Synthesis and characterization of Rh/MnO$_2$-CeO$_2$/Al$_2$O$_3$ catalysts for CO-PrOx reaction

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Abstract

Rh/MnO$_2$-CeO$_2$/Al$_2$O$_3$ catalysts with different manganese-to-ceria ratios have been synthesized, characterized and tested in CO-PrOx reaction. The physicochemical properties of the solids were studied by XRD, Raman spectroscopy, BET surface area, H$_2$-TPR, TGA-DTG and TEM. The differences observed in the textural, structural and redox properties were related to the Mn-to-ceria ratio of the samples. The segregation of Mn species was observed at high Mn-to-Ce ratios. In opposite way, MnO$_2$-CeO$_2$ solid solutions were obtained at low Mn to Ce ones. In this last case, the physicochemical properties of the solids were favored by the intimate Rh-Ce-Mn contact. The effect of the Mn-Ce presence on Rh catalysts which promotes the catalytic behavior towards selective CO oxidation was observed to be better at low temperatures. At higher temperatures, Mn species promote the Reverse Water Gas Shift reaction, whilst ceria promotes the H$_2$ oxidation in the whole range of working temperatures.

Keywords: Manganese oxide, cerium oxide, MnO$_2$-CeO$_2$, CO-PrOx

1. Introduction

During the last decade, there have been important advances in the fuel cells technology for applications in electrical energy generation and co-generation systems (coupled heat and power) in both stationary and mobile systems [1]. Proton exchange membrane fuel cell technology (PEMFC) demands a free-CO hydrogen stream for operation. Since CO is adsorbed on the catalyst surface causing catalyst poisoning, it is necessary to reach CO concentrations of less than 10 ppm for preventing irreversible damage and to facilitate the electrochemical reaction on the Pt electrode. One of the most economical and popular way to produce

hydrogen is the reforming of methane or other hydrocarbons or biomass molecules. However, the high proportion of CO contained in the hydrogen flow produced forces to use clean up reactions to abate the CO levels till less than 10 ppm. In that sense, Water–gas-shift reaction (WGS) in which CO reacts with water to produce CO_2 and H_2 allows achieving an outlet gas composition with a typical CO composition of 0.5–2% (v/v). Afterwards, a final CO abatement is needed. Physical methods (pressure swing adsorption (PSA)) and catalytic methods (methanation and preferential oxidation) have been studied for selective CO removal from a hydrogen-rich stream. Among these, the CO preferential oxidation (CO-PrOx reaction) is preferred for small-scale reforming systems because of its relative simple implementation for portable and on-board applications and auxiliary power units, lower operating costs and minimal hydrogen loss [2-3]. Additionally, CO-PrOx reaction can be performed at atmospheric pressure and the range of working temperatures matches the one at which the fuel cells work [4]. In this reaction, a competition between CO and H_2 molecules for the O_2 ones occurs. A good CO-PrOx catalyst should favor the CO oxidation against H_2 oxidation, in such a way that both high CO conversion and selectivity to CO_2 are desired. In addition, the temperature must be as low as possible, ideally around 150°C, the working temperature of fuel cells, in order to save energy in the full integration process. At higher temperatures, the Reverse Water Gas Shift reaction can be promoted decreasing the CO activity.

The reported promising catalysts for CO-PrOx reaction could be grouped into three classes: (i) Supported noble metal catalysts, such as Pt, Pd, Ir, Ru and Rh [5-9], (ii) Nano-gold catalysts [10] and (iii) Metal oxides catalysts, mainly bulk $CuO-CeO_2$ [11-15] or supported $CuO-CeO_2$ catalysts [12,16], and Co-Ni oxides [17]. Zhou et al. [17] investigated the catalytic properties of Ni, Co and Co–Ni supported on activated carbon for CO-PrOx reaction. They reported the bimetallic system as the most active at lower temperatures. Nowadays highly effective catalysts are required for both the water gas shift (WGS) reaction and the preferential CO oxidation (CO-PrOx) which are considered as purification processes for the production of clean hydrogen. This is normally carried out in fuel processors where WGS and CO-PrOx reactions are coupled as integrated stages. Herein, $CuO-CeO_2$ systems have demonstrated outstanding activity for both mentioned reactions and therefore they are intimately linked to the development of the last generation of hydrogen alimented fuel cells [12,15]. Barbato et al.[11] reported very active catalyst for oxidation reactions based on $CuO-CeO_2$ catalysts prepared by solution combustion

synthesis with respect to the typically ones synthesized by impregnation method [12-15]. Reina *et al.* [12,15] reported that the catalytic system $CuO–CeO_2$ is very active and selective for CO oxidation and WGS reaction in the presence of a large amount of H_2 and that the selectivity increases when gold is also incorporated. Despite the benefits of the inclusion of gold in the formulation of $CuO-CeO_2$ catalysts, the addition of a noble metal (even in low quantities) would increase the cost of the final catalyst. As a way to partially compensate this expense, the amount of copper and ceria can be largely reduced by dispersing the mixed oxide on a high surface carrier as alumina [15]. However only at temperatures above 200^oC some of the alumina based materials reached a better activity/selectivity in comparison with bulk $CuO-CeO_2$ who reached almost full conversion and selectivity at 130^oC.

