The effect of La\(^{3+}\), Ti\(^{4+}\) and Zr\(^{4+}\) dopants on the mechanism of WGS on ceria-doped supported Pt catalysts

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**A B S T R A C T**

Platinum nanoparticles supported on single CeO\(_2\) and TiO\(_2\) metal oxides and Ce\(_{0.8}\)Ti\(_{0.2}\)O\(_2\)-doped ceria solution were prepared to investigate the effect of Ti\(^{4+}\)-doping of ceria on important mechanistic and kinetic aspects of the Water–Gas Shift (WGS) reaction in the 200–300 \(^\circ\)C range, namely: (i) the concentration and chemical structure of active adsorbed reaction intermediates present in the C-path and H-path of WGS, and (ii) the prevailing mechanistic path among “redox” and “associative” both proposed in the literature. The relationship between the chemical nature of dopant (Zr\(^{4+}\), Ti\(^{4+}\) and La\(^{3+}\)) and the concentration of active C-pool and H-pool of reaction intermediates as well as that of specific rate per gram basis (\(r_{\text{co}}\), \(\mu\)mol g\(^{-1}\) s\(^{-1}\)) for the ceria-doped supported Pt is illustrated for the first time based on relevant results previously reported (Zr\(^{4+}\) and La\(^{3+}\)-doped ceria). The 0.5 wt% Pt supported on Ce\(_{0.8}\)Ti\(_{0.2}\)O\(_2\)-doped (Ti\(^{4+}\)-doped CeO\(_2\)) exhibits significantly higher WGS activity in terms of CO conversion (%) and specific kinetic rate (\(\mu\)mol CO g\(^{-1}\) s\(^{-1}\) or \(\mu\)mol CO cm\(^{-1}\) s\(^{-1}\)) compared to Pt/CeO\(_2\), Pt/TiO\(_2\), Pt/Ce\(_{0.8}\)La\(_{0.2}\)O\(_2\)-doped and Pt/Ce\(_{0.8}\)Zr\(_{0.2}\)O\(_2\)-doped catalysts. This was explained mainly by: (i) the larger concentration of active C-pool of reaction intermediates formed around each Pt nanoparticle, and (ii) the higher reactivity of sites (\(k\), s\(^{-1}\)) along the Pt-support interface responsible for CO\(_2\) and H\(_2\) formation. A very good correlation between the concentration of active C-pool and the specific reaction rate, \(r_{\text{co}}\) (\(\mu\)mol g\(^{-1}\) s\(^{-1}\)) as a function of the dopant (Zr\(^{4+}\), La\(^{3+}\) and Ti\(^{4+}\)) was found. The concentration of labile surface oxygen and its mobility in Ce\(_{0.8}\)Ti\(_{0.2}\)O\(_2\)-doped compared to CeO\(_2\) (undoped), La\(^{3+}\) or Zr\(^{4+}\)-doped ceria are also important factors. It is proposed that on Pt/CeO\(_2\)-doped catalysts the WGS reaction follows both the “redox” and “associative formate” mechanisms, where the extent of participation of each mechanism depends on the chemical nature of the dopant (Zr\(^{4+}\), La\(^{3+}\) and Ti\(^{4+}\)).

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1. Introduction

The heterogeneously catalyzed Water–Gas Shift (WGS) reaction (\(\text{CO} + \text{H}_2 \text{O} \leftrightarrow \text{CO}_2 + \text{H}_2\), \(\Delta H = -41.2\) kJ/mol) is one of the key steps in fuel processing systems and in a number of chemical processes, including steam reforming of hydrocarbons, sugars, alcohols and bio-oil for hydrogen production, and the manufacturing of ammonia and petroleum refinery products [1–3].

The low-temperature Water–Gas Shift (LTS) industrial catalyst (Cu/ZnO/Al\(_2\)O\(_3\)) is pyrophoric, and deactivates if exposed to air and condensed water, and it is characterized by low thermal stability [6]. Recently, attempts have been focused towards the development of low-loading robust noble metal-based catalysts with high activity at low-temperatures, and which are non-pyrophoric, in order to reduce catalyst volume and cost [4]. Supported Pt metal catalysts on reducible metal oxide carriers appear to be promising candidates for replacing current industrial low-temperature WGS catalysts [5]. CeO\(_2\) [4,7–13], TiO\(_2\) [14–16], La\(_2\)O\(_3\) [17–20] and ZrO\(_2\) [9–11,21,22] as single or mixed metal oxides have been investigated. However, the stability of these catalytic systems under practical WGS reaction conditions remains one of the problems that need to be solved.

It is generally accepted that the WGS reaction over metal oxide-supported noble metal catalysts operates in a bifunctional manner with the participation of both the dispersed metal phase and the support. Two general mechanistic schemes have been proposed: (i) the “redox or regenerative” mechanism [14,23–27], and (ii) the “adsorptive or associative” mechanism [12–14,28–30]. However, several important kinetic and mechanistic aspects of the WGS over supported metal catalysts still remain controversial, namely: the dominant mechanistic path, the rate-determining step, the chemical nature of the active “carbon-containing” and “hydrogen-containing” intermediates, and their true site location (e.g. support, metal-support interface, metal surface or metal and...
support surfaces) [12,31–35]. Therefore, the fundamental understanding of the WGS reaction at the molecular level is of paramount importance in order to design proper functional catalytic materials for activity, selectivity and stability optimization under industrial WGS reaction conditions. Towards the achievement of this goal, mechanistic aspects of the WGS reaction using in situ spectroscopic and kinetic measurements under reaction conditions (operando methodology) are highly desirable [12–14,20,33,36].

