



Performance enhancement in the water–gas shift reaction of platinum deposited over a cerium-modified TiO₂ support

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Abstract

A novel catalyst consisting of platinum deposited over a cerium-modified titania substrate has been studied. Pt supported on Ce-modified TiO₂ catalyst shows better thermal stability respect to bare TiO₂ support and higher WGS activity than those corresponding to individual titania and ceria supports, indicating a cooperative effect between Pt and the Ce-modified TiO₂ support. XPS and TPR results revealed the intimate contact between Pt and cerium entities in the Pt/Ce–TiO₂ catalyst that facilitates the reducibility of the support at low-temperatures while the Ce–O–Ti surface interactions established in the Ce-modified support TiO₂ decrease the overreduction of TiO₂ at high-temperature. Comparison of catalytic activity with catalysts characterization suggests that the modifications in the reducibility of the support and the stability of metallic particles when platinum is supported on cerium-modified TiO₂ are responsible of the better catalytic behaviour of this sample in the water–gas shift reaction.

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1. Introduction

Nowadays, there is renewed interest in WGS because it is a critical component of fuel processors used to supply hydrogen for fuel cell power generation. Commercial WGS catalysts (high-temperature shift Fe₂O₃–Cr₂O₃ and low-temperature Cu–ZnO–Al₂O₃) are unsuitable for use in fuel processors due to its complex and time-consuming activation protocol before use and their instability in contact with air. Consequently, it is a critical point to develop new WGS catalysts with high activity and stability over a wider operating temperature window than is currently possible with the commercial shift catalysts. Alternative catalysts containing noble metals such as Pt, Rh, Ru [1], Pd [2], Au [3], supported on oxide and mixed oxide substrates have been proved very effective for the WGS reaction.

Among the various noble metal-support examined in the literature, the Pt/TiO₂ catalysts are promising candidates for water–gas shift reaction [4–6].

It is generally accepted that the WGS occurs in a bifunctional manner with the participation of both the noble metal and the support. One of the proposed mechanisms is the redox process [2,7], whereby CO adsorbed onto the metal is oxidized by the support. The other mechanism used to describe the WGS reaction is the associative mechanism [8,9] in which surface formates produced from CO reaction with active OH groups of supports participate as intermediates decomposing to hydrogen and unidentate carbonate, prior to the liberation of CO₂. Whichever is the mechanism operating on the WGS catalysts, it is clear that support is a crucial component of catalysts mainly on account its role in stabilizing metal dispersion and the ability to reversibly exchange oxygen ions during oxidation/reduction.

The redox and surface properties of TiO₂ support are primarily dependent upon various factors such as particle

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size, phase modifications, structural defects/distortion and chemical non-stoichiometry. Of course, the redox and surface properties of TiO_2 are strongly influenced when it is combined with other transition metals or rare earth oxides. Ceria is particularly interesting as candidate to mix with TiO_2 substrates because cerium ions have surface properties very useful for WGS [10,11]. Besides Ti^{4+} ions can be replaced for Ce^{4+} ions improving the thermal stability and redox properties of TiO_2 [12,13].

With this background, in the present study we investigated a cerium-modified TiO_2 substrate as new support of platinum for the WGS reaction. The effect of the support on the textural, structural and surface catalyst properties were determined by N_2 adsorption–desorption isotherms, XRD, TPR and XPS and related to the activity/selectivity results in the WGS reaction of gas mixtures simulating typical compositions of reformat streams.

2. Experimental

2.1. Catalyst preparation

TiO_2 support (Titanium (IV) oxide, catalyst support Alfa Aesar 150 m^2/g BET area) was stabilized by thermal treatment at 773 K for 4 h. The cerium-modified TiO_2 support (6.6 wt.% Ce) was prepared by impregnation of the calcined TiO_2 with aqueous solutions of cerium nitrate (Alfa Aesar, REacton 99.5%). The impregnate was dried under air at 383 K for 8 h and subsequently calcined at 773 K for 8 h. Supported Pt catalysts (0.5 wt.% Pt) were prepared by impregnating each of the above supports, under stirring at 343 K for 2 h using aqueous solutions of H_2PtCl_6 metal precursor (Aldrich, 99.9%). After Pt loading, the samples were dried in air at 383 K, followed by calcination in air at 773 K for 3 h.