Concerning to noble metal catalysts, Pt/Al_2O_3 was proposed by Los Alamos National Laboratory in 1963 as an effective catalyst for preferential oxidation of CO in the H_2-rich gas mixture [18]. Later on, Oh and Sinkevitch [19] carried out CO-PrOx tests with synthetic reformate gases (0.85% H_2, 900 ppmv CO, and 800 ppmv O_2) from room temperature to 300°C with Al_2O_3-supported noble metals (Rh, Ru, Pt and Pd). They found that Rh/Al_2O_3 and Ru/Al_2O_3 catalysts had a superior activity for CO oxidation and reached a complete CO conversion at temperatures lower than those for Pd/Al_2O_3 and the most widely used Pt/Al_2O_3 catalysts. In addition, Rh/Al_2O_3 catalyst was the most selective among all the catalysts tested. Many other Rh-based catalysts have been studied extensively for CO-PrOx [20-24] because of their good performance at lower temperatures compared with other noble metals based catalysts. These systems are claimed to facilitate the elimination of CO in a single step under realistic space velocities (120000 mL/g h) and O_2 concentrations ($O_2/CO=1$) without compromising the CO_2 selectivity, and to operate in a wider temperature window which yield CO outlet concentration of less than 30 ppm even in the presence of H_2O and CO_2 ($180 -200^oC$) in comparison with Pd and Pt/Al_2O_3 systems.

The key role played by the support composition and properties in a CO-PrOx catalyst is well known. A large variety of supports (for instance, CeO_2, $Ce_xZr_{(1-x)}O_2$, $SiO_2–Al_2O_3$, Al_2O_3, SiO_2, La_2O_3 and MgO), with different redox, acidic and basic properties have been usually used in oxidation reactions. Among them, γ-alumina is commonly used as a support due to its high thermal and chemical stability, and high surface area. However, to increase the catalytic

conversion, the support must supply oxygen to the CO oxidation process. For some practical applications dopants such as transition and non-transition metal ions may be introduced in the lattice of support like CeO_2, increasing its temperature stability and ability to store and release oxygen [25-27]. Metallic cations with ionic radius and electronegativity close to those of cerium are thought to be the most appropriate modifiers of structural and chemical properties of ceria [28]. The similarity in the ionic radii is the criterion to predict the formation of a solid solution. Thus rare earth elements (Gd, La, Y, Eu, Pr, Sm, Nd) are a good choice for this [26-27]. In fact oxide of rare earth elements have been widely used as structural or electronic promoters to improve the activity, selectivity and thermal stability of CeO_2 through the formation of solid solution [26-27,29]. When doping with lanthanide cations an increase in the concentration of oxygen vacancies in the ceria structure is expected. This feature promotes the migration of oxygen ions through the lattice oxide and provides a material whit high oxygen ion conductivity. In addition the presence of oxygen vacancies have been correlated with an increase in the catalytic performances of the solids attributed to the direct interaction of the surface defects with the reactive gas phase [25,30]. These oxygen vacancies act as oxygen activation sites, able to produce very active oxygen species, such as peroxide and superoxide ones, generating very active oxidation catalysts [15]. For metal supported catalysts on CeO_2 (i.e Au, Pt, Rh) the presence of punctual defects on the metal oxide facilitates the interaction of the metallic phase with the support surface allowing a high dispersion and special dynamic interaction (electronic enrichment, redispersion process etc) [31]. Additionally modifying the chemical composition of CeO_2 with other oxides (i.e ZrO_2, MnOx) also greatly improves the catalyst activity [32, 33]. It is known that the introduction of zirconium enhances oxygen mobility even further by the formation of solid solution improving the redox properties and the oxygen buffering action observed for the Ce oxides [34]. Ceria–zirconia mixed oxides are also thermally stable and the oxygen storage capacity is retained even after many consecutive cycles of reduction at high temperature followed by re-oxidation. These properties improve even more the catalytic activity in oxidation, reforming and WGS reactions.

On the other hand, MnO_2-CeO_2 mixed oxides could exhibit much better redox properties than ceria alone due to multi-valence state and strong interaction between ceria and manganese [35-36]. Manganese is believed to favor greatly the oxygen storage capacity of CeO_2 and the oxygen mobility on the surface of the ceria by forming MnO_2-CeO_2 solid solution [37]. MnO_2-

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CeO_2 oxides have been found to be highly actives for oxidation of light oxygenates compounds [38-46]. Venkataswamy *et al* [47] compared the CO oxidation performance of MnO_2-CeO_2 supported on alumina prepared by deposition-coprecipitacion method with respect to CeO_2 /Al_2O_3 and MnOx /Al_2O_3. The enhanced activity of mixed oxide was mainly attributed to high surface area, large amount of oxygen vacancies and excellent redox behavior. This quite promising activity compares favorably with other catalysts based on noble metals in oxidation reactions [48-49]. Additionally, it is indispensable to enhance the desired properties of Ce-Mn oxides by dispersing them over a thermally stable and high surface area support material. In this case alumina is a good carrier, especially for the industrial applications because of its ideal cost-efficiency and stability. Therefore, MnO_2 $_-CeO_2$ oxides supported in alumina could increase the catalyst surface area, thus maximize the oxygen vacancies concentration, which are very useful for catalytic oxidation reaction. However, to our knowledge, MnO_2-CeO_2/Al_2O_3 support effect on the physicochemical properties of the Rh-based catalysts and additionally their catalytic response on CO-PrOx reaction have not been reported. With this background the aim of this work was to study the physicochemical properties of the catalysts Rh/ MnO_2-CeO_2/Al_2O_3 as a function of Mn/Ce ratio fixing the Rh and Al_2O_3 loading. Thus, the high surface area supplied by alumina support simultaneously with the enhanced redox, textural and structural properties of the ceria by the formation of MnO_2-CeO_2 solid solution were discussed and related with the catalytic activity behavior in a CO-PrOx reaction as catalytic test.

