

# Phosphorus poisoning during wet oxidation of methane over Pd@CeO<sub>2</sub>/Graphite model catalysts

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## Abstract

The influence of phosphorus and water on methane catalytic combustion was studied over Pd@CeO<sub>2</sub> model catalysts supported on graphite, designed to be suitable for X-Ray Photoelectron Spectroscopy / Synchrotron Radiation Photoelectron Spectroscopy (XPS/SRPES) analysis. In the absence of P, the catalyst was active for the methane oxidation reaction, although introduction of 15% H<sub>2</sub>O to the reaction mixture did cause reversible deactivation. In the presence of P, both thermal and chemical aging treatments resulted in partial loss of activity due to morphological transformation of the catalyst, as revealed by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) analysis. At 600 °C the combined presence of PO<sub>4</sub><sup>3-</sup> and water vapor caused a rapid, irreversible deactivation of the catalyst. XPS/SRPES analysis, combined with *operando* X-Ray Absorption Near Edge Structure (XANES) and AFM measurements, indicated that water induces severe aggregation of CeO<sub>2</sub> nanoparticles, exposure of CePO<sub>4</sub> on the outer layer of the aggregates and incorporation of the catalytic-active Pd nanoparticles into the bulk. This demonstrates a temperature-activated process for P-poisoning of oxidation catalysts in which water vapor plays a crucial role.

**Keywords:** Phosphorus, catalytic converters, methane, palladium, ceria

## 1. Introduction

Palladium-based catalysts are the most active materials for oxidation of methane at low temperatures [1,2], and especially high activity can be achieved when the Pd is in the presence of reducible promoters such as ceria ( $\text{CeO}_2$ ) [3–5]. The promoter helps stabilize PdO (the most active phase) against thermal decomposition to less active Pd, improving the catalytic performance by activation and spillover of oxygen from the promoter to the Pd phase [2,4,5]. Indeed, recent work has shown that the activity of ceria-supported Pd catalysts increases with the interfacial contact between the Pd phase and ceria [6]. Therefore, to maximize this contact, some of us recently used self-assembly methods to synthesize hierarchical, core-shell catalysts, designated here as Pd@CeO<sub>2</sub>, that consist of Pd nanoparticles surrounded by a thin porous shell of ceria [7]. These catalysts show remarkable activity for CH<sub>4</sub> combustion under some conditions and offer significant potential to improve the performance of catalysts required to reduce methane emissions. However, despite their high intrinsic activity for methane oxidation, Pd-based catalysts can deactivate under real conditions, especially in the presence of water vapor, sulfur and phosphorus species [8–14].

Phosphorus is a particularly serious poison for CeO<sub>2</sub>-promoted catalysts and is a primary agent for irreversible deactivation of automotive catalytic converters under real operating conditions [15–17]. The presence of phosphorus compounds ( $\text{P}_2\text{O}_5$  or  $\text{H}_3\text{PO}_4$ ) in vehicle exhaust is due to decomposition/volatilization of motor oil anti-wear additives, such as zinc dialkyldithiophosphate (ZDDP) [18,19]. These additives are present in most available motor oils in concentration up to 1–2% (although this can vary depending on the final application) and their effect on catalytic converters is well documented [15–17]. Based on studies of simplified, model systems ( $\text{CeO}_2$  and  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ ) [18–25], it is known that mixed phosphates (Zn, Ca and Mg) form glassy overlayers on the washcoat surface and also react with the catalyst to form  $\text{CePO}_4$  and  $\text{AlPO}_4$  [25].

$\text{CePO}_4$  formation is irreversible and detrimental to the catalytic activity due to loss of oxygen storage capacity (OSC), which is caused by locking of the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  pair in the 3+ state [24,25]. Both the direct reaction of  $\text{CeO}_2$  with phosphorus compounds in the gas phase and the reaction of  $\text{CeO}_2$  with P-containing species on the catalyst (e.g. aluminum phosphate) can lead to the formation of  $\text{CePO}_4$  [22]. Based on evidence from total reflection X-ray fluorescence (TXRF), XPS and <sup>31</sup>P NMR data on P-poisoned  $\text{CeO}_2$ , phosphates species formed on the surface and sub-surface region dramatically decrease OSC. Cerium phosphate is also very stable and cannot be removed from either pure  $\text{CeO}_2$  or  $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$  by calcination treatments to 1000 °C [21,26]. A few studies indicated partial removal of phosphate species by washing the spent catalyst with oxalic acid [18] or chlorine containing species [27]. However,  $\text{CePO}_4$  persists even after these treatments [18], implying that alternative methods need to be developed to address the problem of P-poisoning.

Despite previous work on regenerating P-poisoned catalysts, relatively little is known about the conditions in which  $\text{CePO}_4$  is formed. In studies regarding commercial catalysts, the effect of P-aging is evaluated by comparing fresh samples and samples aged for 30, 000 - 160,000 km in conventional automobiles [15–17]. In model systems studies the aging treatment is typically simulated by depositing phosphates by impregnation of the catalyst with  $\text{NH}_4\text{H}_2\text{PO}_4$  solutions followed by calcination to get a final P content of 0.04–4.5 wt% [19,21,23]. In one study,  $\text{CeO}_2$  aging was performed for only 10 hours by introducing 85 ppm  $\text{H}_3\text{PO}_4$  through the gas feed [22]. Notably, aging effects were similar in model systems and real catalysts, even if the chosen

conditions, the materials studied and method of P addition were different. This suggests that model systems studies are relevant to real applications, and also that aging can be very fast as soon as phosphates reach the catalytic bed at a certain temperature of formation. Despite this, to our best knowledge, time-on-stream deactivation studies on commercial or model systems are still too limited. Also, the temperature threshold at which  $\text{CePO}_4$  is formed was only reported by Xu *et al.* [22] for pure  $\text{CeO}_2$  under lean conditions (600°C). However, in their study, gas-phase  $\text{P}_2\text{O}_5$  was introduced by thermal decomposition of aqueous  $\text{H}_3\text{PO}_4$ , resulting in 5%  $\text{H}_2\text{O}$  in the reaction atmosphere. In the present study, we show that the introduction of  $\text{H}_2\text{O}$  in methane combustion reaction mixture enhances the effect of phosphorus poisoning, leading to deactivation. This is particularly relevant to lean-burn engines converters and other real applications, in which water is typically present in 5-15% vol. concentration [13,14].

