

Geometric and electronic structure of Au on Au/CeO₂ catalysts during the CO oxidation: Deactivation by reaction induced particle growth

Ali M. Abdel-Mageed¹, Gabriela Kučerová¹, Ayman Abd El-Moemen², Joachim Bansmann¹, Daniel Widmann¹, and R. Jürgen Behm^{1,*}

¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

²Chemistry Department, Faculty of Science, Suez Canal University, Ismailia, Egypt

*Corresponding author: juergen.behm@uni-ulm.de

Abstract. Changes of the geometric and electronic structure of gold on Au/CeO₂ catalysts induced by different pre-treatments (oxidative and reductive) and by the CO oxidation reaction at 80°C were followed by *operando* XANES / EXAFS measurements. The results showed that i) oxidative pre-treatment (O₂) leads to larger Au nanoparticles than reductive pre-treatment (CO), that ii) Au is predominantly metallic during CO oxidation, irrespective of the preceding pre-treatment, and that iii) there is a reaction induced Au particle growth. Correlations with the activity of the respective catalysts and its temporal evolution give insights into the origin of deactivation of these catalysts under reaction conditions, in particular on reaction induced changes in the Au particle size.

1. Introduction

Supported Au catalysts have attracted enormous interest in recent years because of their exceptionally high activity in a number of oxidation and reduction reactions [1]. One of the most prominent examples is the (preferential) CO oxidation reaction. Despite extensive efforts many important aspects of this reaction are still under debate, such as the active Au species or the physical origin of the pronounced deactivation during the reaction [1], which is relevant also for practical applications.

In the meantime there has been increasing evidence that the exact nature and working principle of Au catalysts depends strongly both on the nature of the support and the reaction and catalyst pre-treatment conditions [2,3]. While for CO oxidation on Au/TiO₂ at temperatures around 80 °C and higher Au is exclusively present in form of Au⁰ nanoparticles (NPs), which are also the active Au species [3,4], this may be different for other supports and reaction conditions. Furthermore, detailed information on the geometric structure and on the electronic structure and state of the gold species in these catalysts has so far mainly been provided by *ex situ* techniques such as transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements. Considering that these properties may be different under reaction conditions, *in situ* information is highly desirable.

For the CO oxidation on highly active Au/CeO₂ catalysts, previous results led to contradicting conclusions on the nature of the active Au species. While some groups claimed that gold in ionic form (Au⁺, Au³⁺) is predominantly responsible for the activity of the Au catalysts [5], other groups suggested that metallic Au⁰ NPs represent the active species during reaction [6]. Likewise, deactivation of Au/CeO₂ catalysts during CO oxidation had been proposed to mainly originate from (i)



effects associated with changes of the formal oxidation state of Au [5,7], (ii) the build-up of surface poisoning carbon containing species at the perimeter of the Au-support interface [8], and/or (iii) sintering of Au NPs during reaction [7,9]. Due to the considerable differences in the pre-treatment and reaction conditions in the different studies, a more general understanding of the active Au species and its role in the reaction and deactivation process can hardly be derived from these data.

We here present results of a combined kinetic and *in situ* XAS (XANES / EXAFS) study where we investigated the structural and electronic properties of the Au species in a Au/CeO₂ catalyst upon pre-treatment in either oxidative (O₂/N₂) or reductive (CO/N₂) atmosphere and during subsequent CO oxidation at 80°C, and their correlation with the catalyst activity and its evolution with time, to unravel the role of changes in the Au particle size and in its electronic state in the deactivation of the catalyst.

2. Experimental Section

The *operando* XANES / EXAFS measurements were performed on a highly dispersed 4.5 wt.% Au/CeO₂ catalyst with a surface area of 188 m²·g⁻¹, at the XAFS beamline at the Elettra Synchrotron (Trieste) using a Si(111) double crystal monochromator [10] and a specially designed reaction cell [11]. The catalyst was prepared by a deposition-precipitation procedure described elsewhere [12]. EXAFS/XANES data were recorded before and after the pre-treatment as well as during reaction at the Au L₃-edge (11919 eV) in the fluorescence mode, using a Si drift diode detector (KETEK GmbH). The pre-edge region was measured from 11616 - 11885 eV, followed by the XANES (11885 - 11970 eV) and the EXAFS region (11970 - 12500 eV). The EXAFS spectra were evaluated using XDAP software. The theoretical references were calculated by FEFF 8.0, and calibrated by measured reference spectra (Au foil and Au₂O₃ powder)[13]. About 20 mg of the diluted catalyst (1:3 with SiO₂) were placed in the reaction cell (catalyst bed size: 2 x 10 mm). Next, the catalyst was pre-treated either in oxidative (O400: 10% O₂ in N₂) or in reductive (CO400: 10% CO in N₂) atmosphere. This included first heating up to 400°C in N₂, then holding the catalyst for 30 min in the respective gas mixture at 400°C, and afterwards cool-down in N₂ to the reaction temperature of 80°C (all at 1.0 atm). Subsequently, the CO oxidation was performed in an idealized gas mixture (1% CO, 1% O₂, 98% N₂) at 1 atm and 80°C. Kinetic measurements were performed under identical conditions.

