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Chemical and Electronic Changes of the CeO₂ Support during CO Oxidation on Au/CeO₂ Catalysts: Time-Resolved Operando XAS at the Ce L_{III} Edge

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Abstract: While being highly active for the CO oxidation reaction already at low temperatures, Au/CeO₂ catalysts suffer from continuous deactivation with time on stream, with the activity and deactivation depending on the initial catalyst activation procedure. In previous X-ray absorption measurements at the Au L_{III} edge, which focused on changes in the electronic and geometric changes of Au, we found a modest increase of the Au particle size during reaction, with the Au nanoparticles (NPs) present in a dominantly metallic state during reaction, regardless of the pretreatment. Here we aim at expanding on these insights by examining the changes in electronic and chemical composition of the CeO₂ support induced by different pretreatment procedures and during subsequent CO oxidation at 80 °C, by following changes at the Ce L_{III} near edge region in time-resolved operando X-ray absorption measurements. The results indicate a strong dependence of the initial concentration of Ce³⁺ ions on the pretreatment, while during subsequent reaction this rapidly approaches a steady-state value which depends on the oxidative/reductive character of the reaction gas mixture, but is largely independent of the pretreatment. These results are discussed and related to earlier finding on the electronic properties of Au nanoparticles under identical reaction conditions.

Keywords: CO oxidation; Au/CeO₂; XANES; Ce L_{III} edge; operando spectroscopy

1. Introduction

For over 3 decades, the intriguing catalytic properties of supported gold catalysts have inspired a large number of scientists, both from a fundamental and application-oriented points-of-view [1–3]. The number of studies on Au based catalysts is still increasing rapidly, not only because of their exceptionally high catalytic activity for a variety of very different reactions such as CO oxidation [4], methane activation [5], (reverse) water gas shift (R)WGS reaction [6,7], anaerobic oxidation of alcohol [8], propene oxidation [9,10], or CO/CO₂ reduction to methanol [11–14], but also since they can be considered as attractive model systems for studies of fundamental reaction mechanisms. Metal oxide supported Au nanoparticles, in particular, have been found very promising as heterogeneous catalysts. The activity of these catalysts was found to rely decisively on the nature of oxide support, specifically the support reducibility. According to an early systematic study of this parameter by Schubert et al., these oxides were classified as inert and active supports [4]. The first type was identified as non-reducible oxides, inert toward oxygen activation, while the latter type of active supports are reducible oxides (e.g., Fe₂O₃, TiO₂, NiO_x, and CoO_x), which are able to actively adsorb, dissociate, and store oxygen, and then re-supply active oxygen species for oxidation reactions. Among these, CeO₂ is considered as one

of the most important oxides in catalysis due to its remarkable oxidation/reduction characteristics related to the facile transfer of electrons from O^{2-} ions to the two adjacent Ce^{4+} atoms, forming Ce^{3+} species [15–18], which make ceria an ideal oxygen storage material.

Gold nanoparticles (NPs) were proposed to strongly modify the surface properties of the ceria support by electronic interactions between support and Au NPs, allowing facile removal of lattice oxygen already at temperatures around ambient temperature [19]. Furthermore, Au NPs in close contact with (surface) O-vacancy defects were proposed to act as active sites in the (R)WGS reaction [19]. The participation of O-vacancy defects in the ceria support in contact with the Au NPs in the reaction, most likely via formation and re-oxidation of these sites, was derived later also from dynamic measurements in a temporal analysis of products (TAP) reactor [20,21]. Finally, the important role of O-vacancies in this reaction was also verified in recent operando Raman spectroscopy [22,23] and X-ray absorption spectroscopy (XAS) [24] studies.

Focusing on the CO oxidation reaction, where Au/CeO₂ catalysts are also known to be very active [25–30]. Metal-support interactions (MSIs) between Au nanoparticles and CeO₂ support [31,32] and the dynamic formation and replenishment of O-vacancy defects [27,33] were proposed to play a decisive role in the reaction. Furthermore, the nature of the active Au species, in particular, their size and oxidation state [34,35], or the presence and nature of adsorbed surface carbon-containing species [36–38] were claimed to affect the performance of these catalysts, and thus also the deactivation behavior in different ways. While there is ample evidence that each of these effects somehow affects the reaction, direct correlations between the temporal development of these features and of the activity of Au/CeO₂ catalysts in the CO oxidation reaction, under working conditions, have rarely been established [33,39]. This is the topic of the present contribution, where we report results of a time-resolved operando XAS study at the Ce L_{III} near edge region on the oxidation state of the ceria support during the CO oxidation reaction in different gas mixtures. Considering that previous studies had demonstrated considerable effects of the pretreatment procedure [24,30], we applied different oxidative and reductive pretreatment procedures. This study follows a recent report of similar XAS measurements at the Au L_{III} edge, and additional in situ FTIR measurements, focusing on the electronic, chemical, and structural properties of the Au nanoparticles on an Au/CeO₂ catalyst. Those measurements indicated that under present reaction conditions the deactivation of the Au/CeO₂ catalysts originates from a modest growth of Au nanoparticles during reaction and, tentatively, from a slow bulk reduction of the CeO₂ support, where the latter was concluded indirectly from activity differences between differently pretreated catalysts [30,35]. Neither the accumulation of carbon-containing species nor a change of the oxidation state of Au were held responsible for the long-term deactivation. The influence of the oxidation state of the ceria support was demonstrated also for the closely related PROX (preferential oxidation of CO) reaction, where Hernandez et al. reported a significant decrease in the ceria band gap, from 3.09 to 2.82 eV, during the reaction, and where the change in ceria band gap with time on stream followed the deactivation of the low-Au-content catalyst [40]. Therefore, direct probing of the oxidation state of the CeO₂ support during the CO oxidation reaction would be highly desirable for a better understanding of the impact of the CeO₂ oxidation state on the activity and its correlation with the observed deactivation of the catalyst. Since ex situ X-ray photoelectron spectroscopy (XPS) measurements performed under ultrahigh vacuum (UHV) conditions may not reflect the true oxidation state of ceria, due to loss of surface oxygen when being irradiated with Al K_α radiation [41], this requires in situ/operando measurements when using X-rays for spectroscopy, or other techniques sensitive to the ceria oxidation state such as Raman spectroscopy [19,22,23,33,34,39,42,43]. Here it should be noted that, in contrast to Raman spectroscopy, XAS measurements in the near edge region (XANES) allow the ability to quantitatively determine the relative content of Ce^{3+} species and thus of O-vacancies, while Raman spectroscopy is more sensitive to details of the nature of the O-vacancy defect.

