DEVELOPMENT OF A TRULY HOMOGENEOUS AND MONODISPERSE CATALYTIC SYSTEM IN MEANS OF THIOLATE PROTECTED GOLD NANOCLUSTERS

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INTRODUCTION

Catalysis plays an important role in optimizing chemical processes in terms of cost efficiency and energy consumption. Further, the emission of poisonous or greenhouse gases can be reduced, leading to higher health and living standards. Catalytic processes are know for their complexity, which hampers catalysis research. New paths need to be taken to simplify reaction systems for investigations at ambient pressure. In heterogeneous catalysis metal nanoparticles are common active sites. [1] To get around the variation in particle size and size distribution of nanoparticles thiolate protected nanoclusters can be utilized.

Thiolate protected Au nanoclusters $Au_n(SR)_m$ 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 sta-

Figure 1: $Au_{38}(SC_2H_4Ph)_{24}$ nanocluster: 2 center atoms, metallic core, coordinated S–Au–S bonds, complete cluster with ligands

bility under harsher conditions has been overcome by supporting the clusters on solid materials like CeO_2. [2–5] When deposited on a support, the ligands can be successively thermally removed to expose the metal atoms and obtain a truly monodisperse heterogenous catalyst. Different activity and selectivity in catalysis were observed, depending on the atomic composition, degree of ligand removal and pre–treatment. [4–7] 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 $Au_{38}(SC_2H4Ph)_{24}/CeO_2$ catalyst in a CO oxidation model reaction. The structure of this specific cluster is shown in Figure 1.
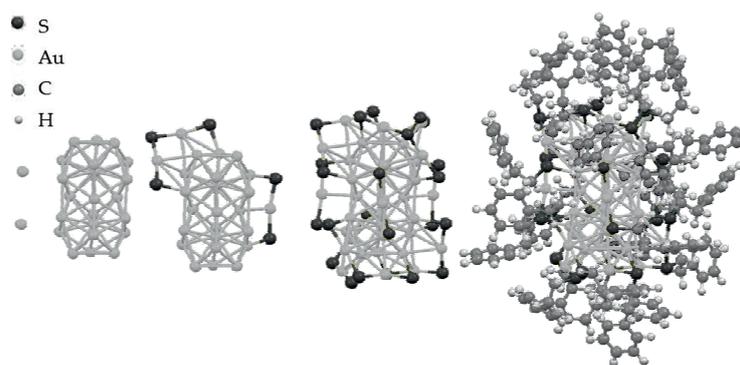
EXPERIMENTAL

$Au_{38}(SC_2H_4Ph)_{24}$ clusters were made by a wet synthesis approach through ligand exchange. To investigate the cluster's stability during pre–treatment and under reaction conditions, XAFS measurements were performed. At CLAESS 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

CO oxidation. CO conversion was followed simultaneously with MS to analyze the catalyst's activity profile. Additional *ex–situ* EXAFS at Au L_3–edge and XANES measurements at S K–edge were performed on samples pretreated under various conditions to investigate the pretreatment effect from the point of view of the ligands. 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.

RESULTS AND DISCUSSION

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. This can be explained by the continuous evolution of new oxidized S species. [6,7] 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.

CONCLUSION

Thus, these results obtained by XAFS, together with complementary studies (XPS, STEM–HAADF), confirm highly active and stable catalysts in form of a well defined cluster catalyst system, which are tunable by atom number, support material, different ligands and through the introduction of dopant atoms to find optimum conditions for different reactions.

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