

## Catalytic Activity of CeO<sub>2</sub> Supported Pt-Ni and Pt-Co Catalysts in the Low Temperature Bio-Ethanol Steam Reforming

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Low temperature bio-ethanol steam reforming (ESR) can be considered a promising method to produce H<sub>2</sub>, owing the increase of thermal efficiency and reduction of capital costs. However, some detrimental effects such as lower H<sub>2</sub> selectivity and catalyst deactivation can occur, making crucial the catalysts selection. The aim of this work is to study bimetallic Pt based catalysts for the low temperature ESR reaction in concentrated reaction mixture. Preliminary results concerning economic aspects are also reported.

### 1. Introduction

Recently, there is a growing interest in the search of clean energy sources such as hydrogen, particularly if produced from renewable feedstock instead of fossil fuels, due to the huge amount of GHG emissions deriving from their conversion processes. Among the others, CH<sub>4</sub> steam reforming is considered the most competitive way to produce H<sub>2</sub>, despite its poor tendency to provide a sustainable energy development (Ni et al., 2007). In contrast, ESR (C<sub>2</sub>H<sub>5</sub>OH+3H<sub>2</sub>O=2CO<sub>2</sub>+H<sub>2</sub>;  $\Delta H^0_{25^\circ\text{C}}=+173.5$  kJ/mol) can be a promising alternative method to produce H<sub>2</sub>, since biomass-derived ethanol is renewable, nontoxic, liquid, easy-to-handle and directly usable as an aqueous solution. Due to the high reaction endothermicity, the ESR reaction was deeply studied at high temperatures, thus enabling high H<sub>2</sub> yield but in turn making less favorite the water gas shift reaction (CO+H<sub>2</sub>O=CO<sub>2</sub>+H<sub>2</sub>,  $\Delta H^0_{25^\circ\text{C}}=-41.2$  kJ/mol) for CO abatement. Therefore, low temperatures ESR reaction simultaneously allows a lower thermal duty and a higher plant compactness, thereby reducing the investment capital costs. However, H<sub>2</sub> selectivity decreasing and catalyst deactivation phenomena due to coke formation, lead to a careful catalyst selection. Typically, noble (Pt, Pd, Ru, Ir, Rh) and non noble (Ni, Co) metals based catalysts supported on reducible (CeO<sub>2</sub>) and non reducible (Al<sub>2</sub>O<sub>3</sub>) oxides are reported in literature (Ciambelli et al., 2010a, Song et al., 2010).

In this work the performance of Pt-Ni and Pt-Co catalysts supported on CeO<sub>2</sub> in the low temperature ESR reaction was investigated, evaluating the effect on catalysts activity and selectivity, of catalyst preparation method, temperature, space velocity (GHSV) and reactants mixture dilution. Preliminary evaluations of several economic aspects are also reported.

## 2. Experimental

### 2.1 Catalysts preparation and characterization

Pt and non-noble metals M (M=Ni or Co) were supported on commercially available CeO<sub>2</sub> (Aldrich, BET surface area of 60 m<sup>2</sup>/g after calcination). The catalysts were prepared by wet impregnation and coprecipitation, dried and calcined in air at 600°C for 3 h. For the first method, two sequential impregnations were performed: when the non-noble metal is added to the support before the platinum a Pt/M catalyst was obtained, while in the reverse order a M/Pt catalyst is achieved. Coprecipitated sample were denoted as Pt-M. Metal load is 3 wt% of Pt and 10 wt% of M. Catalysts was characterized by X-Ray Diffraction (XRD), N<sub>2</sub> adsorption at -196°C and Temperature Programmed Reduction (TPR).

### 2.2 Catalysts activity test

The laboratory apparatus employed for the catalytic activity evaluation with concentrated reaction mixture is reported in Figure 1.

The preliminary activity tests were performed in diluted conditions, feeding the reactants, water and ethanol, through saturation of a nitrogen flow at fixed temperature, while in concentrated conditions a feed equipment to carry out the proper liquid fuel vaporization was introduced. The powder catalysts (180÷355 μm) was loaded in a continuous flow fixed bed reactor (18 mm i.d.) placed in a three zone electric oven.