In the following, we will first present and discuss XANES data on the state of the catalyst after different oxidative and reductive pretreatment procedures and compare these with data obtained for reference materials (Section 2.1). Subsequently we will follow the oxidation state of the catalysts

and the activity of the catalysts by operando XANES measurements, after different initial catalyst pretreatments (Section 2.2). This will include also transient changes of the reaction gas mixture, using a standard reaction gas mixture ($\text{CO}:\text{O}_2 = 1:1$) as well as CO-rich and O_2 -rich mixtures with $\text{CO}:\text{O}_2 = 5:1$ and $\text{CO}:\text{O}_2 = 1:5$, respectively. Finally, we discuss the role of Ce^{3+} species/O-vacancies in the CO oxidation reaction in a comprehensive picture (Section 2.3). A brief description of the experimental set-up and procedures is given in Section 3, which is followed by the conclusions (Section 4).

2. Results and Discussion

2.1. State of the Au/CeO₂ Catalysts after Different Pretreatment Procedures

We will start with the pure ceria support and the Ce reference samples, which were used to evaluate the ceria oxidation state and thus quantify the amount of Ce^{3+} species in the Au/CeO₂ catalysts. To obtain well defined reference spectra we recorded X-ray absorption spectra of cerium (III) carbonate hydrate and cerium (IV) oxide at the Ce L_{III} edge without further pretreatment (measured at 80 °C in N₂, see Figure 1). The two references showed significant differences in the onset of the absorption edge, as illustrated by the red and blue solid lines in Figure 1a and in Figure 1b, respectively.

Figure 1. X-ray absorption spectroscopy (XAS) measurements in the near edge region (XANES) spectra recorded at the Ce L_{III} edge (measured at 80 °C in N₂): (a) of the Ce (III) reference ($\text{Ce}_2(\text{CO}_3)_3 \times \text{H}_2\text{O}$, red line); (b) of the Ce(IV) reference (CeO_2) (blue line) and reference data published by Ravel and co-workers (orange lines) [44]. The dashed curves represent the main individual components of Ce as published by Yoshida et al. [45], the solid black lines denote a fit based on these components to our data. For an acceptable agreement with our Ce(IV) reference (blue) the component marked in red, which represents the white line in Ce (III), had to be increased in intensity compared to the fit to Ce(IV) data published by Yoshida (black).

For comparison with our data recorded on CeO₂ we also included a XANES spectrum by Auffan and Ravel [44] (orange lines in Figure 1b), which agrees rather well with our data, except for slightly higher intensities in the two main Ce peaks. The spectrum of the Ce(III) species (Figure 1a) is

characterized by a pronounced white line peak directly at the edge, whereas the Ce(IV) reference spectrum shows a double peak with lower intensities at the Ce L_{III} edge. Furthermore, the inflection point of the spectrum of Ce(IV) is located at about 1.0 eV higher energy compared to that of the reduced Ce(III) species (5725.6 eV). The main contributions to the respective XANES spectra, which are indicated as dashed and dotted lines in the spectra shown in Figure 1 [45], are summarized in Table 1. A detailed discussion of the respective electronic states and transitions contributing to the spectra was given by Yoshida et al. [45]. The solid black lines represent the fits based on these components to our reference spectra.

Table 1. Overview of the individual contributions (peak heights and energy of Lorentzian) to the normalized XANES spectra of our references at the Ce L_{III} absorption edge, with the peaks and peak positions taken from [45]. The respective initial and final states are discussed in that reference.

Peak	A	B ₀	B ₁	B ₂	C ₁	C ₂
Binding energy/eV	5720.2	5726.1	5727.8	5730.2	5736.0	5738.1
Ce(III) reference	0	1.87	0	0	0	0
Ce(IV) reference	0.02	0.2	0.6	0.81	0.02	0.62

The spectra recorded from our Ce references (red and blue lines) agree well with the fit based on the components reported by Yoshida et al. [45] (black curves in both panels of Figure 1). Note that contribution of the electronic transition B₀ (Ce(III) white line marked in red in the Ce(IV) reference spectrum) is higher than in the data reported by Yoshida et al., which denotes a higher amount of oxygen vacancies (Ce³⁺ species) in our Ce(IV) reference than in their sample.

The Ce(III) reference spectrum is characterized by a single Lorentzian peak B₀ plus the transition into the continuum state (Figure 1a), whereas six Lorentzian peaks (see Table 1; in Figure 1b only the four main components B₀–B₂ and C₂ are shown) plus the contribution to the continuum states, where the latter is usually characterized by an arc tangent function, are required to fit the Ce(IV) spectrum. This includes the Ce(III) related peak (red), indicating that there is a small persisting fraction of Ce(III) ions. The presence of six individual Lorentzian peaks in the region close to the Ce L_{III} edge renders a complete quantitative analysis of the electronic state of the ceria nanoparticles complex. To simplify the fitting scenario, we chose the linear combination analysis (LCA) technique, varying only the ratio of Ce(III) and Ce(IV) contributions. Although this analysis might not reproduce the absolute value of the oxidation state with highest accuracy, it is very sensitive to small changes in the oxidation state (see the small contribution of Ce(III) in the Ce(IV) spectrum indicated by the red peak in Figure 1b).

