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Improvement of Catalytic Performance of Perovskites by Partial Substitution of Cations and Supporting on High Surface Area Materials

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Additional information is available at the end of the chapter

Abstract

In this chapter, we present two relevant strategies to improve the activity and selectivity of perovskite-mixed oxides ABO_3 in heterogeneous catalytic reactions such as the oxidation of hydrocarbons, soot combustion and CO selective oxidation, for which the surface sites and lattice oxygen species play important roles for the chemical transformations. Besides, we focus on synthesis of higher alcohols, partial oxidation of methane, oxidative reforming of diesel and dry reforming of methane for which the perovskite is a precursor that leads to a dispersed metal active phase over an oxide matrix. But which strategies are we talking about? First, the partial substitution of cations A and B by different elements, which change atomic distances, causes unit cell distortions, stabilizes multiple oxidation states or induces cationic or anionic vacancies within the lattice. And all these new features perturb the solid reactivity by changing the reaction mechanism on the catalyst surface. Thus, appropriate cations substitutions may lead to better catalysts. The second strategy comprises supporting the perovskite, which usually presents low surface area, on high surface area materials to maximize the exposed surface sites.

Keywords: Catalysis, Partial substitution, Vacancy, Monolith

1. Introduction

Perovskite-type oxides with ABO_3 structure have attracted significant interest in many areas of solid-state chemistry, including catalysis. Several ABO_3 formulations have demonstrated success, especially in total oxidation and partial oxidation of hydrocarbons, carbon monoxide oxidation, alkenes hydrogenation, alkanes hydrogenolysis, alcohols synthesis, dry reforming and water gas shift reaction. However, these materials present some limitations for broader

application in catalysis such as low activity and stability in certain experimental conditions, low metal dispersion when the perovskite structure collapses to form a supported-type catalyst B/AO_x or even low surface area resulting from high calcination temperature.

To overcome these limitations aiming to improve the catalytic activity, selectivity and stability of perovskite-type oxides, one can design these materials by substituting partially and properly the cations A and B or even supporting the perovskite on high surface area materials (porous oxides, monolith-type structure). By substituting the original A and B cations, one can control the extent of substitution and decide for an appropriate cation that will bring significant structural changes, such as lattice distortions, stabilization of multiple oxidation states or generation of cationic and anionic vacancies, all having as a direct consequence the change in catalytic activity. Upon spreading the perovskite on a support, one can choose the best matrix to accommodate the oxide particles and expose the largest amount of active sites in order to improve the catalytic performance.

In this sense, we discuss in the next pages some recent advances that apply perovskite-type oxides for reactions of interest in catalysis and how the above strategies impact on the performance of the catalysts. All visited literature was critically analyzed and here we present well-structured discussions and hypothesis based on extensive experiments and precise characterization techniques.

2. Partial substitution of cations as a strategy to enhance catalytic performance

Perovskite-type oxides ABO_3 can be properly modified by the partial substitution of atoms at A and/or B-sites, creating isostructural $A_{1-x}A_xB_{1-y}B_yO_3$ crystals (or AA'BB'O₃ for simplicity), which may stabilize unusual oxidation states of the B component, induce structural distortions and create cationic or anionic vacancies. The nature and extent of the dopant that substitutes A and B elements impact on the physicochemical properties and catalytic activity of the material [1].

From the catalysis point of view, a solid containing surface and lattice defects presents more structural and electronic instability, which is compensated by the interaction with molecules from gas phase through chemical reactions that break and form bonds. Defects are welcome in catalysis, and the partial substitution of cations within the perovskite lattice tends to enhance the defects density of the crystal structure.

Perovskite oxides may also be considered as catalytic precursors for generating highly active metals dispersed onto a matrix, B/AO_x, that can be obtained *in situ* by reducing the precursor ABO_3 [2–4]. The partial substitution of cations can increase the dispersion of B in reducing treatments and avoid metal sintering during reaction conditions. In this sense, high metal dispersion from perovskite oxides emerges as an interesting alternative to conventional metal supported catalysts.

For instance, several lanthanum-containing perovskites have been considered promising for different applications such as soot combustion in automotive exhaust treatments, oxidation of volatile organic compounds (VOCs) in air pollution control and reforming or partial oxidation of hydrocarbons for hydrogen production [5]. Though perovskites have a remarkable activity and some desired features such as low-cost synthesis and high thermal stability, their industrial application is still missing due to drawbacks related to the low surface area and low density of structural defects, which both can be improved by selecting an appropriate synthesis method to (i) insert different cations into the crystal lattice and (ii) spread the oxide phase over a porous support.

2.1. Perovskites for oxidation reactions

An interesting study about the effect of partial substitution of single-site (A or B) and dual-site (A and B) in the $LaCoO_3$ perovskite on the activity for toluene oxidation and methane oxidation was presented in ref. [5]. This investigation focused onto the effect of single- and dual-site modifications, while most of the researches explain only single-site substitution. The oxidation reactions on perovskite-type oxides usually take place through different mechanisms, either involving weakly chemisorbed oxygen (i.e., α-O in the toluene oxidation, for instance) denoted as suprafacial mechanism, or comprising surface lattice oxygen species (i.e., α'-O in the methane oxidation) denoted as intrafacial mechanism. The latter is directly related to the mobility and amount of oxygen species within the crystal lattice. The following catalysts were prepared by continuous flow hydrothermal synthesis method [5]: $LaCoO_3$ (ABO_3), $LaCaCoO_3$ ($AA'BO_3$), $LaCoMgO_3$ ($ABB'O_3$), and $LaCaCoMgO_3$ ($AA'BB'O_3$). After heat treatments at 700, 800 and 900°C, these materials presented mostly the perovskite phase, but some traces of La_2O_3, Co_3O_4 and MgO (depending on the catalyst) and the specific surface area was lower than 30 m^2/g. Authors evidenced the calcium substitution by verifying distortions in the angle α of the rhombohedral structure of $LaCaCoO_3$, since a significant contraction of the unit cell should not be expected due to the similar ionic radii of Ca^{2+} (0.100 nm) and La^{3+} (0.103 nm). On the other hand, magnesium substitution led to more severe angular distortions and unit cell expansion, because Mg^{2+} has ionic radius (0.072 nm) larger than Co^{3+} (0.063 nm), as well as the oxidation state of Co^{3+} changed to Co^{4+} to guarantee the structural electroneutrality, as revealed by X-ray photoelectron spectroscopy (XPS).

By applying those materials in the oxidation of 500 ppm toluene (in the absence and presence of water 3 vol.%), which is believed to take place through the suprafacial mechanism, the activity sequence was $LaCaCoMgO_3$ > $LaCoMgO_3$ > $LaCoO_3$ > $LaCaCoO_3$. According to XPS measurements [5], the insertion of Ca^{2+} into the perovskite lattice slightly increased the amount of oxygen species chemisorbed on the surface (O^- and O_2^-, denoted as O_{ads}) relating to lattice oxygen (O_{lat}). However, Mg^{2+} insertion had a more relevant impact and practically doubled O_{ads}/O_{lat} ratio, suggesting that Mg^{2+} (with valence lower than Co^{3+} and La^{3+}) generated more oxygen vacancies than Ca^{2+} to ensure charge compensation. As a consequence, the surface vacancies were occupied by oxygen species from gas phase. According to the authors, these findings agreed with the temperature-programmed desorption of oxygen (O_2-TPD) which showed that Mg^{2+}-substituted materials released larger amount of weakly chemisorbed oxygen

(α-O), which were adsorbed on surface oxygen vacancies. Since toluene oxidation makes use of surface oxygen (suprafacial mechanism), we should expect LaCaCoMgO$_3$ and LaCoMgO$_3$ (which contain this type of oxygen) to present higher activity.

