Size control of Pt clusters on CeO₂ nanoparticles via an incorporation-segregation mechanism and study of segregation kinetics.

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KEYWORDS: Pt/CeO₂; segregation kinetics; ionic dispersion; polylol synthesis; in situ XRD

ABSTRACT: Recent literature on Pt/CeO₂ catalysts reveal that ionic Pt species could be incorporated into the CeO₂ lattice. Upon thermal treatment, sub-nanometric Pt clusters maybe segregated on the host lattice surface. Here we present a detailed study of Pt segregation in air and under a reducing atmosphere carried out on thermally treated samples by high resolution XRD and XAS. We further perform a kinetic study by in-situ XRD measurements with the aim to estimate the activation energy for Pt clusters segregation and coalescence in air, which was found to be about 3.88 eV. This high activation energy indicates that Pt clusters are strongly anchored on the CeO₂ surface and that their mobility is activated only at T>900 °C. We demonstrate that an unprecedented control over the size of anchored metallic Pt clusters is achieved using our wet chemical synthesis method combined with an appropriate thermal treatment.

1. Introduction

Despite the fact that the Rare Earth Elements (REE), mainly in the form of oxides, are a worldwide issue due to limited resources and – under the present economic situation – only few countries are controlling the market, their demand – and consequently costs –, have risen dramatically over the past decade.¹

Among REE, cerium-dioxide-based materials have attracted considerable attention in recent years because of their superior performance in several technological fields.²⁻⁴ The high cost of the raw materials is justified by the performance and stability of the derived product materials. In catalysis CeO₂ is used as a support for noble metals, such as Pt or Pd, which act as a catalytic center for a series of reactions, such as CO oxidation. Nowadays it is largely accepted that CeO₂ is not merely a support for the noble metals but it is actively involved in the catalytic process itself. Its action is associated with remarkable redox properties.¹²⁻¹⁵ CeO₂ is able to accommodate a large number of oxygen vacancies, compensated by Ce³⁺ species, resulting in a material with significant oxygen mobility and oxygen storage capacity (OSC).¹⁴⁻¹⁵ As a consequence, the catalytic activity is localized to areas where the noble metal, CeO₂, and the gaseous reactants are simultaneously present (three phase points). In order to increase the number of these catalytic centers the noble metal should be dispersed on the metal oxide surface in entities that are as small as possible. Moreover, such entities should not diffuse on the metal oxide surface in operando otherwise they rapidly coalesce into larger particles with a rapid activity loss. The diffusion of the noble metals entities can be prevented if they are strongly bonded on the CeO₂ surface. Pt and Pd present both a rather stable oxidation state IV and an ionic size compatible with the CeO₂ host lattice, meaning that Pt ions can be accommodated in the Ce positions (PtO₃⁺) without the need for compensation defects. Thus, Ce – O – Pt (or Pd) chemical bonds are possible both on the metal oxide surface and in form of dispersed ions in the fluorite-like CeO₂ lattice. The presence of such surface chemical interactions as well as the ionic dispersion of Pt and Pd into the metal oxide lattice, has been theoretically predicted¹⁶ and experimentally proven.¹⁷⁻¹⁹ In parallel, several authors have reported interesting correlations between the type of interaction and the catalytic activity.²⁰⁻⁴¹

The applied procedure to prepare catalysts and their processing is highly relevant. Traditionally, catalysts are prepared by impregnation or deposition-precipitation methods followed by an appropriate thermal treatment to reduce the deposited metal salts to metal particles. As a result, the active metal particles are poorly anchored to the support and control over the size of the metal particle is questionable.

An innovative alternative approach is to follow a segregative preparation method: the bi-phasic solid nanophase is obtained by promoting phase exsolution from a parent compound. Neagu et al.¹⁵ presented a study on non-stoichiometric perovskites where, upon thermal treat-
ment, the metal oxide particles became decorated by a segregated secondary phase in the form of nanoparticles. A similar approach can be applied to produce Pt/CeO₂ catalysts provided that the parent phase contains Pt ions dispersed into the CeO₂ lattice. Bera et al.⁶ prepared doped CeO₂ materials by combustion synthesis, demonstrating that Pt is ionically dispersed into the CeO₂ host lattice. The catalytic activities were tested for several reactions and the most appropriate conclusion was that the catalytic centres were the noble metal ions incorporated into the CeO₂ lattice. It was also reported that, upon extended thermal treatment at 800 °C in air, Pt segregates out of the host lattice forming metal particles. Nevertheless, during combustion synthesis the local sample temperature and the local oxygen partial pressure is unknown and the segregation of metal Pt clusters during the synthesis itself is plausible as their presence is difficult to identify, in particular on partially sintered samples. Thus, the correlation between catalytic activity and the chemical nature of noble metal is affected by a fair degree of uncertainty.

