**Boosting water activation determining-step in WGS reaction on structured catalyst by Mo-doping**

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**Abstract**

Proton conductors Mo-Eu-Zr mixed oxide systems were synthesized and further mixed with a conventional Pt/CeO2/Al2O3 catalyst to develop a highly efficient water-gas-shift (WGS) catalyst. The designed catalyst, once structured, allows reach the equilibrium conversion at medium temperatures (~350ºC) at 80 L·g-1·h-1 space velocity. The ability of the proton conductor to maintain an elevated water concentration at the metal-support interface by Grotthuss’ mechanism boosts the catalytic activity in WGS reaction.

The Mo-containing proton conductor is extensively characterized allowing to establish the formation of molybdenum oxide phases nucleating on top of the Eu sites in Eu-Zr oxide solid solution. [MoO4]2- to [Mo7O24]6- clusters nucleates at low Mo contents resulting in a α-MoO3 layer on increasing its content. In presence of H2, Mo-bronzes are formed from ~200ºC enhancing water concentration at the surfaces and boosting the catalytic activity in the WGS reaction. These results pave the way for developing lower volume WGS reactors.

**Keywords:** WGS; proton conductor; Pt catalyst; water activation; Mo-doped mixed oxide.

**1. Introduction**

The emergence of fuel processors has renewed the interest on the noble metal catalyzed water-gas-shift (WGS) reaction. As highlighted by excellent reviews [1,2], research efforts in the understanding of how the structure, morphology or growth of the nanoparticles of noble metal-based catalysts has been devoted as a way to tailor the reactivity and selectivity of noble-metal catalysts to target hydrogen production [3] or to design new reactors and concepts [4]. However, to efficiently improve the performances of fuel processors, the design of catalysts able to operate at higher space velocities is mandatory in order to reduce volume and weight of the whole fuel processors [5]. In previous works, our group have evidenced that the mechanical mixing of a non-active WGS solids with a Pt-based WGS catalyst does improve the catalyst performances by favoring the diffusion of water to the noble metal active sites [6]. Our group has demonstrated that by adding a proton conductor to WGS catalysts an increase in its activity is observed [6–8]. Europium doping of ZrO2 results in fluorite-type solid solutions, having oxygen vacancies able to dissociate water. Eu-substituted Zr sites allow a Eu-Zr distance able to accommodate hydroxyl groups bridging Zr and Eu atoms on the solid solution surface. This provides a pathway for proton conductivity according to a Grotthuss’ mechanism for temperatures below ~300 ºC in wet atmospheres [6,9,10]. This path requires the presence of adsorbed water interacting with surface OH species. However, at temperatures above 300 ºC adsorbed molecular water does not longer occur and the Grotthuss’ conductivity contribution ends, becoming similar the ion conductivity of the solid in dry and wet atmospheres. Therefore, to improve the effect of Eu-doped ZrO2 proton conductors on the WGS activity the increase of the conducting properties at high temperatures is required. Mo-containing oxides, including rare earth molybdates, present stable structures showing good ionic conducting properties at high temperatures [11–15]. Therefore, Mo-modified Eu-doped ZrO2 proton conductors seems to be promising solids for enhancing the activity of Pt-based catalysts in the WGS reaction.

Molybdenum compounds usually exhibit mixed ionic and electronic conductivity (MIEC). Their relative contribution to the total conductivity depends on temperature and the amount of Mo [16,17]. Thus, low Mo concentrations results in favoring the proton conductivity, but on increasing the Mo content, the crystal symmetry decreases and the relative contribution of the electronic conductivity increases. Moreover, on ordering oxygen vacancies the ionic conductivity is reduced and the activation energy for conduction increases as observed for other ionic conductors [18–20].

Besides the conducting properties of Mo-based MIEC, Mo oxides have been reported to form bronzes when doped with a few percent of Eu, this generates a semiconductor material capable to hold H2 or water molecules between the α-MoO3 layers [21,22]. In the same way, MoO3 forms bronzes on adding H2 [22–25], that is dissociated and bonded as –OH or –OH2 groups, depending on the H2 concentration. The H2 inclusion in MoO3 phases does not control the electronic properties but has influence in the crystal structure, affecting thereby the hydrogen mobility [26–28]. Proton species can diffuse through the oxide lattice and the –OH or –OH2 groups on the oxide surface provide bridges for the H+ migration [25,29,30]. Ion-exchange properties of bronzes due to their ionic structure have been widely studied [26,31–33]. It is reported that the lattice forming ions are not exchanged, but the protons of the water molecules adsorbed on the surface are [23,26,32]. Because of these properties, Mo bronzes have been considered to numerous applications, among them H2 membrane separation by proton conductivity, sensor or H2 storage devices are found in the literature [14,17,27].

Accordingly, different amounts of Mo oxide are added to Eu-doped ZrO2 proton conductor already studied in the WGS reaction (Eu-doped ZrO2 with 5 mol.% of Eu2O3) [6]. Thus, a typical Pt-based catalyst is physically mixed with the Mo-doped proton conductors in order to provide higher activity in WGS reaction by extra proton conductivity and/or adsorbed water at operation conditions.

Besides catalyst design by structuring the catalyst may result in enhanced performances by improving heat and mass transport characteristics [34]. For instance, the reactor becomes almost isothermal, which avoids high temperature excursion within the reactor resulting in a penalty for the catalytic activity since the reaction exothermicity. This high heat transfer allowing better catalysts’ performances or the use of higher temperatures to promote the kinetics in WGS reaction has been reported and modelled by Palma *et al.* [35,36], where the CFD simulations were used to estimate the temperature profiles along the reactor and to validate the Pt-based catalyst performance supported on Al-foam or as powders. In the present work, we aim to elucidate if the observed improvement in the catalytic activity achieved by the physical mixture of the proton conductor with the Pt-based catalyst in powder systems is due to a thermal or dilution effect by the addition of the ionic conductor as diluent or, indeed, is caused by the proton conducting effect in the reaction mechanism. On choosing a thin metallic foils for structuring the catalyst almost isothermal conditions along the micromonolith are obtained avoiding hot-spots [37]; moreover, this approach favors the cell density per surface unit (cpsi) resulting in an increase in the surface-to-volume ratio and this catalytic layers that may prevent mass transport limitations [34].

**2. Experimental procedure**

**2.1 Synthesis of materials.**

The ionic conductor materials, Mo- and Eu-doped ZrO2 compounds, were prepared by co-precipitation. A 0.1M aqueous solution of ammonium molybdate tetrahydrate ((NH4)6Mo7O24, Alfa Aesar) was slowly added to an aqueous solution resulting of mixing 0.1M of zirconium (IV) oxynitrate hydrate (Sigma-Aldrich) and 0.1M of europium (III) nitrate pentahydrate (Sigma-Aldrich) solutions under continuous stirring in adequate amounts for obtaining the desired compositions; then the pH of the resulting solution ranging between 1 and 2 was raised to 8 by adding a commercial ammonia solution (30 vol.%, Panreac). This solution was aged for 1.5 hours at room temperature under stirring. This procedure results in a white precipitate that was further filtered, washed with distilled water and subsequently dried at 100 ºC overnight. Finally, the solid was calcined in air at 500 ºC for 5 h to remove the nitrate precursors and a pale-yellow solid was obtained. The synthesized solids were named ZrEuMo\_x (where the ZrO2:Eu2O3 molar ratio was fixed at 95:5 and the variable amount of MoO3 is indicated by x = 5, 7 and 10 mol.%).

