The Dynamic Structure of Au\textsubscript{38}(SR)\textsubscript{24} Nanoclusters Supported on CeO\textsubscript{2} upon Pretreatment and CO Oxidation

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\textbf{ABSTRACT:} Atomically-precise thiolate protected Au nanoclusters Au\textsubscript{38}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{24} on CeO\textsubscript{2} were used for in-situ (operando) EXAFS/DRIFTS and ex-situ STEM-HAADF/XPS studies monitoring cluster structure changes induced by activation (ligand removal) and CO oxidation. Oxidative pretreatment at 150°C "collapsed" the clusters’ ligand shell, oxidizing the hydrocarbon backbone but the S remaining on Au acted as poison. Oxidation at 250°C produced bare Au surfaces by removing S which migrated to the support (forming Au-S), leading to highest activity. During reaction structural changes occurred via CO-induced Au and O-induced S migration to the support. The results reveal the dynamics of nanocluster catalysts and the underlying cluster chemistry.

\textbf{Keywords:} Au nanoclusters, catalysis, in-situ XAFS, DRIFTS, CeO\textsubscript{2}

A great challenge in nanocatalysis is to produce truly homogenous, structurally well-defined and highly active nanostructures that can serve for fundamental studies and new applications. Thiolate protected metal nanoclusters (M\textsubscript{m}(SR)\textsubscript{n}) with well-defined structures offer a route towards creating atomically precise and catalytically active sites\textsuperscript{1-14} providing model systems for atomic level studies of catalytic properties\textsuperscript{3,5-6}.

It is well-accepted that Au clusters (with < 100 Au atoms) supported by metal oxides exhibit excellent catalytic activity for (low temperature) oxidation\textsuperscript{4, 7-14} and hydrogenation\textsuperscript{15-17}, especially when compared to larger Au nanoparticles. Au clusters facilitate reactant activation due to higher adsorption energies. Nevertheless, the initially well-defined Au cluster structure may change during pre-treatment and reaction, which is also affected by cluster size and the type of support material\textsuperscript{18-21}. Previously, we have studied structural changes of Au clusters of different size, i.e. Au\textsubscript{x}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{y} (x=25, 38 and 144, y=18, 24 and 60) supported on metal oxides (CeO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2}) upon oxidative pre-treatment and liquid phase reaction. In-situ X-ray Absorption Fine Structure Spectroscopy (XAFS) and High-Resolution Fluorescence Detected – X-ray Absorption Spectroscopy (HERFD-XAS) revealed higher cluster stability on CeO\textsubscript{2} and SiO\textsubscript{2}\textsuperscript{21-23} than on Al\textsubscript{2}O\textsubscript{3}. Here, we refine the structural picture on cluster chemistry by in-situ/operando EXAFS and DRIFTS spectroscopy, to directly monitor the dynamic structure of Au\textsubscript{38}(SC\textsubscript{2}H\textsubscript{4}Ph)\textsubscript{24} clusters on CeO\textsubscript{2}, both during ligand removal and CO oxidation.

CO oxidation has been repeatedly used to assess the catalytic properties/active sites of (mainly CeO\textsubscript{2}) supported thiolated gold nanoclusters, particularly addressing ligand effects\textsuperscript{14, 18, 24-28}. Two different mechanisms were proposed: (i) Mars van Krevelen, with CO adsorbed on Au and active oxygen provided by CeO\textsubscript{2} at the metal/oxide interface\textsuperscript{29} which was supported by Good et al. showing that the reaction of oxygen from the ceria lattice with CO adsorbed on gold was the rate limiting step\textsuperscript{30} (ii) Langmuir-Hinshelwood, with CO and O coadsorbed on neighboring Au sites\textsuperscript{31}. Lopez Acevedo et al. explained the catalytic activity of thiolate protected gold nanoclusters with their HOMO-LUMO energy gap, which matches the binding energy of oxygen on Au\textsuperscript{31}. Hence, for Au\textsubscript{38}(SR)\textsubscript{24} clusters only the removal of ligands turns them into electropositive species that are able to adsorb O\textsubscript{2}. A combination of activated adsorbed and lattice oxygen provides ideal conditions for reaction with adsorbed CO.
Jin and coworkers proposed that not the bulkiness of the hydrocarbon tails but the ligands at the interface between thiolated Au clusters and CeO$_2$ inhibited CO adsorption on Au and reaction with lattice O, hence adversely affecting CO oxidation. Accordingly, pre-treatments removing the ligand shell should have a positive effect on activity.