2. Experimental

2.2 Catalysts synthesis

Rh/MnO_2-CeO_2/Al_2O_3 samples with 1 wt % of Rh were prepared by wet impregnation method using $KMnO_4$ (Panreac), $Ce(NO_3).6H_2O$ (Alfa Aesar) and $Rh(NO_3)_3$ (Alfa Aesar) as precursors. Commercial alumina (SASOL) was impregnated with a solution of $Ce(NO_3).6H_2O$ dissolved in methanol under stirring 24 h. The solvent was removed on rotavapor at 65°C. Then the solid was impregnated with a solution of $KMnO_4$ dissolved in technical grade acetone (Carlo Erba RPE). Additionally, high purity grade ethanol was added as reducing agent [50]. After mixing under vigorous stirring for 60 min, the solvent was removed on rotavapor at 80°C. Finally the

impregnation of $Rh(NO_3)_3$ was done following a similar procedure that was described for ceria precursor. The obtained mixed oxide catalysts were dried overnight at 120°C and calcined at 450°C (2°C/min) for 2 h.

The catalysts were synthesized with different CeO_2/MnO_2 weight ratios (10/40, 20/30, 40/10 wt.%). Always, the total (CeO_2 + MnO_2) content in the samples was 50 wt.%. The another 50 wt.% was constituted by Al_2O_3. The final catalysts were named $RhCe_xMn_yAl$, where Y was CeO_2 wt.% and Z was MnO_2 wt.%. For comparative purposes, catalysts without CeO_2 or MnO_2 ($RhMn_{50}Al$ and $RhCe_{50}Al$ respectively) were also prepared.

2.3 Characterization

X–ray diffraction (XRD) analyses were performed on a Siemens D 500 diffractometer. Diffraction patterns were recorded with Cu Kα radiation (40 mA, 40 kV) over a 2θ-range 20-80º using a position sensitive detector with a step size of 0.05° and a scan rate of 1° min^{-1}. For the determination of crystalline domain size of CeO_2, the Scherrer equation was applied over the most intense XRD peak around 28.5^{o} corresponding to the (111) plane, by using the software X'pert High Score Plus.

Raman spectra were recorded in a dispersive Horiva Jobin Yvon LabRam HR800 microscope with a He–Ne green laser (532.14 nm) working at 5 mW, and with a 600 g mm^{-1} grating (0.87 μm spot laser). The microscope used a 50X objective and a confocal pinhole of 1000 μm. The Raman spectrometer was calibrated using a silicon wafer. The conditions were selected to avoid sample photo decomposition or denaturation since higher laser powers or longer time of acquisition may result in an increase in sample temperature and the transformation of the initial manganese species.

BET specific surface areas were measured through nitrogen adsorption-desorption isotherms at liquid nitrogen temperature in a Micromeritics ASAP 2010 apparatus between 0.1 and 0.995 mmHg. Before analysis, the samples were outgassed for 2h at 150°C in vacuum. The Barrett-Joyner-

Halenda (BJH) method was used for determining the pore size distributions. Always desorption data were used.

HRTEM analysis was performed in a Philips CM 200 working at 200 kV with EDS analysis and CCD camera.

Thermogravimetric analyses were performed in a TA Instruments SOTQ600 thermo-balance using a 50 mL min^{-1} flow of synthetic air. The temperature was increased linearly at a rate of 10°C min^{-1} up to 1000°C.

A Microactivity Reference unit (PID Eng & Tech Company) that allowed the control of temperature and the composition of the feed streams connected to a thermal conductivity detector (TCD) was used for obtaining the H_2-TPR measurements. The reactive gas stream (5 vol.% H_2 in Ar) was flowed at 50 mL min^{-1} over 50 mg of sample and the temperature raised at 15°C min^{-1} from room temperature to 900°C. A molecular sieve 13X was used to retain the reduction products, mostly H_2O and CO_2 that would be desorbed on the surface of the solid. Semi-quantitative analysis was carried out by integration of the reduction signal and comparison with hydrogen consumption of a CuO reference.

2.4 Catalytic activity

Preferential oxidation of CO–PrOx in presence of hydrogen was carried out at atmospheric pressure in a stainless steel fixed bed reactor (9 mm inner diameter) at 60000 cm^3 g_{cat}^{-1} h^{-1}. A reaction mixture composed by 1% CO, 1% O_2, 50% H_2 and N_2 as balance at 100 mL.min^{-1} total flow was used. The catalyst (100 mg, 100 < ϕ < 200μm) was diluted in the adequate amount of crushed glass with the same particle size to obtain a bed height of 5 mm. Prior to all catalytic measurements the samples were treated in 100 vol.%H_2 at 400°C for 2h. Products and reactants were separated and quantified by on-line gas chromatography (Agilent®6890) equipped with HP PLOT Q and HP-5 columns and a TCD detector. The catalytic behavior study was performed between 130°C and 260°C.

The CO and O_2 conversions were calculated according to Eqs (1 and 2) where CO_{in} and O_{2in} are the inlet CO and O_2 concentration and CO_{out} and O_{2out} are the outlet ones.

CO conversion (%) = ([CO]$_{in}$-[CO]$_{out}$/[CO]$_{in}$) x 100   (Eq. 1)

O_2 conversion (%) = ([O$_2$]$_{in}$-[O$_2$]$_{out}$/[O$_2$]$_{in}$) x 100   (Eq. 2)

The selectivity towards CO_2 formation was calculated using Eq. (3)

CO_2 selectivity (%) = ([CO]$_{in}$-[CO]$_{out}$/(2x[O$_2$]$_{in}$-[O$_2$]$_{out}$)) x 100   (Eq. 3)

3. Results and discussion

3.1 XRD

Fig.1 shows the XRD patterns of the synthetized catalysts. Besides the typical diffractions of the primary support (γ-Al$_2$O$_3$, JCPDS 74-2206), in the samples with CeO_2 contents higher than 20 wt.% the diffraction peaks of the cubic antifluorite structure of cerium oxide (cerianite, JCPDS 34-0394) are also observed.