2.2. Catalyst characterization

The chemical composition of the catalysts, previously dissolved in acidic solutions, was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using a Perkin–Elmer Optima 3300DV apparatus. N_2 adsorption–desorption isotherms were obtained at 77 K over the whole range of relative pressures, using a Micromeritics ASAP 2100 automatic device on samples previously outgassed at 423 K for 12 h. Temperature-programmed reduction experiments were obtained by heating the samples under a 10% H_2/Ar flow (50 mL/min) from 233 to 1173 K at a linearly programmed rate of 10 K/min in a U-shaped quartz reactor connected to a Balzer Prisma™ quadrupole mass spectrometer (QMS 200) for on-line gas analysis. The H_2 signal ($m/z = 2$) and the H_2O signal ($m/z = 18$) in the mass spectrometer were continuously recorded in order to follow the reduction processes of metal oxides present in the samples. Platinum dispersion was measured at 193 K, to minimize contribution of hydrogen spillover, by H_2 chemisorption using a dynamic method as

described elsewhere [14]. Prior to chemisorption, all samples were reduced under H_2/Ar flow (50 mL/min) for 1 h at 523 K and subsequently flushed under Ar for 15 min at 15 K above the reduction temperature. To calculate metal dispersion, adsorption stoichiometry of $\text{H}/\text{Pt} = 1$ was assumed [15]. FTIR spectra of CO chemisorbed were collected with a Nicolet ZDX IR spectrophotometer equipped with a DTGS detector. Powder samples were pressed into self-supported wafers. Samples were reduced under H_2 flow at 473 and 553 K. The samples were subsequently outgassed under high vacuum for 0.5 h and the temperature of the cell was set at 303 K. Finally, small CO pulses (50 Torr) were dosed into the cell, recording each FTIR spectrum after CO dosing. X-ray powder diffractograms were recorded following the step-scanning procedure (step size 0.02° , 2θ scanning from 20 to 80°) in a computerized Seifert XRD 3000 P diffractometer ($\text{Cu K}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$). X-ray photoelectron spectroscopy (XPS) was used to study the chemical composition and oxidation state of the catalyst surfaces. Photoelectron spectra were recorded with a VG Escalab 200R electron spectrometer equipped with a $\text{Mg K}\alpha$ X-ray source ($h\nu = 1253.6 \text{ eV}$) and a hemispherical electron analyser operating at constant transmission energy (50 eV). The X-ray source was operated at low X-ray fluxes in order to minimize X-ray-induced reduction of Pt and Ce species. The energy regions of Ti 2p, Ce 3d and Pt 4f core-levels in oxidized and reduced samples were recorded. The C 1s peak at 284.6 eV was used as an internal standard for peak position measurement. The areas of the peaks were estimated by calculating the integral of each peak after subtracting a Shirley background and fitting the experimental peak to a combination of Lorentzian/Gaussian lines of variable proportions.

2.3. Catalytic activity measurements

The catalysts in reduced form (in situ at 548 K for 2 h with 50 mL/min of 10 vol% H_2/N_2 mixture) were tested for the water–gas shift reaction of gas mixtures simulating typical compositions of reformat streams (mol%: H_2 28%, CH_4 0.1%, CO 4.4%, CO_2 8.7% N_2 29.2%, H_2O 29.6%). Activity was measured at atmospheric pressure, under a gas hourly space velocity of $21200 \text{ Lh}^{-1} \text{ Kg}_{\text{cat}}^{-1}$ and temperatures between 498 and 573 K, running from the lowest to the highest temperature. The reaction products were analysed on-line by gas chromatography.

3. Results and discussion

Table 1 shows the chemical compositions, expressed as weight percentages, obtained from ICP-AES analyses and the textural properties of the supports and catalysts. As observed in Table 1, the specific area and pore volume data for the Ce-modified TiO_2 support indicate that the textural properties of the TiO_2 substrate do not change significantly after cerium incorporation.