Nie et al. reported for Au$_n$(SR)$_m$/CeO$_2$ (n=25, 38, m=18, 24) that partial thiolate (ligand) removal led to higher activity than complete ligand removal. According to Wu et al. partial removal of thiol ligands by oxidation around 150°C enabled CO adsorption on the exposed Au surface whereas full removal did not have any further effect. Overall, the effect of thiolate ligands and their removal on the catalytic activity of Au nanoclusters is still controversially discussed.

Recently, we have reported a new effect, i.e., migration of thiolate ligands from the Au clusters to the supporting oxide. Although the assumption had been that thiolate ligands "disappeared" into the gas phase upon oxidative activation, S K-edge XAFS measurements detected that oxidized sulfur species remained on the support. The redistribution and oxidation of S modified the support, which may also alter its catalytic function (e.g., by poisoning interface sites or vacancies).

Herein, we performed more detailed in-situ/operando EXAFS/DRIFTS and ex-situ STEM-HAADF/XPS studies of structural changes of Au$_{38}$(SR)$_{24}$/CeO$_2$ upon pre-treatment and CO oxidation. In-situ XAFS Au L$_3$-edge spectra of Au$_{38}$(SR)$_{24}$/CeO$_2$ upon different oxidative pre-treatment indicated that not only ligands were removed but also that staples collapsed, depositing S atoms on the Au surface (poisoning). At higher temperature, S species migrated from the Au clusters to the support, creating bare active Au surfaces. During CO oxidation further structural changes occurred via CO-induced Au and O-induced S migration to the support. The complex temperature dependence of these structural changes and the formation of Au-S units may explain the conflicting reports in literature on the effect of pre-treatment on catalytic properties.

The atomic structure of Au$_{38}$(SC$_2$H$_4$Ph)$_{24}$ was previously solved by X-ray crystallography with EXAFS confirmation thereafter. The Au$_{38}$(SR)$_{24}$ nanoclusters consist of a symmetric biicosahedral structure Au$_{23}$ core, which is protected by three monomeric (SR-Au-SR) and six dimeric staples (SR-Au-SR-Au-SR; Scheme 1).

As mentioned, oxidative catalyst activation is required and the structural evolution of CeO$_2$ supported Au$_{38}$(SR)$_{24}$ nanoclusters were studied by Au L$_3$-edge XAS (Figure 1).

![Scheme 1. Au$_{38}$(SR)$_{24}$ nanocluster (initial) structure with distances fitted by EXAFS](image)

Figure 1. EXAFS fit (red) in R space of the as-prepared sample, after pre-treatment (150°C or 250°C, in 5% O$_2$ in He) and after CO oxidation reaction.

The Artemis package was applied for EXAFS data treatment, building a cluster model based on the known crystal structure. The fitted values of the three key distances are illustrated in Scheme 1. The Au-Au distance characterizes neighboring Au atoms, e.g., those in the core. There are two different Au-S bond distances, one corresponding to Au$_{v}$core-S and the other to Au$_{v}^{+}$staple-S.
The cluster structural changes upon pretreatment were evaluated via two main EXAFS parameters: R (distance) and N (coordination number of neighboring equivalent atoms). Table S1 and Fig. S3 collect the fitting results, while the deduced structural changes are illustrated in Scheme 2.

As expected, the number of nearest equivalent Au neighbors ($N_{Au-Au}$) increased upon pretreatment (2.59 to 5.08 or 8.09), due to the increasing removal of the ligands, but EXAFS analysis still suggested that the core structure was preserved. However, the N values of Au$^0$core-S and Au$^+$staple-S, which are expected to continuously decrease upon pretreatment, showed a deviating behavior. Apparently, the structural changes are more complex than just a simple successive removal of (entire) ligands.

