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Bimetallic Catalysts for Hydrogen Generation by Low Temperature Ethanol Steam Reforming

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The production of hydrogen through the low temperature-ethanol steam reforming (LT-ESR) reaction requires the development of an efficient catalyst. A bimetallic formulation, based on Pt and Ni and supported on CeO_2 was investigated, in terms of activity, selectivity, stability. Very interesting results were obtained, with a complete ethanol conversion and a perfect agreement between the experimental and equilibrium products distributions, yet at $T \geq 300$ °C, contact time=240 ms and stoichiometric water/ethanol molar ratio. Furthermore, the selectivity towards the desired compounds was very high, with low coke selectivity and appreciable stability, especially with higher water/ethanol ratio. A mechanistic study of the reaction was carried out through the detailed analysis of the experimental evolution of the products distribution as a function of contact time (3 – 600 ms) and temperature (340 – 480 °C). The most significant result was the formulation of a possible $Pt/Ni/CeO_2$ catalysed reaction pathway, that includes the following steps: ethanol adsorption followed by dehydrogenation to acetaldehyde; intermediate decomposition and reforming to CH_4, CO, H_2 and CO_2; CO-WGS and CO_2 methanation reaction. These outcomes were validated by specified characterizations of the exhaust sample, as temperature programmed desorption (TPD) experiments.

1. Introduction

Hydrogen is becoming really attractive as an energy carrier, mainly for fuel cells. There are several method for hydrogen production (Fajardo et al., 2010). Even if steam reforming of natural gas is currently the dominant technology, ethanol steam reforming (ESR) is emerging as a clean and sustainable way (Wang et al., 2010).

The biomass-derived ethanol is characterized by numerous advantages, among which the renewability, non-toxicity and, above all, its direct usability in the ESR reaction as an aqueous solution, avoiding the costs of water separation (Haryanto et al., 2005). In comparison with partial oxidation (POX) and oxidative steam reforming (OSR), the ESR reaction is characterized by higher hydrogen yields at lower temperature, lower reaction rates and a marked endothermicity (Eq. 1).

$$C_2H_5OH + 3H_2O \Leftrightarrow 2CO_2 + 6H_2; \Delta H_{25°C} = 174 kJ/mol \qquad \text{(Eq. 1)}$$

This multi-molecular reaction can lead to a complex equilibrium involving several reactions and giving off numerous by-products such as carbon oxides, methane, ethylene, acetaldehyde, acetone and coke (Ni et al., 2007).

At temperatures higher than 600°C the ESR is thermodynamically favoured while the CO-water gas shift (WGS) reaction it is not promoted; the latter reaction would be necessary because CO is a poison for the PEM fuel cells (Freni et al., 1996). Thus high temperature operations decrease the energy efficiency of the overall energy cycle (Palma et al., 2011) while the low temperature-ethanol steam reforming (LT-ESR) can be helpful for minimizing both the CO formation and the thermal duty (Palma et al., 2012). Several recent papers have proposed different process loops options at low temperatures (Gallucci et al., 2007),

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(Iulianielli et al., 2010) but all these applications have in common the decrease of hydrogen yield at T < 600 °C, in favour of the formation of unwanted by-products, which may in turn be coke precursors (Cavallaro et al., 2003). Therefore, a properly designed catalysts for the steam reforming of ethanol at low temperature (LT-ESR) is considerably important.

Both noble metals (Pd, Pt, Ru, Rh) and non-noble metals (Co, Ni, Cu, Fe) have been studied for ESR reaction (Haga et al., 1998), (Ciambelli et al., 2010); supported on different oxides, as in the following formulations: Al_2O_3, La_2O_3, ZnO, SiO_2, MgO (Yamazaki et al., 2010). Platinum is considered very promising for the ESR and CO-WSG reactions; its high activity and selectivity can be enhanced by using the synergic effect of Co or Ni (Ruggiero et al., 2009).