Recently we presented a new wet synthesis method that overcomes the disadvantages of combustion synthesis, including the high cost, poor control over the process, scalability issues, and the partial sintering of the obtained material. The method allowed for the preparation of Pt-doped CeO₂ NPs, with an average size smaller than 5 nm, using a single-pot procedure.⁶ Similar to the findings presented by Bera et al.,⁶ we were able to produce doped materials containing ionically dispersed Pt, but using instead a scalable and controllable wet-chemistry route. In agreement with the cited literature, Pt particles segregate out of the CeO₂ lattice upon thermal treatment. Thus, by starting from a unique parent phase and tuning properly the thermal treatment, it is possible to produce several scenarios: from ionically dispersed noble metal incorporated into the host lattice, to partially segregated sub-nanometric Pt-clusters, to completely segregated Pt nano- or micro-particles.

The objectives of the present study are to find (a) a rational pathway in order to promote the incorporation of Pt into CeO₂; (b) to measure the Pt metal segregation kinetics upon heating by means of XAS and in-situ XRD; (c) to estimate the activation energy for segregation; (d) to investigate the nature of the segregated clusters or nanoparticles out of the cerium dioxide lattice; (e) to study the influence of the atmosphere on the segregation behavior.

The obtained information would contribute to the understanding of the nature of the active species for a specific reaction, to optimizing the material functionalities, and to minimizing the amount of noble metal required. This study will also provide relevant insights into the structure-performance relationships, thus allowing the preparation of materials with superior performances.

2. Experimental details

2.1. Material. Chemical reagents including cerium(III) nitrate hexahydrate (Ce(NO₃)₃·6H₂O, >99.0%), ethylene glycol (EG, puriss. p.a. >99.5%) and sodium hydroxide (NaOH, >98%) were obtained from Sigma-Aldrich and used as received without further purification. An aqueous solution of hydrogen hexachloroplatinate(IV) (H₂PtCl₆, 8% in H₂O) was prepared from metal Pt (purity 99.99%) as a precursor for the preparation of the doped materials. Reagent grade ethanol and acetone were used for powder washing purposes and obtained from VWR.

2.2. Preparation of Pt doped CeO₂ Nanopowders by Polyol-Mediated Synthesis. The materials were prepared as in a previous work.⁶ In a typical synthesis, a fixed amount of the cerium salt (10 mmol) was heated and dissolved in 100 mL of EG at 80 °C. A second solution containing 30 mmol of NaOH was heated and dissolved in 100 mL EG and 10 mL of milliQ water at 80 °C. After cooling down to room temperature (RT), the two solutions were mixed. The mixture was heated up to 160 °C and held at that temperature for 30 min under magnetic stirring. During this treatment, the color of the liquid changed from white to grey-purple. The suspension was then cooled down and sonicated (Sonics-VibraCell, VCX130, 130 W/20 kHz) at 100% power for 1 min. A defined amount of Pt precursor solution was then added to the CeO₂ nanoparticles suspension in order to achieve a desired loading of noble metal. The mixture was heated up again to 180 °C and held at that temperature for 30 min yielding a black suspension. The suspension was cooled down to RT and the final product collected by centrifugation. The solid was then washed twice in ethanol and once in acetone by redispersing the solids via sonication (100% power, 1 min). Finally, the catalyst was dried at RT overnight. The total noble metal content of the catalyst was determined by chemical analysis (ICP-MS). Two series of samples were prepared with different Pt loading, namely 7 wt% (high load, series H) and 0.7 wt% (low load, series L). The H series served to study by HR-TEM the segregated Pt particles that result from thermal treatments in air. The L series, produced with a composition of common use in catalysis, were pretreated in air (series L_ox) or under a reducing atmosphere (2% H₂, balance Ar, series L_red) in a tubular oven.

The samples with 0.7 wt% of Pt were also used for the in-situ XRD studies of the segregation kinetics. In this case, the powders were pretreated in air for 3 h at 500 °C in a chamber oven (heating rate 3 K min⁻¹) in order to remove the organic residuals. The samples were named the K series.

