Boosting the activity of a $Au/CeO_2/Al_2O_3$ catalyst for the WGS reaction.

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Abstract

Herein a strategy to design highly efficient $Au/CeO_2/Al_2O_3$ based WGS catalysts is proposed. The inclusion of transition metals, namely Fe, Cu and Zn as CeO_2 dopant is considered. All the promoters successfully increased the WGS performance of the undoped sample. The activity improvement can be correlated to structural and/or redox features induced by the dopants. The comparative characterization of the doped samples by means of XRD, Raman spectroscopy and OSC evaluation permits an accurate understanding of the boosted WGS activity arising from the Ce-promoter interaction. This study establishes distinction among both, structural and redox sources of promotion and provides a useful strategy to develop highly active Au/CeO_2 based catalysts for the WGS reaction.

Keywords: WGS, Gold catalysts, cerium oxide, dopants,

1. Introduction

The expected depletion of oil-based energy sources and their associated problems as for example serious pollution and global warming, among others, makes mandatory the investigation on alternative energies more environmentally respectful and with longer lifetime [1]. The H_2-fuel cell technology is recognized as real approach to replace internal combustion engines in vehicles. These devices, use the chemical energy of H_2 to efficiently produce electricity generating only water as a by-product [2,3]. The production of hydrogen for fuel cell applications requires several processing steps, including CO removal by means of the water gas shift (WGS) and the selective CO oxidation and/or methanation since the presence of carbon monoxide inactivates the fuel cell anode [4]. The WGS reaction is the most relevant CO elimination process in terms of CO amount to face (4-10 % vol.) in comparison to the finals steps of the hydrogen purification (few ppm - 1 % vol.). Moreover, the WGS reaction not only eliminates CO but produces an extra amount of H_2 in the stream improving the efficiency of the process. Therefore the development of efficient catalysts for the WGS reaction is of crucial importance to guarantee the success of the hydrogen technology.

Traditionally, the industrial catalysts for the low temperature WGS are based on $Cu-ZnO-Al_2O_3$ mixtures [5-7]. Nevertheless these systems present several drawbacks including its pyrophoricity and obligatorily activation steps [8]. In order to overcome these problems, noble metal based catalysts are under intensive investigation nowadays [6, 9-11]. Pt and Pd based catalysts have been reported as very promising systems for this process, nevertheless they still required activation either by previous reduction or under the WGS stream itself [12-14]. On the other hand, supported gold based catalysts do not present such pre-activation limitation and can be used as prepared. However there is a critical point regarding gold catalysts and the shift reaction:

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contrary to platinum, gold cannot carry out the water activation and requires the indispensable assistance of the support to complete the catalytic cycle [15]. Therefore the choice of the support gains relevancy in the WGS. We have recently reviewed the literature involving gold based materials for the water gas shift in the last 20 years [16]. Despite the diversity of supports employed, cerium oxide outstands as the most convenient option. The suitability of CeO_2 for this process is related to its high oxygen mobility and storage capacity [17,18]. In addition, at medium temperatures and reductive atmospheres, such as the WGS conditions, oxygen vacancies can be created on ceria lattice. Very frequently these punctual defects have been correlated with the catalytic activity in the WGS since they act as water activation sites, being vital to initiate the reaction [19, 20]. Afterwards, the activated water and CO interacts at the $Au-CeO_2$ interface that plays also a major role in the process [21]

Classically gold nanoparticles are dispersed on bulk ceria resulting in very efficient Au/CeO_2 materials for the WGS [22-25]. As an alternative $Au/CeO_2/Al_2O_3$ catalysts can be proposed. This approach provides several advantages compared to the traditional Au/CeO_2 configuration: (i) reduced amount of ceria in the catalysts formulation (ii) greater $Au-CeO_2$ interface (iii) enhanced oxygen mobility, and iv) possibility to potentiate the later by the addition of ceria promoters [26]. These dopants may affect the structural and electronic properties of ceria resulting in a beneficial effect on the WGS activity [27, 28].

With this premises the use of 3 late transition metals Fe, Cu and Zn as ceria promoters of the $Au/CeO_2/Al_2O_3$ catalyst is evaluated in this paper. An accurate comparative study of the $Au/CeO_2-MO_x/Al_2O_3$ catalyst's structural and redox modifications produced by the added metals is then correlated to the observed catalytic behavior.

