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Novel Catalytic Systems for Hydrogen Production via the Water-Gas Shift Reaction

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The present work reports on the development of new catalysts for the production of hydrogen via the water-gas shift (WGS) reaction. In particular, the effect of Ce/La atom ratio on the catalytic performance of 0.5 wt% Pt supported on $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8, 1.0$) mixed metal oxides for the WGS reaction was investigated. It was found that the addition of 20 at.% La^{3+} in CeO_2 lattice increased significantly the catalytic activity and stability of 0.5 wt%Pt/ $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ solid. More precisely, a lower amount of “carbon” was accumulated on the catalyst surface, whereas surface acidity and basicity studies showed that $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ had the highest concentration of labile oxygen and acid sites, and the lowest concentration of basic sites compared to the other $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ mixed metal oxide supports ($x = 0.2, 0.5, 0.8$).

1. Introduction

The heterogeneously catalyzed water-gas shift reaction is an important part of the reaction network for hydrogen production through steam reforming of hydrocarbons, sugars, alcohols, and biooil [1–5]. The reaction is reversible, moderately exothermic, and equilibrium limited:

The WGS reaction can be used to produce H_2 and reduce the level of CO in a hydrogen product stream to less than 10 ppm for fuel cell applications, since CO is deleterious for the fuel cell's electrodes [6]. In the last two decades, the interest of the scientific community for low-temperature WGS (LT-WGS) reaction has grown significantly as a result of the advancements made in fuel cell technologies for electricity production [7].

The conventional WGS catalysts which are used in the industry for more than 70 years are $\text{Fe}_3\text{O}_4/\text{Cr}_2\text{O}_3$ for operation at the high-temperature range of 350–450°C, and

$\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ at the low-temperature range of 180–250°C. These industrial catalysts require long-time period for activation and are pyrophoric, features that make them inappropriate for fuel cells applications [8]. Thus, it is necessary to develop new catalysts, highly preferable to improve the existing WGS catalytic technology, especially at temperatures lower than 250°C. Typical characteristics of novel WGS catalysts should include high stability and activity, no need for activation prior to use, and no pyrophoricity. In recent years, supported Pt catalysts (0.1–0.5 wt% Pt) using CeO_2 and CeO_2 -based supports have been widely studied [9–16]. Jeong et al. [12] have found that Pt/ $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ exhibits higher CO conversions than Pt/ $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ due to the higher Pt dispersion achieved, easier reducibility of support, lower activation energy, and higher oxygen storage capacity (OSC), properties which were induced by the cubic structure and composition of $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ solid support. Linganis et al. [15] reported that Pt/ $\text{Ce}_{0.5}\text{Ca}_{0.5}\text{O}_{1.5}$ catalyst exhibited the best catalytic performance compared to Pt/ CeO_2 . However, it has been reported that under typical conditions of a reformer

outlet, a progressive deactivation of the catalyst takes place. This has been attributed to the irreversible reduction of support [17] and/or to the formation of stable carbonates on the catalyst surface during reaction [8, 18], along with sintering of the metallic phase [19, 20]. It has been reported [8] that the addition of basic oxides to Pt/CeO₂ increases its catalytic activity and stability, favors formate decomposition (formate being considered as an *active* reaction intermediate), and improves ceria reduction.

WGS is generally accepted to occur with the participation of both the metallic and support phases (bifunctional catalytic reaction). Two mechanistic schemes were mainly proposed in the literature [16, 21–23] over reducible metal oxide-supported metal catalysts: (i) the *regenerative or redox* mechanism, and (ii) the *adsorptive or associative* mechanism (nonredox). The nature and true location of these active intermediates (support, metal-support interface or metal) are still controversial.

In the present study, we report the behavior of new Ce_{1-x}La_xO_{2-δ} materials used as supports of Pt noble metal. In particular, the catalytic performance of 0.5 wt% Pt/Ce_{1-x}La_xO_{2-δ} catalysts is investigated with respect to the ratio of Ce/La in the support composition. The aim of this work is to develop stable and sufficiently active LT-WGS catalysts. A physicochemical characterization of catalysts using a variety of techniques, such as XRD, BET, SEM, H₂-TPR, TPD-NH₃, and TPD-CO₂, is presented in an attempt to correlate the physicochemical properties of catalysts with their catalytic activity (CO conversion, X_{CO}, %). Moreover, TPO experiments were carried out in order to measure the amount of carbonaceous species accumulated on the catalyst surface under reaction conditions.