## 2. Experimental Method

### 2.1 Catalyst Synthesis

Potassium tetrachloropalladate(II) (99.95%) and palladium nitrate (99.95%) were purchased from ChemPUR. Cerium ammonium nitrate (CAN, 99.99%), sodium methoxide (25% in methanol), phosphoric acid (85%), 11-mercaptoundecanoic acid (MUA, 95%), dodecanoic acid (99%), triethoxy(octyl)silane (TEOOS, 97.5%), and all the solvents (analytical grade) were obtained from Sigma–Aldrich. Sodium borohydride (98%+) was purchased from Acros Organics. Graphite foils, 0.25 mm thick, were purchased from Alfa Aesar (99.8%, phosphorus-free graphite) and Chempur (99%, graphite containing phosphorus). The foils were cut into 9x9 mm slides and washed with water and acetone prior to use.

The supramolecular  $\text{Pd@CeO}_2$  units were prepared according to published procedures [28]. Briefly, pre-formed Pd nanoparticles protected by 11-mercaptoundecanoic acid (MUA) were mixed with Ce(IV) tetradecyl alkoxide to obtain a Pd:Ce molar ratio of 3.70, leading to the formation of self-assembled units with an intimate Pd-Ce contact. A controlled hydrolysis in the presence of dodecanoic acid leads to the formation of the  $\text{Pd@CeO}_2$  structures, in which small crystallites (~3 nm) of  $\text{CeO}_2$  organize around the preformed metal particles. These units were deposited from solution onto the two types of graphite, one containing phosphates (P-graphite) and one pure (graphite), according to a procedure described in detail elsewhere [30]. The  $\text{Pd@CeO}_2$  batch was diluted 1:10 and the resulting solution was added to the slide 5 times, 0.1 mL at a time, allowing the slide to dry between additions. The  $\text{Pd@CeO}_2/\text{P-graphite}$  and  $\text{Pd@CeO}_2\text{-graphite}$  model catalysts were calcined to 450 °C in air for 5 h. These samples will be referred to as "fresh".

### 2.2 Aging treatments

Aging treatments were performed in a U-shaped quartz reactor, using an alumina tray to hold the model-catalyst slides in place. Reactions were carried out at a total gas pressure of 1 atm, with the inlet composition controlled by varying the flow rates of  $\text{CH}_4$ ,  $\text{O}_2$  and Ar, while maintaining the total flow rate at  $21.3 \text{ mL min}^{-1}$ . The Gas Hourly Space Velocity (GHSV) was  $10^6 \text{ mL g}^{-1} \text{ h}^{-1}$ , using the volume of  $\text{Pd@CeO}_2$  dispersion added to the graphite slides.

The heating and cooling rates in all heating measurements were fixed at  $10\text{ }^{\circ}\text{C min}^{-1}$ . For experiments that included water, the pre-mixed, gaseous reactant mixture was bubbled through a saturator heated to the temperature required for the desired water feed concentration. The composition of the effluent gases was monitored on-line using a mass spectrometer. At the end of the aging treatment, the system was purged with Ar, cooled to room temperature, and finally stored under Ar until rapid transfer to the XPS chamber.

### 2.3 Characterization techniques

The X-ray Photoelectron Spectroscopy (XPS) and Synchrotron Radiation Photoelectron Spectroscopy (SRPES) experiments were carried out at the Materials Science Beamline (MSB) at the Elettra Synchrotron Light Source in Trieste, Italy. The MSB is a bending magnet beamline with a plane grating monochromator that provides light in the energy range of 21-1000 eV. The UHV endstation, with a base pressure of  $1\times 10^{-8}$  Pa, is equipped with an electron energy analyzer (Specs Phoibos 150) and a dual Mg/Al X-ray source. High-resolution, SRPES measurements were performed on the following core levels: O 1s (610 eV), Pd 3d (610 eV), C 1s (425 eV), and P 2p (425 eV). Complementary XPS spectra of Ce 3d, O 1s, C 1s, P 2p, and Pd 3d core levels were recorded at the same end station using the excitation energy of 1486.6 eV (Al  $K\alpha$ ). The apparent degree of reduction of ceria was determined from the Ce 3d spectra using the procedure described in a previous publication [29]. Binding energies are reported after correction for charging using the graphite C 1s as a reference.

Sample surfaces were also examined by means of a field-emission Scanning Electron Microscope (SEM) (Model Tescan Mira 3). High resolution was achieved using an acceleration voltage of 30 kV and a working distance of less than 3 mm. Additionally, a Bruker XFlash® 6 | 10 Energy Dispersive Spectrometer (EDS), mounted on the SEM apparatus, was used to carry out element mapping of the sample. Characteristic X-ray radiation was excited by 20 keV primary electrons.

Atomic Force Microscopy (AFM) was performed using a Nanoscope V (Digital Instruments Metrology Group, model MMAFMLN), in tapping mode in air at room temperature, using an n-type silicon  $\mu\text{mash}^{\circledR}$  SPM probe (HQ:NSC15/AL BS) with tip height of 12-18 $\mu\text{m}$  and cone angle  $<40^{\circ}$  (Resonant frequency 325kHz, force constant of  $\sim 40\text{N/m}$ ).