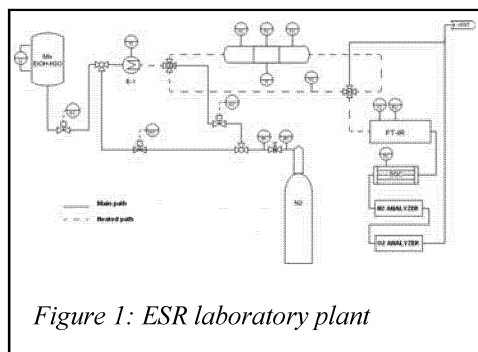


Figure 1: ESR laboratory plant

The reactor outlet concentrations of C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O, CH<sub>4</sub>, CO, CO<sub>2</sub> and other by-products were monitored with an on line Nicolet Antaris IGS FT-IR multigas analyzer, equipped with an heated gas cell operating at temperature up to 185°C and a MCT-A N<sub>2</sub> liquid cooled detector. The data were acquired at 0.5 cm<sup>-1</sup> and cell temperature and pressure were monitored and used to correct gas concentrations. The gas cell used in diluted conditions was characterized by an optical path length of 2 m while in concentrated conditions a new gas cell with an optical path length of 12 cm was re-designed and tested. The H<sub>2</sub> and O<sub>2</sub> concentrations were measured respectively by CALDOS 27 and MAGNOS 206, ABB continuous analyzers.

The catalytic activity tests in diluted environment were carried out in the following operating conditions: P= 1 atm, T= 300°C, GHSV= 15000 h<sup>-1</sup>, Q<sub>TOT</sub>= 1000 Ncm<sup>3</sup>/min, feed gas composition = EtOH/H<sub>2</sub>O/N<sub>2</sub> = 0.5/1.5/98 vol %. In concentrated conditions, at a fixed water to ethanol feed ratio of 3, different dilution ratios defined as  $\frac{\text{moles N}_2}{\text{moles EtOH} + \text{moles H}_2\text{O}}$  (r.d=4, 1.5, 0.67) were used, corresponding respectively to 5,10 and

15% vol of ethanol in the feed stream. The temperature range was 300-500°C, and the GHSV ranging between 7500 h<sup>-1</sup> and 15000 h<sup>-1</sup>.

### 3. Results

#### 3.1 Catalyst characterization

For all the samples, the active species deposition causes a decrease of the specific surface area (SSA) to  $40 \text{ m}^2/\text{g}$ , except for the Co/Pt catalyst ( $25 \text{ m}^2/\text{g}$ ).

In the XRD spectra (Figure 2), all samples showed the peaks relevant to the support and to NiO and  $\text{Co}_3\text{O}_4$ , while the  $\text{PtO}_x$  species were not detected. Ceria and non noble metal oxides crystallites size was about 20 nm, except for the coprecipitated sample, whose  $\text{CeO}_2$  crystallites dimension significantly decreases ( $\sim 7 \text{ nm}$ ).

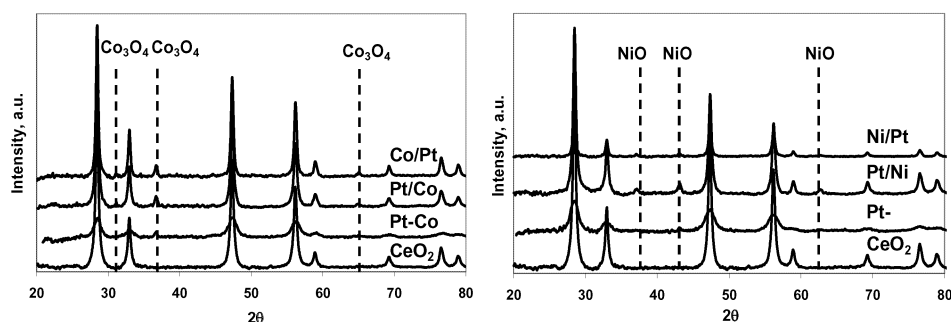


Figure 2: XRD spectra of PtNi and PtCo catalysts

The reduction profiles of PtNi and PtCo catalysts were reported in Figure 3.