2. Experimental

2.1. Catalyst Preparation. The Ce_{1-x}La_xO_{2-δ} ($x = 0.0, 0.2, 0.5, 0.8, 1.0$) supports were prepared by the citrate sol-gel method, where citric acid was used as complexing agent. The metal (M) to complexing agent (CA) ratio was kept to M:CA = 1:1.5, and pretreatment in air (calcination) at 600°C for 10 h was performed. More details on the procedure followed are described elsewhere [24].

The supported Pt catalysts were prepared by the wet impregnation method, using an aqueous solution of H₂PtCl₆·6H₂O (Aldrich). A given amount of precursor solution corresponding to 0.5 wt% Pt loading was used to impregnate the metal oxide support in powder form at 70°C for 4 h. The resulting slurry was dried overnight at 120°C and stored for further use.

2.2. Catalyst Characterization

2.2.1. Ex Situ Powder X-Ray Diffraction (PXRD). Powder X-ray diffraction patterns of Ce_{1-x}La_xO_{2-δ} ($x = 0.0, 0.2, 0.5, 0.8$ and 1.0) solids were collected in the 20–80° 2θ range (scan speed = 2°/min) after calcination in air at 600°C for 10 h, using a Shimadzu 6000 Series Diffractometer (CuKα radiation, λ = 1.5418 Å). The lattice parameter (α) was calculated based on

the following formula, which holds for the fcc structure [25]:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2}, \quad (2)$$

where h , k , and l are the Miller indices.

2.2.2. BET Surface Area Measurements. The texture of the porous solids after calcination in air at 600°C for 10 h was studied by nitrogen adsorption-desorption isotherms at 77 K using a surface area and pores size analyzer (Micromeritics, Gemini model). Before measurements, the samples were degassed at 300°C for 1 h in N₂ gas flow to remove adsorbed atmospheric water and most of CO₂.

2.2.3. Scanning Electron Microscopy (SEM). A Vega Tescan 5136LS scanning electron microscope was used to study the morphology of the secondary particles of Ce_{1-x}La_xO_{2-δ} solids after calcination at 600°C for 10 h. Powdered specimens were spread on the SEM slabs and sputtered with gold. The acceleration voltage was set at 20 kV.

2.2.4. Hydrogen Temperature-Programmed Reduction (H₂-TPR). Hydrogen temperature-programmed reduction (H₂-TPR) studies were conducted in a specially designed gas flow system previously described [26]. Before H₂-TPR experiments, the sample (0.2 g) was first calcined in a 20 vol% O₂/He gas mixture at 600°C for 2 h, purged in He flow for 15 min, and then quickly cooled to 30°C. The feed was then switched to a 2 vol% H₂/Ar (50 NmL/min) gas flow, and the temperature of the solid was increased from room temperature to 800°C in order to carry out a TPR run (30°C/min). The H₂ ($m/z = 2$) and H₂O ($m/z = 18$) signals in the mass spectrometer were continuously monitored in order to follow the kinetics of solid reduction. The H₂-TPR traces obtained were expressed as reduction rate, R_{H_2} (μmol H₂/g·min) versus temperature, after calibrating the MS signal with a standard 4.93 vol% H₂/He gas mixture and using the appropriate material balance equation.

2.2.5. Acidity (TPD-NH₃) and Basicity (TPD-CO₂) Studies. Temperature-programmed desorption (TPD) of NH₃ and CO₂ experiments were conducted in order to probe the surface acidity and basicity characteristics of the Ce_{1-x}La_xO₂ materials. The amount of sample used was 0.3 g, the heating rate was 30°C/min, and the He gas flow rate was 30 NmL/min. The mass numbers (m/z) 15, 30, and 44 were used for NH₃, NO, and N₂O (TPD-NH₃), while the (m/z) 28 and 44 were used for CO and CO₂, respectively (TPD-CO₂). Ammonia (1.11 vol% NH₃/He) or carbon dioxide (5 vol% CO₂/He) chemisorption was conducted at room temperature for 30 min. Before NH₃ or CO₂ chemisorption, the sample was pretreated in 20 vol% O₂/He at 600°C for 2 h.

