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Influence of redox treatments on the low temperature water gas shift reaction over Pt/CeO₂ catalysts

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Abstract

Pt/CeO₂ catalysts are promising for the low temperature water gas shift (LT-WGS) which is an important step to produce H₂ from syngas. When prepared by impregnation of platinum salt and calcination at 500 °C, they contain Pt²⁺ single atoms (SAs) and/or PtOx clusters which need to be converted into Pt⁰ nanoparticles (NPs) to get higher activity for the LT-WGS reaction. In this work, it was shown that reducing pretreatments at 250 °C under H₂ promote the molar activity of catalysts containing from 0.10 to 1.06 wt% of Pt by increasing the number of Pt⁰ NPs formed during reaction at 230 °C. An improvement was also obtained for pretreatment at 500 °C but only for low Pt content catalysts underlying the importance of the pretreatment temperature. Furthermore, it was shown that all prepared Pt/CeO₂ catalysts which slowly deactivate over reaction time can be regenerated by oxidative post-treatment at only 230 °C what is industrially interesting. Even more original, a strong improvement in activity was observed after a 12 h oxidative post-treatment at 500 °C for the low Pt content catalysts. This post-treatment was shown to redisperse and reoxidize Pt atoms into PtOx species different from the initial ones. Such species are highly reducible on the surface of CeO₂ and easily transformed into active Pt⁰ NPs.

1. Introduction

The water gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$) is an important step to produce H₂, by removing CO from syngas in different processes such as the Haber-Bosch one, metal oxide reduction and methanol synthesis.¹ A major effort has been made to develop catalysts for the production of pure H₂ for fuel cells applications because of CO poisoning of the Pt-based electrodes.¹ Among all the catalysts, the Pt/CeO₂ system is promising for the low temperature water gas shift (LT-WGS)¹⁻⁵ compared to Cu-ZnO-Al₂O₃ because of high activity,^{6,7} selectivity and stability.⁸⁻¹¹ The high cost of Pt can be mitigated by using very low noble metal loading what is facilitated by stabilization of Pt single atoms (cations) on ceria.^{12,13} Agglomeration of Pt atoms was previously observed under WGS reaction conditions: Pt/CeO₂ catalyst composed of mostly isolated atoms rapidly forms metallic Pt nanoparticles (Pt⁰ NPs) under WGS conditions above 180 °C.¹⁴ However, there is still a major debate on the nature of the active sites. Recently, a study demonstrated by using environmental transmission electron microscopy (ETEM) that the dynamic nature of the perimeter Pt⁰ – O_{vacancy}–Ce³⁺ sites is a key mechanistic step for the WGS reaction.¹⁴ Furthermore, the necessity to form Pt⁰ NPs to activate the catalyst was evidenced.¹⁵⁻¹⁷ In

particular, Pt NPs of size close to 4 nm were found to be more active for low-temperature WGS than isolated atoms and subnanometric clusters.¹⁶

Redox treatments have often been used to activate Pt/CeO₂ catalysts before CO oxidation,^{18–20} or to regenerate them afterwards.^{21,22} For the WGS reaction, Lee et al. observed the formation of a ceria nanolayer around Pt particles after reduction under H₂ at 250 °C and under N₂ at 800 °C.^{23,24} These treatments slow down the dissociation of H₂ and thus limit its competitive adsorption in favour of CO. Pastor-Pérez et al. showed that the combination of calcination, plasma and H₂ treatments increases the activity of Pt/CeO₂ catalysts by the formation of electron-enriched Pt NPs.²⁵ Furthermore, the size and morphology of Pt nanoparticles and hence the activity of Pt/CeO₂ catalysts can be tuned by low-temperature redox treatments below 500 °C.^{26,27} In particular, an oxidizing post-treatment can re-disperse Pt NPs²⁸ and desorb poisoning carbonates from the surface of CeO₂.²⁹

Our previous study has highlighted a significant influence of Pt content on molar activity of Pt/CeO₂ catalysts for the LT-WGS reaction increasing by a factor of 2.5 from 0.1 to 0.6 wt% and stabilizing above. Below 0.6 wt%, PtOx species initially present are ultradispersed and in strong interaction with CeO₂. Their low reducibility limits their activation under reaction mixture and consequently, their catalytic activity.¹⁷ A suitable reductive treatment can allow their transformation into Pt⁰ NPs active species.

To gain further insights, this work describes the impact of different pre- and post-treatments on the LT-WGS activity of Pt/CeO₂ catalysts with various Pt contents: pre-reduction with and without consecutive oxidation were explored at two different temperatures (250 °C and 500 °C) to favour formation of Pt⁰ NPs active species. An oxidative post-treatment at 500 °C for 12 h to maximize redispersion and another one at the reaction temperature (230 °C) for only 10 min, to approach viable conditions for an industrial process were also attempted. The Pt/CeO₂ catalysts were characterized by microRaman spectroscopy, annular dark-field scanning transmission electron microscopy (ADF-STEM), temperature programmed reduction by H₂ and CO (H₂-TPR and CO-TPR, respectively) and operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in connection with their catalytic activities in order to understand the influence of the different treatments on the structural modifications of Pt species.

2. Experimental

2.1 Preparation

Nine Pt/CeO₂ catalysts with various loadings were prepared by wet impregnation of 2 g of CeO₂ (Solvay Special Chem Company, specific surface area: 150 m².g⁻¹, pore diameter: 7 nm, pore volume: 0.28 cm³.g⁻¹) with 24 mL of deionized water containing between 4 and 80 mg (to get Pt loadings in the range 0.1-1.72 wt%) of [Pt(NH₃)₄](NO₃)₂ (Sigma-Aldrich, >99%) at 60 °C for 4 h under stirring at 400 rpm. Water was then removed with a rotary evaporator at 70 °C and 200 mbar. The obtained powder was finally calcinated under 100 mL.min⁻¹ of synthetic air at 500 °C for 4 h with a heating rate of 10 °C.min⁻¹. The catalysts are labelled xPt in the following where x corresponds to the weight percent of Pt determined by XRF.¹⁷

2.2 Catalytic testing and pre-treatments

A catalyst mass of 200 mg was placed in a straight Pyrex reactor with an internal diameter of 1 cm. Before any catalytic test, an initial oxidizing pretreatment named OX500 was performed under 100 mL.min⁻¹ of a 20% O₂/Ar mixture at 500 °C for 1 h (Figure S1a). To study the influence of reductive pretreatment, a subsequent treatment under 20% H₂ for 1 h was performed at either 250 °C (RED250, Figure S1b) or 500 °C (RED500, Figure S1c). Furthermore, REDOX250 and REDOX500 define a catalyst that has been treated before reaction by the initial oxidizing pretreatment at 500 °C followed by a reducing one under 20% H₂ for 1 h and then an oxidizing one under 20% O₂ flow for 1 h either at 250 °C or at 500 °C, respectively. These protocols are described in Figure S1d and S1e, respectively. Note that a fresh catalyst was used for each pretreatment.

Catalytic testing for the WGS reaction was detailed in a previous study.¹⁷ After pretreatment, measurements were performed at 230 °C under 40 NmL.min⁻¹ of H₂O, 10 NmL.min⁻¹ of CO, 65 NmL.min⁻¹ of Ar and 5 NmL.min⁻¹ of He (feed composition H₂O/CO/Ar/He:33.3%/8.3%/54.2%/4.2%). Helium was used as an internal standard for analysis with Inficon Transpector CPM 3 mass spectrometer. The GHSV was set to 600 mL.min⁻¹.g⁻¹. Preliminary measurements varying the mass of catalyst and its granulometry demonstrated the absence of external and internal diffusion limitations for a large range of conversion. The granulometry was then fixed to 106-180 µm.

The influence of oxidative post-treatments on the activity was also studied. For each catalyst after OX500 pretreatment and WGS reaction, a first short treatment of 10 min under 20% O₂ at 230 °C (ReOx230_1) was performed followed by 1 h of reaction at 230 °C (Figure S1f). Then, a long oxidizing treatment of 12 h at 500 °C under 20% O₂ (ReOx500) was added and also followed by 1 h of reaction at 230 °C. Finally, a last short treatment of 10 min under oxidizing conditions was performed (ReOx230_2) followed by 1 h of reaction at 230 °C (see the complete sequence in Figure S1f).

