27 shows that 2 mol of hydrogen was formed from 1 mol of ethanol over CuO/CeO_2 above 380°C; the amount of hydrogen was found to be twice that over CuO/SiO_2 and CuO/Al_2O_3 without KOH treatment. Acetone and CO_2 were also produced. By-products were ethylene, butanal, ethyl acetate, acetal (1,1-diethoxyethane), and a minute amount of unknown compounds. Molar ratios of acetone, CO_2, and H_2 produced per reacted ethanol were 1/2, 1/2, and 2, respectively (Nishiguchi et al., 2005). The formation of acetone could be described by following reaction (Eq. 51):

$$2C_2H_5OH + H_2O \rightarrow CH_3COCH_3 + CO_2 + 4H_2 \quad (51)$$

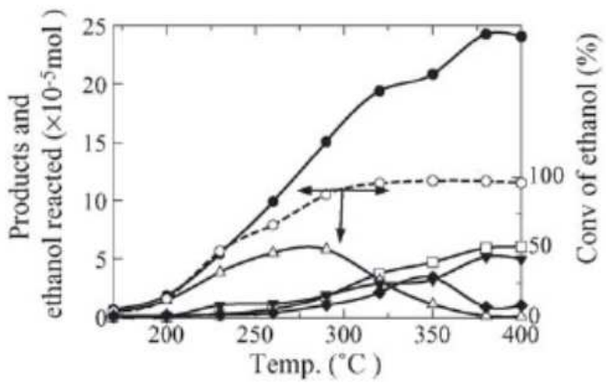


Fig. 27. Steam reforming of ethanol over 20 mol% CuO/CeO_2 (0.5 g): (O) ethanol, (●) hydrogen, (Δ) acetaldehyde, (▼) acetone, (□) CO_2 and (♦) others (Nishiguchi et al., 2005)

4.4 Bimetallic

There is an increasing interest in bimetallic or alloy metal catalysts for ethanol steam reforming; bimetallic catalysts are often used because they have significantly different catalytic properties than either of the parent metals. For example, PtRu catalysts are used in fuel cell applications because of their tolerance to carbon monoxide poisoning. However, it is not easy to predict what to change in catalytic activity will be for a particular bimetallic catalyst.

Ethanol reforming was studied over $Ni/Cu/Cr/Al_2O_3$ catalyst at 300 ÷ 550°C, suggesting that the catalytic effect was more pronounced at lower temperatures (Luengo et al., 1992).

It was found that $Ni\text{-}Cu/SiO_2$ catalyst is more active and selective toward H_2 production in bio-ethanol oxidative steam reforming than Ni/SiO_2 which rapidly deactivates due to coke formation (Fierro et al., 2003). In previous studies, these researchers presented optimization of oxidative steam reforming of ethanol over $Ni\text{-}Cu/SiO_2$ (Fierro et al., 2002; Klouz et al., 2002).

NiZnAl catalysts was prepared by citrate sol–gel method for ethanol reforming at 500–600°C (Barroso et al., 2009). The product distribution was found very sensitive to the alloy

composition. With a Ni loading of 18–25 wt%, high hydrogen selectivity of around 85% was obtained. Ethanol reforming by CeO_2-supported Ni–Rh bimetallic catalyst was studied (Kugai et al., 2005). However, dispersed Ni–Rh redox couple was found instead of a NiRh alloy. The presence of Ni could improve Rh dispersion. Smaller CeO_2- support-crystallite size also improved Rh dispersion and led to strong Rh-CeO_2 interaction.

Cu/Ni/K/γ-Al_2O_3 catalyst exhibited acceptable activity, stability and selectivity to H_2 at 300°C (Mariño et al., 1998, 2001, 2003, 2004). Ethanol dehydrogenation and C–C bond rupture were favored by Cu and Ni, respectively. In addition, K neutralized acidic sites of γ-Al_2O_3, reducing the possibility of coke formation.