2.3. Catalytic Performance Studies. The experimental setup used for evaluating the catalytic performance of the solids was described elsewhere [27]. 0.5 g of catalyst sample was loaded into the reactor and precalcined at 600°C (20 vol% O₂/He) for 2 h and then reduced at 300°C (1 bar H₂) for 2 h prior to any measurements. The WGS reaction feed stream used in all

FIGURE 1: Powder XRD patterns of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8$) solids following calcination in air at 600°C for 10 h. (a) CeO_2 , (b) $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$, (c) $\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$, and (d) $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$. $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid solution: ★, CeO_2 : ■.

experiments was 3 vol% CO , 10 vol% H_2O , and 87 vol% He , and the total gas flow rate was 200 NmL/min. The CO conversion was estimated using the following relationship (3):

$$X_{\text{CO}} (\%) = \frac{(F_{\text{CO}}^{\text{in}} - F_{\text{CO}}^{\text{out}})}{F_{\text{CO}}^{\text{in}}} \times 100, \quad (3)$$

where $F_{\text{CO}}^{\text{in}}$ and $F_{\text{CO}}^{\text{out}}$ are the molar flow rates (mols/min) of CO at the reactor inlet and outlet, respectively.

2.4. Characterization of “Carbon” Formed by Transient Experiments. The amounts of carbon-containing (“carbon”) intermediate species that accumulate on the catalyst surface after 4 h and 70 h of continuous WGS reaction at 325°C and their reactivity towards oxygen were studied as follows. Following WGS reaction (3 vol% $\text{CO}/10$ vol% $\text{H}_2\text{O}/\text{He}$), the catalyst was heated to 800°C in He flow to remove adsorbed water, CO_2 , and/or carbonaceous deposits that could thermally decompose in He flow. The reactor was then cooled quickly in He flow to room temperature, and the gas flow was switched to a 2 vol% O_2/He gas mixture for a temperature-programmed oxidation (TPO) experiment ($\beta = 30^\circ\text{C}/\text{min}$). The H_2 and CO_2 mass spectrometer signals were monitored until they reached their respective baseline value. The H_2 ($m/z = 2$) and CO_2 ($m/z = 44$) MS signals were recorded continuously. Quantification of the H_2 and CO_2 signals was made using standard calibration gas mixtures in He diluent gas for H_2 (4.93 vol% H_2/He) and CO_2 (985 ppm CO_2/He). Transient experiments were conducted in a specially designed gas flow system previously described [26].

3. Results and Discussion

3.1. Structural, Textural, and Morphological Properties of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ Solid Support

3.1.1. Ex Situ Powder X-Ray Diffraction (PXRD) Studies. Figure 1 shows XRD patterns of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ (0078 = 0.0, 0.2, 0.5, 0.8) solids following calcination in air at 600°C for

10 h. In the case of CeO_2 (Figure 1(a)), characteristic peaks of the fcc cubic fluorite structure are noticed [8]. The XRD patterns of mixed metal oxides (Figures 1(b)–1(d)) showed the same diffraction peaks as of CeO_2 , and no other crystalline phases were observed. The above results indicate that the fluorite cubic structure is preserved in the whole range of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ composition investigated ($x = 0.0, 0.2, 0.5, 0.8$). In the case of solids with high La content ($\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$ and $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$), no crystalline phase of lanthana was observed. Nanocrystalline La_2O_3 can be potentially formed, but it might have escaped the XRD detection (>4 nm). All XRD peaks of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.2, 0.5, 0.8$) appear shifted to lower 2θ angles compared to those due to pure ceria. This shift implies that some La^{3+} has been incorporated into the CeO_2 fluorite structure, thus, leading to the expansion of ceria lattice (atomic radii of Ce^{4+} : 0.97 Å and La^{3+} : 1.17 Å) and to the formation of a Ce-La-O solid solution.

Table 1 lists values of the primary crystallite size (d , nm), $d(111)$ (Å), lattice parameter, a (Å), and cell volume ($\text{\AA}^3$) for the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids based on the XRD studies performed. The primary crystallite size of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ was calculated based on the Scherrer formula [28] and the FWHM of the (111) reflection. The primary crystallite size of CeO_2 was found to be 19.5 nm, while a significant decrease to 7.7–3.3 nm after doping of ceria with La^{3+} is obtained; as the La^{3+} content increases, the primary crystallite size decreases. It was found that no significant changes in the mean primary crystallite size were obtained after calcination of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ at 600°C for 42 h compared to 10 h (Table 1), a result that indicates the good thermal stability of the prepared Ce-La-O solids.