Next, we explored the effect of the catalyst pretreatment on the pure CeO₂ support. Figure 2 shows XANES spectra of the pure ceria support recorded in N₂ at 80 °C after an oxidative (O400: blue solid line) and after a reductive (CO400: red solid line) pretreatment, respectively. The spectra exhibit distinct differences, mainly at the onset of the Ce L_{III} absorption edge, but to a lower extent also in the intensity of the two dominant features characteristic of Ce(IV). For comparison, we added the spectra from the two references as dashed curves in this figure.

After oxidative pretreatment (O400), the main features of the spectrum resemble those of the fully oxidized Ce(IV) reference (blue dashed line), only the intensity in the peaks at 5730 eV (B₂, see Table 1) and 5738 eV (C₂) is lower than in the reference spectrum. The small peak at 5720 eV is related to Ce(IV) species (peak A, see Table 1) and has roughly the same intensity as for the Ce(IV) reference. A reductive pretreatment (CO400) on the other hand leads to an absorption spectrum with a higher intensity directly at the absorption edge (photon energy range: 5720–5730 eV), which reflects a higher contribution of the white line of reduced ceria species (cf. Ce(III) reference spectrum, with a peak at 5726 eV (B₀) in Figure 2, dashed line). Quantitative evaluation yields a negligible contribution (1.7%) from Ce³⁺ for the O400 pretreated support, while for the CO400 pretreated support it is about 18%.

Figure 2. Spectra of the high-surface-area CeO_2 support recorded after an O400 (blue solid line) and a CO400 (red solid line) pretreatment. Dashed lines denote the respective data from the Ce references; black: Ce(III), blue: Ce(IV). Note that the Ce(III) reference (black dashed line) has been re-scaled in intensity for similar height as in the other spectra (scale on the right side).

Similar XAS spectra recorded on Au/CeO_2 catalysts at the Ce L_{III} absorption edge are presented in Figure 3. On the first view, these spectra closely resemble those obtained on the pure CeO_2 support (see Figure 2). Reductive pretreatments (H400 and CO400) lead to pronounced contributions from the Ce L_{III} absorption edge, whereas this feature is missing after an oxidative pretreatment (all measurements after pretreatment were performed under a continuous flow of N_2 at 80°C). The black dash-dotted line, which displays the corresponding XANES measurement from the Ce(IV) reference, largely coincides with the spectrum obtained after the oxidative pretreatment.

Figure 3. Spectra recorded on the Au/CeO_2 catalyst at the Ce L_{III} edge after different pre-treatment procedures: H400 (red solid line), O400 (blue solid line), and CO400 (orange solid line). The black dash-dotted line denotes the Ce(IV) reference. The inset (lower right part) displays the respective spectra recorded in transmission at the Au L_{III} edge, together with a spectra of the Au references (dashed line: Au_2O_3 , dashed dotted line: Au foil).

The appearance of the shoulder around 5726 eV at the CO400 pretreated support (indicated by an arrow) is indicative of the presence of Ce^{3+} species. Based on a Linear Combination Analysis (see Section 3.2), it corresponds to a Ce^{3+} contribution of about 6% for the CO400 and 10% for the H400 pre-treated catalysts, whereas this was only about 0.4% after oxidative pretreatment (cf. also Figures 4–6).

Figure 4. Formation rate during CO oxidation in different reaction atmospheres (standard, O_2 -rich, and CO-rich) at 80 °C on a Au/CeO₂ catalyst after oxidative (O400) pretreatment in 10% O_2 in N_2 at 400 °C (black circles) and the relative Ce^{3+} content during time on stream as extracted from LCA analysis of operando X-ray absorption spectra recorded in fluorescence mode during reaction (blue, green, and red symbols). The dashed blue line denotes the initial Ce^{3+} ratio (right scale). Representative error bars are shown for each sequence.

In the inset we additionally show XANES data collected at the Au L_{III} edge at (11919 eV) after oxidative (O400—blue spectrum) and reductive (H400—red spectrum) pretreatments, which were taken from [30,35], respectively, together with spectra from Au₂O₃ and a Au foil (dashed line: Au₂O₃, dashed dotted line: Au metal foil) used as reference materials. Note that a different catalyst was used in these measurements, with a Au loading of 2.5 wt.%, but otherwise rather similar properties as in the present study. The red spectrum of the H400 pretreated sample looks very similar to that of the Au foil and indicates an essentially metallic state of Au in the catalyst, indicative of metallic Au nanoparticles. The blue spectrum, in contrast, shows a contribution of about 40% from the white line, indicative of contributions from an oxidized state of Au [46]. The trend in the chemical state of the Au NPs fits well to that of the ceria support, with a highly oxidized Ce(IV) state after O400 pretreatment and a partly reduced ceria support after (reductive) H400 pretreatment. For a more detailed discussion on the nature of the Au species in the Au/CeO₂ catalysts upon different pretreatments we refer to our previous publications [30,35,46].

Figure 5. Formation rate during CO oxidation in different reaction atmospheres (standard, O₂-rich, CO-rich) at 80 °C on a Au/CeO₂ catalyst after reductive (H400) pretreatment in 10% H₂ in N₂ at 400 °C (black circles) and the relative Ce³⁺ content during time on stream as extracted from LCA analysis of *operando* X-ray absorption spectra recorded in fluorescence mode during reaction (blue, green, and red symbols). Representative error bars are shown for each sequence.

Figure 6. Formation rate during CO oxidation in different reaction atmospheres (standard, O₂-rich, CO-rich) at 80 °C on a Au/CeO₂ catalyst after reductive (CO400) pretreatment in 10% CO in N₂ at 400 °C (black circles) and the relative Ce³⁺ content during time on stream as extracted from linear combination analysis (LCA) analysis of *operando* X-ray absorption spectra recorded in fluorescence mode during reaction (blue, green, and red symbols). Representative error bars are shown for each sequence.

