Comparative Studies of Low Temperature Water Gas Shift Reaction over Platinum Based Catalysts

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Water gas shift reaction (WGS) is normally performed in a two-stage process, a first stage at high temperature (HTS) conventionally carried out at 623 - 873 K on Fe/Cr-based catalyst, to take advantage from a fast reaction, and a second stage at low temperature (LTS) at 423 - 573 K on Cu/Zn-based catalysts, to reach a favourable thermodynamic equilibrium condition. A single-stage process involves at the same time a cost reduction in plant setup as well as operative conditions; however at the moment, due to the lack of efficient catalytic systems the one-stage WGS systems is not widely diffused. Noble metals arise today as a promising solution in this direction, so in this work great attention was focused on the preparation and testing of differently-supported Platinum-based catalysts.

1. Introduction

WGS reaction involves the conversion of CO in CO_2 to increase the H_2 yield in syngas and to provide a H_2/CO mixtures with the appropriate ratio for the production of important chemicals, such as methanol or ammonia. The growing interest towards hydrogen for Fuel Cells employment highlights the relevance of the CO cleaning processes in a H_2 rich stream, especially in the processes intensification direction (Brunetti et al., 2007).

The WGS is an exothermic reaction, thermodynamically favoured at low temperature, however kinetic limitations make it convenient to use a two-stage process, with two different catalytic systems. The first stage (HTS) is conventionally carried out in the temperature range 623-873 K, on Fe/Cr-based catalytic systems; in this stage the most of the CO conversion is obtained, however thermodynamic limitations effect in reduced conversion values. The second stage (LTS) is carried out in the temperature range of 453-633 K on a Cu/Zn-based catalyst; in this phase, although slow kinetics, the thermodynamic conditions allow to obtain high CO conversion (CO in the order of few ppm).

Although this type of configuration is very effective, it shows several disadvantages: as a first, the global system kinetics is very slow, requiring a high mass of catalyst, that in turn results in long activation time; moreover, the presence of the inter-cooling increases not only the energy requirements of the process, but also the plant cost itself; furthermore, the LTS catalyst shows pyrophoricity, resulting not able to sustain frequent start up and shut down stages, and then not suitable for mobile fuel cell applications.

Definitely, the actual WGS plant configuration would be of course the biggest unity of an integrated fuel processor. For these reasons, a process integration is needed. In this context, a single stage WGS appears able to reduce the reactor dimensions and greatly reduce the production costs.

From the above considerations, it is clear that finding a good catalytic formulation is the priority. The most promising catalysts in view of a single-stage process are for sure the noble metal based catalysts (Palma et al., 2012), showing high yields in a wide temperature range even in low concentrations; moreover, they are perfectly compatible with a fuel processor system. Many examples on the use of Gold (Yang et al., 2013), Platinum (Franchini et al., 2012), Rhodium (Cornaglia et al., 2012), Palladium and Rutenium (Mierczynski et al., 2013) are known, however the best performances are reported for Platinum and Gold. The latter in particular has shown excellent activity for LTS, while, at the same time, the tendency to

deactivate rapidly because of sintering phenomena, so complex strategies are necessary to anchor the active phase to the support (Ta et al., 2012). On the other hand, Platinum based catalysts seem to be highly active and stable at the same time, by standing as the best choice for the preparation of a highly productive catalyst. Many studies on platinum based catalysts supported on reducible oxides are already known, for examples Tang et al. (2012) have recently published the preparation by electrospinning of Pt/CeO_2 nanofibers with diameter of 80-120 nm, that show an excellent CO conversion in temperature range of 593-633 K. Kyung-Ran et al. (2013) has reported that the adding of titanium to Pt/ZrO_2 increased the surface area of the support and the dispersion of Pt, enhanced the reducibility of the catalyst and made the formate decomposition rate faster. Azzam et al. (2013) studied the effect of rhenium in $Pt-Re/TiO_2$ catalyst, giving evidence that Re increase the activity by enhancing the activation of water.

As mentioned above, the research was focused on the study of a single stage WGS catalyst; in particular, in this work some differently supported platinum based catalysts (CeO_2, CeO_2/ZrO_2, 14 % $CeO_2/\gamma-Al_2O_3$) were prepared and tested for the LT-WGS; the role of the support was investigated and the performances of potential one-stage WGS catalysts were tested.

