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Study of the water-gas shift reaction over Pt supported on $\mbox{CeO}_2\mbox{-}\mbox{ZrO}_2$ mixed oxides

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ABSTRACT

The water gas shift (WGS) reaction was studied on Pt/CeO₂, Pt/ZrO₂ and Pt/Ce_xZr_{1-x}O₂ catalysts. All the samples were characterized by a variety of physical and spectroscopic techniques. The catalyst activities were evaluated at 250 °C in a recirculating reactor through CO conversion versus time tests and also by in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS). The sample activity for the WGS reaction depended on chemical composition. Pt/Ce_xZr_{1-x}O₂ catalysts with $x \ge 0.5$ were more active than Pt/CeO₂, probably because the addition of Zr to ceria increased both the surface area and the reducibility of ceria. The lowest CO conversion rates were obtained on Pt/ZrO₂ and Zr-rich Pt/Ce_xZr_{1-x}O₂ samples. Based on DRIFTS experiments, this result was interpreted by considering that in the WGS formate associative mechanism the stability of formate species is higher on Zr-rich supports.

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1. Introduction

Successful commercialization of hydrogen based PEM fuel cells in automobile industry needs the development of more efficient water-gas shift (WGS) units for CO cleanup and additional hydrogen production [1]. The WGS conversion, $CO + H_2O \rightarrow CO_2 + H_2$, is moderately exothermic and equilibrium limited, thereby requiring very active catalysts to achieve high CO conversion levels at low temperatures. Conventional Cu-based low-temperature WGS catalysts have been successfully employed in industrial steadystate operations for several years [2,3]. However, they do not meet the activity and stability requirements for onboard polymer electrolyte fuel cells [4]. Thus, increasing research work has lately been performed in order to develop more efficient catalysts for the production of high-purity hydrogen via the WGS reaction under fuel cell processor conditions. Most recent studies have focused on noble metals including Pd [5,6], Ru [7], Rh [8], Pt [9,10] and Au [11,12] supported on reducible single (CeO₂, TiO₂, ZrO₂, ThO₂) and mixed oxides. These studies have shown that the activity of noble metals for the WGS reaction is highly influenced by the nature of the support, essentially because the reaction intermediates and pathways greatly depend on the support redox and reducibility properties.

Platinum-based catalysts have been widely investigated because the CO conversion turnover rate is higher on Pt in comparison to other noble metals [13,14]. In particular, Pt/CeO₂ has been reported as a promising WGS catalyst due to its high activity [15,16]. For example, we recently observed that the WGS turnover rate on Pt/CeO₂ was about two order of magnitude higher than on Pt supported on silica, a non-reducible material [17]. However, Pt/CeO₂ deactivates on stream and also due to shutdown/startup modes for fuel cell applications [18,19]. Several researchers have studied the WGS reaction on Pt/ZrO2 catalysts [20,21]. Zirconia is an attractive support that presents high hardness, good mechanical resistance and thermal stability [22]; it also exhibits interesting acid-base and redox properties [23]. Nevertheless, it was reported that the WGS reaction activity on Pt/ZrO₂ catalysts is lower than on Pt/CeO2 [24]. The WGS reaction has been also studied on Pt supported on binary Ce-Zr mixed oxides [25-27], but conclusions regarding catalysts activity and stability are not conclusive. While several authors reported that Pt supported on Ce-rich $Pt/Ce_xZr_{1-x}O_2$ samples are more active than Pt/CeO₂ [25,26], others did not observe any improvement by doping ceria with Zr [24,27]. In this work, we study the WGS reaction on Pt/CeO₂, Pt/ZrO₂ and Pt/Ce_xZr_{1-x}O₂ catalysts. Results show that $Pt/Ce_xZr_{1-x}O_2$ samples with $x \ge 0.5$ are more active than Pt/CeO_2 , Pt/ZrO_2 and Zr-rich $Pt/Ce_xZr_{1-x}O_2$ are the less active catalysts. In order to interpret these results, a detailed study using in situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) technique that allows studying the evolution of the adsorbed species, intermediates and products inside the cell is presented.