On the other hand, Ca^{2+} insertion decreased the catalyst reducibility (shifting reduction peaks to higher temperature in H$_2$-TPR experiments), which explained higher activity of LaCoO$_3$ instead of LaCaCoO$_3$, since the non-substituted perovskite would release surface lattice oxygen easier to oxidize toluene than LaCaCoO$_3$. Furthermore, the authors estimated the activation energy for the different catalysts in the temperature range of 140–280°C and found out that the dual-insertion of Ca^{2+} and Mg^{2+} into the LaCoO$_3$ perovskite induced the activation energy to decrease from 143 kJ/mol (LaCoO$_3$) to 34 kJ/mol (LaCaCoMgO$_3$), which is comparable or even smaller than some noble metals applied in this suprafacial oxidation process (31–37 kJ/mol on Au/LaCoO$_3$ [6]; 86 kJ/mol on Pt/Al$_2$O$_3$ [7]).

For the oxidation of 1 vol.% CH$_4$ (in the absence and presence of water 3 vol.%), which is believed to occur by an intrafacial mechanism, ref. [5] found the sequence of the catalytic performance LaCoMgO$_3$ > LaCaCoMgO$_3$> LaCoO$_3$> LaCaCoO$_3$ to agree with the sequence of surface lattice oxygen (α'-O) released in O$_2$-TPD measurements, i.e., 19.9 > 13.6 > 6.2 > 2.7 µmol O$_2$/g, confirming the important role of surface lattice oxygen in this type of reaction. Calcium substitution had a negative impact on the generation of surface lattice oxygen (decreasing α'-O which releases during O$_2$-TPD). Differently, magnesium substitution increased considerably surface lattice oxygen species, which participates in methane oxidation reactions (intrafacial mechanism). The estimated activation energy within the temperature range 390–450°C reduced from 152 kJ/mol on LaCoO$_3$ to 80 kJ/mol on LaCoMgO$_3$, which is similar to noble metal-based catalysts (BaZrMO$_3$, M = Rh, Pd, Pt, Mn, Ni, Co, activation energy = 72–106 kJ/mol) [8].

Thus, the dual-site substitution of Ca^{2+} and Mg^{2+} was beneficial for suprafacial oxidation processes by increasing oxygen species chemisorbed on the surface oxygen vacancies, but had a less beneficial effect on intrafacial oxidation processes, for which only the single substitution of Co^{3+} by Mg^{2+} is highly indicated to increase the amount of surface lattice oxygen.

The work of Liu *et al*. [9] brings insights on the role of the partial substitution of La^{3+} by Ce^{4+} into La$_{1-x}$Ce$_x$MnO$_3$ (0 < x < 0.1) which is a very active perovskite for the oxidation of volatile organic compounds (VOCs). The enhancement in activity is usually explained in terms of oxygen excess in the lattice, cationic vacancies, structural defects and the presence of multiple Mn oxidation states (Mn^{3+}/Mn^{4+}). Inserting cerium into the perovskite structure is a great strategy due to the Ce^{3+}/Ce^{4+} redox behavior, which along with Mn^{3+}/Mn^{4+} may increase oxygen transfer within the lattice. These researchers found that the activity of La$_{1-x}$Ce$_x$MnO$_3$ perovskites (all presenting specific area approximately 25 m^2/g) in the oxidation of 1,000 ppm benzene at the temperature range of 100–450°C correlated directly with the extent of cerium substitution (x value), *i.e.*, the higher the cerium content, the higher the benzene conversion according to the sequence x = 0 < 0.025 ≈ 0.05 < 0.075 < 0.1. But how to explain the promoter effect of cerium on the catalytic oxidation of benzene?

Firstly, authors confirmed cerium insertion into the perovskite lattice (using X-ray diffraction measurements, XRD) by verifying absence of segregated CeO_2 phase, presence of lattice distortions and the decrease of $La_{1-x}Ce_xMnO_3$ crystalline domain size as a function of cerium content. That should be expected since the higher Ce^{4+} coordination with their surrounding oxygen atoms (within the same crystal plan) than trivalent La^{3+} tends to inhibit crystal growth, resulting in smaller crystal size.

Then, XPS measurements revealed the existence of Ce^{3+} and Ce^{4+} in the perovskites with higher cerium content ($x = 0.05$; 0.075; 0.10), as well as an increasing Mn^{4+}/Mn^{3+} ratio and decreasing O_{ads}/O_{lat} ratio as a function of cerium substitution, apparently unexpected. Ce^{4+} substitution should induce Mn to have lower oxidation states, or at least decrease Mn^{4+}/Mn^{3+} ratio as a charge compensation mechanism. Similarly, in the presence of Ce^{4+} and Mn^{4+}, the O_{ads}/O_{lat} ratio should increase, representing more oxygen species adsorbed on the surface to compensate the positive cationic charges, but the opposite occurred. According to [9], these findings indicated that cerium substitution created non-stoichiometric Ce-Mn-O compounds on the perovskite surface, and plenty of oxygen was accommodated into the lattice decreasing O_{ads}/O_{lat} ratio as the cerium content increased. Releasable oxygen from lattice justifies the higher activity of cerium-substituted perovskites in the benzene oxidation, which is believed to involve oxygen species supplied by the reducible oxide structure. The H_2-TPR results supported this hypothesis by showing that cerium substitution increased the reducibility, specially at the temperature range of 300–580°C, suggesting that Ce^{4+} increased the amount of oxygen species within the lattice (to reach structural neutrality) and also their diffusion from bulk to the surface.

The reactivity of substituted lanthanum cobaltite perovskites in the carbon oxidation (a solid–solid–gas catalytic reaction) has also been studied [10]. Changes in the $LaCoO_3$ perovskite structure and the existence of gradient in the cobalt valence from bulk to surface were evaluated as a function of partial substitution of La^{3+} by Sr^{2+} and temperature reaction. $LaCoO_3$ and $La_{0.5}Sr_{0.5}CoO_3$ were prepared by spray pyrolysis method (specific surface area < 14 m^2/g), and then ground with carbon at catalyst:carbon = 9:1 ratio (w/w) to give a tight contact. O_2-TPD measurements revealed that the maximum oxidation rate of carbon occurred at 650°C in the absence of catalyst, but $LaCoO_3$ perovskite reduced this temperature to 540°C, and then Sr^{2+} substitution ($La_{0.5}Sr_{0.5}CoO_3$) led to the lowest temperature 510°C. CO and CO_2 were the byproducts in the carbon oxidation. The direct oxidation (absence of catalyst) led to similar amounts of CO and CO_2 (50%/50%), but $LaCoO_3$ and $LaSrCoO_3$ were more selective to CO_2, 89% and 94%, respectively. To explain the improvement in the activity and selectivity, the authors investigated the cations oxidation state and composition of the catalytic systems by using EELS (electron energy loss spectroscopy, which is a bulk sensitive analysis) and XPS (surface sensitive), before, at an intermediate temperature, and after the carbon oxidation process. The conclusions are illustrated in Figure 1, which shows a catalyst–carbon particle model for the catalytic phenomenon.