2.3. Characterizations

The thermally treated samples (H, L_ox, and L_red series) and the in-situ measurements (K series) were performed at the Xo4SA-Materials Science beamline, Swiss Light Source (SLS), Paul Scherrer Institut (PSI), Villigen PSI, Switzerland. The powders were confined in 0.3 mm quartz capillaries and the X-ray beam energy was set to 22 keV. For the in-situ measurements (K series) the capillary was positioned in an oven (STOE furnace), equipped with graphite heating elements, a capillary spinning tool, and 90-deg Kapton X-ray transparent windows. The temperature of the sample was measured in the proximity of the capillary by a thermocouple. The temperature offset
between the sample temperature and the thermocouple signal was determined by a pre-calibration, collecting the diffraction patterns of reference substances across their melting temperatures. For the kinetic study, the XRD patterns were collected every 4.5 minutes at 930, 940, 950 and 960 °C. Cell parameters and phase quantifications were calculated by Rietveld refinement using General Structure Analysis System (GSAS) and the Inorganic Crystallographic Structure Database (ICSD). For screening purposes, X-ray powder diffraction patterns were collected with a Bruker D8 Advance diffractometer (Cu Kα radiation) in the range 15-90° (Δ2θ=0.019) equipped with an Anton Paar hot chamber (XRK 900).

High-resolution transmission electron microscopy (HR-TEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray (EDX) spectroscopy data were obtained with a FEI Tecnai F20ST TEM/STEM microscope operated at 200 kV, enabling High-Angle Annular Dark Field (HAADF) imaging or the detection of reflected Secondary Electrons (SE). The samples for TEM characterization were dispersed in i-propanol and a drop of the suspension was deposited onto either carbon-coated or holey-carbon-coated copper grids allowing the solvent to evaporate in air. In addition, for the STEM data acquisition, some samples were gently cleaned with an Ar(75%)/O(25%) plasma for a few seconds to remove hydrocarbon contamination. Morphological observations and compositional analysis for bulk and individual particles were performed with a Zeiss Ultra-55 Field Emission Scanning Electron Microscope (FE-SEM) operated at 10 keV and equipped with an energy-dispersive X-ray (EDX) detector. The samples were Cr-sputtered.

X-ray absorption spectroscopy was carried out on selected samples of the series L_ox and L_red. The treated powders were diluted with cellulose and pressed into pellets for the measurements. The XAS fluorescence spectra were collected at 80 K at the Pt L_3-edge and at the Ce L_3-edge. The experiments were carried out at the BM08 Beamline at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. As reference materials Pt(IV) oxide (PtO_2), metallic Pt foil (Pt(0), d=50 µm) and Ce(III) and Ce(IV) salts were measured.

Chemical analysis was performed with an Agilent 7700x ICP-MS after digestion of the samples and dilution in milliQ water, using external standard calibration. For the Pt/CeO_2 samples, 20 mg of powders were dissolved in 1 mL HNO_3 (65%). In order to perform a complete dissolution of the samples, a high pressure microwave digestion unit was used. The digested samples were diluted with a two-step process in water solution (milliQ water, 3% HCl, and 1% HNO_3) with a total dilution factor of about 2.5 x 10^6. Calibration and blank solutions were prepared by diluting (single-element) standard solutions down to a range of concentrations between 0 and 20 ppb (mg L^-1). The same acidic matrix containing 3% HCl and 1% HNO_3 was used for the preparation of the calibration and sample solutions.

3. Results

3.1. H series: preliminary study. In this study the samples were thermally treated in a chamber oven in air at different dwell temperatures and durations. Table 1 summarizes the prepared samples. As our previous studies have shown, in the as-prepared samples (H1) Pt is found mainly on the ceria particles surface with oxidation state +2 and +4. Upon thermal treatment at 500 °C in air (H2), Pt is incorporated into the CeO_2 lattice. Samples treated at T < 900 °C showed no evidence of Pt segregation. After being heated at 900 °C for 0.5 h the Pt peaks were not detected from the XRD pattern (sample H6). After a longer time (3, 6, and 12 h for samples H5, H7, and H8, respectively), Pt peaks were clearly detected by XRD. Figure 1 shows the XRD pattern for sample H8 with the Rietveld refinement. The calculated amount of Pt is in agreement with the chemical analysis, confirming that after this treatment, within the experimental error, all Pt is segregated in metal form.

