Influence of re-activation and ongoing CO oxidation reaction on the chemical and electronic properties of Au on a Au/CeO2 catalyst: A XANES study at the Au LIII edge

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ABSTRACT

The influence of oxidative/reductive pretreatment, oxidative re-activation and ongoing CO oxidation on the chemical/electronic properties of a 4.5 wt.% Au/CeO2 catalyst was investigated by in operando X-ray absorption spectroscopy at the Au LIII edge. Experimental data on the electronic structure and the size of the Au nanoparticles are correlated with findings from kinetic and deactivation measurements. The results of this study show that oxidative re-activation as well as reductive and oxidative pretreatment significantly affect the Au electronic structure and, in consequence, the catalytic properties. Independent of the type of the treatment, however, the Au nanoparticles rapidly reach a metallic state during reaction, both after oxidative pretreatment and after oxidative re-activation, and can therefore not be responsible for the long-term deactivation of the catalyst. Correlations between electronic/chemical structure, evaluated in a semi-quantitative model, and the catalytic performance are discussed.

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1. Introduction

Metal-oxide-supported gold catalysts have been subject of significant research activities since Haruta and coworkers reported that these catalysts are highly active for a number of reactions, among them CO oxidation, already at low temperatures [1]. Despite an enormous number of studies, fundamental aspects of these catalysts and their working principle such as the nature of the active Au species, support effects, activation of reactants such as O2, are still discussed controversially. The mechanistic understanding is hampered also by the lack of systematics in the experimental work, where essential details such as catalyst preparation and pretreatment or reaction conditions vary almost from study to study. Accordingly, for CO oxidation on highly active Au/CeO2 catalysts, previous studies arrived at widely different conclusions on the physical origin of the observed deactivation, including (i) effects associated with changes of the formal oxidation state of Au [2,3], (ii) the build-up of reaction inhibiting carbon containing surface species at the perimeter of the Au-support interface [4], (iii) sintering of Au NPs during reaction [3,5], and/or (iv) modification of the ceria support [6]. Also the ceria support itself is known not be inactive in the CO oxidation, a significant contribution can only be expected from temperatures clearly above 80 °C. These questions are highly relevant also from a practical point of view, since industrial applications of these catalysts are mainly hindered so far by their pronounced tendency to deactivation.

Recently we reported results of a comprehensive study on the effect of different pretreatment procedures on the activity and deactivation behavior of Au/CeO2 catalysts in the CO oxidation reaction [6,7]. Among others, this study revealed that already for reaction at 80 °C deactivation can only partly be correlated with the build-up of reaction inhibiting (site blocking) adsorbed species, in particular surface carbonates, since these reach a steady-state situation already after 10–30 min, and this is largely independent of the pretreatment procedure. Longer-term deactivation must therefore originate from other effects, such as slow reaction-induced Au particle growth or slow changes in the electronic properties of the catalysts, either of the Au species or of the ceria support [6]. Changes in the Au particle size were derived from in situ EXAFS
spectroscopy measurements of Au/CeO$_2$ catalysts after CO400 (10\% CO in N$_2$, 400 °C) and O400 (10\% O$_2$ in N$_2$, 400 °C) pretreatments and during/after CO oxidation [7].

Continuing the above study we report new in operando XANES results on the electronic properties of Au nanoparticles after oxidative and reductive pretreatment, during subsequent CO oxidation at 80 °C and after oxidative re-activation and subsequent reaction. The experimental results will be correlated with kinetic data on the catalyst activity/deactivation behavior, aiming at a better understanding of the impact of these processes on the mean size and the electronic state of the Au nanoparticles, and the consequences of subtle changes therein on the activity/deactivation behavior of the Au/CeO$_2$ catalyst. Applying a semi-quantitative model we correlate sometimes subtle changes in the Au L$_2$ XANES region with the activity/deactivation behavior of the Au/CeO$_2$ catalyst.

