

Pt vs. Au in Water Gas Shift Reaction

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Abstract

This work presents a comparison of the gold and platinum based catalysts behavior in the water gas shift (WGS) reaction. The influence of the support, e.g. its composition and electronic properties, studied in details by means of UV-VIS spectroscopy, of the metal nature and dispersion and of the stream composition has been evaluated. The catalytic performance of the samples is directly correlated to the electronic properties modification as a function of metal and/or support. Both metals present high activity in the selected reaction although in a different operation temperature window.

Keywords: gold catalyst, platinum catalyst, mixed oxides, Water Gas Shift (WGS)

INTRODUCTION

Nowadays, steam reforming is the main hydrogen source, especially when the final objective is the generation of pure hydrogen. The hydrogen yields generally increases via water gas shift (WGS) reaction, with the additional value of CO abatement. The WGS reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) is a classic industrial process commonly carried out in a series of adiabatic converters where the effluent from the reformer system is treated in two WGS reactors, a high temperature shift (HTS) and low temperature shift (LTS) ones. The industrial HTS catalysts are based on iron-chromium mixed oxides while the LTS catalysts on copper-zinc mixed oxides [1-3]. Since the WGS reaction is an exothermic and equilibrium-limited reaction, in which the H_2 production decreases with the increase of the temperature, a LTS reactor is preferred for hydrogen yield rising. In spite of the wide use of the copper-zinc LTS catalysts, this catalytic system still requires specific reduction procedures and safety cautions on air exposure due to its pyrophoricity. These drawbacks are well controlled in the hydrogen production plants but when mobile applications are envisaged, the requirements for the WGS catalysts are quite different from those of the traditional catalysts [4]. Thereby, i) a non-pyrophoric low temperature catalyst, ii) an essential reduction of the volume and weight of the reactor and iii) a sufficient withstanding to start-up/shut-down cycles are critical conditions for a successful techno-economic implementation. In response to these needs, noble metals (NM) based catalysts like Pt [1,5] or Au [3,6] are under intense development.

Despite of the extended number of studies concerning platinum or gold-based catalysts for the WGS reaction, still at present in the scientific community no clear

preference for the use of one or another system exists. Burch [6] summarizes the advantages and drawbacks of gold catalysts in comparison to their platinum analogs for the WGS reaction. According to this review, gold catalysts can offer some advantages in the low temperature range (180-250°C) where the platinum catalysts are insufficiently active. However, at higher temperatures the reported inherent activity of the gold catalysts is lower than that of properly activated platinum ones [7].

The pretreatment employed for the Pt based catalysts appears to be essential for their performance which is not the case of gold catalysts, which could be used as prepared. It is very difficult to draw a general conclusion about the importance of one or another NM from the data available in the literature based only on the discussion of the catalytic behavior of the catalysts. No matter the metal, a strong influence of the preparation method is generally reported [8,9]. The gold-based catalysts are only active when present in a highly dispersed state, which imposes, for a proper comparison with the platinum based catalysts, the use of a suitable preparation method. Moreover, the choice of the support is also of primordial importance for both metals [10-12]. In general, the most active formulations are commonly based on NMs supported on reducible oxides as CeO₂ [13-15]. The enhanced activity of the CeO₂ supported NM catalysts is frequently attributed to the ceria ability to undergo fast storage/release of oxygen cycles via a reversible conversion between Ce⁴⁺ and Ce³⁺ oxidation species [16, 17]. These redox cycles implies a mechanism of oxygen vacancies formation that is indirectly correlated with the catalyst ability to activate oxygen species through electronic transfer and hence to the catalytic activity in oxidation reactions. CeO₂ lattice modifications, like the incorporation of trivalent metals ions, allow the improvement of the oxygen exchange ability and, thus the catalytic performances of the catalytic systems. The incorporation of metallic promoters, as for example Fe or Zr, was recently

reported to successfully modify the CeO₂ electronic band structure thus increasing its reducibility and WGS activity [18,19].