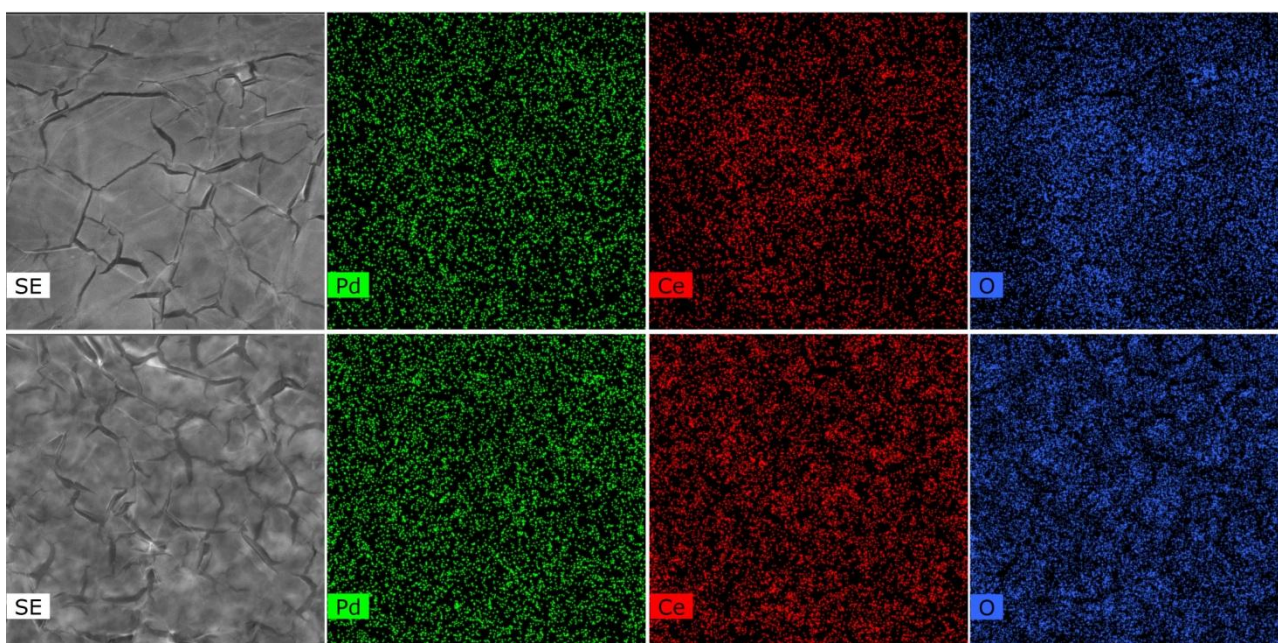
X-Ray Absorption Near Edge Structure (XANES) experiments were performed at the SAMBA beamline at Synchrotron SOLEIL (France) with a Si (220) double crystal monochromator. The monochromator was kept fully tuned and harmonics were rejected by a pair of Pd-coated, Si mirrors. Spectra were recorded in fluorescence mode at the Pd K edge ( $E = 24350\text{ eV}$ ) and Ce  $L_{\text{III}}$  edge ( $E = 5723.4\text{ eV}$ ) using a 35-element Ge detector. *Operando* experiments were conducted using the transmission and fluorescence cell described elsewhere [30]. 3 slides of Pd@CeO<sub>2</sub>/P-graphite catalyst and a total gas flow rate of  $12\text{ mL min}^{-1}$  (0.5 % CH<sub>4</sub>, 2.0 % O<sub>2</sub>, 15.0 % H<sub>2</sub>O if appropriate, and N<sub>2</sub> balance) were used for both Ce  $L_{\text{III}}$  edge experiments and Pd K edge experiments. Product analysis was carried out using a Cirrus-MKS mass spectrometer. The observed activity was comparable to that observed during catalytic testing. The fractions of Ce<sup>3+</sup> and Pd<sup>0</sup> in the samples were determined by fitting the XANES part of the spectrum using a linear combination of spectra for CePO<sub>4</sub> and CeO<sub>2</sub> to fit data for Ce and a combination of spectra for PdO and a Pd foil to fit data for Pd. All measurements were performed during the same beam session.

### 3. Results

The graphitic supports used in this study were analyzed by EDS to determine their P content. As expected, no P was observed on the pure graphite support, while the P-graphite samples contained  $1000 \pm 100$  ppm of P. The P signal did not change appreciably upon deposition of Pd@CeO<sub>2</sub> particles, nor was it affected by any of the aging treatments performed in this study.

Complementary XPS/SRPES analysis was performed on the as-received graphitic supports to determine the chemical state of phosphorus and the surface/bulk distribution. Prior to calcination, there was no P signal on either the P-graphite or the pure graphite. A phosphorus signal, at a Binding Energy (BE) corresponding to that of PO<sub>4</sub><sup>3-</sup> (133 eV) was only observed on the P-graphite after thermal treatment to 450 °C in air (See Figure S1). Similar treatment of the pure graphite did not cause the appearance of a P signal. This suggests that P is initially present only in the bulk of the P-graphite support and is released during the thermal treatment. An O 1s signal at 530.5 eV appeared together with the P signal, indicating the presence of PO<sub>4</sub><sup>3-</sup> species. This fingerprint of PO<sub>4</sub><sup>3-</sup> was present on all Pd@CeO<sub>2</sub>/P-graphite samples, independent of aging conditions and with a similar intensity as was observed following calcination at 450 °C. In accordance to these observations, phosphates can be present as intercalating compounds of graphite foils manufactured by squeezing exfoliated graphite [31].

SEM images of the fresh Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite catalysts are shown in Figure 1 and exhibit very similar surfaces, displaying large, smooth domains of a continuous film, separated by small, shallow cracks. The distributions of Pd, Ce and O signals over the samples were homogeneous, demonstrating that the Pd@CeO<sub>2</sub> particles were well-dispersed and exposed to the gas phase for both supports, an important prerequisite for model catalytic systems.