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2. Experimental

2.1. Catalyst preparation

Ce_xZr_{1-x}O₂ supports were prepared by sol-gel method [28]. The precursor Zr(OC₃H₇)₄ (70% en propan-1-ol, Aldrich) was dissolved in 100 mL of isopropyl alcohol and was slowly added (1 mL min⁻¹) at 30 °C to 100 mL of an aqueous solution of Ce(NO₃)₃·6H₂O (Aldrich) stirred at 500 rpm. The hydrolysis of the mixture leads to the formation of a pseudogel. Three Ce–Zr mixed oxides of different chemical compositions were prepared: Ce_{0.75}Zr_{0.25}O₂, Ce_{0.50}Zr_{0.50}O₂ and Ce_{0.25}Zr_{0.75}O₂. Zirconia was synthesized by using the same preparation method but replacing the cerium nitrate solution by distilled water (100 mL). Ceria was obtained by precipitation of an aqueous solution of Ce(NO₃)₃·6H₂O (Aldrich) with NH₄OH (28%). All the solid precursors were first dried at 60 °C for 1 h in air and then overnight at 120 °C in a drying oven. Finally, the dried powders were calcined in air at 600 °C for 4 h.

Platinum-supported catalysts were prepared by incipientwetness impregnation of the supports at 30 °C with an aqueous solution of tetraamine platinum nitrate $[Pt(NH_3)_4](NO_3)_2$ (Aldrich, 99.9%). The impregnated samples were dried at 120 °C for 14 h and then calcined at 400 °C for 4 h in air. All the catalysts contained 0.4% Pt.

2.2. Characterization

Specific surface areas (S_g) were determined by N₂ physisorption at -196 °C using a Quantachrome Autosorb I sorptometer and BET analysis. Prior to N₂ physisorption, samples were degassed for 3 h at 250 °C.

The crystalline structure and crystal size of supports were determined by X-ray diffraction (XRD) using a Shimadzu XD-D1 powder diffractometer with a monochromated Cu K α radiation source ($\lambda = 0.1542$ nm). Analysis was carried out using a continuous scan mode at 2° min⁻¹ over a 2 θ range of 20–80°. Scherrer equation was used to calculate the mean crystallite size of the samples different oxides.

The thermal decomposition of solid precursors dried at $120 \,^{\circ}$ C was studied by differential thermal analysis (DTA) using a Mettler Toledo System STAR. Samples (15 mg) were heated in dry air at $5 \,^{\circ}$ C min⁻¹ from 25 $^{\circ}$ C to 600 $^{\circ}$ C.

Hydrogen uptakes on Pt/CeO₂ and Pt/Ce_xZr_{1-x}O₂ samples were determined by performing H₂ pulses at -50 °C using a Micromeritics AutoChem II 2920 unit. Samples (150 mg) were reduced in pure H_2 at 400 $^\circ\text{C}$, flushed with Ar at 400 $^\circ\text{C}$ for 30 min and then cooled to $-50 \,^{\circ}$ C in Ar. The H₂ uptake measurements were performed at -50 °C by injecting consecutive pulses containing 0.025 mL of H₂ in a H_2/Ar stream. Pt dispersion (D_{Pt}) on Pt/ZrO₂ was determined by H₂ chemisorption at 25 °C in a conventional vacuum unit. The catalyst was previously reduced in H₂ flow at 400 °C and then evacuated at 500 °C prior to measure the hydrogen uptake by the double isotherm method [29]. The isotherm pressure range was 1-10 kPa. In order to compare experimental H₂ chemisorption methods, the Pt dispersion of Pt/ZrO₂ sample was also determined by performing H₂ pulses at -50 °C as detailed above for Pt/CeO₂ catalyst. In all the cases, an atomic $H_i/Pt_s = 1$ ratio, where Pt_s implies a Pt atom on surface, was used to calculate D_{Pt}.

Temperature-programmed reduction (TPR) experiments were performed using a 5% H₂/Ar mixture (50 mL min⁻¹) in a Micromeritics AutoChem II 2920 unit equipped with a thermal conductivity detector (TCD). Calcined samples (150 mg) were heated at 10 °C min⁻¹ from 25 °C to 600 °C. In order to retain water formed during sample reduction, the exit gas from the reactor was passed through a cold trap before entering the TCD detector.

