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## **LOW TEMPERATURE CO OXIDATION**

**O.H. Laguna<sup>a</sup>, L.F. Bobadilla<sup>b</sup>, W.Y. Hernández<sup>c</sup>, M.A. Centeno<sup>a,\*</sup>**

a) Instituto de Ciencia de Materiales de Sevilla. Centro mixto CSIC-Universidad de Sevilla. Avda Americo Vespucio 49. 41092 Sevilla (Spain)

Email: [centeno@icmse.csic.es](mailto:centeno@icmse.csic.es)

b) Institute of Chemical Research of Catalonia. Avda. Països Catalans, 16. 43007 Tarragona (Spain)

c) Department of Inorganic and Physical Chemistry. Ghent University. Krijgslaan 281, S3, 9000 Ghent (Belgium)

### **Abstract**

Catalytic low-temperature abatement of carbon monoxide becomes essential in environmental pollution control. CO Oxidation, CO Preferential Oxidation (PROX) and Water Gas Shift (WGS) reaction are the conventional technologies used to remove carbon monoxide at low temperature. Perovskite-type oxides have been extensively studied in the last years as catalysts for these reactions due to their high activity and catalytic stability. This chapter describes the state-of-the-art of using perovskite-based catalysts of general formula  $ABO_3$  in these reactions. Key factors such as the type and nature of A and B ions or the formation of oxygen vacancies or interstitials by doping are discussed in the light of the reaction mechanism in each case.

**Keywords:** Perovskite-type oxides; CO abatement, CO oxidation, PROX, WGS reaction; Redox activity; Intrafacial and suprafacial reactions; Oxygen vacancies

## 1. Overview

Catalytic oxidation of carbon monoxide at low temperature remains as an intense and important research topic at present considering its impact on environmental, industrial and academic-related studies [1-3]. The interest of CO oxidation deals with the negative influence of such compound over the environment and its high toxicity for the human and animal life. On the other hand, CO poisons the platinum-based catalysts of the proton exchange membrane fuel cells (PEMFC's), thus being required the abatement of CO from the hydrogen feeding flow at levels below 50 ppm before entering the PEMFC. Consequently, the CO oxidation is a key reaction with a wide range of applications such as trace CO removal in enclosed atmospheres, automotive emission control and H<sub>2</sub> clean-up by Water-Gas-Shift (WGS) and CO preferential oxidation (PROX) processes [4-7].

Perovskites (general formula ABO<sub>3</sub>) are mixed oxides with a well-reported good catalytic activity in CO oxidation reactions at low temperature. Despite that a detailed description of the structural features of perovskites has been presented in previous chapters, some relevant aspects will be briefly summarized below in order to allow an easy understanding of the close relationship between some structural aspects of these materials and their performances in CO oxidation reactions.

The catalytic properties of the perovskite-type oxides depend on aspects such as the morphology, the particle size, and the crystalline structure, among others. The chemical composition also results determinant, just as it is the nature of the A and B site ions and their valence state [8]. The A site ions, in contrast to B site ones, are generally proposed to be catalytically inactive although their nature influence the stability of the solid [9, 10].

Nevertheless, substitution of either or both A and B cations with other heterovalent cation or varying the oxygen content of the structure may enhance the catalytic activity due to the formation of structural defects such as cationic or anionic vacancies (e.g., oxygen vacancies) in the network and/or the modification in the oxidation state of the transition metal cation (B-site ion), generating defective or non-

stoichiometric oxides without altering the perovskite structure. However, it must be emphasized that there is a limit in the amount of defects that can be accommodated in the perovskite structure and a too large number of vacancies can provoke structural deformations. The non-stoichiometry in perovskites has been widely reviewed and discussed by different authors [11-15].

Recently, in a broad and detailed review about CO oxidation reaction over transition metal oxides, Royer and Duprez [7] remarked the wide number of papers where the effect of the transition metals nature settled in the B position on the perovskite oxides has been studied. In this sense, it is notable the attempt for correlating the catalytic activity for CO oxidation of  $\text{LaBO}_3$  perovskites ( $\text{B} = \text{V}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ , or  $\text{Ni}^{3+}$ ) prepared by complexation, with the local symmetry of the solid surface (Figure 1), proposed by Tascon et al. [16].

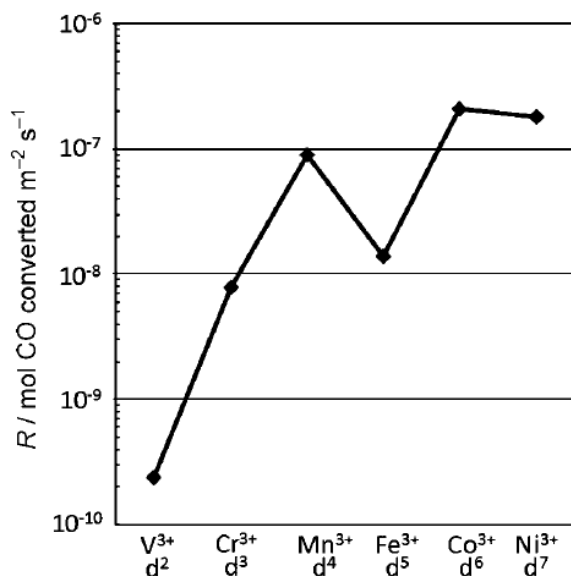


Figure 1. Specific CO oxidation rate obtained for a series of  $\text{LaBO}_3$  perovskite solids, plotted as a function of the number of d electrons of the metal ions (conditions of reaction: 0.66 % CO, 0.66 %  $\text{O}_2$ , balance He. Reaction temperature between 373 K and 673 K. (Reprinted from Tascon et al. [16], with permission from Springer)

The occurrence of structural and/or valence state modifications are related to the different mechanisms of charge compensation needed to maintain the electro-neutrality of the material's structure. These effects are proposed to enhance the oxidation catalytic activity of these types of systems either by facilitating oxygen mobility or by enhancing the redox activity of the  $\text{B}^{n+}$  cation [10, 17-19]. Typical examples of such structural

modifications on perovskite-related materials have been observed on strontium-substituted manganites and ferrites ( $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ , respectively). In the case of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ -type materials, the charge modification induced by the presence of  $\text{Sr}^{2+}$  in the lattice structure is normally balanced by the oxidation of  $\text{Mn}^{3+}$  into  $\text{Mn}^{4+}$  [20, 21]. Such situation is favored on substituted manganites since the formation of  $\text{Mn}^{4+}$  ions mitigates the static Jahn-Teller distortion of  $\text{Mn}^{3+}$  ions [22]. On the other hand, although the presence of  $\text{Fe}^{4+}$  ions have been also reported on  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ -type materials as a mechanism of charge compensation [19, 23], the formation of oxygen vacancies (on the surface and bulk structure) is the principal way to maintain the electroneutrality of lanthanum-substituted ferrites [23, 24]. The oxygen vacancies influence the ionic and electronic conductivity properties reported for these types of materials [25, 26]. Those structural modifications define the nature of the oxygen species participating in the catalysis at a given temperature reaction. Considering the features of catalysis over perovskite oxides, Voorhoeve et al. [17] introduced the concepts of intrafacial and suprafacial reactions, the former being performed by involving the lattice oxygen of the oxide and the second by means of adsorbed (and/or surface) oxygen species. The suprafacial mechanism prevails in the low temperature range, where the adsorption equilibrium of oxygen is thermodynamically favorable. By increasing the temperature, the surface concentration of adsorbed oxygen decreases, but the lattice oxygen becomes more mobile and so more available, bringing a gradual transition to the intrafacial mechanism. Nevertheless, the concept of suprafacial and intrafacial catalysis is rather empirical and mostly depends on the catalyst's composition and the nature of the B-site and B-substituting cations.

