Conference Paper

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 Ce 1−x La x O 2−δ (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/Ce 0.8 La 0.2 O 2−δ solid. More precisely, a lower amount of “carbon” was accumulated on the catalyst surface, whereas surface acidity and basicity studies showed that Ce 0.8 La 0.2 O 2−δ had the highest concentration of labile oxygen and acid sites, and the lowest concentration of basic sites compared to the other Ce 1−x La x O 2−δ 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:

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2, \quad \Delta H^\circ = -41 \text{ kJ/mol} \] (1)

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 Fe 3 O 4 /Cr 2 O 3 for operation at the high-temperature range of 350–450°C, and Cu/ZnO/Al 2 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 cell 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/Ce 0.8 Zr 0.2 O 2 exhibits higher CO conversions than Pt/Ce 0.2 Zr 0.8 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 Ce 0.8 Zr 0.2 O 2 solid support. Linganiso et al. [15] reported that Pt/Ce 0.5 Ca 0.5 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/CeO$_2$ increases its catalytic activity and stability, favors formate decomposition (formate being considered as an active reaction intermediate), and improves ceria reduction.

WGSR 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$_x$O$_{2−δ}$ materials used as supports of Pt noble metal. In particular, the catalytic performance of 0.5 wt% Pt/Ce$_{1−x}$La$_x$O$_{2−δ}$ 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, H$_2$-TPR, TPD-NH$_3$, and TPD-CO$_2$, 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$_x$O$_{2−δ}$ ($x = 0.0, 0.2, 0.5, 0.8, 1.0$) 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 H$_2$PtCl$_6$·6H$_2$O (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$_x$O$_{2−δ}$ ($x = 0.0, 0.2, 0.5, 0.8$ 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]:

\[
a = d_{hkl} \sqrt{h^2 + k^2 + l^2},
\]

where $h, k, l$ 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 N$_2$ gas flow to remove adsorbed atmospheric water and most of CO$_2$.

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$_x$O$_{2−δ}$ 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 (H$_2$-TPR). Hydrogen temperature-programmed reduction (H$_2$-TPR) studies were conducted in a specially designed gas flow system previously described [26]. Before H$_2$-TPR experiments, the sample (0.2 g) was first calcined in a 20 vol% O$_2$/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% H$_2$/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 H$_2$ ($m/z = 2$) and H$_2$O ($m/z = 18$) signals in the mass spectrometer were continuously monitored in order to follow the kinetics of solid reduction. The H$_2$-TPR traces obtained were expressed as reduction rate, $R_C$ (μmol H$_2$/g-min) versus temperature, after calibrating the M$S$ signal with a standard 4.93 vol% H$_2$/He gas mixture and using the appropriate material balance equation.

2.2.5. Acidity (TPD-NH$_3$) and Basicity (TPD-CO$_2$) Studies. Temperature-programmed desorption (TPD) of NH$_3$ and CO$_2$ experiments were conducted in order to probe the surface acidity and basicity characteristics of the Ce$_{1−x}$La$_x$O$_2$ 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 NH$_3$, NO, and N$_2$O (TPD-NH$_3$), while the ($m/z$) 28 and 44 were used for CO and CO$_2$, respectively (TPD-CO$_2$). Ammonia (1.11 vol% NH$_3$/He) or carbon dioxide (5 vol% CO$_2$/He) chemisorption was conducted at room temperature for 30 min. Before NH$_3$ or CO$_2$ chemisorption, the sample was pretreated in 20 vol% O$_2$/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% O$_2$/He) for 2 h and then reduced at 300°C (1 bar H$_2$) for 2 h prior to any measurements. The WGSR reaction feed stream used in all
实验在3 vol% CO, 10 vol% H2O, and 87 vol% He中进行，总气流率为200 NmL/min。CO的转化率是通过以下关系（3）估算的。

\[ X_{CO} = \frac{F_{CO}^{in} - F_{CO}^{out}}{F_{CO}^{in}} \times 100 \tag{3} \]

其中，\(F_{CO}^{in}\)和\(F_{CO}^{out}\)是进气和出气的CO摩尔流率（mol/min）。

2.4. “碳”形成的特性。碳化合物（“碳”）作为一种中间物种在催化剂表面积累，导致连续WGS反应（325°C）和氧气的反应性。WGS反应（3 vol% CO/10 vol% H2O/He）的催化剂在He气流中被加热到800°C。在WO2流下，CO2和/或碳化物沉积在催化剂表面并可能转化为其他物种。反应后，催化剂在He气流中快速冷却。在进气流下，反应后温度和气流速度增加到2 vol% O2/He的气流中，形成一个温度程序氧化（TPO）实验（\(T = 300°C/min\)）。H2和CO2质量信号在达到各自的基线值时被监测。H2（\(m/z=2\））和CO2（\(m/z=44\））MS信号连续记录。H2和CO2信号的定量使用标准校准气混合物在He气流中的H2和CO2（985 ppm CO2/He）。这些实验在专项设计的气流系统中进行。