The partial substitution of La^{3+} by Sr^{2+} created plenty of oxygen vacancies within the perovskite lattice (as a charge compensator mechanism), which also caused the cobalt oxidation state to decrease from Co^{3+} (in $LaCoO_3$) to values between +2.5 and +2.7 (in $La_{0.5}Sr_{0.5}CoO_3$). Authors [10] estimated that the as-prepared Sr-substituted perovskite ($La_{0.5}Sr_{0.5}CoO_3$) presented 50%Co^{3+}

and 50%Co^{2+} (Figure 1a), which was consistent with the unit cell expansion due to the higher ionic radius of Co^{2+} (0.074 nm) related to Co^{3+} (0.063 nm). Surprisingly, the tight contact between carbon and perovskite at room temperature immediately decreased Co^{3+}/Co^{2+} ratio in the bulk, as well as enhanced Co^{2+} (60–70%) on the surface (Figure 1b). This partial reduction of cobalt in the bulk and especially on the catalyst surface suggests oxygen mobility from bulk to surface and a remarkable surface reactivity for carbon oxidation, even at room temperature, which agreed with the increase of carbonate species on the surface, as seen by XPS.
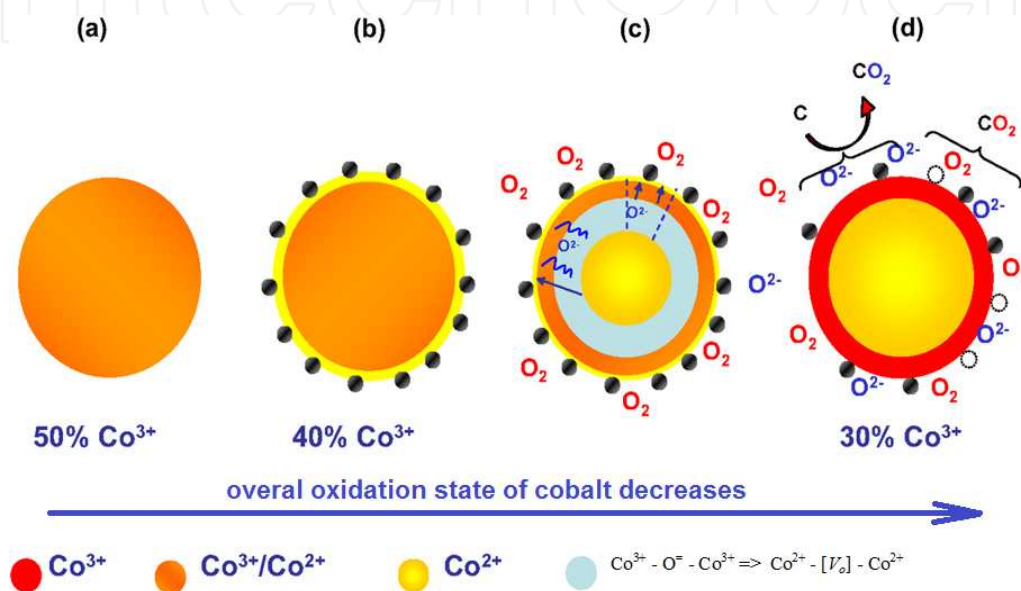

Figure 1. Scheme of cobalt oxidation states distribution within the perovskite $La_{0.5}Sr_{0.5}CoO_3$ as a consequence of the interaction and reaction with carbon particulates: (a) perovskite as prepared (without carbon); (b) after grinding carbon and catalyst at room temperature; (c) heating treatment at 400°C in the presence of 0.5 Torr O_2; (d) final state of the perovskite after removal of carbon by prolonged thermal oxidation. The expressed percentages of cobalt were deduced from EELS calculations. Reprinted from reference [10], copyright (2008) with permission from Elsevier Inc.

As depicted in Figure 1c, by increasing the temperature reaction in the presence of oxygen, the carbon oxidation activity enhanced because O^{2-} species migrated from bulk to surface promoting surface carbonates elimination (as proved by XPS). For this reason, the overall oxidation state of cobalt decreased by the end of reaction and the temperature for the maximum oxidation rate of carbon reduced by 140°C (from 650°C in the absence of catalyst to 510°C on $LaSrCoO_3$). In the presence of oxidative atmosphere, carbon particulates on the catalyst surface were oxidized by O_2 from gas phase and also by lattice O^{2-} anions leading to the consumption of lattice oxygen, which decreased the overall oxidation state of cobalt. After complete carbon oxidation, the perovskite surface presented abundance of Co^{3+} (90–95%) while bulk showed oxygen deficit (Co^{2+}-rich) as shown in Figure 1d, due to the diffusion of oxygen species through the structural vacancies towards surface or re-establishment of the surface lattice with oxygen from gas phase. The overall reaction (1) represents the interaction between the perovskite surface and carbon particles, summarizing the phenomenon in Figure 1 ($[V_o]$ means an anionic vacancy):

$$\left(Co^{3+} - O^{=} - Co^{3+} \right) + C \;\rightarrow\; \left(Co^{2+} - \left[V_{o} \right] - Co^{2+} \right) + CO_{x} \tag{1}$$
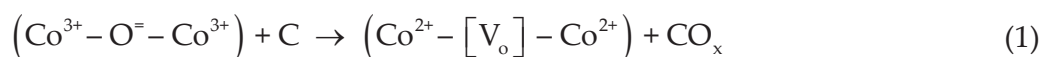
Therefore, Sr^{2+} substitution into the perovskite lattice created oxygen vacancies, increasing cobalt reducibility and enhancing the mobility of lattice oxygen species, which were an additional source of oxygen for the carbon oxidation towards CO_2. But the partial substitution of A and/or B sites into the ABO_3 mixed oxide may lead to consequences other than the generation of anionic vacancies and stabilization of unusual oxidation states, such as the stabilization of the crystal lattice avoiding the segregation of undesired phases (which worsen the catalytic performance), as reported in the reference [11] for $LaCoO_3$ substituted by K^+ and Mg^{2+} applied for the soot oxidation.

$La_{1-x}K_xCo_{1-y}Mg_yO_3$ perovskites ($x = 0 - 0.4$; e $y = 0 - 0.2$) prepared by citric acid complexation [11] showed an increasing segregation of Co_3O_4 as La^{3+} was substituted by K^+ (no Mg substitution then). The phase segregation can be explained because of the larger ionic radius of K^+ (0.133 nm) than La^{3+} (0.103 nm), which caused severe lattice distortions and unstable occupancy of the lanthanum site by K^+ leading to cobalt to segregate as Co_3O_4. However, the increasing Mg^{2+} substitution into the perovskite containing the higher amount of K^+ (*i.e.*, $x = 0.4$: $La_{0.6}K_{0.4}Co_{1-y}Mg_yO_3$) led to a gradual diminishment of segregated Co_3O_4, since the larger ionic radius of Mg^{2+} (0.072 nm) than Co^{3+} (0.063 nm) gave more stability for the crystal lattice avoiding cobalt segregation. This hypothesis was confirmed by XRD, FTIR, TEM and EDS results which evidenced Co_3O_4 phase decreasing as a function of Mg substitution. By replacing both cations K^+ and Mg^{2+} into the perovskite, Co^{4+} was detected by XPS, as a charge compensator mechanism. According to ref. [11], the activity of the perovskites in the oxidation of carbon (using synthetic air 20 vol.% O_2/N_2 and tight catalyst/carbon contact) was established as a function of the temperature for the maximum oxidation rate (T_m). The non-catalyzed reaction (absence of catalyst) presented $T_m = 590°C$, but the perovskite $LaCoO_3$ led to $T_m = 448°C$, which gradually decreased to $T_m = 370°C$ with increasing substitution of La^{3+} by K^+ within the perovskite. By inserting Mg^{2+} into the B site of $La_{0.6}K_{0.4}Co_{1-y}Mg_yO_3$, the structure stability increased and cobalt segregation decreased (ensuring the existence of anionic vacancies useful for oxygen mobility) and as a consequence, the lowest $T_m = 359°C$ was reached on $La_{0.6}K_{0.4}Co_{0.9}Mg_{0.1}O_3$. Therefore, the improvement in the carbon oxidation followed exactly the increasing amount of K^+ up to $x = 0.4$ (into A site) and increasing amount of Mg^{2+} up to $y = 0.1$ (into B site), which is very consistent with the increasing reducibility of the perovskites (and redox properties) as a function of the partial substitution of K^+ and Mg^{2+} (as evidenced by H_2-TPR measurements). In particular, Mg^{2+} stabilized the crystal lattice and reduced cobalt segregation. That ensured the integrity of the perovskite oxide structure and the mobility of lattice oxygen towards surface which enhanced carbon particulate oxidation.