A meaningful comparison for the reported catalytic activity in the WGS reaction of Au and Pt catalysts is difficult since the authors proposed different catalyst formulations that are tested in a variety of feedstock compositions and reaction conditions. For example, Trovarelli et al. [20] have compared Au and Pt supported on zirconia-promoted ceria concluding that the synergism between the precious metal and the oxide can be affected by the chosen synthesis parameters and structural and morphological properties of the support.

On these bases, the aim of this paper is to compare the catalytic behavior of gold and platinum catalysts supported on ceria modified materials in the WGS reaction, correlating its activity to the nature of the support and of the NM. In order to avoid more variables, the same support and metal loading has been kept for all the catalysts. The preparation methods were chosen in order to obtain comparable metal particle size and dispersion during the reaction. The catalytic activity and stability have been measured in both model and simulated realistic post reforming WGS streams.

EXPERIMENTAL:

- Catalyst synthesis:

γ -alumina powder (Sasol) has been employed as a main component of the evaluated materials. The supports (CeO₂/Al₂O₃ and Ce_{0.8}Fe_{0.2}/Al₂O₃) used in this study have been prepared by incipient wetness impregnation using Ce(NO₃)₃·6H₂O (Aldrich) and Fe(NO₃)₃·9H₂O (Aldrich) as oxides precursors. Supports were designed to present 15 wt.% of CeO₂, 2 wt.% of FeO_x and 80-85 wt.% of γ -Al₂O₃. The impregnation was carried out in 50 ml ethanolic solution and evaporated at 50°C at reduced pressure in a

rotatory evaporator till a dry solid was obtained. The solid was then treated with NH_3 solution (10 mol L^{-1}) for 30 min in order to assure the full conversion of the nitrates to hydroxides. The supports were then filtered, dried and finally calcined at 450°C for 4h.

Platinum based catalysts were obtained via aqueous impregnation using tetrammonium nitrate platinate (Johnson Matthey) as Pt precursor at reduced pressure in a rotatory evaporator at 80°C . The as obtained solids were then dried and calcined at 350°C for 8h at a heating rate of $5^\circ\text{C}/\text{min}$.

The gold based catalysts were prepared by the direct anionic exchange method, assisted by NH_3 using HAuCl_4 (Alfa Aesar) as gold precursor [21]. The calcination was carried out in the same conditions than for the platinum based ones but for 4h. The NM total loading was set to 2 wt%. As mentioned above, the preparation methods have been intentionally selected in order to achieve comparable precious metal particle sizes and dispersions.

In the adopted nomenclature the oxygen and the stoichiometric coefficients into the mixed oxide were omitted for simplicity. For example, Pt (2%)/ $\text{Ce}_{0.8}\text{Fe}_{0.2}/\text{Al}_2\text{O}_3$ is named as Pt/CeFeAl.

- *Catalyst characterization:*

X-ray microfluorescence spectrometry (XRMF) was used to determine the chemical compositions and the analysis was performed in an EDAX Eagle III spectrophotometer with a rhodium source of radiation.

The textural properties were studied by N_2 adsorption-desorption measurements at liquid nitrogen temperature. The experiments were carried out on a Micrometrics Tristar

II instrument. Before the analysis, the samples were degassed for 2h at 250°C in vacuum.

X-ray diffraction (XRD) analysis was carried out on a X'Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu K α radiation (40 mA, 45kV) over a 2 θ -range of 10 to 95° and a position-sensitive detector using a step size of 0.05° and a step time of 240 s.

The Raman spectra were recorded in a dispersive Horiva Jobin Yvon LabRam HR800 spectrometer, with a 20 mW He–Ne green laser (532.14 nm) operating 5 mW. The microscope used a 50x objective and a confocal pinhole of 1000 μ m.

The UV-Vis spectra were recorder on a Varian spectroscopy model Cary 100, equipped with an integrating sphere using BaSO₄. All spectra were collected in diffuse reflectance mode and transformed to a magnitude proportional to the extinction through the Kubelka-Munk function $F(\alpha)$.

CO chemisorption measurements were performed on fresh and post-reacted platinum samples by using a Micromeritics Autochem II apparatus. Prior to chemisorption, the samples were heated with a ramping rate of 10°C/min from ambient temperature to 350°C and treated with flowing hydrogen (10% H₂ in Helium) for 2 h at this temperature. The samples were then cooled to room temperature under vacuum. It was assumed that each surface platinum atom was one CO chemisorption site.

