SUPPORTED GOLD NANOCLUSTERS: EFFECT OF CLUSTER SIZE AND OXIDE MATERIAL UNDER OXIDATION PROCESSES

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INTRODUCTION

Heterogeneous catalysis by metal nanoparticles supported on oxides is often limited in activity/selectivity, due to variations in metal particle size, surface structure and bonding to the support. Thiolate-protected Au nanoclusters have shown enhanced catalytic activity in several processes in comparison with the common nanoparticle catalysts. Atomically designed metal clusters offer the possibility to design well-defined and truly homogeneous surfaces, leading to optimal catalysts for reaction mechanism studies. However, understanding the stability of the cluster structure and type of interaction with the support during the thiolate ligand removal treatments and under reaction conditions represent key understanding for their catalytic application [1].

EXPERIMENTS

The interaction and stability of $Au_{25}(SC_2H_4Ph)_{18}$ and $Au_{144}(SC_2H_4Ph)_{60}$ clusters on different oxide materials (SiO_2, TiO_2 and ZrO_2) have been studied by (UV-Vis, TGA, FTIR, HRTEM, XRD and XAFS). Supported clusters were pretreated under air (a common industrial pretreatment) at 150°C for a partial removal of ligands and at 250°C for a total removal of ligands. In order to establish correlations between morphology and catalytic properties, cyclohexane oxidation was employed as a model reaction, as it is a well-known industrial process where gold is required to activate the molecular oxygen.

RESULTS AND DISCUSSION

TGA studies showed that the removal of ligands takes place around 200°C. In order to find out more about cluster´s stability under harsh conditions, particle size images were measured after loading and after both pretreatments. HRTEM images showed that there is a negligible increase of particle size after 150°C, while a significant increase was observed after 250°C.This size increase was also noticeable via diffuse reflectance spectroscopy. The spectra changes considerably after 250°C pretreatment, a new band is observed at 520 nm corresponding to the surface plasmon resonance band, characteristic of particles bigger than 2 nm and reflects the collective excitation behaviour in metallic state. Measurements of pretreated and unpretreated samples were also performance using synchrotron radiation. We observed a higher structural stability of $Au_{144}(SC_2H_4Ph)_{60}$ compared to $Au_{25}(SC_2H_4Ph)_{18}$.

Moreover, we compared the catalytic activity and selectivity of both clusters supported on SiO_2, TiO_2 and ZrO_2 as well as the pretreatment influence in the catalytic activity. Cluster´s stability after reaction was also probed with XRD, the results confirm that the structure is preserved after 10 hours reaction, making this clusters recyclable.

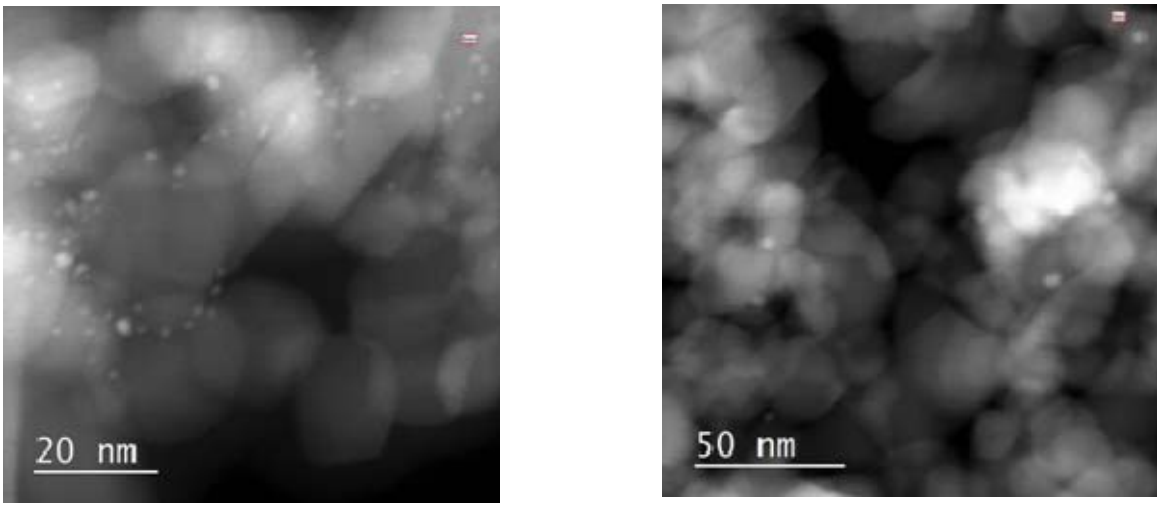

Figure 1: HRTEM images of 2% wt $Au_{144}(SC_2H_4Ph)_{60}/TiO_2$ after 150°C pretreatment (left) and after 250°C (right)

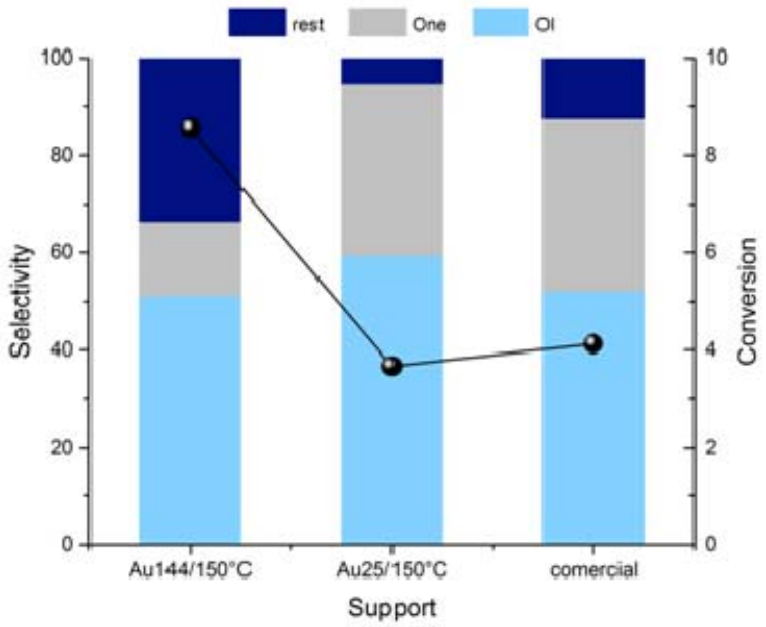

Figure 2: Conversion and selectivity in cyclohexane oxidation after 10h.
The main products are cyclohexanol (ol) and cyclohexanone (one).
Peroxide was used as a iniciator.

CONCLUSION

It was observed that a 150° leads to a partial removal of ligands, activating the catalyst as well as preserving the particle size. $Au_{144}(SC_2H_4Ph)_{60}$ supported in TiO_2 lead to the best values of selectivity and conversion, compared with traditional commercial nanoparticles and with smaller clusters. This high activity may be associated with the unique geometric structure (icosahedron). We can also conclude that TiO_2 not only stabilizes the cluster, but also plays an active role in the reaction. The results here opens doors for further application of thiolate gold clusters in liquid phase reactions.

REFERENCES

[1] Zhang, B.; Kaziz, S.; Li H.; Hevia, M.G.; Wodka, D.; Mazet, C.; Bürgi, T.; Barrabés, N. *J. Phys.Chem. C.* **2015**, 119, 11193