2.2. Perovskites for CO selective oxidation

Carbon monoxide selective oxidation reaction (CO-SELOX) is an interesting and economic approach to remove CO from H_2-rich gas streams, but a selective catalyst should avoid H_2 consumption since CO and H_2 oxidation reactions compete each other. Pt-supported catalysts

are typically used because CO adsorbs more strongly on Pt surface than H_2. Other classes of CO selective oxidation catalysts comprise non-noble metals such as Ag, Au and also oxides, e.g., $CuO-CeO_2$, CeO_2, $Cu-LaO_2-CeO_2$ as well as cobalt-based oxides. Literature reports bulk and supported cobalt oxides applied for SELOX, but rarely cobalt-based perovskites. The main constraint for cobalt oxides application is their low stability in H_2-rich stream and consequent metallic cobalt formation on the catalyst surface which catalyzes undesirable reactions such as H_2 oxidation and methanation. For instance, CoO_x/ZrO_2 showed high CO conversion at 175°C, but above this temperature H_2 oxidation took place, and methanation reaction occurred above 250°C [12].

For this reason, a suitable catalyst for CO selective oxidation should not only be able to keep the oxide structure during the process but also allow oxygen mobility through the crystal lattice in order to enhance the CO oxidation rates towards CO_2 on the surface active sites. Cobalt-containing perovskites seem to satisfy all these requirements.

Magalhães *et al.* [13] applied Ce-substituted $LaCoO_3$ perovskites in the CO-SELOX reaction in H_2-rich feedstream (1% CO, 1% O_2, 60% H_2, He balance, vol.%) and found out the new structures containing cerium increased the resistance to undesirable reactions and did not damage the high selectivity to CO_2 presented by the non-substituted perovskite. They obtained single phase $La_{1-x}Ce_xCoO_3$ perovskites (x = 0; 0.05 and 0.10) with low surface area (< 15 m^2/g) and verified, by Rietveld refinements, that the Ce^{4+} substitution into La^{3+} sites decreased both cell parameters of the rhombohedral unit cell and crystalline domain sizes, since the ionic radius of Ce^{4+} is smaller than La^{3+}, exactly as verified by ref. [9] for $LaCeMnO_3$. Figure 2 illustrates the effect of cerium insertion into the perovskite on the CO conversion to CO_2 and H_2O byproducts during temperature-programmed reactions: region 1 evidenced the selective CO oxidation in which CO and O_2 were exclusively converted to CO_2, and one can note that the presence of cerium affected the reaction kinetics shifting CO conversion to higher temperatures. In region 2 the undesired H_2 oxidation gained importance leading to water formation, and finally methanation reaction occurred at higher temperatures at region 3 (leading to CH_4 and H_2O formation). Though cerium substitution shifted the range of temperature for CO-SELOX reaction up to 240°C, all the undesired reactions also shifted to higher temperature.

Authors [13] affirmed that Ce^{4+} changed some Co^{3+} to Co^{2+} to keep the charge neutrality within the structure, consequently decreasing the amount of active Co^{3+} sites on the surface and decreasing the activity for CO conversion (for this reason, $La_{0.90}Ce_{0.10}CoO_3$ showed CO conversions at higher temperature than $LaCoO_3$ in Figure 2). However, the formation of cationic vacancies into A and B sites as a second mechanism to keep the charge neutrality would stabilize the entity Co^{3+}/O_2 on the surface, ensuring high CO_2 selectivity for cerium-substituted perovskites. At temperatures higher than 350°C, Co^{n+} species coexist with metallic Co^0 which leads to undesirable methanation reaction. This hypothesis was supported by H_2-TPR experiments that showed perovskite reduction above 300°C (i.e., $T_{reduction}$ > 300°C). These results clearly evidenced that Co^{3+} as part of a perovskite structure is more resistant to reduction when compared to typical supported cobalt catalysts, such as CoO_x/CeO_2 ($T_{reduction}$ > 275°C) [14], CoO_x/ZrO_2 ($T_{reduction}$ > 250°C) [12] and $Co_3O_4/CeZrO_2$ ($T_{reduction}$ > 200°C) [15].
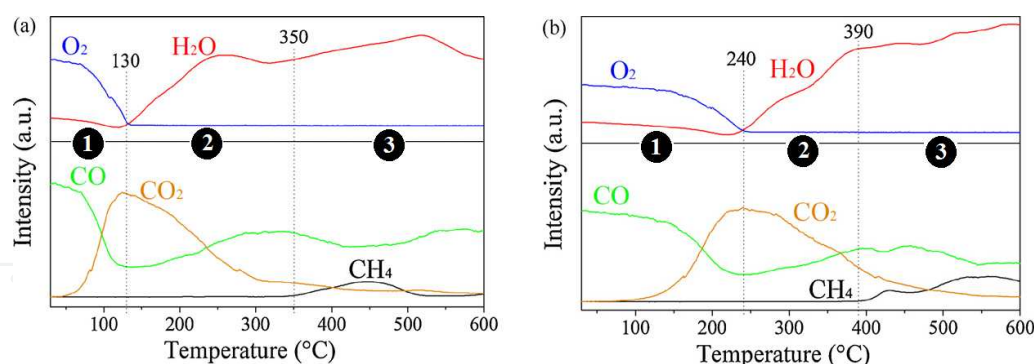
Figure 2. Effect of temperature and cerium substitution on compounds distribution in the CO-SELOX reaction for (a) $LaCoO_3$ and (b) $La_{0.90}Ce_{0.10}CoO_3$ (1% CO, 1% O_2, 60% H_2, He balance, vol.%). Reprinted from reference [13], copyright (2010) with permission from Elsevier B.V.
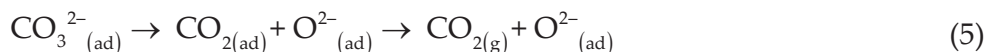
Schmal *et al.* [16] investigated the effect of strontium insertion into $La_{1-x}Sr_xCoO_3$ (x = 0; 0.05) on the catalytic performance in the CO-SELOX reaction. Differently from cerium, Sr^{2+} as a cationic dopant is expected to increase cobalt oxidation state and/or create oxygen vacancies within the crystal lattice, which could enhance oxygen mobility and provide lattice oxygen for CO oxidation on the surface. These researchers found out evidences for complete Sr^{2+} substitution into the rhombohedral crystalline structure of the perovskite (by means of XRD and Raman spectroscopy), which led to distortions and expansion of the unit cell volume, since the ionic radius of Sr^{2+} (0.132 nm) is larger than La^{3+}. XPS indicated that Sr^{2+} did not modify the cobalt oxidation state (Co^{3+}) in $La_{0.95}Sr_{0.05}CoO_3$, suggesting that anionic vacancies have been created within the lattice as a charge compensator. This hypothesis was supported by the enhancement in both activity to CO conversion and selectivity to CO_2 after Sr^{2+} substitution: the temperature to convert 50% of CO decreased from 170°C ($LaCoO_3$) to 155°C ($La_{0.95}Sr_{0.05}CoO_3$), and selectivity to CO_2 (at 29% isoconversion of CO) increased slightly from 87% to 91%. Interestingly $La_{0.95}Sr_{0.05}CoO_3$ was more stable than $LaCoO_3$ on stream at 170°C, presenting constant CO conversion 75% for 48 h, while the non-substituted perovskite showed decreasing CO conversion from ca. 75% to 45% at the same conditions.