The XRD patterns were also measured against time and temperature by in-situ XRD using standard lab equipment. The CeO_2 and Pt peak evolution is summarized in Figure S1 (supporting information), where it is confirmed that the Pt peaks are XRD visible only after 1 h at 900 °C.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dwell Temperature (°C)</th>
<th>Dwell time (h)</th>
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</thead>
<tbody>
<tr>
<td>H1</td>
<td>as prepared</td>
<td>-</td>
</tr>
<tr>
<td>H2</td>
<td>500</td>
<td>3</td>
</tr>
<tr>
<td>H3</td>
<td>700</td>
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<tr>
<td>H4</td>
<td>800</td>
<td>3</td>
</tr>
<tr>
<td>H5</td>
<td>900</td>
<td>0.5</td>
</tr>
<tr>
<td>H6</td>
<td>900</td>
<td>6</td>
</tr>
<tr>
<td>H7</td>
<td>900</td>
<td>12</td>
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<td>H8</td>
<td>900</td>
<td>12</td>
</tr>
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</table>

Figure 1. Diffraction pattern of the sample H8 (collected at 22 keV). The crosses are the experimental points and the red line represents the result of the Rietveld refinement. The 2θ positions and relative intensities of the Pt and CeO_2 peaks are also marked.
The samples were investigated by TEM and HAADF-STEM. Below the segregation threshold temperature of $T = 900 \, ^\circ\text{C}$ traces of metal Pt could not be detected in the EM images, in agreement with the XRD results. The powders are loosely packed and show a rather narrow size distribution even at elevated temperatures (such as $800 \, ^\circ\text{C}$ for $3 \, \text{h}$, sample $H_4$); only minor particle-particle necking was identified (Figure 2).

HR-TEM micrographs for sample $H_6$ are shown in Figure S2 (supporting information). Because of the thermal treatment, the CeO$_2$ particles grow up to about 10-15 nm, maintaining their equiaxed shape. Several particles were analyzed but no evidence of Pt segregation could be detected, in agreement with the XRD analysis. The EDX chemical mapping did not show any zone with distinct higher Pt content (SI, Figure S3). After longer thermal treatments ($6 \, \text{h}$), Pt segregation was detected by TEM as well.

The HAADF-STEM micrograph of sample $H_7$ is shown in Figure 3. Bright spots in the HAADF-STEM images became visible and correspond to Pt particles of about 1-2 nm. This preliminary XRD study clearly defines the experimental conditions in terms of temperature and duration to be set for the detailed in-situ kinetic study.

3.2. $L$ series: ex-situ Pt segregation by XRD, STEM and XAS. Table 2 summarizes the samples prepared for the $L$ series. The samples were treated in a tubular oven and then analyzed by XRD, EM imaging and XAS. Due to the low amount of Pt, reliable XRD data can be collected only by using a synchrotron radiation facility.

Figure 4 shows the evolution of the XRD patterns against time and temperature of the $L_{\text{ox}}$ and $L_{\text{red}}$ series. In both series the evolution towards bigger CeO$_2$ crystallites against temperature can be easily deduced from the peak broadening (Figure 4a). Under oxidizing atmosphere the Pt peaks are detectable only after $3 \, \text{h}$ of thermal treatment at $900 \, ^\circ\text{C}$ ($L_{\text{ox}7}$) whereas they are not present if the treatment is done at $850 \, ^\circ\text{C}$ ($L_{\text{ox}5}$, $L_{\text{ox}5}$). The anomalies on the shape and intensity of the Pt peak in Figure 4b is discussed in chapter 4.

Under reducing conditions, Pt peaks were already detectable at $550 \, ^\circ\text{C}$. A clear evolution against temperature towards bigger particles (from the peak broadening) and increasing amount of Pt (from the normalized peak intensity) can be deduced in the temperature windows $500 - 650 \, ^\circ\text{C}$. At higher temperature ($650 - 900 \, ^\circ\text{C}$) the peaks’ shape and normalized intensity do not change anymore. Due to the low amount of the metallic phase the calculation of phase composition and Pt crystallite size is affected by a significant error and could be not more than a speculation.

The Secondary Electron (SE) STEM micrographs on the $L_{\text{ox}7}$ revealed bright spots on the CeO$_2$ surface corresponding to Pt nanoclusters of about 0.5 nm (Figure 5a). Such spots were not detected on other samples within the $L_{\text{ox}}$ series. The chemical nature of the bright spots was confirmed by EDX spectroscopy (Figure 5b). On the other hand HR-TEM revealed few intragranular particles with higher contrast with a size of a few nanometers. According to the nominal composition of the samples, the

Figure 2. TEM micrographs of Pt-doped CeO$_2$ treated at $800 \, ^\circ\text{C}$ for $3 \, \text{h}$ ($H_4$). (a) Even after thermal treatment at elevated temperature the particle are loosely packed and shown a relatively narrow size distribution. (b) At higher magnification, the lattice fringes of the crystalline material become clearly visible; metal Pt particles, however, cannot be detected.
XRD patterns, and the XAS spectra (as described later) it is plausible to consider these internal particles as Pt (Figure 5c and 5d). On the CeO$_2$ surface such particles were not detected after several hours of STEM observation and in several repetition of sample L$_{ox7}$. Larger sample areas (350x300 $\mu$m$^2$) at lower magnification were observed by FE-SEM. In the overall EDX mapping some spots (1 over about 5000 $\mu$m$^2$ of scanned surface) with a higher Pt concentration (SI, Figure S4) are visible. These spots correspond to micrometric-sized Pt particles deposited on the CeO$_2$ agglomerates (Figure 6).

