ON THE REACTIVITY OF $Au_n(SR)_m$ NANOCLUSTERS CATALYSTS: LIGAND, STRUCTURE AND SUPPORT EVOLUTION

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INTRODUCTION

In nanocatalysis, a great challenge is to obtain truly homogenous and well-defined highly active nanostructures on surfaces. Ligand protected metal nanoclusters is an emerging class of functional nanomaterials consisting of less than 100 atoms, with atomic precision, well-defined molecular structure. These properties are also sensitive to the metal composition, which allows tuning properties by removing, adding or replacing (doping) one or more au atoms with heteroatoms. We successfully doped different cluster sizes by metal as Pd, Pt, Cu or Ag, producing bimetallic and trimetallic nanoclusters with atomic precision. Insights in the structural and properties changes were obtained by several spectroscopic studies (XAFS, XPS, MALDI…) correlated with DFT calculations[1, 2].

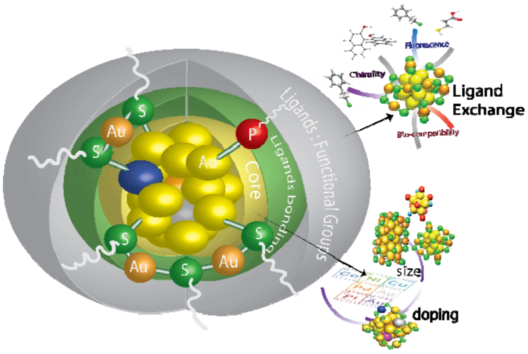

Figure 1: Scheme monolayer protected clusters and the possible route for fine-tunning of their properties (doping and ligand exchange)

Heterogeneous catalytic research of atomically precise gold nanoclusters is an emerging field opening new opportunities for accurate studies of size-dependent properties, atomic structure effects and reaction mechanisms in catalysis. An enhancement of the catalytic properties by metal nanoclusters has been observed, when compared to classical nanoparticles of similar size. By *in situ* spectroscopic techniques we study the influence of the cluster structure and support material in their stability and reactivity, during pretreatment and in different gas and liquid phase reactions

RESULTS AND DISCUSSION

Generally, the supported nanoclusters undergo ligand removal treatments, in order to increase the active surface accessible for reaction. We studied the structural changes of different atomic sizes of $Au_x(SC_2H_4Ph)_y$ (x=25,38 and 144) supported on various metal oxides (CeO_2, Al_2O_3 and SiO_2) upon thermal treatments and reaction conditions. *In situ* XAFS measurements revealed the strong influence of the cluster structure and support material in their stability.[3-5] Whereas high stability of the cluster is obtained with CeO_2 and SiO_2 supports, Al_2O_3 leads to an increase in particle size. These studies confirmed that the cluster core structure was stable upon deposition and post-treatment, but focused only on the Au kernel. However, the fate of the thiolates (ligands) during deposition of the clusters on an oxide support and post-treatments was not considered. Up to now, it was believed that the ligands of cluster catalysts

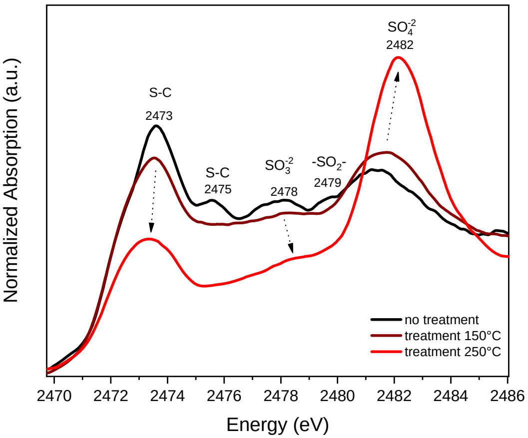

Figure 2: XANES spectra at S K-edge of Au_{38}/CeO_2 catalysts fresh and treated at 150°C and 250°C under oxygen atmosphere

"disappeared" (into the gas phase) upon activation. The field is in fact moving towards applications and many involve the deposition of clusters on solid surfaces (supports). This motivated us to study the fate of the thiolate ligands upon supporting clusters on surfaces. S K-edge measurements revealed for first time ligand migration from the gold clusters to the support, manifested by formation of unexpected oxidized sulfur species on the support.[3] The redistribution and oxidation of the ligands modified the support surface, a factor that may alter its properties.

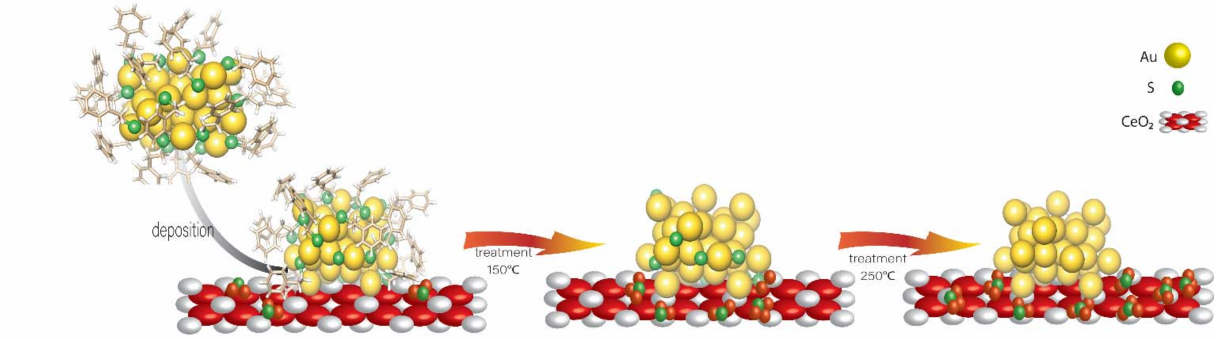

Figure 2. Scheme of thiolate ligands evolution upon cluster deposition on CeO_2 and oxidative treatments

In situ XAFS Au L_3-edge studies under CO oxidation reaction conditions show the high stability of the main core cluster structure but a reversible mobility of the Au-S units[6]. The flexibility of the cluster structure and the mobility of atoms was observed in our previous work by in situ QXAFS of metal exchange reaction between Au_{38} and Ag_xAu_{38-x} clusters[7]. The mobility of the Au-S units can explained the different catalytic behaviour depending on the treatment also confirmed by *in situ* DRIFTS measurements.

CONCLUSION

Insights into the interaction between the monolayer protected nanocluster and the oxide support are obtained leading to a better understanding on the different catalytic behavior of this class of nanocatalysts. In summary, we have shown that upon supporting thiolate protected gold clusters, the thiolates are redistributed between cluster and support, leading to oxidized sulfur species that alter the electronic and adsorption properties of the support. This effect has completely been neglected up to now but we believe that it must be taken into account to fully understand the complex selectivity patterns of supported thiolate-protected clusters in catalysis.

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