# Characterizations of $Pt/CeO_2$ during model redox sequences

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**Abstract:** The shape, size and electronic properties of Pt nanoparticles supported on ceria have been tailored during model redox sequences based on successive $H_2$ (reduction) and $O_2$ (oxidation) 1 hour treatments at moderate temperatures (250 °C and 500 °C). Raft shaped Pt nanoparticles of around 1 nm size are produced on the surface, in strong interaction with ceria, then boosting the oxygen transfer from the oxide towards Pt. *In situ* techniques establish the presence of Pt cations in an intermediate oxidation state, probably $Pt^{2+}$, in interaction with peroxo oxygen species.

**Keywords: Pt rafts, ceria, diesel exhaust.**

## 1. Introduction

The tailoring of Pt based diesel oxidation catalysts is crucial to enhance the efficiency of the diesel vehicles after treatment. For instance, specific interactions between Pt and ceria can improve the thermal stability of Pt nanoparticles (NPs) in an oxidizing atmosphere as in diesel exhausts, through the formation of rigid Pt-O-Ce bonds[1]. More recently, Jones et al.[2] have evidenced the stabilization of Pt single atoms and clusters on ceria surface steps, strongly suggesting the doping of ceria subsurface by Pt cations in good agreement with recent DFT studies[3] which also predict $Pt^{2+}$ cations incorporation between surface oxygen ions species of the support. We have recently demonstrated[4] the dynamic nature of Pt NPs on ceria under reducing/oxidizing sequences at temperatures below 500 °C. Lean/rich pulses can be used to control the formation of Pt NPs and enhance their catalytic activity for CO oxidation[4]. This study aims to get new insights into the impact of redox sequences on the $Pt/CeO_2$ interactions.

## 2. Experimental

Ceria provided by Solvay Special Chem. Company was dry impregnated with Pt (0.9 wt %) and calcined 4 h at 500 °C. Before each characterization or catalytic test, the catalyst was systematically pretreated in $O_2$ for 1 h at 500 °C to get a reference state. Model redox sequences were composed of a first reduction step of 1 h in 10% $H_2$ followed by an oxidation one also of 1 h in 20% oxygen. They were performed at different temperatures: 500/500 °C (reduction/oxidation), 250/250 °C and 250 °C/RT. Catalytic performances were measured for CO and propylene oxidation in a lean mixture (10% $O_2$, 1000 ppm CO, 500 ppm NO, 500 ppm $C_3H_6$, 10% $H_2O$ in He) that simulates diesel exhaust gas. Temperature-Programmed Reduction (TPR) experiments were conducted with a Inficon JPC400 mass spectrometer. *Post mortem* STEM observations were performed with an Environmental Transmission Electron Microscope (Ly-ETEM, FEI TITAN ETEM operated at 300 kV). The spatial distribution of surface oxygen species and $PtO_x$ clusters were assessed by Raman spectroscopy mapping at the micrometric level (200 µm x 200 µm) recorded at RT in oxygen. HRXANES was also implemented to *in situ* follow the oxidation degree of Ce cations in the catalyst.

## 3. Results and discussion

As previously observed with rich/lean pulses[4], model redox sequences can achieve outstanding catalytic performances for CO and $C_3H_6$ oxidation, much higher than those recorded at the reference state. TPR experiments have shown that redox sequences increase the reducibility of ceria (Fig. 1a). The $H_2$ consumption only starts above 150 °C on the first TPR, suggesting the absence of Pt NPs able to chemisorb $H_2$ below this temperature, as confirmed by STEM observations. Successive redox sequences (TPR 2 and TPR 3) promote the formation of Pt NPs in strong interaction with ceria as shown by the excellent reducibility of the support as early as the room temperature. The lower the temperature of the redox sequences, the greater the reducibility. Variations of the Raman band associated with $PtO_x$ at 690 $cm^{-1}$ (Fig. 1b) demonstrate that such species evolve upon redox sequences with stabilization of Pt cations in another oxidation state, probably $Pt^{2+}$, as suggested by XPS measurements and DFT calculations[3]. These $Pt^{2+}$ cations are in interaction with peroxo oxygen species (Raman bands at 860 $cm^{-1}$). No $Ce^{3+}$ cations were detected both by Raman spectroscopy and HR-XANES measurements, confirming that these oxygen peroxo species did not re-oxidized ceria but are stabilized on the surface.

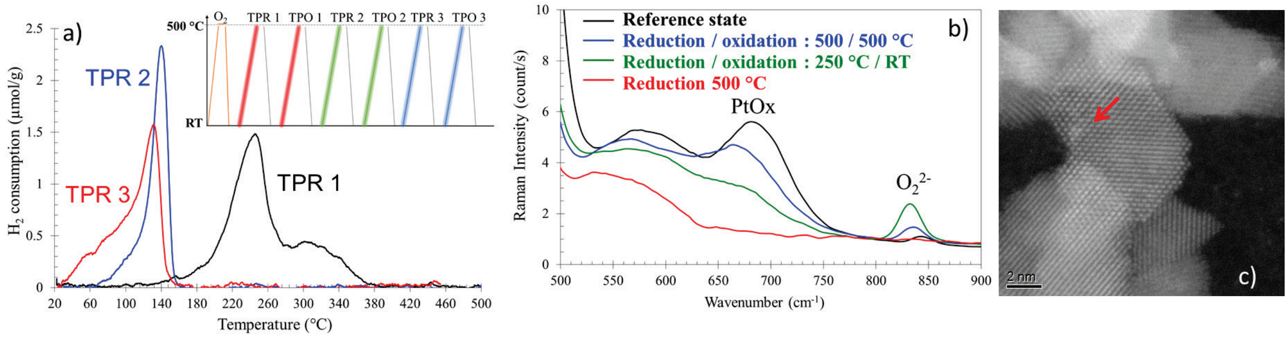

**Figure 1.** a) TPR spectra up to 500°C in 1%$H_2$/He recorded according to the protocol described in the insert diagram, b) Raman spectra recorded at RT in 20% $O_2$/He after different pretreatments, c) STEM images after a reduction step at 250°C.

The shape of the Pt NPs was followed along the redox sequences. After the first reduction step, only raft shaped particles or single atoms are observed on the surface (Fig. 1c). This morphology is not modified after a subsequent oxidation step but the surface mean diameter of Pt rafts slightly increases from 1 to 1.3 nm, maybe due to Pt oxidation. Statistics on the ratio between the number of rafts and single atoms were tricky to estimate. However, CO chemisorption performed after each reduction step shows no significant modification of the Pt dispersion along the redox cycles.

## 4. Conclusions

Model redox sequences at mild temperatures can stabilize raft shaped Pt nanoparticles and Pt single atoms in closed interaction with ceria. This maximizes the Pt/ceria interface, promoting the oxygen transfer from the support towards Pt which is a key step in the CO oxidation mechanism. Pt cations are stabilized in an intermediate oxidation state, probably $Pt^{2+}$, in interaction with peroxo oxygen species, confirming the high availability of oxygen species for oxidation reactions.

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