How to explain that? The dopant Sr^{2+} caused distortions in the lattice due to its size and oxidation state, giving rise to anionic (oxygen) vacancies, which initially neutralized the structure charge but then enhanced the oxygen transfer through the lattice, i.e., from bulk to surface during reaction (indeed, the full redox process also comprises the re-establishment of lattice oxygen from oxygen coming from gas phase). As a consequence, this oxygen supplying from the lattice enhanced the CO oxidation on the catalyst surface.

A short communication [17] highlighted the influence of cerium substitution in $La_{1-x}Ce_xNiO_3$ (x = 0; 0.05; 0.1) on the catalysts properties and performance in the CO-SELOX reaction (2.5% CO, 5% O_2, 33% H_2 and N_2 balance, vol.%). The surface area of the catalysts with rhombohedral structure did not change with cerium addition, which usually takes place only at Ce content above x > 0.4 simultaneously to the appearance of segregated CeO_x phases [18]. CO conversion was higher for the cerium-doped perovskites than for $LaNiO_3$ at the entire range of 150–230°C,

and undesirable H_2 oxidation took place only above 230°C (H_2 conversion < 12%). The authors discussed the promoter effect of cerium in terms of (i) very active surface Ce^{3+}/Ce^{4+} redox cations that directly adsorbs and activates O_2, (ii) stabilization of reduced Ni^{n+} species ($n < 3$), not discarding (iii) the enhanced lattice oxygen mobility from bulk to surface supplying oxygen for the CO oxidation.

Literature reports that CO oxidation over perovskites proceeds through a suprafacial mechanism involving weakly chemisorbed oxygen. The following mechanistic proposal has been suggested by Tascon *et al.* [19] to explain CO oxidation on $LaCoO_3$: molecular oxygen chemisorbs on Co^{2+} cations as an O_2^- anion, dissociating to form atomic oxygen (O^-) on the cobalt sites. Simultaneously, CO chemisorbs on surface oxide ions yielding a labile species that interacts with adsorbed atomic oxygen, producing carbonates (the rate-determining step) which decompose towards CO_2 and oxygen.

$$O_{2(g)} \rightarrow O_2^-{}_{(ad)} \rightarrow 2O^-{}_{(ad)} \tag{2}$$

$$CO_{(g)} \rightarrow CO_{(ad)} \tag{3}$$

$$CO_{(ad)} + 2O^-{}_{(ad)} \rightarrow CO_3^{2-}{}_{(ad)} \text{ rate-limiting step} \tag{4}$$

$$CO_3^{2-}{}_{(ad)} \rightarrow CO_{2(ad)} + O^{2-}{}_{(ad)} \rightarrow CO_{2(g)} + O^{2-}{}_{(ad)} \tag{5}$$

Though the mentioned mechanism (equations (2)–(5)) does not clarify about the role of the lattice oxygen within the elementary steps, we may infer that those mobile oxygen species, specially the surface lattice oxygen, participate more easily in the redox process and contribute in some extent into the elementary step (4).

2.3. Perovskite as a catalytic precursor

Considering only geometric factors, the Goldschmidt tolerance factor (t) for perovskites indicates that lanthanum, which is the largest lanthanide ion in the series, leads to the most stable perovskite structure [20]. However, the thermal stability of ABO_3 perovskites strongly depends on cations at both positions A and B. Particularly, the thermal stability in a reducing atmosphere such as H_2, during reduction treatments or redox cycles, has been the focus of research because the metal B can reach high degree of dispersion over an AO_x matrix when Figure 2 these treatments. Considering the importance of dispersed metals in heterogeneous catalysis, the reduction or reduction–oxidation of perovskites under controlled conditions and atmosphere may offer a promising methodology for the preparation of highly active and dispersed catalysts [20]. In this sense, we can face a perovskite-type oxide as a catalytic precursor for a dispersed metal catalyst.

Copper-substituted materials have been widely investigated in the literature, not only in perovskite oxides, since copper may modify the carbon formation mechanism avoiding coke deposition. Tien-Thao *et al.* [21] verified that replacing cobalt by copper into $LaCo_{1-x}Cu_xO_3$ perovskites ($0 < x < 0.6$; specific surface area 10–60 m^2/g) increased the reducibility and caused strong cobalt–copper interaction that enhanced metallic dispersion of cobalt and prevented metal sintering. The main catalytic consequence of Cu^{2+} substitution was the notable selectivity to higher alcohols in the syngas conversion (H_2/CO = 2 diluted to 20 vol.% in He, 1000 psi, 275°C) by using the perovskites partially reduced in H_2. According to these authors, X-ray diffraction of the as-prepared materials proved the copper substitution due to the clear structure distortions, which affected the redox properties and stability of these mixed oxides. Temperature-programmed desorption of O_2 showed large amount of oxygen releasing from Cu^{2+}-substituted perovskites, reflecting a high concentration of surface oxygen vacancies (Co^{3+} substituted by Cu^{2+} creates anionic vacancies for charge compensation). The partially reduced $LaCo_{1-x}Cu_xO_3$ perovskites were tested in the syngas conversion and yielded a homologous series of linear hydrocarbons (from methane to undecane) and a set of linear primary alcohols with the chain growth probability values ranging from 0.34 to 0.42.

The authors of ref. [21] expressed they did not expect to have higher alcohols on the cobalt-based perovskites, since cobalt is indeed known as a good Fischer-Tropsch catalyst (forming higher hydrocarbons) but not active for higher alcohols. However, the basic properties of the amorphous matrix La_2O_3 catalyzed or promoted in some extent the synthesis of these alcohols (Fischer-Tropsch metal catalysts can yield alcohols when promoted with a base). And at the reaction conditions, dispersed metallic cobalt and copper species were expected to coexist over intermediate oxides ($La_2Co_{0.75}Cu_{0.25}O_{4\pm\delta}$ and La_2O_3) as evidenced by XRD for samples partially reduced in H_2. Furthermore, Tien-Thao *et al.* [21] emphasized the selectivity to higher alcohols showed to be dependent on the content of intra-lattice copper in the perovskite. The selectivity to alcohols (36.5–49.5%) and productivity (a maximum at 49.6 mg/(g_{cat}.h) for $LaCo_{0.7}Cu_{0.3}O_3$) indicated that by increasing copper content, the selectivity to alcohol (C_2 $^+$OH) also increased simultaneously with a decrease in the selectivity to methane and C_2 $^+$ hydrocarbon. Those authors stated that a uniform distribution of the metallic cobalt–copper on the catalyst surface, as well as a high metal dispersion, seem to be the key for the synthesis of higher alcohols, but they did not prove that copper increased the cobalt dispersion. However, this kind of evidence was discussed in ref. [22] in the reduction of cobalt-based perovskites substituted with copper.

