

# The Pt-CeO<sub>2</sub> interface as key for low temperature CO oxidation identified by spatially resolved structure-activity relationships

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**ABSTRACT:** Pt/CeO<sub>2</sub>-based catalysts are attractive for emission control applications, because of their outstanding CO oxidation performance at low temperature compared to the Al<sub>2</sub>O<sub>3</sub>-based counterpart. A detailed study of the Pt electronic structure by means of *operando* X-ray methods together with a spatially resolved assessment of the catalytic activity along the catalytic reactor allowed to spectroscopically identify the catalytically active Pt species at low temperature in Pt/CeO<sub>2</sub> as reduced and CO-covered Pt nanoparticles with active metal-support interface sites. The insight was gained by spatially resolved *operando* X-ray absorption near edge structure (XANES) experiments in high energy resolution fluorescence detection (HERFD) mode combined with CO concentration profiles along the catalyst bed using a capillary technique. The selection of methods allowed to elucidate the interplay between catalytic activity, oxidation state and CO coverage on Pt nanoparticles in Pt/CeO<sub>2</sub> and to unravel the special nature of Pt/CeO<sub>2</sub> by comparison to Pt/Al<sub>2</sub>O<sub>3</sub>. At low temperature, the Pt surface is covered by CO in both catalysts according to HERFD-XANES. In contrast to Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/CeO<sub>2</sub> converts CO in the presence of CO covered Pt nanoparticles. CO concentration profiles reveal the contribution of the Pt-CeO<sub>2</sub> interface sites to be crucial and they allow a higher CO oxidation rate of Pt/CeO<sub>2</sub> compared to Pt/Al<sub>2</sub>O<sub>3</sub> along the catalytic reactor at low temperature. This demonstrates the importance of correlative and advanced *operando* spectroscopic techniques in a spatially resolved manner. Furthermore, it consolidates the outstanding role of the noble metal-support interface in Pt/CeO<sub>2</sub>-based catalyst systems for low temperature CO oxidation.

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## 1. Introduction

For many chemical and physical applications the interface between a metal oxide and a noble metal is critical for high performance, e.g. in photocatalytic and photovoltaic devices,<sup>[1]</sup> sensors<sup>[2]</sup> and heterogeneous catalysts.<sup>[3-7]</sup> In the latter case, understanding, manipulating and controlling the synergy between reducible oxide supports like ceria and catalytically active metal components promises a substantial improvement of today's catalytic materials. This is particularly important for processes which rely on expensive noble metals, e.g. platinum, in exhaust gas abatement commonly applied as small nanoparticles (NPs). Important insight has advanced the field in the past years and has led to speculations with respect to the origin of the beneficial nature. For example,

- electron transfer from oxide support to the noble metal interface,<sup>[8-9]</sup>
- oxygen transfer from ceria to noble metal NPs<sup>[10-11]</sup> and
- stabilization of high noble metal dispersion or even single sites as well as their capability to redisperse noble metal NPs under oxidizing conditions.<sup>[12-14]</sup>

In particular, ceria-based catalysts have become outstanding candidates for the removal of automotive exhaust gas pollutants in three-way catalysts, diesel oxidation catalysts and those for VOC-removal.<sup>[15-17]</sup> In addition, the potential of Pt/CeO<sub>2</sub> catalysts for low-temperature CO oxidation has been highlighted in recent studies.<sup>[11, 14, 18]</sup> However, the underlying working principle is still under strong debate.<sup>[19]</sup> Pt based catalysts commonly suffer of a prominent issue: “CO self-poisoning” of the noble metal surface.<sup>[20-22]</sup> Due to strong CO adsorption, Pt sites are blocked and not accessible for oxygen adsorption. This substantially diminishes the catalytic activity at low-temperatures.<sup>[23-25]</sup> Recent studies argue that for ceria-based catalysts the CO oxidation reaction occurs at the noble metal-support interface sites, which are less affected by CO poisoning<sup>[18]</sup> and, hence, promise a more efficient use of the expensive precious metals. However, to the best of our knowledge the spectroscopic evidence for the catalyst state, namely catalytically active CO covered Pt NPs, has so far not been presented. This missing link has not been unraveled, because heterogeneous catalysts are complex materials, which undergo structural changes under reaction conditions in space (along the reactor) and time (during start-up, operation and the entire catalyst lifetime). This complexity