The present work reports on the effects of ceria doping with Ti4+ cations on the catalytic behaviour and important kinetic and mechanistic aspects of the WGS in the low-temperature range of 200–325 °C over Ti4+-doped ceria-supported Pt. This work is a continuation of previous ones [20,36], where the effect of doping of ceria with La3+ [20] and Zr4+ [36] cations was reported. In the present work it is demonstrated how the concentration (μmol g⁻¹) of the active C-pool and H-pool, and the extent (∆x, nm) of a reactive zone formed around each Pt nanoparticle are influenced by the presence of Zr4+, La3+ or Ti4+ cation dopant in the ceria support matrix. Also, correlations between the active C-pool and H-pool and the specific WGS reaction rate as a function of dopant (Zr4+, La3+ and Ti4+) are probed. To our knowledge, this is the first time that such relationships are derived for the WGS reaction on ceria-doped supported Pt catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

The Ce0.8Ti0.2O2−δ Solid solution (Ti4+-doped CeO2) and the single metal oxides of CeO2 and TiO2 used as supports of Pt (0.5 wt%) were synthesized using a modified citrate sol–gel technique described in detail elsewhere [20]. The supported Pt catalysts were prepared by impregnating the oxide supports with a given amount of diluted aqueous solution of H2PtCl6 (8 wt% solution in water, Aldrich) so as to yield a 0.5 wt% Pt nominal loading. Prior to catalytic measurements, the fresh catalyst sample was in situ pretreated in 20 vol% O2/He (50 N mL min⁻¹) gas mixture at 600 °C for 2 h followed by reduction in H2 (1 bar, 50 N mL min⁻¹) at 300 °C for 2 h.

Platinum particle size distribution and a mean Pt particle size (d32, nm) for the 0.5 wt% Pt/CeO2, 0.5 wt% Pt/TiO2 and 0.5 wt% Pt/Ce0.8Ti0.2O2−δ Catalysts were directly high by Direct Analytical dark Field (HAADF) images obtained using a 200 kV JEM-2100 (Jeol Ltd) transmission electron microscope [20]. Platinum dispersion was estimated after considering the relationship: D (%) = 1.1/dPt (nm) × 100.

2.2. Steady-state WGS reaction

Steady-state WGS catalytic measurements were conducted in the experimental set-up previously described [37]. The reaction feed composition used consisted of 3 vol% CO/10 vol% H2O/He, and the total volume flow rate was 200 N mL min⁻¹, resulting in a GHSV of about 40,000 h⁻¹ (L/Lcat/h). The powder catalyst’s particle size was between 0.1 and 0.2 mm, and the amount of catalyst sample used was 0.5 g. The catalytic performance of Pt/3Ce1−xTi xO2−δ (x = 0.0, 0.2 and 1.0) solids in terms of XCO (%) versus the reaction temperature was evaluated in the 200–325 °C range over an in situ pre-reduced catalyst in H2 flow (1 bar, 50 N mL min⁻¹) at 300 °C for 2 h. The effluent gas stream from the micro-reactor after removing the water (Peltier Gas Cooler, model ECP1000, M&C TechGroup) was directed to a mass spectrometer (Omnistar, Balzer) for on line monitoring the H2, CO and CO2 gas composition. The purity of H2, He, CO, and Ar gases (Linde Gas, Greece) was higher than 99.95%.

2.3. SSITKA-mass spectrometry studies

The SSITKA-MS experiment performed to follow the hydrogen-path of the WGS reaction involved the switch 3 vol% CO/10 vol% H2O/Ar/Kr (T, 30 min) → 3 vol% CO/10 vol% D2O/Ar (T, t), whereas that to follow the carbon-path of WGS involved the switch 3 vol% CO/10 vol% H2O/Ar/He (T, 30 min) → 3 vol% CO/10 vol% H2O/Ar (T, t). The effluent wet gas stream from the reactor was first passed through a condenser (Peltier system of low volume), the exit of which was directed to a mass spectrometer for on line monitoring the normal and isotope-containing (D, 13C) reactants and products composition (e.g. H2, HD, D2, 12CO, 13CO, 12CO2 and 13CO2). The isotopes used in the SSITKA experiments were 13CO (99.9 atom% 13C, Spectra Gases) and deuterium oxide (D2O, 99.96 atom% D, Aldrich). The mass of the catalyst was adjusted in every SSITKA-MS experiment so as to keep the CO conversion below 15%; the total mass of catalytic bed was 0.5 g (catalyst + SiO2 for dilution when needed). More details on the SSITKA-MS experiments and the micro-reactor used were previously reported [12,20,36,38–40].

2.4. Probing the H-exchange between —OH groups of support and D2O or D2 gases

In order to account for possible H-exchange between the —OH groups of support and the D2O(g) and D2(g) during the SSITKA-MS experiment at 300 °C for measuring the active H-pool, the following experiments were performed:

(a) The catalyst sample was first treated in 10 vol% H2O/Ar (100 N mL min⁻¹) at 300 °C for 30 min, and then the feed was switched to an equivalent mixture of 10 vol% D2O/Ar, and the transient evolution of HD. H2 and D2 gases at the latter switch was followed with time on stream by mass spectrometry.

(b) The catalyst sample was first treated with 10 vol% H2O/Ar (100 N mL min⁻¹, 30 min) at 300 °C followed by an Ar (100 N mL min⁻¹) purge at 300 °C for 10 min. The feed was then switched to an x vol% D2/Ar gas (100 N mL min⁻¹), and the transient evolution of HD and H2 gases was followed with time on stream. The x vol% composition of D2 was chosen to be the same as that achieved in 3 vol% CO/10 vol% D2O/He gas treatment under steady-state WGS reaction conditions at 300 °C.

2.5. SSITKA-DRIFTS studies

SSITKA-DRIFTS experiments with 13CO (99.9 atom% 13C, Spectra Gases) involved the switch 3 vol% 13CO/10 vol% H2O/Ar/He (T, 30 min) → 3 vol% 13CO/10 vol% H2O/Ar (T, t) at a total flow rate of 200 N mL min⁻¹ which potentially allows determining the chemical structure of the active intermediates and spectator species of the WGS reaction. All the SSITKA-DRIFTS experiments were performed in a specially designed gas flow-system described in detail elsewhere [39]. Signal averaging was set to 128 scans per spectrum (averaged), and the spectra were collected in the 4000–500 cm⁻¹ range at the rate of 0.2 s/scan (MCT detector), and using a resolution of 4 cm⁻¹. The background spectrum of the solid was taken under 10 vol% H2O/Ar flow at the desired reaction temperature. After background subtraction, a baseline correction was performed according to the provided software (PerkinElmer Spectrometer, v.10.03.02). More details on the SSITKA-DRIFTS experiments and the DRIFTS reactor cell used were reported [12,14,20,36,39,40].