2.3 Characterization

Diffuse reflectance infrared Fourier transform (DRIFT) spectra with a spectral resolution of 4 cm⁻¹ were obtained from a Thermo Scientific Nicolet IR-TF 6700 spectrometer equipped with a ceramic source. Operando DRIFTS analyses were performed in a Harrick-HVC-DRP cell similar to a fixed bed reactor with a gas feed from the top to the bottom and a powdered solid (around 50 mg) retained by a stainless-steel grid. A calibration of the powder bed temperature as a function of the cell temperature was carried out using an IR pyrometer. The DRIFT cell was equipped with ZnSe windows absorbing weakly in the IR. The IR beam scattered at the surface of the sample was analysed by a high sensitivity MCT detector cooled by liquid nitrogen. During operando analysis, the feed composition was H₂O/CO/He:2%/0.5%/97.5 with a GHSV value of 1000 mL.min⁻¹.g⁻¹. Water vapor was added using a saturator at 18 °C. Analyses were performed every minute during the reaction with background subtraction performed at 230 °C after OX500 pretreatment. An Inficon Transpector CPM 3 mass spectrometer was placed at the vent to analyse the inlet and outlet gases and determine the catalytic activity, similarly to the method used during catalytic tests. The protocol of oxidative pretreatment and post-treatments performed during the catalytic tests (Figure S1) were directly applied to the catalysts in the DRIFTS cell.

MicroRaman spectra were recorded with a LabRAM HR (Horiba) spectrometer equipped with an Open Electrode CCD detector cooled at -75 °C. The Ar ion laser at 514 nm

(power limited to 0.3 mW) was focused with an x50 objective, leading to a spatial resolution of ca. 2 μm . The backscattered light was recollected, sent to an edge filter to remove the Rayleigh light, and spatially dispersed using a 300 lines. mm^{-1} diffraction grating, leading to a spectral resolution of 4 cm^{-1} .

A Titan ETEM G2 80-300 kV (FEI) microscope equipped with a spherical aberration corrector was operated at 300 kV for the analyses, which were mainly carried out in Annular Dark Field-Scanning Transmission Electron Microscopy (ADF-STEM) mode with a resolution of 0.136 nm. For each preparation, a few milligrams of sample were ground and ultrasonically suspended in ethanol. Two to three drops of the suspension were deposited on the surface of the holey carbon film covering a 300 mesh copper grid.

Temperature-Programmed Reduction (TPR) curves were obtained using a 9 Omnistar GSD 301 O2 (Pfeiffer Vacuum) mass spectrometer. The sample (50 mg) was placed in a U-shape reactor (internal diameter of 4 mm) on a quartz fiber pad and heated by a tubular furnace. The sample was pre-treated under 40 $\text{mL}\cdot\text{min}^{-1}$ of 20% O_2/N_2 at 500 $^\circ\text{C}$ for 1 h. Then, it was reduced under 40 $\text{mL}\cdot\text{min}^{-1}$ of either 1% H_2/He or 1% CO/He by heating from 25 $^\circ\text{C}$ to 500 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. When the temperature reached 500 $^\circ\text{C}$, the feed was replaced by pure H_2 or CO and maintained for 1 h before cooling down.

3. Results and Discussion

3.1 Influence of reductive and redox pre-treatments on the WGS activity

Only peaks of cubic ceria were observed by X-ray diffraction up to 1.06 wt% of Pt after oxidizing pretreatment at 500 $^\circ\text{C}$ (OX500) indicating high dispersion of Pt species. This is consistent with the low Pt surface density (below 0.22 $\text{Pt}\cdot\text{nm}^{-2}$) due to high surface area of CeO_2 support. Additionally, X-ray photoelectron spectroscopy (XPS) showed that Pt species mostly contain Pt^{2+} cations.^{17,26} Therefore, one can conclude that Pt/ CeO_2 catalysts contain ultra-dispersed oxidized Pt species (i.e. Pt^{2+} SAs and PtO_x subnanometric clusters).

The WGS molar activity at 230 $^\circ\text{C}$ strongly increases up to 0.6 wt% Pt and stabilizes above (Figure 1).¹⁷

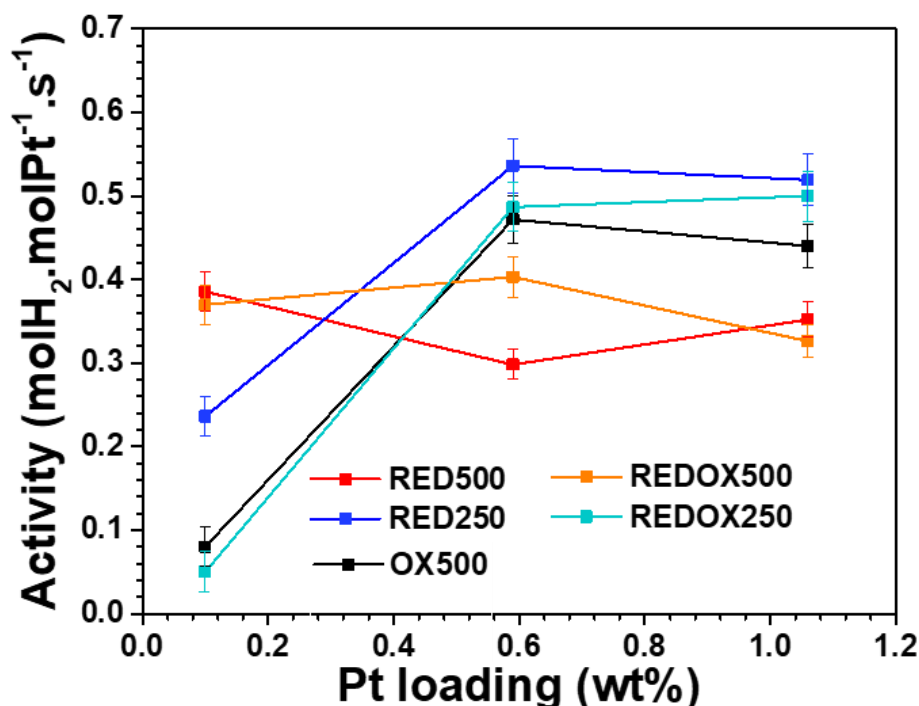


Fig.1 Evolution of molar activity with Pt loading after oxidizing OX500, reducing RED250 and RED500, redox REDOX250 and REDOX500 pre-treatments. Reaction conditions: 230 °C, H₂O/CO/Ar/He:33.3/8.3/54.2/4.2 vol% feed, GFSV = 600 mL.min⁻¹.gcat⁻¹, time on stream: 45 min.

Thus, different reductive and redox pre-treatments (see the protocols in Figures S1a-e) were attempted for three representative catalysts: 0.10Pt, 0.59Pt and 1.06Pt. For each catalyst, the activity rose up to a maximal value after few minutes (time called t_{opti}) and then slightly decreased over time (Figure S2). Therefore, data are compared both at t_{opti} and after 45 min in the following.

The evolutions over time in molar activity and CO₂/H₂ ratio are provided for 0.10Pt, 0.59Pt and 1.06Pt catalysts in Figure S3, S4 and S5, respectively. The latter parameter was significantly higher than 1 during the first 5 min of the reaction after the OX500 pretreatment due to the reduction of both PtO_x and ceria induced by CO.¹⁷ Interestingly, the reductive pretreatment at 500 °C, named RED500, and the redox one REDOX500, strongly increase the molar activity of 0.10Pt catalyst by a factor of 5 (Figure 1). Conversely, the RED500 pretreatment significantly decreases the activity of 0.59Pt and 1.06Pt catalysts (by about 25%-50%). For the reductive pretreatment at 250 °C, named RED250, the molar activity of the three catalysts slightly increases especially for 0.10Pt. The WGS molar activity of the three catalysts reduced at 250 °C and reoxidized at 250 °C before reaction (protocol REDOX250 in Figure S1d) is close to the reference values measured after OX500 pretreatment. However, this is not the case after REDOX500 pretreatment, suggesting that the structural modification of Pt species is reversible at 250 °C but not at 500 °C.