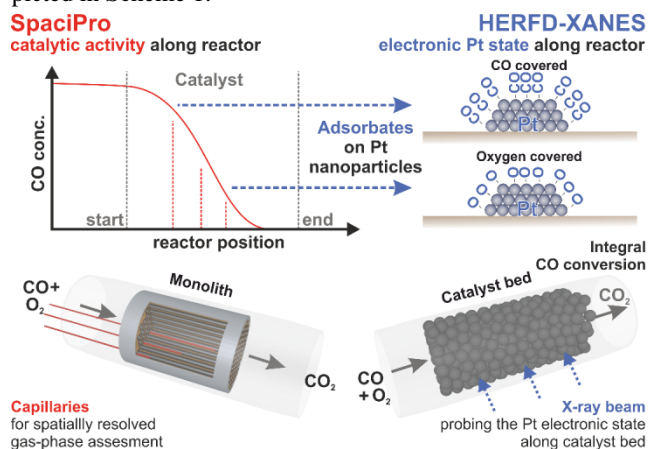
requires the identification of the active center to consolidate the understanding of the reaction mechanism for a robust theoretical treatment as well as for advancing the design of the catalytic material and process.

For this purpose, catalyst characterization needs to be conducted *operando*, meaning relevant reaction conditions for a robust correlation between catalytic activity and catalyst structure.<sup>[26-28]</sup> In this regard, X-ray based methods like X-ray absorption spectroscopy (XAS) are attractive. Here, we use the more sophisticated photon-in/-out-technique *high energy resolution fluorescence detected X-ray absorption near edge structure* (HERFD-XANES),<sup>[29-31]</sup> which is especially powerful, since it employs highly penetrating X-rays and it provides in-depth information on the noble metal atomic and electronic structure.<sup>[32-34]</sup> HERFD-XANES can recognize the impact of adsorbates on the noble metal electronic structure, and it is thus able to probe CO adsorption on Pt.<sup>[35]</sup> This is a unique opportunity because it allows the study of CO adsorption directly from the perspective of the Pt component, as compared to IR-based methods, which are generally used to approach such questions. The latter characterizes the electronic structure of Pt species indirectly by studying changes in the CO stretching frequency.<sup>[36-37]</sup> Therefore, the adsorption of CO is a prerequisite, which prevents the acquisition of information on short-lived adsorbed CO species during CO oxidation. Hence, Pt species not suitable for CO adsorption are practically hidden from the experimentalist. Although HERFD-XANES has been demonstrated powerful for gathering information on adsorbates,<sup>[38-39]</sup> there are still only few studies which use the method to elucidate reaction mechanisms in heterogeneous catalysis.<sup>[24, 31, 40-42]</sup>

Apart from further developing *operando* techniques, recording them in a spatially resolved manner becomes now important as the concentration and temperature often strongly changes along the catalyst bed and just measuring at one location in the device, i.e. the reactor, is not sufficient. In fact, recent spectroscopic studies underline the need and potential of a spatially resolved assessment of the catalyst bed or catalytic reactor for the establishment of a robust mechanistic understanding, as well as to elucidate the catalytically active component.<sup>[28, 43-44]</sup> These studies generally aim at unraveling atomic-scale properties like the structure of noble metal NPs, their oxidation state or adsorbate coverage along the catalyst bed. This allows to elaborate on gradients, how they evolve and how they are related to macro-scale processes like temperature hot-spots, heat transfer and mass transport.<sup>[45-49]</sup> Their information becomes particularly powerful when correlated to spatially resolved catalytic activity data, obtained e.g. by spatial profiling of the gas phase using a thin capillary coupled with a sensitive gas analysis (SpaciPro).<sup>[50-54]</sup> Whereas such studies were conducted with respect to concentration, temperature and structure over Pt/Al<sub>2</sub>O<sub>3</sub>, even during oscillatory conversion,<sup>[45, 55]</sup> neither a direct comparison of a ceria and alumina based catalyst with such an approach, nor a combination with structural studies has been reported yet.

In the present study we thus probe the different CO oxidation mechanisms over Pt/Al<sub>2</sub>O<sub>3</sub>- and Pt/CeO<sub>2</sub>-based catalysts by comparing the CO gas phase concentration along the catalyst bed under reaction conditions and by correlating it to the electronic structure of platinum (oxidation state and coverage by CO). In this way, the special role of the Pt-ceria interface for

the CO oxidation catalysis can be directly identified and unraveled. For this purpose, a 1wt.%Pt/Al<sub>2</sub>O<sub>3</sub> and a 1wt.%Pt/CeO<sub>2</sub> with similar Pt particle size were probed using the SpaciPro technique for determining the conversion profiles and *operando* XAS, including more advanced HERFD-XANES to identify catalytically active CO covered Pt NPs in Pt/CeO<sub>2</sub> and to elaborate on their mechanistic role for low-temperature CO oxidation (cf. Figure 1). The catalysts were coated as a layer of 50-100 μm on cordierite honeycombs for concentration profiles by SpaciPro and a sieve fraction of 100-200 μm in a 1.5 mm thick microreactor was used for spectroscopic studies. The experiments were correlated via integral mass spectrometric information. The central idea and course of the experiment is depicted in Scheme 1.