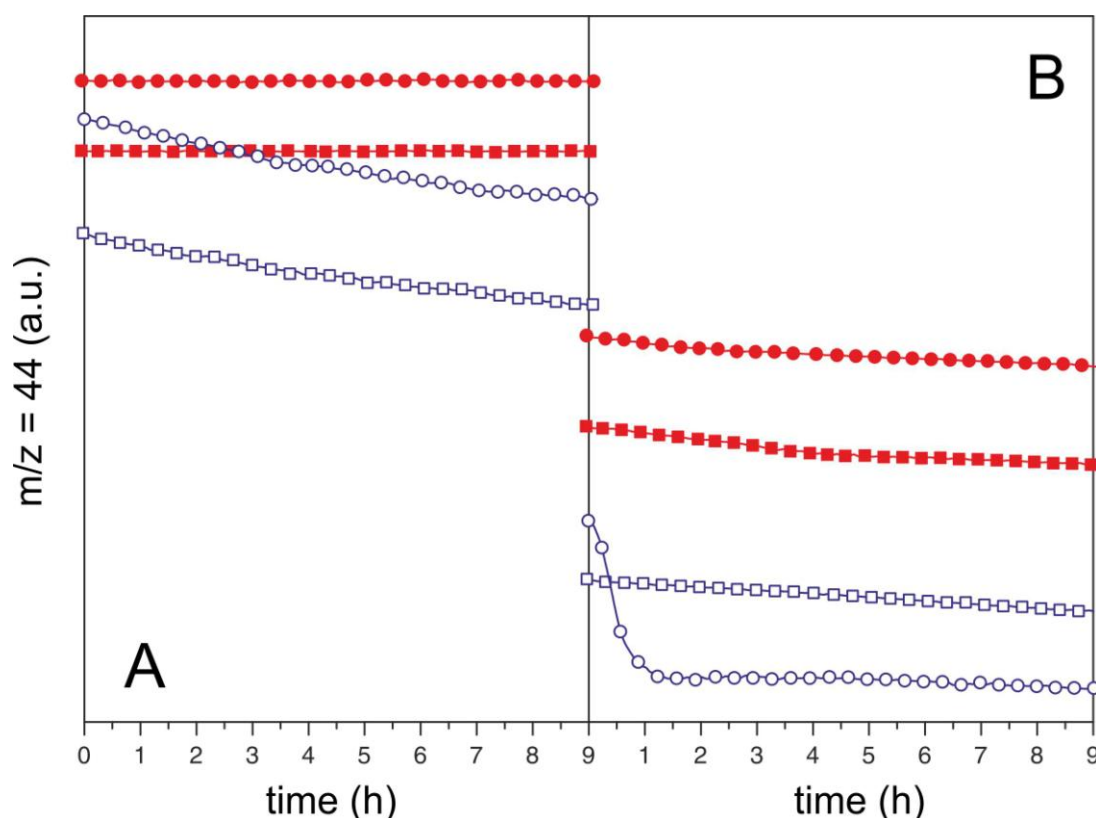


**Figure 1:** 20  $\mu\text{m}$  viewfield SEM images and EDS mapping of Pd, Ce and O signals of fresh Pd@CeO<sub>2</sub>/graphite (top row) and Pd@CeO<sub>2</sub>/P-graphite (bottom row) samples.

The “fresh” catalysts were then aged for 0 min, 30 min, 1 h, or 9 h at catalytic reaction conditions, at 500 °C and 600 °C, in dry and wet conditions. In all experiments, the catalyst was ramped to the desired temperature in 0.5% CH<sub>4</sub>, 2.0% O<sub>2</sub> and 15.0% H<sub>2</sub>O (for wet conditions) and held at that

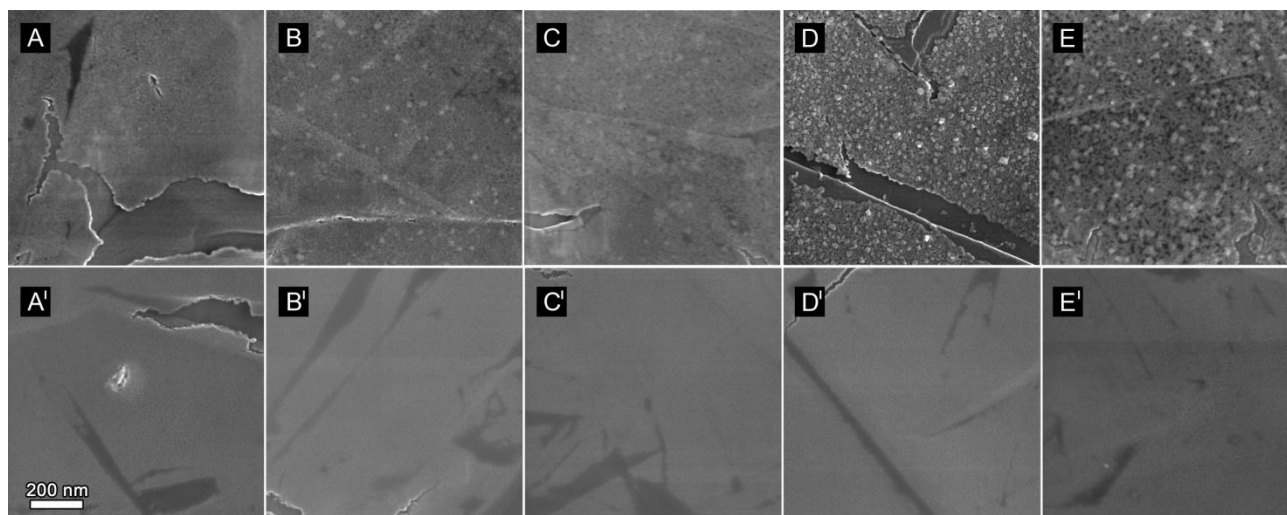
temperature for the chosen time span. After aging, the gas flow was switched to pure Ar and the samples cooled to room temperature before being transferred to either the SRPES/XPS line or to the SEM.

As shown in Figure 2A, the fresh model Pd@CeO<sub>2</sub>/graphite catalyst showed significant and constant evolution of CO<sub>2</sub> as result of CH<sub>4</sub> oxidation at both 500 and 600 °C. While rates were stable under dry conditions, the rate of CO<sub>2</sub> production decreased with time at both temperatures when water was added. The Pd@CeO<sub>2</sub>/P-graphite samples were less active for methane oxidation (Figure 2B). Most notably, there was a fast and irreversible deactivation during wet aging at 600 °C. After 1 h of isothermal treatment under these conditions, the sample was almost completely inactive.