Gold dispersion was estimated through High-Angle Annular Dark Field-Scanning Transmission Electron Microscopy (HAADF-STEM). The images were recorded on a JEOL2010F instrument. The HAADF-STEM studies were performed using an electron probe of 0.5 nm diameter and a diffraction camera length of 10 cm. It should be pointed that the chemical composition of the sample was studied in STEM mode using an

Energy-dispersive X-ray spectrometer (Oxford Instrument, Inca Energy-200). Loose powder samples were supported on a holey carbon-coated copper grid without using any liquid. The excess of sample was removed from the grids using a flow of N₂. This approach allows us to obtain electron transparent thin regions.

Catalytic activity

The water gas shift reaction was carried out placing 1g of catalyst in a tubular flow reactor at atmospheric pressure in the 180-350 °C temperature range using two reaction schemes named model and realistic conditions. Pt based catalysts were activated during 2h at 350 °C in a H₂ stream (10% vol.) while a pretreatment was not necessary for gold based samples. For the model WGS reaction just water and CO diluted in nitrogen were used while for the realistic WGS reaction a reformat gas surrogate containing hydrogen and carbon dioxide was selected. The experimental mixtures and conditions are summarized in the Table 1. The model reaction mixture is the one usually employed for testing catalysts for the clean H₂ production via WGS. The conditions used to test the catalysts using the reformat gas surrogate simulate the outlet of a typical ethanol reformer and they are known as CO clean-up conditions. All the solids were sieved and the 600-800 µm fraction retained. The CO and CO₂ content was analyzed with an ABB gas analyzer and the activity expressed in terms of CO conversion.

RESULTS AND DISCUSSION

The textural properties of the studied systems are summarized in Table 2. All the samples are mesoporous materials with textural properties mainly governed by the presence of the primary γ -Al₂O₃ support. Regarding the supports, a decrease on the specific surface area, pore volume and pore size was observed when ceria is added to alumina. This effect was enhanced with the inclusion of Fe as ceria doping agent,

leading to materials with smaller pores and lower specific surface areas than those of the CeAl sample.

As reported elsewhere for gold catalysts, the NM addition increases the surface area in all the samples respect to their corresponding supports. The increase of the surface area is related to the observed increase in the pore volume. This effect has been previously explicated by Somorjai et al. [22] claiming that the inclusion of gold nanoparticles in the pore structure would lead to a pore widening and therefore to an increase in the specific surface area. On the contrary, the opposite effect is observed for the platinum based catalyst pointing to a slight blocking of the pores by the presence of platinum species.

The chemical composition of the solids is presented in Table 3. All the samples show chemical compositions close to the target values. Nevertheless, in the case of bare alumina supports, a metal loading below the target one was obtained irrespectively of the NM (Au or Pt) pointing to a weak interaction between the γ -Al₂O₃ support and the metals. The presence of ceria and ceria mixed oxides leads to stronger metal-support contact, resulting in an enhanced metal loading. In any case, the obtained metal loadings and the target ones are closer for platinum than for gold and this must be related to the different synthetic procedure. Gold deposition was carried out under a high basic media. According to Moreau and Bond, the gold uptake depends on several factors such as pH, temperature and specific surface area of the support [23]. Working at pH above the isoelectric point of the solid (pH ~ 7.2 in our ceria containing samples) involves a change of charge in the support becoming increasingly more negative. This results in an electrostatic repulsion of gold containing anions limiting their deposition.