Regarding the presence of manganese peaks, no manganese crystalline species are detected at low Mn contents (RhCe$_{40}$Mn$_{10}$Al and RhCe$_{20}$Mn$_{30}$Al samples). Therefore, the inclusion of Mn into the ceria lattice forming solid solution could not be completely discarded. In this sense, it has been reported that the solubility of manganese in the ceria network strongly depends on the preparation method, the calcination conditions and the MnO_2/CeO_2 molar ratio used. MnO_2 segregation is normally observed for MnO_2/CeO_2 molar ratios above 3.0 [51]. Below this value the solid solution is expected. From here, the presence of MnO_2-CeO_2 solid solution for RhCe$_{40}$Mn$_{10}$Al and RhCe$_{20}$Mn$_{30}$Al samples could be suggested, at least partially, since these catalysts have MnO_2/CeO_2 molar ratios of 0.5 and 3.0, respectively. According to H. Li *et al* [46] the incorporation of Mn into the CeO_2 network must result in a decrease of the ceria lattice parameter, exposing preferentially the (111) crystal plane of ceria. The lattice contraction is due to the lower ionic radius of Mn^{n+} (0.053 nm for Mn^{4+} and 0.0645 nm for Mn^{3+}) compared to that of Ce^{4+} (0.094 nm). These authors also report that in the MnO_2-CeO_2 mixed oxides there are at

least three types of MnO_2 species with different structural locations: in ceria-lattice defect sites, in framework Ce^{4+} locations, and in interstitial locations.

The lattice cubic parameters of ceria in these two samples were estimated and the values are presented in Table 1. $RhCe_{40}Mn_{10}Al$ and $RhCe_{20}Mn_{30}Al$ solids exhibit a certain degree of ceria lattice contraction, showing an *a* parameter lower than those of the bare cubic ceria (5.414 Å) [52] and $RhCe_{50}Al$ sample (5.401 Å). In addition, the cubic lattice parameter of these samples decreases linearly with the concentration of MnO_2 (Fig. 2). Thus, the formation of the solid solution in both samples can be claimed.

For the samples with higher manganese contents (40 wt.%, $RhCe_{10}Mn_{40}Al$ and 50 wt. %, $RhMn_{50}Al$), reflections of crystalline MnO_x were detected rather than those of ceria, Fig.1. β-MnO_2 (Mn^{4+} pyrolusite, JCPDS 24-0735) and $K_2Mn_4O_8$ ($Mn^{3.8+}$, JCPDS 16-0205) phases are noticeable. The (Mn_4O_8) structure results from the presence of mainly Mn^{4+} and only small amounts of Mn^{3+} [44]. In addition, diffraction peaks of α-Mn_2O_3 (Mn^{3+} bixbyite, JCPDS 41-1442) are also observed. Simultaneously some diffraction peaks of potassium nitrate (JCPDS 01-0493) are also observed for $RhMn_{50}Al$ sample. For $RhCe_{10}Mn_{40}Al$ solid the segregation of MnO_x species is expected since the MnO_2/CeO_2 molar ratio is 7.9. Additionally no XRD peaks that could be assigned to any Rh crystalline phases are observed in the samples pointing out the lower crystalline domain or the lower amount of such species. This could indicate a high Rh dispersion in the samples.

Interesting information can also be extracted from XRD concerning the CeO_2 crystalline domain size. As shown in Table 1, a generalized decrease is produced by the introduction of Mn. From here, it can be suggested that the incorporation of manganese into ceria lattice greatly inhibits the crystalline growth. This observation has been already reported for CeO_2 doped with Me^{n+} (Me = metal) cations and correlated with a retarding or stabilizing effect of the dopant element on the growth of the crystal oxide [53-54]. Smaller ceria particles drive to a greater MeO_x/CeO_2 interface which is crucial for an enhanced activity in catalytic processes.

3.2 Raman spectroscopy

Raman spectra of fluorite type oxide structures are dominated by bands due to oxygen lattice vibrations, which are sensitive to the crystal symmetry. Fig. 3 shows the Raman spectra obtained for the synthesized materials. $RhCe_{50}Al$ exhibit a main band centered at about 462 cm^{-1}, which is assigned to Ce F2g mode due to symmetrical stretching of Ce–O vibrational unit in octahedral coordination [34]. It is well known that the position and width of this band depends on several factors, such as phonon confinement, strain, inhomogeneity of the sizes distribution, presence of defects and dopants and variation in phono relaxation with the particles size. In particular, when the ceria particle size decreases, the band shifts to lower energies, broadens and becomes asymmetric [55-57]. In our case, we observed a blue shift of the F2g mode for the $RhCe_{40}Mn_{10}Al$ and $RhCe_{20}Mn_{30}Al$ catalysts dispersed on alumina compared to the $RhCe_{50}Al$ sample. This blue shift could be ascribed to a decrease on the average ceria particle size in good concordance with the XRD data discussed above. Besides this, the inclusion on manganese ions into the ceria lattice forming the MnO_2-CeO_2 solid solution, also evidenced by XRD, could contribute to the observed displacement of the band.