2. Experimental

2.1. Catalyst preparation

Support preparation

The supports were synthesized by a conventional co-precipitation method. The necessary amounts of metal nitrate precursor (cerium, copper, iron or zinc nitrate - Sigma-Aldrich) were impregnated on γ-alumina powder (Sasol). The impregnation was carried out in 50 mL of ethanol, evaporated in rotary vapour till dry solid obtaining at reduced pressure and 50 ºC. The solid was then treated with NH_3 solution (10 mol L^{-1}) during 30 min in order to assure the full conversion of the nitrates to hydroxides, except for the Cu where an important loss of the metals as amino complexes should be avoided. The support was then filtered, dried and calcined at 500 ºC during 4 hours. The intended composition of the samples was 15 wt. % of Ce-M mixed oxide (M= Zn, Cu, Fe,) with 2 wt. % of doping metal oxide. According to previous results of our group, 2 wt.% of metal oxide is the optimum amount of dopant for this kind of systems [26, 28]

Gold deposition

The gold was deposited by the direct anionic exchange method (DAE), assisted by NH_3 as described elsewhere [29]. A 10^{-4} mol L^{-1} aqueous solution of the gold precursor $HAuCl_4$ (Alfa Aesar) was used in order to obtain a final Au loading of 2 wt. %. The support was sieved and the 100-200 μm fractions retained. After Au deposition, the solid was dried at 100 °C overnight and calcined in air at 350°C for 4 h. To simplify the nomenclature, oxygen is omitted from the labels. For example, the Au/CeCu/Al solid theoretically contains 2 wt.% of Au and 15 wt.% CeO_2-CuO mixed oxide dispersed on alumina.

2.2. Catalyst characterization

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

The specific surface area was determined 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 250ºC in vacuum. BET equation was applied to obtain the specific surface area of the studied samples.

X-ray diffraction (XRD) analysis was carried out on X`Pert Pro PANalytical instrument. Diffraction patterns were recorded using Cu Kα radiation (40 mA, 45kV) over a 2θ-range of 10 to 80º and using a step size of 0.05º 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 μm.

For the oxygen storage capacity (OSC) measurements 100 mg of catalyst were loaded and activated into a U-shaped quartz reactor at 350 ºC during 1 hour in 5% O_2/ He flow (50 mL/min). Then, the system is cooled and set to the desired temperature (150, 250 and 350 ºC). For each temperature, ten O_2 pulses of 1 mL were injected every 2 min. The sample is then subjected after 10 min He degasification to four alternating series of pulses ($CO–O_2–CO–O_2–CO–O_2-CO–O_2$). The OSC is determined by the average amount of CO_2 per pulse formed after the first CO pulse of the alternated ones. This method is based on the one presented by Duprez *et al.* [30,31]. The

gas composition at the exit of the reactor was analyzed by a mass spectrometer PFEIFFER Vacuum PrismaPlus controlled by Quadera® software.

Several assumptions were contemplated for the OSC calculations. Concretely, it was considered that i) only oxygen atoms bonded to the cerium participate in the oxygen storage process; ii) the surface is assumed homogeneous iii) only one of the four oxygen atoms is involved in the storage ($CeO_2 \rightarrow Ce_2O_3 +$ "O"); and iv) null gold metal contribution to the reduction, e.g. the gold metal could not be reoxidized.

2.3. Catalytic Activity

Water-gas shift reaction was performed in a stainless steel tubular flow reactor (0.75 cm ID) at atmospheric pressure in the 140-350 ºC temperature range .The catalysts were pelletized and sieved with the 600-800 μm fraction employed for the test. The following conditions were applied: catalyst bed volume 1.5 cm^3, space velocity 4000 h^{-1} and gas composition: 30% vol. H_2O + 4.5% vol. CO balance in N_2. Water was injected into flowing gas stream by HPLC pump, vaporized and homogenized with the gas feed before entering the reactor. The CO and CO_2 content was determined by on line ABB gas analyzer and the activity expressed in terms of CO conversion.

The most active sample was submitted to long-term stability test, using gas composition imitating the outlet of an ethanol reformer - 30% H_2O, 9% CO, 11% CO_2 and 50% H_2.

3. Results and discussion

The actual composition of the prepared catalysts and their parent supports is presented in **Table 1.** All the samples are composed mainly by alumina (more than 80 wt. %) and about 15 wt. % of cerium oxide. The dopants loadings are close to the targeted value (2 wt. %) except for the Zn doped sample for which only 50 % of ZnO is incorporated to the catalyst. Most likely the ammonia treatment caused partial dissolution and loss of Zn during the filtration process. Regarding gold loadings, all the catalysts presented gold amounts very close to the nominal value pointing that the gold deposition was successfully carried out. Curiously, the doped supports admit slightly higher quantities of gold. It is well accepted that gold uptake depend on the point of zero charge (PZC) of the support [32], hence this result indicates that dopants could have smoothly modified this parameter. In addition, the presence of dopants may involve the creation of oxygen vacancies on ceria. These vacancies are viewed as electron rich sites where gold particles tend to nucleate [33, 34]. Therefore, the enhanced gold uptake observed for the doped ceria samples could suggests also higher concentration of oxygen vacancies on these systems compared to the unmodified one.

