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Pt-Re Based Catalysts for the Realization of a Single Stage Water Gas Shift Process

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The excellent performance of the Pt/Re/CeZrO$_4$ catalyst, for the CO Water Gas Shift reaction, is presented. A preliminary comparative study, on the activity of some bimetallic catalysts, Platinum-based (PtM/CeZrO$_4$, M=Re,La,Rh), highlighted the great ability of the Rhenium to enhance the activity and stability of the catalyst, even at very low temperatures. The effect of the preparation method, in terms of sequence of impregnation of the two active metals, was evaluated, showing a low impact on the performance of the final catalyst. The reported results indicate that the Platinum-Rhenium system represent a concrete possibility for the realization of a single stage WGS process.

1. Introduction

The water gas shift (WGS) is an exothermic reversible reaction, between carbon monoxide (CO) and steam, widely used downstream reforming processes, to reduce the CO concentration and to increase the hydrogen (H$_2$) concentration in the reformate stream (Newsome, 1980).

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \Delta H°_{298} = -41 \text{ kJ/mol}$$

The WGS industrial process provides two adiabatic stages, firstly a high temperature stage (HTS), carried out in the temperature range 580-723 K over Fe/Cr-based catalysts, followed by a low temperature stage (LTS), carried out in the temperature range 473-620 K over Cu/Zn-based catalysts (Smith et al., 2010). The exothermicity of the reaction generate, in adiabatic conditions, a temperature gradient with a much higher temperature at the outlet of the catalytic bed, disfavouring the kinetics at the inlet and limiting the conversion at the outlet. In the HTS stage, the inlet temperature is near 580 K, while the outlet temperature reaches 800 K, obtaining a CO conversions of 90%; the LTS stage provides an inlet temperature of 490 K and an outlet temperature of 570 K, reaching a final conversion on 99-99,7%; moreover an intermediate intercooler complete the global process. The actual process configuration is profitable because allows to overcome this limitations, exploiting fast kinetics in the HTS stage and allowing to reach high conversions in the LTS stage however, at the same time, it presents many disadvantages, such as the high energy consumption in the inter-cooling stage, the high costs of realization and maintenance of the two plants, the slow system kinetics and the not feasibility for small scale applications.

As evident from these considerations, the WGS industrial process requires a substantial process intensification; moreover all the industrial processes based on exothermic reactions suffer of similar problems so, an effective improvement on the WGS, could easily be extended to the others. Flatten the thermal profile over the catalytic bed is theoretically possible through the backdiffusion of the reaction heat, from the outlet to the inlet of bed, favouring kinetics and increasing the CO conversion, caused by the higher inlet temperature and the lower outlet temperature. This kind of process intensification can be obtained by the use of structured catalysts based on highly conductive carriers, such as metallic foams (Palma et al., 2015) or ceramic honeycombs, prepared by washcoating these supports with catalytic formulations at high surface area. A good structured catalyst, highly active, in a wide temperature range, intermediate between the activity temperatures of the actual catalysts for HTS and LTS, would allow to realize a single stage process. The actual catalytic formulations, used in HTS and in LTS processes, suffer of many disadvantages, among which the pyrophoricity of the Cu/Zn-based catalysts and the low activity of the Fe/Cr-based catalysts at low temperatures, much more promising, for a single stage process, are the noble metal based catalysts, highly active in a wide range of temperatures at low concentration and compatible with fuel processor systems. The Au-based catalysts are highly active, showing good CO conversion even at 420 K, however the preparation methods are rather laborious and the resulting catalysts show a low stability (Pérez et al., 2016). The Rhodium based catalysts show high initial activities but deactivate rapidly, due to the irreversible adsorption of oxygenated residues. The Platinum based catalysts have shown much better performance (Palma et al., 2014), the preparation methods are easily workable and the deactivation occurs slowly. In a previous works we have shown that is really possible to flatten the temperature profile over the catalytic bed, by using highly conductive open cell aluminum foams (Palma et al., 2016a), obtaining a real improvement in the CO conversion at low temperatures, with respect to the powder catalyst, having the same chemical composition of the catalytic washcot used in the preparation of the structured catalysts. The formulations of our structured catalysts provide the use of Pt/CeO_2, $Pt/CeZrO_4$ or $Pt/CeO_2/Al_2O_3$ that, despite the excellence results in term of process intensification, show low activity at temperature below 470 K and the methanation occurrence over 620 K. A possible solution comes from the use of promoters or stabilizers, such as Sodium (Yang et al., 2015) that is able to stabilize the Platinum sites through the formation of –O ligands, Molibdenum that increases the turnover frequency up to a factor of 4000 (Sener et al., 2016), Tin that depress the methanation side reaction (Palma et al., 2016b). Interesting results were reported also with Rhenium (Choung et al., 2005),