The literature revision presented as follow describes the utilization of perovskite-type materials as CO oxidation catalysts, doing special emphasis on the effect of the materials composition in their catalytic efficiency. Aspects such as the participating oxygen species (adsorbed oxygen and/or bulk-mobile  $\text{O}^{2-}$  species), surface redox properties and the CO affinity of the considered catalysts will be discussed.

## **2. Low-temperature CO oxidation reaction**

Recent excellent papers have reviewed the latest works focused in the applications of perovskites-type oxides for low-temperature CO oxidation [6, 7, 9, 27].

Lanthanum-based perovskites containing a transition metal in the B-site ( $\text{LaBO}_3$ , B = Co, Fe, Ni or Mn) have shown catalytic activities close to that of supported-noble metals for such reaction. Nevertheless, most of those perovskites exhibit their highest performances at relatively high temperatures, being their low-temperature activity still far from the well-disperse noble-metal-based catalysts [28]. Doping is usually adopted for preparing perovskites in order to boost their catalytic performance; however, depending on the nature of the dopant ion and its crystallographic position (A and/or B-site partial replacement) diverse catalytic efficiencies and bulk-surface-gas interactions can be achieved. More recently, the utilization of perovskite-type oxides as active supports for noble metals (such as Au and Pd) have gained interest as an alternative to improve the catalyst efficiency of these types of catalyst while maintaining a low noble metal loading [29-31]. This section considers three main families of perovskite-related materials as catalysts for the low-temperature CO oxidation reaction: un-doped  $\text{ABO}_3$ -type perovskites, A, B substituted materials and noble metal-perovskite hybrid materials.

## 2.1. $\text{LaBO}_3$ -type perovskites

Lanthanum-undoped perovskites are not the most frequently used catalysts for CO oxidation reaction since their catalytic performance is not good enough at low temperatures. Nevertheless, the study of these types of materials represents a good opportunity to differentiate just the effect of the nature of the B-site ion in the catalytic activity and structural properties of the mixed oxide.

It has been generally accepted that the catalytic activity of  $\text{LaBO}_3$  catalysts (B = first-row transition element) is related to its defect nature and density, oxygen adspecies, and reducibility [9]. Among the lanthanum-based perovskites, Mn, Co, and Fe-containing structures has been reported as the most active and promising catalysts for the CO oxidation reaction [32, 33]. The  $\text{LaCoO}_3$  solid has been extensively studied being proved as catalysts for such catalytic process, obtaining high performances [9, 34, 35]. For these types of catalysts, it is well accepted that the oxidation reaction proceeds according to the suprafacial mechanism: CO first reacts with oxygen adspecies to give  $\text{CO}_2$ , and  $\text{O}_2$  molecules are activated to be active oxygen adspecies by a  $\text{B}^{(n+1)+} \Leftrightarrow \text{B}^{n+}$

redox process [35]. Thus, a high redox activity of the B-site ion will facilitate the activation and stabilization of surface oxygen species (denoted as  $\alpha\text{-O}_2$  from TPD- $\text{O}_2$  measurements) during the reaction. Levasseur et al. [36] studied and compared the reducibility of  $\text{LaMnO}_3$ ,  $\text{LaCoO}_3$  and  $\text{LaFeO}_3$  perovskites synthesized by reactive grinding. The  $\text{H}_2$ -TPR profiles showed that, on  $\text{LaCoO}_3$  and  $\text{LaFeO}_3$  materials,  $\text{B}^{3+}$ -site ions were able to be totally reduced, up to the metallic state ( $\text{M}^0$ ), while the reducibility of Mn in  $\text{LaMnO}_3$  material stops at the  $\text{Mn}^{2+}$  state. For all the analyzed materials, the first step of reduction ( $\text{B}^{n+}$  to  $\text{B}^{2+}$ ) occurs at temperatures below 500 °C (Figure 2). Concerning the  $\text{LaMnO}_3$  solid, the presence of a low temperature reduction peak (as a shoulder) and a higher  $\text{H}_2$  consumption above 0.5 mol of  $\text{H}_2$  per B atom, were clear evidences of the presence of  $\text{Mn}^{4+}$  cations. Similar results were reported by Liu et al. [35] on  $\text{LaMnO}_3$  and  $\text{LaCoO}_3$  perovskites with a typical hollow spherical morphology.

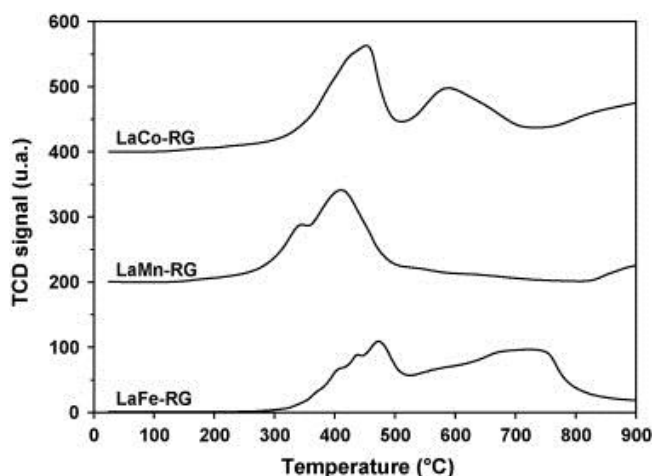


Figure 2.  $\text{H}_2$ -TPR profiles of  $\text{LaBO}_3$  perovskites (Reprinted from Levasseur et al. [36], with permission from Elsevier)

From XPS analyses, the coexistence of  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  species was evidenced in  $\text{LaMnO}_3$  material, while the  $\text{LaCoO}_3$  one showed the presence of  $\text{Co}^{3+}$  and  $\text{Co}^{2+}$  at the same time. Additionally, these authors established a higher  $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$  molar ratio on  $\text{LaCoO}_3$  perovskite than that observed for the  $\text{LaMnO}_3$  one. This phenomenon, observed at the surface of the material, along to improve the low-temperature reducibility of  $\text{LaCoO}_3$  material, where the catalyst's properties claimed to be responsible of the remarkable catalytic performance of the cobalt-based perovskite for the CO oxidation reaction. Other authors have also remarked the importance of the presence of  $\text{Co}^{3+}$  species as active sites for the adsorption of CO [37-39]. For instance, by using DRIFT spectroscopy, Natile et al. [37] showed that the reactivity of  $\text{LaCoO}_3$  powders respect to

carbon monoxide occurs through the Lewis acidic sites distributed on the surface of the sample, that is,  $\text{Co}^{3+}$  species, while oxygen is preferably adsorbed as molecular  $\text{O}_2^-$  species on  $\text{Co}^{2+}$  ions. This behaviour can also explain the improved capacity of cobaltites-type perovskites as CO oxidation catalysts compared with manganite and ferrite ones.