The catalyst Pt/CeO2/Al2O3 (named PtCeAl) was prepared by wet impregnation. The platinum was loaded over commercial Puralox CeO2/Al2O3 (20:80 ceria/alumina mass ratio). A convenient amount of the Pt precursor (tetraammine platinum (II) nitrate solution, Johnson Matthey) was previously mixed with acetic acid solution 1M in a Pt:Acid molar ratio of 1:1,1. Then, the Pt solution was added over the commercial support and shaken at room temperature. Thereafter, the solvent was evaporated at reduced pressure in a rotary evaporator and the obtained solid was dried at 100 ºC for 12 h. Finally, the dry solid was calcined at 350 ºC for 8 h with a heating rate of 5 ºC/min.

**2.2 Slurry and micromonoliths preparation.**

Metallic FeCrAlloy – Iron/Chromium foil (Fe72.8/Cr22/Al5/Y0.1/Zr0.1, GoodFellow) 0.05 mm thick was used for the manufacture of the micromonoliths. Flat and corrugated sheets were rolled together resulting in cylindrical metallic micromonoliths with 17 mm in diameter and 30 mm in height (Figure 1) with a cell density of 1588 cpsi and 540 cm2 of exposed surface. A detailed description of the manufacturing procedure and oxidation treatment prior to catalyst coating has been described elsewhere [38,39].

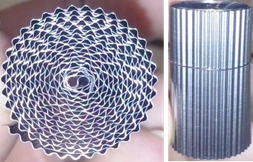


Figure 1. Manufactured metallic micromonolith.

A washcoating procedure was used to deposit either the catalyst or the physical mixture of the catalyst and the ionic conductor on the metallic substrate. Details for this procedure have been given elsewhere [40]. In brief, slurries with adjusted rheological properties were prepared optimizing both the viscosity and the Z potential of the suspension. The freshly prepared suspension to washcoat the micromonolithic support consists in 80 wt.% deionized water, 6 wt.% of a commercial aqueous solution of colloidal Al2O3 (20 wt.% of alumina, Nyacol) and 14 wt.% of the sieved catalyst with particle sizes below 50 µm. The slurry, once formulated, is aged under continuous stirring for 24 h in a closed vessel. The micromonoliths were washcoated by successive immersion/emersion cycles until the desired load is achieved. After every cycle, the excess slurry was eliminated, by blowing air to avoid their obstruction and the micromonolith was dried at 100 ºC for 30 minutes. This process is repeated until the desired amount of catalyst is loaded. Finally, the structured catalyst was calcined at the same temperature than the original catalytic powder but with a heating ramp of 2 ºC·min-1, in order to slowly remove the leftovers without creating porosity or fissures.

**2.3 Water Gas Shift reaction.**

The WGS reaction has been carried out at atmospheric pressure in a home-made rig coupled to an on-line ABB gas analyzer (AO2020) equipped with an IR detector in a tubular fixed bed reactor of 9 mm in diameter for powder catalysts and of 18 mm for structured catalysts. The catalytic tests were carried out in the 180 ºC - 350 ºC temperature range using two different feeds named model conditions (4.5% CO, 30% of H2O and N2 as balance) and industrial conditions (9% CO, 30% of H2O, 11% CO2 and 50% H2). In all the experiments 0.1 g of the PtCeAl catalyst was always loaded. The powder catalysts were either tested separately or physically mixed with the synthesized ionic conductors using a 1:5 (catalyst:ionic conductor) mass ratio. Prior to the catalytic tests the powder were sieved and particles in the 600-800 µm particle size range were selected for the experiments, keeping constant the bed volume for all the tests adding inert quartz chips in the same particle range when needed. The structured catalysts were prepared in such a way that the final catalyst loading was 0.1 g and the PtCeAl catalyst: ZrEuMo\_5 ionic conductor set in a 1:5 mass ratio. All experiments (either powder or structured catalysts) were performed at a constant space velocity of 80000 mL·h-1·gcat-1.

**2.4 Characterization.**

The structural analysis of the synthesized samples and calcined slurries was performed by XRD (X-ray diffraction) on an X’Pert Pro PANalytical instrument. Diffraction patterns were obtained using Cu Kα radiation (40 mA, 45 kV) over a 2θ-range of 10-90º and using a step size of 0.05 º and a step time of 80 s. The chemical composition of the prepared materials was determined by X-ray fluorescence spectrometry (XRF) using an AXIOS PANalytical spectrometer with Rh source of radiation, working at 40 kV. For the experiments, the samples were previously dispersed in boric acid pellets and covered by thin wax film. Synthesized samples and structured catalysts were degassed in vacuum at 250 ºC for 4 h and analyzed by N2 adsorption at liquid nitrogen temperature with a Micromeritics Tristar II instrument in order to determine their textural properties.

X-ray photoelectron spectra (XPS) of the ionic conductors were recorded on a Leybold-Hereus LHS-10/20 spectrometer equipped with an ultra-high vacuum (UHV) system operating at 5·10-9 Torr and a dual X-ray source, of which the Al Kα (1485 eV) was used. Binding energy correction was performed by fixing C 1s level at 284.6 eV. Spectra were analysed with CasaXPS software and Gaussian-Lorentzian (70:30) curves were used for the fittings. High resolution scans were acquired at binding energy intervals associated with the Zr 3d, Eu 3d, Mo 3d, O 1s and C 1s levels. In order to quantify the band areas and obtain superficial atomic percentages, Zr 3d5/2, Eu 3d5/2 and Mo 3d5/2 peaks areas corrected with their respective Scofield factors for Al Kα source were used.

Raman spectroscopy analysis of the ionic conductors were performed in a dispersive Horiva Jobin Yvon LabRam HR800 microscope. Raman spectra were obtained by using a 532.14 nm (green) laser excitation source with a ×50 microscope objective. The power of the laser on the sample is 20 mW with a 600 g·mm-1 grating. Two types of filters were used: D1 filter which reduces the laser to 2 mW to avoid a saturated signal in the 1000 – 4000 cm-1 range and D0.6 filter to have a laser of 5 mW for the 200 – 1000 cm-1 range. A confocal pinhole of 1000 µm was employed for all the measurements reported. Prior to the analysis, the Raman spectrometer was calibrated using a silicon wafer reference. Moreover, due to the Eu luminescence and in order to observe the molybdenum oxide structure, a 785 nm (red) laser excitation source with a ×100 microscope objective was also used in the same conditions. The UV–vis spectra were recorded on an Avantes spectrometer model AvaLight-DH-S-BAL. All the spectra were collected in absorbance mode using BaSO4 as reference. Finally, the ionic conductors were analysed by Temperature Programed Reduction (TPR) experiments carried out with a flow of 5 vol.% of H2 in Ar using a heating ramp of 10 ºC·min-1 from RT to 950 ºC. For the quantitative analysis the TCD signal was calibrated with a CuO pattern (Strem Chemicals 99.999%).

An estimate of the stability of the slurries is obtained by measuring the Z potential of the colloidal suspension of the catalyst in deionized water with a Zetamaster Malvern Instrument (BFi Optilas). The Z potential was measured from pH 1-2 to 10-11 to obtain the complete curve. Moreover, each point was determined as the media of 9 measurements. The viscosities of the prepared slurries were measured in time (1h) and at different rpm (from 150 to 250 rpm) in a programmable rheometer Brookfield Model DV-III equipped with RV Spindle set.