The activation of catalysts after reducing treatments under H₂ could be due to an increase in the amount of Pt⁰ NPs active for the LT-WGS reaction by decreasing the amount of Pt²⁺ cations strongly anchored in the subsurface layers of ceria.^{30,31} To address this question, the influence of pre-treatments on the nature of Pt species and the redox properties of Pt/CeO₂ catalysts was investigated by H₂-TPR analysis and operando DRIFT spectroscopy.

3.2 Impact of the reductive and redox pre-treatments on the nature of Pt species and redox properties of Pt/CeO₂ catalysts

For the nine Pt/CeO₂ catalysts and the CeO₂ support, a first H₂-TPR analysis (named TPR1) was performed after the initial OX500 pretreatment. Structural modifications during TPR1 are assumed to be similar to that during RED500 since a temperature plateau at 500 °C under H₂ was applied in both cases. TPR1 was followed by an oxidative treatment at 500 °C for 1 h leading to a catalyst state equivalent to that after REDOX500 pretreatment. The second H₂-TPR analysis (named TPR2) subsequently carried out allows comparison of reducing properties after OX500 and REDOX500 pre-treatments. The curves plotted in Figures S6a and S6b, respectively contain one main non-symmetrical reduction peak. For TPR 1 achieved after OX500 pretreatment, the peak temperature is above 250 °C for Pt loading below 0.59 wt% (Figure 2a). According to Resasco et al., this high-temperature reducibility arises from the presence of Pt SAs at the surface of CeO₂.³² For Pt content from 0.59 to 1.06 wt%, the reduction temperature which ranges between 211 and 222 °C could be related to the presence of PtO_x clusters.³²

Finally, the reduction temperature is much lower for 1.43Pt and 1.72Pt catalysts (125 and 93 °C, respectively). Such low-temperatures reveal that either Pt⁰ NPs are present at the beginning of the TPR analysis, or are easily formed under H₂.

For the second TPR analysis (TPR2) used to probe reducing properties after REDOX500 pretreatment, the peak temperature is shifted below 150 °C for all the prepared Pt/CeO₂ catalysts (Figure 2a). This indicates the presence, even for low Pt content (LPC) catalysts of Pt⁰ clusters or NPs which are already present after REDOX500 pretreatment or easily formed from highly reducible PtO_x species. Indeed, metallic Pt species are able to dissociate H₂, leading to the surface reduction of CeO₂ by H-spillover.^{33,34}

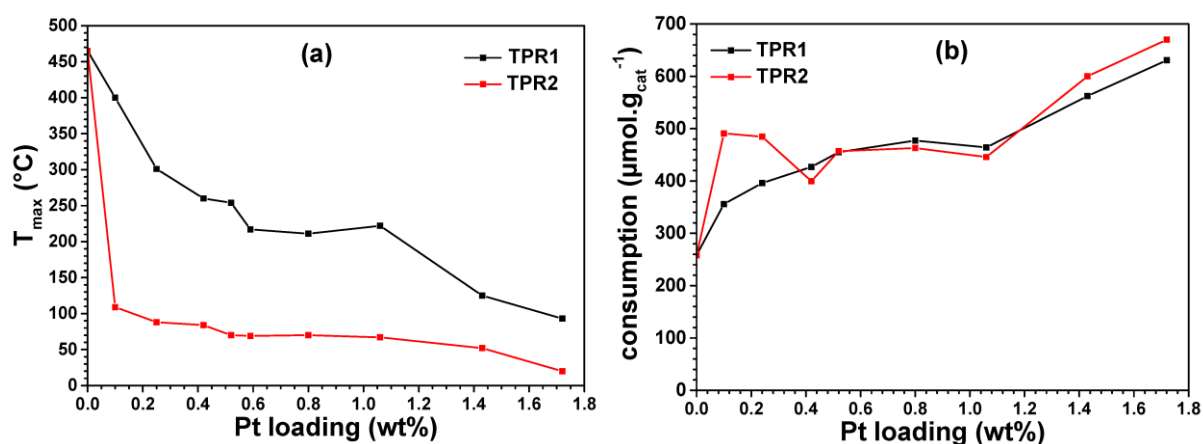


Fig.2 Evolution of (a) T_{max} peak temperature and (b) total H₂ consumption with Pt loading for TPR1 and TPR2 analyses from RT up to 500 °C under 1% H₂/He flow.

Hence, the reducibility improvement of 0.1Pt catalyst reflects a major structural change of Pt species after REDOX500 pretreatment compared to OX500. Pt⁰ NPs can then be easily formed under reaction mixtures leading to a strong enhancement of molar activity of 0.10 catalyst (Figure 1). Interestingly, REDOX500 pretreatment did not reoxidize and redisperse Pt atoms as at the initial state, in agreement with the changes of activity observed

after REDOX500 pretreatment compared to OX500 (Figure 1). Note that irreversible structural changes after such a redox cycle were previously proposed from the decrease in intensity of the PtO_x Raman band.^{26,35}

The reducibility of Pt/CeO₂ catalysts was reported to be a key parameter determining the activity.^{6,11,36–38} In this work, improvements of reducibility and activity seem to be related for LPC catalysts, typically 0.10Pt. However, REDOX500 pretreatment leads to a decrease in activity for 0.59Pt and 1.06Pt in spite of a significant improvement of reducibility. It shows that for these Pt contents, other parameters determine the catalytic activity. The decrease in activity after RED500 and REDOX500 pre-treatments could arise from Pt aggregation and poisoning by carbonates.^{29,39–41} However, ADF-STEM images of 1.06Pt catalyst recorded after RED500 pretreatment (Figure S7) did not reveal the presence of Pt NPs significantly larger than 1.4 nm, typical size determined after WGS reaction at 230 °C.¹⁷ Therefore, if Pt aggregation occurs during RED500, it should be limited to the subnanometric species and should have no impact on catalytic activity since they are poorly active.¹⁷

The total H₂ consumption rates measured between RT and 500 °C during TPR1 are much higher than the quantity required to reduce PtO to Pt⁰ (Table S1). This reveals a high reduction rate of CeO₂ and hence the presence of a high amount of oxygen vacancies and Ce³⁺ cations at the surface of CeO₂. Furthermore, the rate increases with Pt loading (Figure 2b) which can be explained by a higher number of Pt⁰ NPs leading to higher extent of H-spillover.⁴²

The H₂ consumption rates during TPR2 are significantly higher for 0.10Pt and 0.25Pt catalysts compared to TPR1 (Figure 2b and Table S1). For LPC catalysts, reduction at 500 °C under H₂ could favour extraction of Pt²⁺ cations anchored in the subsurface layers of ceria increasing the number of Pt atoms available to form Pt⁰ NPs at the surface.^{17,43} A higher number of Pt⁰ NPs both favours reduction of ceria and catalytic activity.¹⁷ However, no significant change is observed for high Pt content (HPC) catalysts (Figure 2b) showing that in this case, reduction at 500 °C has no impact on the number of Pt⁰ particles and the H-spillover over the CeO₂ surface.

A strong increase in activity of 0.10Pt catalyst was also observed during operando DRIFT analysis after RED500 pretreatment (Figure S8). Furthermore, the spectrum recorded after this pretreatment contains $\nu(\text{CO})$ bands contrary to the one after OX500 (Figure 3a). Indeed, the absence of $\nu(\text{CO})$ band after the oxidative pretreatment arises from the presence of Pt²⁺ SAs which weakly adsorb CO and are poorly active for the reaction.^{17,32,44} After reduction, Pt NPs are formed on CeO₂ with characteristic $\nu(\text{CO})$ bands at 2063, 2046 and 2009–1969 cm⁻¹ corresponding to CO molecules adsorbed on the terrace, edge and periphery sites, respectively (see Ref.17 and references therein) leading to observation of a broad band for 0.1Pt catalyst.

