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Steam Reforming of Ethanol to H_2 over Bimetallic Catalysts: Crucial Roles of CeO_2 , Steam-to-Carbon Ratio and Space Velocity

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Hydrogen has been proposed as an energy carrier which could reduce atmospheric pollution, GreenHouse Gases (GHG) emissions, and dependency on fossil fuels.

In this context, one of the most environmentally friendly process for hydrogen production is ethanol steam reforming (ESR). In addition, the biomass-derived ethanol is renewable and also able to significantly reduce NO_x, SO_x emissions. Furthermore, ethanol is easier to reform than gasoline or natural gas as well as ready to be used in ESR reactions as an aqueous solution, thus, avoiding the water separation costs. When the reaction is carried out at low temperature, with the aim to reduce the thermal duty and promote the Water Gas Shift (WGS) reaction, the role of the catalyst is especially important. Various formulations have been proposed in literature but this work focuses on the development of innovative formulations; with this purpose, several CeO_2-supported samples, based on the synergic activity of a noble and a non-noble metal, were investigated. The results showed that Pt can positively interact with Ni or Co, allowing the complete ethanol conversion, yet at $T < 600$ °C. The selectivity towards the desired compounds was one of the key parameters for the selection of the optimal catalyst, through specified tests in the following operating range: pressure=1 atm, temperature (300 – 600 °C), contact time = 240 – 720 ms, water-to-ethanol molar ratio = 3. Another central study was relevant to the stability of the sample, through Time-on-Stream (TOS) tests carried out at 430 °C and 10 vol.% of ethanol in the feed stream. The coke selectivity and coke formation rate were calculated and compared with current literature. The reaction pathway over the most interesting catalytic formulation was obtained, thanks to a detailed experimental campaign in which the evolution of the product distribution *vs.* contact time (0.600 ms) and temperature (300-600°C) was analysed. In addition, the ethanol adsorption and the subsequent Temperature Programmed Desorption (TPD) experiments were performed. The results were also evaluated in terms of reaction rate, by considering the contribution of each possible reaction along the catalytic bed.

1. Introduction

The helpfulness of hydrogen as an energy carrier has been validated by several publications in the current literature, with a particular focus on its use as a fuel for fuel cells: they are devices able to produce clean energy with high efficiency (Fajardo et al., 2010)

Hydrogen can be produced through several method, the most common being the steam reforming of natural gas (Wang et al., 2010). Nevertheless, the latter is not a green process, thus the steam reforming of biomass-derived ethanol can be considered advantageous, combining the renewability of the feedstock with the well-known technology (Haryanto et al., 2005)..

The biomass-derived ethanol is renewable, non-toxic and directly usable in the ESR reaction as an aqueous solution (Freni et al., 1996). The overall desired reaction

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

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leads to the production of 2 moles of carbon dioxide and 6 moles of hydrogen, with a stoichiometric water-to-ethanol feed ratio (Ni et al., 2007). In this way, it takes into account the contribution of the WGS reaction for CO removal (Palma et al 2011), that is necessary because carbon monoxide is a poison for fuel cells (Palma et al., 2012).

The ESR reaction is endothermic, thus it is typically carried out at high temperatures; unfortunately, these conditions cannot promote the WGS reaction, that is promoted at low temperature, being exothermic. Therefore, the high temperature range is helpful for obtaining high hydrogen yield but could negatively affect the overall energy efficiency A possible alternative may be to perform the ESR reaction at low temperature, also reducing the thermal duty (Fishtik et al., 2000). In this case, the role of the catalyst is very crucial for avoiding the selectivity towards undesired products, possible coke precursors (Ioannides, 2001). For all these reason, the optimal catalyst should be active, selective towards hydrogen, stable (Cavallaro et al., 2003) and resistant to coke formation and able to remove carbon monoxide (Ciambelli et al., 2010a)

Several catalytic formulations have already been proposed for ESR reaction (Batista et al., 2004) , based on different active metals - Pd, Pt, Ru, Rh, Co, Ni, Cu, Fe - (Yamazaki et al., 2010) and supports - Al_2O_3, La_2O_3, ZnO, SiO_2, MgO - (Ciambelli et al., 2010b).

The aim of this work is to study the effectiveness of the synergic action of platinum with Ni or Co in CeO_2-supported catalysts for the ESR reaction at T < 600 °C. The activity, selectivity and stability of the samples were studied, with parametric tests by varying the value of the reaction temperature, the feed composition and the contact time.