2.3. Catalytic tests

The WGS reaction was carried out in a glass recirculating unit of 300 mL containing a fixed-bed reactor, a fluid recirculating pump, a system for vacuum generation and pressure measurement, and gas and liquid storage devices. This recirculating reactor minimized heat- and mass-transfer limitations because low CO conversions per pass are obtained. Samples (50 mg) were reduced in situ at 250 °C in a 20% H₂/N₂ flow (200 mL min⁻¹) for 90 min; after evacuation, a gas mixture containing 3% CO, 3% H₂O and balance N₂ was introduced. The recirculating gas flow was approximately 330 mL min⁻¹; it was verified that the CO conversion rate was not changed by increasing the gas flow rate. Samples from the reaction system were collected every 15-30 min for 180 min and analyzed by ex situ gas chromatography using a Shimadzu GC-8A chromatograph equipped with flame ionization detector and a Porapak Q packed column. CO and CO₂ were separated in the chromatographic column, then completely converted to methane by means of a methanation catalyst (Ni/Kieselghur) operating at 400 °C, and finally detected by the flame ionization detector. Carbon monoxide conversion (X_{CO}) was calculated as $X_{CO} = n_{CO_2}/(n_{CO} + n_{CO_2})$. Initial CO conversion rates (r_{CO}^0 , mol CO g⁻¹ h⁻¹) were calculated as $r_{\rm CO}^0 = (n_{\rm CO}^0/W)(dX_{\rm CO}/dt)_{t=0}$, where W is the mass of the catalyst and $(dX_{CO}/dt)_{t=0}$ is the slope of the X_{CO} versus time curve at t=0.

2.4. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

A Shimadzu IR Prestige-21 spectrophotometer equipped with an in situ high-temperature/high pressure SpectraTech cell and a liquid-nitrogen-cooled MCT detector was used to carry out DRIFTS experiments. The sample holder, a ceramic crucible containing a heating resistor and a thermocouple, was placed inside a dome with CaF₂ windows. Scans were taken at resolution of 4 cm⁻¹ and 40 scans were added to improve the signal to noise ratio. The gas flow rates were always 60 mL min⁻¹. Samples (50 mg) were initially reduced in H₂ at 250 °C for 30 min, then treated 10 min in Ar at 300 °C and finally cooled down in Ar to 30 °C. Background spectra of the samples in Ar were taken from 300 °C to 30 °C, at 50 °C intervals. A flow of 5% CO and 10% H₂O in N₂ was admitted at 30 °C and the sample spectrum collected. Then the sample temperature was raised to 300 °C, at 50 °C intervals, for collecting the respective DRIFT spectra. The results given herein are difference spectra, where the background spectra of the sample in Ar served as the reference.

3. Results

3.1. Support characterization

The specific surface areas of all the samples are shown in Table 1. The S_g values were similar for CeO₂ and ZrO₂ single oxides (50–55 m² g⁻¹), but the surface areas of Ce_xZr_{1-x}O₂ mixed oxides increased with cerium content. Consistently, Querino et al. [30] reported that the surface area of zirconia increases with the addi-

Table 1	
Characterization of CeO_2 , ZrO_2 and $Ce_xZr_{1-x}O_2$ mixed oxides.	

Support	Surface area $S_g (m^2 g^{-1})$	Crystallite size (Å)	Lattice parameter a (Å)
CeO ₂	54	159	5.462
Ce _{0.75} Zr _{0.25} O ₂	87	88	5.386
Ce _{0.50} Zr _{0.50} O ₂	75	70	5.367
Ce _{0.25} Zr _{0.75} O ₂	68	64	5.221
ZrO ₂	51	147	-



Fig. 1. XRD patterns of the supports: $CeO_2(a)$; $Ce_{0.75}Zr_{0.25}O_2(b)$; $Ce_{0.50}Zr_{0.50}O_2(c)$; $Ce_{0.25}Zr_{0.75}O_2(d)$; $ZrO_2(e)$. (\bullet) CeO_2 ; (\bigcirc) monoclinic ZrO₂; (*) tetragonal ZrO₂.

tion of cerium, probably because cerium inhibits the crystallite growing and favors the production of smaller particles of monoclinic structure.

The XRD patterns of supports calcined at 600 °C are depicted in Fig. 1. Cerium dioxide displays the peak characteristics of cubic fluorite based structures (diffractogram 1-a) while ZrO₂ (diffractogram 1-e) was mainly monoclinic, although the presence of an additional tetragonal phase was also detected. The addition of 25% Zr to ceria (diffractogram 1-b) shifted the ceria diffraction lines to higher 2 θ values. This shift is indicative of changes in lattice parameter, and has been taken as evidence for the formation of a solid solution between CeO₂ and ZrO₂ [28,31]. The XRD results suggested the presence of a single phase even with the addition of 50% Zr (diffractogram 1-c), but the XRD pattern of Ce_{0.25}Zr_{0.75}O₂ sample (diffractogram 1-d) showed diffraction lines that can be assigned to tetragonal ZrO₂ peaks, thereby suggesting some phase segregation of zirconia.