In this paper we report the results of a comparative study of some promising bimetallic catalysts for the water gas shift reaction and the considerations that make the $Pt\text{-}Re/CeZrO_4$ system a possible catalyst for a single stage WGS process.

2. Experimental

2.1 Catalysts preparation

The $CeZrO_4$ (Actalys® 922, 57.4 %wt of ceria) was provided by Rhodia, the Platinum(IV) chloride (99.9%-Pt) was provided by Strem Chemicals, the Ammonium perrhenate (≥99%), Lanthanum(III) nitrate hydrate (≥99%), Rhodium(III) nitrate hydrate (~36% rhodium basis) were provided by Sigma-Aldrich. The $1Pt/1M2/CeZrO_4$ (M2=La,Re,Rh)catalysts were prepared by two consecutive wet impregnations, by loading 1% of each metal. In the first impregnation was loaded the M2 specie, the support was suspended in a the water solution of the corresponding M2 salt, vigorously stirred and heated until to the complete evaporation of the solvent, the resulting powder was dried at 393 K for two hours and calcined at 873 K for three hours. The resulting derivative was impregnated with the $PtCl_4$ solution, the solvent was evaporated and the resulting powder dried at 393 K for two hours and calcined at 873 K for three hours, to obtain the desired catalyst. The $1Re/1Pt/CeZrO_4$ catalyst was prepared with the same method, previously described, by loading firstly the Platinum and subsequently the Rhenium.

Prior to the H_2-TPR experiments and to catalytic activity tests, all the samples were compacted and sieved to obtain a granulometric distribution between 180 µm and 355 µm.

2.2 Catalysts characterization

The composition of the catalysts was estimated by means of ED-XRF spectroscopy with an ARL^{TM} QUANT'X Thermo Scientific^{TM}; the samples were ground, mixed and compressed to a tablet and analysed with a Fundamental Parameters method to evaluate the elemental composition. The specific surface areas were evaluated with the B.E.T. method by a Sorptometer 1040 K (Constech International); the samples were degased in vacuum for 60 minutes at 423 K and the surface area estimated with adsorption-desorption isotherms of nitrogen at 77 K. The X-ray Powder Diffractograms were obtained with a D8 Brucker Advance, to determine the crystal phases and the crystallite sizes by Scherrer equation; the XRD analysis were performed with a Cu Kα radiation (35kV, 40 mA) in the 2θ range 20-80° (Stp=737; Stp size=0.0814; t/Stp=0.5s). The H_2-TPR experiments were carried out in the same reactor used for the activity tests, with a reducing stream of 1000 Ncc/min of 5% H_2 diluted in nitrogen, a heating rate of 10°C/min, from room temperature to 723 K. The H_2 consumption was calculated by integration the curve, expressing the concentration change of hydrogen vs. temperature. The modifications, induced by adding the metals, on crystalline structure of the support, were evaluated by Raman spectroscopy, with a Renishaw inVia microRaman spectrometer (514 nm excitation wavelength).

2.3 Catalytic activity tests

The activity tests were carried out with a reacting mixture of 8% CO, 30% H_2O diluted in nitrogen at a gas hourly space velocity (GHSV) of 10,000 h^{-1}, in the temperature range 423-673 K, at atmospheric pressure.