2. Experimental

2.1 Catalysts preparation

The CeO_2 and CeO_2/ZrO_2 (57.4 %w/w of ceria) supports were provided by Rhodia, the $\gamma-Al_2O_3$ by Sasol while the 14CeAl (14 %w/w of Ce in $CeO_2/\gamma-Al_2O_3$) was prepared by the method indicated below; the $PtCl_4$ ($\geq$ 99.9 % trace metals basis) and $Ce(NO_3)_3\cdot6H_2O$ (99.99 trace metals basis) were supplied from Sigma-Aldrich.

The 1 % Pt/CeO_2 (PtCe) and 1 % $Pt/CeO_2/ZrO_2$ (PtCeZr) catalysts, both containing 1 %w/w of Platinum, were prepared by impregnation of the support with an aqueous solution of the proper amount of $PtCl_4$, and the mixture was stirred at the boiling point until evaporation occurred. The resulting solid was dried in an oven at 393 K for 3 h and then calcined at 873 K for 3 h.

The 14CeAl was prepared by impregnation of $\gamma-Al_2O_3$ with 4 equimolar aliquots of a water solution of $Ce(NO_3)_3\cdot6H_2O$. In each impregnation the mixture was stirred at the boiling point until evaporation of the water occurred, the resulting solid was dried in an oven at 393 K for 3 h and then calcined at 673 K for 9 h. The $Pt(NO_3)_4$ solution was prepared by the method of Vasilchenko et al (2012 and 2013). The 1 % $Pt/14CeAl$ (Pt14CeAl) was prepared by impregnation of 14CeAl with the proper amount of the platinum nitrate solution and the mixture was stirred at the boiling point until evaporation occurred; the resulting solid was dried in an oven at 393 K for 3 h and then calcined at 673 K for 6 h.

2.2 Catalysts characterization

The effective metal loading of the catalysts was determined through the Energy Dispersive X-ray fluorescence (EDXRF) spectroscopy (Thermo-Scientific Quant'X); the powder XRD patterns (Cu Kα radiation) were recorded by a D8-Advance Bruker WAXRD spectrometer, and the crystallites size was determined; the Raman spectra were obtained by a Renishaw inVia microRaman spectrometer (514 nm excitation wavelength); the specific surface area (SSA) was determined by N_2 adsorption-desorption isotherm at 77 K (B.E.T. method), with a Costech Sorptometer 1,040; the thermogravimetric analysis (TGA) was performed by a Q600 connected to a quadrupole-mass detector Discovery MS TA Instruments: The temperature programmed reduction (TPR) was carried out on 3 cm^3 of samples in powder form, performed in a stainless steel tube having annular geometry. A 5 % H_2/N_2 gas mixture (flow rate: 1,000 Ncm^3/min) was fed to the reactor, and temperature was raised up to 673 K or 873 K (depending on the analyzed sample) with a heating rate of 10 K/min. The hydrogen uptake was recorded by an online Antaris IGS FT-IR analyzer.

2.3 WGS experimental tests

The Water Gas Shift tests were performed at atmospheric pressure, in a temperature range of 423-673 K. The reacting mixture (500 Ncm^3/min) consisted of 5 % CO, 25 % H_2O and Helium balance. The activity of the catalysts was tested in a fixed bed tubular stainless steel reactor having an internal diameter of 18 mm. All the samples were crushed into powder and sieved (180-355 μm) to reach 6 cm^3 of catalyst, diluted 1:1 vol with quartz (500-700 μm), in order to minimize the pressure drops and the thermal effect of the exothermic reaction. The gas hourly space velocity (GHSV) was set up to 5,000 h^{-1}. All the catalysts were reduced by TPR before reaction. Products stream was continuously analyzed by a Hiden Analytical quadrupole Mass Spectrometer, evaluating CO_2, H_2, CO, CH_4 and He.

The catalyst showing the best performances in this initial screening was then tested under different flowing condition (at different GHSV), and also its stability was investigated. The tests were carried out in a stainless steel tubular reactor with annular geometry, the same reactor as described above for the TPR

Table 1: Catalysts characterization: EDXRF Pt content, Specific Surface Area, average crystallites size, TPR H_2 uptake

Sample	Pt load. %w/w	S.S.A. [m^2/g]	Crist. size [nm] (plane)	H_2 uptake [µmol/g]
γ-Al_2O_3	-	158.4	5.35 (440)	-
14CeAl	-	137.46	6.09 (CeO_2 (111))	-
Pt14CeAl	1.08	132.3	6.78 (CeO_2 (111))	134
CeO_2	-	127.2	5.66 (111)	-
PtCe	0.76	125.7	6.60 (CeO_2 (111))	983
CeO_2-ZrO_2	-	64.45	7.21 (111)	-
PtCeZr	0.75	65.35	7.22 (CeO_2-ZrO_2 (111))	1,205

experiments. The influence of contact time on CO conversion was studied by varying the gas hourly space velocity from 6,000 h^{-1} up to 51,000 h^{-1}. The reactants mixture consisted of 8 % CO, 30 % H_2O and N_2 balance and the temperature was set up to 498 K.