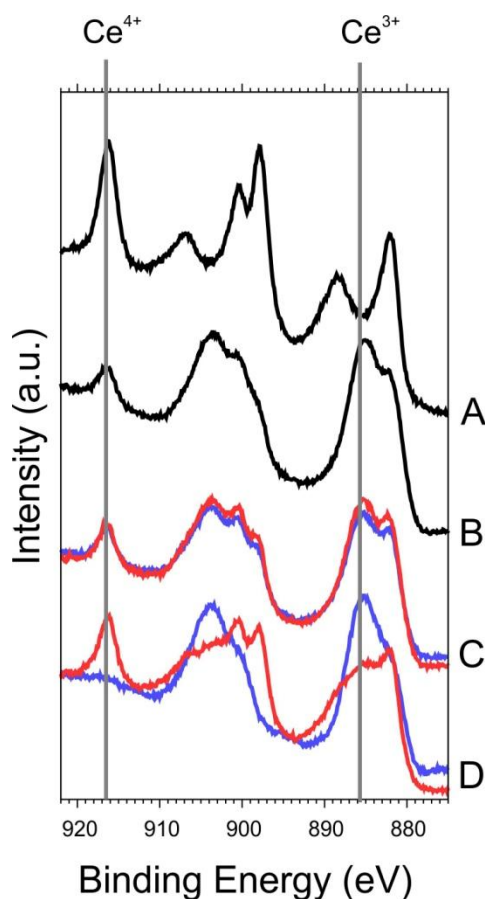
**Figure 2:** CO<sub>2</sub> evolution over time. A: Pd@CeO<sub>2</sub>/graphite; B: Pd@CeO<sub>2</sub>/P-graphite. Circles: 600 °C aging; squares: 500 °C aging; filled symbols: dry conditions (CH<sub>4</sub> 0.5%, O<sub>2</sub> 2%, GHSV: 10<sup>6</sup> mL g<sup>-1</sup> h<sup>-1</sup>); open symbols: wet conditions (15% H<sub>2</sub>O vapor added to reaction atmosphere).

SEM images of the aged samples in Figure 3 show differences between the catalysts supported on graphite and P-containing graphite. The surfaces of the Pd@CeO<sub>2</sub>/graphite samples were not appreciably altered by any of the aging treatments. However, images of the Pd@CeO<sub>2</sub>/P-graphite samples show features having diameters of 10–30 nm, with sizes that are slightly bigger for 600 °C aging treatments. These spots are partially sintered Pd@CeO<sub>2</sub> particles. The SEM analysis suggests that the presence of phosphorus causes partial aggregation of the Pd@CeO<sub>2</sub> units and growth of crystallite sizes that does not occur in the absence of P.



**Figure 3:** SEM of Pd@CeO<sub>2</sub>/P-graphite (A-E) and Pd@CeO<sub>2</sub>/graphite samples (A'-E'). The samples were fresh (A, A') or treated for 9 h under the following conditions: dry reaction conditions at 500 °C (B, B') or 600 °C (D, D'); wet reaction conditions at 500 °C (C, C') and 600 °C (E, E').

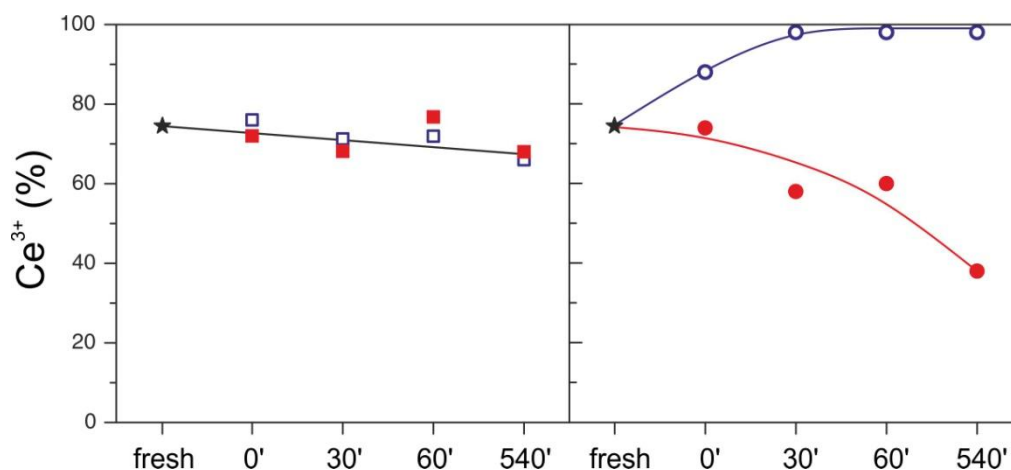
Figure 4 indicates that the Ce 3d region of the XPS spectra is very different for the Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite samples. Spectra on the Pd@CeO<sub>2</sub>/graphite samples were all similar, with features typical of pure CeO<sub>2</sub>. Initially, the apparent O:Ce stoichiometry is 1.94 (12% Ce<sup>3+</sup>) but it increases to 2.0 with aging time. Apparently, a small fraction of the cerium is in the Ce<sup>3+</sup> state in the initial particles but all of the Ce atoms are converted to Ce<sup>4+</sup> under the aging conditions used in this study. This behavior differs from that observed for Pd@CeO<sub>2</sub>/Si-Al<sub>2</sub>O<sub>3</sub> catalysts, which showed a low but constant Ce<sup>3+</sup> fraction for all the treatments [13]. Various factors could contribute to this, including the different surface sensitivity of the techniques used (XPS-XAS) and the different Pd:Ce ratio, but the different calcination temperatures used here (450 °C vs 850 °C) and the different supports (Al<sub>2</sub>O<sub>3</sub> vs graphite) are likely the primary causes. On the Pd@CeO<sub>2</sub>/P-graphite sample, in contrast, the XPS spectra show mainly features of CePO<sub>4</sub> [19,32], even on the fresh sample, for which Ce<sup>4+</sup> is also still observed. Spectra taken after heating to 500 °C under dry and wet aging were similar to each other and showed only small changes compared to the fresh sample. On the other hand, aging treatments at 600 °C resulted in dramatic changes. After 30 min of wet aging at this temperature, the Ce<sup>4+</sup> signal completely disappeared. Spectra obtained after prolonged dry aging (9 h) showed partial oxidation to Ce<sup>4+</sup> with respect to the fresh sample.



**Figure 4:** Representative Ce 3d XPS spectra of: (A) the fresh Pd@CeO<sub>2</sub>/graphite sample; (B) fresh Pd@CeO<sub>2</sub>/P-graphite; (C) Pd@CeO<sub>2</sub>/P-graphite aged at 500 °C; (D) Pd@CeO<sub>2</sub>/P-graphite aged at 600 °C. Dry conditions are shown by red lines and wet conditions by the blue lines. The areas of the presented spectra have been normalized after subtraction of Shirley background and the curves have been offset for clarity. The positions of the most prominent peaks in Ce<sup>4+</sup> and Ce<sup>3+</sup> spectra are marked by grey lines.