Scanning electron microscopy (SEM) analysis of the catalytic layer deposited on the micromonoliths were performed on a Hitachi S4800 SEM-FEG microscope equipped with a cold cathode field emission gun with voltage from 0.5 to 30 kV and resolution of 1nm at 15 kV. The microscope has coupled a Bruker-X Flash-4010 EDX detector with a resolution of 133 eV (at the MnKα line) and a detector with sample holder to work in transmission mode (STEM-in-SEM). The catalyst’ adherence over the metallic support was analyzed by immersing the micromonolith in acetone for 30 min in an ultrasonic bath according to a procedure previously published [41]. The adherence was estimated as the difference in weight with respect to the untreated sample.

**3. Results and discussion**

**3.1 Catalytic activity in WGS reaction.**

The synthesized catalyst PtCeAl and the mixtures of PtCeAl with ZrEuMo\_x ionic conductors in a mass ratio of 1:5 have been tested in the WGS reaction in the same conditions (see section 2.3). The reaction carried out in the two different tested feeds, model conditions (Figure 2a) and industrial conditions (Figure 2b), show higher CO conversion for the physical mixture catalysts than for the bare PtCeAl catalyst. It is worth noting that the ionic conductor does not present activity in the WGS reaction by itself; however, it successfully enhances the WGS catalyst activity in the kinetic regime from ~270 – 280 ºC, when the proper catalyst starts to work. According to the proton conductivity properties of these mixed oxides [6] (see also section 3.2), it may be hypothesized that the presence of the ionic conductor more probably favors the water supply to the PtCeAl catalyst either dissociated or in molecular form. As the water availability increases higher CO conversions are attained. It must be pointed out that the acceleration of the water activation step results in higher reaction rates as has already been demonstrated by García-Moncada *et al*. [37]. Thus, the role of the mixed oxide involves the dissociation of the water and proton conductivity by Grotthuss’ mechanism, which improves the water activation step, whatever the conditions. Therefore, the ZrEuMo\_x samples act as water-enhancer at the service of the catalyst, as is depicted in Schema 1 and according to our previous study [6].

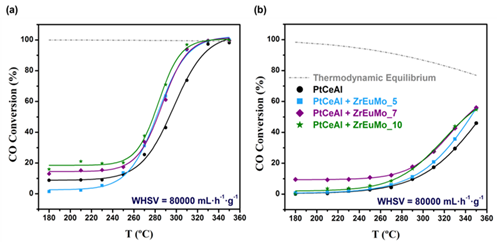
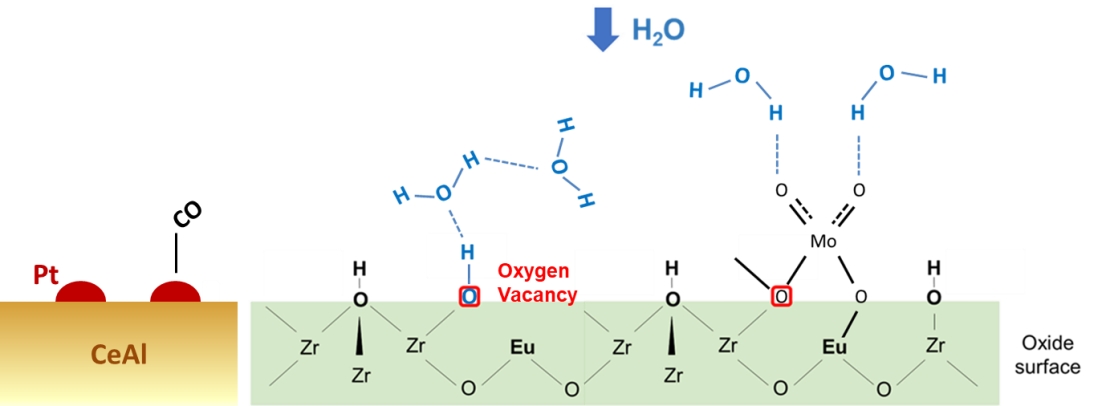


Figure 2. Catalytic tests in WGS reaction on powder catalysts in model conditions (a) and in industrial conditions (b).



Scheme 1. Physical mixture of Pt-based catalyst and Mo-doped ZrEu mixed oxide as proton conductor.

It is also noticeable (figure 2) a deviation of the CO conversion level at values below 20 % (below 250 ºC), mainly in model conditions. This can be explained by high CO capture in the high porosity of the samples, since no CO2 was detected at the outlet yet and carbon balance was inaccurate at these temperatures. Hence, the apparent conversion is based on CO calculation, but negligible considering carbon calance and CO2 production. Besides, at these low conversion levels, also the measured error is important (around 5 %). On the contrary, this apparent CO conversion is not observed on ZrEuMo\_5 sample. According to its highest level to adsorb water (see section 3.2), pores in ZrEuMo are supposed to be easily full of H2O molecules rather than CO. However, no clear effect on molybdenum addition is observed. Similar activities are achieved on increasing the Mo content. Therefore, in order to understand the Mo role in this proton conductor comprehensive characterization tests were conducted and described in the next section. Accordingly, the similar effect obtained for all Mo-doped samples may be due to both Mo-contained samples present the same molybdates phases from the lowest loading, which could mean a similar capacity of adsorbing water and proton-exchanging for both samples (see section 3.2), implying thereby similar catalytic effect. Therefore, considering the lowest amount of Mo and the acceleration observed for PtCeAl + ZrEuMo\_5 sample in industrial conditions at higher temperatures, this sample is also used for the catalytic test on structured catalysts.

In the same way, the structured catalysts over metallic micromonoltih in model conditions (Figure 3a) and industrial conditions (Figure 3b) again exhibit higher conversion on the promoted catalyst. This effect exhibits again the role of the ionic conductor, which neither depends on the mechanism, catalyst, feed conditions nor powdered or structured systems. As observed below in monolithic sample analysis (section 3.3), this structured system with catalytic layers below 20 µm allows to discard mass transfer limitations. Moreover, these metallic monoliths have also shown isothermal conditions measured during WGS reaction kinetic study [37]. Hence, thermal or diluent effects can be discarded by the added material, evincing the promoting effect is due to proton conductivity. It is also highlighted the more significant influence of the mixed oxide for the structured system in industrial conditions. As discussed below in the characterization section and considering no diffusion problems, this effect may be related to such amount of H2 in better contact with the ZrEuMo\_5 sample by structured sample. Thus, the Mo oxide in the surface creates hydrated bronzes from 300 ºC, as is shown below in TPR analysis, which increases the adsorbed water on the surface involved in the reaction mechanism. Therefore, the presence of the Mo provides more adsorbed water, even at higher temperatures, meaning high water-enhancement promoter effect.

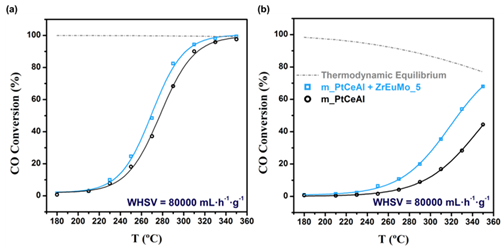


Figure 3. Catalytic tests in WGS reaction on structured catalysts in model conditions (a) and in industrial conditions (b).