A series of Cu–Ni–Zn–Al mixed oxide catalysts were prepared by the thermal decomposition of $Cu_{1-x}Ni_xZnAl$-hydrotalcite-like precursors for ethanol steam reforming. The CuO and NiO were found to distribute on the support ZnO/Al_2O_3. The addition of Cu species facilitated dehydrogenation of ethanol to acetaldehyde, while the presence of Ni led to C–C bond rupture (Velu et al., 2002).

Cu-plated Raney nickel is an active and stable catalyst for low temperature steam reforming of ethanol (250-450°C) (Morgenstern & Fornango, 2005). Methanation was not observed but WGS activity was very poor. The kinetics were modelled by a sequence of two first order reactions: dehydrogenation of ethanol to acetaldehyde (E = 149 kJ/mol) and decarbonylation of acetaldehyde.

Ni–Cu catalysts supported on different materials were tested in ethanol steam reforming reaction for hydrogen production at reaction temperature of 400°C under atmospheric pressure; they were found to be promising catalysts for ethanol steam reforming. Prevailing products can be related to main reactions over catalysts surface. During 8 h of reaction this catalyst presented an average ethanol conversion of 43%, producing a high amount of H_2 by steam reforming and by ethanol decomposition and dehydrogenation parallel reactions. Steam reforming, among the observed reactions, was quantified by the presence of carbon dioxide. About 60% of the hydrogen was produced from ethanol steam reforming and 40% from parallel reactions.

Analysis of reaction products indicated that strong acid sites are responsible for the ethanol dehydration reaction, forming ethylene and diethyl ether, while metallic Ni is responsible for breaking the carbon–carbon bond, increasing the production of C_1 compounds.

The importance of the support for the performance of the Ni–Cu catalysts was evident and indicated a straight relation between support acidity and catalyst efficiency. It was shown that support acidity promotes metal–support interaction, which is a necessary step for the synthesis of catalysts with good stability, high activity and selectivity to the ethanol reforming reaction. However, the acid sites should not be too strong in order to avoid dehydration products, such as ethylene and ethyl ether, which reduce the selectivity to reforming reaction (Furtado et al., 2009).

A parametric study was conducted over Pt-Ni/δ-Al_2O_3 to explore the effect of Pt and Ni contents on the ethanol steam reforming characteristic of the bimetallic catalyst. The best ethanol steam reforming performance is achieved over 0.3wt%Pt-15wt%Ni/δ-Al_2O_3. Kinetic of ethanol steam reforming was studied over this catalyst in the 400-550°C interval using differential and integral methods of data analysis. A power function rate expression was

obtained with reaction orders of 1.01 and -0.09 in ethanol and steam, respectively, and the apparent activation energy of ethanol steam reforming was calculated as 59.3 ± 2.3 kJ mol^{-1} (Soyal-Baltacioglu et al., 2008).

Monometallic Ru and bimetallic Ru-Pt supported nanoparticles, derived from organometallic cluster precursors, were found to be highly efficient ethanol steam reforming catalysts, outperforming all others that were tested under the identical reaction conditions. The high catalytic efficiencies of cluster-derived catalysts are attributed to the very small sizes of the metallic nanoparticles (Koh et al., 2009).

Steam reforming of ethanol was examined over $Co/SrTiO_3$ addition of another metal -Pt, Pd, Rh, Cr, Cu, or Fe- for promotion of the catalytic activity. Ethanol conversion and H_2 yield were improved greatly by adding Fe or Rh at 550°C. Although Rh addition promoted CH_4 formation, Fe addition enhanced steam reforming of ethanol selectively. A suitable amount of Fe loading was in the window of 0.33-1.3 mol%. A comparative study of the reaction over a catalyst supported on SiO_2 was conducted, but no additional effect of Fe was observed on the Co/SiO_2 catalyst. High activity of $Fe/Co/SrTiO_3$ catalyst came from interaction among Fe, Co, and $SrTiO_3$ (Sekine et al., 2009).