XRD diffraction patterns of the employed supports are shown in Fig. 1a. All the supports present the characteristic diffractions of the cubic CeO₂ fluorite structure (JCPDS#00-004-0593) and the γ -Al₂O₃ phase (JCDPS# 00-048-0267). However, no diffraction peaks of any iron-containing crystalline phases were detected either for the small amount of the doping agent or for the possible inclusion of these cations in the ceria lattice resulting in a solid solution formation. Indeed, all the ceria diffraction peaks were shifted toward higher angles when iron was added suggesting the formation of CeO₂-FeO_x solid solution. The CeO₂ lattice parameter was then estimated using the main (111) CeO₂ diffraction line (where no contribution of the γ -alumina phase is observed), the λ factor of Cu filament (1.5405 Å) and the expression that relates the lattice parameter of the fluorite structure with the diffraction angle:

$$a = \sqrt{h^2 + k^2 + l^2} \left(\frac{\lambda}{2\sin\theta} \right)$$

The calculated parameter for the CeAl sample resulted to be 5.407 Å, which is very close to the reported value for a pure ceria powder sample in ref. [18]. The corresponding a parameter for the CeFeAl sample was 5.395 Å. The formation of a substitutional Ce-Fe solid solution must result in a lattice contraction for ceria since Ce⁴⁺ (0.97 Å ionic radius) ions are bigger than Fe³⁺ (0.64Å ionic radius) ions. Recently, for a similar mixed oxide system, the formation of Ce-Fe solid solutions together with the detection of amorphous Fe₂O₃ segregated phases was described [24]. Actually, interstitial and substitutional solid solutions can be obtained when ceria and iron oxides are mixed together. The formation either of interstitial or substitutional solid solutions depends on the relative amount of each oxide component [18,25]. In our case the presence of certain amount of segregated iron species cannot be totally discarded since the small amount of iron limits its detection by XRD. As a secondary effect of the

addition of Fe to the CeO₂ lattice, an increase in the CeO₂ particle size was observed. The calculation using Scherrer equation reveals doubling of the size when Fe is added to the matrix (21 Å for the CeAl and 37 Å for the CeFeAl).

The XRD diffraction patterns of Au and Pt catalysts are presented in Figure 1B and 1C, respectively. Neither gold nor platinum crystalline phases were observed indicating that both NM species are undetectable by XRD, implying good dispersion and an average crystallite size below 4 nm. Moreover, the lattice parameter of ceria remains unaltered upon the addition of the NMs, which indicates that the metallic species are dispersed on the multicomponent support.

An approach to the electronic properties of the studied materials was obtained by UV-Vis spectroscopy. The UV-Vis spectra of the synthesized supports are shown in Fig. 2a. All the supports presented a broad band, centered at *ca.* 280 nm, associated to CeO₂ and assigned to a charge transfer O_{2p} → □Ce_{4f} transition. In the case of the CeFeAl support, the absorption bands are wider than those of the CeAl one. This phenomenon is probably due to the contribution of the iron oxide absorption features at about 530 nm. In fact, Reddy and coworkers ascribed a similar band at 533 nm to d-d transition of α-Fe₂O₃ [26].

For further understanding, the direct and indirect band gaps of the prepared supports were estimated by extrapolating to zero the energy dependence of the [(F(R)hv)^{1/2} and [(F(R)hv)^{1/2} functions, respectively. The results are summarized in Table 4. The CeAl sample presented a direct band gap of 3.05 eV in good concordance with the results obtained in previous studies for CeO₂-Al₂O₃ systems [27]. The experimental band structure of ceria is described considering the valence and conduction bands resulting from O_{2p} and Ce_{5d} states, respectively, separated *ca.* 6 eV. Between these two bands it

appears a flat Ce_{4f} band. For defect-free crystals the later is empty and lies around *ca.* 3 eV above the valence band, but if it becomes partially occupied, their energy separation with the valence band decreases [28]. This description results in a fairly localized picture of the 4f electrons that remain on the cerium ions resulting in Ce^{3+} ions.

The measured band gap for our ceria sample is smaller than that found in ceria single crystals [29,30]. This red-shift band gap has been previously observed for ceria nanoparticles, the shift depending on the particle size [31]. The reason for this shift must be associated to the higher ratio of Ce^{3+} to Ce^{4+} species on decreasing the particle size [32-33]. As Ce^{3+} ions concentration increases, a decrease in the band gap energy is observed. This decrease is associated with the population of the defect states, associated with Ce^{3+} ions and oxygen vacancies. On increasing the 4f level population, as a result of the increase in the defect concentration, a decrease in energy reducing the band gap is observed.