Sample crystallite sizes determined by the Scherrer equation are shown in Table 1. It is observed that crystallites sizes on $Ce_xZr_{1-x}O_2$ samples are significantly lower than on ZrO_2 or CeO_2 , which is in agreement with the specific surface area trend (Table 1). The unit cell parameter *a* for CeO_2 and $Zr_xCe_{1-x}O_2$ fluorite-type cubic structure was calculated from the diffractograms in Fig. 1 and is given in Table 1. The *a* value decreased with zirconium content which is consistent with the formation of solid solutions [32]. Doping ceria with zirconium is very common and the smaller Zr ionic radius ($Zr^{4+} = 0.84$ Å, $Ce^{4+} = 0.97$ Å) induces uniform lattice strain in the material causing the lattice plane spacing changes and the diffraction peaks shifts [33].

DTA thermograms of ZrO_2 , CeO_2 and $Ce_xZr_{1-x}O_2$ samples are shown in Fig. 2. Thermogram of CeO₂ did not exhibit any peaks related to the formation of cubic fluorite-type structure (thermogram 2-a). The XRD diffractogram of CeO₂ precursor dried at 120 °C (not shown here) was similar to diffractogram 1-a corresponding to CeO_2 calcined at 600 °C (Fig. 1), thereby suggesting that the CeO₂ cubic structure was formed during the preparation step. This result is consistent with the absence of peaks observed in thermogram 2-a in Fig. 2. In contrast, the exothermic peak at 445 °C in thermogram 2-e revealed the crystallization of ZrO₂ sample [28]. Sample $Ce_{0.25}Zr_{0.75}O_2$ also exhibited a small exothermic peak at about 410 °C (thermogram 2-d) that can be assigned to crystallization of ZrO₂. Thermal decomposition of Ce_{0.50}Zr_{0.50}O₂ and Ce_{0.75}Zr_{0.25}O₂ presented a single endothermic peak at about 265 and 280 °C, respectively, attributed to the formation of $Ce_x Zr_{1-x}O_2$ solid solutions with cubic structures [34]. In summary, the above



Fig. 2. DTA thermograms of single and mixed oxides: CeO_2 (a); $Ce_{0.75}Zr_{0.25}O_2$ (b); $Ce_{0.50}Zr_{0.50}O_2$ (c); $Ce_{0.25}Zr_{0.75}O_2$ (d); ZrO_2 (e). Heating rate: $5 \degree C \min^{-1}$.

results obtained by DTA and XRD analysis strongly suggest that a solid solution is formed in $Ce_{0.50}Zr_{0.50}O_2$ and $Ce_{0.75}Zr_{0.25}O_2$ samples, with substitution of Ce^{4+} by Zr^{4+} in the lattice.

The TPR profiles of the supports are presented in Fig. 3A. The TPR curve of CeO₂ (curve 3A-a) showed two reduction peaks close to 500 and 850 °C, respectively. According to literature, the low-temperature band corresponds to surface shell reduction step



Fig. 3. Sample characterization by TPR. (A) Supports: CeO_2 (a); $Ce_{0.75}Zr_{0.25}O_2$ (b); $Ce_{0.50}Zr_{0.50}O_2$ (c); $Ce_{0.25}Zr_{0.75}O_2$ (d); ZrO_2 (e). (B) Catalysts: Pt/CeO₂ (a); Pt/Ce_{0.75}Zr_{0.25}O_2 (b); Pt/Ce_{0.50}Zr_{0.50} (c); Pt/Ce_{0.25}Zr_{0.75}O₂ (d); Pt/ZrO₂ (e). Heating rate: $10 \,^{\circ}C \min^{-1}$, W = 150 mg.