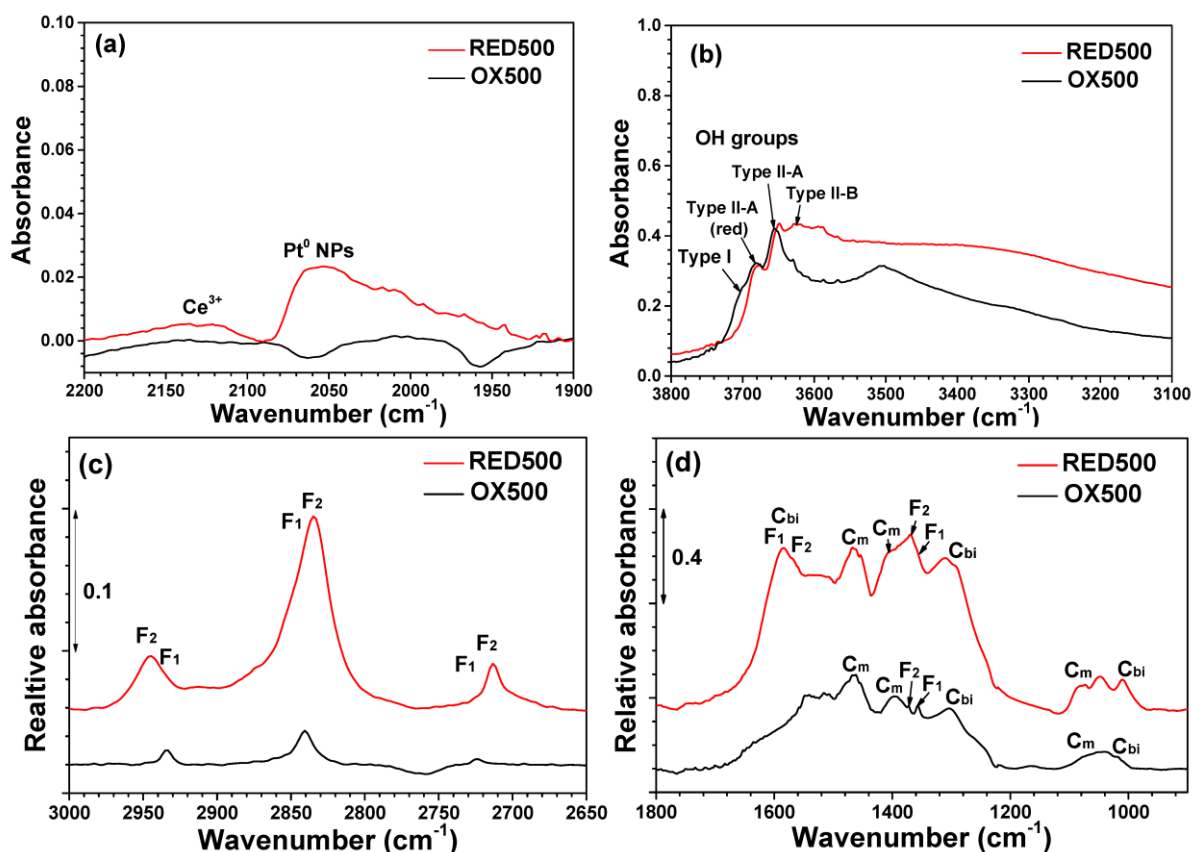


Fig.3 Operando DRIFT spectra of 0.10Pt catalyst after OX500 and RED500 pre-treatments: (a) 1900-2200 cm^{-1} region, (b) 3100-3800 cm^{-1} region, (c) 2650-3000 cm^{-1} region and (d) 900-1800 cm^{-1} region. C_m : monodentate carbonate, C_{bi} : bidentate carbonate, F1 and F2: bridged formates. Reaction conditions: $T=230\text{ }^\circ\text{C}$, $\text{PCO}=5\text{ mbar}$, $\text{PH}_2\text{O}=20\text{ mbar}$, $\text{GHSV}=1000\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. The background corresponds to the spectrum of KBr recorded at $230\text{ }^\circ\text{C}$ and the $\nu(\text{CO})$ gas signal is subtracted.

Furthermore, the formation of Pt NPs is accompanied by the intensification of the band at 2120 cm^{-1} (Figure 3a) due to electronic transition of Ce^{3+} cations^{17,32,45} and of the $\nu(\text{O-H})$ band at 3630 cm^{-1} (Figure 3b) attributed to hydroxyl species near oxygen vacancies (OH type II-B).^{46,47} Note that a broad band around 3400 cm^{-1} typical of H-bonding is superimposed.

These features confirm that a treatment at $500\text{ }^\circ\text{C}$ under H_2 favours the formation of Pt^0 NPs and the reduction of CeO_2 . Moreover, OH groups of type II-B are often considered as the active species for the water gas shift reaction.^{48,49} Hence, the increase in their concentration could arise from the activation of the catalyst. Finally, the formation of Pt^0 NPs is accompanied by an increase in the amount of different formates and carbonates (Figures 3c and 3d) with DRIFT bands similar to those observed on the spectra of the HPC catalysts after OX500 pretreatment (see Ref. 17 and references therein).

In summary, a reductive pretreatment under H_2 at $500\text{ }^\circ\text{C}$ allows the activation of a LPC catalyst, essentially composed of Pt^{2+} SAs, by the formation of Pt^0 NPs more active than oxidic Pt^{2+} SAs and PtO_x clusters.^{16,17,44,48} Inversely, the activity of a HPC catalyst is

decreased by this same reductive pretreatment. It does not appear to result from Pt aggregation but could be due to poisoning by carbonates.^{29,39-41} Note that carbonate formation was observed by DRIFT spectroscopy for both LPC and HPC catalysts but those species are absorbed on the overall surface of CeO₂ while carbonate species poisoning Pt⁰ NPs should be located around them and hence correspond only to a small fraction of the observed carbonates.

3.3 Influence of oxidative post-treatments on the activity of Pt/CeO₂ catalysts

A slight deactivation was evidenced during the catalytic testing whatever the pretreatment (see Figures S2-S5 and relative deviations reported in Table S2). Therefore, two oxidative post-treatments were applied to regenerate the catalysts. The first one called ReOx500 was performed at high temperature (500 °C) for 12 h to boost redispersion of Pt⁰ NPs^{26,27} and removal of carbonates.²⁹ It was limited at 500 °C to avoid sintering of CeO₂. The second re-oxidation called ReOx230 took place at the reaction temperature (230 °C) for only 10 min to approach viable conditions for an industrial process. Consequently, four catalytic tests were successively performed: a first one after OX500 pretreatment, a second one after ReOx230 post-treatment (ReOx230_1), a third one after ReOx500, and finally a last one after a second ReOx230 post-treatment (ReOx230_2).

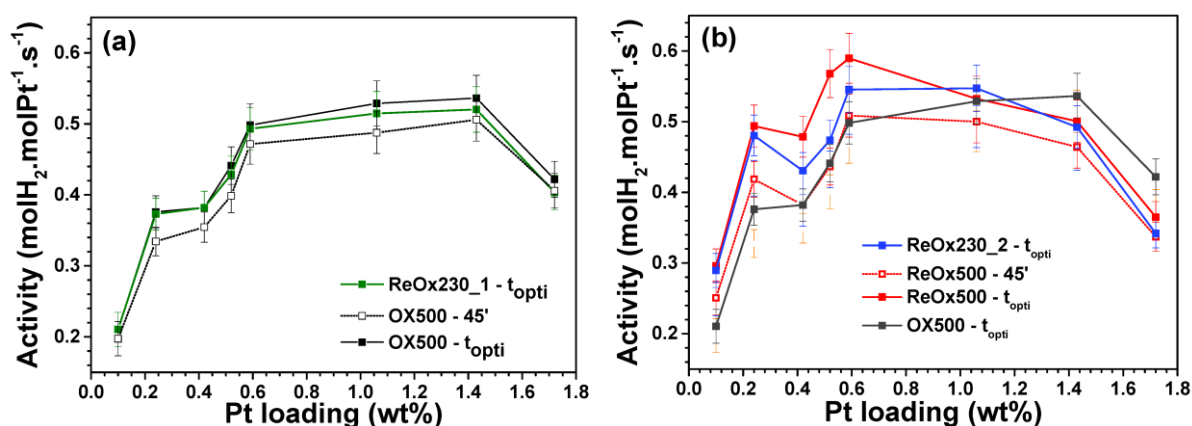


Fig.4 Evolution with Pt loading of molar activity (a) at t_{opti} (maximal value after approx. 1 min on stream), at 45 min of reaction after OX500 pretreatment and at t_{opti} after ReOx230_1 first post-treatment and (b) at t_{opti} after OX500 pretreatment and after ReOx500 post-treatment, at 45 min of reaction after ReOx500 and at t_{opti} after ReOx230_2 second post-treatment.