2.2. Operando X-Ray Absorption Spectroscopy during CO Oxidation

The chemical composition and the catalytic activity of the differently pretreated Au/CeO₂ catalysts during the CO oxidation reaction were characterized as a function of reaction time by recording the CO₂ formation (see Section 3.2) during the XAS experiments. Figure 4 displays a combination of

CO₂ formation rates (black empty symbols) and XAS data (colored symbols) as a function of time on stream after an oxidative pretreatment (O400), where the concentration of Ce³⁺ species (Ce³⁺/(Ce³⁺ + Ce⁴⁺)) during the reaction was evaluated from the XANES spectra (blue, green, and red symbols). The measurements were performed at 80 °C in a reaction gas mixture of 1% CO, 1% O₂ (balance N₂), interrupted by periods in O₂-rich (5% O₂ and 1% CO) and CO-rich reaction gas mixtures (5% CO and 1% O₂). It should also be noted that the XANES measurements shown in Figure 4 require a time of about 30 min per spectrum for acceptable statistics, which limits the time resolution. The CO₂ formation rate shown in Figure 4 starts at a value of slightly less than 0.15 μmol_{CO2} s⁻¹ and decays to about 0.13 μmol_{CO2} s⁻¹ within 1 h on stream in the standard reaction gas mixture (1% CO, 1% O₂, and balance N₂). Then the rate decays only very slowly for the next three hours. The Ce³⁺ concentration after the O400 pretreatment was about 0.4% ± 0.2% and vanished completely (below the detection limit of about 0.2%) within 1.5 h. After approximately 4 h, the gas mixture was changed to an O₂-rich mixture (5% O₂ and 1% CO). Here the CO₂ formation rate increased slightly from 0.125 to 0.14 μmol_{CO2} s⁻¹, followed by a similar slow decrease as before in the standard mixture. During this period and also when returning to the standard reaction gas mixture, where the CO₂ formation rate returned from below slightly below 0.135 to 0.125 μmol_{CO2} s⁻¹, we could not detect any significant variation in the amount of Ce³⁺ species, staying close to zero, as expected for the more oxidative nature of this reaction mixture compared to the standard mixture. This is different when switching to a CO-rich mixture (5% CO and 1% O₂), where both the CO₂ formation rate and the Ce³⁺ concentration increased significantly (CO₂ formation: from 0.12 μmol_{CO2} s⁻¹ to about 0.33 μmol_{CO2} s⁻¹; Ce³⁺ ratio: from close to 0% to about 2.5%). Both CO₂ formation and Ce³⁺ concentration steadily decay with time for about 210 min. Compared to the standard gas mixture the decay in CO₂ formation is about three times faster. The Ce³⁺ concentration seems to follow the CO₂ formation, with the Ce³⁺ concentration decreasing from 2.5% to 1.7% after 210 min on-stream and the CO₂ formation from 0.33 μmol_{CO2} s⁻¹ to 0.29 μmol_{CO2} s⁻¹. Obviously, changing to the CO-rich mixture induces a significant change in the oxidation state of the support, leading to a measurable concentration of Ce³⁺ sites as a result of the formation of O-vacancy defects. The correlation between the concentration of Ce³⁺ ions and thus of O-vacancy sites and the activity for CO oxidation indicates a pivotal role of these sites for the reaction, possibly controlling the activation of molecular oxygen species during reaction. These findings are in good agreement with earlier findings for Au/CeO₂ and Au/TiO₂, which revealed a correlation between CO oxidation activity and the presence of O-vacancy sites [27,47,48].

In the next step, when the reaction gas mixture was returned to the standard composition (1% CO, 1% O₂), the CO₂ formation immediately went down to 0.11 μmol_{CO2} s⁻¹ and the Ce³⁺ species vanished again completely (within the detection limit) within a short time.

Finally, we ‘re-activated’ and fully oxidized the catalyst again by a second O400 treatment. After this treatment the CO₂ formation in the standard gas mixture was in the same range as after the initial O400 treatment, actually it was even slightly higher. Furthermore, similar as after the initial O400 treatment, the CO₂ formation decreased rapidly, with most of the decay occurring during the first 10–15 min. The concentration of Ce³⁺ is below the detection limit, and stays at this level during reaction in the standard reaction gas mixture.

The CO₂ formation rates and the ceria oxidation state can be compared with results of a recent study using the same 4.5 wt.% Au/CeO₂ catalyst, where we performed a rather similar experiment in the same gas mixtures, following in addition the oxidation state of the Au NPs by XANES measurements at the Au L_{III} edge [30]. While in that case similar trends were obtained for the reactivity in standard and O₂-rich gas mixtures, they differed somewhat for the CO-rich gas mixture. In that case the catalyst showed a rather strong deactivation once the reaction in the CO-rich gas mixture commenced, while it increased in the present case. After careful examination of the data we think that this discrepancy is at least partly due to differences in the experimental procedure, and that the present reaction data are correct. This is discussed in more detail in the Supporting Information. Looking at the oxidation state of the catalyst, the previous experiments at the Au L_{III} edge had shown that the oxidation state of the

Au NPs is partly oxidic after the second O400 treatment [30,46], though with a slightly smaller extent than after the first treatment.

To summarize the findings for the O400 pretreated catalyst, the concentration of Ce^{3+} species is very low and at/below the detection limit both after pretreatment and during reaction in a standard or in an O_2 -rich gas mixture, while in the more reductive CO-rich reaction gas mixture it is in the range of 2–3%. The significantly higher Ce^{3+} content goes along with a higher CO_2 formation rate (roughly by a factor of 2.3), and also with a more pronounced deactivation with time on stream. Formally, without considering changes in the reaction constant and the rather high conversion, the higher CO_2 formation rate would correspond to a reaction order in CO of about 0.5, while for O_2 it is about zero. This will be discussed in more detail later. Furthermore, our observations indicated also that the changes in the formation of O-vacancies and the changes in activity as well as the strong dependence of the O-vacancy formation on the partial pressure of CO in the reaction gas are reversible.