**Scheme 1.** Correlating spatially resolved gas-phase concentration profiles (SpaciPro) with spatially resolved information on Pt electronic state and adsorbates (HERFD-XANES) via integral catalytic activity data.

## 2. Experimental

**Catalyst preparation and characterization.** Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> catalysts were prepared by incipient wetness impregnation. In a first step,  $\gamma$ -alumina (Puralox, SASOL) and ceria (MEL Chemicals) were pretreated in air at 700 °C for 5 h. The resulting surface area was 165 m<sup>2</sup>/g for Al<sub>2</sub>O<sub>3</sub> and 30 m<sup>2</sup>/g for CeO<sub>2</sub>. The Pt precursor material, tetraamineplatinum(II)nitrate (STREM Chemicals), was dissolved in water and added dropwise to the support. The resulting powder was dried overnight at 70 °C and calcined at 500 °C for 5 h in static air. The Pt loading was confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES) using an OPTIMA 4300 DV spectrometer (PerkinElmer) at the Institute for Applied Materials at KIT (Karlsruhe, Germany). N<sub>2</sub> physisorption (BELSORP-mini II, Rubotherm) was conducted at -169 °C to estimate the specific surface area according to the Brunauer-Emmett-Teller (BET) method.<sup>[56]</sup> High angle annular dark field scanning transmission electron microscopy HAADF-STEM images were acquired with a FEI OSIRIS microscope operated at 200 kV at the Laboratory for Electron Microscopy at KIT (Karlsruhe, Germany) of pre-reduced catalyst samples (2 % H<sub>2</sub>/N<sub>2</sub>, 2 h at 400 °C). For Pt particle size distributions, the average diameter of >1000 NPs was evaluated assuming an elliptical shape.

This study elaborates on the origin of the outstanding activity of the Pt/CeO<sub>2</sub> catalyst system. Therefore, they will be studied after a reducing pre-treatment, for which highest catalytic activity was observed,<sup>[14, 57-58]</sup> with Pt present as small reduced Pt NPs confirmed.<sup>[14, 59]</sup>

**SpaciPro experiments.** The catalyst powder was coated on cordierite monoliths (cell density: 400 cpsi, 19 mm x 30 mm), and tested in plug-flow quartz tube reactors (WHSV of 60 000 L\*g<sub>Pt</sub><sup>-1</sup>\*h<sup>-1</sup>). Gases were dosed using mass flow controllers (Bronkhorst). The product gases were sampled with a quartz glass capillary (OD = 170 μm) and analyzed using a sensitive mass spectrometer (HPR-20, Hiden Analytics). The impact of such a physical probe within the catalyst has been discussed earlier.<sup>[51]</sup> The catalysts were pre-reduced prior to the catalytic measurement (2% H<sub>2</sub>/N<sub>2</sub>, 2h at 400 °C). The CO concentration was probed along the monolithic reactor in a so-called lean (large oxygen excess) CO oxidation mixture (1000 ppm CO, 10 % O<sub>2</sub>, N<sub>2</sub>) at various temperatures (see ESI). For the comparison, the focus will be on data obtained at ~50 % CO conversion.

**Operando HERFD-XANES.** Operando HERFD-XANES experiments were conducted at ESRF (Grenoble, France) at beamline ID26. The energy of the incident monochromatic X-rays was selected, using a cryogenically cooled Si (311) double crystal monochromator. The X-ray beam footprint on the sample was 700 μm horizontal \* 100 μm vertical. Five spherically bent (R=1 m) Ge (660) analyzer crystals (Rowland geometry) were utilized to select the fluorescence at the maximum of the Pt-L<sub>α</sub> emission line (9442 eV), which was recorded with an avalanche photodiode detector, while the incident energy was scanned around Pt-L<sub>3</sub> absorption edge (11564 eV). As a change of the Pt chemical state has been observed previously upon exposure to an X-ray beam with high photon flux, we used a (311) monochromator (which results in higher energy resolution at the expense of photon flux as compared to the Si(111) reflection) and beam absorber (800 μm Al-foil attenuating 97 % of X-ray photons at 11563 eV) to a point where no changes could be observed upon irradiation of the samples (tested by continuously recording ~5 s quick XANES spectra). The catalysts (sieved fraction 100-200 μm) were loaded in quartz glass capillaries (1.5 mm outer diameter, 0.01 mm wall thickness) and heated by a hot air gas blower.<sup>[60]</sup> Gases were supplied using mass-flow controllers (Bronkhorst) at a WHSV of 60 000 L\*g<sub>Pt</sub><sup>-1</sup>\*h<sup>-1</sup>. The reaction products were monitored with a quadrupole mass spectrometer (Pfeiffer Vacuum, OmniStar GSD 320) and an online FTIR gas analyzer (MKS, Multigas 2030).