$LaCoO_3$ and $LaCo_{0.8}Cu_{0.2}O_3$ perovskite oxides with low surface area (< 10 m^2/g) were obtained by the polymerizable complex route, which is based on the polyesterification between citric acid and ethylene glycol in solution containing the soluble precursor anions. Then, the authors of ref. [22] confirmed the partial substitution of copper due to the increase in cell parameters caused by the larger ionic radius of the hexacoordinated Cu^{2+} and also due to the absence of segregated copper phases. By applying these perovskites in the partial oxidation of methane CH_4/O_2/He = 2/1/37 and 5/1/64, they verified a dynamic structural transformation in which the perovskite collapsed towards lanthanum-based matrix and metallic cobalt and copper species. The perovskites showed comparable performance up to 650°C, but remarkable differences in

between 600 and 900°C in which LaCoO$_3$ favored CH$_4$ dissociation leaving carbon on the surface, while the copper-substituted perovskite was more efficient to produce syngas and suppress carbon deposition (thermogravimetry showed up to 18.5 times less carbon on LaCo$_{0.8}$Cu$_{0.2}$O$_3$ than on LaCoO$_3$). In this study, addition of copper increased the reducibility of the perovskite, decreased the temperature to obtain syngas and inhibited carbon deposition, and authors attributed that to a higher cobalt dispersion caused by copper. And how did they prove that?

According to their results, the presence of copper doubled cobalt dispersion and metal specific area, S_m, (S_m = 6.2 m^2/g$_{Co}$ and 12.1 m^2/g$_{Co}$ for LaCoO$_3$ and LaCo$_{0.8}$Cu$_{0.2}$O$_3$, respectively) since the amount of H$_2$ able to chemisorb on the surface doubled on the sample with Cu as seen in Figure 3 during H$_2$ chemisorption measurements. However, H$_2$ does not chemisorb on copper at such conditions [23], and therefore this finding suggests a higher cobalt dispersion promoted by Cu due to a strong cobalt–copper interaction as proposed by Tien-Thao *et al.* [21] for similar materials. Therefore, copper may be a very important dopant for perovskites applied in reactions with hydrocarbons. Differently from catalytic systems involving transition metals (iron, nickel or cobalt), copper does not tend to catalyze Fisher-Tropsch reactions or processes involving carbonium ion chemistry due to its low activity for breaking C–O bonds or forming C–C bonds, which avoids both wax formation in CO/H$_2$ reactions and coke formation from hydrocarbons [24].
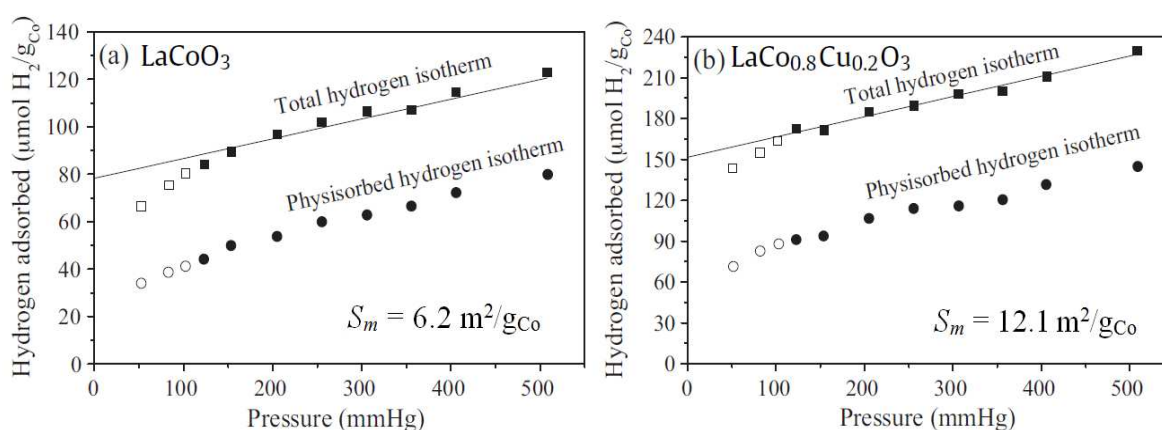

Figure 3. Hydrogen adsorption on (a) LaCoO$_3$ and (b) LaCo$_{0.8}$Cu$_{0.2}$O$_3$ after complete reduction of the perovskite structure. Symbols: (■,□) total H$_2$ isotherm; (●,○) reversible H$_2$ isotherm. In the literature, total H$_2$ uptake is reported to be used for quantifying chemisorbed H$_2$ over cobalt, since the process is activated at 150°C [4, 25–27]. Extrapolation of the straight-line portion of the total adsorption isotherm to zero pressure gives the chemisorbed H$_2$ over cobalt, and full symbols represent the data used to calculate dispersion and metal specific area. Approximately double H$_2$-uptake can be observed for copper-substituted perovskite. Reprinted from reference [22], copyright (2012) with permission from Elsevier B.V.

Reforming and partial oxidation of hydrocarbons aiming syngas production still find the deactivation as the main challenge to be overcome. Noble metals such as Rh, Ru, Pd, Pt and Ir are very active and more stable against coke deposition and metal sintering than Ni, but the latter is highly available and presents a lower price, which makes Ni more appropriate for

industrial applications. By considering perovskite-type oxides ABO_3, nickel can occupy the B position and also be partially substituted by another metal in order to obtain a structure more stable, resistant to carbon deposition and more active ($ABB'O_3$). As discussed previously, the treatment under reducing atmosphere may cause a collapse of the oxide structure, leading the B and B' metals to be dispersed on the surface of AO_x. The dopant B' may contribute to increase dispersion of B, but B' can also be an active phase.

Ruthenium-substituted $LaCoO_3$ perovskites were investigated as catalytic precursors in the oxidative reforming of diesel for hydrogen production [28] and authors concluded that Co substitution by Ru (i) increased the material reducibility, (ii) led to smaller particle size of La_2O_3 and metallic Co^0 phases and (iii) increased the amount of Ru atoms on the catalyst surface, affecting directly the catalytic behavior: the greater $Co^0 + Ru^0$ exposition and higher extension of the $La_2O_2CO_3$ phase derived from the perovskite structure, the higher the activity and stability of the catalysts.