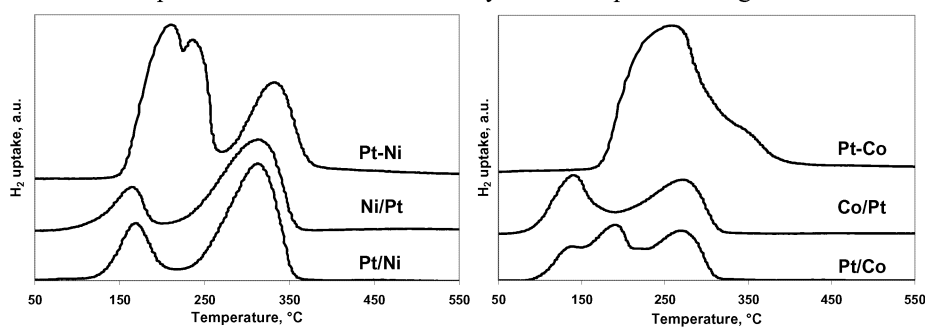


Figure 3: TPR profiles of PtNi and PtCo catalysts

For impregnated samples, two peaks may be observed, that at lower temperature can be ascribed to the  $\text{PtO}_2$  species reduction, that at higher temperature to NiO and  $\text{Co}_3\text{O}_4$  reduction (Ciambelli et al., 2010a), (Heracleous et al., 2005, Paryjczak et al., 1980). The impregnation order and the preparation method have a great effect on catalysts reducibility; furthermore, the catalysts obtained through coprecipitation showed an experimental  $\text{H}_2$  uptake higher than the expected one ( $3339$  vs  $2010 \text{ mmol}/\text{g}_{\text{cat}}$  for PtNi and  $3800$  vs  $2570 \text{ mmol}/\text{g}_{\text{cat}}$  for PtCo), likely due to an higher reducibility of  $\text{CeO}_2$ . This fact may be induced by several effects: lower ceria crystallites dimensions, stronger metal-metal-support interactions and a lower promotion of the spillover effect when the noble metal is not directly available on the support surface (de Leitenburg et al., 1997).

### 3.2 Catalytic activity tests in diluted condition

Results of catalytic activity tests performed in diluted conditions are reported in Table 1.

Table 1: Ethanol and water conversion and hydrogen yield in diluted catalytic tests

Catalyst	$X_{\text{EtOH}}$ [%]	$X_{\text{H}_2\text{O}}$ [%]	$Y_{\text{H}_2}$ [%]
Pt/Ni	100	49	45
Ni/Pt	100	31	31
Pt-Ni	100	28	55
Pt/Co	99.9	41	46
Co/Pt	100	18	55
Pt-Co	87	15	45

The catalysts obtained through impregnation showed a better performance, especially when the non-noble metal is added before the noble one. Coprecipitated samples, in spite of the high  $\text{H}_2$  yield, showed poor and non stable activity towards reactants conversion. Furthermore, the Pt-Co catalyst resulted less selective since acetaldehyde is detected in the output gaseous stream. These results suggest that it could be crucial to have Pt directly available at the gas-solid interface to favour ethanol adsorption (Ciambelli et al., 2010b).

### 3.3 Catalytic activity tests in concentrated conditions

The product distribution at the reactor outlet as function of temperature is reported in Figure 4. At r.d.= 4, for Pt/Ni catalyst there is a good agreement between experimental and equilibrium data while for Pt/Co, in particular at lower temperatures, the two values disagree.

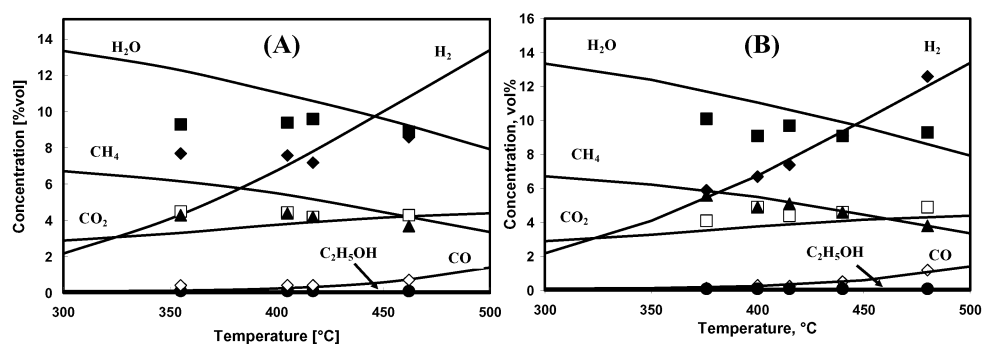


Figure 4: Experimental (points: ■  $\text{H}_2\text{O}$  ◆  $\text{H}_2$  ▲  $\text{CH}_4$  □  $\text{CO}_2$  ◇  $\text{CO}$  ●  $\text{C}_2\text{H}_5\text{OH}$ ) and equilibrium (lines) products distribution as a function of temperature for Pt/Ni (A) and Pt/Co (B) catalysts in concentrated catalytic tests

For the Pt/Ni sample the effect of GHSV was evaluated for also at a lower dilution ratio r.d.=1.5, (Figure 5).