$\text{LaFeO}_3$  perovskites have also been reported as catalysts for the CO oxidation reaction [40, 41]. Although their catalytic performance at low temperatures was not as good as those reported for  $\text{LaCoO}_3$  and  $\text{LaMnO}_3$  catalysts, some improvements have been obtained by modifying their textural and morphological properties through different synthetic routes. Using a nanocasting strategy with mesoporous silica (KIT-6) and  $\text{SiO}_2$  nanospheres as hard template, Deng and coworkers [40] prepared wormhole-like mesoporous  $\text{LaFeO}_3$  with a high surface area (up to  $138 \text{ m}^2/\text{g}$ ). The catalytic activity of such material for the CO and toluene oxidation reactions was improved, compared with that of the bulk material. In fact, the mesoporous material showed a significant increase in the surface  $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$  molar ratio (3.42) in comparison to that of the  $\text{LaFeO}_3$ -bulk (1.07) as well as a high concentration of  $\text{Fe}^{4+}$  species. Those material's features along with a strong redox capability of the perovskite guarantees the occurrence of the suprafacial mechanism where the CO reacts with the oxygen adspecies, while gas phase oxygen is activated by the  $\text{Fe}^{4+}/\text{Fe}^{3+}$  redox cycle.

On the other hand, by using a non-aqueous preparation route, Yang and coworkers [41] reported the synthesis of a nanocrystalline  $\text{LaFeO}_3$  perovskite. Improved oxygen mobility was observed in the nanostructured material by temperature-programmed oxygen isotopic exchange (TPOIE). During the oxidation of CO it was concluded that the higher mobility of oxygen on the surface or even the subsurface as well as a better surface  $\text{Fe}^{3+}$  redox capacity were favorable for the reaction. Actually, these authors have proposed that CO oxidation reaction on the nano- $\text{LaFeO}_3$  proceeds through a redox surface oxidation mechanism in which surface oxygen from the solid is consumed, rather than through a pure suprafacial mechanism.

## 2.2. $\text{La}_{1-x}\text{A}_x\text{B}_{1-y}\text{B}'_y\text{O}_{3\pm\delta}$ -type perovskites

The partial replacement of host A cations in  $\text{ABO}_3$  perovskite-type structures by foreign A ones having a different valence, induces several electronic and ionic defects in the bulk of these materials (e.g. generation of oxygen vacancies), affecting their catalytic properties. A similar scenario may be generated by means of the partial substitution of B-site ions, but mixing two different B-site components, being both catalytically active, can often produce a strong synergetic effect, observed in the catalytic oxidation capacity of the materials.

Among the substituted perovskites used as catalysts for the CO oxidation reaction, the La-based ones are the most popular systems reported in the literature [10, 17, 18, 42, 43]. In general, the partial replacement of  $\text{La}^{3+}$  with cations of other elements with lower oxidation states (such as  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$ ) increases the concentration of oxygen vacancies in the materials structure (favoring their oxygen adsorption/activation capacity) and/or favors the increment in the average oxidation state of the cation in position B (improving the redox properties). Both situations are beneficial for the low temperature CO oxidation activity of these types of catalytic systems. On the other hand, the partial replacement of the B-site ion by other redox-active transition metal ones was also reported as an efficient way to improve the CO oxidation capability of these types of materials [10, 44, 45]. Different B-site combinations have been explored by using the most active metal transition ions reported, i.e. Co, Mn, Fe. In general it is accepted that the presence of a second ionic transition metal facilitates the electronic transport during the catalytic redox cycle, which also enhances the material's reducibility. Besides, the combination of Co, Mn and Fe with Cu in the perovskite structure has shown a very strong influence on the catalytic oxidation properties of these materials [46, 47].

## 2.3. Noble metal-perovskite hybrid materials

As mentioned above, one of the principal aims of using perovskites-type oxides as oxidation catalysts is to avoid the use of expensive and low-thermally stable noble-metal supported catalysts (e.g.  $\text{Pt}/\text{Al}_2\text{O}_3$ ). Thus, by modification of the perovskite



composition using alkaline earth metal or metal transition cations (A and/or B substituted materials) and by improving their textural and defective properties during the synthesis process, it is possible to obtain perovskite-based catalysts as active as noble metal supported ones for the low-temperature CO oxidation reaction. Nevertheless, some authors have recently claimed the utilization of these types of mixed oxides as active supports for the deposition of gold nanoparticles, constituting a very efficient low-temperature CO oxidation catalyst [31, 48, 49]. It is well known that dispersed gold nanoparticles on active supports (such as TiO<sub>2</sub>, CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>) constitute a family of catalysts highly active in this reaction [50-52]. Besides the gold particle size, the choice of an adequate support plays a decisive role in the activation of the gas phase molecules during the oxidation reaction, as well as the stabilization of the gold-active species [51]. In this sense, considering that perovskite oxides exhibit good stability, highly anti-poisoning ability and high catalytic performance in the CO oxidation process, their using as supports for gold nanoparticles have been proved because it is an excellent way to obtain materials with enhanced catalytic activity and stability. Dai et al. [31, 48, 49] have studied the performance of these types of catalysts, focusing their attention on the effect of the perovskite composition and gold loading. In addition, these authors have also proposed the utilization of perovskite supports characterized by a three dimensional macroporous ordered structure (3DOM materials), as a way to improve the surface area of these types of materials, the presence of defects (as oxygen activating centers) and the diffusion of the gas molecules. In fact, for all the perovskites studied, i.e. LaMnO<sub>3</sub> [48], LaCoO<sub>3</sub> [49] and La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> [31], the utilization of 3DOM-structured materials showed a positive effect by itself on the CO oxidation reaction (Figure 3).