3. 结果和讨论

3.1. 结构、纹理和形态学特性

3.1.1. 原位粉末X射线衍射（PXRD）研究

图1显示了Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)（\(x = 0.0, 0.2, 0.5, 0.8\））固体在600°C的气流中形成的XRD图案。在10 h的CeO\(_2\)（图1(a)）中，fcc立方晶格结构的特征峰被注意到[8]。混合金属氧化物的XRD模式（图1(b)–1(d)）显示了相同的特征峰，但没有其他晶型被观察到。这些结果表明，氧化催化剂在Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)（\(x = 0.0, 0.2, 0.5, 0.8\））中，没有其他晶型被观察到。在高La含量的Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)和Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)中，没有观察到新的晶型，La氧合的生长观察到。具有La氧合的CeO\(_2\)可以被潜在地形成，但它可能已经逃逸了XRD检测（>4 nm）。所有WGS反应的Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)（\(x = 0.2, 0.5, 0.8\））在600°C下42 h的气流相比10 h（表1），结果表明催化剂良好的热稳定性。

3.1.2. BET表面积测量

表2总结了特定表面积，SSA（m\(^2\)/g），具体孔体积，\(V_p\)（cm\(^3\)/g），以及平均孔径，\(d_p\)（nm）在气流中得到的Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)固体。很容易看出SSA的Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)固体在高于其他材料时最高，而SSA在42 h的气流中比10 h（表1），结果表明催化剂良好的热稳定性。)

3.1.3. 扫描电子显微镜（SEM）

图2显示了Ce\(_{1-x}\)La\(_x\)O\(_{2-\delta}\)（\(x = 0.0, 0.2, 0.8\））固体在600°C的气流中形成的SEM显微图。
Table 1: Lattice parameters of the Ce$_{1-x}$La$_x$O$_{2-δ}$ mixed metal oxides, primary crystallite size ($d$, nm), $d(111)$ ( Å), lattice parameter, $\alpha$ (Å), and cell volume (Å$^3$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$ (nm)</th>
<th>$d(111)$ (Å)</th>
<th>$\alpha$ (Å)</th>
<th>Cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>19.5</td>
<td>3.1210</td>
<td>5.4057</td>
<td>157.96</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$La$</em>{0.2}$O$_{2-δ}$</td>
<td>7.7</td>
<td>3.1580</td>
<td>5.4698</td>
<td>163.65</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$La$</em>{0.5}$O$_{2-δ}$</td>
<td>4.6</td>
<td>3.2173</td>
<td>5.5725</td>
<td>173.04</td>
</tr>
<tr>
<td>Ce$<em>{0.2}$La$</em>{0.8}$O$_{2-δ}$</td>
<td>3.3</td>
<td>3.2580</td>
<td>5.6430</td>
<td>179.69</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m$^2$g$^{-1}$)</th>
<th>$V_p$ (cm$^3$g$^{-1}$)</th>
<th>$d_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>14.5</td>
<td>0.029</td>
<td>6.7</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$La$</em>{0.2}$O$_{2-δ}$</td>
<td>42.1</td>
<td>0.059</td>
<td>4.1</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$La$</em>{0.5}$O$_{2-δ}$</td>
<td>22.4</td>
<td>0.059</td>
<td>7.9</td>
</tr>
<tr>
<td>Ce$<em>{0.2}$La$</em>{0.8}$O$_{2-δ}$</td>
<td>14.3</td>
<td>0.041</td>
<td>9.3</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>6.7</td>
<td>0.017</td>
<td>9.3</td>
</tr>
</tbody>
</table>

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

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

3.2.1. Hydrogen Temperature-Programmed Reduction (H$_2$-TPR) Studies. Figure 3 presents H$_2$-TPR traces of Ce$_{1-x}$La$_x$O$_{2-δ}$ solids following calcination in 20 vol% O$_2$/He at 600 °C for 2 h. The H$_2$-TPR profiles of Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 Ce$_{0.2}$La$_{0.8}$O$_{2-δ}$ solid presents the highest amount of H$_2$ consumed (437 µmol/g), whereas Ce$_{0.5}$La$_{0.5}$O$_{2-δ}$ the lowest one (282 µmol/g). The amount of H$_2$ consumed for Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ and CeO$_2$ was found to be 400 and 339 µmol/g, respectively. The Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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°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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 µmol/g for $x = 0.0, 0.2, 0.5, \text{and} \ 0.8$, respectively. These results indicate that Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ 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 (m$^2$g$^{-1}$) and acid sites (µmol/g). In particular, it is observed that the concentration of acid sites increases with increasing specific surface area (m$^2$g$^{-1}$) of the solid support.