On considering the Ce-Fe mixed oxide a further decrease in the band gap energy, in comparison with the original CeAl sample, was observed. A similar decrease in the direct and indirect band gaps of Fe-doped ceria has been previously reported [34-35]. However, the average crystallite size does not follow similar trends, either a decrease [36], an increase [37] or even no effect [38] in the crystallite size has been reported on increasing the doping of ceria with iron. Therefore, the band gap modification upon doping ceria with iron cannot be associated to a size effect, but to a modification of the solid solution electronic structure. To elucidate the primary reason for the band gap modification further investigation by Raman spectroscopy of the CeAl and CeFeAl samples was carried out (figure 3). Bare CeO_2 presents a peak at 458 cm^{-1} according to its Raman active F_{2g} mode, and ascribed to the oxygen symmetric breathing vibration around Ce^{4+} [39-41]. The introduction of Fe^{3+} cations into the ceria lattice and the

change of the crystallite size, among other factors, could generate symmetry distortions resulting generally in broadening and/or shift of the F_{2g} Raman signal [10]. For example, an increase of the crystallite size should broaden and shift the band to higher wavenumbers [42], and a strong interaction between Ce and Fe should shift the same band on the opposite direction. Considering that the particle size of the CeO_2 increases when the Fe is introduced, in accordance with the XRD results, a shift to higher wavenumbers is expected. However, a shift to lower wavenumbers and the broadening of the F_{2g} Raman signal is observed and associated with the introduction of Fe^{3+} cations into the ceria lattice. The detected modifications in the shape of the F_{2g} signal evidence the Fe–Ce interaction in the doped systems [12] and suggest its primary role of the electronic properties modification. The distortion of the cubic lattice induced by the formation of the solid solution must be related to changes in the population of the oxygen vacancies in the material and therefore, with the electronic properties [43]. Similarly to our observations, Popovic et al. [43] report the Raman study of a set of iron-doped ceria nanocrystals, $Ce_{1-x}Fe_xO_{2-y}$ ($x = 0, 0.06, \text{ and } 0.12$). Softening and broadening of the Raman F_{2g} mode as a function of dopant oxidation state allow the authors to propose not only the presence of highly localized $4f$ electrons in Ce^{3+} ions but also electron delocalization through $Ce(Fe)-O(V_O)-Ce(Fe)$ orbitals, in highly deficient Fe-doped solid solutions. This electron delocalization results in a split of the $4f$ band inside the ceria band gap in such a way that the $4f^1$ band overlaps with the $O2p$ band. This way, the $4f^0$ band is situated inside the band gap resulting in a band gap decrease with respect to the undoped ceria support. For n-type semiconductors as ceria, the band gap energy value evidences the position and the donating properties of the valence band and can be used as a measure of the basicity of the solid [27,35]. Therefore, the lower the band energy value the higher the easiness of donating electrons.

The UV-Vis spectra of the NM (Au, Pt) supported catalysts are shown in figure 3B. Collective oscillation of the conduction electrons stimulated by the incident light are responsible for the broad absorption band in the 500-600 nm range (plasmon resonance absorption) observed in all the prepared gold catalysts. The size and shape of the metallic particles, as well as the dielectric properties of the support influences the intensity and position of the gold plasmon [44]. As the gold particle size is below 4 nm (as indicated by XRD) and remains approximately constant upon iron doping with ceria, the observed slight shift in the position of the plasmon maximum must be ascribed to the presence of iron. This iron presence favors delocalizing the cerium 4f¹ electrons through Ce(Fe)-O(V_O)-Ce(Fe) orbitals modifying the electronic density of gold as well as the dielectric properties of the iron-doped support. Besides this, both Au and Pt reduce the materials band gap, Table 3, suggesting the insertion of NM levels between the valence and conduction bands of ceria [32].