2.6. Probing CO2 readsoption effects and rival WGS reaction mechanisms

The initial rate of reaction of adsorbed formate and CO with water alone was measured by a novel experiment recently
reported by us [12,20,36], where surface concentrations of the former species were established under steady-state WGS reaction conditions. The experiment involved the following gas delivery sequence: 3 vol% 14CO/10 vol% H2O/Ar (T, 30 min) → 3 vol% 15CO/Ar (T, 10 min) → 3 vol% 13CO/Ar (T, 10 min) → 10 vol% H2O/Ar (T, t), where the transient responses of 12CO2, 13CO2 and H2 were continuously monitored by on line mass spectrometer during the last step gas switch. The initial transient rates of 12CO2 and 13CO2 formation are considered as characteristic rates of the reaction of water with adsorbed non-exchangeable with 13CO(g) active “carbon-containing” (e.g., HCOO−, −COOH or CO2−) and exchangeable active 13CO−s intermediates, respectively. The shape and position in time of the 12CO2 and 13CO2 transient response curves would reflect the kinetics of reaction of the respective intermediates, thus probing the rate of the “redox” versus “associative” WGS reaction path. The amount (µmol g−1) of 13CO2 and 12CO2 reflects the active C-pool formed under WGS reaction conditions and not any reversibly chemisorbed CO2 on non active catalytic sites under WGS, which is measured unavoidably in the SSITKA-MS (carbon-path) experiment (Section 2.3). The difference between the measurement of C-pool by SSITKA and that by the above described transient titration experiment with water, should reflect the extent of reversibly chemisorbed CO2 under WGS reaction conditions.

2.7. 18O/16O isotopic exchange followed by WGS reaction

The catalyst sample (0.3 g) was first pre-treated with 10 vol% 18O2/Ar (600 °C for 30 min), purged with Ar and cooled to 80 °C. The feed was then switched to H2 (1 bar, 80 °C, 20 min) to reduce only PtO2 to Pt. Following this gas treatment, the catalyst was then heated from 80 to 250 °C in Ar flow, and then exposed to the WGS reaction feed stream (3 vol% CO/10 vol% H2O/Ar; 200 N mL min−1). The 18O/16O isotopic exchange performed at 600 °C was monitored with mass spectrometry by recording the evolution of 16O2, 16O18O and 18O2 gaseous species (m/z = 32, 34 and 36). Under the WGS reaction conditions, H2, C16O, C16O2, C16O18O and C18O2 (m/z = 2, 28, 44, 46 and 48) gases were continuously monitored with mass spectrometry.

3. Results and discussion

3.1. Catalytic activity measurements

The effect of ceria doping with Ti4+ cations on the CO conversion (XCO, %) vs. temperature activity profile of the WGS reaction in the 200–325 °C range for the Pt/Ce1−xTiO2−x, (x = 0.0, 0.2 and 1.0) solids is presented in Fig. 1. The CO conversion versus temperature profile at thermodynamic equilibrium conditions is also given (Xeq, Fig. 1) [40]. At all temperatures, Pt/Ce0.8Ti0.2O2−x shows significantly higher activity compared to Pt supported on CeO2 or TiO2 carriers, especially at 250 and 275 °C, where an increase of activity by a factor of 1.7 and 1.9, respectively, is noted.

The specific kinetic rates of WGS per gram basis, rCO (µmol CO g−1 s−1) and those based on the length of the perimeter of Pt-support interface (Ib), rCO (µmol CO cm−1 s−1) at 200 and 300 °C for each catalyst are reported in Table 1. The length of the perimeter of Pt-support interface, Ib (cm g−1) was estimated (Table 1) considering that each Pt nanoparticle has a hemispherical geometry, and after accounting for the Pt loading (wt%) and the corresponding mean Pt particle size [36]. As we have previously reported [12,20,36], the latter analysis is meaningful since the mechanism of WGS on the present catalytic systems involves active catalytic sites at the Pt-support interface and within a reactive zone around each Pt nanoparticle as will be illustrated in the following Section 3.2.3. As it is clearly shown in Table 1, Pt nanoparticles supported on Ce0.8Ti0.2O2−x (Ti4+-doped CeO2) exhibit significantly larger

![Fig. 1. Effect of support chemical composition on the conversion of CO (XCO, %) as a function of WGS reaction temperature over 0.5 wt% Pt/Ce1−xTiO2−x (x = 0, 0.2 and 1) catalysts; GHSV = 40,000 h−1 (L/Lcat h).](image-url)
specific rates both per length of Pt-support interface and per gram of catalyst compared to the bare supports; it is noted that in all three catalytic systems the mean Pt particle size is in the 1.2–2.0 nm range (Table 1). This result could be explained on the basis of intrinsic differences in the site reactivity along the Pt-support interface largely influenced by the support chemical composition and Pt particle size. According to previous studies on Pt/Ce1−xZrO2−δ [36] and Pt/Ce1−xLa2O3−δ [20] catalysts, the site reactivity of Pt across the metal-support interface was increased as a consequence of the introduction of Zr4+− and La3+−-dopant, respectively, into the ceria lattice. It was suggested that the latter enhanced the concentration of labile oxygen and its surface mobility, and the Ce4+→Ce3+ reduction energy, thus increasing the concentration of Ce3+ defect sites. A similar result has also been observed in the present Ti4+−doped ceria supported Pt catalyst to be reported in Section 3.5. The surface concentration of active Ti4+− dopant involved in the reaction path of WGS is another important intrinsic kinetic parameter which is expected to strongly influence the rate of reaction. This is considered in the following Section 3.2.3 to explain the observed differences in the specific reaction rates of Pt supported on the undoped CeO2 and Zr4+−, La3+− and Ti4+−-doped CeO2 catalysts.