**3.2 Catalyst and ionic conductor characterization.**

XRD analysis of the synthesized samples shows the presence of ɣ–Al2O3 [JCPDS: 01-077-0396] and CeO2 [JCPDS: 00-034-0394] phases for the commercial Puralox support for the PtCeAl catalyst with no detectable presence of the Pt active phase (Figure 4a). On the other side, the cubic fluorite type structure is clearly identified for the EuyZr1-yO2-0.5y solid solution [JCPDS: 01-078-1303] corresponding to an amount of Eu dopant of 5 mol.% of Eu2O3 (y≅ 0.1) (Figure 4b). The diffractograms of the Mo-doped EuyZr1-yO2-0.5y solid solution are plotted together with the previously reported XRD pattern of the bare Eu-doped zircona (5 mol.% of Eu2O3, named ZrEu) [6]. As it may be noticed in Figure 4b, molybdenum addition to the Eu-doped zirconium oxide does not modify the diffraction pattern of the solid solution (ZrEu sample). Neither diffraction angles nor line diffraction intensities are modified within the studied range of compositions, which implies that the Mo is not disturbing the Eu-doped ZrO2 solid solution structure. This indicates that the isomorphic substitution of either Eu or Zr in the cubic lattice by Mo atoms may be discarded. By considering the ionic radii of the involved cations, 0.84 and 0.95 Å for Zr4+ and Eu3+ cations, respectively, the formation of a solid solution is thermodynamically possible. However, these radii are meaningful higher than that of Mo(VI). The significantly smaller radius of the Mo6+ cation (0.41-0.73 Å depending on its coordination) may result in either the filling of interstitial tetrahedral holes in the zirconia lattice or in a surface segregation pinning the growth of the Eu-doped zirconia nanoparticles. As the lattice parameter of the zirconia phase remains unaltered as well as the absence of new diffraction lines on Mo doping, it allows to discard the inclusion of the Mo cation in the zirconia lattice. If the hypothesis of a superficial Mo oxide phase is assumed, the absence of diffraction lines for MoOx species may be expected since its loading is well below the monolayer capacity in good agreement with Chary *et al*. [42]. Moreover, it was early shown that adding oxoanions to zirconia stabilizes its surface [43], among them, oxoanions of transition metals in their highest oxidation state (e.g. Cr, W and Mo) [44,45]. Adding molybdates to wet gels, like these samples, the surface tension is modified and the porous structure of the gel is preserved. Therefore, it is concluded that on adding Mo to ZrO2, even in the precipitation stage, formation of surface molybdates occurs hindering zirconia crystallization and favoring high surface areas (Table 1) [46]. However, other characterization techniques are mandatory to identify the molybdenum dopant presence and their structure.

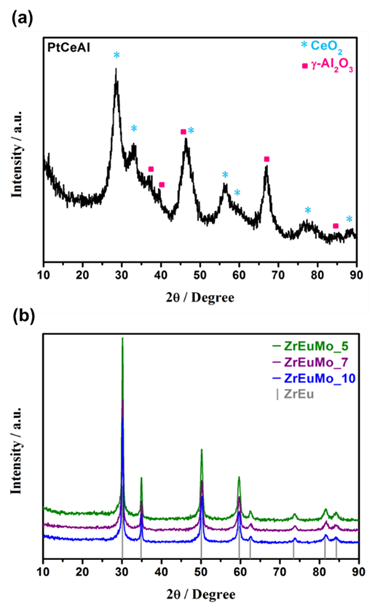


Figure 4. Diffraction patterns of the synthesized samples.

X-ray fluorescence spectroscopy analysis allows determination of the chemical composition of the samples, including Pt loading and Mo content. As it is summarized in Table 1, the composition of the commercial Puralox support exhibits a CeO2:Al2O3 20:80 mass ratio which is in concordance with its technical data [47] as well as the targeted 2 wt.% Pt loading achieved by the used wet impregnation method. A type IV N2 adsorption-desorption isotherm is observed for the PtCeAl catalyst (data not shown) and the sample surface area is slightly lower than 160 m2·g-1, which is the BET surface area of the unloaded commercial CeO2/Al2O3 support [47]. On the other side, the introduction of Mo in the Eu-doped zirconia lattice results in an increase of the BET surface since the ZrEuMo\_x samples exhibit higher surface area than that of Eu-doped ZrO2 mixed oxide (ZrEu sample SBET = 42 m2·g-1). This may support the previously discussed hypothesis of MoOx islands formed on the surface of the mixed oxide. The pore size and pore volume of the Mo-doped solids are not affected by the Mo content being constant for all ZrEuMo prepared samples, although this value is lower for the pore size (2.4 nm) and higher for the pore volume (0.06 – 0.07 cm3·g-1) than the ones observed for the bare ZrEu solid solution, 3.4 nm and 0.02 cm3·g-1, respectively. The ZrEuMo\_x samples also define an isotherm type IV with a pore size monomodal distribution (data not shown), which is again in good agreement with the ZrEu reference sample [6].

Table 1. Summary of physicochemical properties of the prepared samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **SBET (m2/g)** | **Vp (cm3/g)** | **Øp (nm)** | **Chemical composition\* (XRF – wt. %)** |
| **PtCeAl** | 110 | 0.26 | 8.84 | 1.8 Pt (2)  18.8 CeO2 (19.6)  79.4 Al2O3 (78.4) |
| **ZrEuMo\_5** | 74 | 0.06 | 2.4 | 58.4 Zr (60.9)  11.9 Eu (10.7)  4.5 Mo (3.6)  25.2 O (24.8) |
| **ZrEuMo\_7** | 88 | 0.07 | 2.4 | 56.2 Zr (59.6)  11.9 Eu (10.4)  6.5 Mo (5.0)  25.4 O (25.0) |
| **ZrEuMo\_10** | 85 | 0.06 | 2.4 | 55.1 Zr (57.5)  12.2 Eu (10.1)  7.2 Mo (7.1)  25.5 O (25.3) |
| **ZrEu** | 45 | 0.02 | 3.4 | 62.7 Zr (64.3)  12.8 Eu (11.3)  0 Mo (0)  24.50 O (24.4) |
|  |  |  |  |  |

\*Nominal values between parentheses.

The chemical composition of the ZrEuMo\_x compounds determined by XRF (Table 1) shows a very small increase of Eu and Mo content at the expense of Zr percentage in all studied composition range. However, the order of magnitude is preserved and the trend of the increment of the Mo amount follows the targeted one. Since the XRF analysis shows an appropriate chemical composition of the synthesized compounds but the XRD does not exhibit any evidence of the presence of the molybdenum dopant, a XPS analysis was carried out according to the hypothesis of MoOx phase formation on the mixed oxide surface. On analyzing the bulk-to-surface atomic composition of the ZrEuMo\_x samples important differences are revealed. Figure 5 plots the Mo/Zr, Mo/Eu and Eu/Zr atomic ratios for each ionic conductor (ZrEuMo\_x, x = 5, 7 and 10) calculated by XRF, stating thereby the bulk composition, and by XPS showing the surface composition. As can be seen in figure 5c the Eu/Zr ratio measured by XRF is constant whatever the molybdenum content as it should be expected considering that the synthesis procedure fixes a Zr:Eu constant 95:5 molar ratio and that this composition results in a homogeneous solid solution. However, the surface Eu/Zr ratio is noticeable lower than the observed one for the solid solution bulk composition. This indicates either a surface segregation of zirconium cations or that Eu atoms have been selectively covered by Mo, then reducing its surface concentration (Figure 5c). On the contrary, the Mo/Zr surface ratio and bulk ratio are equal within the experimental error (Figure 5a), this ratio increases on increasing the amount of Mo as it should be expected. Figure 5b plots the Mo/Eu surface and bulk ratios, on increasing the Mo content both ratios increase but the higher slope of the surface ratio points to an increase of the Mo surface content at the expenses of Eu surface concentration. The differences increase on increasing the Mo loading. Therefore, it may be hypothesized that molybdenum atoms sit preferentially on surface europium atoms of the solid solution. These observations evidence the idea of a surface segregation of the molybdenum phase on the Zr-Eu solid solution earlier proposed by XRD analysis.