Concerning the textural properties, all the samples are mesoporous materials with specific surface areas neighboring that of the primary support. Compared with a conventional Au/CeO_2 material, these catalysts benefit of larger S_{BET} due to the presence of the Al_2O_3 carrier which can be considered as a textural promoter in the prepared systems.

XRD diffraction patterns of the studied supports and catalysts are presented in **Figure 1A** and **1B** respectively. For all samples the diffraction lines corresponding to cubic CeO_2 fluorite type structure (JCPDS# 00-004-0593) and to γ-Al2O3 phase (JCPDS# 00-048-0367) are detected. No

signals due to the crystalline Cu, Zn or Fe oxide phases are found. The low quantity of doping oxide, its high dispersion, or amorphous character may account for this fact. Similarly, no signals of metallic gold are observed indicating that gold particles are rather well dispersed and under the detection limit of the technique (< 5 nm).

Further relevant information about the structural changes on ceria induced by the dopants can be extracted from the XRD. For example the crystallite size calculations using CeO_2 (111) diffractions points some dissimilarities among the catalysts (**Table 1**). While Zn and Fe doped samples preserve the crystallite size of the undoped solid (about 5.5 nm) the Cu doped solid is composed by slightly larger ceria particles (7.3 nm). Consequently, smaller Au-CeO_2 interface is expected for the Cu promoted sample. In addition, ceria lattice parameter (a) was estimated using the expression that relates the lattice parameter of the fluorite structure with the diffraction angle:

$$a = \sqrt{h^2 + k^2 + l^2}\ \left(\frac{\lambda}{2\sin\theta}\right) \qquad \text{equation 1}$$

The (111) CeO_2 diffraction line (where no contribution of the γ-alumina phase is observed) was selected for this calculation being the λ factor that of Cu filament (1.5405 Å). The obtained values are listed in **Table 1**. From these data it can be concluded that only Fe introduces a notable change in the ceria lattice dimensions in both the support and the catalyst. A contraction of the CeO_2 cell was obtained when iron is used as a dopant indicating the formation of a Ce-Fe solid solution. Actually considering the size of both cations, the decrease of ceria lattice parameter is expected. Indeed, iron oxide fulfills Hume-Rothery´s miscibility rules and the solid solution formation is favored. This phenomenon of Ce-Fe solid solution was broader addressed

elsewhere [26, 34] and basically its main consequence is the formation of oxygen vacancies to balance the lattice charges upon substitution.

Complementary structural information is obtained through Raman spectroscopy experiments. **Figure 2** shows the Raman spectra of the gold catalyst's supports. For all the samples a band centered at about 458 cm^{-1} appeared. This band is ascribed to the F_{2g} Raman mode of ceria fluorite cell corresponding to oxygen symmetric breathing vibration around Ce^{4+} [35]. Shifting and broadening of this vibration mode is observed for all the dopants indicating alterations of ceria structure and/or ceria particle size in good agreement with the XRD data discussed above. Moreover this type of modifications on the shape and position of the F_{2g} Raman mode suggest a change on ceria electronic properties due to the presence of the dopants. In particular the observed blue shift in all doped samples indicates a strong Ce-M interaction [15]. Very importantly, for the Fe doped solid a second band centered at 530 cm^{-1} was detected. This band has been widely reported in literature and is associated with the presence of the oxygen vacancies preferentially placed on the surface of the cubic CeO_2 [36, 37]. As commented in the XRD section, the inclusion of Fe^{3+} cation on the ceria lattice produces the formation of oxygen vacancies in the structure as a result of the Ce-Fe solid solution, confirmed by the Raman experiments providing a spectroscopic evidence of the existence of such punctual defects. This higher oxygen vacancies concentration may also explain the greater gold uptake observed for the Fe doped solid in comparison to the other two dopants.