In addition, a weak band ca. 260 cm^{-1} and another pronounced band at approximately 600 cm^{-1} were detected. These phonons have been previously attributed to the normal Raman inactive (IR active) transverse and longitudinal optical phonon modes at the Brillouin zone center respectively [58]. The band centered at 600 cm^{-1} is especially relevant to discern the defect chemistry of ceria. Normally, this mode should not be observed by Raman Spectroscopy; however, the presence of some defects can involve relaxation of the selection rules. In particular, this band has been indexed to oxygen vacancies (Ov) in the CeO_2 lattice [59] and, in ceria-doped systems, could be considered as an evidence for the solid solution formation [49]. Indeed if Mn^{n+} substitutes Ce^{4+}, oxygen defects should be created to balance the charges. Thus, Raman spectra could confirm the preliminary conclusions extracted from XRD data about the possible existence of MnO_2-CeO_2 solid solution.

It is interesting to compare the intensity of the band centered at 600 cm^{-1} for $RhCe_{40}Mn_{10}Al$ and $RhCe_{20}Mn_{30}Al$ samples. Despite the interference of the MnO_2 band the intensity of the Ov band is seems to be higher for $RhCe_{20}Mn_{30}Al$ than for $RhCe_{40}Mn_{10}Al$ (zoom in Fig. 3). This could suggest either greater concentration of oxygen vacancies for $RhCe_{20}Mn_{30}Al$. This Ov band is also influenced by the ceria particle size and generally its intensity grows up when ceria size

decreases [60] which correlates fairly well with the Scherrer calculations. Also this increase could be related with the high existence of Ce^{3+} ions [56]. The calculation of the area ratio of the oxygen vacancies band and the F2g signal (Ov/F2g) is well accepted as approach to evaluate ceria oxygen vacancies concentration [61-62]. However for $RhCe_{20}Mn_{30}Al$ and RhCe40Mn10Al samples the Ov band overlaps with the MnO_2 band. After a deconvolution process the Ov/F2g area ratio was obtained (table 1). $RhCe_{20}Mn_{30}Al$ seems to exhibit larger concentration of oxygen vacancies than the $RhCe_{40}Mn_{10}Al$ catalysts, which is an advantageous feature given the role played by these defects in oxidation reactions [33,63].

The Raman spectra profiles are different for $RhCe_{10}Mn_{40}Al$ and $RhMn_{50}Al$ catalysts (Fig. 3). The characteristics Raman bands of CeO_2 disappear and those of manganese oxides become evident. Such phenomenon has been previously observed and attributed to the segregation of Mn oxides [64]. Because Mn atoms in the Mn dioxides are always 6-fold coordinated, the Raman bands of MnO_2 materials depend on the MnO_6 octahedral environment (e.g edge/corner-sharing) interaction with water/cations in the tunnels or layers of MnO_2 materials. The Raman spectra for $RhCe_{10}Mn_{40}Al$ and $RhMn_{50}Al$ solids are in good agreement with both the number and the positions of the bands of MnOx species reported for other authors [65]. The observed Raman shifts in the 500-700 cm^{-1} and 200-500 cm^{-1} regions have been assigned to the M-O stretching of MnO_6 octahedral and the Mn-O-Mn bending vibration in the MnO_2 octahedral lattice, respectively [66]. In the Mn-O stretching range, the two sharp bands at high wavenumbers (581 cm^{-1} and 631 cm^{-1}) are indicative of a well-developed tetragonal structure with an interstitial space consisting of 2x2 tunnels, and are assigned to the Ag mode [67]. The other Raman bands at 297, 392, 470 and 509 cm^{-1} for $RhCe_{10}Mn_{40}Al$ and $RhMn_{50}Al$ are related to MnO_2 structure. Somehow this MnO_2 segregation correlates well with the manganese oxide crystalline phases detected trough out the XRD in the samples with the highest MnO_2/CeO_2 ratio.

3.3 Specific surface area and porosity measurements

The nitrogen adsorption-desorption isotherms for all the samples are quite similar (Fig. 4). They indicate the presence of a mesoporous structure (IV type isotherm with H2 hysteresis loop) with complex and heterogeneous size pores. The loop closes at P/P0 circa 0.4 indicating mesoporosity but probably due to pores that are generated by the spaces between the

particles [42]. Table 2 summarizes the textural properties of powder catalysts obtained from the N_2 adsorption–desorption isotherms. A decrease in surface area and pore volume are observed simultaneously with the increase in the MnO_2/CeO_2 weight ratio. The collapse of the textural properties of the primary Al_2O_3 support (with specific surface area of circa 200 m^2/g) is more evident for manganese contents higher than 30 wt.%. This can be related to the segregation of Mn^{n+} oxides (MnO_2 and/or Mn_2O_3) blocking the support porosity.

3.4 Redox properties: H_2-TPR analysis

Fig. 5 shows the H_2-TPR profiles obtained for the synthesized solids. $RhCe_{50}Al$ catalyst presents three main reduction peaks centered at 140°C, 174°C and 277°C. These peaks must be assigned to the reduction of rhodium and cerium species, since alumina support does not show any hydrogen consumption until 1000°C. Usually, ceria presents two broad reduction processes, one due to surface Ce^{4+} species at about 400°C [68], and the other one to bulk CeO_2 to Ce_2O_3 reduction at temperatures higher than 700°C [69]. Moreover rhodium reduction proceeds at much lower temperatures. Ojeda *et al*. [70] reported that Rh/Al_2O_3 catalysts present a broad reduction peak at around 142°C due to the reduction of Rh_2O_3 to metallic Rh. This temperature agrees with the one of the first reduction process of our sample. From here, and taking into account the well-known ability of noble metal oxides to easy the reduction of other surface metal oxide species in intimate contact by hydrogen spill-over processes [71], we can ascribe the three observed reduction peaks to the reduction of both Rh_2O_3 and surface Ce^{4+} in different interaction degree, ranging from free Rh_2O_3 species (140°C), Rh_2O_3-Ce^{+4} in close contact (174°C), and free surface ceria (277°C).