The overall protocol is described in Figure S1f. As this study was achieved with a new series of catalysts, some differences in activity after OX500 can be found mainly for 0.10Pt catalyst.

After the first post-treatment ReOx230_1, the molar activity re-increased during the first few minutes toward to the maximal values measured after OX500 pretreatment at the optimal time t_{opti} (Figures S9 and 4a) and was significantly higher than the value measured after OX500 pretreatment and 45 min on stream (see the relative deviations reported in Table S3 for the different catalysts). Even if the molar activity slowly decreased again after t_{opti}, it remained higher than this value for a similar time (Figure S9). Hence, catalyst regeneration is

obtained after a re-oxidation step at 230 °C for only 10 min. To our knowledge, it was reported that a regeneration of Pt/CeO₂ catalysts can occur by a treatment in air at temperatures higher than 400 °C but not at 230 °C.²⁹

After ReOx500, the molar activity increases compared to the OX500 state for a Pt content below 1.06 wt% (Figures 4b and S10) with an increase comprised between 18 and 41% for the maximal values at topti and between 8 and 27% after 45 min on stream (Table S3). To our knowledge, such improvement in catalytic activity has never been reported. However, for a Pt content higher than 1.06 wt%, a loss of activity is observed after ReOx500, underlying the impact of Pt content on the evolution of activity. Nevertheless, whatever the Pt loading, the molar activity again gradually decreases over time (Figures S10 and S11, Table S3).¹⁷ Therefore, an oxidative post-treatment at 500 °C for 12 h can generate more active sites for LPC catalysts but not suppress the slow deactivation process during WGS at 230°C. However, the second post-treatment ReOx230_2 carried after ReOx500 (Figure S1f) gave rise to activities close to those obtained after ReOx500 both for the maximal values at topti and after 45 min on stream (Figures 4b and S11) confirming the regenerative effect of an oxidative post treatment at 230 °C.

To understand the activation after an oxidative post-treatment at 500 °C for 12 h (ReOx500), catalytic tests were performed on 0.52Pt catalyst after a 12 h oxidative pretreatment instead of the usual 1 h (OX500). The extension of pretreatment time from 1 to 12 h led to an overall decrease in activity of about 7% (Figure S12) which could arise from dispersion of PtOx clusters and anchoring of Pt atoms in the subsurface layers of CeO₂. Note that the evolutions over time were similar with a maximal value after around 4 min on stream and a slow deactivation afterwards. Again, the 0.52Pt catalyst was activated by ReOx500 post-treatment with the same magnitude. Hence, a post-treatment at 500 °C is required to get activation of LPC catalysts. The origin of activation is explained in the following crossing different techniques.

To determine the nanostructure of Pt species on the surface of CeO₂, ADF-STEM images were recorded after the different oxidative post-treatments at 230 °C and 500 °C. After WGS reaction at 230 °C, an average diameter of 1.4 nm was determined from statistical analysis for catalysts with Pt content above 0.42wt%.¹⁷ After the ReOx230_1 first post-treatment (Figures 5a,b), some Pt NPs with similar size were still present at the surface of the support. It reveals that if redispersion occurred, it would involve a limited number of Pt atoms. Hence, regeneration by oxidative post-treatment at 230 °C probably arises from another phenomenon which could be decarbonation of poisoning species upon reoxidation.

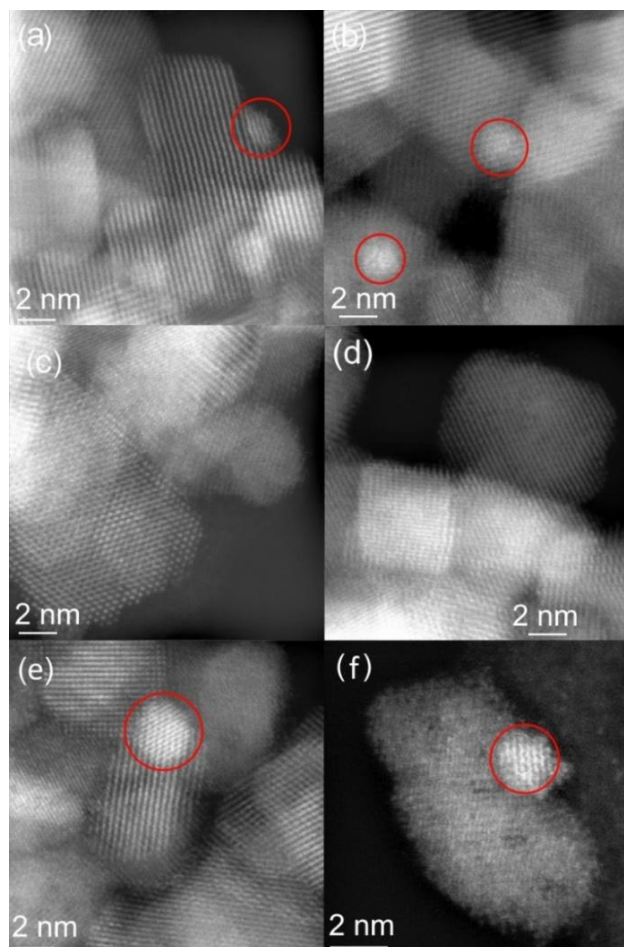


Fig.5 ADF-STEM images of 0.25Pt catalyst after (a,b) ReOx230_1 and (c,d) ReOx500 and (e,f) ReOx_2 post-treatment and WGS reaction. The red circles indicate Pt NPs.

Nevertheless, no Pt NPs are observed after the ReOx500 post-treatment (Figures 5c,d), suggesting a re-dispersion of Pt NPs as Pt SAs and/or clusters not observed in the ADF-STEM images. This re-dispersion does not lead to the initial OX500 state. Otherwise, no activation would be observed. However, Pt NPs with diameter ranging between 1 and 2 nm were again observed on 0.25Pt (Figures 5e,f) after ReOx230_2 post treatment and the last WGS reaction of the post-treatments protocol (Figure S1f) showing such species are stabilized in reaction conditions whatever the post-treatment.

Raman spectra were also recorded to determine the structural changes after the different post-treatments (Figure 6). The main band at 464 cm^{-1} arises from the F_{2g} vibrational mode of cubic CeO_2 and the less intense features at 264 and 402 cm^{-1} are attributed to surface modes of the clean CeO_2 (111) surface.⁵⁰ The band at $550\text{--}600\text{ cm}^{-1}$, also called D band, is attributed to the LO mode, which is activated by the presence of defects such as oxygen vacancies.⁵⁰ The D band is superimposed to a band at 560 cm^{-1} corresponding to $\nu(\text{Pt-O-Ce})$ vibrations.^{51,52} Another band at 650 cm^{-1} is attributed to either $\nu_s(\text{Pt-O-Ce})$ ⁵² or $\nu(\text{Pt-O})$ ⁵¹ stretching vibrations of PtO_x species anchored on the surface of CeO_2 . For the sake of simplicity, it is labelled $\nu(\text{PtO}_x)$ in the following. Finally, the band at 826 cm^{-1} arises from $\nu(\text{O=O})$ vibrations of peroxy species adsorbed on oxygen vacancies.