In summary from both XRD and Raman data an intimate Ce-M interaction can be assumed. This effect influences the structural and electronic properties of the resulting materials. In particular Fe modifies the oxygen vacancies population on ceria structure which may lead to redox altered properties. For an accurate understanding of the redox properties of the presented catalysts the

oxygen storage capacity (OSC) was evaluated at 3 relevant temperatures for the WGS. It should not be disregarded that the WGS is an oxidation-reduction process and therefore the redox skills of the catalysts are of paramount importance. **Figure 3** shows the OSC of the studied materials. As expected, for both supports and catalysts the OSC increases with the temperature. For the supports low oxygen mobility was found at 150 ºC being the Cu-doped material the one exhibiting the highest OSC. At 250 and 350 ºC all the dopants remarkably boost the OSC of the bare Ce/Al support. It is worth mention that at high temperatures iron hardly improves the CeO_2 reducibility while Cu and especially Zn seem to be much stronger redox promoters. Indeed, at 350 ºC CeZn/Al sample presents excellent oxygen mobility. Keeping in mind that the OSC informs about the most reactive and most available oxygen atoms on the catalyst surface directly involved in the redox process, it must be underlined that ZnO is the dopant that widely promotes the lattice oxygen mobility. Similar redox promotion was found by Laguna *et al.* in a bulk ceria zinc doped solid [38] and attributed to intimate ZnO/CeO_2 contact resulting in oxygen vacancies exchange on the oxides interface. Indirectly, this result is reflecting some differences in the transition metals promoter behavior. Two approaches can be envisaged. On one side Fe is the only dopant for which solid solution was formed. On the other side Cu and Zn promoter do not enter on ceria structure and therefore ZnO and CuO particles will be segregated in close contact with the support. Both approaches lead to different defect chemistry involving different ceria-promoter synergy. While Fe directly generates oxygen vacancies on ceria lattice due vacancy compensation, Zn and Cu may potentiates the oxygen exchange in the oxides interfaces. The second option seems to strongly boost cerium oxide OSC. Indeed both Zn and Cu oxides may present oxygen defects that can be transferred to ceria generating the vacancies. For instance,

For the gold catalysts several points should be commented. Firstly, the addition of noble metal notoriously enhanced the oxygen mobility in the whole temperature range. This effect is especially important at low temperatures (150 ºC) where low oxygen mobility was found for the supports. This result agrees with previous OSC studies developed by Bedrane and coworkes [39]. The oxygen storage capacity is widely potentiated by the presence of metal particles in the surface, which act as channel for oxygen migration and storage on the support [39]. The deposition of gold seems to camouflage the dopant influence observed between the supports. Nevertheless, very interestingly, at 250 and 350 ºC the highest OSC was obtained for the Fe doped sample which was the dopant that poorly promotes the OSC among the supports. The gold deposition close to iron (in oxygen vacancies associated to Ce and Fe) could be then imagined resulting in particular metal-support interaction for the gold/Fe doped system.

The catalytic behaviour in the WGS reaction of the prepared solids is presented in **Figure 4**. It is worth to note that the parent supports resulted hardly active in the WGS reaction as reflected in **Figure 4A**. Only at 350ºC the supports showed some activity being the Zn promoted support the most effective. Actually according to the OSC data on **Figure 3** the redox chemistry of this sample is particularly enhanced at this temperature. In any case, the poor WGS activity of the supports highlights the importance gold nanoparticles. As indicated in the introduction part Au/CeO$_2$ based systems in the WGS must be considered as dual materials for which the presence of both metallic phase and an adequate support is mandatory to achieve a good performance. In fact, prove of this point is that the Au/Al$_2$O$_3$ sample evaluated and included in the plot is almost inactive in the whole temperature range remarking the need of ceria to achieve acceptable WGS activity. Regarding the ceria containing materials, a boosted WGS activity was found for all doped samples. While Au/Ce/Al exhibited medium activity in the shift process, the addition of

Cu, Zn and specially Fe promoted the CO conversion. When related to the above analysed physicochemical properties all dopants increase the oxygen storage capacity of the ceria-alumina support, and as a result an enhanced reducibility and greater oxygen availability is observed, explicating the positive effect on the WGS activity. In the same moment, it is interesting to address some differences among the dopants. Although present as main component of the commercial low temperature shift catalyst here the Cu appears the less effective promoter in terms of CO conversion. Despite that the redox skills of CeO_2 are enhanced due to CeO_2-CuO contact, as our OSC data reveal, it seems that copper is a moderate ceria promoter. The larger ceria particle size obtained for this sample could explain this fact. According to Rodriguez´s studies the key factor on a Au/CeO_2 based catalysts is the interface since most of the relevant WGS reaction steps take place there [40]. Therefore, it could be foreseen that larger the metal-support interface better the activity. The bigger ceria particle size of this sample presumably leads to smaller Au-CeO_2 interface attenuating the redox properties promotion. As for the Zn promoted solid an intermediate behaviour is observed, Zn is better promoter that Cu but not as good as Fe. Our XRD data show that Zn does not form solid solution with ceria and from the Raman spectra no oxygen vacancies were observed. However an extraordinarily high redox promotion was detected being the CeZn/Al the support with the uppermost OSC. Therefore, Zn can be considered rather redox than structural ceria promoter. Only the elevated oxygen mobility and as a consequence vacancies number increase during the reaction could account for the boosted catalytic activity of this sample.