2. Experimental

2.1 Catalysts preparation

All the chemicals used in the experiments were Aldrich, HPLC grade. The bimetallic catalysts, based on Pt and Ni or Co and supported on CeO_2, by dispersing the support into an aqueous solution of metal salt. The resulting slurry is stirred on a heating plate and then dried at 120 °C overnight and calcined in air at 600 °C for 3 h (dT/dt= 10 °C/min). Before impregnation, the support is calcined under the same conditions. Commercially available CeO2 (Aldrich, BET = 80 m^2/g) is used as support, while $PtCl_4$, C_4H_6O4Ni·4H_2O and ($C_2H_3O_2$)2Co·4H_2O, as Pt, Ni and Co precursors. To prepare the bimetallic catalysts, two subsequent impregnations were carried out, with a calcination step between the two impregnations.

2.2 Catalysts characterization

The physico-chemical properties of each samples were evaluating through various characterization techniques:

(i) the Energy Dispersive X-Ray Fluorescence (EDXRF) analysis (Thermo-Scientific QUANT'X);

(ii) the N_2 adsorption-desorption isotherm at -196°C (by B.E.T. method) after a pre-treatment at 150 °C for 1 h in He flow (Costech Sorptometer 1040);

(iii) the X-Ray Diffraction (XRD) technique (D-max-RAPID X-ray microdiffractometer);

(iv) the Laser Raman spectroscopy (Dispersive MicroRaman, Invia, Renishaw);

(v) the Thermogravimetric Analysis-Mass Spectrometry (TGA-MS) (TA Instrument Q600 coupled with PFEIFFER ThermoStar Quadrupole Mass Spectrometer;

(vi) the 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;

(vii) the temperature Programmed Desorption (TPD) experiments in N_2 flow, with an heating rate of 10 °C/min, up to 600 °C, after the adsorption of 10 vol.% of ethanol in N_2 flow (Total flow rate = 1000 cm^3/min (STP)) at 40 °C and the desorption in was performed.

2.3 Catalytic tests

The catalytic tests were performed in an experimental set-up (Palma et al., 2012), in which the ethanol/water feed mixture, prepared for simulating a real bio-ethanol stream, is mixed with dilution nitrogen and sent to the PFR reactor; all the stable gaseous products were analysed through a FT-IR online-spectrophotometer, expect H_2, that is monitored thanks to a thermo-gravimetric analyser.

The initial tests were focused on the study of the activity and selectivity of the catalysts. They were performed at P = 1 atm, Flow rate = 1000 cm^3/min (STP); water-to-ethanol molar ratio = 3; ethanol concentration in the feed stream = 5, 10, 15 vol.%, T = 300 - 600 °C, GHSV = 7,500 h^{-1} - 15,000 h^{-1}.

The subsequent tests were carried out with the purpose to compare the samples performance in terms of stability; the TOS tests were carried out at: GHSV = 15,000 h^{-1}, T= 430 °C, 10 vol.% of ethanol in the feed stream.

The evolution of the products distribution was analyzed at different contact times (0 - 600 ms) and temperature (300 - 600 °C).

3. Results and Discussion

3.1 Characterization results

The results of all the characterizations were very useful to understand the catalytic behaviour of the samples, i.e. the results of the XRF analysis revealed a good agreement between the experimental and nominal metals load and the SSA measurement showed a decrease after the deposition of metals on the support. The Table 1 reports the results of the quantitative analysis after the deconvolution of the TPR profiles of 3 wt.% Pt / 10 wt.% Ni / CeO_2 and 3 wt.% Pt / 10 wt.% Co / CeO_2, mentioned as Pt/Ni and Pt/Co.

Table 1: TPR H_2 uptake of Pt and Ni-based catalyst

Catalyst	Temperature [°C]	Experimental H_2 uptake [$mmol_{H2}/g_{cat}$]
Pt/Ni	168	480
	288	856
	319	649
Co/Pt	137	802
	229	840
	275	847

The H_2 uptake due to PtO_x species reduction for Pt/Ni is higher than the theoretical one corresponding to $Pt^{4+} \rightarrow Pt^0$ while the H_2 uptake due to NiO reduction is lower than the expected one. This effect can be explained considering that Ni/CeO_2 is more reducible than pure CeO_2 and that the Pt can promote the spillover phenomenon, reducing the free NiO particles dispersed on the support surface at lower temperatures.

Concerning Pt/Co sample, it is evidenced that the H_2 uptake due to PtO_2 reduction is higher than the theoretical one and the H_2 uptake due to Co_3O_4 reduction is lower than the theoretical one corresponding to the complete reduction to Co. This suggest that, during the calcination step there is an incomplete Co oxidation or that Co_3O_4 starts its reduction already at lower temperatures: it is possible to explain this phenomenon taking into account that the Pt supported on the CeO_2 may very easily reduce the adjacent Co particles, due to the activation of the H_2 via the spillover mechanism.

3.2 Catalytic tests results

After 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, the metals load were optimized as 3 wt.% for Pt and 10 wt.% for not noble metals, by observing the catalytic performance of all the samples.