[15,35,36] and the high-temperature band is due to a bulk reduction from CeO₂ to Ce₂O₃. The TPR profile of Ce_{0.75}Zr_{0.25}O₂ (curve 3A-b) shows that the addition of Zr decreased the peak maximum of the bulk reduction step from 850 °C (ceria) to 820 °C; other authors have already noted that the bulk reduction of ceria is facilitated by doping with Zr [37]. The addition of Zr to CeO₂ also splits the reduction band of surface ceria in two bands and both shift to higher temperatures with the Zr content. Similar results were reported by Ricote et al. [25]. Reduction of ZrO₂ support exhibited two small TPR peaks at 355 and 645 °C attributed to reduction in the surface shell [20].

3.2. Catalyst characterization

The specific surface areas of Pt-based catalysts are shown in Table 2. By comparing the S_g values from Tables 1 and 2 it can be inferred that the addition of Pt to $Ce_xZr_{1-x}O_2$ supports did not change significantly their surface area. In contrast, the Sg values corresponding to ZrO_2 and CeO_2 dropped by 11 and 20%, respectively, following the Pt impregnation step. Accessible metal fractions determined by H₂ chemisorption are also presented in Table 2. The D_{Pt} values on Pt/CeO₂ and Pt/Ce_xZr_{1-x}O₂ samples were obtained by performing H₂ pulses at -50 °C in order to suppress the hydrogen spillover to the support [38]. The Pt dispersion on Pt/CeO₂ (D_{Pt} = 37%) increased slightly with the addition of Zr, reaching about 48% on Pt/Ce_xZr_{1-x}O₂ samples with $x \ge 0.5$. The highest D_{Pt} values were obtained on Pt/ZrO₂; namely, 73% and 76% were determined by using the H₂ uptakes obtained at -50 °C and 25 °C, respectively.

The X-ray diffractograms of Pt-based catalysts (not included here) showed that the incorporation of Pt to supports did not modify significantly the XRD patterns of Fig. 1. Besides, no crystalline phase of Pt was detected probably because of the low Pt loadings.

The TPR profiles of all the catalysts are shown in Fig. 3B. On Pt/CeO₂, the ceria surface reduction is promoted by the presence of Pt that activates the dissociative adsorption of H₂ at lower temperatures and generates reactive atomic protons. Thus, the maximum of the band corresponding to reduction of surface ceria in Fig. 3A (curve 3A-a) was shifted, from 500 °C (CeO₂) to 160 °C (Pt/CeO₂, curve 3B-a). Qualitatively, similar increase of the support reducibility by the presence of Pt was observed for $Pt/Ce_xZr_{1-x}O_2$ and Pt/ZrO₂ samples (curves 3B-b to 3B-e). H₂ consumptions were determined by deconvolution and integration of the reduction bands in Fig. 3B; the obtained values are presented in Table 2. Hydrogen consumptions for $Pt/Ce_{0.75}Zr_{0.25}O_2$ (576 µmol $H_2 g_{cat}^{-1}$) and Pt/Ce_{0.50}Zr_{0.50}O_2 (410 $\mu mol~H_2~g_{cat}^{-1})$ were clearly higher than for Pt/CeO₂ (316 μ mol H₂ g⁻¹_{cat}). By considering that H₂ was totally consumed for reducing Ce⁴⁺ to Ce³⁺ species, these values imply that on Pt/CeO₂ about 11% of the ceria support was reduced, while on $Pt/Ce_{0.75}Zr_{0.25}O_2$ and $Pt/Ce_{0.50}Zr_{0.50}O_2$ the amounts of reduced ceria were 26 and 28%, respectively. On Pt/Ce_{0.25}Zr_{0.75}O₂, the H₂ consumption was 229 μ mol H₂ g_{cat}⁻¹ that represents 31% of ceria reduction. All these results show that the incorporation of Zr

Table 2	
Characterization and cata	alytic activ



^a Determined by H_2 chemisorption at $-50 \degree C$.

 $^{\rm b}\,$ Determined by H_2 chemisorption at 25 $^\circ\text{C}.$



Fig. 4. WGS reaction: CO conversion as a function of time: (○) Pt/CeO₂; (▼) Pt/CeO₂; (◊) Pt/CeO₂; (◊)

increases the ceria reducibility. Finally, the lowest H_2 consumption was obtained for Pt/ZrO₂. In fact, calculations form curve 3B-e show that only 2.7% of the ZrO₂ support was reduced.