When Au$_{38}$(SR)$_{24}$/CeO$_2$ was pre-treated at 150°C, the Au-Au and Au-S distances (R) did not change. In line with ligand removal, N of Au-Au increased and N Au$^+$staple-S strongly decreased, but N Au$^0$core-S unexpectedly increased. The removal of the thiolate carbon backbone seems to collapse the remaining staples, creating new bonds between Au-Au but also between the outer Au atoms of the cluster core and S (Au$^0$core-S). Pre-treatment at 250°C almost completely removed S from the cluster core, as N Au$^0$core-S became almost zero. However, N Au$^+$staple-S was still 0.45, indicating creation of Au$^+$-S configurations, which can only be on the support (staples collapsed at 150°C not reestablished at 250°C).

Figure 2 shows catalytic CO oxidation, comparing pretreated Au$_{38}$(SR)$_{24}$/CeO$_2$ with CeO$_2$. Catalytic activity was monitored by a mass spectrometer (MS) connected to the reaction cell outlet. Au$_{38}$(SR)$_{24}$/CeO$_2$ pretreated at 150°C showed only minute activity even at 150°C. This confirms the structural model, as Au atoms blocked by S were inaccessible for CO and O$_2$ adsorption.

In contrast, Au$_{38}$(SR)$_{24}$/CeO$_2$ pretreated at 250°C was active even below 40°C, being more than 50-times more active than the pret150 sample. Again, this confirms the structural model of bare Au surfaces, as Au-S species are inactive. The as-prepared Au$_{38}$(SR)$_{24}$/CeO$_2$ catalyst with intact ligands was nearly inactive and also sintered, losing the cluster monodispersity, therefore it will not be further considered here.

![Scheme 2. Evolution of the Au$_{38}$(SR)$_{24}$/CeO$_2$ cluster structure derived from EXAFS fit, after pre-treatment at 150 or 250°C and subsequent CO oxidation.](image)

**Figure 2.** CO oxidation on 2wt% Au$_{38}$(SR)$_{24}$ on CeO$_2$ (flow: 3.3% CO, 7% O$_2$, 89.7% He, total flow: 60ml/min, ramp: 5°C/min): CO$_2$ MS traces normalized to the catalyst mass and the He signal, after different pre-treatments.

In order to investigate reaction-induced structural changes the samples were again characterized by EXAFS after CO oxidation (Table S1 and Figure S3). During reaction on the pret250 catalyst, the Au core structure present after pretreatment was preserved, indicated by the only slightly reduced Au-Au coordination numbers, the bond distances and EXAFS fitting (minimal change of $\sigma$$_{Au}$ Au-Au).

However, N Au$^+$staple-S decreased and N Au$^0$core-S increased during the reaction. As S migration back to the cluster is unlikely, this suggests that (isolated) Au$^+$staple-S converted to (agglomerated) Au$^0$core-S on the support and/or that Au$^+$staple-S dissociated. Additionally, more Au atoms may move to the support and merge with S species. Migration of Au atoms under reaction conditions can be explained by CO-induced atom mobility, as observed before, which explains the decrease of N Au-Au. Accordingly, S species are mobile not only during pretreatment, as shown by our previous XANES
study, but also during the catalytic reaction. The two Au-S species will not contribute to catalytic activity, as S is a strong poison. During CO oxidation on the less active pret150 sample with initially S-poisoned Au surfaces, S moved to the support (decreasing N Au$^{6}$core-S and increasing N Au-Au) and merged with CO-mobilized Au atoms (increasing N Au$^{staple}$-S). However, during reaction at 150°C activity did not increase significantly. S may be removed from the clusters, but it will still poison the surrounding ceria.

To address morphological changes, STEM-HAADF images were acquired for the “as-prepared” catalyst and the catalysts after CO oxidation (Fig. S6). In all cases, Au nanoclusters of 2-4 nm size were identified. Smaller entities, like Au-S particles formed by migration of Au and S species during reaction (as indicated by N Au$^{staple}$-S) may be present as well but were beyond detection.

Possible reaction-induced changes in the Au oxidation state were studied by X-ray Photoelectron Spectroscopy (XPS) (Figure S7). For the as-prepared sample the Au 4f$_{7/2}$ signal at 84.2 eV is characteristic of ceria supported Au clusters that are modified by metal-ligand interaction. For ligand-free Au$^{6}$ nanoclusters on ceria$^{42-43}$ a binding energy of 83.8 eV was reported by Huang et al.$^{23,44}$ After pretreatment and reaction, the Au 4f signals were shifted to lower binding energies. For the pret150 catalyst the small shift agrees with the collapse of the staples, while for the pret250 sample the -0.3 eV shift corroborates the formation of bare Au$^{6}$ clusters.