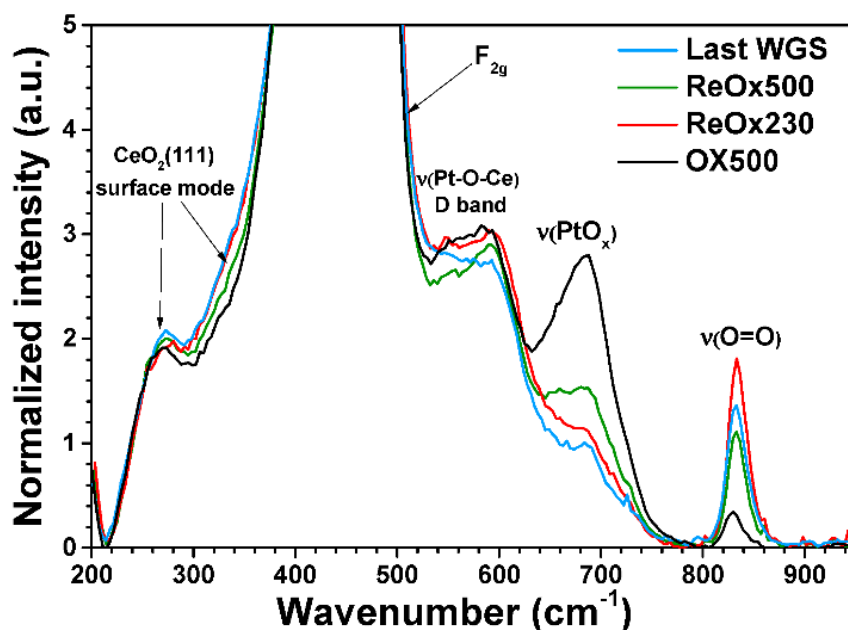


Fig.6 Raman spectra of 0.25Pt catalyst recorded in ambient air after OX500 pretreatment, ReOx230_1 and ReOX500 post-treatments and after ReOx230_2 and WGS reaction. The spectra correspond to the average of spectra recorded from a mapping of 20 analysed areas and are presented after baseline subtraction and normalization to the amplitude of the F_{2g} band.

A reduction of PtO_x species during WGS reaction is evidenced by the damping of the $\nu(PtO_x)$ band.¹⁷ This band was still quite low after ReOx230 (Figure 6) showing that if Pt reoxidation occurs it is limited. Note that the small $\nu(PtO_x)$ feature may result either from the reoxidation of Pt^0 atoms or the presence of Pt^{2+} cations that were not reduced during the reaction. The Raman spectrum recorded after ReOx500 shows a slight increase in the intensity of the $\nu(Pt-O_x)$ band at 680 cm^{-1} reflecting an oxidation of Pt atoms on the surface during the oxidative post-treatment at $500\text{ }^\circ\text{C}$. It is consistent with the redispersion of Pt NPs observed by microscopy. However, the intensity of the $\nu(PtO_x)$ band does not reach the initial one, showing irreversible structural evolution after reduction in reaction conditions. Finally, the $\nu(PtO_x)$ band in the spectrum recorded after ReOx230_2 post-treatment and the last WGS reaction of the sequence (Figure S1f) was quite low showing again reduction of PtO_x species in reaction conditions. Furthermore, the $\nu(O=O)$ band at 826 cm^{-1} reveals the formation of peroxy species on the surface of catalysts after WGS reaction and exposure to ambient air. Those species arise from the reduction of O_2 molecules chemisorbed on oxygen vacancies formed during the reaction. Such reduction induces the reoxidation of Ce^{3+} cations and/or Pt^0 atoms. However, the process stops at this step since the dissociation of peroxy species leading to the formation of O- does not take place.⁵³ Hence, reoxidation is only partial. Either a slight increase or a slight decrease in the $\nu(O=O)$ band is observed after ReOx230 and ReOx500, respectively. However, its intensity remains much higher than after O500 revealing the presence of a higher amount of oxygen vacancies than at the initial state.

From these results, it can be concluded that both reoxidation and partial redispersion of Pt^0 atoms take place during an oxidative post-treatment at $500\text{ }^\circ\text{C}$ for 12 h while only limited re-oxidation occurs during an oxidative post-treatment at $230\text{ }^\circ\text{C}$ for 10 min.

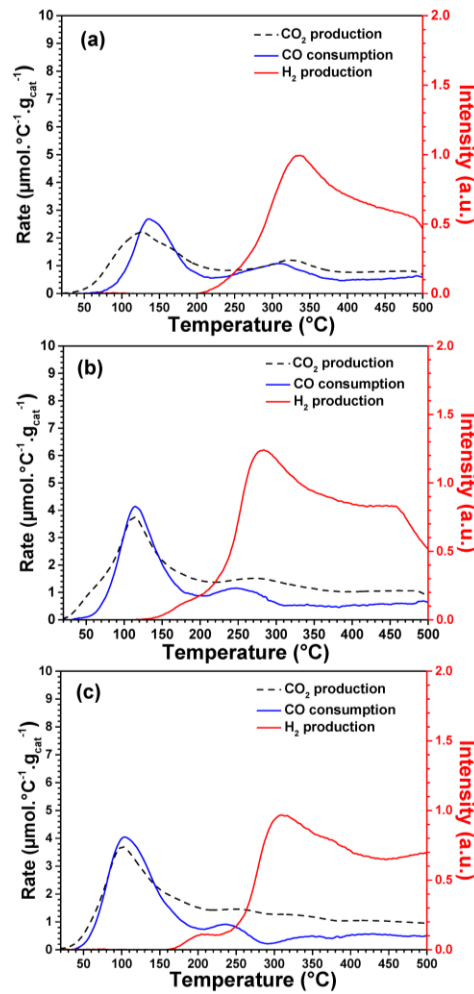
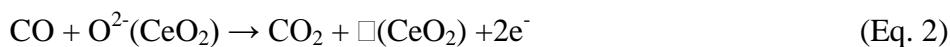


Fig.7 CO consumption, CO₂ production and MS signal intensity at mass 2 (H₂) during TPR analysis under 1%CO/He for (a) 0.10Pt, (b) 0.52Pt and (c) 1.43Pt catalysts after 120 min of WGS reaction at 230 °C and ReOx500 post-treatment.

As CO is more reducing than H₂,²⁷ and is the main reducing molecule in WGS reaction conditions, CO-TPR analysis was preferred to H₂-TPR to probe the reducibility of Pt/CeO₂ catalysts after oxidative post-treatments. Figure 7 shows the production of CO₂ and H₂, and the consumption of CO during CO-TPR analyses between 20 °C and 500 °C for the three chosen Pt/CeO₂ catalysts. They were carried out after 120 min of WGS reaction at 230 °C and ReOx500 post-treatment without air exposure. Very few differences are observed in the CO₂ production and CO consumption profiles for the three Pt contents.

During CO-TPR analyses, CO is adsorbed and rapidly reduces PtO into Pt⁰ and CeO₂ into CeO_(2-x) according to (Eq.1) or (Eq.2), respectively:⁵⁵



with $\square(\text{CeO}_2)$ corresponding to an oxygen vacancy at the surface of CeO₂ support.