Finally, a stability test was made up at a temperature of 473 K on a reactants mixture containing 8 % CO, 30 % H_2O and N_2 balance, with a GHSV = 15,000 h^{-1}.

3. Results

3.1 Characterization

In Table 1 the main results of the characterization of the catalysts were reported.

The hexahydroxy platinic acid (platinum nitrate solution precursor) was analysed by EDXRF to confirm the absence of sodium and by TGA to evaluate the water content.

The specific surface areas recorded for all samples showed that the addition of the active species did not involve a substantial decrease of the s.s.a.

The calcined supports and catalysts were subjected to X-ray diffraction analysis and the results were analyzed by comparing them with the data available in literature. The XRD diffractogram of the ceria support presented the characteristic cubic fluorite type phase, the main peaks were located (JCPDS 34-0394) at 28.6, 33.4, 47.8 and 56.7 °, corresponding to the reflections in the (111), (200), (220) and (311) crystalline planes. The same profile was recorded also in ceria/zirconia diffractogram (Figure 1a), however all the peaks appeared shifted towards higher 2θ values, to indicate the formation of a solid solution between ceria and zirconia (Petkovich et al., 2011). No Platinum peak was observed in all samples, probably due to the too low Platinum loading, below the instrument detection limit. The support crystallites size of the catalysts were determined from X-ray line broadening using the Scherrer equation (Table 1). All the samples had a support average size less than 10 nm. In particular, the Ce and 14CeAl samples showed very similar size, while the CeZr one had a slightly bigger crystallites size. Actually, the addition of the active species caused an increase in the crystallite size of the support for Ce and 14CeAl samples, while no increase was obtained for the ceria-zirconia one.

The Raman spectra of ceria support show the typical strong band at 464 cm^{-1} attributed to the first order F_{2g} mode of the fluorite type phase, while are barely visible the weak bands at 258, 595 and 1,179 cm^{-1} respectively attributed to second-order transverse acoustic (2TA), defect-induced (D) and second-order longitudinal optical modes (2LO) (Wu et al., 2010). On the contrary the calcined PtCe derivate shows the growth of the bands at 258, 595 and 1,179 cm^{-1}, the appearance of a broad band at 657 cm^{-1} and a shoulder at 420 cm^{-1}; the last two bands were attributed to the presence of PtO species (McBride et al., 1991), besides the band at 595 cm^{-1} could be an overlapping between the D-band of ceria and traces of an amorphous phase of α-PtO_2.
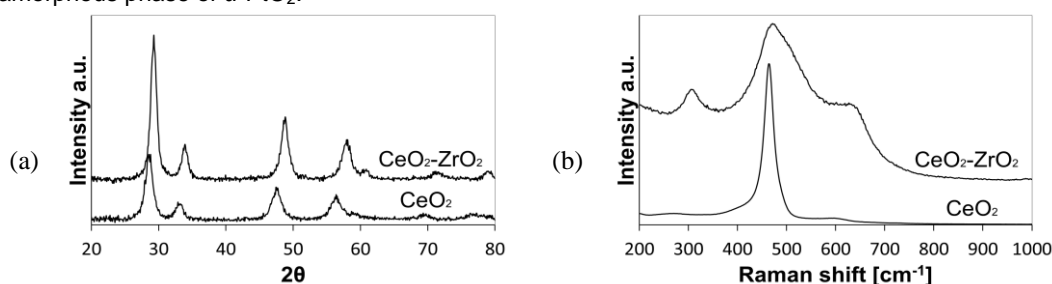

Figure 1: XRD (a) and Raman (b) comparison between CeO_2 and CeO_2-ZrO_2

The comparison between the Raman spectra of ceria and ceria-zirconia (Figure 1b) showed a significantly distorted structure due to the substitution of some Ce^{4+} ions with the smaller Zr^{4+} ions; so, comparing the data with those reported in literature (Ahniyaz et al., 2005), we concluded that the CeO_2-ZrO_2 mixed oxide contained a tetragonal distortion attributable to the metastable t'' phase. The same results were achieved by applying the Bragg formula to the XRD patterns, obtaining a smaller cell parameter for the ceria-zirconia sample (7.3 Å for CeO_2 and 6.9 Å for CeO_2-ZrO_2).

n addition to the bands of CeZr support the Raman spectra of PtCeZr show also bands at 175, 555 cm^{-1} similarly to what happened of PtCe. The Raman spectra of 14CeAl show exclusively the first order band of ceria at 464 cm^{-1}, while the Pt14CeAl shows also the two bands at 655 and 550 cm^{-1}, attributed to the PtO_x phases (Lin et al., 2008).