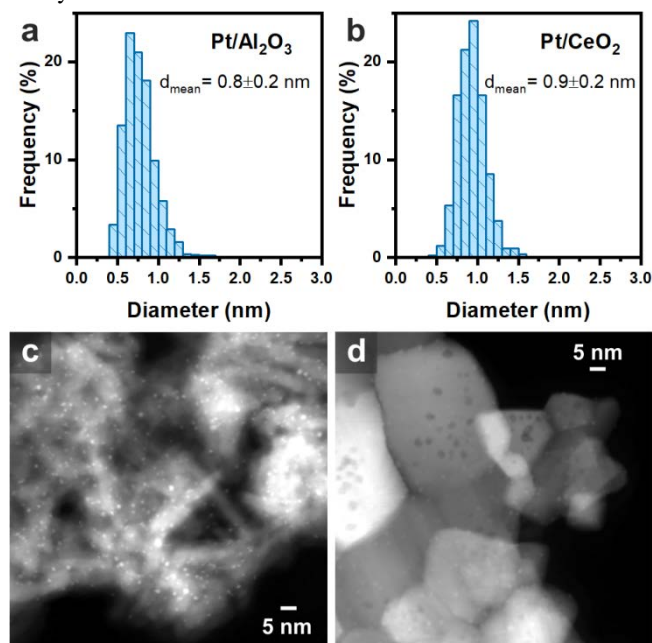
The catalysts were pre-reduced prior to the catalytic measurement (2 % H<sub>2</sub>/He, 30 min at 400 °C). Afterwards the lean CO reaction mixture (1000 ppm CO, 10 % O<sub>2</sub>, He) was applied at room temperature and the temperature was increased stepwise. At each step, HERFD-XANES spectra were obtained at three positions along the catalyst bed (start, middle, end).

Several spectra were merged to increase the data quality and filtered (Savitzky-Golay) before normalization (pre-edge normalization range: -150 eV to -50 eV; post edge normalization range: 150 eV to 400 eV). The data were quantitatively evaluated by linear combination fitting (fitting range: 11560 eV and 11575 eV) using spectra representing Pt in a completely oxidized and surface oxidized state, as well as reduced Pt NPs in He and CO/He atmosphere (see Figure 3a+b). The state ascribed

as “surface oxidized” is represented by the spectrum obtained at the end of the catalyst bed of Pt/Al<sub>2</sub>O<sub>3</sub> at 150 °C under CO oxidation conditions (full CO conversion)

### 3. Results & Discussion

HAADF-STEM images (Figure 1) uncovered very small Pt NPs for both catalysts, 1wt.%Pt/Al<sub>2</sub>O<sub>3</sub> and 1wt.%Pt/CeO<sub>2</sub>, after reductive treatment of the catalyst, with narrow size distribution (more than 99 % of the particles below 1.5 nm) and mean Pt-particle diameters of 0.8 nm and 0.9 nm for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> respectively. Hence, they are ideal model catalysts for comparing their catalytic activity and their structural evolution under reaction conditions as well as for identifying the descriptors responsible for the superior kinetics of the ceria based catalyst.

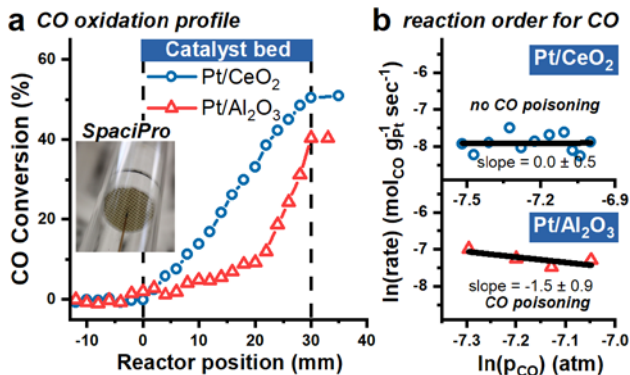


**Figure 1.** Particle size distribution of a) Pt/Al<sub>2</sub>O<sub>3</sub> and b) Pt/CeO<sub>2</sub> together with corresponding HAADF-STEM images of c) Pt/Al<sub>2</sub>O<sub>3</sub> and d) Pt/CeO<sub>2</sub>.