2. Experimental

The preparation of the 4.5 wt\% Au/ CeO$_2$ catalyst as well as the experimental procedures have been described in detail in reference [6]. Prior to the kinetic measurements, the catalyst was conditioned, either in oxidative or reductive atmosphere, for 30 min at 400 °C in a stream (20 Nm min$^{-1}$) of 10\% O$_2$ (O400) or 10\% H$_2$ in N$_2$ (H400), followed by cooling the catalyst to 80 °C in a stream of N$_2$ (20 Nm min$^{-1}$). Kinetic measurements were performed in a quartz tube micro reactor (i.d. 4 mm) under atmospheric pressure (1\% CO, 1\% O$_2$, balance N$_2$, total gas flow of 60 Nm min$^{-1}$). To ensure differential reaction conditions (conversion <15\%), the catalyst powder was diluted with Al$_2$O$_3$, which is inactive for the reaction under these conditions. Analysis of the reaction gases was performed by on-line gas chromatography (Chrompack CP9001).

In situ X-ray absorption spectroscopy (XAS) measurements were performed at the XAFS beamline at Elettra (Trieste, Italy) and the BM26A beamline at the ESRF (Grenoble, France). In both cases, a Si(111) double crystal monochromator was used, details are given in [8,9]. The dimension of the X-ray beam was roughly 7 mm horizontally and 1 mm vertically in all experiments. A stainless steel cylindrical disk with a 10 mm $\times$ 2 mm $\times$ 2 mm slit machined into the flat front side served as reaction cell, which was connected to the incoming and outgoing gas lines via bore holes from the perimeter of the cylinder [10]. The catalyst was packed into the slit, fixed by glass wool at the entrance and exit of the gas lines. In this case we used SiO$_2$ for catalyst dilution (1:3) to have lower flow resistance. The catalyst bed size is sufficient to allow the X-ray beam to hit the sample centrally. The reactor cell was closed off by a catalytically inactive Kapton$^\text{TM}$ window, which allowed incoming synchrotron radiation and emitted fluorescence radiation to pass. A resistive heating element placed in a bore hole in the rear part of the reactor body allowed controlled heating. The XAS spectra (AuL$_\text{III}$-edge, 11919 eV) were collected in fluorescence mode (recording time 30 min), using either a Si drift diode detector (Ketek GmbH, AXAS-M, Elettra) or a 9-element Ge detector (ESRF). For the EXAFS analysis and for comparison with the XANES data, reference spectra were collected in transmission mode also on a pure Au foil and on Au$_2$O$_3$ powder.

3. Results and discussion

3.1. Activity and deactivation measurements

Following our previous approach [6], we used two pretreatment procedures which result in catalysts with widely differing chemical/catalytic properties. This is illustrated in Fig. 1, which shows the evolution of the Au mass normalized catalytic activity during CO oxidation at 80 °C as a function of time on stream (TOS).

Here it should be noted that the first GC measurement was initiated 10 min after the reaction was started, which means that the deactivation in the initial 10 min on stream is not detected. In agreement with previous findings [6], the initial activity is significantly higher, by a factor of 2, than the oxidative (O400) pretreatment than after oxidative (H400) pretreatment, but the former catalyst exhibits also the stronger deactivation (34% after 1000 min on stream) compared to the latter one (20% after 1000 min on stream). Nevertheless, the activity of the H400 catalysts is always significantly lower than that of the O400 catalyst. Even after 1000 min on stream, the activity is only 60\% of that of the O400 catalyst at that time.

In addition to these measurements, which largely reproduced our previous findings [6], we tested the effect of exposing the deactivated O400 catalyst to a second O400 (O400-2) treatment, directly after this was on stream for 1000 min. As illustrated in Fig. 1, this led to an increase of the activity, but the initial activity of the catalyst could not be restored. After reactivation, only 75\% of the initial activity was recovered, indicative of a partly irreversible loss of the CO oxidation activity during time on stream. Interestingly, the subsequent deactivation, after the reactivation procedure, largely followed the trend during the first reaction phase, only at a lower level. After another 1000 min TOS, the catalyst reached a similar activity as the H400 pretreated catalyst after 1000 min.