Table 1
Textural properties, chemical composition (wt.%) and metal dispersion of supports and catalysts

	BET area (m ² /g)	Pore volume (cm ³ /g)	Pt (%)	CeO ₂ (%)	Pt dispersion (%)
TiO ₂	62	0.232			
Ce–TiO ₂	70	0.306			
Pt/TiO ₂	65	0.249	0.52		57
Pt/Ce–TiO ₂	62	0.312	0.56	9.6	60

Fig. 1 shows the X-ray diffraction patterns of the supports. XRD profile of Ce-modified TiO₂ support (T-C in Fig. 1) presents reflections of crystalline anatase phase (at 25.3°, 48.1° and 53.9° JCPDS 84-1286) with a very weak peak around 28.6° corresponding to the strongest line [111] from cerianite phase (JCPDS 34-394). From XRD pattern of Ce–TiO₂ there is not evidence of substantial modification of particle size of TiO₂ nor changes in lattice parameters of TiO₂ after Ce addition.

The results of the TPR-MS experiments performed on the supports are shown in Fig. 2. The figure includes the TPR-MS traces for H₂ consumption ($m/z = 2$) and H₂O evolution ($m/z = 18$). The H₂ consumption profile corresponding to TiO₂ support (Fig. 2a) shows a broad band centered at 919 K with simultaneous H₂O evolution indicative of some surface reduction of Ti⁴⁺ ions [16]. MS trace for H₂O also shows a strong peak at 564 K without H₂ con-

sumption which can be assigned to the thermal surface dehydroxylation [17,18] because weakly adsorbed H₂O was observed at 433 K in the inert pretreatment done prior to reduction. The TPR profile for the Ce-modified TiO₂ support (Fig. 2b) displayed a broad hydrogen consumption peak with components at 879 K and 920 K. This hydrogen consumption involves, besides reduction of Ti ions observed for pure TiO₂ at 920 K, the reduction of cerium ions that, in accordance with the literature addressing reducibility of ceria, may be related with easily reducible surface oxygen from ceria entities of low particle size [19] or with the reduction of some Ce–O–Ti surface structures [12,20]. Compared with TPR of individual TiO₂, the surface reduction in Ce-modified TiO₂ support increases in intensity. The TPR profile for Ce-modified TiO₂ support (Fig. 2b) displayed two sharp water evolution peaks, at 487 K and 566 K, without hydrogen consumption associated to the thermal desorption of water from recombination of hydroxyl surface groups from TiO₂ (564 K) and highly dispersed ceria entities (487 K). The TPR-MS profiles of the platinum-containing samples are depicted in Fig. 3. The reduction profiles of platinum species indicate differences in the interaction between Pt species and the supports. For platinum deposited on bare TiO₂ (Fig. 3a), two main hydrogen consumption peaks at 360 K and 634 K were observed. According to previous studies conducted over supported Pt catalysts [6,21–23] the reduction peak at 360 K could be assigned to the reduction of surface PtO_x species. The hydrogen consumption for the reduction of these species is not accompanied by a simultaneous H₂O evolution indicating readsorption of H₂O formed on the TiO₂ support. The second hydrogen consumption peak on Pt/TiO₂ sample at 634 K occurs with simultaneous H₂O production. This reduction peak could be attributed to the reduction of the surface oxygen of TiO₂. This reduction step shifts towards lower temperature respect to the reduction temperature observed during the reduction of bare TiO₂ support. This fact agrees with literature studies on the reducibility of Pt–TiO₂ catalysts that generally recognized the promotional effect of Pt in the surface reduction of TiO₂ [16,24–26]. In the case of the sample supported on Ce-modified TiO₂ (Fig. 3b) hydrogen consumption peaks at 370 K and 700 K were observed. As it was indicated in the case of Pt–TiO₂ catalysts, the hydrogen consumption peak at low-temperature is related with the reduction of surface PtO_x. Quantification of hydrogen consumed in the reduction peak at 370 K indicates that reduction at this temperature includes Pt species together with species of support since the measured value of hydrogen consumption was higher than the amount expected for the complete reduction of platinum precursors to Pt⁰. The support species involved in this reduction are related with cerium phases because the intensity of the reduction increases with the ceria content. The reduction of platinum species and the concomitant ceria surface reduction indicate a close interaction between Pt and ceria surface phases, in agreement with previous findings [27]. The