At higher temperature, a CO₂ production peak is accompanied by H₂ production (see the H₂ signal intensity in Figure 7) and can be attributed to the WGS reaction with hydroxyl species according to (Eq.3):⁵⁴

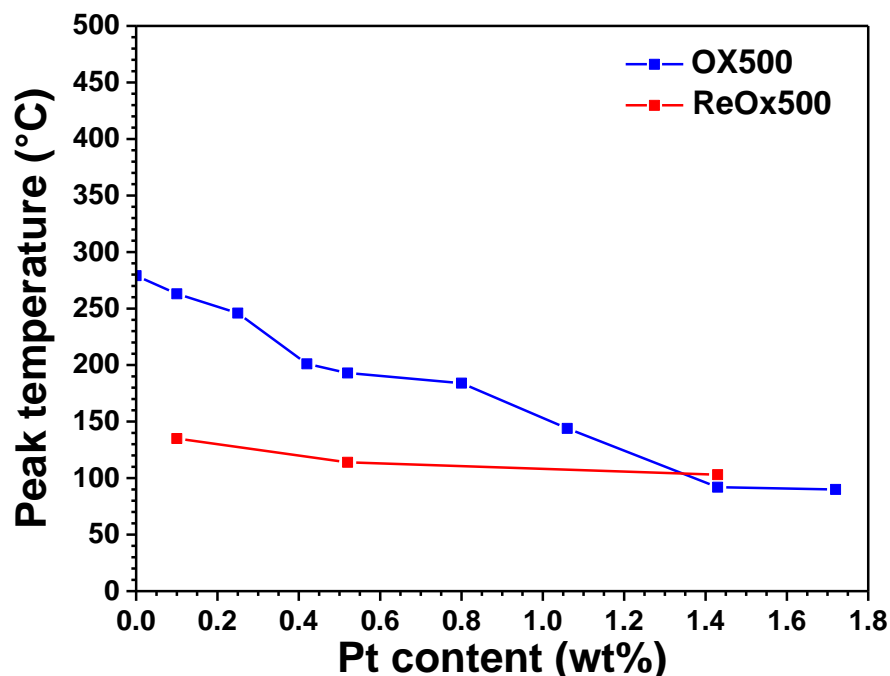
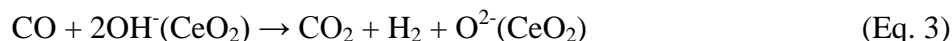


Fig.8 Evolution of peak temperature of CO₂ production after OX500 pretreatment (OX500) and after 120 min of WGS reaction at 230 °C followed by ReOx500 post-treatment.

On LPC catalysts, both CO₂ production and CO consumption take place at much lower temperatures after ReOx500 post-treatment than after OX500 pretreatment (Figure S13). In particular, the peak temperatures of CO₂ production after ReOx500 are much lower (Figure 8) with values below 150 °C which were obtained only for HPC catalysts after OX500.¹⁷

Thus, combining WGS reaction conditions and ReOx500 post-treatment strongly increases the reducibility of LPC catalysts revealing an easy formation of Pt⁰ NPs under CO, which in turn leads to reduction of CeO₂.¹⁷ Note that the same trends were observed for H₂-TPR analysis (see Figure S14 and associated comments) which is quite sensitive to the presence of Pt⁰ NPs because it allows reduction of CeO₂ by dissociative adsorption of H₂ and H-spillover.^{33,34}

Operando DRIFTS studies were carried out in order to better understand the origin of the activation of LPC catalysts after ReOx500. It was important to check that the same activity trends were obtained in the DRIFTS cell as in a conventional fixed bed reactor. The activities of the different Pt/CeO₂ catalysts during operando DRIFTS experiments are compared in Figure S15. Again, an activation is observed after ReOx500 for the LPC catalysts (0.10Pt, 0.25Pt and 0.52Pt). It is even more pronounced, which may be due to differences in feed composition.

The temporal evolutions of operando DRIFTS spectra between 1800 and 2200 cm⁻¹ of the 0.25Pt, 0.52Pt and 1.06Pt catalysts are plotted for the first 10 min of reaction in Figures

9a-c. For the three catalysts, the first spectrum recorded under reaction conditions after OX500 contains a $\nu(\text{CO})$ band at 2090 cm^{-1} indicating the presence of PtO_x clusters (Figures 9a-c).^{32,55} This observation may seem to contradict the H_2 -TPR analysis which indicates the presence of Pt^{2+} SAs for Pt loading below 0.59 wt% (Figure 2a). However, PtO_x clusters are probably rapidly formed at $230\text{ }^\circ\text{C}$ under reaction mixture by the cleavage of Pt-O-Ce bonds and Pt diffusion, are therefore immediately observed during operando DRIFT experiments. Indeed, reactive adsorption of CO was previously shown even at RT.¹

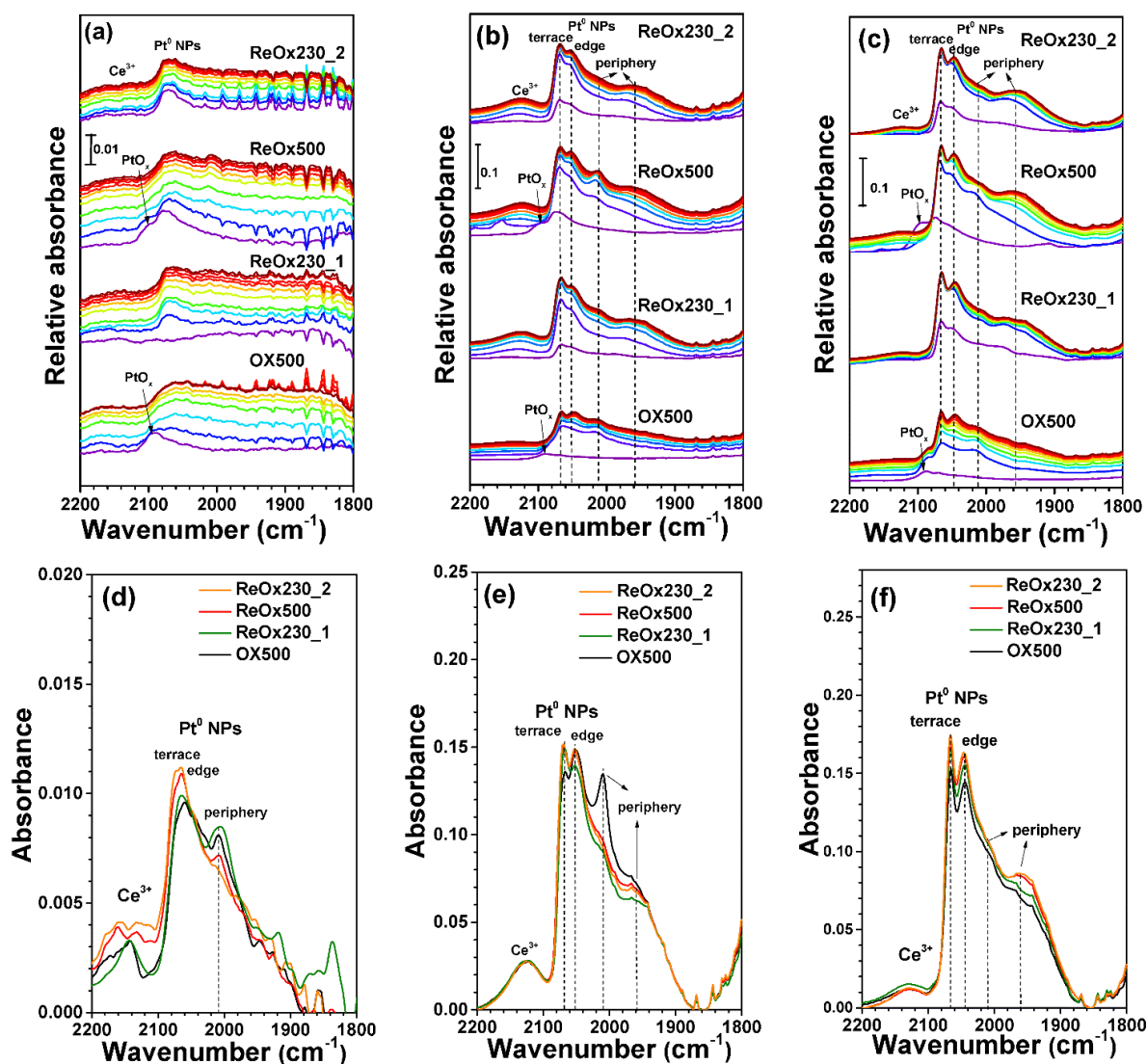


Fig.9 Operando DRIFT spectra recorded between 1800 and 2200 cm^{-1} during the first 10 min and at apparent steady state after 1 h of WGS reaction for the (a,d) 0.25Pt, (b,e) 0.52Pt and (c,f) 1.06Pt catalysts after OX500 pretreatment, ReOx230_1, ReOx500 and ReOx230_2 post-treatments. For the temporal evolution, the spectra are plotted from purple to dark red each spectrum corresponding to approximately one minute under reaction conditions. Reaction conditions: $T=230\text{ }^\circ\text{C}$, $\text{PCO} = 5\text{ mbar}$, $\text{PH}_2\text{O} = 20\text{ mbar}$, $\text{GHSV} = 1000\text{ mL}\cdot\text{min}^{-1}\cdot\text{g}^{-1}$. The background corresponds to the spectrum of KBr powder recorded at $230\text{ }^\circ\text{C}$ and the $\nu(\text{CO})$ gas signal is subtracted.