The gas hourly space velocity was calculated as the ratio between the volumetric flow rate and the volume of the catalyst. The tests were carried out in a fixed bed tubular stainless steel reactor with an internal diameter of 23 mm, and performed with 6 cm^3 of catalyst (180-355 µm) diluted with 6 cm^3 of quartz (500-700 µm) to minimize the pressure drop and the thermal effects. The stream coming from the outlet of the reactor was dried by condensation with a thermocryostat Julabo F12-Dcontinuously and the resulting composition was monitored by an ABB system, equipped with a nondispersive infrared photometer Uras 14 for CO, CO_2 and CH_4 and the a thermal conductivity analyser Caldos 17 for hydrogen. The catalytic performances were evaluated in terms of carbon monoxide conversion and hydrogen yield, defined, the first as ratio between the difference of the moles, between input and output, and the input moles (Eq(1)), the second as the ratio between the hydrogen moles produced and the carbon monoxide moles fed (Eq(2)).

$$X_{CO} = \frac{COin - COout}{COin} \qquad (1)$$

$$Y_{H_2} = \frac{H_2out}{COin} \qquad (2)$$

3.Results and discussion

3.1 Characterization

In table 1 the effective metal loading, the specific surface area and the crystallites size, for all the calcined catalysts, are summarized. The effective metal loadings, evaluated by ED-XRF analysis, showed a good agreement with the theoretical, the B.E.T. specific surface areas showed no significant difference between the catalysts, in any case, the loading of the second metal has brought to a reduction of the S.S.A., with respect the monometallic counterpart.

Table 1: Metal loading, specific surface area and crystallite size.

Sample	Pt %wt	M2 %wt	S.S.A. [m^2/g]	Cryst. Size [nm] $CeZrO_4$ (111)
$1Pt/CeZrO_4$	0.90	-	49.1	9.0
$1Pt/1Re/CeZrO_4$	0.92	0.95	47.3	8.9
$1Pt/1La/CeZrO_4$	0.92	0.99	48.0	8.9
$1Pt/1Rh/CeZrO_4$	0.97	0.98	47.9	9.0
$1Pt\text{-}1Re/CeZrO_4$ (c)	0.94	0.96	47.5	9.4

The average crystallite sizes, evaluated by Scherrer equation, from the broadening of the (111) reflections centred at 2 ϴ 29.4 (Figure 1), showed similar results for all the catalysts except for the co-impregnated 1Pt-1Re/$CeZrO_4$ (c), for which a higher value was obtained. This result was attributed to the possible incorporation of the metals into the lattice of the support, that brought to the increase of the grain size.

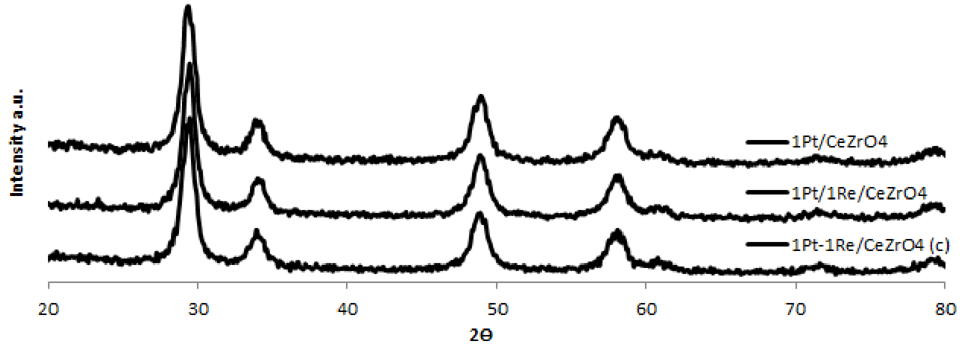

Figure 1: Comparison of the X-ray diffractograms for 1Pt/$CeZrO_4$, 1Pt/1Re/$CeZrO_4$ and 1Pt-1Re/$CeZrO_4$ (c) catalysts

In table 2, the experimental hydrogen uptake, evaluated by integration of the hydrogen concentration curve from the H_2-TPR experiment, and the temperature main reduction peak, for all the calcined catalysts were reported. For all the catalysts the hydrogen uptake is much higher than the theoretical, probably due to the spillover effect of Platinum over ceria/zirconia support, however, for the 1Pt/1Rh/$CeZrO_4$ the value is much lower, probably due to a stronger interaction between Platinum and Rhodium, that weakens the interaction between Platinum and the support.