3.1.2. BET Surface Area Measurements. Table 2 summarizes the specific surface area, SSA ($\text{m}^2\cdot\text{g}^{-1}$), specific pores volume, V_p ($\text{cm}^3\cdot\text{g}^{-1}$), and average pores size, d_p (nm) obtained over the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids. It is clearly observed that the SSA of $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ solid is the highest among the other materials, while SSA becomes lower with increasing La^{3+} content in the material. Alifanti et al. [29] reported that as Zr^{4+} content increases, the SSA of $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ solid drops. The V_p of the mixed metal oxides was found to be larger than that of single-phase oxides (Table 2). The d_p was found to decrease by 39% after incorporating 20 at.% La^{3+} in the CeO_2 lattice, and this becomes higher with increasing La^{3+} content in the material.

Based on the diffraction peak (111) and (2), the lattice parameter a (Å) of each solid was calculated. The latter was found to be 5.4057 Å for CeO_2 (Table 1), which is smaller than that estimated for the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid solution. The lattice parameter (a) increased by 1, 3, and 4% after 20, 50, and 80 at.% La^{3+} incorporation in the ceria lattice, respectively. The cell volume ($\text{\AA}^3$) values obtained indicate the expansion of ceria lattice after La^{3+} introduction.

3.1.3. Scanning Electron Microscopy (SEM). Figure 2 presents SEM micrographs of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.8$) solids after calcination at 600°C for 10 h. A spongy morphology was

TABLE 1: Lattice parameters of the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ mixed metal oxides, primary crystallite size (d , nm), $d(111)$ ($\text{\AA}$), lattice parameter, a ($\text{\AA}$), and cell volume ($\text{\AA}^3$).

Sample	d (nm)	$d(111)$ ($\text{\AA}$)	a ($\text{\AA}$)	Cell volume ($\text{\AA}^3$)
CeO_2	19.5	3.1210	5.4057	157.96
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$	7.7	3.1580	5.4698	163.65
$\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$	4.6	3.2173	5.5725	173.04
$\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$	3.3	3.2580	5.6430	179.69

TABLE 2: BET-specific surface area (SSA, $\text{m}^2\cdot\text{g}^{-1}$), specific pores volume (V_p , $\text{cm}^3\cdot\text{g}^{-1}$), and average pores size (d_p , nm) obtained over $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids.

Sample	SSA ($\text{m}^2\cdot\text{g}^{-1}$)	V_p ($\text{cm}^3\cdot\text{g}^{-1}$)	d_p (nm)
CeO_2	14.5	0.029	6.7
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$	42.1	0.059	4.1
$\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$	22.4	0.059	7.9
$\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$	14.3	0.041	9.3
La_2O_3	6.7	0.017	9.3

achieved in all cases, with a mean secondary particle size of about 200 nm.

3.2. Surface Properties of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ Solid Support

3.2.1. Hydrogen Temperature-Programmed Reduction (H_2 -TPR) Studies. Figure 3 presents H_2 -TPR traces of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids following calcination in 20 vol% O_2/He at 600°C for 2 h. The H_2 -TPR profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ present mainly two hydrogen consumption peaks. The low-temperature hydrogen reduction peak observed in the 370 – 700°C range is due to metal oxide surface reduction, whereas above 700°C is due to bulk reduction [30, 31]. It is seen that doping of ceria with 20 at.% La^{3+} facilitates its reduction process, shifting surface reduction profile to lower temperatures. Instead, after the addition of 50 and 80 at.% La^{3+} in ceria lattice, reduction of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ becomes more difficult, and surface reduction profile is shifted to higher temperatures. By integrating the H_2 -TPR trace, the amount of H_2 consumed and the concentration of labile lattice oxygen species can be obtained. The $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$ solid presents the highest amount of H_2 consumed ($437 \mu\text{mol/g}$), whereas $\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$ the lowest one ($282 \mu\text{mol/g}$). The amount of H_2 consumed for $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ and CeO_2 was found to be 400 and $339 \mu\text{mol/g}$, respectively. The $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ support exhibits the highest concentration of labile oxygen species, and this property is correlated with its highest catalytic activity (Section 3.3).