Results of a similar experiment performed on a reductively pretreated catalyst, after H400 pretreatment, are presented in Figure 5. In general, the trends are rather similar to those observed after oxidative O400 pretreatment, although the absolute values are different. E.g., the CO_2 formation rate is generally about 40% lower than after oxidative pretreatment, but with similar trends in O_2 -rich and CO-rich reaction atmospheres as after O400 pretreatment. Although it may look different because of the different time scales in Figures 4 and 5, the deactivation rate is nearly identical in all reaction gas mixtures. Only in the first hour after H400 pretreatment the decrease in the CO_2 formation rate is less pronounced than after O400 pretreatment. Differences appear, however, in the Ce^{3+} concentration. It starts with a rather high value of 11%, meaning that pretreatment in the reducing gas mixture (10% H_2 in N_2) at 400 °C results in a considerable formation of O-vacancies/ Ce^{3+} species, which is more than one order of magnitude higher than observed during reaction of the O400 pretreated catalyst in the CO-rich gas mixture. During operation in the standard gas mixture, this value decreases rapidly to a concentration of about 1%. Though rather low, this is nevertheless higher than during reaction after O400 pretreatment, where after an initial phase the Ce^{3+} concentration was negligible. Reasons for this discrepancy will be discussed after the next change in gas mixture.

Changing to an O_2 -rich gas mixture, the Ce^{3+} concentration quickly decreases to values around $0.5 \pm 0.1\%$, except for an initial small drop to slightly lower values. This level is maintained also when returning to the standard gas mixture. We explain this remaining fraction of measurable Ce^{3+} species, which is still present after reaction in O_2 -rich mixture, by deeper lying O-vacancy defects, which could be generated during pretreatment at 400 °C, due to the higher mobility of these vacancy defects at elevated temperatures, but not be replenished during reaction at 80 °C, not even in O_2 -rich atmosphere (see below). In the initial phases in standard mixture and again in the O_2 -rich gas mixture the accessible O-vacancies were replenished by surface reaction, which required that they could diffuse to the ceria surface. From the fact that there is (i) only little change in Ce^{3+} content when changing from the initial reaction in standard reaction gas to the O_2 -rich mixture and (ii) no significant change in Ce^{3+} content when changing from O_2 -rich to standard reaction mixture we conclude that the standard gas mixture is sufficiently oxidative to replenish most of the surface near O-vacancy defects.

When changing to the CO-rich reaction atmosphere, the difference between the differently pretreated catalysts (O400 and H400) seems to disappear, in both cases the Ce^{3+} ratio is about 1.4–2.5%, with decreasing Ce^{3+} content during reaction. However, when changing again to the standard mixture, we again see a residual Ce^{3+} content of about 0.5%, which is on a similar level as in the previous phases on this catalyst (except for reaction in the CO-rich gas mixture). Obviously, the residual amount of deeper lying O-vacancies created during H400 pretreatment is still present. Interestingly, similar as after O400 pretreatment, the Ce^{3+} content shoots up when changing to the CO-rich mixture, and then decays again. This is very different from the behavior expected intuitively, namely an exponential increase of the Ce^{3+} concentration to a new steady-state value. We speculate that this behavior may be related to the simultaneous formation of carbonate species, but cannot provide a more detailed picture at present.

After the second H400 treatment the resulting Ce^{3+} content is even slightly higher than after the initial H400 pretreatment, but subsequent reaction in the standard mixture causes this to quickly return to the value of about 1.0%, which is similar to that observed after the first pretreatment.

In total, these results seem to indicate that upon reaction most of the O-vacancies in the surface region are replenished, independent of pretreatment (O400 or H400), and that only a small fraction of deeper lying O-vacancies and Ce^{3+} species are metastable on the time scale of these experiments at 80 °C, which had been generated during the reductive H400 pretreatment.

Finally, we performed a similar reaction sequence after another reductive pretreatment in 10% CO in N_2 (CO400). The resulting CO_2 formation rate and Ce^{3+} concentrations are displayed in Figure 6. These data differ significantly from the trends in Figures 4 and 5. Here, the CO_2 formation rate is close to zero after the CO400 pretreatment and increases steadily with time on stream. This general trend is qualitatively similar for the different reaction atmospheres. Even after almost 1000 min on stream in different reaction atmospheres the reaction has not yet reached steady-state conditions. At this point the CO_2 formation rate in a standard gas mixture is only about $0.03 \mu\text{mol}_{\text{CO}_2} \text{s}^{-1}$, which is much lower than the values obtained for the H400 (O400) pretreated catalysts of about $0.06 \mu\text{mol}_{\text{CO}_2} \text{s}^{-1}$ ($0.11 \mu\text{mol}_{\text{CO}_2} \text{s}^{-1}$).

The observation of an initially almost inactive catalyst and subsequent slow activation resembles recent findings for CO oxidation on Au/TiO₂ catalysts after a CO400 pretreatment, which was explained by a very low CO adsorption energy and hence a very low CO_{ad} coverage on the negatively charged Au NPs in the initial reaction phase [49]. Only with increasing re-oxidation, i.e., upon increasing replenishment of the O-vacancies during reaction CO adsorption on the Au NPs and CO oxidation rate increased. For the Au/CeO₂ catalysts, one may expect similar effects, i.e., an over-reduction of the Au/CeO₂ catalyst by the CO400 pretreatment, which strongly reduces the activity of that catalyst. This does not fit, however, to the fact that the content of Ce^{3+} is lower after CO400 than after H400 pretreatment, and also not to the fact that the Ce^{3+} that the XANES detected Ce^{3+} concentration rapidly decays to a value of about 1%, which is unlikely to represent an over-reduction of the catalyst. In that case we tentatively assign the distinctly lower activity of the CO400 pretreated catalyst to a pronounced blocking of the catalyst surface by carbonate species formed during/after CO400 pretreatment. A high tendency for surface carbonate formation during CO400 pretreatment was indeed observed in [30]. In that case the slowly increasing activity would reflect a slow decomposition of the surface carbonates.