3.3. Catalyst activity

Catalyst activities for the WGS reaction were determined at 250 °C. Prior to catalytic tests, samples were reduced in pure H₂ at 250 °C for 90 min. This H₂ pretreatment reduces completely oxidized Pt to Pt⁰ and partially the support surface (Fig. 3B). It was verified that single and binary Ce–Zr oxides were inactive for the WGS reaction at 250 °C. In Fig. 4, CO conversions (X_{CO}) are represented as a function of $t W/n_{CO}^0$, where t is the reaction time, W is the catalyst weight, and n_{CO}^0 is the initial mol of CO. The local slope of each curve in Fig. 4 gives the CO conversion rate at a specific value of CO conversion rate (r_{CO}^0 , mol h⁻¹ g⁻¹) by calculating the initial slopes in Fig. 4 according to:

$$r_{\rm CO}^0 = \left[\frac{dX_{\rm CO}}{d(tW/n_{\rm CO}^0)}\right]_{tW/n_{\rm CO}^0 = 0}$$
(1)

From r_{CO}^0 values we calculated the initial turnover frequencies (TOF, s⁻¹). The obtained r_{CO}^0 and TOF values are shown in Table 2. Turnover frequencies followed the order: Pt/Ce_{0.75}Zr_{0.25}O₂ > Pt/Ce_{0.50}Zr_{0.50}O₂ > Pt/CeO₂ > Pt/Ce_{0.25}Zr_{0.75}O₂ > Pt/ZrO₂; i.e. Pt/Ce_xZr_{1-x}O₂ samples with $x \ge 0.5$ were the most active catalysts. Other authors have already noted that the activity for the WGS reaction of Pt supported on binary Ce–Zr oxides was higher than on single CeO₂ or TiO₂ supports [25,26]. In order to obtain more insight on the effect of support Ce/Zr ratio on catalyst activity additional in situ DRIFTS studies were performed.



Fig. 5. In situ DRIFTS spectra recorded at increasing temperatures on Pt/ZrO₂ (A) and Pt/Ce_{0.75}Zr_{0.25} (B) (5% CO + 10% H₂O in N₂; W_{cat} = 50 mg; P = 101.3 kPa; F_{ν} = 60 mL min⁻¹).

3.4. In situ DRIFTS studies

Fig. 5A presents the DRIFTS spectra obtained on stream during the WGS reaction on Pt/ZrO₂ at increasing temperatures, from 30 °C to 300 °C. CO adsorption on metallic Pt showed two IR bands that are assigned to linear (v_{CO} , 2044 cm⁻¹) and bridge-bonded $(v_{CO}, 1822 \text{ cm}^{-1})$ CO, respectively [39,40]. The bridged CO band diminished with the temperature increase and disappeared at about 200 °C. The two bands corresponding to gaseous CO were detected at 2185 and 2112 cm⁻¹ [41]. The bands at 2349 and 2312 cm^{-1} arising from gaseous CO₂ [42] appeared at about 200 °C and increased with increasing temperature which confirmed the catalytic results in Fig. 4 showing that Pt/ZrO_2 is active for converting CO to CO₂ via the WGS reaction. Spectra in Fig. 5A also showed IR absorption bands at 2962 and 2870 cm⁻¹ associated to C-H stretching vibration of adsorbed formate species. The presence of formates was also confirmed by characteristic bands of asymmetric (v_{asCOO} , 1570 cm⁻¹) and symmetric (v_{sCOO} , 1367 cm⁻¹) OCO stretches [43,44]. The IR formate bands appeared at about 150 °C and evolved with the reaction temperature similarly to gaseous CO₂.

DRIFTS spectra obtained on Pt/Ce_{0.50}Zr_{0.50}O₂ are presented in Fig. 5B. Linear and bridge adsorption bands of CO on Pt appeared at 2041 and 1824 cm⁻¹, respectively. An additional band was formed at 1980 cm⁻¹ on Pt/CeO₂ at about 150 °C and developed with the reaction temperature. A similar band was observed in previous studies on the CO adsorption over Pt/CeO₂ [45] and was assigned to CO adsorbed on metallic atoms interacting with Ce³⁺ ions of the support. The C-H stretching vibration bands (2860 and 2954 cm⁻¹) revealing the formation of formates appeared at about 150 °C and developed with the reaction temperature. A similar qualitative evolution with the temperature was noted in Fig. 5B for the gaseous CO_2 band at 2358 cm⁻¹, reflecting the progress of the WGS reaction. In contrast with the DRIFTS spectra obtained on Pt/ZrO₂ (Fig. 5A), in the 1000–1700 cm⁻¹ region of spectra in Fig. 5B it is observed the formation of carbonate bands that hinder the univocal identification of surface formate species in this region. Qualitatively, the spectra shown in Fig. 5B are very similar to those obtained on Pt/CeO_2 that we presented in a previous work [17].