The CO conversion profiles recorded along the central channel of the two monolithic catalysts by SpaciPro during CO oxidation are shown in Figure 2a (increase of the temperature leads to a smaller oxidation zone, cf. further profiles in Figure S1). The profiles were obtained at temperatures of ~50 % overall CO conversion (denoted T<sub>50</sub> or light-off temperature) of the respective catalysts (95 °C for Pt/CeO<sub>2</sub>, 140 °C for Pt/Al<sub>2</sub>O<sub>3</sub>) after a reductive pre-conditioning step. The superior integral CO oxidation activity for Pt/CeO<sub>2</sub> compared to Pt/Al<sub>2</sub>O<sub>3</sub> is in a good agreement with previous studies.<sup>[14, 18]</sup>

As illustrated in Figure 2a, prominent differences in the concentration profiles along the monolith channels are found for the two catalysts. For Pt/CeO<sub>2</sub>, CO was converted at a similar rate at all positions along the catalyst bed, with a linearly increasing CO conversion corresponding to a reaction order of zero (Figure 2b). In contrast, a negative reaction order with respect to CO was observed over Pt/Al<sub>2</sub>O<sub>3</sub>.<sup>[18]</sup> Hence, after two thirds of the catalyst about 10 % CO conversion were observed for Pt/Al<sub>2</sub>O<sub>3</sub> at 140 °C, whereas for Pt/CeO<sub>2</sub> 30 % CO

conversion was achieved at the same position of the catalyst bed already at 95 °C. This reflects the impact of the CO concentration on all Pt surface sites in the case of Pt/Al<sub>2</sub>O<sub>3</sub> in contrast to Pt/CeO<sub>2</sub>.

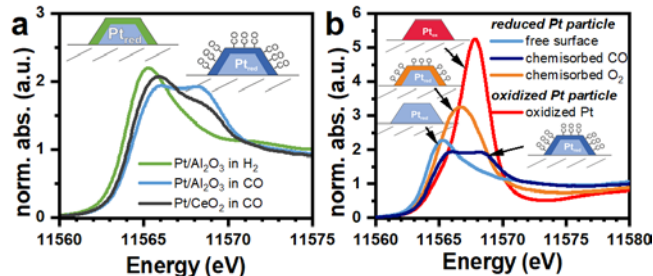


**Figure 2.** a) CO conversion along pre-reduced Pt/CeO<sub>2</sub> (blue circles) and Pt/Al<sub>2</sub>O<sub>3</sub> (red triangles) coated monoliths at ~50 % integral CO conversion (1000 ppm CO, 10 % O<sub>2</sub>, N<sub>2</sub>). b) Linear regression of logarithmic plot of the CO oxidation rate as function of the CO partial pressure along the catalyst bed. The slope indicates the reaction order of the CO oxidation rate.

