# CATALYTIC ACTIVITY OF THIOLATE-PROTECTED GOLD NANOCLUSTERS SUPPORTED ON $TiO_2$, $SiO_2$ AND $ZrO_2$

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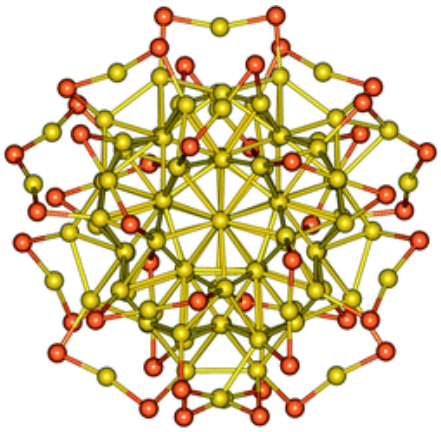
## INTRODUCTION

Thiolate-protected gold nanoclusters are an interesting emerging class of materials due to their stability, optical and electronic properties. Since the first report in 1994 by Brust et al. [1], atomically precise synthesis and separation protocols and final chemical and structure determination have been widely studied. This made possible to treat $Au_n(SR)_m$ clusters as well-defined nanostructures. Their stability and electronic states were found to be related to the highly symmetrical metallic core, which is protected by multiple gold-thiolate staples (-SR-Au-SR-), monomeric in case of $Au_{144}(SC_2H_4Ph)_{60}$) and dimeric staple bands in $Au_{25}(SC_2H_4Ph)_{18}$



**Picture 1:** $Au_{144}(SC_2H_4Ph)_{60}$

Heterogeneous catalysis by metal nanoparticle supported on oxides, are often limited in their activity/selectivity, due to variations in metal particle size, surface structure and bonding to the support. Thiolate-protected Au nanoclusters had shown enhancement catalytic activity in several processes in comparison with the common nanoparticles catalysts. Atomically designed metal clusters offer the possibility to design well-defined and truly homogeneous surfaces leading to optimal catalysts for reaction mechanism studies. Although, the stability of the cluster structure and type of interaction with the support during the thiolate ligands removal treatments and under reaction conditions represent key understanding for their catalytic application.

## EXPERIMENTS

Therefore, an in-depth investigation of the effect of the cluster size ($Au_{25}$ vs $Au_{144}$), the staple configuration (short vs long staple) and the ligand interactions depending on the material support nature ($TiO_2$, $SiO_2$ and $ZrO_2$) is the focused on the present work, key information for their catalytic studies.

In order to evaluate the influence and effect of each parameter (size, staple, and support), the catalytic activity of the supported clusters is studied in Water-gas shift reaction (WGS). WGS reaction is an important industrial chemical process for the production of hydrogen and plays an important role in the production of methanol, each of which may be directly used as a fuel for various applications. The current conventional low-temperature catalysts have important drawbacks, as the deactivation of Cu-ZnO when it is exposed to air and /or water condensation[2]. Due to the enhancement of the catalytic performance by supported nanoclusters, the studied systems represents also an alternative in this process.

## RESULTS AND DISCUSSION

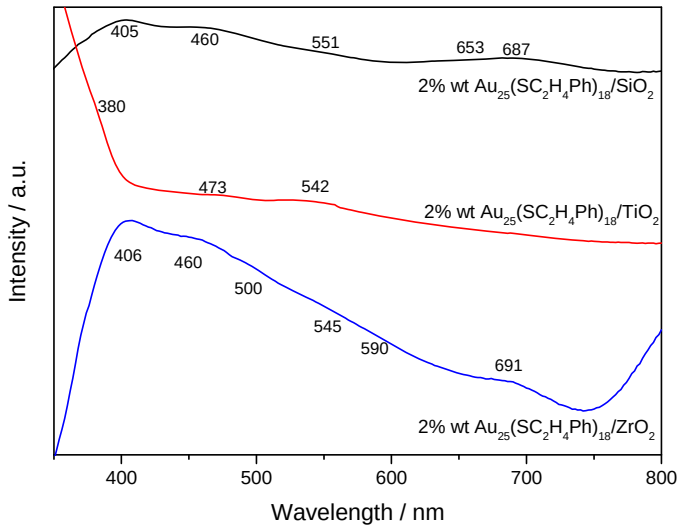



**Chart 1:** UV-Vis solids spectra

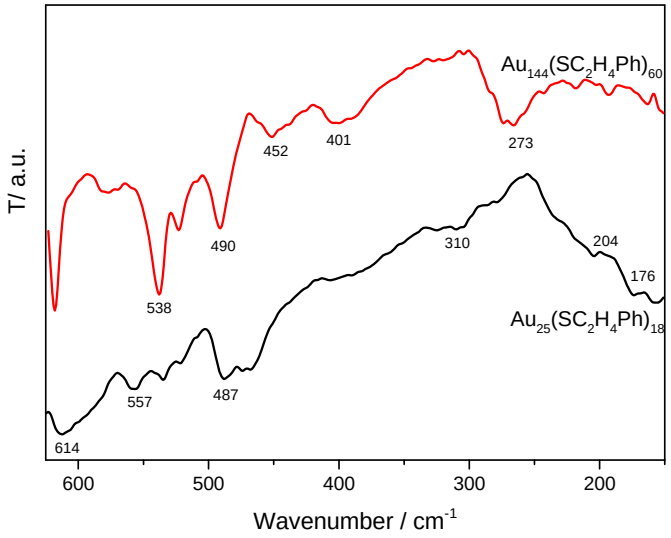



**Chart 2:** Far-Infrarred spectra

$Au_{25}(SC_2H_4Ph)_{18}$ and $Au_{144}(SC_2H_4Ph)_{60}$ clusters has been synthesized and isolated based on reported studies. The cluster purity and properties have been characterized by UV-Vis, FTIR and MALDI[3]. Each clusters has been supported on the different oxide materials ($SiO_2$, $TiO_2$ and $ZrO_2$) with a 2% wt by impregnation. The cluster characterization have been performance using optical spectroscopy (UV-vis) and infrared spectroscopy (FIR and MIR). By means of V-Vis solids it has been shown that there are different kinds of interactions denoted with the changes of the bands in the UV-Vis spectra depending on the supports. It is also confirmed the presence of the clusters without decomposition. Vibrational spectroscopy also showed the characteristic bands for both clusters.

## CONCLUSION

Thermogravimetrical studies (TG), X-ray diffraction studies and XPS will be applied. The catalytical behavior will be measured via mass spectrometry. In terms of scientific community this study represent a bridge between the model catalysis and the real catalysis, due that with supported cluster catalysis it is possible to obtain structure-resolved active sites with 100% homogeneity (completely defined surface) normally just obtain by single crystals. In model catalysis, ultra-high vacuum conditions are required in all the studies whereas we operated at real conditions (atmospheric pressure).

## REFERENCES

[1] Brust, M, J Chem Soc Chem Comm, 801, 1994

[2] J. A. Rodriguez, J. Phys. Chem. C, 116, 2012

[3] Huifeng Q. Rongchao J; Chem. Mater, 23, 2011