The effect of replacing nickel by zinc in $LaNi_{1-x}Zn_xO_3$ perovskites ($0 < x < 1$) on the methane dry reforming ($CH_4/CO_2/He = 1/1/1$, 750°C) was studied in ref. [29], showing that, for $x \leq 0.4$, the partial substituted oxides were highly active towards syngas production. Particularly, $LaNi_{0.8}Zn_{0.2}O_3$ presented the highest CH_4 and CO_2 conversions and also the highest resistance to carbon deposition among all the catalysts. Characterization before and after catalytic evaluation showed decomposition of the rhombohedral structure of the perovskite towards metallic Ni^0 and hexagonal La_2O_3 phases (for high Zn content, ZnO and La_2NiO_4 phases also emerged). Authors found out that the partial substitution of Ni by Zn in $LaNiO_3$ increased the reduction temperature of the perovskite, suggesting a more stable structure under reaction conditions which could avoid Ni sintering. For this reason $LaNi_{1-x}Zn_xO_3$ samples ($x \leq 0.4$) presented activity and stability improvements in the methane dry reforming, opposite to the lower activity shown by $LaNiO_3$ and Zn high-content perovskites (the latter containing insufficient active nickel phase). Other investigators claim that $LaNiO_3$-derived catalysts form oxycarbonate species such as $La_2O_2CO_3$ during methane dry reforming, due to CO_2 adsorption on La_2O_3, and these species electronically stabilize nickel particles inhibiting metal sintering [30].

Therefore, the above discussion comprises the application of perovskites for important catalytic reactions and points out the efforts made to better comprehend the role of the active sites on perovskite-type oxides. Investigations focus on elucidating why the *substituting cations* enhance the activity and stability of this type of oxide structure or how they modify the characteristics of the supported metal catalysts obtained from the precursor perovskite under reducing treatments.

More examples are found in details in the literature: [31] studied $LaSrCoO_3$ perovskites and concluded that Sr substitution could increase the amount of chemisorbed oxygen species over the perovskite, improving the catalytic performance in the toluene oxidation. Refs. [32] and [33] showed that by substituting La^{3+} by Ca^{2+} into $LaFeO_3$ lattice, iron valence changed from Fe^{3+} to Fe^{4+}, improving the catalytic performance in oxidation reactions. Similar substitution of La^{3+} by Ca^{2+} into $LaCoO_3$ increased the surface oxygen vacancy density, yielding higher catalytic activities in the propane oxidation [34]. A series of B site substitutions over $LaCoO_3$

perovskite showed that Mn^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} dopants could enhance CO oxidation [35]. All these interesting researches illustrate the relevance of perovskites as catalytic precursors or as active oxides for direct application in heterogeneous catalysis. Efforts on *in situ* studies are a strong tendency and will bring important insights about the physicochemical properties and dynamic transformations of the perovskites under relevant conditions in catalysis.

3. Supporting perovskites on high surface materials as a strategy to enhance catalytic performance

Bulk perovskites prepared via conventional procedures exhibit rather surface area lower than 30 m²/g [36], which strongly limits the application of these materials as catalysts. The La-CoO₃ reported in [37] showed high CO oxidation activity, but authors observed a decrease in the catalytic activity for samples synthesized at high temperatures, which was ascribed to the abrupt loss of surface area. An alternative to overcome this drawback is to support perovskites on traditional porous solid matrices such as Al_2O_3 and SiO_2 in order to spread the perovskite particles and increase the exposed active sites.

LaCoO₃ perovskite (low surface area < 10 m²/g) has been supported on alumina, x%LaCoO₃/γ-Al₂O₃ (x = 10, 20, 40 wt.%) by using a physical mixture and thermal treatment [38], leading to materials with higher surface area: 146, 131 and 96 m²/g, respectively. As the perovskite load increased on alumina (164 m²/g), the overall surface area and mesopore volume decreased due to blocking of support pores. The 40%LaCoO₃/γ-Al₂O₃ catalyst presented the best performance in the CO-SELOX reaction showing the lowest temperature for 50%CO conversion $T_{50\%CO}$ = 168°C, while bulk LaCoO₃ had intermediate activity with $T_{50\%CO}$ = 240°C. The higher effective exposition of the perovskite active phase over the alumina support explains the catalytic performance. The authors estimated the metal cobalt surface from H_2-chemisorption experiments as an indirect measurement of the oxide perovskite dispersion on the alumina surface (since the active catalyst in the CO-SELOX reaction is indeed the oxide perovskite and not the reduced structure, a H_2-reduction pretreatment was exclusively performed only before H_2-chemisorption measurements, and not before the catalytic tests). The supported 40%LaCoO₃/γ-Al₂O₃ perovskite had ca. twice as many metallic area than LaCoO₃ (13.5 and 6.2 m^2/g_{Co}, respectively), which suggests that the particles of oxide perovskite over the alumina-support also presented approximately twice exposed surface area than the bulk perovskite. For this reason, 40%LaCoO₃/γ-Al₂O₃ showed higher CO conversion. Besides, the catalyst with higher load of perovskite showed the highest selectivity to CO_2 (>75%) at the temperature range of 100–170°C, above that the H_2 oxidation side reaction also took place decreasing CO_2 selectivity for all the catalysts. By comparing the performance of 40%LaCoO₃/γ-Al₂O₃ with noble metal-based catalysts, this supported perovskite showed higher selectivity to CO_2 (i.e., 75% at $T_{50\%CO}$ = 168°C) than 1wt% Pt/Al₂O₃ (46%) evaluated in the CO-SELOX at similar conditions of space velocity and isoconversion [39]. The physical mixture between support and perovskite and thermal treatment as described in ref. [38], allowed a tight contact between those phases, but not a uniform spreading of the perovskite over the alumina as revealed by electron microscopy and energy-dispersive X-ray spectroscopy (EDS). In this sense, new methodolo-

gies should be investigated in order to improve the formation of smaller perovskite particles and their uniform distribution on the support. Simple methods such as precipitation, coprecipitation and wet impregnation should be considered.

Once again, these findings indicate that supported perovskites may be a very good alternative for CO-SELOX reaction. Other investigations also took advantage of supporting perovskite oxides on Al_2O_3-La_2O_3 [40], $Ce_{1-x}Zr_xO_2$ [41], ZrO_2 [42] and MCM-41 molecular sieve [43] to enhance the catalytic performance by increasing the number of exposed perovskite active sites.

Also attempts to support perovskites onto a monolithic structure have been reported, onto a metallic [44–46] or ceramic one [35, 46–48]. The ceramic monoliths are usually made of synthetic cordierite, which is wash-coated with γ-Al_2O_3 to increase the contact area between gas phase and solid surface. Monolith, by itself, presents several advantages over conventional catalysts, such as good mass transfer, easier product separation, good thermal and mechanical properties, easy scale up and low pressure drop, making this structure particularly suitable for high gas space velocities. Compared to conventional powdered perovskites used in fixed-bed reactors, monolith-supported perovskites have some unquestionable advantages: the pressure drop remains very low for high-cell density monoliths, and the desired extent of conversion is obtained with a smaller amount of perovskite.

Brackmann *et al.* [47] coated the cordierite substrate with γ-Al_2O_3 by repeating six times the wash-coating procedure and obtained 10 wt.% alumina well dispersed on the cordierite. The alumina had high adherence, since negligible mass loss was verified after the alumina/cordierite pieces underwent ultrasonic bath for 30 min. Then, $LaCoO_3$ synthesized by Pechini route was deposited on?γ-Al_2O_3/cordierite by successive dip coatings, in which 11 immersion cycles led to 10 wt.% mass increment on the support. This technique was efficient for depositing $LaCoO_3$ perovskite on γ-Al_2O_3/cordierite by avoiding formation of other oxides and by promoting a good adherence of the perovskite phase, since only 3.5% mass loss was verified after pieces underwent ultrasonic bath for 30 min. The pH of the perovskite suspension in the presence of γ-Al_2O_3/cordierite was properly controlled to increase electrostatic repulsion among particles and avoid agglomeration. This procedure tends to promote a uniform distribution of the perovskite on the γ-Al_2O_3/cordierite. Figure 4 shows pieces of the cordierite structure coated with γ-Al_2O_3 and $LaCoO_3$/γ-Al_2O_3 calcined at 500 and 700°C, respectively.