It should be noted that on a first view this slow activation seems to be in contrast to earlier experiments, where the CO reaction rate was found to decrease continuously, similar to that after O400 and the H400 pretreatments [30,35]. The apparent difference results, however, from the different CO concentrations in the pretreatment process, which was 2% in the earlier experiments published in [30], but 10% in the present experiments and also in those performed on an Au/TiO₂ catalyst [49]. A test measurement performed after CO400 pretreatment in 2% CO in N_2 confirmed our previous results (see Figure S2, Supporting Information). Thus, the CO concentration in the pretreatment gas mixture has a pronounced effect on the CO oxidation activity of the resulting catalyst; a lower concentration of CO (e.g., 2% CO in N_2) in the pretreatment gas mixture results in a much higher CO_2 formation at present pretreatment and reaction conditions. Arguing along the lines above this can be explained by a lower amount of site blocking surface species such as surface carbonates.

The slope of the activity vs. time curve and also the absolute value of the CO_2 formation rate change little when switching to O₂-rich reaction gas, while after returning to the standard reaction mixture the slope is somewhat lower than initially. Even at the end of the second reaction phase in the standard mixture, the CO_2 formation rate reaches only about $0.024 \mu\text{mol}_{\text{CO}_2} \text{s}^{-1}$, which is significantly less than that obtained for the H400 pretreated catalyst at this stage ($\sim 0.06 \mu\text{mol}_{\text{CO}_2} \text{s}^{-1}$). Interestingly, for reaction in the CO-rich mixture we not only find a significantly higher CO_2 formation rate, but also an increase with time on stream. The latter is opposite to the decrease in CO_2 formation rate observed for the O400 and H400 pretreated catalysts. In contrast, the significant decrease in the Ce^{3+} concentration during time on stream in CO-rich gas mixture from 2.0% to 1.7%, similar, resembles the

trend for the O400/H400 pretreated catalysts. One may speculate that in the present case the activation due to carbonate decomposition overcompensates the competing deactivation as observed for the other catalysts.

The second CO400 treatment leads again to a significant increase in the Ce^{3+} content, reaching 13.0%, which is significantly higher than after the first CO400 pretreatment procedure and comparable to that after H400 pretreatment. During subsequent reaction in a standard reaction mixture the CO_2 formation rate is significantly higher than after the first CO400 pretreatment, where it was negligible, but still only about half of that obtained directly after H400 pretreatment. We assume that the higher Ce^{3+} content obtained after the second CO400 treatment is more typical and that the lower value obtained after the first CO400 period was still kinetically limited.

In total, these data indicate that the two reductive pretreatment procedures, H400 and CO400, result in very different catalysts, both in terms of their catalytic activity and their (de)activation behavior. The fraction of Ce^{3+} species in the whole reaction period (in the different reaction atmospheres) is approximately identical after CO400 and H400 pretreatments, therefore the distinctly lower initial activity of the CO400 pretreated catalyst cannot be explained over-reduction effects. Moreover, this value (Ce^{3+} concentration) is nearly constant in the standard reaction gas mixtures, while the reaction rate continuously increases with time on stream. The slow activation during time on stream is therefore mainly assigned to the decomposition of by-products formed during the CO400 pretreatment such as surface carbonate species.

2.3. Role of Ce^{3+} Species/O-Vacancies in the CO Oxidation Reaction

Finally, in Figure 7 we provide an overview on the Ce^{3+} concentrations in the different reaction gas mixtures for the three differently pretreated catalysts. For these values we took the average of the last 3–5 individual Ce^{3+} concentrations obtained for each gas mixture. The data illustrate the distinct differences in the Ce^{3+} concentration after the different pretreatment procedures, and the generally similar trends in the Ce^{3+} concentrations during reaction, independent of the initial pretreatment. This means that concentration of Ce^{3+} species and thus of O-vacancies in the surface region equilibrates rather quickly. Except for reaction in the CO-rich gas mixture, the activity of the catalysts closely follows this for the O400 and H400 pretreated catalysts, where the activities are rather stable with time on stream. This seems to indicate that the oxidation state of the ceria has a decisive influence on the reactivity of the Au/ CeO_2 catalyst. It should be kept in mind, however, that the differences in the CO_2 formation rate can also be explained by differences in the coverage of adsorbed species (CO_{ad} , reactive oxygen). Formally, the first explanation would be reflected by a change in the rate constant, while the latter would be represented by a change in reactant coverages. From the present data we cannot discriminate between these two possibilities.

The data furthermore demonstrate that, in good agreement with the previous Raman spectroscopy data [22,33,39], there are (at least) two different types of O-vacancies/ Ce^{3+} species, one which is in the surface region and can easily be formed and replenished at 80 °C, and another one which is formed only at higher temperatures (400 °C) and cannot be replenished upon exposure to CO/ O_2 mixtures at 80 °C, at least not on the time scale of these experiments.