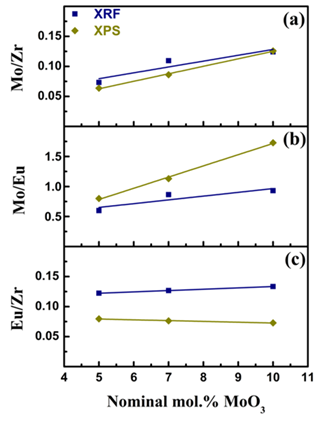


Figure 5. Atomic ratios in the bulk analysed by XRF and in the surface analysed by XPS for all ZrEuMo\_x samples (where x shows the nominal amount of MoO3, x= 5, 7 and 10 mol.%). (a) Mo/Zr ratio, (b) Mo/Eu ratio and (c) Eu/Zr ratio.

In the light of the exposed results, it can be concluded that the used synthesis method results in a homogeneous Eu-doped zirconia solid solution in which a homogeneous oxygen vacancies distribution is expected. On adding Mo, a surface segregated molybdenum phase appears on top of the Zr-Eu solid solution whose crystalline structure is not altered. This Mo oxide phase may vary from isolated tetrahedral [MoO4]2-, octahedral polymolybdates ([Mo7O24]6- and/or [Mo8O26]4-), clusters formation till α-MoO3 monolayer formation for high loadings [22,48–50]. Chippindale and Cheetham [22] using a synthesis procedure similar to the one described in this work have reported paramolybdate species ([Mo7O24]6-) as the most convenient precursor for the preparation of α–MoO3 layers. In the same way, a MoO3 phase is formed above 300 ºC upon decomposition of heptamolybdate [51].

Similar systems have been studied by several authors. For instance, Hu *et al*. [52] have studied by Raman spectroscopy and EXAFS the different phases formed upon impregnation of an ammonium heptamolybdate solution on different supports like ZrO2 as a function of Mo loading. They observed that the support nature, its isoelectric point and the solution pH affect the nature of the supported phase, which may result in octahedral (MoOx phase) or tetrahedral (hydrated molybdates) structures; however, they could not observe any influence of the preparation method. The Mo oxides supported on ZrO2 in Hu’s work exhibit isolated tetrahedral structures (MoO42- in aqueous solution) for low loadings and high pH values, but octahedral ordering for high amounts of Mo. For these authors a ca. 4 wt.% of MoO3 is required to create a monolayer coverage on ZrO2. This loading results in surface structures that present Raman signals corresponding to crystalline MoO3. This loading accounts for a Mo density of ca. 4,5 Mo atoms/nm2. A slightly higher Mo loading (5 Mo atoms/nm2) is determined by Xie *et al*. [53] to form a MoOx monolayer on ZrO2, which is in accordance with other authors [54–57]. Chary *et al*. [42], in a similar study with different loadings of MoO3 on ZrO2, reports a 6,6 wt.% of MoO3 as necessary to complete a monolayer. All these values are close to the 0.16 wt.% of MoO3 per m2 of support proposed by Van Hengstum *et al*. [55].

Estimating our Mo surface density is not an easy task since the synthesis procedure implies the coprecipitation of Zr, Eu and Mo phases, not the impregnation of an already prepared ZrEu mixed oxide support. Two alternatives may be envisaged, the first one would consider a support of 45 m2·g-1 as reported in table 1 whereas a Mo-containing phase is on the surface of the mixed oxide. This may be consistent with a decrease in pore radius from 3,4 to 2,4 nm but cannot explain the increase in pore volume. In the second approach the Mo-containing phase is in the surface of the mixed oxide but its relatively low concentration does not alter the surface of the solid, therefore the surface area is in the range 74-88 m2·g-1. This approach is consistent with a porous volume higher than in the support precipitated in the absence of molybdenum. As it is easily seen, the surface density of molybdenum is quite different depending on the approach, in the first case a MoO3 monolayer should be attained for ca. 7,5 wt.% of MoO3 assuming Van Hengstum *et al*.’ calculations [55], while in the second one between 12 and 14 wt.% of MoO3 is required for obtaining a statistical MoO3 monolayer. A conservative approach may suggest that the monolayer capacity is in between these two extreme alternatives and, therefore, assume that the MoO3 coverage in ZrEuMo\_5 and ZrEuMo\_7 is below the monolayer while for ZrEuMo\_10 a close to unity coverage has been attained. The absence of diffraction lines (Figure 4b) associated to any Mo-containing phase may indicate either the formation of a monolayer all over the support in which tetrahedral molybdates dominates or the existence of islands of α-MoO3 phase with sizes below the detection limit of the XRD diffractometer. XPS data (Figure 5) seems to better support the second hypothesis: small MoO3 islands nucleating on Eu sites of the solid solution.

Therefore, in an attempt of finding the structure adopted by surface MoOx phase in the ZrEuMo\_x samples, Raman and UV-Vis spectroscopy analysis of the synthesized samples in ambient conditions were carried out. The UV-Vis spectra (Figure 6) only show a shift of the edge energy (Eg) from ~270 nm (4.6 eV) to ~340 nm (3.6 eV) on increasing the Mo content associated to Mo-O-Mo bonds. According to Tian *et al*. [48], this shift indicates that ZrEuMo\_5 sample shows predominantly isolated monomeric [MoO4]2- species, whose UV-Vis excitation band is found at more narrow and lower wavelength range, characteristic of this Mo-O bond. On increasing the Mo concentration, [Mo7O24]6- clusters are formed and even an α-MoO3 layer for the ZrEuMo\_10 sample may appear, making wider the UV-Vis excitation Eg band (lower energy required) due to more Mo-O-Mo bonds. These structures are also in good agreement with the literature discussed above. Moreover, the UV-Vis spectra have been presented together with the reference ZrEu sample for comparison, where the luminescence by f-f transitions of Eu has been hidden by the red shift of Eg on increasing the Mo content.

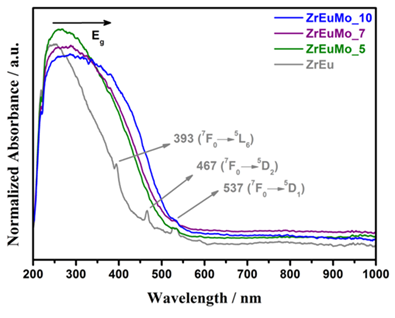


Figure 6. Normalized UV-Vis spectra of ZrEuMo\_x samples compared with ZrEu sample as reference.