### Table 1

Effect of Ce/Ti ratio on the specific kinetic rate of WGS reaction per gram of catalyst, r_CO (μmol g cat−1 s−1) and total length of perimeter of Pt−Ce1−xTiO2−δ interface (l_α, cm g−1). R_CO (μmol cm−1 s−1) at 200 °C and 300 °C (P_CO = 0.03 bar, P_O2 = 0.1 bar, P_H2 = 0.87 bar).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>d_α (nm)</th>
<th>r_CO (μmol g cat−1 s−1)</th>
<th>l_α (cm g cat−1)</th>
<th>R_CO (μmol cm−1 s−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CoO</td>
<td>1.2 (±0.3)*</td>
<td>0.24</td>
<td>1.9 × 10^11</td>
<td>1.3 × 10^−12</td>
</tr>
<tr>
<td>Pt/CoO0.7TiO2.3</td>
<td>1.7 (±0.2)*</td>
<td>0.78</td>
<td>1.3 × 10^11</td>
<td>6.0 × 10^−12</td>
</tr>
<tr>
<td>Pt/CoO0.4TiO2.6</td>
<td>2.0 (±0.2)*</td>
<td>0.20</td>
<td>7.0 × 10^−11</td>
<td>2.8 × 10^−12</td>
</tr>
</tbody>
</table>

* According to HAADF/STEM studies; d_α (nm) = 1.1/D (%) × 100.

### 3.2. Quantification of the active reaction intermediates (SSITKA-Mass spectrometry)

#### 3.2.1. Hydrogen-path of WGS

Fig. 2a presents transient concentration response curves of H2, HD, D2 and Kr obtained after the SSITKA isotopic switch 3 vol% CO/10 vol% H2O/Ar/Kr (300 °C, 30 min) → 3 vol% CO/10 vol% D2O/Ar (300 °C, t) was made over the Pt/CoO2 catalyst. The concentration (μmol g cat−1) of active “H-containing” reaction intermediates, named H-pool, which are found in the H-path of WGS, is estimated based on the transient response curves of H2, HD and Kr as previously reported [12–14,20,36,39,40]. The formation of HD(g) (Fig. 2a) includes the result of the recombination of adsorbed H and D on the Pt surface but likely also the exchange of H of −OH group of support with D from D2(g) and/or D2O(g) under the 12CO/D2O/Ar gas switch. The latter side exchange reactions were checked according to the experiments described in Section 2.4. Fig. 3 presents transient response curves of HD(g) and H2(g) obtained over the Pt/CoO2 (Fig. 3a), Pt/CoO2 (Fig. 3b), Pt/Co0.8TiO2.5 (Fig. 3c) and Pt/Co0.8La0.2O2−δ (Fig. 3d) solids following the switch to x vol% D2/Ar gas mixture at 300 °C according to the gas delivery

Fig. 3. Transient response curves of H2 and HD obtained at 300 °C during the gas delivery sequence 10 vol% H2O/Ar (30 min) → Ar (10 min) → x vol% D2/Ar (t) over (a) Pt/CoO2 (x = 0.75); (b) Pt/CoO2 (x = 0.25); (c) Pt/Co0.8TiO2.5 (x = 0.42); and (d) Pt/Co0.8La0.2O2−δ (x = 0.5) WGS catalysts.
sequence: 10 vol% H₂O/Ar (30 min) → Ar (10 min) → x vol% D₂/Ar (t). It is clearly observed that exchange of D₂(g) with the −OH groups of support does occur in all four catalysts with different extent and kinetics as reflected by the shape and position in time of the H₂(g) and HD(g) transients (Fig. 3a-d). The quantity of H-exchange on Pt supported on CeO₂, TiO₂, Ce₀.₈Ti₀.₂O₂−δ and Ce₀.₈La₀.₂O₂−δ catalysts was found to be 100, 20.4, 114.4, and 255 μmol g⁻¹, respectively. It should be noted that the extent of H-exchange was found to be closely related to the BET (m²g⁻¹) area of the catalyst. Pt/TiO₂ and Pt/Ce₀.₈La₀.₂O₂−δ with the lowest and highest BET area (3.5 vs. 42 m² g⁻¹) were found to exhibit the lowest and highest amount of H-exchange, respectively. Table 2 reports the concentration of the active H-_pool (μmol g⁻¹), after subtracting the amount of H-exchange (Fig. 3). Also, the equivalent amount of the active H_pool in terms of surface Pt monolayers (θ) is included in parentheses. The amount of H-exchange on the four catalysts is determined by the kinetics of hydrogen production via the H-path of WGS. According to the experimental results (Table 2), no HD(g) and HD(g) were observed at the switch 10 vol% H₂O/Ar → 10 vol% D₂/Ar (t) at 300 °C.

The surface coverage of the active H_pool (θ_H) in all cases was found to be significantly larger than one (Table 2). This result strongly suggests that the “H-containing” species largely reside on the support surface. The chemical nature of these active intermediates is considered to be labile hydroxyls (−OH) and atomic hydrogen (H) both produced via water dissociation. Atomic hydrogen species should be regarded as attached on support’s surface oxygen anions, O²⁻. It was suggested [9,10,14,20,42] that oxygen vacancies (Ce³⁺−O−Ce³⁺) in partially reducible metal oxides (e.g. CeO₂, TiO₂ and La₂O₃) are specific sites for H₂ activation. Formate (HCOO−) and carboxyl (−COOH) species could also be considered as active “H-containing” intermediates based on SSITKA-DRIFTS and other transient isotopic experiments to be presented next.

Based on the SSITKA-MS results (Fig. 2a), the rate of H₂(g) formation appears to be larger than that of D₂(g) by a factor of 1.2. This result implies the existence of a normal kinetic isotopic effect (NKIE), where an elementary reaction step associated with the breaking/formation of a chemical bond that involves H can be considered as rate-determining step. According to the present results of SSITKA-DRIFTS (Section 3.3) and other transient isotopic experiments (Section 3.4), both “redox” and “associative formate with −OH group regeneration” mechanisms appear important at 300 °C over the present ceria and Ti₄⁸−doped ceria supported Pt catalysts. The O−H bond breaking producing mobile H species and/or the water dissociation on surface oxygen vacant sites of ceria might be considered as one of the slow elementary reaction steps in WGS. However, as will be shown in the following Section 3.2.2, a good correlation between the concentration of active C_pool and the specific WGS reaction rate exists, suggesting that the C−H bond breaking in the formate (HCOO−) species, the latter being also a major reaction intermediate (see Section 3.3), must be considered as a slow step in the respective “associative formate with −OH group regeneration” reaction path.