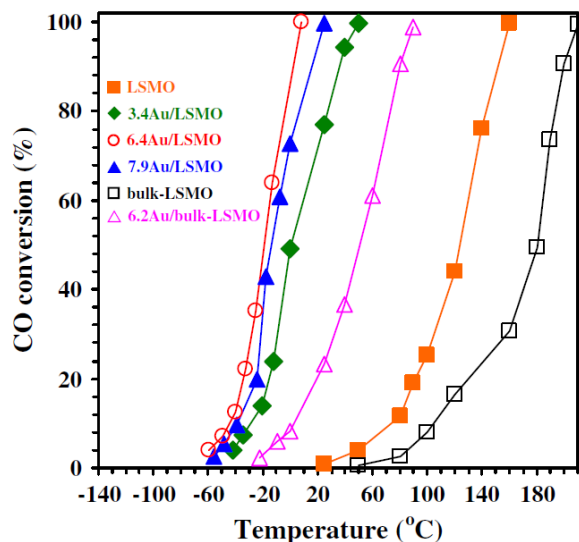


Figure 3. CO conversion as a function of temperature over the LSMO and xAu/LSMO catalysts (Reprinted from Dai et al. [31], with permission from Elsevier)

Therefore, the presence of gold in a relatively high loading (3 to 8 wt.%) strongly boosted the efficiency of the catalysts, even at the sub-ambient temperature range (see Table 1).

Table 1 Catalytic activity reported as  $T_{90\%}$  (temperature at which a 90% CO conversion is achieved) and surface-oxygen composition of several perovskite-related materials.

Catalyst	$T_{90\%}$ (°C)	$O_{ads}/O_{latt}$ molar ratio	Ref.
LaMnO <sub>3</sub> -bulk	259	0.87	[48]
LaMnO <sub>3</sub> -3DOM	179	1.08	
4.9Au/LaMnO <sub>3</sub> -3DOM	91	1.57	
LaCoO <sub>3</sub> -bulk	204	1.6	[49]
LaCoO <sub>3</sub> -3DOM	178	1.9	
6.2Au/LaCoO <sub>3</sub> -3DOM	102	2.1	[31]
La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> -bulk	200	1.02	
La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> -3DOM	152	1.27	
6.4Au/ La <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> -3DOM	3	2.43	

For all the catalysts studied by these authors, it was concluded that the high catalytic performance might be associated to the relatively high surface area, an improved  $O_{ads}$  concentration (measured by XPS analysis; table 1), their improved low-temperature reducibility, and the strong interaction between the gold nanoparticles and the perovskite-support (as established by H<sub>2</sub>-TPR measurements). Hence, the oxidation of CO proceeds via suprafacial mechanism where the presence of gold favors two main

catalytic aspects: i) improvement of the surface reduction of the B-site cation in the perovskite structure, promoting the generation of oxygen vacancies. These defects are able to activate the gas phase O<sub>2</sub> molecules to produce active oxygen species. ii) The addition of Au can significantly promote the adsorption of CO, enhancing the migration of chemisorbed CO to the Au-perovskite interface where the oxidation takes place with the active oxygen species.

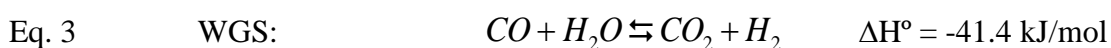
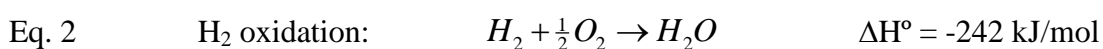
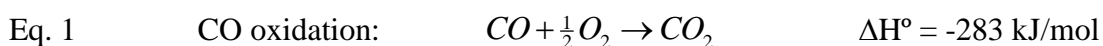
Noble-metal-promoted perovskites have also been synthesized and used as CO oxidation catalysts by considering a different approach; it is the incorporation of noble metal ions (such as Pd, Pt and Ru) in the perovskite structure [29, 53, 54]. Such synthetic approach was initially thought to prevent the sintering and losses of the metallic phase due to volatilization at high operating temperatures in three way converters, and to avoid reactions with the support that lead to catalyst deactivation [55]. Sigh et al. [29] established that the partial replacement of Ce by Pd in the structure of the BaCeO<sub>3</sub> perovskite promotes the catalytic oxidation of CO through the increased oxygen vacancy concentration, which facilitates oxygen ion transport and thus diffusion through the bulk to the surface. In that case, the presence of metallic palladium (generated by a reductive treatment of the perovskite) decreases the CO oxidation capacity of the catalyst due to the low accessibility of the metallic nanoparticle as well as its poor interaction with the CO molecule. The presence of Ru<sup>4+</sup> ions in the structure of La<sub>0.7</sub>Sr<sub>0.3</sub>Cr<sub>1-x</sub>Ru<sub>x</sub>O<sub>3</sub> perovskite resulted to be very effective for improving the CO oxidation capacity at low temperature [53]. Nevertheless, XPS characterization showed an important segregation of strontium and particularly ruthenium from the bulk to the surface in the solids with higher substitution degree. In this sense, the presence of dispersed Ru<sup>4+</sup> species stabilized as SrRuO<sub>3</sub> and RuO<sub>2</sub> oxides were concluded as the feasible phases present on the higher Ru-loaded materials. Finally, the concentration of such Ru<sup>4+</sup> species in the surface and its stability was established as the determining factor for the CO oxidation activity of these types of catalysts.

On the other hand, Gao et al. [54] reported an opposite behavior for Pt-doped BaTiO<sub>3</sub> and CaTiO<sub>3</sub> perovskites during the CO oxidation reaction. Through a reduction treatment of those catalysts, metallic platinum was produced and thus favored the interaction of CO with the catalyst surface. These results remark the importance of the

nature of the noble metal used as active place for the CO oxidation reaction, especially considering its role as CO adsorption/activation site.

### 3. H<sub>2</sub> purification-related CO oxidations: Water-Gas-Shift and PROX reactions

It is widely recognized the interest on developing a sustainable infrastructure for the approaching of H<sub>2</sub> as an energetic vector [56]. This purpose has motivated important efforts in many researches devoted to improve the production of H<sub>2</sub> and its transformation to electric energy using fuel cells [57, 58]. Among these devices, the polymer electrolyte membrane fuel cells (PEMFC) are very interesting because their high efficiency and low temperature operation (50 °C - 100 °C) [59]. However, as was mentioned above, the anode of the PEMFC's is commonly manufactured in Pt or Pt-Ru, being extremely sensitive to be deactivated by the irreversible adsorption of CO (< 50 ppm). Since H<sub>2</sub> is commonly produced by reforming reactions of any hydrogen-containing compounds (typically methane but also methanol, ethanol, and biomass, among others), a large proportion of CO (>10% v/v) always accompanies it, acting as poison and decreasing the lifetime of the fuel cells. For this reason, CO-cleaning-up processes are required in order to purify the H<sub>2</sub> flow used for feeding such PEMFC's. A first CO abatement process after the reforming unit is the WGS reaction that may be carried out in different units working at high and low temperature, reducing CO contents to 0.5-2%. Nevertheless, these CO levels are still above the allowed ones for feeding the PEMFC's, thus additional CO cleaning-up process is required. The one of choice is the preferential oxidation of CO (PROX) [57]. PROX reaction principally implies the CO oxidation (Eq. 1), but the presence of high contents of H<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> in the mixture of reaction may produce collateral reactions such as the oxidation of H<sub>2</sub> (Eq. 2), and the reverse water-gas-shift (R-WGS) (Eq. 3) [4, 28, 60]. Consequently, not only high active but also very selective catalysts are required.