Afterwards, PtO_x species are rapidly reduced to form metallic NPs giving rise to characteristic $\nu(\text{CO})$ bands at about 2065, 2045, and 2005 cm^{-1} attributed to CO chemisorption on terrace, edge and periphery sites of Pt^0 NPs.¹⁷ The typical band at 2090 cm^{-1} was not observed after ReOx230_1 post-treatment, indicating that such treatment cannot form stable PtO_x clusters from Pt^0 NPs or very few. However, after ReOx500 , the first spectrum of the three catalysts contains a shoulder at 2100 cm^{-1} showing the formation of PtO_x clusters during this post-treatment (Figures 9a-c). Furthermore, the spectra exhibit an intense band at 2010 cm^{-1} during the first minutes of reaction, which is then damped. For instance, it vanishes after 2 min of reaction for 1.06Pt catalyst (Figure 9c). This feature reflects the decrease in the amount of Pt atoms at the periphery of Pt NPs, and thus their agglomeration.

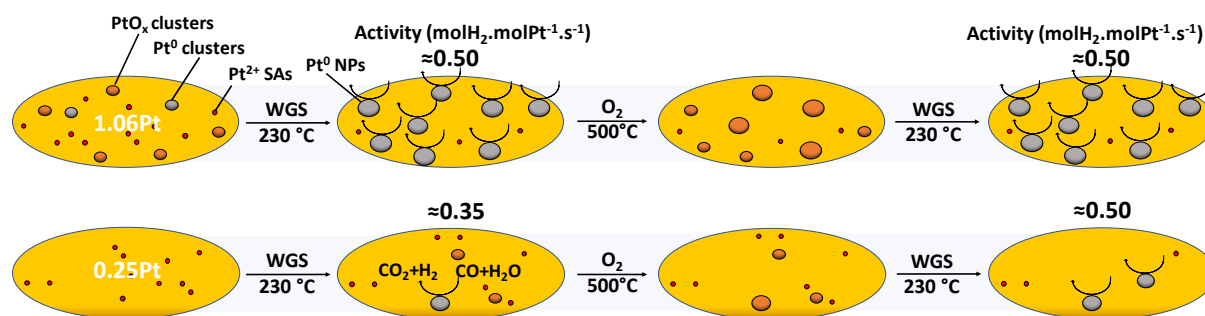


Fig.10 Scheme of the influence of oxidative post-treatment at 500 °C for 12 h after reaction on Pt species formation during the water gas shift reaction for 0.25Pt and 1.06Pt catalysts.

Moreover, the formation rate of Pt^0 NPs is higher after ReOx500 than after OX500 for LPC catalysts: Indeed, for 0.25Pt and 0.52Pt catalysts after ReOx500 , the DRIFT spectra rapidly evolve like the 1.06Pt one after OX500 pretreatment leading to spectra typical of Pt^0 NPs. Thus, the redispersion of Pt^0 NPs during the oxidative post-treatment at 500 °C results in higher number of reducible PtO_x clusters than after OX500 .

After 1 h on stream, no signal was detected on 0.10Pt even after ReOx500 (Figure S16). However, for 0.25Pt, a higher absorbance of the $\nu(\text{CO})$ bands at 2076-2065 cm^{-1} is observed after ReOx500 than after OX500 together with a lower absorbance of the band at 2010 cm^{-1} (Figure 9d). For 0.52Pt, the $\nu(\text{CO})$ absorbance decreases sharply after ReOx230_1 and the band at 2050 cm^{-1} is slightly blue-shifted after ReOx500 (Figure 9e), which is attributed to the presence of less defects in Pt^0 NPs.⁵⁶ As expected from the absence of impact of the oxidative post-treatments on the molar activities of 1.06Pt and 1.43Pt catalysts, no significant modification of the relative intensity of the bands at 2067, 2046 and 2012 cm^{-1} is observed at the steady state (Figure 9f and S16b).

Regarding the other spectral ranges, very few differences are observed between the three Pt contents. Between 3300 and 3800 cm^{-1} (Figure S17), the bands at 3680 and 3630 cm^{-1} are attributed to OH species of type II-A and II-B, respectively.^{46,47,57} Furthermore, two types of formates, denoted F1 and F2, and characterized by bands at 2935, 2842 and 2723 cm^{-1} and at 2944, 2831 and 2713 cm^{-1} were identified (Figure S18). As it was proposed from DFT calculations that bidentate formates are not stable on CeO_2 contrarily to bridged ones,⁵⁸ these bands could be attributed to two types of bridged formates. Finally, the 900-1800 cm^{-1} spectral range contains bands due to free, monodentate and bidentate carbonates as well as the

two types of bridged formates (Figure S19). Hence, even if some species could be desorbed during the ReOx230 and ReOx500 post-treatments, the adsorbed species observed at the steady state of WGS reaction remain similar.

Thus, the oxidative post-treatment at 500 °C for 12 h triggers the formation of PtO_x clusters on LPC catalysts which can rapidly evolve to Pt⁰ NPs active species in WGS conditions at 230 °C, as schematized in Figure 10, and then promotes the molar activity of ca 50% reaching the values obtained for HPC catalysts. However, they remain lower than the maximal value obtained for Pt content around 0.6wt% which was ca 0.6 molH₂.molPt⁻¹.s⁻¹ (Figure 4).

4. Conclusions

The low reducibility in WGS conditions of Pt²⁺ SAs and/or PtO_x clusters limits the operando formation of Pt⁰ NPs, active for the WGS reaction at the surface of LPC catalysts. This study has shown that reducing pre-treatments at 250 and 500 °C under H₂ as well as an oxidative post-treatment under O₂ at 500 °C can promote their reducibility. The gain in activity was attributed to an increase in the number Pt⁰ NPs formed under LT-WGS conditions.

For reductive pretreatment, it was concluded that the choice of the temperature is critical to activate the catalyst. Indeed, a reduction temperature of 250 °C increases the activity whatever the Pt content. However, after a reducing pretreatment at 500 °C, a 4-fold increase in activity compared to the initial state was measured for 0.1Pt catalyst which contains mostly SAs. Conversely, catalysts with higher Pt content containing PtO_x clusters and Pt⁰ clusters are deactivated by the same reductive treatment. The results support that a reductive pretreatment and the reaction conditions irreversibly modify the structure of Pt species, even if an oxidizing treatment is carried out afterwards.

Despite a slight deactivation of Pt/CeO₂ catalysts, a recovering of activity was demonstrated after oxidative post-treatment at 230 °C for only 10 min what is industrially interesting. Such regeneration does not arise from re-dispersion of Pt NPs.

Finally, an original highlight of this work is the strong increase in activity observed after a 12 h oxidative post-treatment at 500 °C for LPC catalysts. Even if this treatment allows for redispersion and oxidation of Pt atoms, the initial Pt²⁺ SAs and/or PtO_x clusters are not recovered. In fact, such treatment leads to the formation of highly reducible PtO_x clusters on the surface of CeO₂, which are easily transformed into Pt⁰ NPs active species.

Conflicts of interest

The authors declare that there are no conflicts of interest.

Data availability statement

The data supporting this article are available in the published article and its Electronic Supplementary Information (ESI).

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