According to the XRD analyses, the evolution and growth of Pt peaks in the L$_{red}$ series already occur at much lower temperatures. This was confirmed by the HAADF-STEM micrographs and EDX elemental mapping, where Pt particles on the CeO$_2$ surface were clearly identified (Figure 7). Because of the thermal treatment under reducing atmosphere, the CeO$_2$ particles growth was developed with partial sintering and pronounced faceting.

Selected samples were analyzed by X-ray Absorption Near Edge Structure (XANES) spectroscopy. The measurements at the Pt L$_3$ edge allowed clear insight into the average Pt oxidation states. The amplitude reduction and shift of the white line are clearly showing the increase of the Pt(0) signal upon thermal treatment.

According to the previous HR-XRD results, the evolution of Pt peaks is expected to occur between 875 – 900°C under oxidizing conditions (Figure 8a), whereas the reducing atmosphere promotes the occurrence of XRD-detectable metal Pt already after a thermal treatment at 550°C (Figure 8b). Correspondingly, changes of the EXAFS signals were also detected (not shown; the details of the EXAFS spectra were out of the scope of the present study).

In the L$_{ox}$ series, the contribution of Pt$^0$ increases rapidly at the threshold temperature of 900°C, whereas under reducing condition, L$_{red}$ series, Pt is in metallic form already at 500°C, even if not yet XRD detectable. Specifically, under oxidizing conditions at T < 900°C, most of the Pt is still in ionic form.

A similar XAS study was carried out on the Ce L$_3$-edge. Measured spectra indicated the presence of Ce(IV) only, whilst Ce(III) was not detected in any of the samples (not shown), regardless of thermal treatment or atmosphere.

Table 2. Samples from the L$_{ox}$ series (left) and L$_{red}$ series (right).

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Dwell Temperature (°C)</th>
<th>Dwell time (h)</th>
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<tbody>
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<td>L$_{ox1}$</td>
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<td>3</td>
</tr>
<tr>
<td>L$_{ox2}$</td>
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<td>900</td>
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<tr>
<td>L$_{ox8}$</td>
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</tr>
<tr>
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</tr>
<tr>
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Figure 4. High resolution XRD patterns of the $L_{ox}$ and $L_{red}$ samples collected at the energy of 22 keV for the samples of Table 2. (a) Patterns normalized by the maximum intensity of the CeO$_2$ (111) peak; (b) Blow-up of the Pt (111) peak region for patterns of selected samples normalized by the integrated intensity of the CeO$_2$ (111) peak.
Figure 5. EM micrograph of a Pt/CeO₂ sample treated at 900 °C for 3 h under oxidizing atmosphere ($L_{ox7}$). (a) SE-STEM micrograph: the lighter spots on the CeO₂ crystal corresponds to surface sub-nanometric Pt clusters as confirmed by EDX spectroscopy (shown in (b)). In (c) and (d) HR-TEM micrographs: the arrows are indicating intragranular Pt particles of few nanometers.
Figure 6. (a) FE-SEM micrograph and (b) EDX Pt mapping of sample \(L_{\text{ox}7}\). Few large (2-3 µm) well-faceted Pt particles deposited on the CeO\(_2\) agglomerates can be detected.

Figure 7. Pt/CeO\(_2\) sample treated at 900 °C for 3 h under reducing atmosphere \(L_{\text{red6}}\): (a) HAADF-STEM micrograph and (b) EDX elemental mapping. The bright spots in the HAADF image can be identified as Pt particles (red) in the EDX mapping.
Figure 8. Pt L3-edge XANES spectra of selected samples and references Pt(0), and Pt(IV)-oxide compounds (dotted blue and red, respectively). (a) Samples $L_{ox4}$ (violet) and $L_{ox7}$ (blue); (b) Samples $L_{red1}$ (red), $L_{red2}$ (green) and $L_{red3}$ (violet).

Figure 9. (a) Evolution of the Pt (111) peak intensity over time collected in situ at 930, 940, 950 and 960 °C ($K_1$, $K_2$, $K_3$ and $K_4$, respectively). Each line belongs to a pattern accumulated for 4.5 minutes. (b) Normalized integrated intensities of the Pt (111) peak ($I_{Pt(111)}$) over time at 930, 940, 950 and 960 °C. The crosses depict the measured values and the circles are the values chosen for the linear fits. The calculated slopes are used to determine the kinetic constant $k$ at the respective temperature. (c) Arrhenius plot derived from the slopes of the normalized Pt (111) peak intensities. The error is estimated to be 0.1% and 1% on the horizontal and vertical axis, respectively.
3.3. K series: in-situ Pt segregation kinetic by XRD.