DRIFTS spectra obtained on our Pt-based catalysts are compared at $250 \,^{\circ}$ C in Fig. 6. Qualitatively, similar spectra containing the characteristic bands corresponding to gaseous CO ($2180-2110 \,\mathrm{cm}^{-1}$) and CO₂ ($2360-2320 \,\mathrm{cm}^{-1}$), linear CO adsorbed on Pt⁰ ($2061-2036 \,\mathrm{cm}^{-1}$), C–H stretching modes of formate species



Fig. 6. In situ DRIFTS spectra at 250 °C on Pt/CeO₂ (a); Pt/Ce_{0.75}Zr_{0.25}O₂ (b); Pt/Ce_{0.50}Zr_{0.50} (c); Pt/Ce_{0.25}Zr_{0.75}O₂ (d); Pt/ZrO₂ (e) (5% CO+10% H₂O in N₂; $W_{cat} = 50 \text{ mg}; P = 101.3 \text{ kPa}; F_{\nu} = 60 \text{ mL min}^{-1}$).



Fig. 7. In situ DRIFTS spectra in the formate υ_{C-H} region on Pt/CeO₂ (a); Pt/Ce_{0.75}Zr_{0.25}O₂ (b); Pt/Ce_{0.50}Zr_{0.50} (c); Pt/Ce_{0.25}Zr_{0.75}O₂ (d); Pt/ZrO₂ (e): (A) purged in Ar at 200 °C; (B) purged in Ar at 250 °C.

(2970–2841 cm⁻¹) and OCO stretches of formates and carbonates were obtained. However, it is worth to note in Fig. 6 that the Zr addition to CeO₂ shifted the formate v_{C-H} band to higher wavenumbers, from 2841 cm^{-1} (Pt/CeO₂) to 2868 cm^{-1} (Pt/ZrO₂). This band shift suggested that the formate species stability increases with the Zr content in the sample. To confirm this result, additional DRIFTS experiments were carried out. Specifically, after recording the DRIFTS spectra at 300 °C (see Fig. 5), we purged the system with Ar at 200 and 250 °C. The spectra obtained on all the samples in the region corresponding to C-H stretching vibration of adsorbed formate species following the Ar purges are presented in Fig. 7. The presence of formate species was detected on all the samples following the Ar purge at 200 °C (Fig. 7A), although the formate band intensity increased with the Zr content in the sample. After the Ar treatment at 250 °C, the formate species were detected only on Pt/ZrO₂ and Pt/Ce_{0.25}Zr_{0.75}O₂ (Fig. 7B). The higher stability of adsorbed formate species on Zr-rich $Pt/Ce_xZr_{1-x}O_2$ samples was therefore confirmed by these results showed in Fig. 7.

4. Discussion

There is much controversy in the literature regarding the WGS mechanism on Pt supported over reducible supports. In general, authors have explained the catalyst activity results essentially in basis of the redox and the associative mechanisms, or by a combination of both of them [46]. In the case of Pt/CeO₂, several works have lately proposed [25,46] that the WGS occurs via a formate associative mechanism as depicted below:

$$Pt + CO_{(g)} \leftrightarrow Pt - CO$$
 (2)

 $Pt-CO+S-OH \Leftrightarrow S-HCOO+Pt$ (3)

$$H_2O_{(g)} + S \leftrightarrow S - H_2O \tag{4}$$

$$S-HCOO + S-H_2O \leftrightarrow CO_{2(g)} + H_{2(g)} + S-OH + S$$
(5)

where Pt and S are platinum and support surface sites, respectively. This mechanism involves the interaction of CO adsorbed on platinum with terminal OH groups of partially reduced ceria forming bridge formates that are converted to bidentate formates by coadsorbed water and finally decomposed toward H₂ and CO₂.