In the present study the reaction of ethanol steam reforming at temperature lower than 600 °C on a commercial CeO_2-supported Pt/Ni catalyst was carried out. The dependence of the catalytic performance on the reaction temperature, the feed composition and the contact time was studied. Time-on-stream (TOS) experiments were also performed for evaluating the catalyst stability and possible coke formation phenomena. A reaction pathway for the desired reaction was proposed through a mechanistic study of the kinetic of the $Pt/Ni/CeO_2$-catalysed process.

2. Experimental

The catalyst $Pt/Ni/CeO_2$ was prepared by sequential wet impregnations using aqueous nickel acetate $C_4H_6O_4Ni{\cdot}4H_2O$ (Aldrich) and platinum chloride $PtCl_4$ (Carlo Erba Reactants) solutions, respectively, with an intermediate and a final calcination at 600°C. The support was commercially available CeO_2 (Aldrich, BET=$80m^2/g$), calcined at 600 °C (heating rate = 10°C/min).

The effective metal load was determined through the Energy Dispersive X-Ray Fluorescence (EDXRF) analysis (Thermo-Scientific QUANT'X). The specific surface area (SSA) was determined by N_2 adsorption-desorption isotherm at -196°C (B.E.T. method) after a pre-treatment at 150°C for 1 h in He flow, with a Costech Sorptometer 1040. The crystallites phases were detected through X-Ray Diffraction (XRD) technique, using a D-max-RAPID X-ray microdiffractometer, with a cylindrical imaging plate detector. Before each ethanol steam reforming test, the catalyst underwent a temperature programmed reduction (TPR) in situ under 1000 cm^3/min (STP) flow rate of a gas mixture containing 5 vol. % of H_2 in N_2, up to 600°C with a 10°C/min heating rate. The coke formation was detected through the Laser Raman spectroscopy, with a Dispersive MicroRaman (Invia, Renishaw), equipped with 785 nm diode-laser, in the range 100-2500 cm-1 Raman shift. The coke selectivity was calculated through the Thermogravimetric Ananlysis-Mass Spectrometry (TGA-MS), performed through TA Instrument Q600 coupled with PFEIFFER ThermoStar Quadrupole Mass Spectrometer. Temperature Programmed Desorption (TPD) experiments after ethanol adsorption were used as a support for the results of the kinetic studies. The adsorption of 10 vol.% of ethanol in N_2 flow (Total flow rate = 1000 cm^3/min (STP)) was realized at 40 °C and the desorption in N_2 flow was performed, with an heating rate of 10 °C/min, up to 600°C.

The catalytic tests were performed in an experimental set-up, previously reported and described in details (Palma et al., 2011). All the gases employed in this work come from SOL S.p.A with a purity degree of 99.999 %. As a first approach, the catalytic tests were performed with a simulated bio-ethanol mixture, obtained by mixing bidistilled water and pure ethanol, according to the desired water/ethanol ratio, without considering the effect of contaminants like methanol and diethyl ether. The catalytic activity and selectivity tests were performed at a fixed water-to-ethanol molar ratio, equals to 3: it was selected from a thermodynamic analysis, considering that it is the minimum value to avoid coke formation, and considerably lower than the values of a real bio-ethanol mixture (Freni et al., 1996). The other operating parameters were: feed composition = 5 vol. % of ethanol/ 15 vol. % of water/ 80 vol. % of nitrogen; T = 250-600°C; GHSV = 7500 h^{-1}-15000 h^{-1}. The catalytic performance was evaluated through the conversion of reactants, the selectivity towards the main products and the hydrogen yield. The operating conditions of the TOS tests were critical, with the objective to underline the possible coke formation: GHSV = 15000h^{-1}, T= 450°C10 vol.% of ethanol in the feed stream (Carrero et al., 2010).

The evolution of product distribution with contact time, in the range 0-600 ms, and temperature, in the range 350 - 500°C, was investigated. The results were used for the formulation of the LT-ESR reaction pathway over the catalyst $Pt/Ni/CeO_2$.