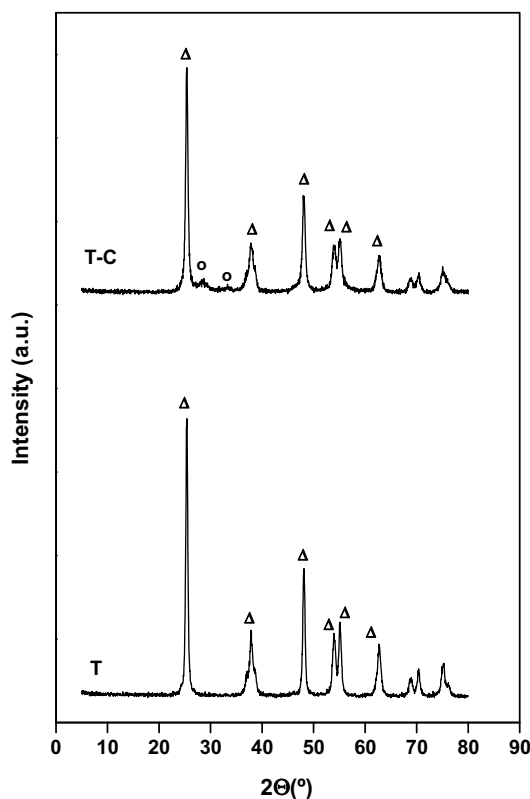


Fig. 1. Powder X-ray diffraction patterns of TiO₂ (T) and Ce–TiO₂ (T-C) supports ((Δ) Anatase, (○) Cerianite).

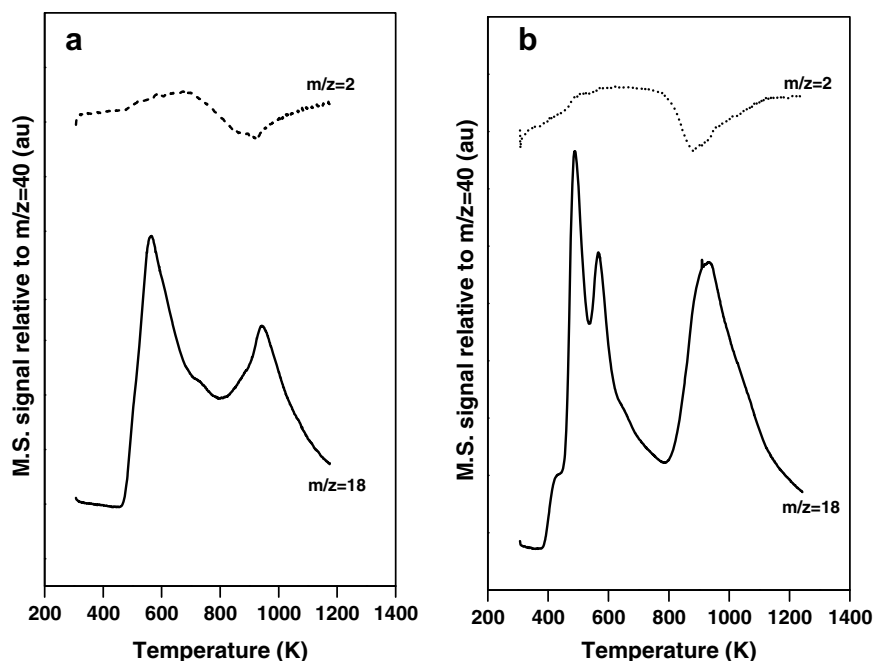


Fig. 2. Temperature-programmed reduction-MS profiles of: (a) TiO_2 and (b) Ce-TiO_2 calcined supports.