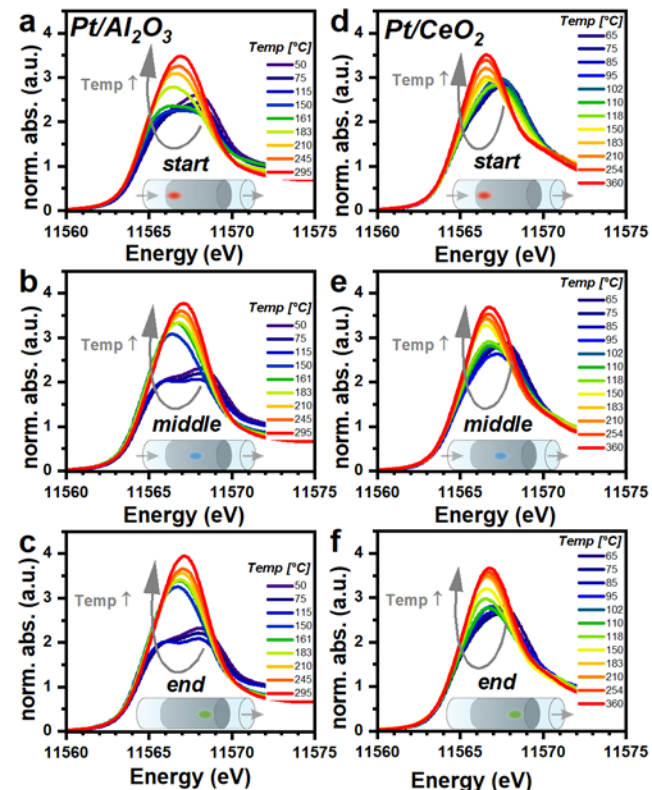
In order to probe the structure of Pt and CO coverage on Pt along the reactor, X-ray absorption spectroscopy (HERFD-XANES at the Pt-L<sub>3</sub> edge) was applied. Spatially resolved data were obtained by moving the catalyst bed in the focused X-ray beam. Pt-L<sub>3</sub> edge HERFD-XANES spectra contain additional information on the adsorption of CO on Pt in comparison to conventional XANES.<sup>[35]</sup> The unique opportunities to probe CO on Pt and its oxidation state are illustrated in Figure 3a where CO was dosed to the pre-reduced Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> catalysts. After reduction at 400 °C in H<sub>2</sub> the spectra obtained at room temperature revealed the well-known white-line profile (~11564 eV) of reduced Pt.<sup>[35, 61]</sup> Upon dosing 1000 ppm CO in He to the reduced catalyst, the absorption intensity increased at higher energies (~11569 eV) and a pronounced double peak feature evolved in the case of Pt/Al<sub>2</sub>O<sub>3</sub>, which was earlier attributed to the atop adsorption geometry of CO on Pt.<sup>[35]</sup> In contrast, in the case of Pt/CeO<sub>2</sub> a shoulder was recognized at 11569 eV similar as in the case of Pt/TiO<sub>2</sub>.<sup>[61]</sup> This feature also originates from CO adsorption and was previously assigned to CO adsorbed to Pt in a bridged mode, based on calculations for unsupported Pt<sub>6</sub> cluster with a CO molecule adsorbed on different Pt sites.<sup>[35]</sup> Upon exposure to oxygen the white-line intensity increased and the spectrum was dominated by a feature at around 11167 eV (Figure 3b). Very high absorption was observed for oxidized Pt NPs resulting in a narrow peak at 11568 eV (Figure 3b).

In a next step, *operando* HERFD-XANES data were recorded at selected temperatures in a model lean CO oxidation mixture (1000 ppm CO, 10 % O<sub>2</sub>, He). At each temperature during the CO oxidation light-off the catalyst bed was probed at start, middle and end position, while the outlet CO concentration was simultaneously monitored. *Operando* HERFD-XANES data are presented for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> in Figure 4a-f (full data set in Figure S2-S5). The data were furthermore quantitatively evaluated with linear combination fitting (LCF, Figure 5, further information Figure S6+S7), using spectra representing Pt

in a bulk oxidized and surface oxidized states, as well as reduced Pt NPs in He and CO/He atmosphere (Figure 3a+b). The contributions of the references for CO and oxygen covered Pt NPs to the fit of the experimental data are presented for Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> in Figure 5 (indicated as colored circles) and compared to their respective CO oxidation activity (indicated as grey triangles). Upon addition of oxygen to the reaction atmosphere at room temperature, Pt partially oxidized as indicated by an increase of the white-line intensity at higher energies (~11568 eV), particularly in the case of Pt/CeO<sub>2</sub> (Figure 3, further details in Figure S4).



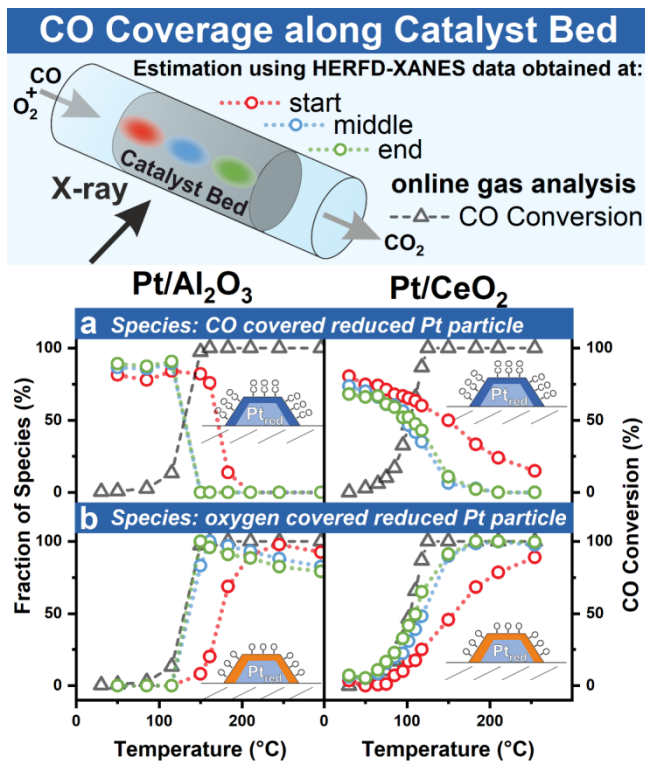
**Figure 3.** Variation of Pt L<sub>3</sub> HERFD-XANES spectra by CO adsorption a) CO covered and CO free reduced Pt NPs in Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> and b) reference states: reduced Pt NPs with free, CO covered and oxygen covered surface, as well as oxidized Pt NPs. Low absorption intensity with a broad feature indicates adsorption of CO on reduced Pt, while high absorption intensity results from oxidation of Pt.