Mechanistic aspects of the ethanol steam reforming on Pt, Ni, and PtNi catalysts supported on γ-Al_2O_3 are investigated. The main reaction pathway for ethanol steam reforming over the three catalysts studied was found to be the ethanol dehydrogenation and subsequent acetaldehyde decomposition. For Ni and PtNi catalysts, a second reaction pathway, consisting in the decomposition of acetate intermediates formed over the surface of alumina support, became the main reaction pathway operating in the steam reforming of ethanol once the acetaldehyde decomposition pathway is deactivated (Sanchez-Sanchez et al., 2009).

The influence of the addition of Ni on the catalytic behaviour of a Rh/Y_2O_3-Al_2O_3 catalyst (Rh/Y-Al) was evaluated in the ethanol steam reforming reaction in the presence of methyl-2-propan-1-ol as impurity. It was established that the catalytic behaviour of the Rh/Y-Al base catalyst is widely improved by the addition of Ni. Nickel incorporation leads to the formation of both dispersed nickel phase and nickel aluminate species. Basic properties of the support were not modified by the addition of Ni but it was concluded to a rearrangement of acid sites. $NiAl_2O_4$ phase leads to an increase of the Lewis acid sites (LAS) of weak strength, generating a decrease of the production of coke and higher catalytic stability. It has been shown that the incorporation of Ni on the Rh/Y-Al catalyst increases the rhodium accessibility and stabilizes the rhodium particles size. The higher performances of RhNi/Y-Al catalyst were correlated to an increase in the methane steam reforming activity (Le Valant et al., 2010).

The effect of Fe, Ni, Cu, Cr, and Na (1%) addition over ZnO-supported Co (10%) honeycomb catalysts in the steam reforming of ethanol (ESR) and water gas shift reaction (WGS) for the production of hydrogen was studied. Catalysts promoted with Fe and Cr performed better in the ESR, and the sample promoted with Fe showed high activity for WGS at low temperature. Alloy particles in catalysts promoted with Fe and Cr exhibited a rapid and higher degree of redox exchange between reduced and oxidized Co, which may explain the better catalytic performance (Casanovas et al., 2010).

The catalytic activity of NiM/La_2O_3-Al_2O_3 (M= Pd, Pt) catalysts with different noble metal contents was investigated in the steam reforming of ethanol. Experimental tests of ethanol

steam reforming showed that the catalysts produced a hydrogen-rich gas mixture It was seen that the addition of noble metal stabilized the Ni sites in the reduced state throughout the reaction, increasing ethanol conversion and decreasing coke formation, irrespective of the nature or loading of the noble metal. In the experiments performed at 450°C, the catalysts showed lower H_2 formation and higher acetaldehyde production than the promoted catalysts. Moreover, the bimetallic catalysts showed a higher ethanol conversion and higher hydrogen yield than he Ni/La_2O_3-Al_2O_3 catalyst, irrespective of the nature or concentration of the noble metal (Profeti et al., 2009).

Steam reforming of ethanol for H_2 production was studied over a catalyst prepared by copper and nickel retention on zirconia microsphere. It was concluded that high temperature (550°C), higher water/ethanol molar ratio (3:1) promote on $Ni/Cu/ZrO_2$ high hydrogen yield (60 %) (Bergamaschi et al., 2005).

A series of Co-Ni catalysts has been studied for the hydrogen production by ethanol steam reforming. The total metal loading was fixed at 40% and the Co-Ni composition was varied (40-0, 30-10, 20-20, 10-30 and 0-40). All the catalysts were active and stable at 575°C during the course of ethanol steam reforming with a molar ratio of H_2O:EtOH=3:1. The 40Ni catalyst displayed the strongest resistance to deactivation, while all the Co-containing catalysts exhibited much higher activity than the 40Ni catalyst. The hydrogen selectivities were high and similar among the catalysts, the highest yield of hydrogen was found over the 30Co-10Ni catalyst (He et al., 2009).