3.2 Activity and Selectivity WGS test

The catalytic activity results are summarized in Figure 2, in terms of CO conversion and selectivity to CO_2 and H_2 as functions of temperature. The activity data at each temperature were determined after stabilization of the concentration of the species, and no deactivation was detected during the tests.

All the samples showed a very good activity for the WGS, since the thermodynamic equilibrium approach was observed for temperature above 513 K. The activity of the catalysts was in the following order: PtCeZr > PtCe > Pt14CeAl. In particular, Pt14CeAl approached the equilibrium in the range 513-673 K, but at 473 K the conversion fell to 5 %. The same happened for the PtCe sample, but in this case the CO conversion at 473 K was still very high (90 %), while it decayed to 60 % at 453 K. The PtCeZr catalyst was above all the most active, reaching the equilibrium value even at 453 K, and also showing a very appreciable activity at 423 K (CO conversion was about 30 %).

With regard to the selectivity towards the Water Gas Shift reaction, all the catalysts showed appreciable behaviors in the whole investigated range. Only the PtCeZr showed a slightly lower selectivity, related to a little amount of methanation reaction at the highest operating temperatures.

3.3 Catalyst performance by varying GHSV and stability test

As already mentioned above, in the conditions investigated PtCeZr resulted, among the others, the best catalyst in terms of activity and selectivity: on this formulation, the effect of GHSV on catalytic performances was investigated. The results are shown in Figure 3.
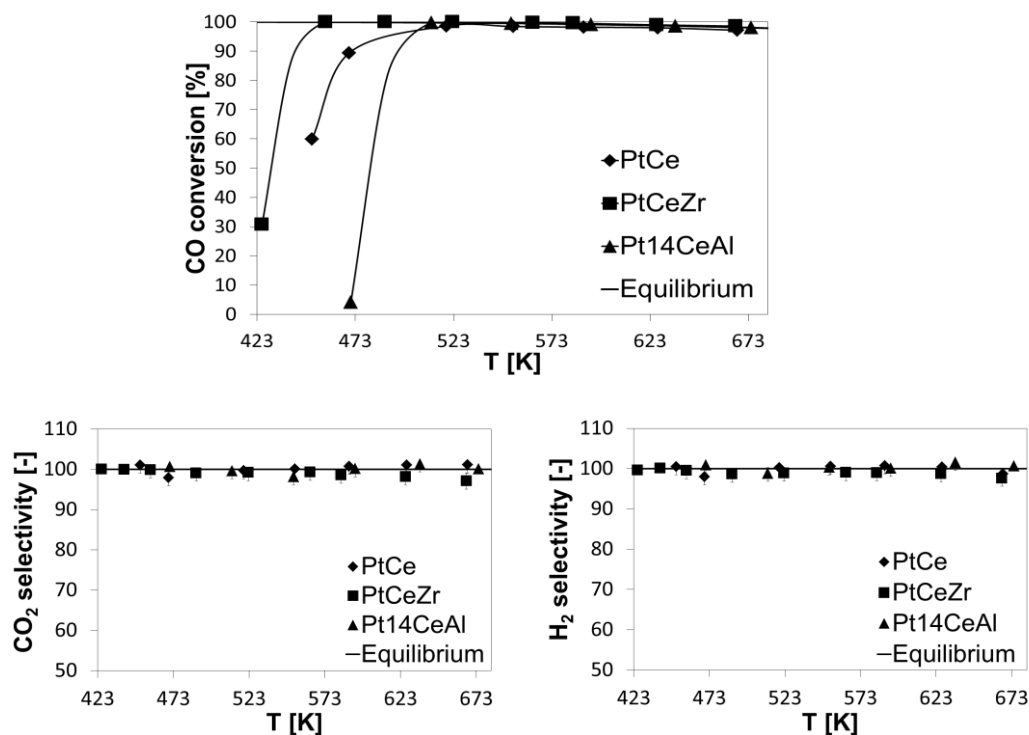