**Figure 4.** *Operando* Pt-L<sub>3</sub> HERFD-XANES obtained at the start, middle and end of the catalyst bed of Pt/Al<sub>2</sub>O<sub>3</sub> (a-c) and Pt/CeO<sub>2</sub> (d-f) during CO oxidation (1000 ppm CO, 10 % O<sub>2</sub>, He) at various temperature plateaus.

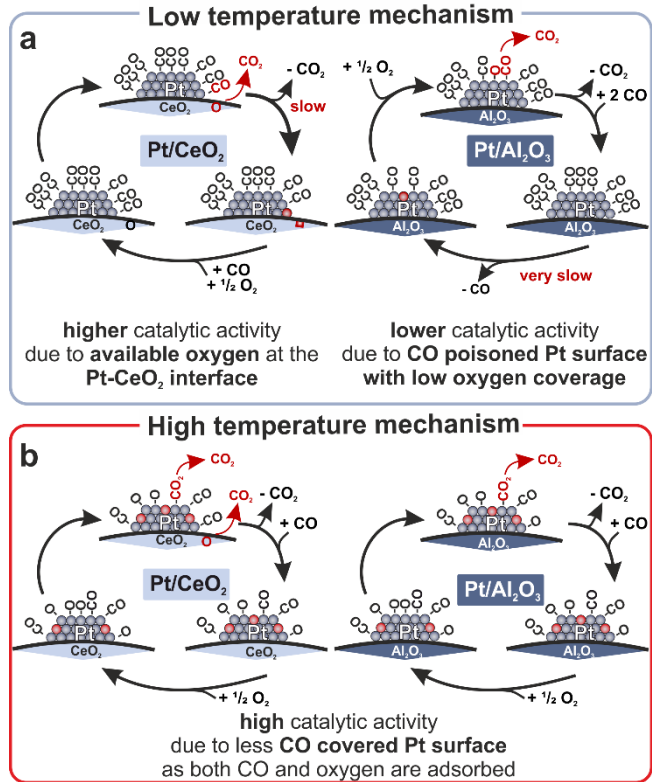
During heating in the CO oxidation mixture, a distinct gradient in CO adsorption along the catalyst bed evolved in the case of Pt/Al<sub>2</sub>O<sub>3</sub>. At low temperatures (below 115 °C), this catalyst showed low CO conversion (Figure 5, <15 % CO conversion) while the LCF analysis of the HERFD-XANES data revealed CO adsorption on Pt NPs at all catalyst bed positions, underlining a strong poisoning effect by CO. In fact, the initial partial oxidation of Pt was reversed within this stage, and the white-line double feature characteristic for CO adsorption on Pt was observed for all positions at 115 °C (Figure 4). This reduction of Pt appears to play an important role for the catalyst activity, as it just precedes the transition from the low to the high active regime. The same Pt oxidation state evolution was also identified with conventional time-resolved XAS measurements presented in Figure S8.

At 150 °C full CO conversion was observed for Pt/Al<sub>2</sub>O<sub>3</sub> behind the reactor. However, while at the beginning of the catalyst bed Pt NPs were still covered by CO (Figure 5a), they were covered by oxygen at the middle and end position (Figure 5b). Due to significant CO conversion at positions closer to the start, the amount of CO was substantially diminished for the rest of the catalyst bed. Therefore, oxygen could readily access the Pt surface, which could cause surface oxidation and, at higher temperature, also bulk oxidation of Pt particles (see also Figure S6 for further details of the LCF analysis). At the start of the catalyst bed, the same evolution was also observed above 160 °C.



