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Bio-Ethanol Steam Reforming Reaction Over Bimetallic Ceria-Supported Catalysts

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Hydrogen is mainly produced through the steam reforming of natural gas. Despite the advantages related to the well known technology, this method has some drawbacks due to the non renewability of the feedstock and to the production of harmful emissions. The use of bio-ethanol as the raw material for the steam reforming process could overcome these limits, in particular at the low temperature it is possible to reduce the thermal duty and the production of carbon monoxide. Considering that also by-products productions coudl occur, a very active and stable catalyst is needed, able to minimize CO and coke formation. This work focuses on the performance of bimetallic catalysts for the low temperature-ethanol steam reforming (LT-ESR reaction), investigated in terms of activity, selectivity, stability and reaction mechanism.

1. Introduction

The growing demand for environmental sustainability lead the attention of researchers on the replacement of fossil fuels for energy production, since they produce harmful emissions and are not renewable. As an alternative fuel hydrogen is ideal, producing little or no emissions, with a plentiful supply available. The full environmental benefit of a society transition to hydrogen as a new energy source is achieved only when the hydrogen can be derived from renewable feedstocks. In particular biomass-derived ethanol (bio-ethanol) presents several advantages such as natural availability, storage and safe handling (Yamazaki et al., 2010). Hydrogen can be produced from ethanol using different reforming reactions, including ethanol steam reforming (ESR), partial oxidation (EPO), oxidative steam reforming (OESR) and ethanol decomposition (ED). The ESR reaction based process seems to be the most convenient method since: (1) the water present in bio-ethanol can be used as a reactant; (2) the product, H_2, is insoluble in water without the necessity of separation costs; (3) the process ensures the production of 6 moles of hydrogen from 1 mole of ethanol, using a well know technology (Aupretre et al., 2005). Thermodynamic analysis have shown that, under steam reforming conditions, the reaction system is more complex and ethanol can undergo some secondary reactions with various undesired by-products, possible coke precursors. Silveira et al. (2009) showed that high temperature and low pressure, together with a high water-to-ethanol molar ratio in the feed stream, have been found to be the best operating conditions to favour the direct conversion of ethanol toward H_2 and CO_2. On the other hand, the main hydrogen application as an energy vector is the feed of fuel cells, and the CO impurity in the hydrogen stream from the ESR products cause poisoning of the fuel

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cell anode catalyst. As a consequence, some downstream purification processes are required such as the exothermic water gas shift (WGS) reaction, that further converts CO and produces H_2.

The high temperature ESR reaction coupled with the low temperature WGS one suffers from thermal inefficiencies (Roh et al., 2006). In this perspective, despite its endothermic nature, the ESR reaction could be carried out at low temperature, in order to depress CO formation and, simultaneously, allow the overall thermal efficiency be increased and the costs be reduced (Ciambelli et al., 2009). Nevertheless, reduced H_2 yield with lower catalyst selectivity and durability could be the main disadvantages linked to these operating conditions. Thus kinetic rather than thermodynamic control of the reaction is required (Ciambelli et al., 2010a).

Studies of ethanol steam reforming catalysts have therefore increased significantly in recent years to find the optimal catalyst for the process, but only few papers are available concerning the low temperature operating range. The ESR over noble metals such as noble and transition metals has been reported. The noble metals (Rh, Pt, Pd) promote dehydrogenation, decomposition and WGS reactions, that are in favour of H_2 production. Noble metals supported on different ionic oxides such as Al_2O_3, TiO_2 and CeO_2 have been studied and found promising. Their performance was improved by the presence of water and oxygen. The non noble metals (Ni, Co, Mg) have been investigated in ESR reaction, on various supports. They are able to break the C-C bonds on surface intermediates to produce CO and CH_4 (Diagne et al., 2002). Ceria is the most commonly used support, since it has a lot advantages such as redox properties and oxygen storage/release capacity, that favour coke removal reactions (Muroyama et al., 2010).