Despite the thermodynamic limits relevant to the use of a lower dilution ratio, the experimental values agree with the equilibrium data, in particular with increasing contact time.

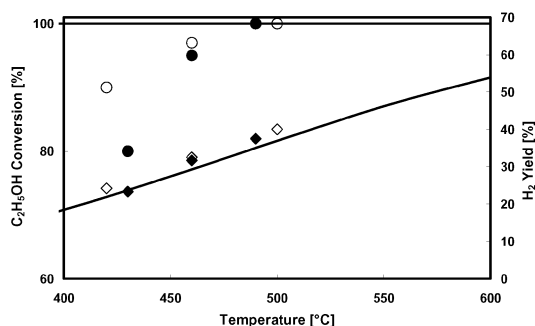


Figure 5: Experimental (full points  $GHSV=15000h^{-1}$ , empty points  $GHSV=7500h^{-1}$ ) and equilibrium (lines)  $C_2H_5OH$  conversion and  $H_2$  yield as a function of temperature for Pt/Ni catalyst in concentrated catalytic tests

#### 4. Techno-economic Evaluation

Ciambelli et al. (2009) suggested a competitive and innovative application of low temperature ESR reaction, by considering it as a pre-reforming stage into a multi feed hydrogen production. Two main configuration have been proposed: the first configuration as a prereforming step alone, the second coupled with a membrane for  $H_2$  separation in an open architecture process scheme (Figure 6). This solution allows, not only a reduction of the radiant section of the reforming section, but since the extraction of the heat to convert the ethanol is carried out from the sensible heat of the flue gases generated by reforming the methane left over, an increase of the overall energy of the unity in the energy in the range of 8-10%.

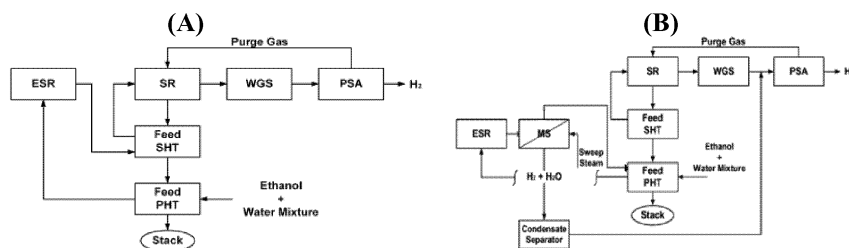


Figure 6. Block diagrams of ESR-SR hybrid system in a stand alone configuration (A) or coupled with  $H_2$  selective membrane separator (B)

Logistic and bio-ethanol procurement cost, plant capacity and  $H_2$  production final cost have to be considered but, preliminary, the Capital Investment (ISBL) and a tentative production cost have been calculated, to finally obtain the cost of ethanol mixture which makes the production cost equal to natural gas based. For a capacity of  $1500 \text{ Nm}^3/\text{h}$  of  $H_2$ , the reforming section can be considered 85% of the conventional one, then the reforming duty will pass from 1417 to 1205 Mkal/h, feeding 784 kg/h of ethanol rather than  $620 \text{ Nm}^3/\text{h}$  of natural gas and the Capital Investment will become 4.0 MEUR while

for the conventional steam reforming it was assumed to be 5.0 MEUR. Considering as variable cost only the cost of feed and assuming for fixed cost a working life of 15 years and a return on investment (WACC) of 9.5%, the production cost has been calculated equal to 0.113 EER/Nm<sup>3</sup> of H<sub>2</sub>. At 0.14 EUR/kg of ethanol in a water ethanol mixture, the production makes economically sense.

## 5. Conclusions

The performance of bimetallic PtNi and PtCo catalysts supported on CeO<sub>2</sub> has been investigated in low temperature ethanol steam reforming in both diluted and concentrated reaction mixtures. The results showed that the catalytic activity is deeply affected by the preparation method. In concentrated conditions, the effect of temperature, dilution ratio and GHSV on the gaseous stream composition has been investigated. As a result, Pt/Ni catalyst seems to be promising for the low temperature ESR reaction, since it shows the best performance in terms of activity, selectivity and stability among the investigated catalysts. The evaluation of the economic feasibility of two hybrid proposed processes showed that there is a consistent reduction of the reforming section and elimination of desulphurization section.

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