

Operando XAFS studies on stability and reactivity of a $\text{Au}_{38}(\text{C}_2\text{H}_4\text{Ph})_{24}/\text{CeO}_2$ nanocluster catalysts in oxidation reactions

Stephan Pollitt, Noelia Barrabés, Günther Rupprechter (IMC, TU Wien (AUT))
pollitt.stephan@gmail.com

Thiolate protected Au nanoclusters $\text{Au}_n(\text{SR})_m$ supported on oxides have been proven to be active in several catalytic reactions with high yields. In contrast to nanoparticles, which usually have a size distribution, nanoclusters are well defined with resolved structures and offer the possibility to atomically design a truly homogenous system. This leads to optimal conditions for reaction and mechanism studies in catalytic research. Limited stability under harsher conditions has been overcome by supporting the clusters on solid materials like CeO_2 .¹⁻⁴ When deposited on a support, the ligands can be successively thermally removed to expose the metal atoms and obtain a truly monodisperse heterogeneous catalyst. Different activity and selectivity in catalysis were observed, depending on the atomic composition, degree of ligand removal and pre-treatment.³⁻⁶ However, surface studies on the state of the cluster structure and ligand effects after pretreatment or during catalytic reactions have not been performed yet, but are crucial for a mechanistic understanding. The present work represents the first operando XAFS studies of monolayer protected gold cluster catalysts under pretreatment and reaction conditions. Investigations were performed with a $\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}/\text{CeO}_2$ catalyst in a CO oxidation model reaction.

$\text{Au}_{38}(\text{SC}_2\text{H}_4\text{Ph})_{24}$ clusters were made by wet synthesis through ligand exchange. At CLAES beamline of ALBA Synchrotron, in-situ XANES studies at Au L_3 -edge of the catalyst were performed during thermal treatment in oxidizing atmosphere and during a CO oxidation model reaction. CO conversion was followed simultaneously with MS. Additional ex-situ EXAFS at Au L_3 -edge and XANES measurements at S K-edge were performed on samples pretreated under various conditions. Investigation of the oxidation state and particle size of the support and the deposited clusters before and after reaction were done by XPS and STEM-HAADF, respectively.

The XAFS measurements represent the first evidence for a redistribution of the thiol ligands between nanoclusters and support. Further conversions of oxidation state in the S species were observed upon thermal pre-treatment, leading to different activity profiles in the model reaction. The selectivity changes in several reactions, depending on the level of ligand removal can be explained by the continuous evolution of new, oxidized S species.⁵⁻⁶ Au L_3 -edge measurements point out the importance of a soft pretreatment in order to obtain a stable catalyst. The XANES spectra of the unpretreated samples during CO oxidation reaction evidence the changes of the clusters, related to modifications in both the ligand shell (Au-S) and also the remaining Au core (Au-Au). Once the samples had been pretreated, no relevant changes in the XANES spectra were observed, denoting the high stability of these catalysts.

Thus, these results obtained by XAFS, together with complementary studies (XPS, STEM-HAADF), confirm highly active and stable catalysts in the form of a well defined cluster catalyst system.

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