In this work, we aimed to prepare bimetallic catalyst that possess high activity, selectivity and durability for low temperature ESR reaction. Starting from our previous results (Palma et al., 2011), some catalysts, based on Pt and Ni or Co, and supported on ceria were investigated for the desired reaction, with focus on the effect of main macroscopic parameters, such as the reaction temperature, the N_2 dilution ratio (r.d.), and the water-to-ethanol molar ratio (r.a.).

2. Experimental methods

2.1 Catalyst preparation

In this work different bimetallic catalysts have been tested, based on Pt (3 wt%) and Ni or Co (10 wt%) and supported on commercially CeO_2, Aldrich, BET surface area of 60 m^2/g after calcination. They were prepared by wet impregnation: it was necessary the dispersion of the calcined support into an aqueous solution of one the two active metals precursors, that were platinum chloride $PtCl_4$, nickel acetate $C_4H_6O_4Ni \cdot 4H_2O$ and cobalt acetate $(C_2H_3O_2)_2 \cdot 4H_2O$. All chemicals used were HPLC grade obtained from Aldrich. To add the second metal, the just impregnated support was dried at 120 °C overnight and calcined in air at 600 °C for 3 h (dT/dt= 10 °C/min) in a muffle furnace. After the second impregnation step, the resulting solids was dried and calcined.

2.2 Catalyst characterization

The catalysts were characterized by different techniques. The chemical analysis was performed by Energy Dispersive X-Ray Fluorescence (XRF), using a Thermo-Scientific QUANT'X. X-ray diffraction (XRD) patterns were collected on a D-max-RAPID X-Ray microdiffractometer, with a cylindrical imaging plate detector, that with Cu-Kα radiation allows to collect the diffraction data from 0 to 204° (2θ) horizontally and from -45 to 45° (2θ) vertically. N_2 adsorption at -196 °C (BET method) was used to measure the specific surface area of the catalyst after calcination. The instrument was a Costech adsorption equipment, SORPTOMETER 1040 "Kelvin" by Costech Analyitical Technologies. TPR were carried out in the laboratory apparatus before ESR test, reducing the catalyst in situ with 5 %vol of H_2 in N_2, at 600 °C for 1 h at 10 °C/min. The thermogravimetric analysis (TG) was carried out through a thermogravimetric analyzer *TA Instrument Q600*, coupled with a PFEIFFER ThermoStar Quadrupole Mass Spectrometer (MS).

2.3 Catalytic tests

Catalytic performance tests were performed in a specifically developed lab-scale plant (Figure 1). The liquid water-ethanol-mixture, controlled through a Coriolis controller (Brooks-Quantim), is diluted with gaseous N_2, sent into a boiler and then inside a tubular stainless steel (AISI-310) reactor. The catalyst powder (180-355 μm) is located in the annular section of the reactor (18 mm i.d.), placed in a three zone electric oven. Effluent gases were analyzed through an online Nicolet Antaris IGS FT-IR multigas analyzer, equipped with an heated gas cell, designed with an optical path length of 12 cm, operating at temperature up to 185 °C and a MCT-A N_2 liquid cooled detector. The data were acquired at 0.5 cm^{-1} and cell temperature and pressure were monitored and used to correct gas concentrations. The H_2 and O_2 concentrations on dry base were measured respectively by CALDOS 27 and MAGNOS 206, ABB continuous analyzers.

All the catalytic activity tests were carried out in the following operating conditions: total gas flow rate= 1000 cm^3/min(STP); r.a.= 3; r.d.= 4, 1.5 and 0.67, corresponding to an ethanol concentration of 5, 10 and 15 % vol in the feed stream, respectively; T= 250 ÷ 600 °C, GHSV= 7,500÷15,000 h^{-1}. The stability tests were performed by fixing the following values : GHSV= 15,000h^{-1}, r.d.= 1.5, T = 450 °C; r.d.= 3.