Although perovskites have demonstrated a high activity in low temperature CO oxidation reactions, the number of papers focussed in these energetic and industrial applications, WGS and PROX reactions, are really scarce and their detailed revision, up to our knowledge, absent from the open literature.

### **3.1. Perovskites for the Water Gas Shift Reaction (WGS)**

For the WGS reaction, the temperature strongly influences the achieved CO conversion, since this is a reversible and exothermic reaction. In addition, the reaction rate is limited by kinetics at low temperatures thus, catalysts with high performance are necessary to provide the adequate activity [61, 62].

Commonly in the industry, the applying of the WGS reaction for the purification of hydrogen is carried out in two stages. The first one, generally achieved at temperatures around 300-500 °C, is considered as a high temperature process and for that reason named as high temperature water gas shift reaction (HT-WGS). The second stage, often know as low temperature water gas shift reaction (LT-WGS), is carried out at temperatures near to 150-250 °C. For the LT-WGS reaction, mainly Cu-Zn mixed oxides has been employed as catalysts. However, these materials are pyrophoric and usually require long and complex activation steps before using. Therefore, the development of a new generation of catalysts for the LT-WGS with high activity and stability is a current scientific and industrial challenge. Most of the present research in this topic is devoted to the structural and redox aspects of such desired catalysts, and the decisive role played by the oxygen vacancies of the solid has been highlighted [63, 64].

Considering the kinetic limitations of the WGS reaction, the development of catalysts for such process should deal with the requirement of generating active sites able to adsorb and activate the CO and H<sub>2</sub>O molecules, being particularly a retardant stage the activation of the last compound. In this sense, structured oxides like perovskites are ideal candidates for such reaction, due to its ability to stabilize structural vacancies leading to a high electronic conductivity and oxygen mobility. The presence of ionic vacancies directly influences the catalytic activity by favoring or disfavoring the adsorption of reactant from the gas phase [65]. In addition, perovskites exhibit a considerable thermal stability, superior than that of many metals oxides [66]. Despite

these interesting properties of perovskites, the use of these materials as WGS catalysts is relatively recent and limited. For that reason, although the scope of the present chapter is the application of perovskites on low temperature CO abatement reactions, the most relevant conclusions of those papers focused in the use of these materials not only in the LT-WGS reaction, but also in the HT-WGS reaction will be reviewed.

Maluf et al. [67] evaluated the catalytic performance of  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_4$  perovskites on the low temperature WGS reaction. They observed that all studied perovskites are active at 290 °C, and a promoter effect of Ca is described. They found that the partial substitution of La by Ca enhanced the stability of the perovskites and increased their reduction temperature. The calcium amount incorporation increased the oxygen vacancies population in the bulk, nor on the surface of the solids. As Merino et al. [66] reported, oxygen vacancies play an important role in oxidation reactions since they are responsible for the adsorption–desorption properties, easing the diffusion of lattice oxygen from the bulk to the surface [64]. Therefore, the different amount of surface and bulk oxygen vacancies formed by replacement of La by Ca influences the catalytic performances, decreasing the activation energy of the reaction, for samples with up to 15% of Ca. The same authors investigated the performance of  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  perovskites (where  $M = \text{Sr}, \text{Ca}$  or  $\text{Ce}$ ) prepared by co-precipitation. [68] The best catalytic activity of the cerium containing samples was explained by the higher surface area, the higher copper content on the surface and a higher stabilization of the  $\text{Cu}^{2+}$  oxidation state, favored by the cerium. Also, it is widely known that the catalytic activity of the perovskite oxides is related to the unusual oxidation states of the transition metal ions, the amount of non-stoichiometric oxygen, and the structural defects of the lattice. The increase in the copper oxidation state could facilitate the catalyst performance in a redox cycle, in which the copper is reduced, supplying the necessary oxygen for the oxidation reaction.

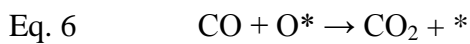
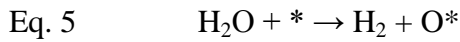
The  $\text{H}_2$  production via the WGS reaction was also studied by Su et al. [69, 70] over  $\text{La}_{(0.9-x)}\text{Ce}_x\text{FeO}_3$  perovskite-like catalysts, in the 450-600 °C temperature range and at atmospheric pressure. The catalysts were prepared by a low-temperature thermal decomposition method in order to obtain materials with large BET surface area and a high level of chemical homogeneity. They found that these catalysts exhibited higher activity at high temperatures compared to that of a commercial high temperature iron-

chromium catalyst. The LaFeO<sub>3</sub> perovskite structure and CeO<sub>2</sub> redox properties play an important role in enhancing the water-gas shift activity. Addition of a high Ce content leads to the formation of segregated phases of Fe<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and La<sub>0.25</sub>Ce<sub>0.75</sub>O<sub>1.9</sub> which inhibits the formation of the LaFeO<sub>3</sub> perovskite structure and decreases the catalyst activity. The same authors performed a kinetic study of the WGS reaction over a La<sub>0.7</sub>Ce<sub>0.2</sub>FeO<sub>3</sub> perovskite-like catalyst in the temperature range of 550-600 °C [70]. It was found a power-law rate expression (Eq. 4), which involved six variables and correlates with the experimental data with good accuracy:

$$\text{Eq. 4} \quad r = 10^{0.866} \exp\left(\frac{-85600}{RT}\right) P_{CO}^{0.73} P_{CO_2}^{-0.23} P_{H_2}^{-0.046} \left(1 - \frac{1}{K} \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}\right)$$

where, K is the equilibrium constant for the WGS reaction, r is the reaction rate, T is the temperature, R is the universal gas constant, and  $P_i$  is the partial pressure of gas component  $i$ . As expected, the presence of both reactants and products has an effect on the overall WGS reaction rates.

Among the possible reaction mechanism proposed in the literature, the regenerative mechanism is generally the most accepted to describe the WGS reaction, in which water molecules are adsorbed and dissociated on reduced sites to generate hydrogen while oxidizing the site (Eq. 5). Subsequently, CO is oxidized to CO<sub>2</sub> and reduces the oxidized site to complete the catalytic cycle (Eq. 6), where \* is a vacant oxygen site [71, 72].



Hence, oxygen vacancies and oxygen mobility play an important role in maintaining the high catalyst activity for the WGS reaction. Two types of oxygen are identified to take part in the adsorption-desorption of oxygen from the outermost layers of the ABO<sub>3</sub> perovskite structure, which form the 'active surface' of the material: low-temperature  $\alpha$ -oxygen desorbed in the temperature range of 300-600 °C, and high temperature  $\beta$ -oxygen desorbed at 600-900 °C. The  $\alpha$ -oxygen is accommodated in the oxygen vacancies formed by the partial substitution of A site cations by low valence

ions or even by vacancies and involves diffusion of oxygen ions through the lattice with the formation of neighboring high valence metal ions.  $\beta$ -oxygen is observed for both substituted and unsubstituted samples; the O diffusion inside the lattice is accompanied by the A and/or B ionic diffusion and, therefore, it is activated at higher temperatures than  $\alpha$ -oxygen [73]. It is likely that these  $\beta$ -oxygen species could take part in the WGS reaction to increase catalyst activity at high temperatures.