The Pt/Ni and Pt/Co samples showed very promising results, as reported in Table 2. At 600 °C and 240 ms, the selectivity towards the desired products was very high. A very low CO concentration was obtained over Pt/Ni and the product distribution was in perfect agreement with the equilibrium calculations in all the temperature range; the H_2 concentrations obtained over Pt/Co were higher than the equilibrium values.

Table 2: Product concentrations at the reactor outlet during ESR reaction (P = 1 atm, T = 580 °C, feed composition: 5 vol.% C_2H_5OH / 15 vol.% H_2O / 80 vol.% N_2)

Catalyst	C_2H_5OH [vol.%]	H_2O [vol.%]	CH_4 [vol.%]	CO [vol.%]	CO_2 [vol.%]	H_2 d.b. [vol.%]
Pt/Ni	0.00	7.05	1.63	3.44	4.29	17.11
Pt/Co	0.00	6.78	1.54	3.93	4.25	18.41

The carbon mass balance is closed up to 99 %, when considering C_2H_5OH, CO, CH_4 and CO_2 as C-containing products. This result, coupled with very stable product distributions observed during the TOS, may lead to the exclusion of any deactivation effect. Nevertheless, during the TOS a strong increase in the pressure drops was observed, and this can be due to the reactor plugging. Some characterization of the exhaust samples showed a very few carbon deposition. The comparison of the coke selectivity, plugging time and coke formation rate was helpful to select the most stable catalyst; the results related to Pt/Ni and Pt/Co was reported in Table 3.

Table 3: Product concentrations at the reactor outlet during ESR reaction (P=1 atm, T=580 °C, feed composition: 5 vol.% C_2H_5OH / 15 vol.% H_2O / 80 vol.% N_2).

Catalyst	Plugging time [min]	Coke selectivity [%]	Coke formation rate [$g_C/(g_{cat}$ h]
Pt/Ni	300	0.6	0.00675
Pt/Co	800	0.2	0.000211

It is worth to note that the coke selectivity is lower than 1 % and that the results of the current literature in conditions more advantageous (higher temperature, higher r.a. values and higher contact times), are in the range 0.0156-2.7334 $g_C/(g_{cat}$ h) [17].

3.3 Reaction pathway

Differently from previous publications (Palma et al, 2012), the kinetic aspects was preliminarily studied in this paper. Pt/Ni catalyst was selected for this detailed analysis, based on the consideration that this sample showed the products distribution closest to the equilibrium,. A preliminary kinetic study together with ethanol adsorption-desorption experiments was undertaken in order to appreciate the reaction pathway. The effect of contact–time (0 - 600 ms) on products distribution was investigated at constant temperature in the range 300 – 600 °C and water to ethanol molar ratio = 3.

The interpretation of the evolution of products distribution was joined with additional characterization, i.e. during the ethanol adsorption at 40 °C (Figure 1a), the signal of H_2 is in agreement with the tendency of ethanol, confirming the formation of an ethoxy species and the formation of two atoms of hydrogen that form the molecule of H_2. This justify the assumption of the dehydrogenation of ethanol to acetaldehyde as the first reaction of the system (Sannino et al., 2012), also considering that the acetaldehyde was detected in the FT-IR spectrum of the outlet gas stream (Figure 1b).

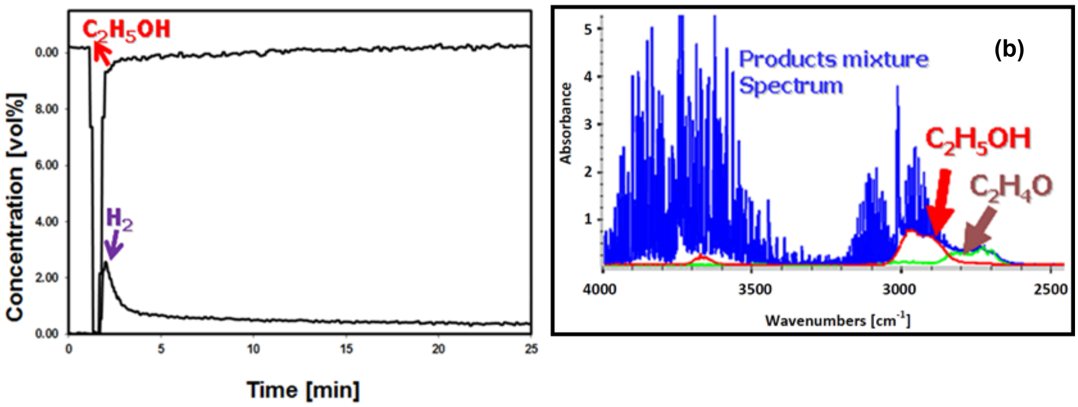

Figure 1: Ethanol and hydrogen concentration (a) and FT-IR spectrum (b) during ethanol adsorption on calcined and reduced Pt/Ni

By analysing the evolution of the C-containing products during the desorption (Figure 2), two peak for both CH_4 and CO, overlapped at 150 and 410 °C, were detected.