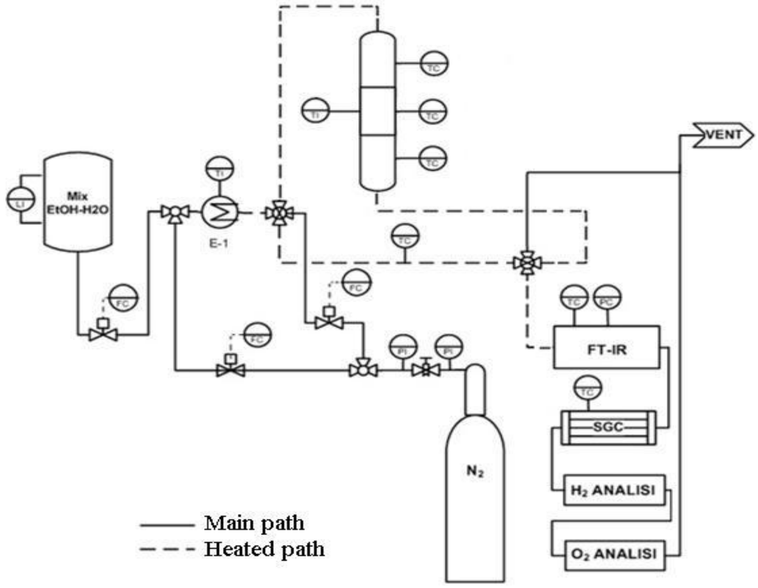

Figure 1: ESR laboratory plant

3. Results and discussion

3.1 Catalyst characterization results preparation

In Table 1 all specific surface area values of the support and the catalysts after calcination are reported, showing that the deposition of the active species causes a specific surface area decrease.

Table 1. Specific surface area (SSA) of catalysts and support

Catalyst	SSA [m^2/g] after calcination
Pt/Ni	42
Ni/Pt	39
Pt/Co	39
Co/Pt	25
CeO_2	60

3.2 Catalytic activity tests

The tests were performed in very severe conditions, in particular in terms of r.a. (since, from the thermodynamic analysis, 3 has been evaluated as the minimum value to avoid coke formation when thermodynamic equilibrium occurs) and temperature (since the desired reaction is favored at temperatures higher than 600 °C). In Fig. 2 there are the products distributions at the reactor outlet for some catalysts after catalytic tests, in comparison with the equilibrium expected trend. According to the equilibrium calculation, the ethanol should be almost completely converted . Moreover, the H_2 yield and CO and CO_2 selectivities should increase with temperature increasing while CH_4 selectivities should decrease with temperature increasing. The catalytic performances of the tested catalysts are very promising. In particular, using the 3 wt% Pt / 10 wt% Ni / CeO_2 catalyst, it is possible to obtain the best agreement with the thermodynamic trend, yet at low contact times, as shown in Figure 2. The Ni/Pt catalyst leads to a products composition that is in worse agreement with the equilibrium calculations (Figure 3), especially at low temperatures, where the H_2 and CO concentrations are higher than the thermodynamic ones and the ethanol conversion is not complete.