Unfortunately, as it can be noticed in Figure 7 where the Raman spectra of ZrEuMo\_x samples are also compared with ZrEu reference sample, the intense luminescence of europium atoms hinders the Raman signals of the molybdenum species that show bands in the 200 – 400 cm-1 and 600 – 950 cm-1 ranges. The europium f-f transitions corresponding to transitions from 7F0 state towards 7FJ states (at high wavelengths) or from 7FJ levels towards excited 5D1 state (Raman shifts less than ~1000 cm-1, *i.e*. wavelengths below 560 nm) are exhibited [58]. Luminescence spectra of europium compounds are deeply discussed elsewhere [6,58–62]. Interestingly, in general the presence of Mo has implied the widening and the shifting towards lower wavelengths (red shift) of the bands indicating that the f-f transitions are more favored, especially those that include an excited state (like 7F1 → 5D1, 7F2 → 5D1, 7F2 → 5D0 and 7F3 → 5D0 transitions, Figure 7). Contrary, the 7F0 → 5D0 transition appears at higher energy (blue shift) and the intensity is increased when the Mo is added but keeping constant on increasing the molybdenum loading. This transition (7F0 → 5D0 at ~1530 cm-1 Raman shift, *i.e.* 579 nm) is exhibited when the symmetry of Eu3+ atoms is low. Thus, the increment of its intensity reveals the contact between Mo and Eu atoms reducing the symmetry of the latter. Moreover, the 7F1 → 5D0 transition identified at ~591 nm (around 1880 cm-1 Raman shift) splits in three components between 588 and 594 nm due to the association between the oxygen vacancies and the Eu atoms of the Zr-Eu solid solution that necessarily indicates that the symmetry is orthorhombic or less. As the Mo is added, the splitting becomes broader due to the presence of many different Eu sites which stablishes again the influence of the Mo atoms in the Eu coordination. Analogously, it is not surprising that the 7F2 → 5D0 transition (also known as hypersensitive transition) shows the most significant modified Eu luminescence by the presence of Mo atoms [58], stating again the influence of the Mo atoms in the Eu surrounding. Furthermore, according to several authors [60–63], the relative high intensity of the 7F2 → 5D0 transition with respect to the 7F1 → 5D0 transition is expected. The intensity ratio (7F2 → 5D0)/(7F1 → 5D0) relates to the symmetry of the Eu coordination environment, so that the higher the ratio, the lower the site symmetry. Thus, in these samples the increment of the Mo content increases the intensity of the (7F2 → 5D0)/(7F1 → 5D0) ratio from 1.54 for ZrEu sample to 2.56, 3.24 and 5.90 for ZrEuMo\_5, ZrEuMo\_7 and ZrEuMo\_10 sample respectively, meaning a decrease of the Eu symmetry. Therefore, the changes in intensity and the shifts exhibited in Eu luminescence of ZrEuMo\_x samples again evidence the intimate contact between the Mo and Eu atoms, supporting thereby the conclusions obtained by XPS analysis where Mo is preferentially positioned over Eu atoms in the proton conductor.

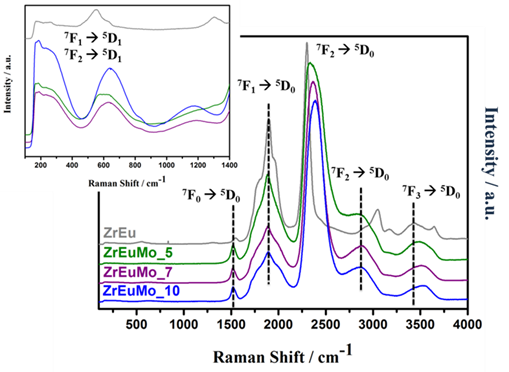


Figure 7. Normalized Raman spectra using a green excitation laser (532.14 nm) at RT of ZrEuMo\_x samples compared with the bare ZrEu sample.

To avoid luminescence as much as possible and get a further insight into the Mo-containing phase structure, Raman analysis were carried out again but with an excitation laser of 785 nm (red light) in the same ambient conditions. The use of this excitation wavelength allows to eliminate Eu luminescence in the 700-1000 cm-1 Raman shift range (Figure 8). This approach succeeds and Raman bands, distinguishable from these of the bare ZrEu sample, associated to Mo-containing phases appear. A broad complex band between 700 and 1000 cm-1 Raman shift develops on adding Mo to the ZrEu sample. This band shows clear maxima at *ca.* 830, 890, 960 and 990 cm-1. The intensity of all of these bands increases on increasing coverage but the one at *ca*. 990 cm-1. Collection of overlapping bands may be associated to stretching modes of both MoO3 islands and molybdate clusters. Terminal Mo=O bonds of isolated tetrahedral species appear at 924 cm-1 according to Hu *et al*. [52]. These authors indicate that this band shift to 952 cm-1 on increasing Mo coverage on MoO3/ZrO2 indicating the formation of clusters containing octahedral Mo species (hydrated octahedral [Mo7O24]6- and [Mo8O26]4-). On further increasing the Mo coverage a band at 820 cm-1 appears that is characteristic of MoO3 species. Tian *et al*. [48] studied among others the MoO3/ZrO2 system as a function of Mo coverage. They ascribed bands at 919 cm-1 to isolated [MoO4]2- anion, bands at 952 and 880 cm-1 that reflects the existence of [Mo7O24]6- clusters and a band at 820 cm-1 that assign to MoO3 nanoparticles and corresponds to asymmetric stretching mode of bridging Mo-O-Mo bonds. Finally, the weak band at 989 cm-1 is ascribed to the symmetric stretching mode of terminal Mo=O bonds of the MoO3 layer according to several authors [42,48].

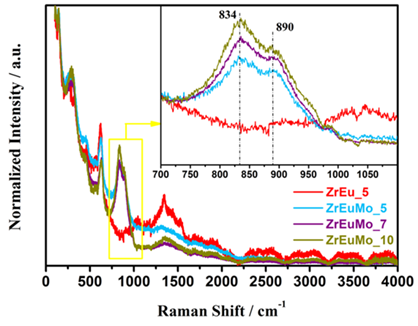


Figure 8. Normalized Raman spectra using a red excitation laser (785 nm) at RT of ZrEuMo\_x samples compared with the bare ZrEu sample.

According to this, it must be concluded that whatever the Mo loading in these synthesized ZrEuMo\_x samples, MoO3 nanoparticles (band at 820-830 and 989 cm-1) together with the presence of polymolybdate clusters, [Mo7O24]6- and [Mo8O26]4- (bands at 890 and 961 cm-1) are always present. However, the line profile of the Raman spectra between 700 and 1000 cm-1 may not allow discarding the existence of isolated molybdate ions since their characteristic mode at 919 cm-1 may be hidden in the broad and complex band shown in Figure 8.

The analysis of the UV-Vis spectra together with the densities estimate allowed to propose a model for MoO3 deposits consistent with molybdate and polymolybdate species dispersed on the ZrEu mixed oxide at coverages below or close to the monolayer. The Raman data above clearly state the presence of Mo-containing phases of high nuclearity MoO3 and polymolybdate clusters even for the lowest loading tested. This seems to discard the formation of a continuous monolayer and support the XPS data that points to islands of high nuclearity Mo species sitting on Eu sites.

Finally, TPR analysis of both PtCeAl and ZrEuMo\_x samples allow understand the behavior of these materials under reducing atmospheres present in the WGS reaction. Concretely in this work, this reaction will be studied using a surrogate of natural gas reformate (previously named industrial conditions) and, therefore, the feed stream will contain *ca.* 50 % of H2. Moreover, for the PtCeAl catalyst, this analysis will provide information to stablish the Pt activation step conditions. In general, the platinum reduction process strongly depends on the metal loading, the metal dispersion, the nature of the support, the synthesis method and the temperature treatment [64–66]. The H2-TPR profile of the PtCeAl catalyst has been then compared in Figure 9a with the CeAl support in order to analyze the reduction associated to ceria, as well as with a 2 wt.% Pt supported on an undoped commercial alumina support also prepared by wet impregnation. As Al2O3 is a non-reducible oxide, the H2 consumption in this Pt/Al2O3 sample must be entirely assigned to the reduction of the platinum species, whose process will appear at different temperatures depending on the Pt particle size and its interaction metal – support. Thus, Merlen *et al*. [67] observed three different reduction peaks around 100, 180 and 300 ºC associated to PtOx species with different particle sizes and metal – support interactions: the smaller the particles, the stronger the interaction and hence the higher the temperature of reduction [68,69]. As it can be noticed in Figure 9a, two general reduction processes at ~220 and ~361 ºC are described in the prepared catalyst PtCeAl. Taking into account that the reduction processes appear at relatively high temperatures (220 and 361 ºC) respect to those reported in literature and considering that platinum phases were not detected by XRD, the TPR data seem to indicate small Pt particle sizes in the prepared sample, with a high interaction between Pt and ceria support.