Recently, it has been proposed that oxygen vacancies in ceria may cluster [45], the groups of exposed Ce³⁺ ions in these clusters would become a potent surface site for catalysis, as adsorbed gases or reaction intermediates could interact simultaneously with several Ce³⁺. The interaction of these surface clusters with gold atoms results in a strengthened Au adsorption ions [46]. In this gold adsorption, the role of Ce 4f states is of paramount importance. The partially occupied *f* states of reduced cerium ions, resulting from the removal of oxide ions, act as an electron donor stabilizing the adsorbed Au atoms. This donor-acceptor concept implies that Ce³⁺ ions are re-oxidized and gold atoms become reduced generating an ionic bonding between negatively charged gold atoms and the surrounding cerium atoms [47]. DFT studies of the Pt/CeO₂ interface showed a similar picture to that shown by gold atoms adsorbed on ceria. Platinum atoms sit on oxygen vacancies acting the partially filled *f* sates of Ce³⁺ ions as

donors and *5d* states of Pt as acceptor levels [48]. Our HAADF-STEM data, Figure 4, shows that gold nanoparticles sit always on iron-doped ceria nanoparticles supporting the NM-ceria interaction.

The band gap observed for the Au catalyst is lower than the one estimated for the Pt sample, Table 3, which can be explained on the basis of the electronic structure of both catalysts. The presence of metal induced gap states (MIGS) is the result of the interaction between the NM and the iron-doped ceria surface. The ionic interaction between the negatively charged NM atoms and the surface vacancy clusters results in overlapping of Pt *5d* states with the O *2p* states, while Au *5d* states lies in between the O *2p* and Ce *4f* levels. Whatever the MIGS configuration, accommodation of the extra electrons would result in the transfer of electronic density from the Ce(Fe)-O(V_O)-Ce(Fe) ensemble to the NM being the negative charge on platinum higher than the one supported by gold.

Water-gas shift behavior

Both gold and platinum based catalysts were evaluated in the WGS. Figure 5a compares their catalytic activities using the named model conditions. Although comparison of both catalysts is not an easy task, it is clear that gold and platinum based catalysts exhibit different conversion trends no matter the support. The NM supported catalysts on bare Al_2O_3 show the lowest conversion for both metals confirming the strong influence of the support nature on the catalytic properties. Whatever the temperature, the gold catalysts presents higher conversion when supported on CeFeAl and lower when the support is the bare alumina. Also for platinum catalysts, the conversions are hardly modified when supported on CeFeAl or CeAl being, for temperatures below 300°C, always higher than supported on the bare alumina. By comparing the observed different catalytic activities, it may be stated that the support

nature has a stronger influence on the gold catalysts than on the platinum ones. In this context, it is worth noting that at low temperatures, gold catalysts are always more active than the corresponding platinum catalysts but the reverse is true for temperatures above 200 °C.

Generally, the NM based catalysts supported on CeO₂ or ceria mixed oxides are often described in the literature as very efficient systems [6,49]. Cerium containing systems show enhanced activities with respect to the bare alumina catalysts, being this usually attributed to fast Ce⁴⁺/Ce³⁺ redox cycles that results in the promotion of the WGS reaction redox mechanism. In this mechanism, the formation of carboxyl species in the oxygen vacancies of the support is often reported [50]. Consequently, the differences in the activity between similar gold and platinum catalysts may be explained on the basis of different reaction pathways.

In this redox mechanism, CO adsorbs on NM surface sites and is oxidized by oxygen species from CeO₂, which, in turn, is re-oxidized by water that adsorbs on the oxide surface generating hydroxyl groups bound to the oxygen vacancies. In other words, it involves the reaction of the reactants, CO and H₂O, with the surface: CO with the oxide ion of the ceria (to yield CO₂) and H₂O with the anion vacancies on ceria (generating OH groups and, eventually, H). Cerium re-oxidation upon water adsorption has been previously described for Au/CeO₂ catalysts [51]. An important role of the metal is to adsorb/activate CO and to create oxygen vacancies at the metal-ceria interface [1]. Through a microkinetic modeling of the low temperature WGS reaction on Pt/CeO₂, it has been proposed that the most significant reaction pathway proceeds via a carboxyl (COOH) intermediate [52]. This reaction pathway implies the nucleophilic attack of a surface hydroxyl group to an adsorbed CO molecule generating the carboxyl species adsorbed on the NM. Further decomposition of this species results in the

formation of CO₂ and H₂. The thermal decomposition of this carboxyl species was proposed as responsible for CO₂ evolution on supported gold catalysts as the simpler and more probable mechanism [53]. More recently, Rodriguez et al. [54] propose also carbonate or bicarbonate species as intermediates in the low temperature WGS.