Overall, the data presented above and considering also results of previous in situ/operando XANES [24,30,35,46] and Raman studies [22,23,33,34,39,43] result in the following picture on the role of Ce^{3+} species/O-vacancies in the CO oxidation reaction on Au/ CeO_2 catalysts:

1. While oxidative O400 pretreatment results in a fully oxidized CeO_2 support with negligible Ce^{3+} contents, reductive H400 or CO400 pretreatment leads to the significant formation of Ce^{3+} species, between 6% and 10% in the catalyst region accessible by XANES under present conditions, and hence formation of O-vacancies (cf. upper panel of Figure 8). At the same time, Au species are fully reduced after reductive pretreatment, while the formation of oxidic Au species was reported after oxidative O400 pretreatment [30,46];

2. The concentration of Ce^{3+} species on the pure CeO_2 support (without Au NPs) seems to be slightly higher than on the Au/ CeO_2 catalyst, with 1.7% and 17% Ce^{3+} species after O400 and CO400 treatment, respectively. The higher Ce^{3+} content compared to those obtained on the Au/ CeO_2 catalysts seems to contradict earlier claims that the presence of the Au NPs enhances the formation of O vacancies [19,27,48]. This apparent contradiction may arise from the rather high temperature of the reductive pretreatment, where ceria reduction is facile also without additional enhancement by Au NPs;
3. During the reaction in formally oxidative gas mixtures (standard gas mixture and O_2 -rich gas mixture), most of the Ce^{3+} species are rapidly re-oxidized. Due to the high mobility of O-vacancies, the bulk O-vacancies are essentially in equilibrium with those in the surface near region. In the O400 pretreated sample, this leads to complete removal of Ce^{3+} species/O-vacancies, while on the reductively pretreated samples a small fraction of Ce^{3+} species/O-vacancies ($\sim 0.5\%$) remains, which cannot be re-oxidized under present reaction conditions. They are attributed to deeper lying defects, which can be created during pretreatment at 400°C , but are metastable during reaction at 80°C due to the limited mobility of O-vacancy defects under these conditions. This agrees fully with findings from operando Raman studies, which also identified surface and bulk type defects and could discriminate between them [22,33,39,43];
4. On the Au/ CeO_2 catalysts the steady-state concentration of Ce^{3+} species/O-vacancies in the surface region is determined by the reaction gas composition, it is negligible in the standard and O_2 -rich gas mixtures, and in the range of 1%–2% in the CO-rich mixture, independent of the pretreatment (cf. lower panel in Figure 8);
5. Based on the rapid re-oxidation of Ce^{3+} species/surface vacancies during reaction at 80°C in oxidative gas mixtures and their stable concentration at longer reaction times we can exclude that the slow deactivation of the catalysts under these conditions is mainly related to an over-reduction of the catalyst support, in the sense that a reduced catalyst state is generated which is less active. Considering also previous reports this seems to be related to the slow build-up of site blocking surface species, mainly surface carbonates;
6. The build-up of such surface species during pretreatment in CO rather than over-reduction is also proposed as main reason for the very low initial activity of the CO400 pretreated sample and the very slow increase in activity during time on stream, considering that the concentration of Ce^{3+} species/O vacancies is similarly high after pretreatment in H_2 (H400), where such effects were not observed, as in CO (CO400). This is supported also by the fact that the concentration of Ce^{3+} species/O vacancies decreases rapidly during the time on stream, while the increase in activity during the reaction is very slow. We attribute this to a slow, possibly oxygen-induced decomposition of site blocking surface species;
7. Considering that reduction/re-oxidation of the surface region is rather fast on the time scale of these measurements, it is not possible to decide from these measurements whether changes in the CO_2 formation rate upon changing the composition of the reaction gas atmosphere are (mainly) caused by changes in the support oxidation state, leading to a modification of the rate constant, or by changes in the adsorbate coverages. This is mainly relevant when going to CO-rich gas mixtures with their higher CO_2 formation rate, while increasing the O_2 content has little effect on the CO_2 formation rate.

Figure 7. Overview about changes in the Ce^{3+} concentration in Au/CeO_2 catalysts during CO oxidation (a) after CO400 pretreatment, (b) after O400 pretreatment, and (c) after H400 pretreatment in a sequence of varying reaction gas atmospheres. The left and right parts refer to the reaction in standard reaction gas mixture following the first and the second treatment.

Figure 8. Schematic overview illustrating the O-vacancy and Ce^{3+} concentration in Au/CeO_2 catalysts after oxidative (top left) and reductive pretreatments (top right) and during CO oxidation (bottom) in the different reaction gas mixtures used in this study (left: O_2 rich or standard reaction gas mixture, right: CO rich gas mixture).

3. Experimental

3.1. Catalyst Preparation and Characterization

The Au/CeO_2 catalysts were prepared by a deposition–precipitation procedure described in detail earlier [26]. In brief, the supporting CeO_2 material (HSA 15, Rhodia, calcined in air at 400 °C for 4 h) was dispersed in water at 60 °C, then an aqueous solution of the gold precursor ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.5%,

Merck) was added drop-wise, while adjusting the pH to ~6 by addition of 0.16 M Na_2CO_3 (Aldrich) solution. Then the as-prepared Au/CeO₂ catalyst was filtered, washed three times with deionized water, and dried at room temperature (25 °C) overnight. Finally, the catalyst was collected and stored in a fridge to reduce ageing effects. This resulted in a Au loading of 4.5 wt.%, as determined by inductively coupled plasma atom emission spectroscopy (ICP-AES, Spectro ICP Modula S). The specific surface area of the catalyst of 188 m²·g^{−1} was determined via N₂ adsorption measurements (Porotec Sorptomatic 1990 system). For the CO₂ formation measurements, we used about 60 mg of the diluted catalyst powder, with the Au/CeO₂ catalyst diluted with SiO₂ at a ratio of 1:3. This resulted in a catalyst bed length of about 1 cm. Note that the SiO₂ (calcined at 1200 °C for 24 h) is chemically and catalytically inert under present reaction conditions. Prior to the CO oxidation measurements, the diluted catalyst was pretreated in situ, either in an oxidative or in a reductive atmosphere. This involved first heating to 400 °C (10 K·min^{−1}) in a flow of 20 Nml·min^{−1} N₂, then the respective pretreatment gas mixture (O400: 10% O₂/N₂, H400: 10% H₂/N₂, or CO400: 10% CO/N₂, 20 Nml·min^{−1}) was introduced for 30 min at 400 °C. Finally, the catalyst was cooled down in 20 Nml·min^{−1} N₂ to the reaction temperature (80 °C).