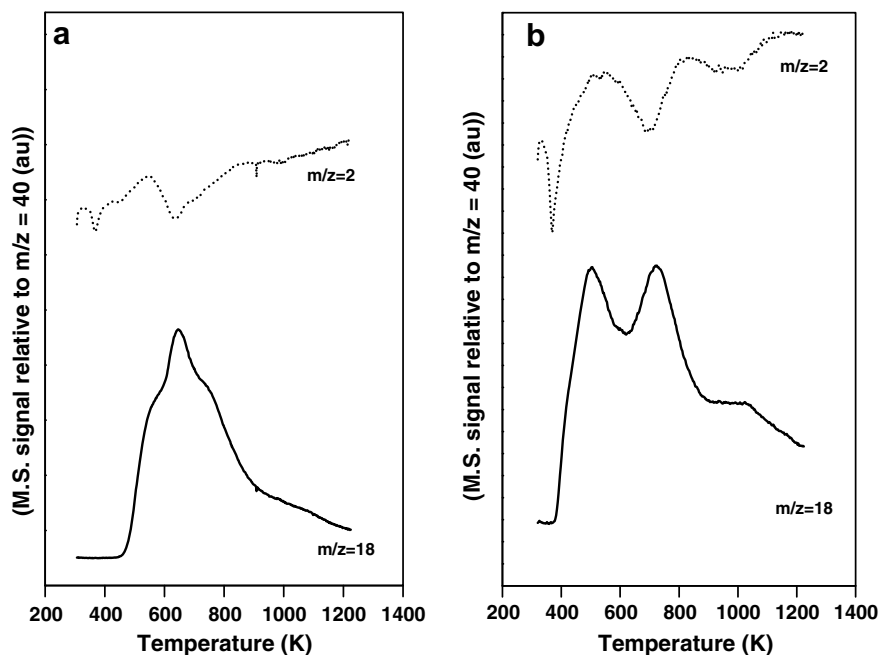


Fig. 3. Temperature-programmed reduction-MS profiles of (a) Pt/TiO_2 and (b) Pt/Ce-TiO_2 calcined catalysts.

second hydrogen consumption peak on Pt/Ce-TiO_2 observed at 634 K could be attributed to the reduction of the surface oxygen of TiO_2 . This reduction step shifts towards higher temperature respect to the reduction temperature observed during the reduction of Pt/TiO_2 catalyst. The modification of Ti reducibility by the presence of Ce is indicative of some Ce-O-Ti surface interaction [12,20].

The chemical species present on the catalyst surfaces and their proportions were evaluated by XPS. The binding

energies of core-electrons and the surface atomic ratios of the calcined supports are summarized in Table 2. The Ti 2p spectra of TiO_2 and Ce-modified TiO_2 supports were deconvoluted in two components at 458.5 and 464.2 eV that correspond to Ti^{4+} ions in stoichiometric TiO_2 surfaces [28,29]. Comparing the envelopes of u and v peaks (using the nomenclature of Burroughs [30]) of the Ce 3d level for the bulk CeO_2 and the Ce-TiO_2 support, it is observed for the latter a growing of the v' component

Table 2

Binding energies (eV) of core electrons and surface atomic ratios of calcined supports

	Ti 2p _{3/2}	Ce 3d _{5/2}	Ce ³⁺ (%)	Ce/Ti
TiO ₂	458.5			
Ce–TiO ₂	458.5	882.1	42	0.171

together with a significant decrease in the v'' and u''' peak intensities. After the deconvolution of the Ce 3d spectra, the percentage contribution of u''' to the total Ce 3d (4.3%) indicates a very high degree of reduction (50% ca Table 2) of the cerium introduced in the support. The stabilization of Ce³⁺ ions on TiO₂ may be the result of different factors, such as small particle size of ceria entities [31], changes in the coordination of Ce atoms [32] and/or net charge due to anion sharing with TiO₂. Considering both the low calcination temperature used and the difference in ionic radii between Ti⁴⁺ and Ce³⁺ ions, stabilization of cerium due to its incorporation into the titania lattice appears unlikely. Taking into account the low Ce/Ti = 0.032 atomic ratio of the substrate, the formation of Ti–O–Ce bonds in an interfacial phase Ce_{1–x}Ti(IV)O_{2–y}, as reported and explained in the earlier literature reports [12,33] is, probably, the type of surface interaction responsible of the high surface exposure and reducibility of cerium ions detected by XPS on the Ce–TiO₂ support. For the sample supported on Ce–TiO₂, it is observed a decrease in the Ce/Ti XPS atomic ratio of the support after Pt incorporation (Table 3); this could correspond to preferential coverage of the ceria phase with platinum or to the formation of some specific compound between them. The chemical changes in the catalysts after reduction in H₂ at 623 K were also investigated by XPS. As shown in Table 3, the Pt 4f_{7/2} level for the Pt/TiO₂ and Pt/Ce–TiO₂ catalysts after reduction contains a single peak at 71.5–71.7 eV indicative of the presence of Pt⁰ species. Small electropositive shift in Pt XPS peaks after reduction in catalysts supported on Ce–TiO₂ may be interpreted in terms of charge transfer from metal to ceria consequence of the close Pt–Ce interactions [34,35]. After the H₂ treatment, the binding energies of Ti did not change with respect to the fresh counterparts, indicating that these species were scarcely affected by reduction at 623 K. Treatment under hydrogen, however, produced changes in the Ce state. As shown in Table 3, a substantial