3.2. XANES/EXAFS measurements on the H400 and O400 pretreated Au/ CeO$_2$ catalysts

In order to investigate the chemical state of the Au/ CeO$_2$ catalysts in situ before and after pretreatment (H400 and O400) as well as during CO oxidation, XAS spectra were recorded at the Au L$_\text{III}$ edge. Fig. 2 shows the resulting XANES spectra of (from top to bottom) a Au$_2$O$_3$ reference (black line), of the Au/ CeO$_2$ catalyst in its native state before pretreatment (green line), after H400 pretreatment (blue line), followed by 5 spectra (red lines) recorded after different time intervals (2 min, 23 min, 1 h, 3 h, 5.5 h) during CO oxidation. The bottom curve in Fig. 2 refers to a reference spectrum recorded on a thin metallic Au foil (black line). The photon energies were carefully calibrated using the reference samples (Au foil and Au$_2$O$_3$ powder) and XAS Au standards in the open access program Hephaestus [11].

The XANES spectra of the Au/ CeO$_2$ catalyst in its native state, before any pretreatment, closely resemble the Au$_2$O$_3$ reference spectrum, with a strong white line (peak position at 11920 eV).
Upon H400 pretreatment, the oxidic feature in the XANES spectra vanished completely (blue curve), and the data largely resemble those recorded from the metallic Au reference (black line in the bottom of Fig. 2). During subsequent CO oxidation at 80 °C, no further changes appear in the respective XANES spectra, they represent metallic Au nanoparticles. The suppression of the small features in the Au/CoO2 spectrum visible in the spectrum of the Au metal foil indicates the presence of very small Au particles [12]. Analysis of the corresponding in situ EXAFS data resulted in values of about 0.7 nm (before) and 0.8 nm after CO oxidation (up to 175 min on stream). Only Au–Au scattering events were found to contribute to the EXAFS data [6], which in agreement with the distinct similarity of XANES spectra of the H400 catalyst and the metal Au reference. 

Fig. 2. XANES spectra recorded (from top to bottom) on a Au2O3 reference (black curve), from a native Au/CoO2 catalyst (green curve), after H400 pretreatment (blue), during CO oxidation (red, time intervals see text), and on a Au foil reference. The vertical dashed line indicates the metallic Au LIII absorption edge at 11919 eV (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Ex situ XRD measurements resulted in slightly larger mean Au particle sizes of 1.8 ± 0.5 nm both before and after reaction, where the differences may result from the XRD detection limit for small particles (~1.5 nm) and a certain underestimation of particle sizes in EXAFS (for details, see [6]). Clearly, the deactivation of at least 20% of the H400 catalyst cannot be explained by the negligible particle growth observed during CO oxidation. (Note that the deactivation during the first 10 min on stream, which is not detected by the GC measurements, is not included in this value).

For the O400 pretreated catalyst, the XANES spectrum obtained directly after pretreatment (Fig. 3, blue curve) differs from that obtained after H400 pretreatment (Fig. 2, blue curve). After O400 treatment, the spectrum shows a pronounced white line close to the peak maximum of the Au2O3 reference. The presence of this feature shows that at least part of the Au atoms are oxidized or positively charged. The peak position is shifted by about 1 eV to higher photon energies compared to the Au2O3 reference. With the onset of the CO oxidation, the situation changes again and already after a few minutes the XANES spectrum resembles that recorded on the metallic Au foil used as reference (black curve, bottom of Fig. 3). Thus, the chemical state during reaction seems to be independent of the respective pretreatment. This will be discussed further with the spectra in Fig. 4.

Fig. 3. XANES spectra recorded (from top to bottom) on a Au2O3 reference (black curve), a native catalyst (green curve), an O400 pretreated catalyst (blue curve), during CO oxidation (red curves, started after 1 and 210 min on stream, dashed line: middle spectrum of the H400 sequence in Fig. 2), after reactivation (blue curve, O400-2), during CO oxidation (red curve, recorded after 300 min on stream), and on a Au foil reference (black curve). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

After the second O400 treatment the XANES spectra show again an increase in the white line, with an intensity/area close to that obtained the first O400 pretreatment. Thus, the chemical state after re-calcination is nearly identical to that obtained after the initial O400 pretreatment. When switching again to reaction conditions, the XANES spectra at the Au LIII edge immediately change back to a metallic state and show, similar as in Fig. 2, no further variation (Fig. 3). EXAFS analysis of the Au nanoparticles after re-calcination confirms the presence of oxygen (Au-O scatterers), but the coordination number (CN) of this contribution is about 1/3 smaller than after the first calcination (Table 1), indicating that the mean size of Au-O ‘domains’ is smaller after the second O400 treatment than after the first one.