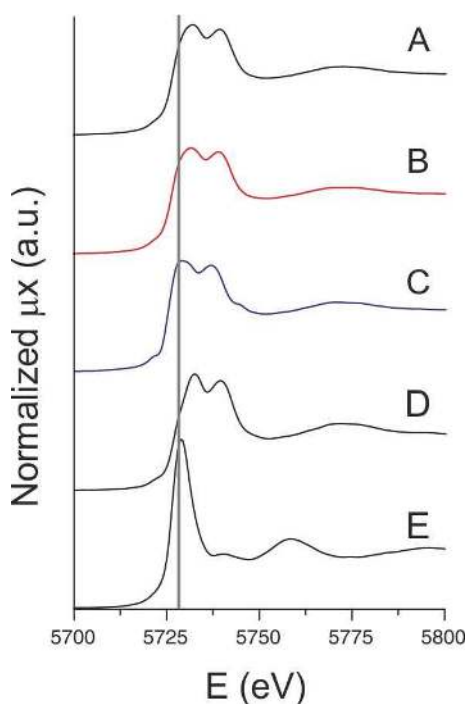
Figure 5 shows the percentage of Ce<sup>3+</sup> on the Pd@CeO<sub>2</sub>/P-graphite sample for the different aging conditions. Since, in the absence of P, the Ce in the Pd@CeO<sub>2</sub> particles is almost completely oxidized to Ce<sup>4+</sup> after the initial calcination and after all aging treatments, the trends observed for the Ce<sup>3+</sup> percentage in this case are indicative of CePO<sub>4</sub> formation on the surface of the particles sampled by XPS. The fresh sample contains 75% Ce<sup>3+</sup>, demonstrating that the particles are extensively covered by CePO<sub>4</sub> already after calcination. For aging at 500 °C, the percentage of Ce<sup>3+</sup> does not change appreciably, regardless of the aging conditions (dry or wet). However, aging at 600 °C changed the sample dramatically. Wet aging caused an increase in Ce<sup>3+</sup> percentage to 100% after 30 min, while dry aging decreased the Ce<sup>3+</sup> content, to 40% Ce<sup>3+</sup> after 9 h. These results indicate a crucial role for water in the formation, accumulation, and stabilization of phosphates on ceria.





**Figure 5:** Calculated  $\text{Ce}^{3+}$  percentage for  $\text{Pd@CeO}_2/\text{P-graphite}$  samples, determined by fitting of Ce XPS spectra. Fresh samples: star. Squares: aged at 500 °C (filled: dry conditions, empty: wet conditions). Circles: aged at 600 °C (filled: dry conditions, empty: wet conditions). The solid lines are guides to the eye.

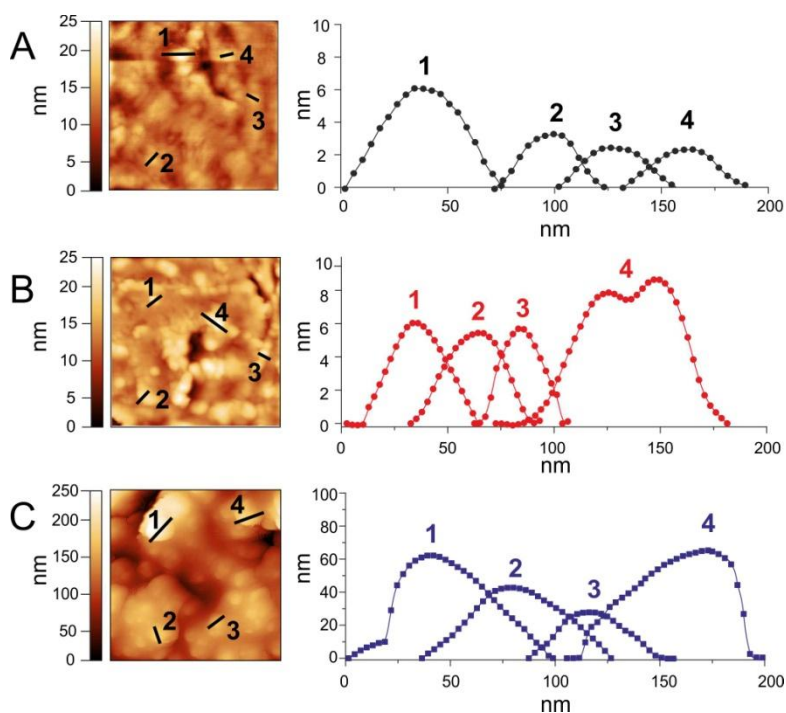
To gain further insights into the extent of  $\text{CePO}_4$  formation and the extent of cerium reduction, *operando* and *ex-situ* XANES measurements were performed on the  $\text{Pd@CeO}_2/\text{P-graphite}$  catalysts, with representative results shown in Figure 6. In all cases, only minor differences were observed between fresh, dry-aged and wet-aged samples, at both 500 °C and 600 °C. In contrast to the XPS results, the  $\text{Ce}^{3+}$  percentage did not evolve during aging treatments and ranged from 15% to 18% in all the samples studied. Indeed, these results are similar to recent *in-situ* EXAFS data on a  $\text{Pd@CeO}_2/\text{Si-Al}_2\text{O}_3$  powder having a similar  $\text{Pd@CeO}_2$  composition with no P poisoning. That study also indicated the presence of 20%  $\text{Ce}^{3+}$  in the fresh catalyst [13].



**Figure 6:** *Operando* XANES spectra of  $\text{Pd@CeO}_2/\text{P-graphite}$  sample at Ce  $L_{III}$  edge: (A) fresh; (B) during dry aging at 600 °C; (C) during wet aging at 600 °C. Reference spectra:  $\text{CeO}_2$  (D),  $\text{CePO}_4$  (E).