Besides the direct use of perovskites as catalysts for the WGS, these materials have been explored as noble metals support, obtaining highly active catalytic systems. Particularly, precious metals supported on  $\text{LaBO}_3$  perovskites have been recently described as very promising catalysts for the low temperature WGS. Jijil et al. [74] reported the use of platinum doped barium cerate as catalysts for WGS reaction. They found a maximum CO conversion at 350 °C and observed that the oxygen vacancies population of the system increase with the Pt substitution. Similar results were reported by Rajesh et al. [75] who investigated the doping of  $\text{BaCeO}_3$  perovskite with different amounts of Pt for the WGS reaction and they found that ionic Pt species are stabilized in lattice points of the  $\text{BaCeO}_3$  structure increasing the oxygen vacancies of the material as increasing the Pt incorporation.

From here,  $\text{BaCeO}_3$  was proposed to be an ideal perovskite lattice to stabilize ionic Pt, maintaining it not only active but also avoiding its sintering under WGS conditions. The same authors investigated the role of oxygen vacancies in WGS reaction on  $\text{BaCeO}_3$  perovskite co-doped with platinum and yttrium [76], concluding that the controlled addition of yttrium allows to tailor the oxygen vacancies concentration in the material, as a consequence of the Y(III) to Ce(IV) substitution. Structural and activity studies reveal that the compound with a 6% Y in its composition has the most symmetric B site coordination environment and exhibits the highest WGS activity (Figure 4). Hence, a dependence of the activity with the crystallographic characteristics of the perovskite more than on the concentration of oxygen vacancies is proposed. Symmetric coordination around B ions facilitates water adsorption and dissociation by lowering the energy barriers due to the creation of an isotropic environment. On the other hand, the oxygen vacancies act as water activation centers, favoring the dissociation of the water molecule and generating an oxide/hydroxide ion on the surface. This indicates an important role played by oxygen vacancies in WGS



reaction. Similar conclusion has been clearly demonstrated for Au/CeO<sub>2</sub> WGS catalysts [77], where the decisive role played by the oxygen vacancies in the water activation procedure has been evidenced.

Sekine et al. [78] investigated the WGS reaction at low temperature (300 °C) over Pt and Pd catalysts supported on several LaBO<sub>3</sub> (B = Cr, Mn, Fe, Co and Ni) perovskite oxides prepared using the Pechini method. They observed that perovskite oxides without active metal showed no activity for the WGS reaction while those loaded with Pt and Pd exhibited good WGS activity. Interaction between Pt or Pd and the support promotes the WGS reaction. They found that both Pt/LaCoO<sub>3</sub> and Pd/LaCoO<sub>3</sub> catalysts have high catalytic activity, although Pt/LaCoO<sub>3</sub> catalyst deactivated immediately, and Pd/LaCoO<sub>3</sub>, although initially less active, exhibited superior stability. The cause of deactivation of Pt/ LaCoO<sub>3</sub> was attributed to the reduction of Co and Pt cations.

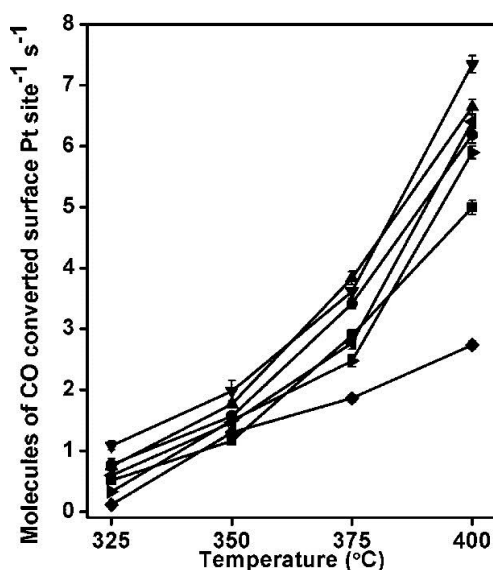


Figure 4. Specific activity of BaCe<sub>0.98-x</sub>Y<sub>x</sub>Pt<sub>0.02</sub>O<sub>3-δ</sub> under WGS conditions: (■)  $x = 0$ , (●)  $x = 0.02$ , (▲)  $x = 0.04$ , (▼)  $x = 0.06$ , (◄)  $x = 0.10$ , (►)  $x = 0.20$ , and (◆)  $x = 0.30$ . Reformate composition: 40.3% H<sub>2</sub>, 35.1% N<sub>2</sub>, 10.1% CO, and 14.5% CO<sub>2</sub> with a steam to CO ratio of 4.5 and GHSV of 5000 h<sup>-1</sup>. (Reprinted with permission from T. Rajesh et al. [76]. Copyright 2014 American Chemical Society)

Recently, Rajesh et al. [79] studied the oxidation state of Pt incorporated in perovskites LaBO<sub>3</sub> (B = Mn, Co, Fe) for WGS activity. They observed that Pt doped Mn-perovskite showed very poor activity likely attributed to the sintering of Pt particles

on the surface, while Pt doped Co and Fe perovskite catalysts showed almost 90% CO conversion above 300°C. XPS measurements indicate that Pt could be stabilized in ionic form in Co and Fe perovskites but not in LaMnO<sub>3</sub> one. This result suggests a possible key influence of the oxidation state of Pt as well as of the enhanced presence of oxygen vacancies in the doped samples, in the activity. It is possible that ionic Pt species in tandem with oxygen vacancies capable of acting as water adsorption and activation sites may enhance the WGS activity of the perovskite. In other study, the same authors synthesized Pt doped LaMnO<sub>3</sub> perovskites [80]. Characterization studies evidenced that a structure with an oxygen excess, as LaMnO<sub>3</sub>, presented a substantial resistance to B site doping with Pt. This behavior was different from other oxygen deficient perovskites, such as LaCoO<sub>3</sub> and LaFeO<sub>3</sub>, in which the lattice was able to stabilize the active species against sintering. In doped samples, a strong interaction of Pt species with a persistent amorphous phase prevents the sintering, enhancing the activity when compared with impregnated sample. The study revealed a possible mechanism in which only metallic Pt species were active, with the perovskite oxide playing a minimal role in the system due to the resistance to lattice incorporation. The authors concluded that crystalline PtO<sub>x</sub> species were not as active as Pt<sup>0</sup> for WGS reaction.