3.2.2. Acidity (TPD- NH_3) and Basicity (TPD- CO_2) Studies. Figure 4 presents TPD- NH_3 profiles recorded over $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids ($x = 0.0, 0.2, 0.5, 0.8$). It is observed that doping ceria with 20 at.% La^{3+} increases the concentration of weak and medium strength acid sites (e.g., peak intensity increase at $>200^\circ\text{C}$) and presents one additional peak at higher temperatures (450 – 600°C), which corresponds to strong acid sites. Increasing further the La^{3+} content to 50

and 80 at.% in the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid results in a decrease of the concentration of weak and medium strength acid sites, while the peak which corresponds to strong acid sites shifted to higher temperatures (550 – 800°C). By integrating the TPD- NH_3 response curves, the total concentration of surface acid sites can be estimated. This was found to be 27, 42, 26, and $23 \mu\text{mol/g}$ for $x = 0.0, 0.2, 0.5$, and 0.8 , respectively. These results indicate that $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ presents the highest concentration of surface acid sites compared with the other supports. It is pointed out that there is a correlation between BET-specific surface area ($\text{m}^2\cdot\text{g}^{-1}$) and acid sites ($\mu\text{mol/g}$). In particular, it is observed that the concentration of acid sites increases with increasing specific surface area ($\text{m}^2\cdot\text{g}^{-1}$) of the solid support.

Figure 5 presents TPD- CO_2 profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8$) solids. Pure CeO_2 presents five desorption peaks centered at 68, 128, 160, 250, and 650°C , and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ solid exhibits also five desorption peaks (70, 125, 275, 690, and 780°C). $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$ exhibits four desorption peaks centered at 68, 140, 370, and 800°C , whereas $\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$ exhibits three desorption peaks slightly shifted to lower temperatures (50, 340, and 780°C). The peak at the highest temperature (600 – 800°C) is due to strongly bounded carbonate species. Increasing the La^{3+} content in the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid to 50 and 80 at.% results in the increase of peak area corresponding to strong basic sites, indicating the enhancement in the concentration of strong basic sites. These results indicate that La^{3+} induces the formation of strong basic sites on the surface of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids [32]. Zhang et al. [33] found that CO_2 desorption from CeO_2 and Ce-La-O solids depends on the ratio of Ce/La . In particular, CO_2 desorption from CeO_2 takes place mainly at low temperatures (ca. 120°C) [33]. In the case of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid solution, with Ce content higher than 50 at.%, the main CO_2 desorption peak appeared at 180°C , and for Ce content lower than 50 at.%; a CO_2 desorption peak at 296°C was reported [33]. The strong influence of La^{3+} in tuning the surface basicity of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ is illustrated in the inset of Figure 5. In principle, the species that act as surface acid and basic centers are coordinatively unsaturated metal cations (Lewis acid) and oxygen anions (Lewis base), respectively. Hydroxylation results in surface $-\text{OH}$ groups, which can have acid or base character (Brønsted theory) depending on the polarisation strength of the hydroxyl group and the influence of the chemical environment [34].

The total concentration of surface basic sites was found to be 780, 256, 104, and $47 \mu\text{mol/g}$ for $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$, $\text{Ce}_{0.5}\text{La}_{0.5}\text{O}_{2-\delta}$, $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$, and CeO_2 , respectively. These results corroborate that surface basicity increases with increasing La^{3+} content in the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid. It is noted that no correlation was found between the BET area and the total concentration of basic sites for the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids, suggesting that the site density of basic sites (no sites/ nm^2) is different for each of the $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solid.

3.3. Catalytic Performance Studies. Figure 6 presents catalytic performance results in terms of CO conversion (X_{CO} , %) as a function of WGS reaction temperature over the 0.5 wt%

FIGURE 2: SEM images of (a) CeO_2 , (b) $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_{2-\delta}$ and (c) $\text{Ce}_{0.2}\text{La}_{0.8}\text{O}_{2-\delta}$ solids after calcination in air at 600°C for 10 h.

FIGURE 3: H_2 -TPR profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids ($x = 0.0, 0.2, 0.5, 0.8$).

FIGURE 5: TPD- CO_2 profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ mixed metal oxides ($x = 0.0, 0.2, 0.5, 0.8$).