reduction of cerium occurred in the case of the Pt/Ce–TiO₂ catalyst (u''' percentage equivalent to 70% of Ce³⁺ species, Table 3). The increase in the degree of reduction of ceria as compared to the Ce–TiO₂ support alone (Table 2) implies a close contact between metallic Pt and ceria surfaces.

The amount of exposed platinum in the reduced catalysts, as determined by H₂ chemisorption, is given in Table 1. As Table 1 shows, the change in Pt-support interaction when cerium is incorporated to TiO₂ did not change significantly the surface platinum exposure respect the value observed on bare TiO₂.

Chemisorption of CO was used to reveal the nature of the Pt metal surface sites in reduced catalysts. The IR spectra of CO chemisorbed on the Pt/TiO₂ and Pt/Ce–TiO₂ catalysts after reduction at 473 and 553 K are shown in Fig. 4. As expected for Pt supported on CeO₂ or TiO₂ [36,37], the infrared spectra of CO adsorbed on reduced catalysts are consistent with the formation of linear forms of chemisorbed CO (2090–2000 cm^{−1}). For catalysts reduced at 473 K, the band of linearly adsorbed CO appears shifted at higher wavenumbers when platinum is supported on Ce-modified TiO₂. Keeping in mind that the particles sizes of Pt after reduction are similar in both supports (Table 1), the higher CO vibration frequency observed on Ce–TiO₂ support is indicative of some electron-deficiency in the electronic configuration of Pt atoms deposited on this support. The variation of the electronic character of Pt on Ce–TiO₂ observed by FTIR of CO is in line with the small electropositive shift in Pt previously observed by XPS and interpreted in terms of charge transfer from metal to ceria consequence of the close Pt–Ce interactions [34,35]. On both samples, IR bands evolve differently when the reduction temperature rises to 553 K. For the Pt/TiO₂ catalyst the intensity of linear CO band decreases significantly after reduction at 553 K while in the case of Pt/Ce–TiO₂ the variation is considerably less accentuated. The decrease in intensity observed for Pt/TiO₂ catalyst may be related to the following processes: (a) sintering of metallic particles, (b) modification of electronic properties of Pt from its interaction with partially reduced Ti³⁺ sites [36] or, (c) generation of strong metal-support interactions [37]. In the present case, the loss in intensity with the increase in reduction temperature is probably related with particle sintering and/or modification of Pt with partially reduced Ti³⁺ sites since no decoration of the metal particles with TiO_x

Table 3

Binding energies (eV) of core electrons and surface atomic ratios of calcined and reduced Pt supported catalysts

		Pt 4f _{7/2}	Ti 2p _{3/2}	Ce 3d _{5/2} (%Ce ³⁺)	Pt/Ce	Pt/Ti	Ce/Ti
Pt/TiO ₂	Calcined	71.7 (28.8%) 73.0 (71.2%)	458.4			0.007	
	Reduced	71.1 (100%)	458.4			0.002	
Pt/Ce–TiO ₂	Calcined	71.9 (23.2%) 73.4 (76.7%)	458.7	882.0 (50)	0.854	0.094	0.110
	Reduced	71.5 (100%)	458.5	882.0 (70)	0.126	0.009	0.071

moieties is expected taking in mind that strong metal-support interactions is believed to occur at reduction temperatures higher than 573 K [37].