3.2.2. Carbon-path of WGS

Fig. 2b presents dimensionless gas-phase transient concentration (Z) response curves for ¹²CO₂, ¹³CO₂ and He obtained after the isotopic switch 3 vol% ¹²CO/10 vol% H₂O/He (300 °C, 30 min) → 3 vol% ¹³CO/10 vol% H₂O/Ar (300 °C, t) was made (probing the carbon-path of WGS). No ¹³C-isotopic kinetic effect was observed, whereas the ¹²CO₂(g) and ¹³CO₂(g) transient response curves in time under the ¹³CO/H₂O switch cross each other at Z=0.51 instead of 0.5 according to the SSITKA theory (~2% experimental error).

The concentration of active "carbon-containing" reaction intermediates, named C_pool, and which are found in the carbon-path of WGS can in principle be estimated based on the ¹³CO₂ and He response curves as described previously [12–14,20,36,39,40] if no external (within the catalytic bed) and internal (readsoption of CO₂ on non active catalytic sites) effects are present. These effects were carefully considered for the quantification of the active C_pool as described in Section 2.6. The external CO₂ readsoption effect was considered after varying the amount (W) of catalyst within the same volume of catalytic bed (catalyst + SiO₂) and extrapolating the C_pool (Fig. 2b) to W=0 [13]. Fig. 4 presents the results observed under the 10 vol% H₂O/Ar switch (see Section 2.6) over the Pt/Ce₀.₈Ti₀.₂O₂−δ catalyst. It is observed that most of the CO₂ is evolved as ¹³CO₂ (109.7 μmol g⁻¹cat⁻¹ or θ_H=5.9) with only a small amount of ¹²CO₂ (4.5 μmol g⁻¹cat⁻¹). It is noted that reversibly chemisorbed CO₂ formed under WGS was desorbed under the ¹²CO/Ar and ¹³CO/Ar treatments (background value at m/z = 44 after the 10-min ¹³CO/Ar switch was obtained).

Part of the ¹³CO₂ is due to the reaction of water with the adsorbed ¹³CO−S (formed upon the exchange of ¹²CO−S under the


3.2.3. Effect of dopant (Zr$^{4+}$, La$^{3+}$ and Ti$^{4+}$) on the C-pool and H-pool

The results reported in Table 2 for the surface concentration of active carbon-containing and H-containing WGS reaction intermediates indicate that, when expressed in terms of surface Pt monolayers ($\theta$), these species cannot be considered as residing on the Pt surface but the majority of them must be located within a reactive zone [20,36] around each Pt nanoparticle. Fig. 5a and b illustrates the effect of doping of ceria with Zr$^{4+}$, La$^{3+}$ and Ti$^{4+}$ cations on the active C-pool and H-pool, respectively, along with the corresponding length of a reactive zone ($\Delta x$, nm) within which these species were formed under steady-state WGS at 300 °C over the 0.5 wt% Pt/ceia-doped catalysts. Fig. 5c illustrates the very good correlation found between the concentration of C-pool ($\mu$mol g$^{-1}$) and the specific reaction rate, $r_{CO}$ ($\mu$mol g$^{-1}$ cat$^{-1}$ s$^{-1}$) as a function of the chemical nature of the dopant used (Zr$^{4+}$, La$^{3+}$ and Ti$^{4+}$) in the ceria support. Results for the Zr$^{4+}$ and La$^{3+}$ dopants were obtained from our previous works [20,36], and considering also the results of Fig. 3a and d for the Pt/ceia and Pt/ceiaLa$_{0.2}$O$_{2-\delta}$ catalysts. It should be noted that the 1.0% dopant concentration used in these catalytic systems is the optimum one found towards the CO conversion in the WGS reaction at 300 °C [36,43].

The results shown in Fig. 5c revealed the importance of one of the kinetic parameters that explain the order of activity observed among the undoped and Zr$^{4+}$-, La$^{3+}$- and Ti$^{4+}$-doped ceria used as supports of Pt. This kinetic parameter is the concentration of the active C-pool formed around each Pt nanoparticle and within a reactive zone of 5–28 Å (Fig. 5a). As will be shown in the following Sections 3.3 and 3.4, the majority of these species must be of the formate/carboxylate chemical nature and not of carbonate type. The significantly higher activity of Pt supported on Ti$^{4+}$-doped ceria

13CO/Ar gas treatment), and this adsorbed 13CO-s was formed under WGS reaction conditions. Given the fact that the maximum $\theta_{c}$ value on Pt is one (1:1 stoichiometry), most of the 13CO$_2$ response is then due to formate species residing on the support (see Section 3.3). Reaction of adsorbed 13CO-s and H$^{13}$COO-s species (formed under the 13CO/Ar treatment, see Section 3.4) with OH/H derived from water dissociation corresponds to 1:1 stoichiometry for CO$_2$ formation, and this is indeed confirmed by the estimated amount of hydrogen response (125.8 $\mu$mol g$^{-1}$). The concentration of C-pool estimated from this transient titration experiment (Fig. 4, 114.2 $\mu$mol g$^{-1}$) must be seen as the true concentration of the active CO-s and HCOO-s species (see Section 3.3), where the reversibly adsorbed CO$_2$ (as carbonate species) that did form mainly on the internal non catalytic surface sites, and which unavoidably was measured during the SSITA switch (Fig. 2b) is not accounted for. As an example, the concentration of C-pool measured during SSITA was found to be 580 $\mu$mol g$^{-1}$ (includes both external and internal adsorption) to be compared to the value of 114.2 $\mu$mol g$^{-1}$ measured during the transient isotopic titration experiment with water presented in Fig. 4. Table 2 reports the true active C-pool free of any CO$_2$ readorption effects for the Pt/ceia$_{1-x}$Ti$_x$O$_{2-\delta}$ ($x=$ 0.0, 0.2 and 1.0) catalytic systems.