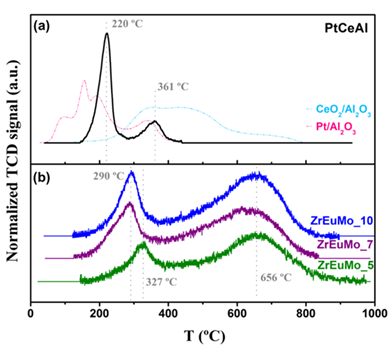


Figure 9. H2 - TPR profiles of (a) PtCeAl catalyst compared with the unloaded Puralox commercial support CeO2/Al2O3 and the 2 wt.%. of Pt on commercial Al2O3 support and (b) ZrEuMo\_x samples.

A quantitative analysis of the reducibility of the sample has been carried out after calibrating the TCD signal using a standard CuO pattern (Strem Chemicals 99.999%). Thus, the reducibility has been defined as:

[1]

Accordingly, the total H2 consumption (up to ~ 450 ºC) respect to the theoretical one, assuming Pt4+ species (PtO2 + 2 H2 ⇆ Pt + 2 H2O), indicates a 366 % of reducibility. This over-consumption could be due, besides the Pt reduction process, to other processes like Ce4+ reduction or carbon deposits hydrogenation reactions. Considering only the first observed reduction process around 220 ºC, the calculated reducibility still shows over-consumption (270 %). Consequently, from ~300 ºC the Pt is assumed to be completely reduced. Moreover, by comparison of the TPR profiles of Pt/Al2O3 and CeO2/Al2O3 samples, the last peak at around 361 ºC should be associated to the reduction of ceria or to the hydrogenation of carbonaceous species. According to the TPR data and taking into account the calcination temperature of the PtCeAl sample, a reduction at 350 ºC in a 10 % of H2/N2 flow for 30 min was selected as the catalyst activation step to completely reduce the Pt particles and to avoid high calcination temperatures that favor the particle sintering.

On the other side, not surprisingly the H2-TPR profile for the bare ZrEu sample does not show any reduction process. However, the introduction of reducible Mo atoms in these materials (ZrEuMo\_x) exhibit two well defined reduction processes around 300 and 650 ºC (Figure 9b). According to several authors [42,51,70], the reduction of MoO3 essentially happens in two steps (MoO3 → MoO2 and MoO2 → Mo), where shoulders or weaker peaks can appear according to intermediate phases like Mo4O11. The reduction process of bulk MoO3 normally starts over 600 ºC. However, the required temperature to achieve the reduction of molybdenum oxide can vary depending on the amount of water in the system, the heating rate, the sample amount or the calcination temperature in the sample preparation process [70]. Moreover, if the sample is a supported MoO3 instead of a bulk, other parameters like MoO3–support interaction or particle size also modify the reduction temperatures. For instance, Chary *et al*. [42] reported reduction temperatures as low as 400-420 ºC for the low-temperature peak of MoO3/ZrO2 samples while the high-temperature peak occurs at 800-940 ºC. The first reduction peak is assigned to the reduction of octahedral species ([Mo7O24]6- and [Mo8O26]4- clusters) and the high temperature one to the reduction of tetrahedral species more strongly bound to the support. In addition, they observed that the temperature at which both reduction processes develop shifted to lower temperatures on increasing the Mo content up to reaching the monolayer coverage. Besides, Ressler and co-workers [71] reported the hydrogen is introduced in the Mo oxide structure forming bronzes over ~200 ºC forming HxMoO3. On increasing the temperature, from ~380 ºC, reduced nuclei MoO2 phases start to appear. Finally, for temperatures above ~450 ºC, the reduction of MoO3 to MoO2 is the main process, where formation of intermediate Mo4O11 phase is not discarded. According to these two works, the observed behavior of ZrEuMo\_x TPRs perfectly matches with that described by Chary *et al*., where a shift to lower temperatures is shown on increasing the Mo loading up to ZrEuMo\_7, from which the amount of Mo oxide probably exceeds the monolayer formation at expense of octahedral species according to previously discussed data. Moreover, these ZrEuMo\_x samples show the reduction processes even at lower temperatures, which are in good agreement with those reported by Ressler *et al*.

The quantitative analysis of the TPR leads to a ratio of the areas A2/A1 (considering A1 the first reduction process at lower temperature and A2 the area of the second reduction peak) of 3.3, 3.1 and 3.1 for ZrEuMo\_5, ZrEuMo\_7 and ZrEuMo\_10, respectively. However, no elemental proposed reduction steps (Equations 2 to 5 or 2 and 5) provide a H2 consumption ratio of 1:3 according to the calculated areas ratio:

[2]

[3]

[4]

[5]

Moreover, the calculations lead to a total reducibility (Equation 1) around 400 %. If only the first reduction process is considered (A1), which is the temperature range of interest in this work, according to reduction process proposed in Eq. 2, the calculated reducibilities are 116, 107 and 77 %, respectively. According to this, Mo oxide presents over-reducibility and, in agreement with Ressler’s work [71], the formation of bronzes (HxMoO3 type-structures) and some reduced MoO2 phase below 350 ºC are expected and should be kept in mind for future catalytic experiments.

**3.3 Analysis and characterization of the slurries and structured catalyst.**

The final formulation for the slurries preparation for the two selected samples (PtCeAl catalyst, named m-PtCeAl, and the physical mixture of PtCeAl + ZrEuMo\_5 in mass proportion of 1:5, named m\_PtCeAl+ZrEuMo\_5) was optimized as described above in order to have a stable slurry during the complete washcoating process, to avoid the particle agglomeration and to obtain well-controlled homogeneous thin layer deposited on the micromonolith to prevent diffusional problems, fractures or peeling and catalyst loss. Thus, the solid samples were grinded and sieved to achieve particle sizes below 50 µm and the Z potential of each suspension was studied. The Z potential curves of the samples (Figure 10a) have been fitted to a Boltzmann equation. The solids present Z potential within the 6 – 8 pH range indicating that, for a stable slurry, the pH of the suspension must be far from this range. In addition, the viscosity of the slurry was analyzed at different stirring velocities. The same variation of the viscosity was observed for both slurries, being the value obtained at 250 rpm around 2.5 cp lower to the optimally suggested according to literature of 5 cp [40]. These data correspond to the final slurry formulation using only colloidal alumina (Nyacol ®) as additive, whose role is to help the adhesion of the catalyst. The summary of the measured pH and viscosities of each slurry is reported in Table 2 and Figure 10.