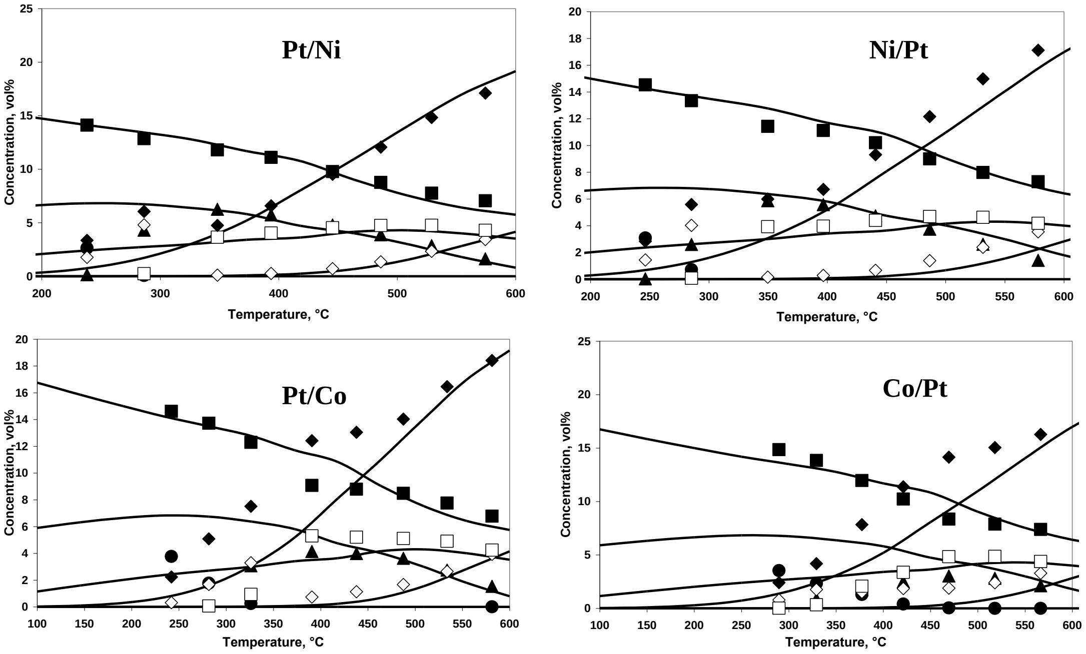

Figure 2: Experimental (points: ■ H2O ♦H2 ▲ H4 □ CO2 ◊ CO ● C2H5OH) and equilibrium (lines) products distribution as a function of temperature for different catalysts in concentrated catalytic tests (Total flow rate=1000 Ncc/min; GHSV=15,000 h-1; r.d.=4; r.a.=3)

It can be observed that the products trend is not so close to the thermodynamic one in the case of the Pt- and Co-based catalysts is case and the H_2 production is higher than the expected one, notwithstanding the method used to prepare the catalyst. Also for the Co-based catalyst, the inversion of the impregnation order decreases the catalytic activity, despite higher H_2 yields values.

From these preliminary results, the catalysts prepared in the impregnation order Pt/M (M=Ni, Co) are more selective and active, suggesting that platinum should be direct available on the catalyst, in according with literature (Yakimova et al., 2009; Ciambelli et al., 2010b; Palma et al., 2011).

The catalytic activity and selectivity have been tested, at different temperature, in more concentrated reaction mixture (r.d.=1.5, 0.67). The catalysts performance is negatively affected by the higher ethanol content in the feed stream, in particular at low temperatures but the products distribution obtained with the Pt/Ni catalyst in more concentrated conditions (Figure 3) is still interesting. At temperature lower than 450 °C, it is possible to observe a strong disagreement between the experimental products distribution and the equilibrium trend. The effect is stronger in the most concentrated conditions (r.d. = 0.67), corresponding to 15 wt% of ethanol in the feed stream. The influence of the higher ethanol amount in the gas reaction mixture is more evident when observing the ethanol conversion. Its trend suggests that kinetic limitations occur: probably the reaction rate, in these highly concentrated feed conditions, is lower than the minimum required to achieve the complete ethanol conversion.

3.3 Stability tests

The stability of the catalysts has been preliminarily tested. The time-on-stability tests were performed by fixing the following values : GHSV= 15,000 h^{-1}, r.d.= 1.5, T=450 °C; r.d.= 3. A strong concentrated feed mixture has been used to further underline possible catalyst deactivation phenomena.

In Figure 4A, the products distribution as a function of time is reported, for the Pt/Ni sample during the stability test. Any apparent deactivation phenomena occur on the products distribution when the ESR has been carried out on this catalyst, but a simultaneous dramatic increase in the pressure drop has been observed during the experiment (Figure 4B). This result can be explained considered that the formation of carbonaceous fibres occurs in the catalytic bed, causing the reactor plugging. Since the gas products distribution is not affected during the experiment, 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.