The concentration of the active C-pool in terms of $\theta_{c}$ was found to be in the 0.4–6.5 range for all Pt/ceia$_{1-x}$Ti$_x$O$_{2-\delta}$ ($x=$ 0.0, 0.2 and 1.0) catalysts at 300 °C (Table 2). In the case of Pt supported on CeO$_2$, $\theta_{c}$ is larger by a factor of 16 and 3.8 compared to TiO$_2$ and CeO$_2$, respectively. This result illustrates that addition of Ti$^{4+}$ cations into the ceria lattice leads to significant enhancement in the surface concentration of active intermediates involved in the carbon-path of WGS. This in turn provides an additional explanation for the observed enhanced activity of Pt/CeO$_{2-x}$Ti$_x$O$_{2-\delta}$ compared to the other solids (Fig. 1, Table 1). The active “C-containing” intermediates formed during WGS and which lead to the CO$_2$(g) formation can be potentially considered as those of adsorbed CO formate (HCOO−), carboxyl (−COOH) and carbonates, CO$_3^{2−}$. The first three species are considered to be active species according to the results reported in Sections 3.3 and 3.4.

The fact that a single symmetrical 13CO$_2$ peak is observed (Fig. 4) may reasonably suggest that the rate of reaction of adsorbed CO-s and formate with water are similar. The 12CO$_2$ response obtained with its peak maximum shifted to higher reaction times compared to that of 13CO$_2$ peak (45 vs. 51 s) is due to the presence of a very small concentration of formate that reacts with water (see Section 3.4), and which is irreversibly formed by the interaction of CO with −OH groups (not exchangeable with 13CO(g)). This small concentration was not possible to be seen during the SSITA-DRIFTS experiment (see Section 3.3).
compared to the other dopants can also be related to the high concentration of the active H-pool (−OH/H species) formed upon water chemisorption on the Ce0.8Ti0.2O2−δ support surface as shown in Fig. 5b. After comparing the results shown in Fig. 5b (H-pool vs. dopant) with those of CO vs. dopant in Fig. 5c, it is seen that no correlation among these kinetic parameters can be seen. It might be reasonable to suggest that the carbon-path than the hydrogen-path of WGS is more detrimental in influencing the kinetic rate of reaction over the present supported Pt catalysts.

For the present Pt/TiO2 catalytic system, the size of the C-pool and H-pool were found to be 5.3 (θH = 0.4) and 67.4 μmol g−1 (θH = 4.7), respectively (Table 2) providing a reactive zone length, Δx = 1.8 nm for the H-pool.

3.3. Determination of the chemical structure of active intermediates (SSITKA-DRIFTS)

In order to determine the chemical composition of the active “carbon-containing” intermediates formed in the C-path of WGS and that of spectator species also formed, SSITKA-DRIFTS experiments at 300 °C were performed. The IR bands corresponding to a given vibrational mode for an active intermediate must show the red isotopic shift due to the replacement of 12C-containing active intermediates with the corresponding 13C-containing ones during the switch 12CO/H2O → 13CO/H2O. In the case that a particular adsorbed species is not active (spectator), then the IR spectra under the 13CO/H2O feed gas stream must not provide the red isotopic shift. In situ DRIFTS spectra recorded in the 3050–1200 cm−1 range on Pt/Ce0.8Ti0.2O2−δ during SSITKA-DRIFTS at 300 °C are presented in Fig. 6. The 3050–2750 cm−1 range (Fig. 6a) corresponds to the vibrational modes of adsorbed formate, HCOO− (νCH and δCH + νCOO), that of 2100–1850 cm−1 (Fig. 6b) to adsorbed CO on Pt [42,44–46], and that of 1650–1250 cm−1 (Fig. 6c) to the O−C−O stretching vibrational modes of formate, carbonate or carboxylate species [9,11,28,47,48]. The various IR bands observed in Fig. 6a–c under the 12CO/H2O (solid line spectra) and 13CO/H2O (dotted line spectra) feed gas streams were obtained following appropriate deconvolution and curve fitting procedures [12,36].

The IR bands centred at 2178 and 2119 cm−1, labelled as 1 and 2, respectively in Fig. 6b (solid line spectrum) are due to gas phase 12CO, whereas those at 2068, 2050, 2023 and 1974 cm−1 (IR bands 3–6) correspond to different kinds of linearly adsorbed carbon monoxide, COδ. The IR bands 3 and 4 are related to a high-frequency (HF) linearly bound CO on Pt, whereas the infrared band 5 (2023 cm−1) to a low-frequency (LF) linearly bound CO on Pt atoms present in small platinum particles (P5) of low coordination (dp < 1.5 nm) [12,49]. The IR band 6 recorded at 1974 cm−1 is attributed to CO adsorbed on isolated very low-coordinated Pt atoms in strong interaction with the support [12,49,50]. A similar IR band located in the 1940–1980 cm−1 region was reported on various noble metal catalysts dispersed on reducible supports [12–14,20] including ceria and titania. In fact, it was proposed [12–14,36] that the IR band observed at larger than 2000 cm−1 concerns terminal CO adsorbed on Pt sites which are in contact with M” at the metal support interface, Pt−Cδ−M” (where, M = Ce3+ or Ti4+). The very small IR band at 1835 (band 7) corresponds to bridged adsorbed carbon monoxide, COδ. It was suggested [51] that the latter IR band is associated with COδ at the metal-support interface with CO interacting with the support via either the carbon (bonding with 0− of MO), or the oxygen atom (bonding with M” of MO, where MO = metal oxide). As depicted in Fig. 6b (bottom spectrum), all IR bands due to molecularly adsorbed CO show the red isotopic shift upon the switch 12CO/H2O → 13CO/H2O (bands labelled with *), except the IR band of 7 COδ which is considered to be an inactive intermediate (spectator). Based only on the observed red isotopic shift, it cannot be safely stated that these COδ species are all active intermediates, since an adsorbed spectator species (12CO−δ) formed on the catalyst surface could interact reversibly with 13CO(g) resulting in the observed red isotopic shift. Thus, additional transient isotopic experiments were performed to assign the role of such an adsorbed COδ being or not an active or spectator species (see Section 3.4). On the other hand, at least one adsorbed COδ−s must be considered as an active intermediate in the
carbon-path of WGS since CO is the only “C-containing” reactant species.