Ni-based catalysts doped with copper additives were studied on their role in ethanol steam reforming. The effects of Cu content, support species involving Al_2O_3-SiO_2, Al_2O_3-MgO, Al_2O_3-ZnO, and Al_2O_3-La_2O_3, on the catalytic performance were studied. Activity tests showed that Ni-Cu-based bimetallic catalyst had the best catalytic performance when Cu content was 5 wt%, with the H_2 selectivity for 61.2% at 400°C and 92.0% at 600°C. TPR showed much higher Cu content made the interaction between the support and NiO weak. On the basis of the optimal Cu content, Ni-Cu-based bimetallic catalysts supported on Al_2O_3-M_yO_z (M=Si, La, Mg, or Zn) were prepared to study the effect of composited support on the catalytic performance in the steam reforming reaction of ethanol. The catalysts supported on Al_2O_3-MgO and Al_2O_3-ZnO have much higher H_2 selectivity than that on Al_2O_3-SiO_2 (Zhang et al., 2009).

Ni/Al-SBA-15 mesoporous catalysts have been synthesized in order to study the influence of Al incorporation on their properties and catalytic performance in ethanol steam reforming. It was found that several properties such as mesostructure ordering, acidity, Ni dispersion and nickel-support interaction of Ni/SBA, depend on the Si/Al ratio of SBA-15 support. Ni/Al- SBA presents larger Ni phase particles size and stronger of the metal-support interaction. All catalyst were active in ethanol steam reforming and were selective to hydrogen, but although Ni/Al-SBA catalysts keep almost complete ethanol conversion for Si/Al ratios lower than 60, they showed lower selectivity towards main products. The incorporation of Al atoms into SBA-15 structure is responsible for the formation of catalyst acid sites; therefore Al has a great influence on the product distribution. Support acidity promotes ethanol dehydration, generating high coke amounts and disminishing hydrogen selectivity. Thus, the best catalytic results, in terms of highest hydrogen selectivity and lower coke deposition, were reached with Ni/SBA-15 catalyst (Lindo et al., 2010).

ZnO-supported Ni and Cu as well as bimetallic Co-Ni and Co-Cu catalysts containing ca. 0.7 wt% sodium promoter and prepared by the coprecipitation method were tested in the ethanol steam-reforming reaction at low temperature (250-450°C), using a bioethanol-like mixture diluted in Ar. Monometallic ZnO-supported Cu or Ni samples do not exhibit good catalytic performance in the steam-reforming of ethanol for hydrogen production. Copper catalyst mainly dehydrogenates ethanol to acetaldehyde, whereas nickel catalyst favours ethanol decomposition. However, the addition of Ni to ZnO-supported cobalt has a positive effect both on the production of hydrogen at low temperature (<300°C), and on catalyst stability (Homs et al., 2006).

Since on Pt/CeO_2 catalysts the maximum amount of hydrogen produced is limited by the inability to activate CH_4 at low temperature, a possibility is adding a secondary metal to catalyst composition: nickel, cobalt and silver were selected as secondary metal. The bimetallic Pt-Ni and Pt-Co catalyst supported on CeO_2 exhibited a synergic effect of the active species, giving a H_2 and CH_4 rich stream without any catalyst deactivation, in very diluted reaction conditions. When platinum is present along with nickel, acetaldehyde is converted into H_2 and carbon oxides. Increasing platinum loading the hydrogenation capability of nickel is enhanced; this is confirmed by an increasing in CH_4 selectivity. Higher temperature is not favorable in order to obtain an H_2 and CH_4 rich stream. Over bimetallic Pt-Ni catalyst the formation of CO is favored increasing temperature to 450°C. Long term stability tests reveals that the catalyst 3 wt.% Pt/10 wt.% Ni/CeO_2 is very effective in ethanol steam reforming reaction at 300 °C exhibiting no deactivation in about 13 h of time on stream with no CO formation. No improvement in the performance of Pt-Ni catalysts is observed substituting nickel with cobalt or silver in bimetallic catalysts. The cobalt performance in ethanol steam reforming reaction at 300°C was similar to nickel in bimetallic Pt based catalysts supported on CeO_2. The catalyst 3 wt.% Pt/10 wt.% Co/CeO_2 is highly selective to steam reforming products, also CH_4 selectivity is higher with a stability of about 13 h of time on stream without CO production. The best temperature condition in the low and middle temperature range is 300°C (Ruggiero A., PhD Thesis, University of Salerno, 2009).