Among the dopants Fe resulted to be the best ceria promoter. Several reasons may justify this fact. To begin with, our XRD data reveal the formation of a Ce-Fe solid solution implying an intimated Ce-Fe contact and structural vacancies formation. These oxygen vacancies, as electron

rich sites, benefits the WGS in many ways: (i) they are considered as water activation sites (a fundamental necessity in the WGS), (ii) they are envisaged as preferential gold nucleation points thus enhancing gold dispersion, which in turn affects positively the gold/support interface and in consequence the catalytic performance and (iii) they seem to potentiate the gold uptake during the synthesis. In addition mainly due to the later, the Au/CeFe/Al sample presents the highest OSC at 250 and 350 ºC which increases additionally the vacancies population during the WGS reactions. The highest oxygen mobility suggests also a strong electronic metal support interaction (EMSI) for this sample. The EMSI effect is a phenomenon reported in literature that correlates electronics perturbations in the catalyst surface with metal-support contact [41]. This contact may arise from the presence of special sites at the perimeter of the metal particles, where the electronic properties of both metal and support atoms influence the adsorbed species and module the catalytic activity. In summary, Fe can be consider as both structural and redox promoter resulting in superior WGS behaviour.

As a final test, the Au/CeFe/Al sample was submitted to a long term stability study under realistic WGS conditions (including elevated quantities of CO_2 and H_2 in the stream). It should be kept in mind that for a practical application, for instance, the use of WGS unit in an integrated fuel processing device, the catalyst obligatorily should tolerate H_2 and CO_2. On one hand, high H_2 concentrations may produce the over-reduction of the support thus suppressing the activity. On the other hand, the CO_2 could motivate the formation of carbonaceous species blocking the arrival of H_2O and CO to the catalytic active sites. **Figure 5** shows the result of the stability test under these exigent conditions. A depletion of the CO conversion was observed at the first stages of the reaction. However, after 60 hour of continuous operation the catalysts reached the steady state and conserved relatively high conversion during the following 80 hours. This result is very

promising weather a stationary application is desired. This catalyst is able to abate high amounts of CO under a surrogate reforming mixture for long periods of time without considerable activity loss. From previous studies a close relationship between ceria oxidation state and catalytic activity in the WGS process was found [42]. In particular XANES data points out that formal oxidation state of Ce +3.3 is the optimum value [42]. In principle, the highly reductive mixture employed in the aging test should completely reduce ceria and deactivate the catalyst. However the presence of Fe mitigates process, iron redox pair (Fe^{3+}/Fe^{2+}) helps to avoid ceria over-reduction allowing good WGS performances even under greatly reductive environment.

As a final remark, it must be pointed out that the excellent skills exhibited for this material are achieved using less than 15 wt. % of CeO_2 and low quantity of gold in the catalyst formulation. The strategy of dispersing ceria on alumina together with the use of dopants produces encouraging results coupled with economical viability and should be further explored.

Conclusions

The inclusion of small amounts of late transition metals, Fe, Cu, and Zn as cerium oxide dopants remarkably promotes the activity of the $Au/CeO_2/Al_2O_3$ catalyst in the WGS reaction. Mainly two reason accounts for the boosted activity (i) enhanced redox properties and (ii) structural promotion. The former is the effect produced by Cu and Zn that broadly enhanced the OSC of the primary Ce/Al support. Among them Zn is best redox promoter manifesting very high OSC values. For the Fe dopant both structural and redox promotion are coupled resulting in an excellent WGS activity thus converting the Fe in the best choice of promoter. Together with the

excellent WGS activity, the Au/CeFe/Al catalyst exhibited a great stability under a surrogate reforming mixture suggesting its suitability for a real application.

Overall the results presented in this study provide a methodology to follow in order to improve the activity of Au/CeO$_2$ based catalyst for the WGS by the use dopants. It seems that a good dopant candidate should produce a cumulative promotional effect: electronic plus structural features must be enhanced resulting in a substantial performance improvement.

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