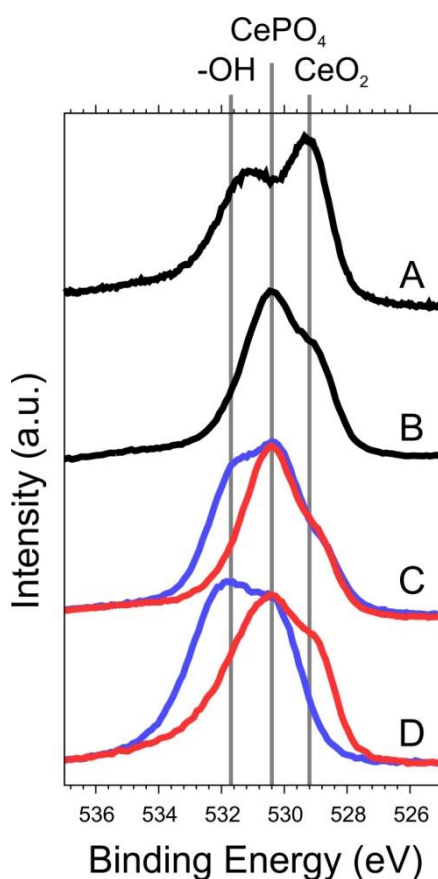
The dramatic difference in the valence ratios calculated from XPS and XANES implies that the surface and bulk concentrations can be very different on these samples. Since the inelastic mean free path in CeO<sub>2</sub> of the photoelectrons originating from Ce 3d level in the XPS study is approximately 1.2 nm and the expected dimensions of the CeO<sub>2</sub> crystallites in the Pd@CeO<sub>2</sub> particles is 3 to 4 nm [6,30], the large difference between surface and bulk concentrations cannot be explained by the presence of CePO<sub>4</sub> at the surface of the initial Pd@CeO<sub>2</sub> core-shell particles. Rather, the data indicate that thermal sintering or partial aggregation of ceria crystallites must occur under wet aging at 600 °C.

To further investigate the evolution of the Pd@CeO<sub>2</sub> particles dimensions during aging, the Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite samples were characterized by AFM topographic analysis. Figure 7 shows images and height profiles for the Pd@CeO<sub>2</sub>/P-graphite sample, both fresh and after 9-h aging at 600 °C. Results for the Pd@CeO<sub>2</sub>/graphite sample are not shown but were essentially identical to that observed for fresh Pd@CeO<sub>2</sub>/P-graphite, even with various aging treatments. For both Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite, the fresh and dry aged samples showed small features, approximately 10 nm in height, similar to what was observed for Pd@CeO<sub>2</sub> particles deposited onto YSZ(100) single crystals [33] (Figure 7A and B). Wet aging did not appreciably change the Pd@CeO<sub>2</sub>/graphite sample at either 500 °C or 600 °C. However, wet aging at 600 °C caused dramatic sintering on the Pd@CeO<sub>2</sub>/P-graphite sample, leading to the appearance of features that were 50-60 nm high and 50-70 nm wide, distributed over a corrugated surface (Figure 7C). The changes in particle size help explain how the bulk and surface compositions can be so different.



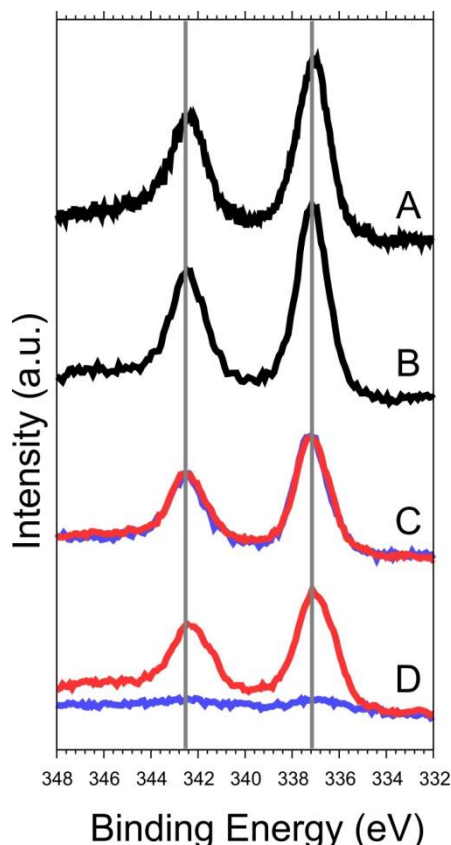
**Figure 7:** AFM topography images with representative line scans for Pd@CeO<sub>2</sub>/P-graphite: (A) fresh; (B) aged at 600 °C under dry conditions for 9 h; (C) aged under wet conditions at 600 °C for 9 h. Please note the different scales in part C.

Figure 8 shows XPS/SRPES spectra for the O 1s region of the Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite samples and the results support the conclusions reached from the Ce 3d core level. The spectrum of the fresh Pd@CeO<sub>2</sub>/graphite sample, Figure 8(A), shows two peaks at 529.2 eV and 531.6 eV. The peak at lower BE can be assigned to bulk CeO<sub>2</sub>, while higher BE peak is likely due to hydroxyl species [34]. However, the presence of other species having similar BE cannot be entirely ruled out. Carbonates arising from reaction with the graphite supports are not expected to form during the thermal treatments performed here; also, similar O 1s spectra were observed for Pd@CeO<sub>2</sub> on Au (not reported here). When the Pd@CeO<sub>2</sub>/graphite sample was aged under wet conditions, Figure S2, the intensity of the peak at 532 eV was enhanced and a slight shift to higher binding energies was observed, further supporting the assignment of the signal to hydroxyl species [9,13,34]. With Pd@CeO<sub>2</sub>/P-graphite, the spectrum of the fresh sample, Figure 8B, again showed a peak near 529 eV due to bulk CeO<sub>2</sub> but the largest peak was centered at 530.4 eV, which can be assigned to CePO<sub>4</sub> basing on the preliminary analysis performed on the P-containing graphite. There was very little change in the spectrum of samples aged under dry conditions at either 500 °C or 600 °C, but wet aging at either temperature gave increased intensity in the region assigned to hydroxyls. After wet aging at 600 °C, the peak associated with bulk CeO<sub>2</sub> essentially disappeared. This is consistent with the disappearance of the Ce<sup>4+</sup> signal in the Ce 3d region of the 600 °C wet-aged samples.