To monitor adsorbed species, in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was performed during CO oxidation. Figure 3 displays temperature-dependent operando DRIFT measurements of the highly active Au$_{38}$(SR)$_{24}$/CeO$_{2}$ catalyst pretreated at 250°C. Spectra were taken from room temperature to 150°C (ramp 1°C/min, then isothermal for 4h).

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Operando DRIFTS during CO oxidation on Au$_{38}$/CeO$_{2}$ pretreated at 250°C, from room temperature to 150°C (background corrected with pure CeO$_{2}$ pretreated under the same conditions). (a) 2500-2000 cm$^{-1}$, (b) 1600-1200 cm$^{-1}$.

CO adsorbed on Au$^{6}$ (2130 cm$^{-1}$) was observed below 118°C, corroborating clean Au surfaces (Figure S8). CO$_{2}$ formation was already observed at room temperature by MS (Fig. S12) and gas-phase bands between 2300 and 2400 cm$^{-1}$ (Figs. 3a and S9). In the lower wavenumber region (Figure 3b) the typical monodentate carbonates, frequently observed during CO oxidation and bonded to ceria, were observed via an increasing signal at 1468 cm$^{-1}$. For sulfation of CeO$_{2}$, Waqif et al. reported distinct IR bands of surface SO$_{2}$ (or S$_{2}$O$_{2}$) and SO$_{3}$ (1x S=O, 3x S-O-Ce),$^{46}$ which were also present here (Fig. S10 and S11). Bulk SO$_{4}$ was absent (missing bands at 1196, 1128 cm$^{-1}$ in Fig. S11).$^{46-47}$ Surface SO$_{3}$ and SO$_{4}$ increased over time, becoming more pronounced close to maximum temperature in Figure 3b. Thus, sulfur from Au-S species, which have migrated to the support during pretreatment, reacted to surface SO$_{3}$ and SO$_{4}$.

The detailed evolution of the structure of Au$_{38}$(SR)$_{24}$ nanoclusters supported on CeO$_{2}$ was monitored upon pre-treatment and CO oxidation. Whereas unpretreated samples tend to sinter, oxidative pretreatment at 150°C collapsed the staples structure. Unlike the hydrocarbon backbone, sulfur was not removed to the gas phase but remained on the Au core, thus inhibiting adsorption of CO and oxygen. Pretreatment at 250°C fully removed S and created clean Au$^{6}$ clusters with intact core structure. The removal of ligands was beneficial for CO oxidation, why the pret250 sample had the highest activity, being already active at room temperature. During reaction, mobile Au and S species formed additional (inactive) Au-S entities. Operando DRIFTS detected CO adsorption on Au$^{6}$ below 118°C, in addition to carbonates on the ceria support. A slow continuous transformation to SO$_{3}$ and SO$_{4}$ was observed (during ~6h), becoming more pronounced close to the maximum temperature. The current results are particularly relevant for further studies of cluster chemistry and functionality. It is important to understand the role and fate of staples/ligands and their interaction with the support, as this strongly affects catalytic performance.

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Sample preparations were performed by S.P. and C.G.. EXAFS measurements were performed by N.B., V.T. and S.P.. EXAFS fitting was carried out by W.O.. Operando DRIFTS measurements and data analysis were done by S.P.. XPS measurements and analysis was carried out by T.H. and V.T.. STEM-HAADF measurements with analysis were performed by J.L.. Final interpretation and manuscript preparation was led by S.P., N.B. and G.R., with contributions of all authors. Funding was acquired by G.R.

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ABBREVIATIONS
EXAFS, Extended X-ray Absorption Fine Structure; DRIFTS, Diffuse Reflectance Infrared Fourier Transform Spectroscopy; STEM-HAADF, Scanning Transmission Electron Microscopy – High Angle Annular Dark-Field Imaging XPS, X-ray Photoelectron Spectroscopy; MS, Mass Spectrometry; Au30(SR)24/Co3O4, catalyst: Au30(SC2H4Ph)24 cluster supported on CeO2; pret150, catalyst sample pretreated at 150°C; pret250, catalyst sample pretreated at 250°C

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