The kinetic data were measured at four temperatures, namely 930, 940, 950 and 960 °C. Each diffraction pattern was measured with an accumulation time of 4.5 minutes and the samples were analyzed for several hours. The collected patterns were background-corrected and the integrated intensity for the Pt (111) peak \( I_{\text{Pt(111)}} \) and for the CeO\(_2\) (111) peak \( I_{\text{CeO}_2(111)} \) were calculated. Because of sintering at the measuring temperature, the material in the capillary shrinks. Thus, the normalized Pt peak intensities, \( I_{\text{Pt(111)}}/I_{\text{CeO}_2(111)} \), were calculated as:

\[
\frac{I_{\text{Pt(111)}}}{I_{\text{CeO}_2(111)}} = \frac{I_{\text{Pt(111)}}}{I_{\text{CeO}_2(111)}} = \frac{I_{\text{Pt(111)}}}{I_{\text{CeO}_2(111)}} \quad \text{Eq 1}
\]

The Pt segregation could be represented by a simplified model, such as the chemical equation:

\[(\text{Pt}, \text{Ce})_2\text{O}_3 \rightarrow x\text{Pt}^0 + y\text{CeO}_2 + z\text{O}_2\]

where \((\text{Pt}, \text{Ce})_2\text{O}_3\) and Pt\(^0\) represent a generic Pt ion dissolved in the CeO\(_2\) lattice and the segregated metallic Pt, respectively. More complex reactions, involving Ce\(^{3+}\) and Pt\(^{2+}\) ions and oxygen vacancies, could be speculated upon without adding significant insight on the segregation path.

The evolution of the Pt (111) peak over time for the four experimental datasets is shown in Figure 9a, whereas the value of \( I_{\text{Pt(111)}} \) against time is shown in Figure 9b. From the experimental data an extended linear behavior can be seen which could be associated with an apparent zero-order kinetic reaction, such as:

\[
\frac{d(\text{mass of segregated Pt}^0)}{dt} = k(T) \quad \text{Eq. 2}
\]

The Arrhenius plot of the peak growth rate is given in Figure 9c. The calculated activation energy for the Pt segregation from the CeO\(_2\) lattice in air corresponds to 3.88 eV (374 kJ mol\(^{-1}\)). The extracted numerical values for the Arrhenius plot are reported in Table T1 (Supplementary Information).

4. Discussion: incorporation and segregation pathways

The reported experimental evidences, combined with our previous findings\(^8\) are summarized in Figure 10. The as prepared material is composed by CeO\(_2\) NPs of about 5 nm where Pt is in form of Pt\(^{2+}\) and Pt\(^{4+}\) ions on the CeO\(_2\) surface. Upon calcination two different pathways can be discerned, namely under oxidizing (air) or reducing (2%H\(_2\), balance Ar) atmosphere. In Figure 10, the oxidizing pathway is indicated by red arrows, whereas the reducing pathway is described by the blue arrow.

Under the oxidizing atmosphere and in the temperature range 500 < T(°C) < 900, Pt ions diffuse into the CeO\(_2\) lattice. This fact is validated by a sensible CeO\(_2\) lattice contraction in highly doped samples\(^8\) and by the spectroscopic evidence presented in Figure 8a. Accordingly, evidence of crystalline Pt particles is found neither with XRD (Figure 4b) nor with EM (Figure 2). XANES spectra show that after 3 h of thermal treatment at 800 °C Pt is mainly present in its ionic form (Figure 8a). The ionically dispersed Pt acts as a sintering and crystal growth inhibitor.\(^18\) At T ≥ 900 °C Pt sub-nanometric clusters are segregated on the CeO\(_2\) particles surface (Figure 5a-b). The metallic nature of Pt at 900°C is spectroscopically proven (Figure 8a). Few Pt nanometric particles (<5 nm) are detected within the CeO\(_2\) crystals (Figure 5c-d) and few micrometric particles (2-3 µm) are deposited on the CeO\(_2\) agglomerates (Figure 6). These few large particles give rise to the Pt peaks in the diffraction patterns (Figure 4b).