3.2. Operando Catalyst Characterization

Operando X-ray absorption spectroscopy (XAS) measurements were performed at the XAFS beamline of the electron storage ring Elettra in Trieste (Italy), using a Si(111) double crystal monochromatic; details regarding the beamline can be found in [50]. The cross sectional size of the beam was roughly 6 mm horizontally and 1 mm vertically. For the measurements, we used a home-made stainless-steel tube flow reactor with a cylindrical channel (i.d. 2 mm) along the axis of the tube. The catalyst was packed such that it results in a bed size of ca. 10 mm (length) × 2 mm × 2 mm, at 45° with respect to the detector. Under reaction conditions, the cell was closed on the top by a catalytically inactive Kapton window. Heating of the cell was achieved using resistive heating elements, which were placed in bore holes in the reactor body. This allowed homogeneous heating of the reactor. The XAS spectra at the Ce L_{III}-edge (5723 eV) were collected in fluorescence mode, using a Si drift diode detector (Ketek GmbH, AXAS-M, München, Germany). X-ray absorption spectra from cerium oxide references were collected both in transmission and fluorescence mode on standard compounds (cerium(IV) oxide (CeO₂) as well as cerium(III) carbonate hydrate (Ce₂(CO₃)₃ × H₂O, both Alfa Aesar, Karlsruhe, Germany). While the reaction measurements were performed under operando conditions, this was not possible for the pure supports and Au/CeO₂ catalysts during pretreatment. From experimental reasons, these measurements were carried out in a flow of N₂ at 80 °C (30 Nml min^{−1}, without further pretreatment) after annealing in the respective pretreatment gas mixtures.

For data evaluation, we used the free XAS data processing software Athena 0.9.26 [44], especially the Linear Combination Analysis (LCA) module for XANES spectra. This method, which involves a fit to the experimental data by summing over-weighted contributions of reference spectra of the different components, in the present case of Ce³⁺ and Ce⁴⁺, allows a straightforward analysis of the material as long as there are no additional types of that species involved.

Operando XAS measurements include a simultaneous analysis of the gas outlet from the XAS cell during CO oxidation. In the present case, the gas phase signals of CO and CO₂ were monitored by a home-built analysis system consisting of a Bruker Alpha single-beam transmission IR-spectrometer (Ettlingen, Germany) and a substrate-integrated hollow waveguide (iHWG) device for signal enhancement [51]. In all measurements the signals of CO₂ and CO were calibrated using standard test gas mixtures (1% CO, 1% O₂, 0.5% CH₄, balance N₂) to quantify the CO conversion and CO₂ formation. The calculated overall CO₂ formation rates are based on the formation of CO₂, where the detection is more sensitive than for CO (larger IR absorption cross-section for CO₂). Note that because of the relative amounts of catalyst required for the spectroscopic measurements the resulting conversions were up to 80%, which is well above the limits of differential reaction conditions. Therefore, we could not calculate Au-mass normalized reaction rates.

For the CO oxidation measurements, we used three different gas mixtures, (i) a close-to-stoichiometric ‘standard’ reaction gas mixture (1% CO, 1% O₂, and 98% N₂), (ii) an O₂-rich gas mixture (1% CO, 5% O₂, and 94% N₂), and (iii) a CO-rich gas mixture (5% CO, 1% O₂, and 94% N₂), respectively. All gas mixtures were prepared using mass flow controllers from Hastings (HFC-202) at a total flow rate of 60 Nml·min^{−1} using high-purity gases (CO 5.0, O₂ 5.0, N₂ 6.0, Westfalen AG).

4. Conclusions

Based on results of in situ/operando XANES measurements on the oxidation state of the CeO₂ support (ratio of Ce³⁺ to Ce⁴⁺ species) after different oxidative and reductive pretreatment procedures and during reaction in different atmospheres, at 80 °C and 1 bar, we could derive a detailed, quantitative picture of the influence of the pretreatment procedure and the composition of the reaction gas mixture on the oxidation state of the Au/CeO₂ catalyst support and its influence on the CO oxidation activity. Overall, the data indicate that under most reaction conditions Ce³⁺ species/O-vacancies in the surface region have little effect on the CO reaction, as they are rapidly re-oxidized by the reaction gas mixture. Only in strongly reducing CO-rich gas mixtures they are present under steady-state conditions in measurable amounts and may affect the reaction over longer times. Furthermore, the study illustrates the benefit of quantitative operando spectroscopy data for solving issues that have been debated controversially over long periods such as the role of catalyst over-reduction in this reaction.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/10/785/s1>, Figure S1: CO₂ formation rate upon reaction gas exchange on an O400 pretreated (10% O₂, balance N₂) commercial 1 wt.% Au/CeO₂ catalyst (Haruta Gold Inc.), Figure S2: CO₂ formation rate after a CO400 pretreatment in 2% CO (balance N₂) on a commercial 1 wt.% Au/CeO₂ catalyst in a standard reaction gas mixture: 1% CO, 1% O₂, balance N₂ at 80 °C, Figure S3: CO₂ formation rate on a commercial 1 wt.% Au/CeO₂ catalyst in different reaction gas atmospheres after a O400 pretreatment in 10% O₂ (balance N₂), Figure S4: CO₂ formation rate after an O400 pretreatment in 10% O₂ (balance N₂) on a commercial 1 wt.% Au/CeO₂ catalyst in different reaction gas atmospheres at 80 °C, Figure S5: CO₂ formation rate after a CO400 pretreatment in 10% CO (balance N₂) on a commercial 1 wt.% Au/CeO₂ catalyst in different reaction gas atmospheres at 80 °C, Table S1: Relative content of Ce³⁺ species on a commercial 1 wt.% Au/CeO₂ catalyst after oxidative (O400) and reductive (CO400) pretreatment and during subsequent reaction in different reaction gas mixtures at 80 °C.

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