3. Results and discussion

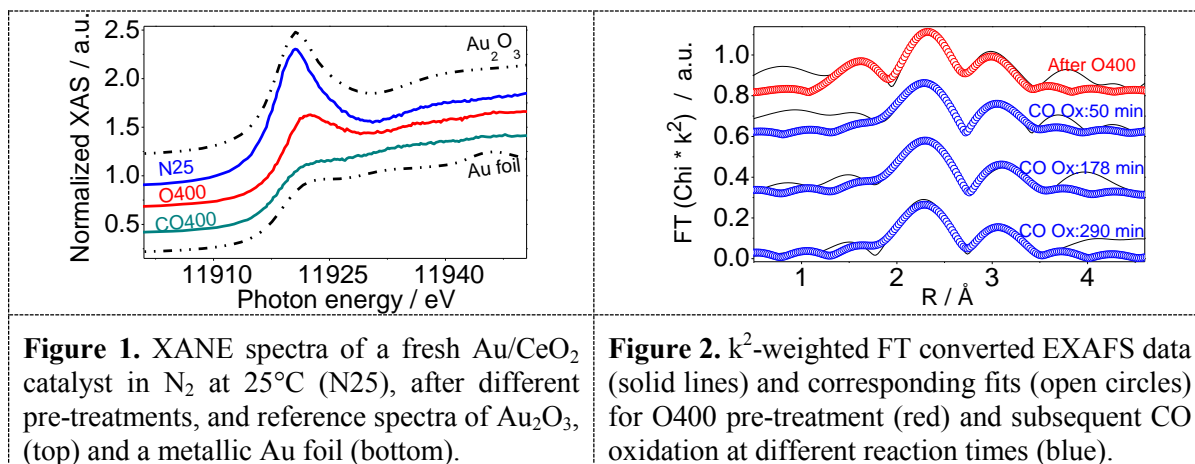
3.1. Influence of pre-treatment on the nature and dispersion of Au nanoparticles

The influence of the pre-treatment on the nature of the Au species as well as on the initial metal dispersion was determined by recording XANES/EXAFS at the Au L₃-edge in N₂ at 80°C after the respective pre-treatments (see above) and in N₂ at 25°C for the fresh sample (N25). A comparison of the normalized XANES spectra (see Fig.1) clearly demonstrates that the fresh Au/CeO₂ catalyst shows almost identical features as the Au₂O₃ reference (inflection point: 11918 eV; peak: 11921 eV). Hence, it largely consists of ionic Au³⁺ species. The strong oxide peak visible on the fresh sample, however, disappeared almost completely after CO400 pre-treatment, and instead a fully metallic Au⁰ species is formed. After the O400 pre-treatment, in contrast, a significant fraction of oxidic species is still present, although to a much lower extent compared to the fresh sample (N25). These results agree well with EXAFS data obtained after the different pre-treatments. After CO400 pre-treatment, the spectrum can be fitted with only metallic Au-Au scatterers, while for O400 pre-treated catalyst it has to be fitted with a model containing both metallic (Au-Au) and oxidic (Au-O) shells (see Table 1 and Fig. 2) [14].

Table 1. Structural parameters for Au NPs obtained from EXAFS after O400 and CO400 pre-treatments at 80°C. CN: coordination number, DW: Debye-Waller factor, R: distance, E₀: energy shift.

Pre-treatment	Scatterer	CN	DW / 10 ⁻³ Å ²	R / Å	E ₀ / eV	Dispersion / %
O400	Au-Au / Au-O	6.3 / 0.5	9.7 / 1.0	2.84 / 1.96	0.65 / 19.7	54
CO400	Au-Au	3.9	12.0	2.80	-1.65	100

These findings confirm the presence of oxidic Au species after O400. Hence, the ionic gold species present on the fresh Au/CeO₂ catalyst sample are reduced to Au⁰, either partly (O400) or completely (CO400). Furthermore, the pre-treatment procedure results in remarkable differences in the Au-Au CN and, hence, in the Au NP size, with the higher dispersion / smaller Au particle size for CO400. While the Au-Au CN is 6.3 after O400, it is only 3.9 after CO400. Assuming hemispherical Au NPs one can also calculate the corresponding dispersion, which is much higher after CO400 (100%) as compared to O400 (54%), and the Au particle size, which is much smaller after a CO400 pre-treatment (table 1).