Table 1

<table>
<thead>
<tr>
<th>State</th>
<th>Scattering</th>
<th>CN</th>
</tr>
</thead>
<tbody>
<tr>
<td>After O400-1</td>
<td>Au-Au/Au-O</td>
<td>6.13/1.32</td>
</tr>
<tr>
<td>During CO oxidation (200 min TOS)</td>
<td>Au-Au</td>
<td>6.7</td>
</tr>
<tr>
<td>After O400-2</td>
<td>Au-Au/Au-O</td>
<td>7.94/0.9</td>
</tr>
<tr>
<td>During CO oxidation (300 min TOS)</td>
<td>Au-Au</td>
<td>8.34</td>
</tr>
</tbody>
</table>

In the following, we present a semi-quantitative analysis of the XANES spectra obtained on the 400 pretreated Au/CeO2 catalysts at different stages, after initial pretreatment (O400), during CO oxidation, and after reactivation (O400-2). The analysis is based on an approach reported by Panteloups et al. [13] and considers two contributions: (i) a peak with a pseudo-Voigt line shape representing electronic transitions from the Au 2p3/2 (Au LIII) state into empty 5d states, the so-called 'white line', and (ii) a transition into 6s continuum states, where the intensity is described by an arctan function. Parameters such as the width of both functions were kept constant in this analysis, except for the relative weight of each contribution and its energy position (peak maximum/inflection point). It should be noted that for metallic Au there is a small probability for transitions into empty 5d states (see also lower part in Fig. 4), even though for a single Au atom the electronic structure is [Xe]4f145d106s1, with completely filled 5d states.

Starting with the Au2O3 reference, we find the highest white line of all Au species investigated here. The shape of the XANES spectrum of the Au/CeO2 catalyst before pretreatment (native catalyst) is quite similar to that of the Au2O3 reference. After the O400 pretreatment, the white line contribution decreases significantly. When setting the area of this peak for Au2O3 to unity, the respective area (which in some way represents the relative contribution of charged AuO+ species, see below) is ~0.66 after the first O400 pretreatment, ~0.60 after O400-2, and 0.30 during/after CO oxidation. For the Au metal foil we obtain a value of 0.25. The energy positions of these peaks shift only slightly between 11920 eV and 11921 eV, which is close to the limits of the deconvolution procedure. In general, the higher energies are found after the O400 treatments. Also the inflection points shift with increasing oxidation state, from 11920.5 eV (AuO) to ~11923 eV for Au3+ species. This trend in the shifts of the inflection points agrees well with previous findings [13].

Assuming a linear correlation between mean Au oxidation state and the relative peak area (relative to those in Au2O3 (Au+) and in metallic Au (Au0)) in the white line [13], one formally gets Au oxidation states of +1.5 for the O400-1, +1.35 for the O400-2 treatment, and +0.15 during CO oxidation. These results can be compared with XPS data measured ex situ on the same catalysts after identical treatment, where we found rather small amounts of AuO+ species (19% after O400 pretreatment, 14% after CO oxidation), but higher amounts of Au2+ species (52% after O400, 25% after CO oxidation) [6]. For the situation after the first O400 treatment, the XPS based value (mean oxidation state +1.1) seems to agree reasonably well with the mean oxidation state derived from XANES. Under CO oxidation conditions/after CO oxidation, the differences are more significant, with mean oxidation states of +0.15 (XANES) and +0.67 (XPS), indicating the limitations of this comparison. Small differences might be related to re-oxidation of the catalysts during their transport from the reactor to the XPS measurement. Modification in the XANES spectra due to self-absorption effects at the Au LIII edge should be negligible because of the very low amount of gold in the sample and since the Au particles are well distributed and thus highly diluted in the Au/CeO2 samples. This underlines the value of the in situ XANES measurements for reliable chemical analysis of the catalyst at different processing and reaction stages. The data presented before reveal significant effects of the different pretreatment and re-activation procedures on the oxidation state of the Au/CeO2 catalysts compared to the native state and the state under reaction conditions. While the oxidative O400 treatment results in a significantly oxidized state of the Au NPs, independent of the state before (native state (pre-treatment) or after longer time on stream in the CO oxidation reaction (re-activation)), the reductive H400 treatment leads to purely metallic Au NPs. The oxidation state during CO oxidation (under present reaction conditions), on the other hand, is always close to the metallic state. However, the presence of a small amount of oxidic Au species cannot be ruled out from these data. Similarly, this study cannot decide on the question whether oxygen is provided from the ceria support or not, which was suggested earlier on the basis of TAP (temporal analysis of products) reactor measurements [14].