$LaCoO_3$/γ-Al_2O_3/cordierite was active for syngas production in the partial oxidation of methane (800°C; CH_4/O_2 = 4/1; 1 atm; W/F = 6.67 × 10^{-5} g_{cat}.min.cm^{-3}) yielding the following byproducts distribution: 42, 54, 3.5% to H_2, CO, CO_2, respectively, at 36% CO conversion for 30 h. The H_2/CO ratio lower than unit was ascribed to the reverse water–gas shift and dry reforming of methane reactions taking place at those conditions [47]. The high stability was discussed in terms of (i) basic properties of La_2O_3 (which originated from the perovskite collapse during activation in H_2), (ii) stable and dispersed cobalt particles onto La_2O_3/Al_2O_3/cordierite, (iii) dispersion of metal cobalt on the top of carbon nanotubes (which grow up at reaction conditions). The monolith structure was pointed out as a promising support to increase the exposition of the perovskite phase, showing excellent adherence properties for γ-Al_2O_3 and $LaCoO_3$.
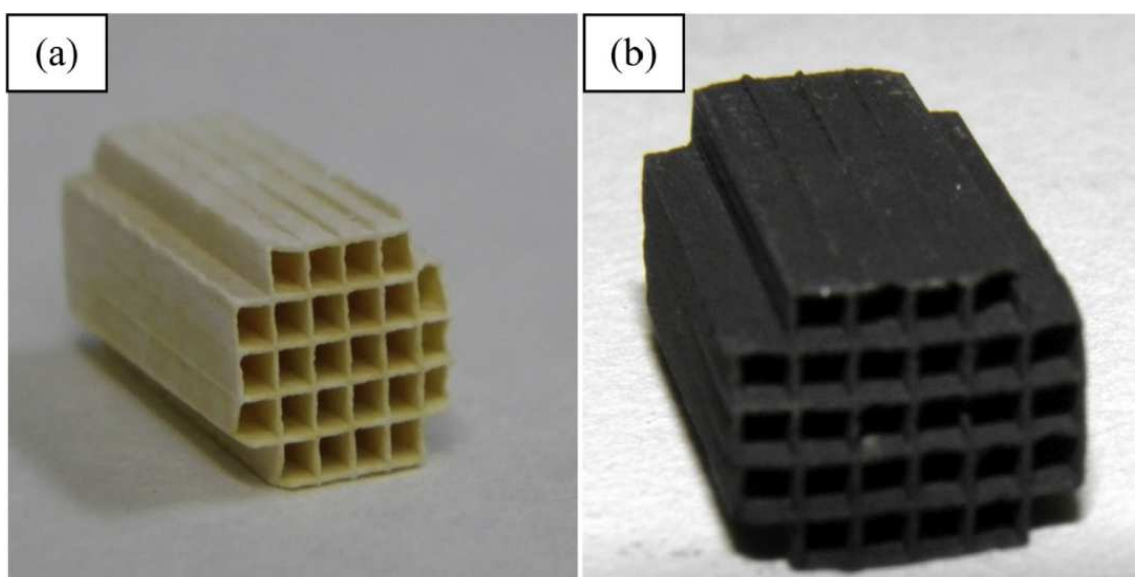
Figure 4. Pieces of honeycomb-type cordierite structure approximately 1.5 cm length, 0.8 cm wide, 0.65 cm high, cell density of 400 cell/in². (a) γ-Al_2O_3/cordierite calcined at 500°C and (b) $LaCoO_3$/γ-Al_2O_3/cordierite calcined at 700°C. Wash-coating and dip coating procedures were efficient to load alumina and perovskite phase onto the honeycomb-type cordierite. The perovskite $LaCoO_3$ was previously prepared by Pechini route. Reprinted from reference [47], copyright (2014) with permission from Hydrogen Energy Publications LLC and Elsevier Ltd.

An important progress on the synthesis of supported perovskites on monolith structure has been reported by ref. [48]. Initially, three different catalysts based on typical $LaCoO_3$ perovskite were obtained as (i) powder $LaCoO_3$ prepared by citrate method, (ii) $LaCoO_3$/monolith prepared by traditional wash-coating and (iii) $LaCoO_3$/monolith directly synthesized by a modified citrate route, all calcined at 650°C/6 h and then tested in the oxidation of CO and hydrocarbons (environmental applications) as a model reaction to validate the direct synthesis, which showed to be simple, sustainable, fast and reproducible. Results confirmed the expected formation of crystalline $LaCoO_3$ for the powdered sample (low surface area 9.8 m²/g) and also over the cordierite (which presented 21 m²/g) for both methods (ii) and (iii). By supporting the perovskite on the cordierite using the traditional wash-coating, a minimum of eight cycles were mandatory to achieve a uniform coating, since only afterwards the XPS revealed the cordierite species to disappear from the surface spectra. SEM images also confirmed that eight cycles were necessary to completely cover the cordierite and form a grain-type morphology. Activity measurements indicated that more than eight cycles (in the wash-coating procedure) did not lead to further significant increase of catalytic activity. Therefore, we can learn from wash-coating method that a significant number of cycles is required as well as lots of labor and time in order to ensure reproducibility and a uniform coating (which is a requisite for high activity).

The direct synthesis of the perovskite on the bare monolith (no γ-Alumina supported in advance) was carried out in a single step by immersing the monolith pieces in a solution containing La^{3+} and Co^{2+} precursors, the piece was then calcined [48]. XPS measurements

proved the interaction between the cordierite and the deposited perovskite, and SEM images indicated a layer of porous perovskite on the cordierite, and this layer can be modulated by using a precursor solution with appropriate concentration and by controlling the immersion time. The directly synthesized $LaCoO_3$/monolith proved to be as effective as the best wash-coated catalyst (obtained after 8 cycles) in the oxidation of CO, C_3H_6 and C_3H_8 (environmental applications) leading to similar performances. Thus, we can learn that the direct method is simpler, faster, reproducible and does not deal with organic solvents, making it very attractive for industrial application through a sustainable process.

4. Conclusion

This chapter presented two strategies to overcome some limitations of perovskite-type oxides in catalysis: (1) the partial substitution of cations, which stabilizes unusual oxidation states of the metal components and creates anionic or cationic vacancies within the perovskite lattice. This is interesting for oxidation reactions, since vacancies can increase oxygen mobility from lattice to surface, increasing the catalytic activity of oxidation or improving the selectivity to products of interest. If the perovskite is a precursor, the partial substitution of cations can increase the reducibility and metal dispersion of the catalyst. The strategy (2) comprises to support perovskites on porous materials like a monolith or a conventional high surface area material to increase the number of exposed perovskite active sites.

Nomenclature

CO-SELOX: carbon monoxide selective oxidation reaction

EDS: energy-dispersive X-ray spectroscopy

EELS: electron energy loss spectroscopy

FTIR: Fourier transform infrared spectroscopy

H_2-TPR: temperature-programmed reduction (by H_2)

O_2-TPD: temperature-programmed desorption of oxygen

SEM: scanning electron microscopy

TEM: transmission electron microscopy

VOCs: volatile organic compounds

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

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