The Pt peak in Figure 4b, sample L_0x7, shows anomalies (detectable only using high resolution synchrotron X-ray diffraction) which are poorly reproducible and – if occurring – affect all Pt peaks in the respective XRD pattern. Moreover, the angular gap between the maximum and the shoulder is \(\theta\)-independent, which excludes the possibility of two populations of particles with slightly different lattice parameters and other crystallographic features (such as strain effects). The reason for the peak’s irregular profile (a visible shoulder, Figure 4b, bottom) is attributed to the poor particle statistics.\(^46\) In fact, considering the sample volume probed by the beam, the overall concentration of Pt (0.7wt.%), and the size of the Pt particles (about 3 µm), the number of such Pt particles can be estimated to be less than 4000. Moreover, it is worth mentioning that only a small fraction of these particles (0.3%, Supporting Information) are in average in scattering condition for each peak. Thus, the number of contributing grains to each Bragg peak is estimated to be 10-20, which is not enough to give a statistically consistent profile.

Coherently, the peaks of L_red series are rather broad and with a regular profile: in these cases no micrometric Pt particles can be detected and the Pt grains responsible of the diffraction are those highlighted by Figure 7, which are present in a statistically appropriate number.

The evolution of Pt peaks is studied in situ in the temperature range 930-960 °C by high resolution XRD (Figure 9a). Also in this case – and in particular for the experiment done at 940 °C – the peak shape is affected by the aforementioned anomalies, even against time. Since the acquisition is done at high temperature, the resolution is not as high as the one reported in Figure 4b (collected at RT) and the shoulder is only partially resolved. Coherently, the peak position at high temperature is shifted towards lower angles due to the thermal lattice expansion. The initial velocity for segregation and coagulation of Pt clusters into larger crystalline particles is experimentally evaluated and the activation energy is estimated to be about 3.88 eV (Figure 9b-c). Since it is clear that Pt is occurs in its metallic form (Figure 8a) and the particles responsible for the diffraction peaks are the large particles, the evolution of the Pt peak corresponds to the depletion of the Pt clusters on the CeO\(_2\) surface. Thus, the measured high activation energy indicates that the Pt clusters are strongly stabilized (anchored) on the CeO\(_2\) surface.
**Figure 10.** Incorporation-segregation pathways for Pt doped CeO$_2$ nanopowders. The thermal treatment under oxidizing conditions (blue arrows) promotes the ionic dispersion of Pt into the CeO$_2$ lattice, whereas treatments above a threshold temperature of $T \geq 900$ °C lead to Pt segregation and the formulation of sub-nanometric Pt metal clusters on the CeO$_2$ and few intragranular Pt particles. At $T=900$ °C and long dwell time, Pt segregate in micrometric-size particles (not showed in this figure). On the other hand, thermal treatment under reducing conditions (red arrow) promotes the direct formation of relatively large Pt particles (3-10 nm) on CeO$_2$. 

Under reducing atmosphere, CeO$_2$ particles sintering and ripening are promoted at lower temperature and are more pronounced than under oxidizing conditions. For instance, the sample $L_{ox5}$ (treated at 850 °C for 3 h) shows a peak broadening similar to the sample $L_{red4}$ (treated at 650 °C for 3 h) and the particles facetting of sample $L_{red6}$ is more marked than for sample $L_{ox7}$. This behavior is well-known and due to the high solid state ionic mobility in the presence of oxygen vacancies, which are promoted when the material is treated under reducing conditions. The experimental results show that the Pt(IV)-rich layer of the as prepared material is directly reduced to Pt metal particles. These particles rapidly grow up to 3-10 nm, which are easily detected by X-ray diffraction (Figure 4b), by XAS (Figure 8b) and by EM (Figure 7).

The results clearly indicate that in order to prepare a nanometric CeO$_2$ material decorated with Pt clusters, a defined pathway has to be followed. Specifically, (a) a synthesis method able to produce CeO$_2$ nanoparticles surface doped with Pt have to be considered; (b) a mild thermal treatment in oxidizing condition in order to incorporate Pt ions into the CeO$_2$ lattice is required; and (c) a controlled thermal treatment in oxidizing condition is crucial to being able to tailor the segregation of sub-nanometric Pt metal clusters on the CeO$_2$ surface, preserving the loosely packed nanostructure. The so obtained material is thermally stable and Pt clusters become mobile only at $T > 900$ °C, thus they are strongly anchored at a lower working temperature, i.e. up to 800 °C. If the material is treated at high temperature (such as 900 °C) for several hours, the Pt cluster disappears, larger Pt particles are formed and the material could lose the catalytic properties. If a thermal treatment under a reducing atmosphere is performed on the as prepared material, Pt ions are not incorporated into the particle but directly reduced on the CeO$_2$ surface. The obtained material is equivalent to that produced by standard impregnation techniques where the deposited Pt particles are relatively large and poorly anchored on the support material. As a consequence, even if small Pt particles can be produced on the catalyst surface (Figure 4b), they rapidly grow into larger particles at a relatively low temperature (<650 °C) and the material is easily deactivated in operando.