For $RhMn_{50}Al$ a narrow reduction process centered at around 254°C is detected. Several small maxima are discernible which probably indicates the overlapping of different reduction processes. The existence of different maxima could be related with the reduction processes of the different manganese oxides detected by XRD (Fig. 1). Besides this, the reduction of rhodium and manganese species overlaps, which imply that rhodium reduction is in fact, shifted to higher temperatures with respect to isolated Rh_2O_3 in $RhCe_{50}Al$. It has been described that the reduction of manganese supported alumina samples are generally described to proceed by two step reduction profiles in the 320-350°C and 400-500°C temperature ranges, due to the

sequential $MnO_2/Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$ reduction [72-73]. The deeper reduction from MnO to Mn(0) is not produced even in contact with rhodium [73]. The observation in the RhMn$_{50}$Al sample of a unique reduction process at 254°C suggests a close and different contact between rhodium and manganese species with respect to the obtained for rhodium and cerium species in RhCe$_{50}$Al. Similarly that in the case of the reduction of surface ceria in the RhCe$_{50}$Al catalyst, rhodium oxide favors the reduction of manganese oxides by spill-over resulting in a one-step reduction process but at higher temperatures.

The TPR profiles of the catalysts containing Rh, Mn and Ce can be explained on the basis of that explained for RhCe$_{50}$Al and RhMn$_{50}$Al. When increasing the Mn-to-Ce ratio, the individual reduction processes of free Rh_2O_3 and free surface Ceria shift to higher temperatures and diminish in intensity until they become undistinguishable, being observable an only broad peak due to the combined reduction of manganese, cerium and rhodium species. A similar behavior have been described early for Rh doped manganese alumina [73] and Ce-Mn mixed oxides [72,74-75]. The TPRs shown in Fig. 5 suggest that manganese presence changes the interaction among all reducible species (Mn, Rh and Ce), inducing a unique reduction process displaced at higher temperatures with the increase of manganese concentration. The Mn species segregation observed by XRD could promote this displacement at higher temperatures. In opposite way, the formation of a Mn-Ce solid solution at low manganese-to-ceria ratio facilitates the reducibility of the species at lower temperature.

The experimental hydrogen consumption per gram of sample and the reducibility percentage (RP) of the samples obtained by comparing the experimentally consumption with the theoretical one are presented in Table 3. For the RP calculation we have assumed that all cerium, rhodium and manganese species are in the form of Ce^4, Rh^{4+} and Mn^{4+} ones, and they are reduced to Ce^{3+}, Rh^0 and Mn^{2+}, respectively. High RP values are obtained in all cases, which evidences that the presence of rhodium favors the reducibility of the samples. Besides this, RP increases with the manganese addition to the ceria, obtaining a maximum value for the RhCe$_{20}$Mn$_{30}$Al sample, very close to the total reduction one. Again, this can be related with the Mn-Ce solid formation and the better Rh-Mn-Ce contact that increase the oxygen vacancies (Ov), which favors the reducibility of the sample. The decrease in the RP values observed for the samples with higher manganese-to-cerium ratio is probably due to the segregation of

manganese oxides with manganese oxidation state lower than 4+ ($K_2Mn_4O_8$ and α-Mn_2O_3) detected in such samples, which underestimates the calculated RP.

3.5 HRTEM microscopy of reduced samples

Fig. 6 shows several HRTEM images of $RhMn_{50}Al$ sample after reduction at 400°C. The reduction protocol was similar to the one used to reduce the catalysts before the catalytic reaction. Simultaneously a characteristic electron diffraction pattern is also shown in Fig. 6b. In this case the rings observed are due to the typical reflection of MnO. The presence of this oxide reinforces the idea of the reduction of Mn^{4+} to Mn^{2+} after reduction postulated by TPR analysis. However the analysis of HRTEM images (Fig. 6c) reveals *d*-interplanar spacing of 0.5 nm which is consistent with Mn_3O_4 phase. Therefore both MnO and Mn_3O_4 phases coexist after reduction of $RhMn_{50}Al$. This indicates that part of Mn^{4+} is partially reduced to $Mn^{2.5+}$ (Mn^{2+} and Mn^{3+}). The spherical nanoparticles observed of MnOx have an average size of approx. 50 nm. Simultaneously smaller particles of Rh are also detected. These particles are better observed in Fig. 6d. From here the Rh particles size are between 1.5-2 nm. In good agreement, it has been described that MnO_2 lead to suppression of migration of noble metal atoms, decreasing that way the rate of growth of metallic particles [76] and favoring their surface distribution.

Similar HRTEM images were observed for the reduced $RhCe_{40}Mn_{10}Al$ and $RhCe_{20}Mn_{30}Al$ samples. For comparative purpose only the HRTEM micrographs for $RhCe_{20}Mn_{30}Al$ are shown in Fig. 7. The characteristic electron diffraction pattern is also included in Fig. 7b. In this case the rings observed are characteristic of the cubic fluorite structure of mixed oxide Ce-Mn-O. Also some minority reflections of MnO are also detected. The HRTEM images clearly display nanoparticles with the average particle sizes of 5-6 nm, which are in close agreement with the XRD result. The observed lower particle size of $RhCe_{20}Mn_{30}Al$ sample than that of $RhMn_{50}Al$ is due to the highly dispersion of Ce-Mn-O nanoparticles over the alumina surface probably motivated by the solid solution formation. Further the images clearly show the well-crystallized (111) lattice plane with a *d*-spacing of 0.3 nm (Fig. 7c), which confirms the fluorite type of the CeO_2 crystal [77]. Similar *d*-spacing were observed for reduced $RhCe_{50}Al$ sample. Therefore the HRTEM analysis for $RhCe_{20}Mn_{30}Al$ confirms the existence of a surface layer of CeO_2 (as Ce-M-O solid solution) on the alumina support, which is strongly supported by XRD results. Additionally

smaller Rh particles are observed in Fig. 6c. These particles are better observed as dark spots in the white areas of the image. Its size is less than 2 nm. These important results confirm the high Rh dispersion and the lower crystalline domain of Rh particles suggested by XRD results. In this case the metal support interaction seems to play a decisive role in the stabilizing the metallic dispersion.