The performance of bimetallic PtNi and PtCo catalysts supported on CeO_2 has been investigated in low temperature ethanol steam reforming in both diluted and concentrated reaction mixtures. The catalysts were prepared by two different method, wet impregnation and coprecipitation, to monitor the effect of the preparation technique on the catalysts performances: the catalytic activity is deeply affected by the preparation method, leading to prefer the impregnated samples. The influence of reaction temperature (in the range 250-600°C), dilution ratio, water-to-ethanol molar ratio (in the range 3-6), space time (in the range 7500h-15000h^{-1}) was also studied with respect to catalysts activity, selectivity and durability. The results, in very concentrated conditions, close to the raw bio-ethanol stream conditions, showed that the Pt/Ni catalyst seems to be very promising for the low temperature ESR reaction, since it shows the best performance in terms of activity and selectivity among the investigated catalysts, yet at low contact times (Palma et al., 2010).

A comparative study between the different tendency to produce coke of all the catalysts were also performed, showing that coke formation occurs using the Pt/Ni sample, even if the products distribution doesn't change in an appreciable way during the experiment. This effect can be explained considering that the formation of carbonaceous fibers occurs in the catalytic bed, causing the reactor plugging. Since the gas products distribution is not

affected during the experiment, it could be desumed that the plugging effect is not directly linked to the catalytic site. In fact there aren't evidence of any loss of activity by site blockage or support degradation effect.

From some characterization after the stability test, it could be assumed that the reactor plugging (due to the high pressure drop values reached) is related to the coke deposited on the catalyst, since, about 1% of the overall carbon fed during the test has been found as coke in the sample analysed after the stability test.

A higher water to ethanol seems to be helpful to improve the catalyst durability since the pressure drops increasing occur at higher reaction times, probably due to the strong influence of water in the coke gasification reactions.

The cobalt-based catalysts, despite their not perfect agreement with the equilibrium products distribution, seems to be more durable, in the same operating conditions.

A deeper study of the coke formation mechanism together with the evaluation of the kinetic parameters will be necessary to better know the proposed process, that appears economically feasible and industrially attractive.

5. Conclusion

Although catalytic steam reforming is widely used for hydrogen production, it is not a green process since hydrocarbons are not a renewable source and harmful emissions are produced. Bioethanol is an excellent candidate to replace in the perspective of a hydrogen-based economy. Thermodynamically, the ethanol steam reforming requires relatively high temperatures and low pressures. When the reaction is carried out at moderate temperatures, in order to reduce the thermal duty and the CO amount in the outlet gas stream, the catalyst role is particularly crucial.

Starting from the catalysts proposed in this and other papers, the development of a more advanced catalyst formulation, is necessary and is still a challenge for the scientific research. It is recommended to pay more attention to the reaction mechanism, since there are few studied on this aspect, particularly at low temperatures.

Moreover, the literature mainly deals with the steam reforming of bio-ethanol in which the feed stream is simulated through a mixture of ethanol and water, prepared with the desired water-to-ethanol-molar ratio. Nevertheless, the steam reforming of crude ethanol differs from that of pure ethanol by the fact that the impurities present in the crude ethanol feed may influence the hydrogen yield and the catalyst stability. Very few studies report the use of crude ethanol for hydrogen production by steam reforming but this aspect is very important to consider, since a catalyst more resistant to deactivation could be necessary.

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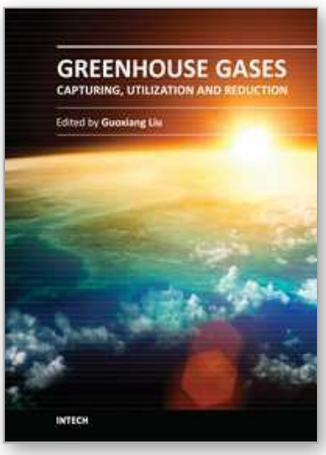
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