The peaks at lower temperature can be related to the reactions of dehydrogenation of ethanol to acetaldehyde, followed by acetaldehyde decomposition and reforming. The second peak could be linked to additional decomposed acetaldehyde, in agreement with the results of the model and with literature, mainly producing CO and CH_4. 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. The hydrogen and water profiles were in agreement with the above hypothesis, thus validating the kinetic evaluation.

In addition, the evolution of the reactions rate along the catalytic bed (Figure 3) showed that the first reactions are r1 (dehydrogenation of ethanol), r2 (decomposition of ethanol), r4 (steam reforming of acetaldehyde), followed by acetaldehyde decomposition and CO-WGS and CO_2-methanation.

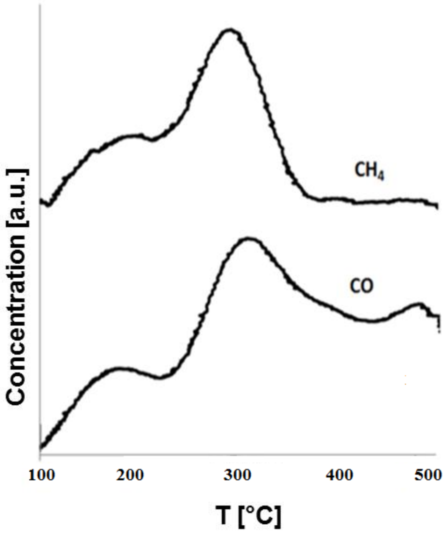

Figure 2: TPD in N_2 flow (Flow rate = 1,000 Ncc/min; 10°C/min up to 600 °C)

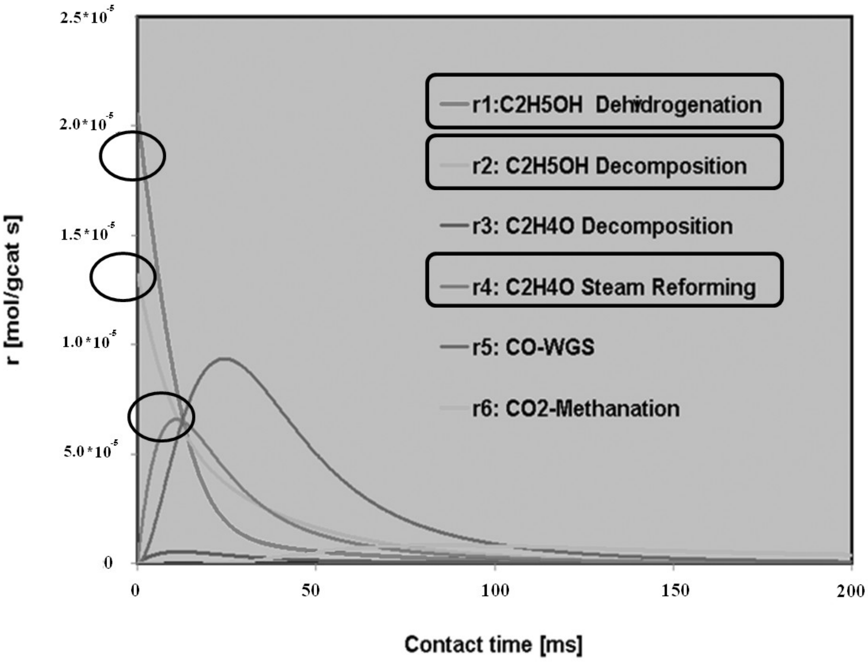

Figure 3: Evolution of the rate of each reaction along the catalytic bed (T = 370 °C)

3.4 Conclusions

The ethanol steam reforming reaction at low temperature was carried out on several catalysts. Besides the cooperative and synergic effect between Pt and Ni or Co activities, the use of cerium oxide as a support: it is convenient for its mechanical and chemical resistance under reaction condition. The ethanol is completely converted at low temperatures and contact times and the hydrogen selectivity is considerably higher than the CO and C ones. Finally, the great novelty of this work is the reaction pathways proposed over Pt/Ni: the ethanol is dissociatively adsorbed, then dehydrogenated and decomposed; the acetaldehyde obtained from the dehydrogenation is decomposed and reformed; the CO is converted into CO_2 through WGS and CO_2 and H_2 produce CH_4 and water through methanation reaction. it has not been considered the steam reforming of methane, that is included in some works. The reason is related to the relatively low temperatures used for the above experiments: at T ≤ 400 °C the methane is not typically converted through reforming.

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