3.6 Thermogravimetric analysis

The TGA-DTG curves in synthetic air of the studied catalysts are shown in Fig. 8, the results being summarized in Table 4. The sample without manganese (RhCe$_{50}$Al) presents an only process of weight loss (1.3%) at 61°C due to desorption of adsorbed water. For the samples with manganese in their composition, several additional weight loss processes are detected at higher temperatures. According to the described thermal behavior of manganese oxides in the literature [78-80] and the well-known ability of these materials to adsorb water [81], the first weight loss observed below 100°C is due to the removal of physisorbed water, meanwhile those observed in the 100-400°C range are produced from the desorption of chemisorbed water, namely, interlayer water and OH-water [81]. The number of processes in this temperature range, the maximum in temperature of the process, and the total amount of water released increase with the amount of manganese in the sample. These processes are then related with the desorption of "structural water" from the catalyst (table 4), and must be associated with the presence of protons connected to cation vacancies; and Mn(III) ions in the structure. This observation matches with the XRD and TPR results, and reinforces the idea of the segregation of different manganese oxides at high manganese-to-cerium ratios. In fact, for RhCe$_{40}$Mn$_{10}$Al sample, any chemisorbed water desorption process is detected, probably confirming the formation of a Ce-Mn solid solution.

At higher temperatures, two weight loss processes occur, one in the 550-800°C range and the second at temperatures higher than 950°C. These processes are well described in the literature and are due to the oxygen loss associated to the MnO$_2$ to Mn$_2$O$_3$ and Mn$_2$O$_3$ to Mn$_3$O$_4$ phase transformations, respectively [82]. As in the case of chemically bound water released processes, the temperature at which these phase transformation proceed shifts to high values with the

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increase in the amount of manganese in the material, indicating a higher thermal stability of the manganese oxide (Table 4).

3.7 Catalytic test: preferential oxidation of CO in presence of H_2 (PROX)

The catalytic activity of the synthesized materials for CO oxidation, their selectivity to CO_2 and conversion of O_2 as a function of the reaction temperature are shown in Fig.9. Methane was not detected in any case, a clear indication that undesirable CO or CO_2 methanation reactions are absent. Accordingly, the CO conversion in the low temperature window (130–200°C) increases with the ceria content. The best CO conversion is shown by the manganese-free solid, $RhCe_{50}Al$ (around 60% at 150 °C). However, this solid is poorly selective to CO_2 formation (less than 40% at 150°C). In fact, a full oxygen conversion is achieved in all the temperature range studied, indicating that it is very active in H_2 oxidation reaction. This can be understood taking into account the lower enthalpy of the hydrogen oxidation reaction with respect to CO one (-242 versus -283 KJ mol^{-1} respectively [83]). In any case, due to the use of an O_2 concentration above the stoichiometric for the CO oxidation, the selectivity values are not very high, since an excess of O_2 molecules able to react with H_2 exits [84].

The catalytic behavior of the catalysts is clearly dependent on the MnO_2/CeO_2 ratio. The increment of the MnO_2/CeO_2 ratio dramatically decreases the oxidation capabilities of the catalyst at low temperature, decreasing the CO, O_2 and H_2 conversions, but resulting in a more selective CO oxidation solid. These results are in agreement with the characterization results, in particular with the reducibility of the samples, in such a way that lower the temperature of reduction, higher the total oxidation capabilities of the solid at lower temperatures. The increment in the selectivity of the CO oxidation with the increase in manganese concentration must be related with the intimate contact of ruthenium with the reducible species of the support, promoted by the manganese presence. It is also observed that high RP values are obtained in all cases, which evidences that the presence of rhodium and manganese favors the reducibility of the samples. Besides this, RP values increase with the manganese addition to the ceria. Therefore, in $Rh/MnO_2–CeO_2/Al_2O_3$ catalysts the enhanced catalytic behavior observed at lower temperatures is related to a better redox and also to the better structural and textural properties of the solids, promoted by the formation of the MnO_2-CeO_2 solid solution.

Conversely, at high manganese-to-ceria ratios, the detected MnO_x phase segregation decreases the catalytic behavior towards CO oxidation in the low temperature window.

The increment in temperature drives to an increment in the CO conversion, reaching a maximum in the 200-240°C range, where full oxygen conversion is also reached. Again, the support nature determines the maximum CO conversion achieved. All catalysts arrive to the thermodynamic CO conversion except $RhCe_{40}Mn_{10}Al$ one which only converts around 70% of the initial CO introduced. Conversely, at lower temperature the high activity and selectivity towards CO oxidation can be achieved when manganese and ceria forms a solid solution.