The catalysts were tested for the water–gas shift reaction of gas mixtures simulating typical compositions of reformate stream. Fig. 5 compares the CO conversion achieved in the WGS reaction over the catalysts supported on TiO₂ and Ce-modified TiO₂. The conversion achieved over a reference Pt catalyst supported on pure CeO₂ of similar surface area of the TiO₂ based catalysts is also shown for comparison. As Fig. 5 shows, significant differences in WGS activity were observed for the Pt catalysts depending on the support. Pt/CeO₂ reference catalyst is significantly the less active tested catalyst. Pt/TiO₂ sample is considerably more active than the later but shows low stability at high-temperatures that implies a decreasing in its WGS activity for temperatures higher than 573 K. Pt supported on Ce–TiO₂ showed better thermal stability with respect to the bare TiO₂ and higher WGS activity than those corresponding to individual titania and ceria oxides indicating the cooperative effect in activity between Pt and Ce-modified support.

It is generally accepted that WGS reaction occurs with the participation of both metallic phase and support. Results of the present study show important differences in activity of platinum catalysts in spite that Ce-modified TiO₂ support did not improve significantly the initial platinum surface exposition achieved on bare TiO₂ (Table 1). This implies that properties other than the number of

metallic platinum sites affect the catalytic activity of the sample when ceria was added to TiO₂ support. Studies of the reaction pathway of WGS over CeO₂ and TiO₂ supported catalysts have shown that the physicochemical characteristics of the support are critical for generating the active germinal OH groups on support (associative mechanism) and/or for generating reducing centers on support (redox mechanism). From the point of view of associative mechanism, the differences in WGS activities are related with the type, density and reactivity of surface OH groups present on WGS catalysts. In spite that characterization done in this work does not allow to distinguish type and reactivity of surface OH groups, it is clear that addition of Ce to TiO₂ increases the hydroxyl concentration on support (Fig. 3a and b) which is in accordance with the higher activity at low-temperature observed for the sample Pt/Ce–TiO₂. From the point of view of redox mechanism, the differences in WGS activities may be related to the effect of ceria addition to TiO₂ on the redox properties of support. Physicochemical characterization of Ce–TiO₂ support presented here clearly shows that ceria entities are present in a highly dispersed state with a close interaction with Ti atoms. Over this support, platinum species interacts in different way to that operating on bare TiO₂ establishing, as XPS indicates, a direct interaction between Pt and ceria entities. As observed in Fig. 3b, the intimate contact between Pt and cerium entities in the Pt/Ce–TiO₂ catalyst facilitates the reducibility of the support at low-temperatures ($T < 400$ K). This better reducibility of support at low-temperature is in line with the higher WGS activity at low-temperature observed for this sample (Fig. 5). Taking into account the changes that catalysts may suffer under reaction at high-temperature, the differences in support reducibility and stability of Pt particles associated to the presence of Ce in the support may also be the cause

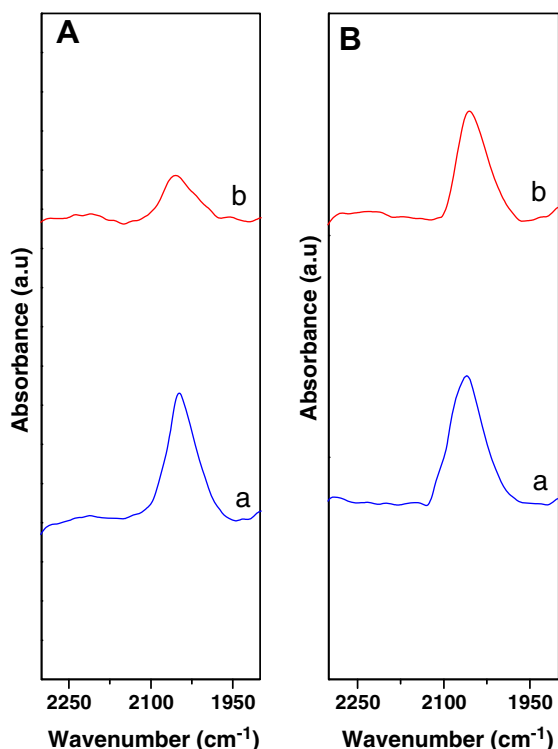


Fig. 4. FTIR spectra of chemisorbed CO on Pt/TiO₂ (A) and Pt/Ce–TiO₂ reduced at: 473 K (a) and 553 K (b).