**Figure 8:** Representative O 1s XPS spectra: (A) fresh Pd@CeO<sub>2</sub>/graphite; (B) fresh Pd@CeO<sub>2</sub>/P-graphite; (C) Pd@CeO<sub>2</sub>/P-graphite aged at 500 °C; (D) Pd@CeO<sub>2</sub>/P-graphite aged at 600 °C. The red lines were obtained after aging under dry conditions and the blue lines under wet conditions. The areas of the presented spectra have been normalized to the CePO<sub>4</sub> contribution (B,C and D) and the P free sample (A) has been adjusted to comparable intensity. The curves have been offset for clarity. The positions of assigned O 1s contributions are marked with grey lines.

XPS spectra of Pd 3d region on representative samples are shown in Figure 9. For both Pd@CeO<sub>2</sub>/graphite and Pd@CeO<sub>2</sub>/P-graphite, the fresh samples show two peaks at 337.2 eV and 342.4 eV, which are almost certainly due to PdO. The two peaks are due to the Pd spin-orbit split doublet (Pd 3d<sub>5/2</sub> and Pd 3d<sub>3/2</sub>). The BE of the doublet is actually close to the BE expected for PdO<sub>2</sub> [35]; however, a shift to higher binding energy is often observed for metal and metal-oxide nanoparticles, including Pd and PdO [36–42]. For example, the 3d<sub>5/2</sub> signals of both PdO and Pd nanoparticles have previously been reported to shift to approximately 1.0 eV higher BE due final-state effects [36,40]. The fact that our samples contained PdO was confirmed by *operando* and *ex-situ* XANES measurements on both the graphite and P-graphite supported catalysts (Figure S4).



**Figure 9:** Representative Pd 3d XPS spectra: (A) Pd@CeO<sub>2</sub>/graphite; (B) fresh Pd@CeO<sub>2</sub>/P-graphite; (C) Pd@CeO<sub>2</sub>/P-graphite aged at 500 °C; (D) Pd@CeO<sub>2</sub>/P-graphite aged at 600 °C. Aging under dry conditions is indicated by the red lines while wet aging is indicated in blue. The curves have been offset for clarity.

Neither wet nor dry aging had any effect on the XPS spectrum for Pd on the Pd@CeO<sub>2</sub>/graphite sample; however, the same was not true for Pd@CeO<sub>2</sub>/P-graphite. While dry aging did not affect the spectrum, wet aging of the P-containing sample at 600 °C resulted in the complete disappearance of the Pd signal. Since EDS and XANES results demonstrate that Pd is not lost under these conditions (Figure S4), the loss of Pd signal in XPS must be due to burial of Pd under the CePO<sub>4</sub>. This agrees with the SEM results, showing that the Pd@CeO<sub>2</sub> particles undergo severe sintering during wet aging when P is present.

#### 4. Discussion:

One of the main objectives of this work was to study the effect of P poisoning on the catalytic performance of Pd-CeO<sub>2</sub> catalysts. Similarly to other P-poisoning studies, phosphorus was deliberately introduced in the system during the catalyst preparation [19,21,23], rather than introducing it from the gas feed during aging treatments [22]. In this way, H<sub>2</sub>O is not introduced in the reaction mixture by decomposition of H<sub>3</sub>PO<sub>4</sub> to P<sub>2</sub>O<sub>5</sub> and the effect of water addition can be studied separately. The combined results in this study demonstrate that the presence of phosphorus in the vicinity of a Pd/ceria catalyst results in the rapid formation of CePO<sub>4</sub> at temperature as low as 450 °C. Since vapor pressure of phosphates is negligible under these conditions, the formation of CePO<sub>4</sub> indicates that there is a high affinity of Ce and P. This agrees with previous results from Xu et al, who observed formation of CePO<sub>4</sub> from the reaction of CeO<sub>2</sub> with AlPO<sub>4</sub> [22]. Notably, the distribution of CePO<sub>4</sub> in the surface and subsurface of CeO<sub>2</sub> particles is in agreement with other observations from the literature [19,22–25], even if the source of phosphorus and aging conditions were different.

Interestingly, the phosphorous-poisoned catalysts maintain a relatively high activity under dry conditions, despite being extensively covered by phosphates. Indeed, the XPS spectra even indicate that cerium phosphate can be partially removed from the surface of ceria particles at 600 °C under dry conditions. In agreement with this, López Granados et al. reported that, on P-poisoning of CeO<sub>2</sub> by addition of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, followed by calcination to 600 °C [19] some of the CeO<sub>2</sub> surface was not converted to CePO<sub>4</sub> and was still available for oxygen exchange with gas-phase oxygen, even for samples having a high P:Ce ratio.

The presence of water changes things completely, and a rapid, irreversible deactivation is observed at temperatures above 600 °C. At these temperatures, CePO<sub>4</sub> becomes highly mobile and causes severe aggregation of ceria particles and Pd encapsulation. The results of this study indicate that water and phosphorus have a cooperative effect and take part in a deactivation mechanism activated by high temperature. For the first time, the deactivation of Pd-CeO<sub>2</sub> catalysts in the presence of P was studied in steady-state experiments, revealing that poisoning occurs in very short time under conditions relevant for real applications [22,23,25]. Although surface blockage by CePO<sub>4</sub> is reported in the literature as the main effect of P-poisoning on ceria-based catalysts, our work reveals that phosphorus can also cause deep morphological transformations of the catalyst and dramatic loss of activity, especially in the presence of water.

## 5. Conclusions

The effect of phosphorus poisoning on the catalytic combustion of methane over Pd@CeO<sub>2</sub>/graphite catalysts was found to be dramatically influenced by temperature and presence of H<sub>2</sub>O. When P was not introduced in the catalyst formulation, the catalysts were active and stable under all studied conditions (500-600 °C; dry and wet conditions). On the other hand, P-poisoned catalysts were less active and stable because of partial thermal sintering. Water vapor causes rapid and complete deactivation at higher temperatures by inducing severe aggregation of ceria nanoparticles, incorporation of Pd active phase in the bulk of the crystallites and exposure of CePO<sub>4</sub> to the catalyst surface. The combination of XPS/SRPES, *operando* XANES measurements, SEM/EDS and AFM techniques provide evidence of a temperature dependent, water-driven P-poisoning of Pd and CeO<sub>2</sub>-based oxidation catalysts.

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