At temperatures higher than 220°C, a decrease in the CO conversion is detected in all manganese-contained samples. This decrease is due to the concurrence of the R-WGS which is favored at these temperatures [85] increasing the concentration of CO at expenses of CO_2 and H_2. The loss in CO conversion is different for all catalyst, being maximum for $RhCe_{40}Mn_{10}Al$ and almost inexistent for the one without manganese, $RhCe_{50}Al$. This behavior suggests that the R-WGS occurrence is seems to be more promoted by the manganese presence at higher temperatures. In fact the decrease in CO_2 selectivity is more pronounced in these solids (Fig. 9c) at temperature range of 130-200°C, reaching the same constant value (circa 50%) for all catalysts in the 200-240°C region, except $RhCe_{40}Mn_{10}Al$, once full oxygen conversion is achieved and then decreases at higher temperatures, where R-WGS takes place. For RhCe50Al the CO_2 selectivity remains always in lower values in the whole range of temperature. This lower CO_2 selectivity has been also related to that the rate of hydrogen oxidation exceeds that of carbon monoxide oxidation at higher temperatures [12]. In this case the hydrogen oxidation is seems to be more promoted by the Ce presence than Mn since for $RhCe_{50}Al$ the O_2 conversion is always 100%. Similar behavior has been described for cryptomelane-type MnO_2 catalysts [44]. In that case, the decrease of selectivity with temperature was explained because of the higher activation energy of the H_2 oxidation compared to that of CO. The constant value attained in the 200-240°C interval is due to the arrival to the thermodynamic CO conversion, and the total consumption of oxygen. In fact, taken into account the λ value used in our experiments (λ= $2x[O_2]_{in}/[CO]_{in}$ = 2, that means that the amount of oxygen in stream is twice the stoichiometric amount needed to oxidize all the CO supplied $[CO]_{in}=[O_2]_{in}$), and Eqs.1, 2 and 3, when oxygen

conversion is 100%, the calculated CO_2 selectivity must be half of the measured CO conversion, having the fixed maximum observed of 50% for all catalysts.

Therefore the synergic effect of Mn and Ce presence promoting the catalytic behavior is better observed at lower temperatures when selectivity towards CO oxidation is enhanced. In opposite way at higher temperatures the presence of Mn favored the Reverse Water Gas Shift reaction and the catalyst supported only on Ce promoted the H_2 oxidation in all range of studied temperatures. The synergistic effect between cations in a mixed-oxide has been extensively discussed in many publications [87-88]. It is well known that they can work in a cooperative way catalysing different steps of a chemical process. Also the mixed-oxide can terminate with multiple surface functionalities and expose cations in multiple oxidation states. Thanks to these interesting features the Mn-Ce oxides have been used as catalysts in different interesting reaction as catalytic oxidation and reaction of NOx among others [88].The cooperative work between Mn and Ce is promoted when a solid solution is obtained. In other way when the segregation of Mn species appears this synergetic effect decreased. In fact the catalytic behavior was different in samples $RhCe_{10}Mn_{40}Al$ and $RhMn_{50}Al$ in comparison with $RhCe_{40}Mn_{10}Al$ and $RhCe_{20}Mn_{30}Al$ probably due to the presence of Rh-Mn-Ce species and most precisely Mn-Ce forming a solid solution. Currently the synergic effect of the Rh-Mn-Ce in the catalytic behavior of Rh/MnO_2-CeO_2/Al_2O_3 catalysts in increasing the CO adsorption or the oxygen activation is under study. It will be published elsewhere.

Conclusions

In this work the preparation of Rh/MnO_2-CeO_2/Al_2O_3 catalysts was carried out by using wet impregnation method. The prepared solid were tested in CO-PrOx reaction. The results obtained from characterization data demonstrated that the formation of MnO_2-CeO_2 solid solution can be achieved at low MnO_2/CeO_2 ratios. In this case, the intimate Rh-Mn-Ce contact promoted the redox, structural and textural properties of the samples. On the other hand, the segregation of Mn species was observed at high ratios. In opposite way at higher temperatures the presence of Mn favored the Reverse Water Gas Shift reaction and the catalyst supported only on Ce promoted the H_2 oxidation in all range of studied temperatures.

Although these catalysts do not show an optimal performance for CO-PrOx reaction, the enhanced physicochemical properties promoted by the simultaneous presence of Rh, Mn and Ce favored the catalytic activity and selectivity of the catalysts at lower temperatures, producing interesting catalysts for this reaction. The synthesis method employed promoted the Mn-Ce solid solutions formation at low MnO_2/CeO_2 molar ratios, avoiding the Mn oxides segregation. This study can be taken as a starting point to obtain different active catalysts supported on $MnO_2\text{-}CeO_2/Al_2O_3$ through the optimization of the metal-support interaction and the decrease of the Mn segregation.

Acknowledgments

Figures labels

Fig.1. XRD patterns for the synthesized materials. ω: CeO_2, β: MnO_2, ε: $K_2Mn_4O_8$, α: Mn_2O_3, X: γ-Al_2O_3, $\blacksquare$$KNO_3$.

Fig. 2. Lattice cubic parameters as a function of the concentration of CeO_2

Fig.3. Raman spectra for the synthesized materials. ω: CeO_2, β: MnO_2

Fig.4. N_2 absorption/desorption isothermal plot for the synthesized materials

Fig 5. H_2-TPR profiles for the synthesized materials

Fig. 6. HRTEM images and electron diffraction pattern for $RhMn_{50}Al$

Fig. 7. HRTEM images and electron diffraction pattern for $RhCe_{20}Mn_{30}Al$

Fig.8. (A) TGA, (B) DTG curves for the synthesized materials in synthetic air

Fig. 9. (A) CO conversion, (B) O_2 conversion and (C) CO_2 selectivity with the reaction temperature for the preferential oxidation of CO in presence of hydrogen over the powder synthesized materials.

Tables

Table 1. CeO_2 crystallite size and lattice parameter and Ov/F2g area ratio

Table 2. Textural properties for the synthesized materials

Table 3. H_2-TPR results: Experimental hydrogen consumption and Reducibility percentage (RP) of the samples

Table 4. Temperature (in ºC) and weight loss (in parenthesis, %) of the different process from TG-DTG experiments

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