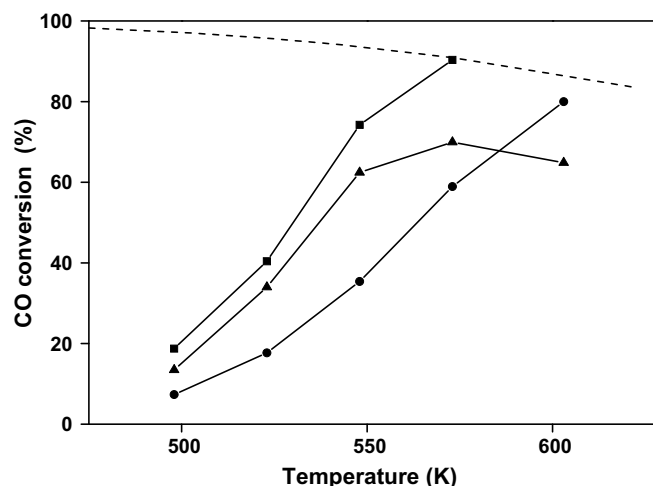


Fig. 5. CO conversion for the WGS reaction on supported Pt catalyst: (▲) Pt/TiO₂, (■) Pt/Ce–TiO₂, (●) Pt/CeO₂ (reference). Reaction conditions: total pressure 1 atm, GHSV = 21200 Lh⁻¹ kg_{cat}⁻¹, feed gas composition (mol%): H₂ 28%, CH₄ 0.1%, CO 4.4%, CO₂ 8.7%, N₂ 29.2%, H₂O 29.6%. Dotted line shows thermodynamic equilibrium limit.

of the better thermal stability of the sample supported on Ce-modified TiO_2 under reaction at temperature higher than 548 K (Fig. 5). As observed in Fig. 3a and b, the reduction of the surface oxygen of TiO_2 in the Pt/ TiO_2 catalyst occurs at lower temperature than in the case of Pt/Ce- TiO_2 counterpart as consequence of the Ce–O–Ti surface interaction developed in the latter. As observed in Fig. 4, the increase in reduction temperature implies a significant loss of CO chemisorption for the sample Pt/ TiO_2 , while in the case of Pt/Ce- TiO_2 the CO chemisorption capacity was maintained. The changes in CO chemisorption capability of Pt/ TiO_2 as consequence of the modification of electronic properties of Pt from its interaction with partially reduced Ti^{3+} sites and/or Pt particle sintering may affect its WGS activity. Therefore the better thermal stability of Ce-modified TiO_2 catalyst is probably associated with the lower over-reduction of TiO_2 under reaction at high-temperature as consequence of the Ce–O–Ti surface interaction established in the modified support together with the better stability of Pt particles on this support. Comparison of catalytic activity with catalysts characterization suggests that the modifications in the reducibility of the support and stability of metallic particles when platinum is supported on cerium-modified TiO_2 are responsible of the better catalytic behaviour of this sample in the water–gas shift reaction.

4. Conclusions

A novel catalyst consisting of platinum crystallites deposited over a cerium-modified titania substrate was found to be highly active and stable in the water–gas shift reaction. Characterization of catalyst revealed the intimate contact between Pt and cerium entities in the Pt/Ce- TiO_2 catalyst that facilitates the reducibility of the support at low-temperatures while the Ce–O–Ti surface interactions established in the modified support TiO_2 decrease the over-reduction of TiO_2 at high-temperature. The cerium-mediated modifications in both the support reducibility and metallic stability on Pt/Ce- TiO_2 catalyst were reflected in an increase of the active sites responsible of the high WGS activity observed over this catalyst. The high activity in the CO removal from real reformat gaseous streams indicates that catalysts based on Pt deposited on cerium-modified titania substrate may be considered as a promising formulation for the WGS reaction applied to fuel processors used to supply hydrogen for fuel cell power generation.

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