Our results in Table 2 showed that Pt supported on $Ce_xZr_{1-x}O_2$ mixed oxides with $x \ge 0.5$ are more active catalysts for the WGS reaction than Pt supported on the corresponding single oxides, i.e. CeO₂ or ZrO₂. According to elementary step (3) in the associative mechanism, the formate formation rate would increase with the concentration of surface OH groups. Previous works have shown that the formation of WGS active OH groups occurs on Ce^{3+} defect sites resulting from the reduction of ceria support [8,25]. Results in Fig. 3B and Table 2 showed that the reduction extent of surface ceria on $Pt/Ce_xZr_{1-x}O_2$ samples with $x \ge 0.5$ was clearly higher than on Pt/CeO₂ which is consistent with theoretical calculations showing that introduction of zirconia into the ceria lattice decreases the Ce⁴⁺/Ce³⁺ reduction energy [47]. The higher reducibility of Ce-rich $Pt/Ce_xZr_{1-x}O_2$ samples in comparison to Pt/CeO₂ has been specifically explained by considering that the introduction of more electronegative Zr⁴⁺ ions to ceria induces significant lattice distortions that increase both the oxygen mobility and the oxygen vacancies in the lattice [25]. Thus, the superior WGS activity exhibited by $Pt/Ce_xZr_{1-x}O_2$ samples with $x \ge 0.5$ in comparison to Pt/CeO₂ may be explained by considering that a higher concentration of surface OH groups is formed on Ce-rich $Pt/Ce_xZr_{1-x}O_2$ during the sample reduction step.

The lowest WGS turnover rates were observed on Pt/Ce_{0.25}Zr_{0.75}O₂ and Pt/ZrO₂ samples (Table 2). In particular, the TOF value on Pt/ZrO_2 was four times lower than on Pt/CeO_2 . Our DRIFTS spectra in Fig. 6 showed that the formate C-H stretching bands on $Pt/Ce_{0.25}Zr_{0.75}O_2$ and Pt/ZrO_2 appeared shifted to higher wavenumbers in comparison to that obtained on Pt/CeO_2 , thereby suggesting that the stability of formate species is higher on Pt/ZrO_2 and Zr-rich $Pt/Ce_xZr_{1-x}O_2$ samples. This assumption was corroborated by DRIFTS spectra in Fig. 7B showing that formates remained adsorbed only on Pt/Ce_{0.25}Zr_{0.75}O₂ and Pt/ZrO₂ samples after purging with Ar at 250 °C. In previous works [15], it has been proposed that on Pt supported over ceria-based solids the rate limiting step in the WGS mechanism is the surface formate decomposition (elementary step (5) in the formate associative mechanism depicted above), essentially by taking into account the relative stability of formates on ceria at low temperatures as it was observed on our DRIFTS spectra. If this is true, then the lower WGS activity exhibited by Zr-rich $Pt/Ce_xZr_{1-x}O_2$ and Pt/ZrO_2 samples

can be associated with the higher stability of the formate species formed on these samples.

In summary, our results show that the WGS activity on $Pt/Ce_xZr_{1-x}O_2$ catalysts depends on Ce/Zr ratio. $Pt/Ce_xZr_{1-x}O_2$ samples with $x \ge 0.5$ are the most active catalysts while Zr-rich $Pt/Ce_xZr_{1-x}O_2$ samples are less active than Pt/CeO_2 . Changes in sample reducibility and formate species stability with the chemical composition account for these observed differences for the WGS activity.

5. Conclusions

The WGS activity on $Pt/Ce_xZr_{1-x}O_2$ catalysts depends on the chemical composition of support. On $Pt/Ce_xZr_{1-x}O_2$ samples with x > 0.5, the WGS turnover rate is higher than on Pt/CeO₂. Introduction of zirconia into ceria lattice increases both the surface area and the reducibility of ceria and, as a consequence, increases also the concentration of surface OH groups that are formed on Ce³⁺ reduced sites. The WGS associative mechanism on Pt supported on ceria-based solids would occur via the formation of intermediate formate species that is promoted by the presence of terminal OH groups on partially reduced ceria. Thus, the superior WGS activity exhibited by Ce-rich $Pt/Ce_xZr_{1-x}O_2$ samples may be explained by considering that a higher concentration of surface OH groups is formed on these samples during the sample reduction step. In contrast, the WGS activity on Pt/Ce_{0.25}Zr_{0.75}O₂ is lower than on Pt/CeO₂ because the formate species stability increases on Zr-rich $Pt/Ce_xZr_{1-x}O_2$ samples thereby lowering the formate decomposition rate that would be rate-limiting in the WGS associative mechanism.

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