Table 2: Experimental H_2 uptake and temperature of the main reduction peak

Sample	Exp. H_2 uptake [mmol/g]	T. of the main reduction peak [K]
1Pt/CeZr	0.81	523
1Pt/1Re/CeZrO4	1.09	540
1Pt/1La/$CeZrO_4$	0.91	497
1Pt/1Rh/$CeZrO_4$	0.50	374
1Pt-1Re/$CeZrO_4$ (c)	1.00	505

3.2 Activity tests

The activity tests were performed by comparing the performance of the monometallic 1Pt/$CeZrO_4$ catalyst with the bimetallic systems 1Pt/1M/$CeZrO_4$, where M=Re,La,Rh; moreover the effect of the impregnation sequence was evaluated for the Pt/Re bimetallic system. The tests were carried out in the conditions described in the section 2.2, and were evaluated in terms of CO conversion (Figure 2), hydrogen yield (Figure 3) and methane concentration (Figure 4).

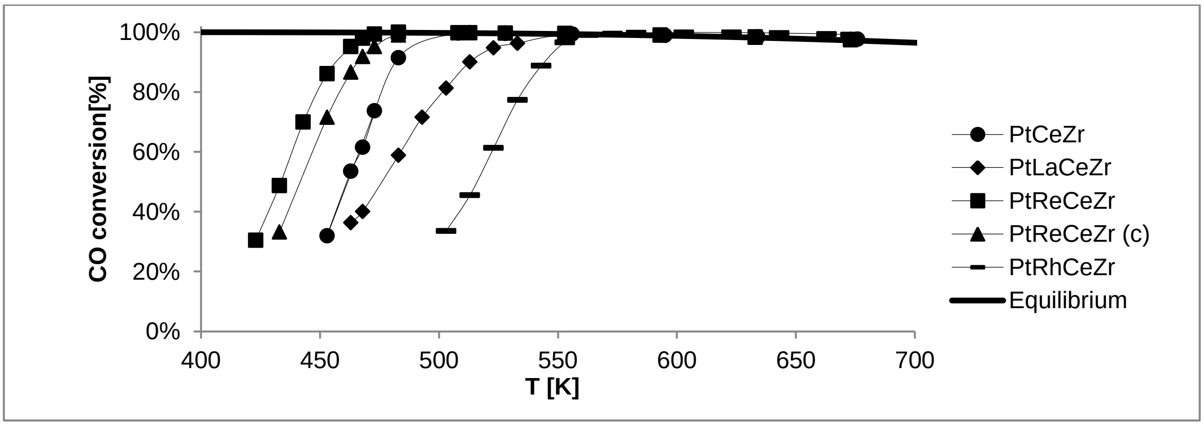

Figure 2: Comparison of the CO conversion for 1Pt/$CeZrO_4$, 1Pt/1La/$CeZrO_4$, 1Pt/1Re/$CeZrO_4$, 1Pt-1Re/$CeZrO_4$ (c) and 1Pt/1Rh/$CeZrO_4$ catalysts.

The CO conversion trend showed an evident dependence from the nature of the bimetallic system used. The conversion obtained with the monometallic 1Pt/$CeZrO_4$ catalyst approached the equilibrium over 510 K, while decreased for lower temperatures until reaching the 30% at 453 K.

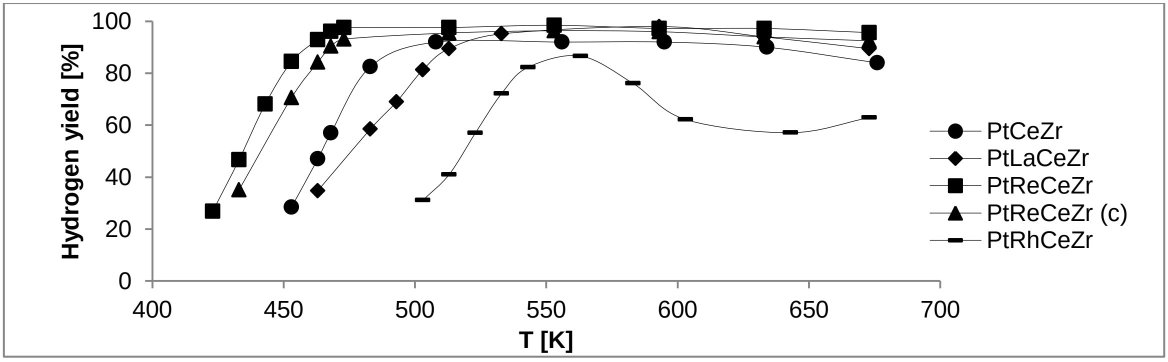

Figure 3: Comparison of Hydrogen yield for 1Pt/$CeZrO_4$, 1Pt/1La/$CeZrO_4$, 1Pt/1Re/$CeZrO_4$, 1Pt-1Re/$CeZrO_4$ (c) and 1Pt/1Rh/$CeZrO_4$ catalysts.