### **3.2. Perovskites for the preferential CO oxidation in the presence of H<sub>2</sub> (PROX)**

Only few reports are specifically devoted to the preferential oxidation of CO in presence of H<sub>2</sub> in the open literature. However, since this reaction is very close to the oxidation of CO in the absent of hydrogen, many of the principal observations extracted from the very popular and reviewed above studies dedicated to CO oxidation, may be adapted for studying the potential application of perovskites in the PROX reaction. In both cases, the key point is the contribution of the structure of defects of such networks. For instance Peña and Fierro [9] showed the comparison of the CO oxidation reaction carried out with O<sub>2</sub> or with N<sub>2</sub>O on BaTiO<sub>3</sub> solids. Differences in the activation energy of these reactions near the Curie temperature of the catalyst and a very slow reaction rate in the temperature range from 373 to 473 K were observed, being limited by the desorption of CO<sub>2</sub> under steady-state conditions. These features were considered for proposing that the CO oxidation proceeds via surface defects, confirming that the defects into the perovskite structures are crucial for their application in the oxidation of CO.

In the same review, in a section devoted to oxidation reactions over perovskites [9], there is an interesting summary of how the CO oxidation proceeds according to a suprafacial process where the band structure near the Fermi level seems to be important in the electronic transfer, being influenced by the temperature and the O<sub>2</sub> partial pressure. For LaBO<sub>3</sub> perovskites (being B = transition elements from V to Ni), the LaCoO<sub>3</sub> proved to be one of the most active and the LaCrO<sub>3</sub> among the least active for the CO oxidation. In this sense Tascon et al. [39] have proposed a mechanism for the CO oxidation on LaCoO<sub>3</sub>. Oxygen is adsorbed as molecular O<sub>2</sub><sup>-</sup> on Co<sup>2+</sup> and then is dissociated in atomic O<sup>-</sup>. On the other hand, CO adsorbs on surface oxide ions, producing labile species that interacts with adsorbed atomic oxygen for producing carbonate species which is then decomposed to afford adsorbed CO<sub>2</sub> and oxygen.

In other study about nonstoichiometric LaCuO<sub>3-δ</sub> (δ = 0.05-0.45) perovskites, it was highlighted how the concentration of oxygen vacancies can be gradually changed by controlled annealing at higher temperatures and oxygen pressures. Additionally, it was observed that catalytic activity in CO oxidation is largely controlled by the number of oxygen vacancies present in the crystal structure as has been confirmed in other works [81, 82]. It means that the ability for controlling the kind and concentration of defects into the structure of the perovskite oxides results relevant for the performance of such materials in oxidation processes. Modulation of the defective structure in perovskites may be carried out through the doping with different cations such in the case of doped Ln<sub>1-x</sub>Sr<sub>x</sub>NiO<sub>3</sub> (Ln = Pr, Sm, Eu) reported by Falcón et al. [83]. The catalytic activity evaluation of the different materials demonstrated that the doped solids were considerably more active than the undoped ones, being especially active those solids doped with Pr.

Considering many possible applications of perovskites where the defects in the structure are important, not only the creation but also the mobility of defects is relevant. This last subject has motivated studies on examining principally the oxygen mobility [84], because the application of perovskites as ion conductors has been approached in several fields [9, 81]. In the case of the preferential oxidation of CO, the oxygen mobility results determinant for the activation of the CO molecules and their transformation into CO<sub>2</sub>. Uberuaga et al. [84] studied the migration mechanisms of

interstitials and vacancies in perovskites with different chemical compositions ( $\text{SrTiO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ ,  $\text{LaAlO}_3$ ), varying the potential to simulate long time dynamics. They found that the migration mechanisms for the various interstitial and vacancy species are very similar regardless of the potential used of the chemistry of the perovskite, though the energy barriers associated to those mechanism are sensitive to both parameters. Additionally, oxygen and A cation interstitials (in a  $\text{ABO}_3$  structure) diffuse in a complex manner, exhibiting one- or two-dimensional diffusion mechanisms that are detected in the long-time simulations. The demonstration of the high oxygen mobility in these materials may agree with the required ability of a PROX catalyst of providing oxygen species from the structure where the concentration of  $\text{O}_2$  in the gas mixture of reaction is deficient. On the other hand, the high ionic mobility in perovskites may also contribute to the enhancement of the mass transport phenomena during the catalytic process, which is a relevant aspect for the scaling up of the PROX reaction and its linkage to a fuel processor.

The specific applying of perovskites in the PROX reaction has been proposed in some works such as that published by Maluf et al. [85] where  $\text{LaNiO}_3$ ,  $\text{La}_{0.95}\text{Ce}_{0.05}\text{NiO}_3$  and  $\text{La}_{0.90}\text{Ce}_{0.10}\text{NiO}_3$  have been synthesized by co-precipitation of the adequate amounts of La, Ce and Ni nitrates. The TPR results showed that reduction of these mixed oxides proceeds in three steps and, in the case of the solids with cerium, the reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  species occurred at lower temperatures by the enhancement of the oxygen mobility. Concerning the catalytic activity, none of the samples presented CO conversion at temperatures below 150 °C but the solids doped with Ce presented a better catalytic activity. However, comparing between these samples, the excess of Ce in the  $\text{La}_{0.90}\text{Ce}_{0.10}\text{NiO}_3$  reduced dramatically the interaction Ce–Ni by the promoted increment of defects, allowing the formation of segregated phases and reducing the ionic mobility. In this sense, an optimal concentration of defects for enhancing the CO oxidation abilities of the analyzed perovskites is suggested.

Gosavi et al. [86] studied the PROX reaction over platinum supported on lanthanum ferrite-ceria ( $\text{Pt/LaFeO}_3\text{-CeO}_2$ ) catalysts, modifying the loading of Pt (0.5, 1.0, 2.0 and 5.0 wt.%). The supports were synthesized using chitosan complex and, an additional  $\text{LaFeO}_3$  system was prepared by the sol-gel method in order to evaluate differences in the textural properties promoted by the synthesis procedures and their

influence in the catalytic activity. The using of chitosan complex allowed an improved crystallinity and homogeneity of the material, together with a higher porosity and open morphology. These properties resulted in a strong Pt-support interaction, producing a high catalytic performance of the materials, combining high CO conversion and selectivity to CO oxidation. In other work [87], the same authors have proposed a study where various oxides including perovskites with a kind of oxygen defective structure ( $\text{CeO}_2$ ,  $\text{CuLa}_2\text{-CeO}_2$ ,  $\text{La}_2\text{CuO}_4$ ), widely employed as superconductor, were used as supports for supporting 0.1 Pt wt.%. The obtained materials were tested in the cited catalytic reaction and the authors have observed that the  $\text{La}_2\text{CuO}_4$  solid presented a considerable CO conversion. Whereas, 0.1 wt.% Pt/ $\text{CuLaO}_2\text{-CeO}_2$  presented not only the highest CO conversion levels but also high selectivity. Although there was not a deep analysis on this manuscript and the applied characterization techniques were scarce, the highest catalytic performance of the 0.1 wt.% Pt/ $\text{CuLaO}_2\text{-CeO}_2$  was attributed to the enhancement of the WGS reaction at the interface of Pt-metal oxide besides the relatively higher oxidation activity of the metal oxides. Surely, the presence of defects in the structure promoted by the mixture  $\text{CuLaO}_2\text{-CeO}_2$  did allow the promotion of dispersion of Pt and the activation of the CO molecules due to the highly mobile oxygen species.