Table 2. Properties of the prepared slurries, catalyst loading on micromonoliths by washcoating and weight loss measured by the adherence test.

|  |  |  |
| --- | --- | --- |
| Structured sample | m\_PtCeAl | m\_PtCeAl+ZrEuMo\_5 (1:5) |
| pHa  (Z pot. = 0) | 7.12 | 7.77 |
| pH slurry | 5.35 | 3.87 |
| Viscosity slurry (cp) | 2.6 | 2.0 |
| Catalyst loading (g) | 0.1281 | 0.5482 |
| Adherenceb (%) | 94,46 | 94,44 |

apH at zero Z potential of the colloidal suspension (Figure 10a).

bCatalyst’ adherence (%) calculated by the difference between the catalyst loading before and after the adherence test of the structured catalysts.

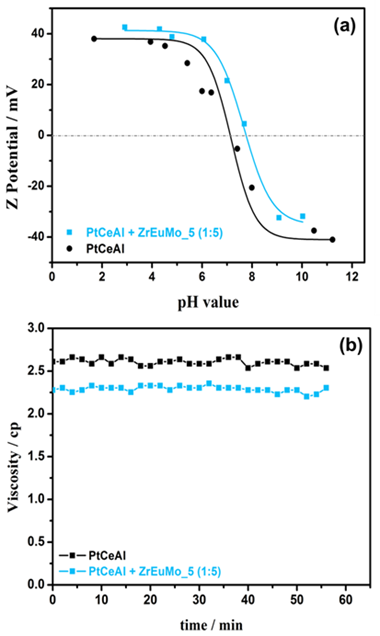


Figure 10. Properties of the prepared slurries: (a) Z potential and (b) viscosity at 250 rpm.

Then, the monoliths were impregnated following the process described in the experimental section until the PtCeAl catalyst loading was 0.1 g in both cases, it means, 0.1 g of PtCeAl and 0.6 g of PtCeAl + ZrEuMo\_5 mixture of 1:5 mass ratio. Finally, the structured catalysts were subjected to an adherence test based on the one proposed by Yasaky *et al*. [41] (see experimental section). The adherence based on the difference in weight of the loading on the micromonolith measured before and after the adherence test is summarized in Table 2. The weight losses (around 5 %) are acceptable and comparable to those studied by Frias *et al*. [72] for similar structured systems and within the conventional limits for good adherence [40].

After the washcoating process, the remaining slurries were dried and calcined in the same conditions as loaded micromonoliths. The calcined slurries were then analyzed by XRD in order to compare them with the original powders and to observe if any modification during the coating process occurs. The intensities and positions of the diffraction peaks of both samples (m\_PtCeAl and the m\_PtCeAl+ZrEuMo\_5) are not modified by the slurry preparation and all present phases are preserved for the structured catalysts as expected (Figure 11).

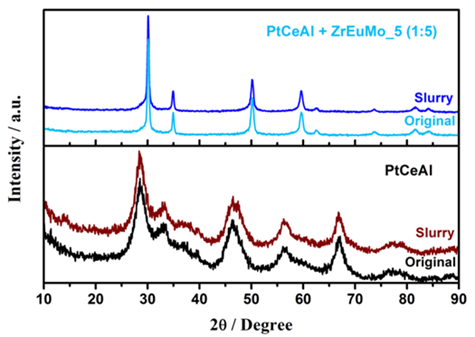


Figure 11. Diffraction patterns of the dried and calcined remaining slurries after whascoating process and the XRD of their original powders for comparison.

The structured catalysts were analyzed by N2 adsorption (Table 3). A slightly increase of the specific surface of the m\_PtCeAl catalyst respect to the original powder (see Table 1) was observed, due to the addition of colloidal alumina for the slurry stabilization. On the other side, the specific surface of m\_PtCeAl+ZrEuMo sample was compared to the calculated value for the original powders (PtCeAl and ZrEuMo) considering the mass proportion of 1:5. These values are 80 m2/g of SBET, 0.09 cm3/g of porous volume and 3.473 nm of porous diameter. The value of 5.3 nm as pore size provide from the contribution of two pore sizes found in the distribution plot (data not shown), where distinguished fractions at ~3 nm and at ~8 nm appears corresponding to the initial pore sizes of the original ZrEuMo\_5 and PtCeAl powders, respectively (see Table 1).

Table 3. Textural properties of the structured catalysts and the calculated theoretical thickness of loaded catalytic layers.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Structured sample | SBET (m2/g) | Vp (cm3/g) | Øp (nm) | Theoretical thickness of the catalytic layer (µm) |
| m\_PtCeAl | 134 | 0.24 | 7.0 | 0.9 |
| m\_PtCeAl+ZrEuMo\_5 (1:5) | 85 | 0.15 | 5.3 | 2.8 |

Finally, scanning electron microscopy (SEM) technique was used to observe the homogeneity and thickness of the catalytic layer on micromonolith. In Figure 12a SEM image of the manufactured micromonolith after thermal treatment and before the catalytic layer impregnation is shown, where the characteristic needle-like shape alumina layer is identified [72,73]. In Figure 12b, the transversal cross section of the m\_PtCeAl+ZrEuMo\_5 sample is presented, where the measurement of the layer reveals *c.a*. 3 µm in thickness, in a good concordance with the calculated theoretical layer (Table 3) and comparable to other reported similar structured catalysts [74]. Thickness theoretical calculations are based on the compact structure density, the textural properties (porosity and BET surface), the exposed surface of the micromonolith (540 cm2) and the catalyst loading. The m\_PtCeAl+ZrEuMo\_5 sample presents the highest loading and, consequently, its layer is thicker. Thus, both structured catalysts present active layers below 3 µm, which allows us to neglect possible diffusional problems, in agreement with other studies, where such problems become important within the 10 – 20 µm range thickness [75,76].

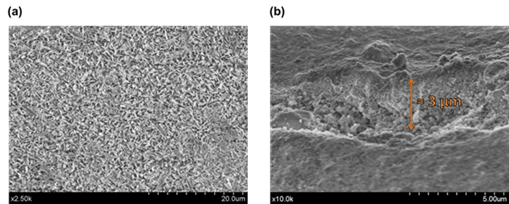


Figure 12. SEM images of (a) the created Al2O3 layer of the treated micromonolith and (b) transversal section of the m\_PtCeAl+ZrEuMo\_5 layer loaded on the micromonolith.

**4. Conclusions**

According to the determining role of the water activation in WGS reaction in H2 production process, promoted catalysts based on physical mixture of a Pt-based catalyst and proton conductor mixed oxides have been prepared. The addition of MoOx to Eu-doped ZrO2 mixed oxide generates proton conducting materials composed by a Zr and Eu solid solution with molybdates clusters located on the surface, preferentially over Eu sites. The increment of Mo content show the promotion of MoOx clusters to α-MoO3 islands or monolayers for high Mo loadings. Moreover, TPR analysis exhibited the reducibility of Mo phases at really low temperatures and possible bronzes formation. In addition to the previously demonstrated proton conductivity of the Eu-doped zirconia solid solution, these Mo-based structures are reported to be able to adsorb water and present ion-exchange in the temperature range of interest in order to improve the WGS catalyst performance. Indeed, catalytic tests with these promoted catalysts on WGS reaction exhibit higher activity in terms of CO conversion, which is related to its water-enhancer effect that improves the water activation step of the WGS reaction.

The structuration of these catalysts allows to discard thermal or diffusional effects supporting thereby the water-promoter effect by the ionic conductor. The better activity achieved by this structured promoted catalyst (m\_PtCeAl+ZrEuMo\_5) in industrial conditions at the tested high space velocity makes it quite promising for future mobile devices applications, as well as it fosters new WGS catalysts design based on proton conductors.

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