A change of the Au oxidation state during the reaction, either relative to the pretreated catalyst or relative to the native catalyst, was mentioned earlier as a possible reason for the deactivation of Au/CeO2 catalysts during CO oxidation [23]. Obviously, this does not agree with our present findings, which show that the oxidic peak in the XANES spectra at about 11921 eV disappears in a few minutes, while the pronounced decrease in activity (Fig. 1) extends at least over the first 2 h under present reaction conditions. Hence, the change in Au oxidation state occurs on a much shorter timescale than the deactivation. Here it should be kept in mind that a possible deactivation during the initial few min on stream, i.e., during the change in oxidation state of the Au NPs, is not detected in this work because of the much slower GC measurements.

The loss of activity over longer time on stream (long-term deactivation) must therefore be related to other and partly irreversible processes, where the latter is indicated by the fact that upon re-activation we could not recover 100% of the initial activity (Fig. 1). Most likely, this is at least partly related to an irreversible Au NP growth with time on stream, which cannot be reverted by the present re-activation procedure. This is illustrated also by the EXAFS data (Au–Au scatterers) obtained in situ during the sequence shown in Fig. 3, which showed an increase in the Au–Au coordination number (i.e., Au particle growth) (Table 1) from 6.1 after the first O400 treatment via 6.7 during CO oxidation (after 200 min TOS) to 7.9 after reactivation (O400-2) and finally 8.3 after ~300 min in the second CO oxidation run. The fact that the O400-2 re-activation procedure results in an initially higher activity despite of a simultaneous increase in Au particle size must mean that the deactivation encountered during time on stream also contains reversible contributions, which can be reversed during O400 re-activation, but they are not dominant. From the same reasons (different time scales), we can exclude that the reactivation is solely related to the removal of surface carbonates. Accordingly, the deactivation must include additional processes such as modifications of the electronic state of the ceria support. The latter would agree with observations by Widmann et al. who reported that the ceria support of Au/CeO2 catalysts is slightly surface reduced during CO oxidation in a gas mixture of 1% CO/1% O2/balance N2 [14].

4. Conclusion

Studying the influence of different pretreatment and re-activation procedures on the electronic/chemical properties and size of Au nanoparticles on a Au/CeO2 catalyst in situ X-ray absorption spectroscopy (XANES/EXAFS) measurements at the Au LIII edge in combination with kinetic measurements we found:

(i) That oxidative (O400) and reductive (H400) pretreatment results in Au nanoparticles with distinctly different oxidation...
state, with fully metallic particles resulting from H400 treatment, while differences in particle sizes are small;
(ii) that independent of the pretreatment the Au particles assume a fully metallic state after a few minutes on stream;
(iii) and that oxidative treatment of a deactivated catalyst (O400 re-activation) results in a similar state as O400 pretreatment, but cannot fully recover the initial activity.

The rapid change from an oxidized to a metallic state during reaction indicates that this cannot be responsible for the longer-term deactivation of the catalyst. The latter is tentatively associated with slow irreversible growth of the Au nanoparticles. Overall, the study illustrates the value of in situ XANES for chemical characterization of catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.elspec.2017.01.002.

References


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