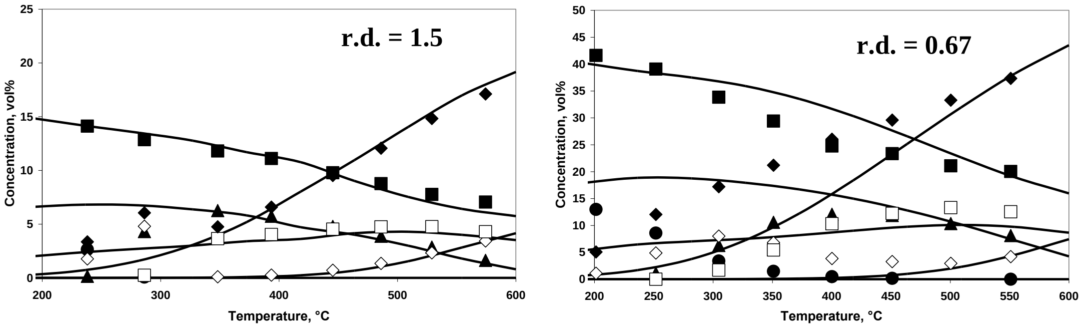

Figure 3: Experimental (points: ■ H2O ♦H_2 ▲ CH_4 □ CO_2 ◊ CO ● C_2H_5OH) and equilibrium (lines) products distribution as a function of temperature for different catalysts in concentrated catalytic tests (Total flow rate=1000 Ncc/min; GHSV=15,000 h-1; r.a.=3)

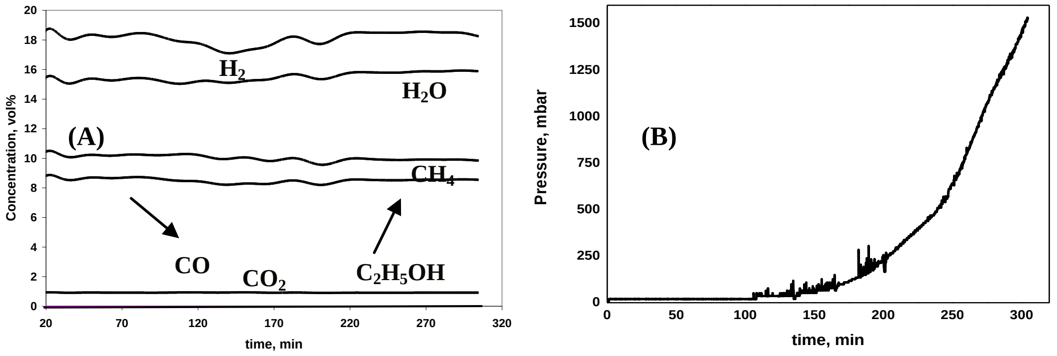

Figure 4: Experimental product distribution (A) and pressure drops profile (B) as a function of time during the stability test in concentrated catalytic tests for Pt/Ni catalyst (Total flow rate = 1000 Ncc/min; GHSV = 15,000 h^{-1}; r.d.= 4; r.a.=3)

From TG analysis performed after the 300 min of 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.

The same problems occur with the other samples, even if the same amount of coke has been detected in the impregnated Pt- and Co-based catalysts after a higher reaction time (about 800 min).

4. Conclusions and perspective

Bimetallic Pt-Ni and Pt-Co catalysts supported on CeO_2 were prepared by impregnation, characterized with various techniques and tested for low temperature ESR reaction. The effect on the catalysts properties of the preparation method and some parameters such as temperature and dilution ratio and GHSV has been investigated through a careful analysis of the gaseous stream composition.All the tested catalysts are very interesting and effective for the desired reaction in terms of H_2 production, in particular, when the noble metal is added as the last one), in terms of activity and selectivity. The Pt/Ni catalyst is the most activity and selective one towards the low temperature-ESR reaction, among the tested samples. It is still interesting in very concentrated conditions and in terms of stability. Concerning to the catalyst stability, the considerations are different: coke formation occurs using the Pt/Ni sample, even if the products distribution doesn't change during the experiment. 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 deep study of the reaction mechanism will better explain all the differences between the catalysts performance.

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