Starting from the same as prepared material with tunable Pt loading and applying the incorporation-segregation pathways of Figure 10, the nature of Pt can be tuned according to the specific material requirements. A variety of scenarios can be realized: from a material composed of Pt ions dispersed in the CeO$_2$ lattice to CeO$_2$ nanoparticles decorated by strongly anchored sub-nanometric Pt clusters. On the other hand, a material with relatively large Pt particles supported on CeO$_2$ can be produced by a thermal treatment under a reducing condition. This flexibility allows the study of the structure-property relationships with the aim of understanding the nature of catalytically active centers. This allows one to minimize the amount of precious metal required, and to increase the lifetime of catalytically active materials. Moreover, the applied synthesis and processing methods for the preparation of the advanced material are fully scalable. For instance the material can be produced using the Segmented Flow Tubular Reactor (SFTR) technology.

**5. Conclusions**

The rational incorporation-segregation pathways for the system Pt-CeO$_2$ are clearly outlined. The major outcomes and findings are summarized as follows:

(a) the preparation of nanometric CeO$_2$ surface doped with Pt ions is achieved using a scalable and cost-effective processes;

(b) the condition to promote the incorporation of Pt ions into the CeO$_2$ lattice is defined. It results that a mild thermal treatment in air condition is mandatory;

(c) the condition to segregate sub-nanometric Pt clusters on the CeO$_2$ nanoparticles is described and it occurs at $T = 900$ °C.
(d) the metallic nature of the segregated clusters is confirmed by X-ray absorption near edge structure (XANES) spectroscopy and EDX analyses;
(e) the size of Pt clusters is proven by Secondary Electron (SE) STEM;
(f) the segregation kinetics are followed by in-situ high resolution X-ray diffraction collected at the Swiss Light Source at T > 900 °C. It results that the activation energy for Pt clusters segregation and coagulation is about 3.88 eV, which strongly suggest that the clusters are strongly anchored on the CeO₂ surface.

With this study we show that unprecedented control over strongly anchored metallic Pt clusters on the surface of CeO₂ nanoparticles is achievable using a wet chemical synthesis method combined with an appropriate thermal treatment. The strategy can be applied to other material with aim to deeply investigate the structure-properties relationships and the nature of catalytically active centers. The combination of scalable processes and reliable control over the material nanostructure paved the way towards the development of advanced materials of industrial application.

ASSOCIATED CONTENT
Supporting Information. The in-situ XRD patterns to screen the CeO₂ and Pt peak evolution of sample H₂ up to 900 °C are reported in Figure S1; HR-TEM micrographs of sample H₆ with high Pt-load above the segregation temperature, but below the segregation duration are reported in Figure S₂, including the corresponding Fast Fourier Transformed image; the EDX chemical mappings of sample H₆ are reported in Figure S₃; the EDX chemical mapping of sample L₁₋₀ₓ₇ is reported in Figure S₄; the values for the determined kinetic constant k for the respective samples of the K series are reported in Table T₁. A comment on particle statistics is reported as well. This material is available free of charge via the Internet at http://pubs.acs.org.

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FP carried out the synthesis of the material and substantially contributed to the manuscript preparation. AT wrote the paper and coordinates the scientific activity. ACa contributed to the experiments at the beamlines and to samples preparation. CP did the microscopic characterization of the samples. ACe coordinated the scientific activity at the beamline and contribute to the diffraction patterns analysis. CL provided the financial support and contributed to the paper reviewing. All authors have given approval to the final version of the manuscript.

ACKNOWLEDGMENT
We thank A. Trapananti for her contribution to the XAS characterization. The XRD and XAS data were collected at the X04SA-MS beamline of the Swiss Light Source (SLS-PSI) and the LISA beamline of the European Synchrotron Radiation Facility (ESRF), respectively. The HRTEM data were collected with the help of A. Falqui at the Italian Institute of Technology in Genoa and N. J. Zaluzec at the Argonne National Laboratory. Use of the Center for Nanoscale Materials, including resources in the Electron Microscopy Center, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. We thank E. Müller Gubler for STEM imaging, using the facilities at PSI and at ScopeM ETH Zurich. We thank M. Tariq for the chemical analysis of our samples. We gratefully acknowledge E. De Boni for SEM-EDX analyses. We thank M. Dzambevogic for the realization of the 3D figures. Financial support was provided by PSI and the Swiss National Foundation (SNF) project no. 200021_144302.

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