3. Results and Discussion

3.1 Characterization results

The metal load was optimized through a preliminary screening of different relative amounts of the noble and non-noble metal in the range 1-5 wt.% as Pt and 5-20 wt.% as NiO respectively (Ruggiero et al., 2009).

The results of the main characterization techniques are reported in Table 1.

Table 1 Results of XRF, N_2 adsorption and XRD analysis

Catalyst	Metals content [%]		SSA [m^2/g]	dCeO_2 [nm]	dNiO [nm]
	Pt	Ni			
Pt/Ni/CeO_2	2.8	9.8	60	60	17

3.2 Catalytic activity and selectivity tests

The catalytic performance of the Pt/Ni sample for the ESR reaction is very promising, especially concerning H_2 production and ethanol conversion. The experimental products distribution values are in very good agreement with the thermodynamic equlibrium in the overall temperature range, yet at the low contact time of 240 ms. The carbon mass balance is closed up to 99%, when considering C_2H_5OH, CO, CH_4 and CO_2 as C-containing products. Fig. 1 shows for the same sample and test conditions, the results in terms ethanol conversion (X_{C2H5OH}), hydrogen yield (Y_{H2}) and products selectivity (S_{CH4}, S_{CO}, S_{CO2}) vs. temperature. The ethanol is completely converted, yet at T of about 290°C, and the performances, in terms of H_2 yield, improves with temperature. The CH_4 selectivity showed an opposite trend, and decrease with temperature.

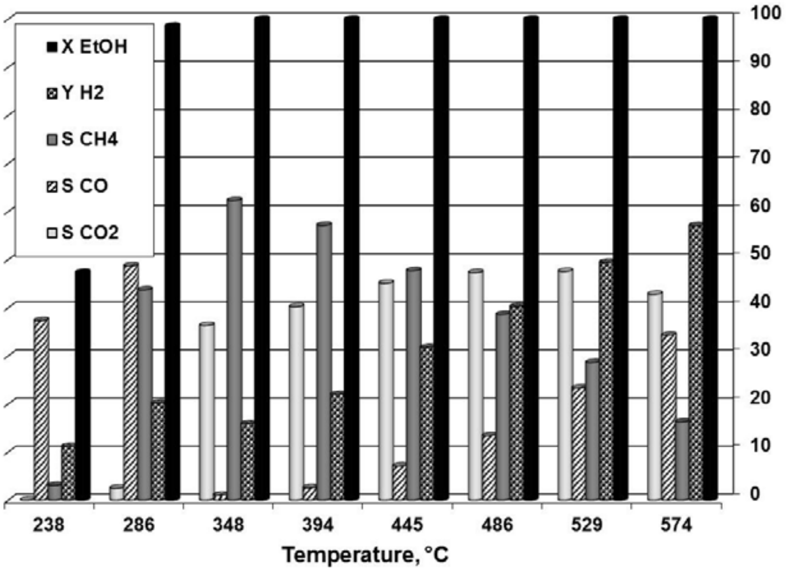

Figure 1 Ethanol conversion (X_{C2H5OH}), Hydrogen Yield (Y_{H2}) and Products selectivity (S_{CH4}, S_{CO}, S_{CO2}) vs. temperature for the Pt/Ni/CeO_2 sample. Operating conditions: GHSV=15000 h^{-1}, feed composition 5vol.%EtOH/15vol.%H2O/80vol.%N_2.