The IR bands centred at 2952, 2909 and 2850 cm⁻¹ (Fig. 6a, upper spectrum) correspond to the νC, δCH + νCOOₐ and δCH + νCOOᵦ vibrational modes of adsorbed HCOO⁻. The true site location of the latter species, e.g. Pt versus metal oxide support, is difficult to be resolved based only on the resulting position of IR bands [9,11,48,52]. However, based on the surface concentration of this species, which is estimated to be greater than one Pt monolayer (see Section 3.2.2), most of the active HCOO⁻ species reside on the support surface, and the concept of having an active zone around each Pt nanoparticle can be established as previously described.

The IR bands recorded at 1581 (band 2) and 1375 cm⁻¹ (band 5) under the ¹²CO/H₂O gas mixture (Fig. 6c, upper spectrum) are assigned to OCOₐ and OCOᵦ vibrational modes of formate (HCOO⁻) and carbonate species, respectively, depending predominantly on support’s micro-structural features [30]. The IR band at 1518 cm⁻¹ (band 3) corresponds to carboxylate species, whereas the IR bands centred at 1469 (band 4) and 1417 cm⁻¹ (band 5) to carbonate species and bicarbonate-type chemisorbed carbon dioxide [30]. The IR band 1 (1643 cm⁻¹) is due to the bending mode of water molecule.

After the new steady-state in ¹³CO/H₂O gas mixture was reached, all recorded IR bands due to formate species formed under ¹²CO/H₂O gave the red isotopic shift (Fig. 6a, bottom dotted-line spectra). On the contrary, the IR bands related to carboxylate and carbonate species do not show any red isotopic shift under the ¹³CO/H₂O treatment (Fig. 6c), providing evidence that the latter species are considered merely spectators. The above described SSITKA-DRIFTS results lead to the conclusion that formate species populated on the metal and support surfaces could be considered as active intermediates of the WGS at 300 °C. However, we have previously reported [39] that if the reaction step of an adsorbed CO with –OH group is a reversible step, and considering that H¹²COO⁻ species does not further react to produce CO₂ and H₂ (inactive or spectator), then during the ¹³CO/H₂O switch formate is expected to be labelled as H¹³COO⁻. Meunier et al. [34] have reported that the decomposition rate of formate towards CO₂ formation under WGS reaction conditions on Au/Ce(La)O₂ catalyst was smaller compared to the overall WGS reaction rate. For this reason formate was not considered as an important reaction intermediate. Therefore, based only on the SSITKA-DRIFTS results one cannot conclusively decide whether formate could be a true active WGS reaction intermediate.

SSITKA-DRIFTS spectra were also recorded over Pt/CeO₂ and Pt/TiO₂ at 300 °C, and these are shown in Figs. 7 and 8, respectively. In the case of Pt/CeO₂, all IR bands due to molecularly adsorbed CO on Pt (Fig. 7b), formate, carbonate or carboxyl species adsorbed on the support (Fig. 7a and 7c) show the red isotopic shift (bands labelled with *). As previously mentioned, the existence of a red isotopic shift cannot be considered alone as a safe criterion to judge whether the related adsorbed species is an active reaction intermediate. Thus, even though formate (Fig. 7a and c) on the support had given the red isotopic shift, these species may not be important active reaction intermediates. The same reasoning also applies for the formation of carboxyl species on Pt [53]. Furthermore, it is seen that the IR band 3 due to carbonate species (Fig. 7c) showed also the red isotopic shift. The latter result is related either to the CO₂ readesorption effect in which part of the carbonate species formed under WGS is due to reversibly chemisorbed CO₂, as illustrated in Section 3.2.2, or to carbonates that could be considered as true active reaction intermediates based on a “redox” mechanism (see Section 3.5). In fact, according to other transient isotopic studies conducted on Pt/CeO₂ [12], Pt/Ce₁₋ₓZrₓO₂₋δ [36] and Pt/Ce₁₋ₓLaₓO₂₋δ [20], formate was proposed to be an active reaction intermediate at T> 250 °C, although its contribution to the overall WGS reaction rate was small.

![Fig. 7. SSITKA-DRIFTS spectra recorded under WGS reaction conditions at 300 °C in the (a) 3050–2750, (b) 2250–1800 and (c) 1800–1200 cm⁻¹ range over 0.5 wt% Pt/CeO₂. Solid-line spectra were recorded under 3 vol% ¹²CO/10 vol% H₂O/Ar/He, and dotted-line spectra under 3 vol% ¹³CO/10 vol% H₂O/Ar gas mixtures. Deconvoluted DRIFTS spectra are also shown.](Image)
Fig. 8. SSITKA-DRIFTS spectra recorded under WG5 reaction conditions at 300 °C in the (a) 2250–1800 and (b) 1800–1200 cm⁻¹ range over 0.5 wt% Pt/TiO₂. Solid-line spectra were recorded under 3 vol% 12CO/10 vol% H₂O/Ar/He and dotted-line spectra under 3 vol% 13CO/10 vol% H₂O/Ar feed gas mixtures. Deconvoluted DRIFTS spectra are also shown.

Fig. 9 shows in situ DRIFT spectra recorded in the 1200–3000 cm⁻¹ range under the 10 vol% H₂O/Ar gas switch following the gas delivery sequence ¹²CO/H₂O (30 min) → ¹²CO/Ar (10 min) → ¹³CO/Ar (10 min) → H₂O/Ar (t) at 300 °C over the Pt/Ce₀.₈Ti₀.₂O₂–δ catalyst (see Sections 2.6 and 3.2.2). Fig. 9a presents spectra in the characteristic region of vCH stretching vibrational mode of formate (HCOO⁻). The spectrum marked with t = 0 s corresponds to that recorded at the end of the ¹³CO/Ar gas treatment (10 min) of the catalyst, where a red isotopic shift for the observed IR bands was noted. This result strongly indicates that formation of formate species involves the reversible step: CO(g) + OH₃ ↔ HCOO₃. It is clearly seen that within ~115 s under the H₂O/Ar gas treatment, all adsorbed formate species were depleted (Fig. 9a). The rate of formate decomposition under Ar flow is small at 300 °C, since after the switch CO/H₂O → Ar and waiting 10 min in Ar flow only a small decrease in the intensities of formate’s IR bands was noticed (not shown). Thus, the results of Fig. 9a strongly suggest that depletion of formate concentration is largely due to the presence of water, and this leads to the formation of CO₂(g) and H₂(g) as evidenced by mass spectrometry analysis.