FIGURE 4: TPD- NH_3 profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids ($x = 0.0, 0.2, 0.5, 0.8$).

$\text{Pt}/\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8$, and 1.0) catalysts. It is shown that Pt/CeO_2 is more active than $\text{Pt}/\text{La}_2\text{O}_3$. It is clearly seen that doping of ceria with La^{3+} at the level of 20 at.% improves the catalytic performance of 0.5 wt% Pt

FIGURE 6: Effect of support chemical composition on the conversion of CO as a function of WGS reaction temperature over 0.5 wt% $\text{Pt}/\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8, 1.0$) solids.

FIGURE 7: TPO (2% O₂/He) profile obtained over 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} and 0.5 wt% Pt/Ce_{0.2}La_{0.8}O_{2-δ} solids after WGS reaction for 70 h and 4 h on stream, respectively.

deposited on the support towards the WGS reaction. For example, at 275°C the CO conversion increased by a factor of 1.3 after doping ceria with 20 at.% La³⁺. However, there is a threshold for the La³⁺-induced improvement, since the increase in La³⁺-dopant concentration up to 80 at.% resulted in a significant decrease in the CO conversion. In particular, at 275°C the CO conversion decreased by a factor of 3.0 after increasing La³⁺ dopant concentration in the support from 20 to 80 at.%. It is noted that no methane was formed within the whole temperature range over the Pt/Ce_{1-x}La_xO_{2-δ} solids, showing that these systems do not facilitate the undesirable methanation reaction ($\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$).

As indicated in the H₂-TPR studies (Section 3.2.1), the Ce_{0.8}La_{0.2}O_{2-δ} support presents the highest rate of H₂ consumption at low temperatures (<400°C), which is attributed to the availability of labile oxygen species (O/OH) that can potentially migrate from the support to the metal surface through the metal-support interface, leading eventually to CO oxidation over the Pt surface. Thus, the superior activity observed with the Ce_{0.8}La_{0.2}O_{2-δ} support could be understood based on the chemical composition of the particular support which led to minimum Ce⁴⁺/Ce³⁺ reduction energy thus higher oxygen mobility. The latter appears as a very important parameter in the kinetics of WGS reaction [23, 35, 36].

Based on the TPD-NH₃ studies, a clear correlation between catalyst surface acidity and WGS activity is observed. The order of surface acid sites concentration was as follows: Pt/Ce_{0.8}La_{0.2}O_{2-δ} > Pt/CeO₂ > Pt/Ce_{0.5}La_{0.5}O_{2-δ} ≈ Pt/Ce_{0.2}La_{0.8}O_{2-δ}. It should be noted that the catalytic activity followed also the same order. These results point out that the best (Pt/Ce_{0.8}La_{0.2}O_{2-δ}) and worst (Pt/Ce_{0.5}La_{0.5}O_{2-δ} and Pt/Ce_{0.2}La_{0.8}O_{2-δ}) catalyst compositions exhibit the highest and lowest concentrations of surface acid sites, respectively. According to the H₂-TPR and TPD-NH₃ studies, Pt/Ce_{0.8}La_{0.2}O_{2-δ} with the best catalytic activity exhibits also the highest concentration of M^{x+}-O^{y-} sites (present in the support) that potentially participate in the WGS via

FIGURE 8: Stability test recorded during WGS reaction at 325°C over the 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} catalyst.

the dissociative chemisorption of water to form active -OH groups.

Regarding the surface basicity of the five Ce_{1-x}La_xO_{2-δ} ($x = 0.0, 0.2, 0.5, 0.8$, and 1.0) solids, it is seen that the addition of 20 at.% La³⁺ in ceria lattice causes an increase in the population of weak to medium strength surface basic sites and the formation of strong basic sites. Increasing the La³⁺ content in the Ce_{1-x}La_xO_{2-δ} solid (50, 80 at.%) results in a significant enhancement of the concentration of strong basic sites. The highest CO conversion obtained over Pt/Ce_{0.8}La_{0.2}O_{2-δ} might be related to the enhancement of weak to medium basic sites in the support. It is well known [37] that support basicity enhances the water dissociation, leading to the formation of active -OH species. The enhancement of basic sites in the support leads also to the promotion of carbon gasification ($\text{C} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$) [37–39]. The lower CO conversion observed in La³⁺-rich catalysts (Pt/Ce_{0.5}La_{0.5}O_{2-δ} and Pt/Ce_{0.2}La_{0.8}O_{2-δ}) may be due to the presence of strong basic sites in the respective support.