The main difference between the tested NM may reside on water dissociation. Thus, while CO activation only occurs on the metal particle, water dissociation may take place either on the support, as for gold catalysts, or in the support and the metal particle as in the case of platinum catalysts. This effect can be clearly seen for alumina-supported NMs, the activity for the platinum catalyst increases with temperature reaching the equilibrium conversion at *ca.* 300°C; on the contrary the gold catalyst present a very low conversion (~10% CO conversion) hardly dependent on temperature. DFT calculations have found that water dissociation is highly endothermic on Au(111) and slightly endothermic on Pt(111) [55]. Therefore, in the absence of a support able of activating water dissociation only, the Pt catalysts will be active in the WGS. For that reason, the influence of the support nature in the WGS activity of gold catalysts might be far more important than for platinum based ones [8,10].

The modification of the alumina support alters the concentration of oxygen vacancies and hence, reduces the band gap and increases the Lewis basicity of the support. The catalytic activities of the gold catalysts follow parallel trends for the different supports, in such a way that for all the temperature range the CO conversions for the Au/CeFeAl and Au/CeAl catalysts are around $8,6 \pm 0,8$ and $4,7 \pm 0,6$ times that of the Au/Al catalyst respectively. Therefore on increasing the concentration of oxygen vacancies, the band gap decreases and the basicity increases favoring water dissociation and hence the CO conversion rate.

As mentioned above the existence of oxygen vacancies is not required for reaching the equilibrium conversion in the case of platinum catalysts. However, a detailed analysis evidences that the cerium-containing catalysts reach the equilibrium conversion at lower temperature (230°C) than the un-doped Pt/Al catalyst. According to this, it might be stated that the presence of a support with enhanced redox properties is also required for achieving good performances with Pt systems. It must be noticed however that the support ability for water dissociation is the same for Pt or Au catalysts and therefore the differences in catalytic activity must be associated to the CO adsorption properties on the metal surface.

The support band gap is the energy difference between the $O(2p)$ band and the localized $Ce(4f)$ states. The measured band gap in the NM supported catalysts, smaller than the corresponding to the pure support, accounts for the difference in energy between the NM $5d$ states and the $4f$ levels of cerium [27]. The catalytic activity of the samples is a function of this band gap, in such a way that the higher the band gap the higher the activity. This behavior can be explained in terms of separation between energy levels, showing that the higher catalytic activity is obtained when the energy levels introduced by the NM are closer to the $O(2p)$ ones that means, when the easiness of the electron transfer between oxygen atoms of ceria and the NM is higher and therefore this excess electron density weakens the CO bond strength through back-bonding and facilitates the formation of the carboxyl intermediate.

For a proper comparison of the catalytic data, WGS specific reaction rates (expressed in $molCO_{conv}/gmetal \cdot s^{-1}$) at two different temperatures have been calculated for the prepared materials, Table 5. Besides, in the Table 6 the turnover frequencies (TOFs) are presented in two temperatures. Two values are reported for Pt/CeFeAl, for fresh and post-reaction catalysts as a sinterization occurs during the reaction. For

Au/CeFeAl no agglomeration is observed and only one TOF value is reported for both fresh and post-reaction samples. Particle sizes calculated from TEM data and/or CO chemisorption were used to estimate NM dispersion. TEM data allows establishing a gold dispersion of 32%, corresponding to an average particle size of 4 nm, figure 4. CO chemisorption experiments led to a Pt dispersion of 70% for the platinum fresh catalyst corresponding to Pt nanoparticles of 2.2 nm, which is close to the average particle size estimated by TEM experiments (figure 4b). As stated in a previous work [56], the average particle size of gold nanoparticles after the WGS reaction remains while platinum nanoparticles sinter upon reaction resulting in 28% dispersion which accounts for an average particle size of 5.8 nm. Platinum sintering during the WGS reaction was also observed by Farrauto's group [8] reporting values for pre- and post- reaction particle sizes quite similar to those reported in this work. Once the platinum catalyst is stabilized, the particle size and metal dispersion of Au and Pt nanoparticles are quite similar and so, any effect on the differences in activity between both NM associated to particle size and/or dispersion may be discarded.