**Figure 5.** Evaluation of a) CO and b) oxygen coverage of Pt NPs by linear combination fitting (LCF) analysis of Pt-L<sub>3</sub> edge *operando* HERFD-XANES spectra obtained on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/CeO<sub>2</sub> during CO oxidation. The contribution to the LCF for each component along with conversion of CO is presented for Pt/Al<sub>2</sub>O<sub>3</sub> (left) and Pt/CeO<sub>2</sub> (right) along the catalyst bed (start in red, middle in blue and end position in green). The contribution of completely oxidized Pt and Pt NPs with a free surface are shown in Figure S8.

For Pt/CeO<sub>2</sub> the LCF analysis of the HERFD-XANES data revealed a strikingly different evolution (Figure 5). CO was already significantly converted at lower temperature (~100 °C) with less pronounced gradients in the Pt state along the catalyst bed. In fact, also at high CO conversion (>80 %) Pt NPs were still substantially covered by CO (>30 %) at downstream positions (Figure 5) compared to Pt/Al<sub>2</sub>O<sub>3</sub>. Only above 110 °C the white-line intensity started to increase at the end of the catalyst bed. Since in the front part of the catalyst bed most of CO was converted, Pt NPs were oxidized at the end. For this case, the CO oxidation rate was found to be independent of the position along the catalyst bed for Pt/CeO<sub>2</sub> (Figure 2). As Pt NPs were still prominently covered by CO, the Pt-ceria interface probably enabled CO oxidation. The same behavior was found at the middle at temperatures above 120 °C (>85 % conversion) and at the start of the catalyst bed above 150 °C (full CO conversion).



**Scheme 2.** Dominant CO oxidation reaction pathways for Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> at a) low temperature and b) high temperature.

In summary, SpaciPro unraveled an equally high catalytic activity along the catalyst bed for Pt/CeO<sub>2</sub> at low temperatures (Figure 2). In the light of the HERFD-XANES characterization of the Pt component (Figs. 4 and 5), the origin of the superior catalytic properties can be assigned to CO covered Pt NPs. Although CO covered, these Pt NPs on ceria are able to oxidize CO despite of CO-poisoning of the Pt particle, by exploiting the oxygen species at the noble metal-ceria interface. In contrast, for the Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, partial desorption of CO is a prerequisite to allow the access of oxygen to Pt sites for the onset of CO oxidation (Figure 5). These two different reaction pathways are also reflected by the SpaciPro data (Figure 2), which show the participation of the entire catalyst bed in the case of Pt/CeO<sub>2</sub>

and of mainly the end of catalyst bed for Pt/Al<sub>2</sub>O<sub>3</sub> catalyst (including a negative reaction order for CO) to achieve about 50 % CO conversion.

This difference explains the substantially lower light-off temperature over Pt/CeO<sub>2</sub> and the resulting mechanism is illustrated in Scheme 2a. In addition, the altered reaction pathways for Pt/CeO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> at elevated temperature are shown in Scheme 2b. At high temperature CO oxidation is efficiently catalyzed on the Pt surface for both catalyst systems. However, when the Pt surface gets covered by CO at lower temperature and the oxidation reaction on the Pt surface is inhibited, the Pt-CeO<sub>2</sub> interface still provides oxygen from the support to the CO covered surface.

#### 4. Conclusion

In conclusion, this unique combination of spatially resolved catalytic (SpaciPro) and structural studies (*operando* HERFD-XANES) allowed to identify CO covered, yet catalytically active Pt NPs on ceria and to elaborate on the role of the Pt-CeO<sub>2</sub> interface. The results highlight the importance of the metal-support perimeter and the study provides a toolbox for unraveling its chemistry and catalysis. The enhancement of the low temperature activity does not originate in an improved reaction ignition behavior, but in an enhanced activity of the interface sites between ceria and pre-reduced Pt NPs along the entire catalyst bed. This holds important implications for the atomic- and macro-scale design of catalysts. It underlines the importance of hierarchical characterization of catalytic reactors with respect to the atomic and macroscale as well as the correlation of structure and activity in a spatiotemporal manner. For the present case, the enhanced catalytic activity of the metal-support interface can be exploited to substantially improve today's exhaust gas catalysts. However, this demands an integrative approach which considers the role of the metal-support interface within the macroscopic catalyst design and operation conditions is taken into consideration. Hence, the study demonstrates the demand and the potential of spatially resolved structure analysis combined with spatially resolved gas-phase analysis to unravel the mechanisms and interplay in catalytic reactors and related physico-chemical devices.

#### ASSOCIATED CONTENT

**Supporting Information.** Supplementary SpaciPro data (Figure S1), *operando* HERFD-XANES data (Figure S2-S7) and *operando* XAS data (Figure S8)

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#### Notes

The authors declare no competing financial interest

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