Worse results were obtained with $1Pt/1La/CeZrO_4$ and $1Pt/1Rh/CeZrO_4$, in particular the latter showed a conversion higher than the equilibrium over 550 K, because of the occurrence of the methanation reaction. Excellent results were obtained with the $1Pt/1Re/CeZrO_4$ catalyst that approached the equilibrium 470 K and showed the 30% of conversion at 423 K. This catalyst showed also a great hydrogen selectivity in the temperature range studied; as evident from the Figure 3 and 4, no evidence of occurrence of the methanation reaction was observed, until 650 K. Similar results were recently reported for the $Pt-Re/TiO_2$ catalyst (Azzam et al., 2007), in which the presence of Rhenium seems to stabilize the Pt/TiO_2 system, increasing the activity and preventing the Pt sintering, because of the presence of oxidizing form ReOx.

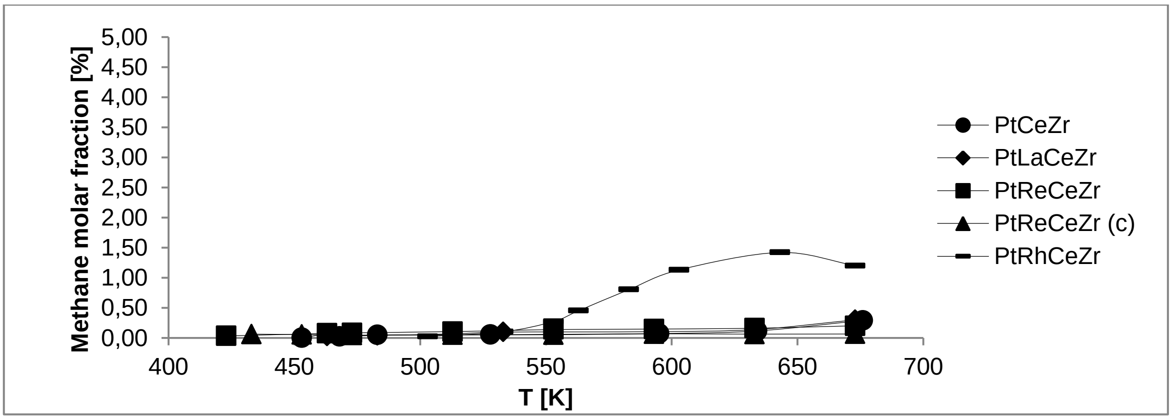

Figure 4: Comparison of the methane molar fraction for $1Pt/CeZrO_4$, $1Pt/1La/CeZrO_4$, $1Pt/1Re/CeZrO_4$, $1Pt-1Re/CeZrO_4$ (c) and $1Pt/1Rh/CeZrO_4$ catalysts.

Comparable results were obtained with the co-impregnated $1Pt-1Re/CeZrO_4$ (c) catalysts, it left the equilibrium at 480 K and showed a significant conversion of 30% at 433K. The slight differences found between the latter two catalysts were explained in terms of formation of smaller particle size, for the the $1Pt/1Re/CeZrO_4$ catalyst, due to a different distribution of the metals over the surface of the support.

4.Conclusions

A comparative study on the activity of bimetallic Pt-based catalysts for the water gas shift reaction was presented; the activity tests showed the superior performance of the 1Pt/1Re/CeZrO4 catalytic system, both in terms of CO conversion and of hydrogen selectivity. The effect of the sequence of the loading of the two metals was evaluated, highlighting the performance of the catalysts in which was firstly loaded the Rhenium. The results obtained show, without doubt, that 1Pt/1Re/CeZrO4 constitutes the ideal catalytic formulation, in view of the realization of a single-stage process. Coupling the performance of a so active catalyst, in a wide range of temperatures, and the capacity of a structured carrier to redistribute the heat along the bed, it is theoretically possible to provide a catalyst for the single stage process. In our laboratories we are currently under way to prepare structured catalysts, with such features.

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