3.3 Time-On-Stream tests and characterization on the used sample

The TOS tests were performed in the following conditions: GHSV= 15000h^{-1}; r.d.= 1.5; r.a.= 3. T=450°C, where r.d. is the dilution ratio, defined in Eq. 2, and r.a. is the water/ethanol molar feed ratio, defined in Eq. 3.

$$r.d. = \frac{moles_{N_2}}{moles_{C_2H_5OH} + moles_{H_2O}} \qquad \text{(Eq. 2)}$$

$$r.a. = \frac{moles_{H_2O}}{moles_{C_2H_5OH}} \qquad \text{(Eq. 3)}$$

These conditions are particularly severe, and were specifically chosen to enhance the coke formation and the catalyst deactivation phenomena. The results of the TOS test revealed a few coke deposition: after 300 min of time on stream there was no appreciable change in the products distribution but a sensible increase in the pressure drops up to 1 bar, making necessary stopping the experiment. Some characterizations after the time on stream test were carried out; from XRD analysis on the used sample, no considerable variation are evidenced in the dimensions of CeO_2 and NiO crystallites, excluding any sintering phenomena. A considerable increase in the SSA value of the same after the TOS test was noticed, changing from 40 to 60 m^2/g: this could be likely related to the formation of micro-porosity into the catalyst particles and/or the presence of some solid species characterized by a higher SSA, i.e. carbonaceous compounds. The deposition of coke on the catalyst surface was also confirmed by the Raman spectrum, where it was possible to detect the typical peaks of carbonaceous species at a Raman shift of about 1350 cm^{-1} and 1590 cm^{-1} (Lin et al., 2009). From TGA-MS analysis after the TOS, it was measured a weight loss of about 3.4% in the range 400-600°C, corresponding to the CO_2 formation in the gas phase and observed in the MS data for the m/z=44, confirming the presence of carbonaceous compounds on the used sample. For the previous test relevant to the Pt/Ni sample, the quantitative analysis revealed a very low carbon selectivity (about 0.6%), thus not quantifiable from the carbon mass balances and not able to deactivate the active sites during the test time.

In addition, the coke formation tendency could be further reduced by changing the operating conditions. For instance, the TOS test was also performed at r.a. = 6, 9 an 18. As shown in Figure 2, by doubling the water-to-ethanol molar ratio, the time required to reach 1 bar of pressure drop was about doubled (600 min), the SSA value doesn't significantly change after the TOS test and the coke selectivity is lower. In addition, by further increasing the water-to-ethanol molar ratio up to 18 (close to the S/C ratio of the real bio-ethanol stream), any change in the pressure drops profile is visible.

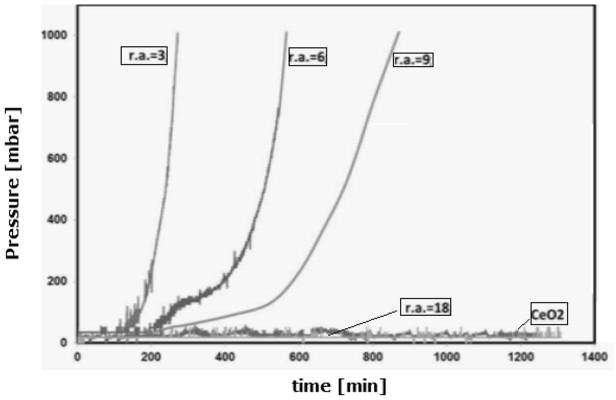

Figure 2 Pressure drop vs. time during the stability test in concentrated catalytic tests for the Pt/Ni/CeO_2 catalyst (Total flow rate=1000Ncc/min; GHSV=15000h^{-1}; r.a.=3 - 18) and CeO_2 (Total flow rate=1000Ncc/min; GHSV=15000h^{-1}; r.a.=3)