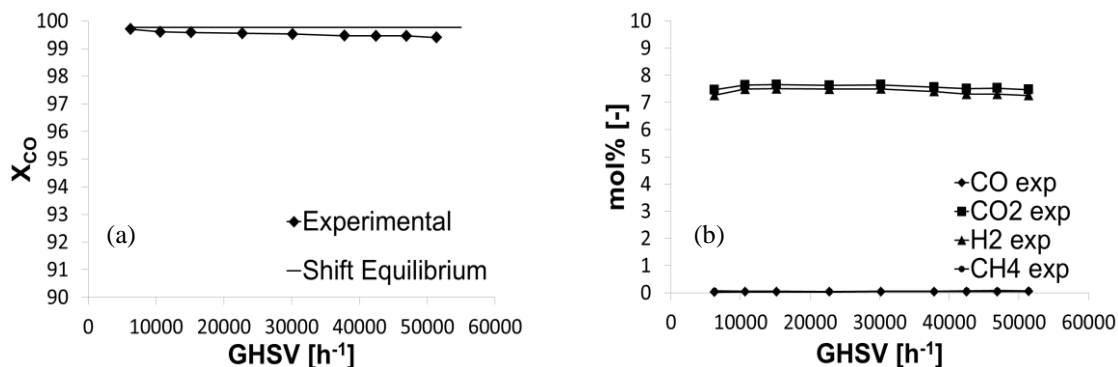Figure 2: PtCeZr: X_{CO} vs T (up); CO_2 and H_2 selectivity vs T (down)

Figure 3: PtCeZr: X_{CO} vs GHSV (a) and molar concentration vs GHSV (b)
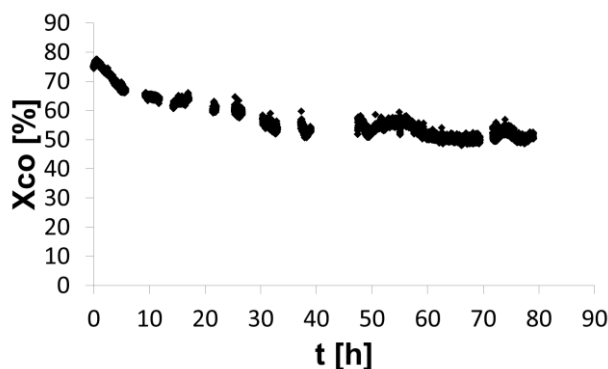

Figure 4: PtCeZr, stability test (T = 473 K; GHSV = 15,000 h^{-1})

As reported, this catalyst showed an excellent activity, also at high space velocity, both in terms of conversion that selectivity. A slight reduction in catalytic activity did not affect the very good performance of the proposed formulation.

Stability test results, performed on PtCeZr, are summarized in Figure 4. It is observed that, under the selected operative conditions, typically very stressful for the WGS catalyst, the CO conversion during the first 40 h decreased from an initial value of 75 % to a value of 50 %, then the conversion did not change anymore. The main reasons for this behavior are still not clear, and further experiments need to be carried out. However, it can be assumed that probably sintering phenomena may causes the initial deactivation, leading to a constant value of the CO conversion when sintering was completed.

4. Discussion and conclusions

During the last years the catalytic behavior of the ceria supported catalysts for the Water Gas Shift reaction has been largely studied. It has been demonstrated also the synergism between the noble metal and the oxide support, operating together into the reaction mechanism; so, it has been established that the main reason for having a high active WGS catalyst has been referred to the redox properties of the ceria support, i.e. the capability to provide oxygen atoms due to the high oxygen mobility into the bulk of the support. Therefore, it is clear that the presence of ceria is of primary importance. The approach used in this work has been to prepare different platinum based catalysts supported on ceria, trying to modify the support composition to show the importance of the reasons discussed above. In fact, the modification of the ceria bulk by the introduction of Zr atoms brought to a lower cell parameter, as detected by XRD; this phenomenon has created a distortion in the crystal cell, and may have been the main cause of the better activity of the PtCeZr catalyst. Moreover, it is well known that ceria, when used in a WGS catalyst, undergoes the carbonation phenomenon, this limiting the catalyst overall activity. So, the presence of zirconium could have also limited this, enhancing the activity also at lower temperatures.

The PtCeZr catalyst could be really a very attractive catalyst for the one-stage WGS process, showing a 30 % CO conversion at 423 K, which is a very low temperature; moreover, it could be used also in a membrane reactor, where the operating condition of course could be favorable, leading to savings in terms

of energy consumption, and where the presence of the membrane is useful to reach higher conversion by removing selectively one product from the reaction mixture.

Actually, also the Pt14CeAl could be a promising catalyst for the WGS process, taking into account the limited supply of ceria and zirconia, as rare earths, because in this catalyst there is a reduction of the ceria content of about 85 %; this, together with the low platinum loading, would provide a very active catalyst with also a competitive price.

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