According to the above results, the best catalytic activity performance obtained with the Pt/Ce_{0.8}La_{0.2}O_{2-δ} solid could be explained based on the “redox” and “associative” WGS reaction mechanisms. In the “redox” mechanism, CO is first adsorbed on the metal (e.g., Pt), where it is then diffused towards the metal-support interface. At this place it reacts with surface lattice oxygen of support to produce CO₂, where at the same time Ce⁴⁺ is reduced to Ce³⁺ by the creation of an oxygen vacancy. The catalytic cycle is closed by the reoxidation of support via water chemisorption (fill in of the oxygen vacancy) to form H₂. The reduction of support is also involved in the “associative” mechanism. In particular, in this mechanism, CO is first adsorbed on Pt and diffuses then towards the metal-support interface, where it reacts with -OH groups to form formate (HCOO⁻) or carboxyl (-COOH) species, which then decompose by the likely aid of Pt to form CO₂; H. Kalamaras et al. [40] proposed that the WGS reaction on Pt/CeO₂ at 200°C is governed by a “redox”

mechanism, while at 300°C the “associative formate with –OH group regeneration” mechanism applies but to a small extent compared to the “redox” mechanism.

3.4. Amount of Carbonaceous Species Formed during WGS Reaction and Catalyst Stability. Figure 7 presents CO₂ transient response curves obtained during TPO studies (2 vol% O₂/He flow) performed over the 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} and 0.5 wt% Pt/Ce_{0.2}La_{0.8}O_{2-δ} solids run for 4 h in WGS reaction. The 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} catalyst showed two CO₂ peaks at 610 and 780°C, which correspond to the oxidation of two different kinds of carbonaceous species, formed under WGS reaction conditions. On the other hand, the 0.5 wt% Pt/Ce_{0.2}La_{0.8}O_{2-δ} catalyst presents only one peak centered at 800°C, which suggests the formation of a less reactive “carbon-containing” intermediate formed on the catalyst surface during WGS. The total amount of “carbon” formed was found to be 1.8 and 14.5 μmol/g for the 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} and 0.5 wt% Pt/Ce_{0.2}La_{0.8}O_{2-δ} catalysts, respectively. The latter result shows that the lowest catalytic activity observed over the 0.5 wt% Pt/Ce_{0.2}La_{0.8}O_{2-δ} solid could be partially associated with the “carbon” deposits, which may result to a gradual deactivation of the catalyst. It has been reported [18] that deactivation of Pt/CeO₂ during WGS is due to the formation of carbonates on the catalyst surface. The carbonates cover the support surface and could block also the Pt-support interface. As mentioned above, the 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} catalyst has shown the highest concentration of weak to medium basic sites, which leads to the promotion of “carbon” gasification thus to catalyst stability, as presented in Figure 8. The catalyst was tested for 70 h of continuous WGS reaction at 325°C, where the CO conversion decreased from 86 to 74% (14% drop in activity over 70 h on reaction stream). Temperature-programmed oxidation (TPO) experiments performed after 70 h of continuous WGS reaction allowed to estimate the amount of “carbon” accumulated on the catalyst surface, which was found to be 10.2 μmol/g. It is pointed out that this amount was found to be lower than that estimated for the Pt/Ce_{0.2}La_{0.8}O_{2-δ} catalyst after only 4 h of WGS reaction.

4. Conclusions

The atom ratio of Ce/La in Ce_{1-x}La_xO_{2-δ} solid largely affects its structural, textural, surface, and bulk properties and in turn the catalytic performance towards WGS reaction performed on Pt supported on it. The 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} (Ce/La = 4) catalyst exhibits the best catalytic performance and stable activity for a long period (70 h of testing). The same catalytic composition presents the highest concentration of labile oxygen species, acid sites and weak to medium strength of basic sites, and the lowest amount of accumulated “carbon.” Based on the open literature, the present 0.5 wt% Pt/Ce_{0.8}La_{0.2}O_{2-δ} catalyst exhibits high WGS activity at $T < 300^\circ\text{C}$, a result that makes this system as a starting point for the optimization of its composition for further enhancement of its catalytic activity.

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