In other work presented by Magalhães et al. [88],  $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$  ( $x = 0, 0.05$  and  $0.1$ ) perovskite-type oxides were prepared, characterized and evaluated in the PROX reaction. For the synthesis of the materials, a citrate synthesis methodology was applied, favoring the formation of perovskites with rhombohedral structure. TPR studies demonstrated that the inclusion of Ce inhibited the formation of intermediates during the reduction process and generated modifications in the perovskite lattice. All the studied materials presented a similar catalytic performance where the maximum CO conversion (near to 100 %) has been achieved around 200 °C. Higher temperatures enhanced the hydrogen consumption by the probable side reactions (R-WGS and methanation). The  $\text{LaCoO}_3$  and  $\text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3$  solids exhibited a good stability during 48 h of continuous operation. Moreover, the influence of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  was a relevant aspect also considered by the authors, since these components are the main products of the reaction and it is important to verify their influence over the catalytic performance of the studied materials. For such analysis, the  $\text{LaCoO}_3$  catalyst was tested under constant temperature (180 °C) and space velocity ( $40,000 \text{ cm}^3_{\text{cat}}^{-1}\text{h}^{-1}$ ). Initially the solid

was submitted to a mixture of reaction A (A = 1 Vol.% CO + 1 Vol.% O<sub>2</sub> + 60 Vol.% H<sub>2</sub> + balance He) during 2 h. Then, the inclusion of CO<sub>2</sub> and/or H<sub>2</sub>O was analyzed with the mixtures of reaction B (A + 4 Vol.% CO<sub>2</sub>), C (A + 3 Vol.% H<sub>2</sub>O) and D (A + 4 Vol.% CO<sub>2</sub> + 3 Vol.% H<sub>2</sub>O) and the results are presented in Figure 5.

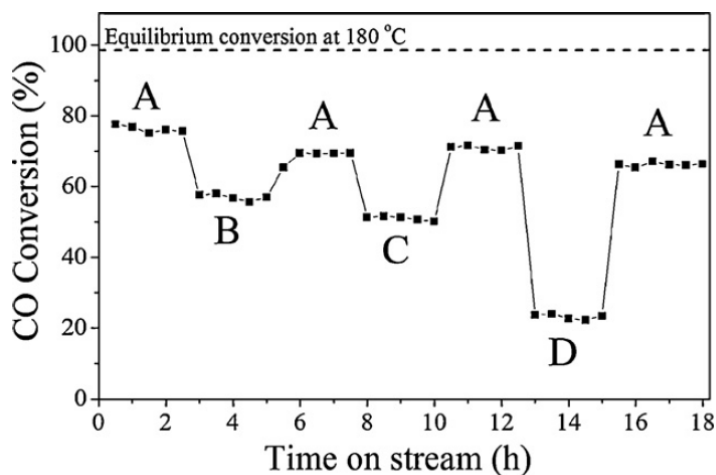


Figure 5. CO conversion for LaCoO<sub>3</sub> catalyst at 180 °C under distinct inlet flows. (A = 1 vol.% CO, 1 vol.% O<sub>2</sub>, 60 vol.% H<sub>2</sub> + balance He ; B = A + 4 vol.% CO<sub>2</sub>; C = A + 3 vol.% H<sub>2</sub>O; D = A + 4 vol.% CO<sub>2</sub> + 3 vol.% H<sub>2</sub>O). (Reprinted from Magalhães et al. [88], with permission from Elsevier)

Their results demonstrated that the presence of both components in the mixture of reaction (which is more close to realistic conditions in a catalytic reformer) has a negative influence in the CO conversion. In the case of CO<sub>2</sub>, this may be competing for being adsorbed over the active sites with the CO molecules, delaying the CO oxidation reaction. As for the effect of water, this molecule may be physisorbed over the surface of the catalyst establishing a physical blocking of the active sites. Beside the negative effect of CO<sub>2</sub> and H<sub>2</sub>O over the catalytic activity, this may be restored by allowing desorption of the carbonaceous species and water molecules over the surface of the catalysts. Therefore the deactivation process was not due to a structural modification of the perovskite, pointing out the high stability of such materials for the PROX reaction.

Chagas et al. [89] also worked with the LaCoO<sub>3</sub> perovskite for preparing catalysts for the PROX reaction. The perovskite structure was obtained by the Pechini's method that implies the polyesterification between citric acid and ethylene glycol, employing La(NO<sub>3</sub>)<sub>3</sub> and Co(NO<sub>3</sub>)<sub>2</sub>. Subsequently the obtained material was physically mixed with pretreated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in different proportions (10, 20 and 40 wt.% in

perovskite) and finally calcined at 500 °C for 24 hours. Although the synthesis of the  $\text{LaCoO}_3$  was successfully achieved, the deposition over the alumina did not result in a highly disperse perovskite phase. In any case, the use of this method did not cause structural changes in the active phase after supporting and heat-treatment steps. The bulk  $\text{LaCoO}_3$  and the 40 wt.%  $\text{LaCoO}_3/\text{Al}_2\text{O}_3$  sample presented the highest catalytic performances. In the case of the deposited system, although a high dispersion was not achieved, the observed enhancement of the catalytic activity may indicate a large exposition of available area of perovskite for the reaction.

#### **4. Concluding remarks**

The good catalytic activity of perovskite-type oxides in the CO oxidation reaction is well-known for more than 40 years. During this period of time, a large number of researchers have centered their attention in the study and comprehension of the main factors governing such catalytic performances.

Most of the works agree in the key role played by the structure of defects of the perovskite arrangement, which can be tailored adjusting the composition of the solid, mainly by substituting (total or partially) the A and B cation by other ones with the same or different oxidation state. The generation of such cationic or anionic defects alters (normally improving), the electronic, redox, ionic transport and surface properties of the material, and it is generally considered as decisive in the catalytic activity shown by the solid.

The high CO oxidation activity of bulk perovskites can be even increased if they are used as supports of any other active metal, particularly noble metal ones. In this case, the settlement of the noble metal on the surface or inside the perovskite structure, as well as the nature of the A and B cations, is determinant.

In the latest years, the increasing interest in developing catalyst able to abate CO at low temperature from hydrogen streams for feeding fuel cells, besides the recognized capabilities of perovskites in CO oxidation, and their encouraging and promising characteristics and properties briefly reported above, has motivated the renewed attention in such solids and in their possible application in the  $\text{H}_2$  clean-up processes, such as WGS and PROX ones.

## 5. Acknowledgements

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