Several points should be considered regarding the obtained results. First, gold based systems exhibit superior catalytic activity in terms of rates than the platinum ones in the low temperature range. However, the tendency changes at high temperature being more active the platinum based catalysts. Second, all the ceria containing solids presented higher activities compared to Au/Al and Pt/Al. The iron to ceria promotion is also evidenced by the increase of the reaction rates for both metals observed for the iron loaded solids once compared with their un-promoted parent catalysts. Confirming the specific rate trend, the TOF values for the catalysts at 180°C show the superiority of the gold sample in this temperature range. However, at 250°C the platinum based catalysts doubled the TOF obtained for the gold system with a similar dispersion, thus converting

platinum is a better choice in this temperature range. The evaluated gold-based catalysts presented higher CO rates and turnover frequencies at 180°C than some well referenced Au/CeO₂ and Au/CeO₂-MO_x systems tested in the same conditions [57,58]. Regarding the Pt materials, the specific reaction rates of our Pt based materials are superior compared to the results obtained by the group of Efstathiou using a similar WGS inlet stream [59].

As a general remark, no matter the support, the gold based catalysts behave always better at the lowest measured temperature (180°C), and the platinum based catalysts take the advantage at temperatures above 200°C.

Taking into account all the information presented above, the study of the behavior of the catalysts in the reformat gas surrogate is mandatory. Thus, the most active Au and Pt catalysts, those supported on the CeFeAl material, were selected for the catalytic evaluation in a stream with the composition shown in table 1. The catalytic performances of both samples are presented in Fig. 5b. Both activity curves show a shift to higher temperatures with respect to those obtained under model conditions, as expected on the bases of Le Chatelier's principle.

However, it must be pointed out that the gold-based catalyst does not reach the equilibrium conversion in the whole range of studied temperatures. As proposed by Rodriguez et al. [60] the redox mechanism with a carboxyl intermediate can explain the behavior of Au/CeO₂ based catalysts. In this mechanism, it is crucial to achieve some ceria reduction degree to promote the water splitting into the ceria oxygen vacancies. Recent in-situ XANES studies revealed that in a Au/CeO₂-FeO_x/Al₂O₃ system, the highest WGS performance was achieved for a Ce formal oxidation state of 3.3 [56]. However, in order to close the catalytic cycle, water has to be able to reoxidize the

partially reduced support in the studied temperature range. This redox behavior is easily maintained in the model mixture due to the softer reductive conditions. Nevertheless, the ability of water to reoxidize the ceria-iron support in the presence of a high amount of hydrogen is limited decreasing remarkably the reaction rate.

Regarding the catalytic results presented in Table 6 in a realistic mixture, a general decrease of the TOF values compared with the model mixture is obtained indicating the negative effect of the presence of CO₂ and H₂ in the mixture. Again gold seems better at 180°C as in the model mixture. However at temperatures higher than 250°C, platinum showed not only higher rate but also better tolerance to the composition of the stream (same TOF in model and realistic mixture).

Conclusions

The catalytic activity of the samples is a function of the supports electronic properties and more precisely on the samples band gap, in such a way that the higher the band gap the higher the activity. The higher catalytic activity is obtained when the energy levels introduced by the NM are closer to the *O(2p)* ones that means, when the easiness of the electron transfer between oxygen atoms of ceria and the NM is higher.

For all the systems (gold or platinum) the presence of ceria or mixed CeFe oxide is beneficial for the WGS activity, being the gold based systems more influenced by the electronic properties of the support.

No matter the stream composition, the gold based catalysts present superior activity than the platinum ones at 180°C, thus shifting its operation window to the lowest temperature range. Nevertheless, the platinum based systems are much more

versatile since they are able to withstand changes in the stream composition with higher TOF than its gold homologues and attained the equilibrium conversion at temperatures close to 250 °C.

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