Figure 5 presents TPD-CO$_2$ profiles of Ce$_{1-x}$La$_x$O$_{2-δ}$ ($x = 0.0, 0.2, 0.5, 0.8$) solids. Pure CeO$_2$ presents five desorption peaks centered at 68, 128, 256, 500, and 630 °C, and Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$ solid exhibits also five desorption peaks (70, 125, 275, 690, and 780 °C). Ce$_{0.2}$La$_{0.8}$O$_{2-δ}$ exhibits four desorption peaks centered at 68, 140, 370, and 800 °C, whereas Ce$_{0.5}$La$_{0.5}$O$_{2-δ}$ 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ solids [32]. Zhang et al. [33] found that CO$_2$ desorption from CeO$_2$ and Ce-La-O solid 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 Ce$_{1-x}$La$_x$O$_{2-δ}$ 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 –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 µmol/g for Ce$_{0.2}$La$_{0.8}$O$_{2-δ}$, Ce$_{0.5}$La$_{0.5}$O$_{2-δ}$, Ce$_{0.8}$La$_{0.2}$O$_{2-δ}$, and CeO$_2$, respectively. These results corroborate that surface basicity increases with increasing La$^{3+}$ content in the Ce$_{1-x}$La$_x$O$_{2-δ}$ solid. It is noted that no correlation was found between the BET area and the total concentration of basic sites for the Ce$_{1-x}$La$_x$O$_{2-δ}$ solids, suggesting that the site density of basic sites (no sites/nm$^2$) is different for each of the Ce$_{1-x}$La$_x$O$_{2-δ}$ solid.

3.3. Catalytic Performance Studies. Figure 6 presents catalytic performance results in terms of CO conversion ($X_{\text{CO}}$, %) as a function of WGS reaction temperature over the 0.5 wt%
Figure 2: SEM images of (a) $\text{CeO}_2$, (b) $\text{Ce}_{0.4}\text{La}_{0.6}\text{O}_{2-\delta}$ 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: $\text{H}_2$-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 4: TPD-NH$_3$ profiles of $\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ solids ($x = 0.0, 0.2, 0.5, 0.8$).

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/$\text{CeO}_2$ is more active than Pt/$\text{La}_2\text{O}_3$. It is clearly seen that doping of ceria with $\text{La}^{3+}$ at the level of 20 at.% improves the catalytic performance of 0.5 wt% Pt

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 6: Effect of support chemical composition on the conversion of CO as a function of WGS reaction temperature over 0.5 wt% Pt/$\text{Ce}_{1-x}\text{La}_x\text{O}_{2-\delta}$ ($x = 0.0, 0.2, 0.5, 0.8, 1.0$) solids.
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.% La^{3+}. However, there is a threshold for the La^{3+}-induced improvement, since the increase in La^{3+}-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 La^{3+} 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_{x}O_{2−δ} solids, showing that these systems do not facilitate the undesirable methanation reaction (CO + 3H_{2} ⇌ CH_{4} + H_{2}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 on 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 Ce^{4+}/Ce^{3+} 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_{0.9}La_{0.1}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^{3+}−O^{2−} sites (present in the support) that potentially participate in the WGS via the dissociative chemisorption of water to form active −OH groups.

Regarding the surface basicity of the five Ce_{1−x}La_{x}O_{2−δ} (x = 0.0, 0.2, 0.5, 0.8, and 1.0) solids, it is seen that the addition of 20 at.% La^{3+} 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 La^{3+} content in the Ce_{1−x}La_{x}O_{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_{1.0}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 (C + H₂O ⇌ CO + H₂) [37–39]. The lower CO conversion observed in La^{3+}-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 Ce^{4+} is reduced to Ce^{3+} 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 (−COO−) 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 CO$_2$ transient response curves obtained during TPO studies (2vol% O$_2$/He flow) performed over the 0.5wt% Pt/unsupported catalysts solids run for 4h in WGS reaction. The 0.5wt% Pt/unsupported catalyst showed two CO$_2$ 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 0.5wt% 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 mol/g for the 0.5wt% Pt/unsupported and 0.5wt% Pt/Ce$_{0.2}$La$_{0.8}$O$_{2−δ}$ catalysts, respectively. The latter result shows that the lowest catalytic activity observed over the 0.5wt% 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/CeO$_2$ 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 0.5wt% Pt/Ce$_{0.2}$La$_{0.8}$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$_{x}$O$_{2−δ}$ 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 0.5wt% 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 0.5wt% Pt/Ce$_{0.8}$La$_{0.2}$O$_{2−δ}$ catalyst exhibits high WGS activity at $T < 300^\circ$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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