Fig. 9b presents similar DRIFT spectra for the characteristic region of O–C–O vibrational modes in formate, carbonate and...
carboxylate adsorbed species. It was found that after 115 s in H2O/Ar flow IR bands related to carboxinate- and carboxyl-type species strongly persist, whereas those due to formate significantly decreased, in agreement to the results shown in Fig. 9a. Also, no changes in the IR bands due to carboxinate- and carboxyl-type species were seen for times larger than 10 min in H2O/Ar gas flow. These results strongly suggest that a large part of the latter species is inactive towards water, and only a small part of it reacts towards water with a lower rate than formate species does react.

Fig. 9c shows in situ DRIFT spectra in the region of adsorbed CO (linear and bridged) after deconvolution and curve fitting was applied. It is observed that after 5 min in H2O/Ar treatment there were refractory adsorbed CO species towards water for all five types of adsorbed CO (see section 3.3, Fig. 6b). In fact, only a small decrease in the intensity of the IR bands due to LF-linearly bonded CO on small platinum particles and to CO adsorbed on Pt–Ce1−xMx+ solid solutions was observed. On the other hand, the least refractory species was the HF-linear CO, where about half of its surface coverage reacted with water towards CO2 and H2 (Fig. 9c, IR band at 2000 cm−1). It should be noted that only the four types of linearly adsorbed CO gave the red isotopic shift under the 13CO/Ar gas treatment (reversible chemisorption), as opposed to the case of bridged CO species. Based on these results and previous studies [20], it is proposed that co-adsorbed surface species (e.g. −COOH and HCOO−) on Pt hinder reactions of adsorbed CO with water and likely diffusion of CO towards the interface for reaction with lattice oxygen and −OH groups (redox and associative formate mechanism, respectively).

3.5. Effect of dopant (Zr4+, La3+ and Ti4+) on the mechanism of WGS

Based on the initial rates of 12CO2 and 13CO2 observed in the transient isotopic experiment depicted in Fig. 4 over the Pt/CeO2 [12] and Pt/Ce0.5Zr0.5O2 [36] catalysts, and fact that during the 13CO/Ar gas treatment formate (HCOO−) infrared bands have not provided red isotopic shift, it was concluded that the “redox” instead the “associative formate” mechanism largely controls the WGS reaction rate over these catalytic surfaces at 300 °C. On the contrary, in the case of Pt/Ce0.5La0.5O2 [20] and the present Pt/Ce0.8Ti0.2O2−x catalysts (Figs. 4 and 9a), both “redox” and “associative formate” reaction mechanisms seem to control the WGS reaction rate. However, the extent of participation of each mechanism to the overall reaction rate cannot be quantified from the results of the present work.

The concentration (μmol gcat−1) of lattice oxygen participating in the WGS reaction path along with that of exchangeable surface and bulk 16O-lattice oxygen (mmol 16O gcat−1) obtained at 600 °C on Pt/TiO2, Pt/CeO2 and Pt/Ce0.8Ti0.2O2−x (see Section 2.7) are summarized in Table 3. The possibility that formation of C18O2 and C16O218O might also be due to the simple exchange of C16O2(g) formed under WGS with 18O-lattice oxygen of support was carefully checked according to our previous work [20]. It was found that the transient kinetics of isotopic exchange of 18O-lattice oxygen with C16O2 is totally different from the transient behaviour of the rate of formation of these carbon dioxide isotopic species due to reaction of lattice 18O with CO under WGS as observed in the Pt/Ce1−xLa0.3O2−y catalyst [20]. Based on the results reported in Table 3, it is seen that only a small fraction of available 18O-lattice oxygen in the catalyst can participate in the WGS reaction. This lattice oxygen must be regarded as inherently present at the vicinity of Pt-support interface. Also, on the basis of the results reported in Table 3, it is illustrated that introduction of Ti4+ into the ceria lattice enhanced both the 18O-isotopic exchange and the amount of lattice oxygen participating in the WGS reaction. Given the fact that WGS over the present three catalytic systems proceeds via the redox mechanism in parallel to the associative mechanism (via formate and carboxyl intermediates) as previously discussed, the presence of a larger concentration of labile oxygen and oxygen vacancies in Ce0.8Ti0.2O2−x must contribute to the observed enhanced surface coverage of active intermediates and their site reactivity. The latter parameters are influenced by the presence of Ti4+ in the ceria lattice (Ti4+-doped ceria), thus leading to the observed enhanced catalytic activity presented in Fig. 1 and Table 1.

4. Conclusions

The following conclusions can be considered from the results of the present work:

(a) The enhanced WGS catalytic activity (μmol gcat−1 or μmol cm−1 s−1) exhibited by Pt/Ti4+-doped CeO2 compared to Pt/CeO2 and Pt/TiO2 solids can be explained considering the existence of (i) a higher site reactivity (k) and a larger concentration for active “H-containing” and “C-containing” intermediates formed within a reactive zone around each Pt nanoparticle, and (ii) a larger concentration of labile oxygen and oxygen vacancies present in the Ti4+-doped CeO2 support which participate in WGS via the “redox” mechanism.

(b) The mechanism of WGS on Pt supported on CeO2-doped carrier (Zr4+, La3+ and Ti4+ dopant) at 300 °C was found to proceed via the “redox” bifunctional mechanism in parallel to the “associative with −OH group regeneration” mechanism. The extent of participation of each reaction path to the overall kinetic rate of WGS depends on the dopant used.

(c) The HF-linear adsorbed CO formed on Pt and formate (HCOO−) on the support are considered as active intermediates present in the C-path of WGS at 300 °C over Pt supported on Ce1−xTi0.2O2−x (x = 0.0, 0.2, and 1.0) solids.

(d) A very good correlation between the active C-pool and the specific WGS reaction rate (μmol gcat−1 s−1) at 300 °C as a function of dopant (Zr4+, La3+ and Ti4+ dopant) was found.

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