3.2. Reaction induced changes: Au oxidation state and Au particle size

During kinetic measurements (see Fig. 3) the CO oxidation activity over Au/CeO₂ catalysts was found to be i) lower after CO400 than after O400 and ii) strongly decreasing with time on stream for both pre-treatments (deactivation after 1000 min on stream: 36% for O400 and 46% for CO400).

To obtain more information on the Au oxidation state of the Au/CeO₂ catalysts, XANES data were recorded at different times on stream during the CO oxidation. While for the CO400 pre-treated catalyst (Fig. S1) they did not show significant changes during the reaction (only metallic Au species), the respective data after O400 pre-treatment (Fig. S2) revealed a fast decrease of the oxidic peak upon changing from N₂ to the reaction gas mixture, leading to complete disappearance in less than 5 min. Thus, independent of the pre-treatment, we always find mainly Au⁰ species after a few minutes on stream. Similar observations of Au⁰ NPs as dominant Au species during CO oxidation had been reported earlier for other Au catalysts, e.g., for Au/TiO₂ [4]. This strong decrease of ionic Au species in the O400 pre-treated sample occurs on a rather short time scale compared to the catalyst deactivation, which is less than 5% within the first 10 min. In contradiction to previous reports [5,7], who claimed that cationic gold species are responsible for the high CO oxidation activity of Au/CeO₂, we conclude that the decrease in activity under present reaction conditions is not mainly related to changes in the Au oxidation state, e.g., from Au³⁺ to Au⁰. This is also supported by the respective data for the CO400 pre-treated catalyst, which equally showed a significant decrease in activity.

Additional information on the Au-Au CN and Au NP size under reaction conditions were derived from EXAFS measurements (see Table S1). These data show a pronounced increase of the Au-Au CN, from 6.3 to 8.0 and from 4.1 to 5.9 for O400 and CO400 pre-treated samples, respectively, within 175 min of reaction. For the first series, the corresponding k²-weighted Fourier Transformations of EXAFS data are shown in Fig. 2 after different time intervals. This increase in CN reflects a decrease in the dispersion of the Au NPs from 54% to 34% (O400) and from 100% to 60% (CO400), indicating a reaction-induced particle growth (see Fig. 4). Although a direct comparison of the activities after O400 and CO400 is not possible due to the rather different catalyst state after both pre-treatments, it is obvious that for both samples the activity decreases with increasing Au particle size, similar to other Au catalysts [8]. Moreover, also on a quantitative scale the loss of activity and the loss of Au

dispersion are of similar order of magnitude. The dispersion decreases by a factor of ~ 0.6 for both pre-treatments within 175 min on stream, while the decrease in activity (within the same time) is 0.81 and 0.57 for O400 and CO400, respectively. Considering the (comparable) time scales of deactivation and Au particle sintering (in contrast to changes in the Au oxidation state) and their similar magnitudes, we conclude that under present reaction conditions reaction-induced Au particle size growth contributes significantly to the catalyst deactivation. Nevertheless, especially in the beginning of the reaction other factors such as changes in the catalyst oxidation state or site blocking by adsorbed surface species e.g., by carbonates or formate species, may contribute to the initial fast deactivation.

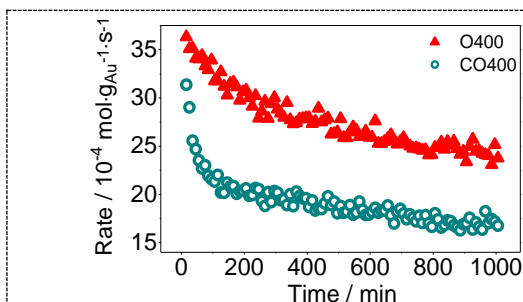


Figure 3 Au mass-normalized CO oxidation activity in 1% CO, 1% O₂, balance N₂ at 80 °C (O400: red; CO400: green) with time on stream.

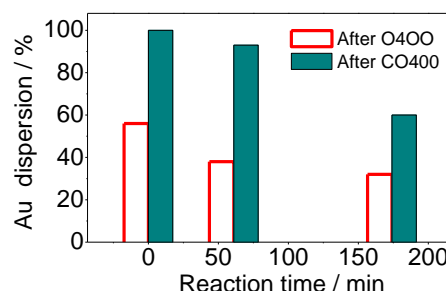


Figure 4. Time evolution of the Au dispersion during CO oxidation (O400: open red column; CO400: green filled column).

In summary, different pre-treatments lead to different initial states of the Au/CeO₂ catalyst. While Au NPs after O400 pre-treatment contain a significant amount of oxidic species, only metallic Au species could be detected after CO400 pre-treatment. During CO oxidation only metallic Au NPs are present, which grow in size for both pre-treatments. Accordingly, the relatively strong deactivation of Au/CeO₂ catalysts with time on stream is mainly attributed to reaction-induced Au particle size growth.

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