3.4 Mechanistic study of the reaction

The behaviour of the products distribution at 370 °C in the range 0-600 ms revealed that at very low contact time, for values lower than 4 ms, no ethanol and steam conversion is obtained. This could be an index of a characteristic time for the adsorption of the reactants before activating the reaction. Few ms later, only the acetaldehyde appears in the gas phase, and simultaneously the ethanol concentration decreases. Starting by 8 ms, the hydrogen is revealed in the gas phase, together with the CH_4 and CO, and a lower CO_2 concentration. The CO profile reaches a maximum at about 16 ms and after decreases, while the CO_2 and H_2 concentrations still increase, in very good agreement with the stoichiometry of the WGS reaction. In the range 20-45 ms, CO, CO_2, CH_4 and H_2 still increase while C_2H_5OH and C_2H_4O is totally converted. Up to about 100 ms, the H_2 concentration and the H_2O uptake increasing simultaneously, where a maximum is observed for CO_2 and H_2. After this point, another reaction occurs between the CO_2 and the H_2, driving the system to the equilibrium composition. In fact, in the range 100-400 ms the concentration changes in the gas phase follows the stoichiometry of the methanation reaction. At contact times ≥ 400 ms, the gaseous composition is in perfect agreement with the equilibrium. This evolution of products distribution suggests a set composed by different reactions, activated at different contact times: ethanol dehydrogenation (Eq. 4), ethanol decomposition (Eq. 5), acetaldehyde steam reforming (Eq. 6), acetaldehyde decomposition (Eq. 7), CO-WGS (Eq. 8) and CO_2-methanation (Eq. 9).

$$C_2H_5OH \leftrightarrow C_2H_4O + H_2; \Delta H_{25°C} = 68 kJ/mol \tag{Eq. 4}$$

$$C_2H_5OH \leftrightarrow \frac{1}{2}CO + \frac{3}{2}CH_4; \Delta H_{25°C} = -74 kJ/mol \tag{Eq. 5}$$

$$C_2H_4O + H_2O \leftrightarrow 2CO + 3H_2; \Delta H_{25°C} = 213 kJ/mol \tag{Eq. 6}$$

$$C_2H_4O \leftrightarrow CH_4 + CO; \Delta H_{25°C} = -134 kJ/mol \tag{Eq. 7}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2; \Delta H_{25°C} = -41 kJ/mol \tag{Eq. 8}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O; \Delta H_{25°C} = -253 kJ/mol \tag{Eq. 9}$$

The results of these tests and of the analysis of the recent literature suggested us to hypothesize a specified set of reactions, that were used for the formulation of the reaction pathway over Pt/Ni/CeO_2. the reaction pathway at 370°C includes different consecutive or parallel steps: the ethanol could undergo a dissociative adsorption on the catalyst surface, as confirmed by literature (Sannino et al., 2012a), (Murcia et al., 2012) and observed by the results of TPD experiments. It has been considered that the adsorbed ethanol could dehydrogenates to form an acetaldehyde intermediates (Sannino et al., 2012b.), (Murcia et al., 2012b). Subsequently, the acetaldehyde may undergoes a C-C bond rupture through two competitive reactions: decomposition to CO and CH_4 and steam reforming to CH_4, CO and H_2 (Song et al., 2010). The obtained carbon monoxide is converted into CO_2 and additional H_2 through the CO-WGS reaction. The last step is the methanation reaction, that enables the system to reach the equilibrium composition (Barroso et al, 2009).

4. Conclusions

The performances of a bimetallic catalytic formulation, based on Pt and Ni and supported on CeO_2, was investigated for the ethanol steam reforming at 250 – 600 °C. The catalyst 3wt.%Pt/10wt.%Ni/CeO_2 showed high activity in the desired reaction, with a products distribution in agreement with the equilibrium calculation (yet at a low contact time equal to 240 ms), a complete ethanol conversion (yet at T > 300 °C); high H_2 yield and a very low coke selectivity (less than 1%). By increasing the water-to-ethanol molar ratio up to 18, it is possible to obtain a coke selectivity equal to zero, index that the carbon formation and the carbon gasification rates are comparable. The evolution of the products distribution as a function of contact time (0 – 600 ms) and temperature (340 – 480 °C) was also examined with the purpose to formulate the possible reaction pathway. The set of reactions involved in the process was detected and it was proposed a possible reactions sequence at 370°C including the following steps: ethanol adsorption followed by dehydrogenation to acetaldehyde; intermediate decomposition and reforming to CH_4, CO, H_2 and CO_2; CO-WGS and CO_2-methanation reaction.

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