

# Pd DOPING EFFECT ON THE CATALYTIC PROPERTIES OF GOLD NANOCCLUSERS SUPPORTED ON OXIDES

Clara García, Noelia Barrabés\*, Günther Rupprechter

E165 - Institute of Materials Chemistry, TU Wien, Vienna, Austria

## INTRODUCTION

Atomically designed metal clusters offer the possibility to design well-defined and truly homogeneous surfaces leading to optimal catalysts for reaction mechanism studies. Thiolate-protected metal clusters supported on metal oxides have been shown enhanced catalytic activity in several reaction processes, both in liquid phase and gas phase [1]. These structures can be tuned by different strategies: modifying the ligands (ligand exchange reactions), by size (varying the synthetic procedure) or by heteroatom doping (varying the metal composition). In the case of  $Au_{25}(SR)_{18}$  clusters, Pd have a preferential position in the core centre, leading to an increase in stability and reactivity [2,3]. Previously we studied the effect of support and nanocluster size on the catalytic properties in liquid phase oxidation reactions (cyclohexane oxidation) [4,5]. Clear influence was observed, related with the cluster stability. Therefore, we further investigate the effect of Pd doping in the cluster structure stability under pretreatment and reaction conditions, in addition to the catalytic properties.

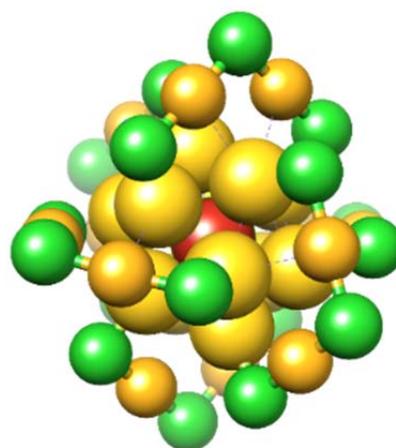


Figure 1.  $PdAu_{24}(SR)_{18}$  core structure  
(●Pd, ● $Au^0$ , ● $Au^+$ , ●S)

## EXPERIMENTS

$PdAu_{24}(SC_2H_4Ph)_{18}$  and  $Au_{25}(SC_2H_4Ph)_{18}$  have been synthesized and supported on  $SiO_2$  and  $TiO_2$  based on reported methods [1]. The samples have been pretreated to remove the ligand shell previous the catalytic test in the cyclohexane oxidation reaction. At each step, fresh, pretreated and after reaction, the samples have been characterized by several techniques (MALDI, UV-Vis, STEM, TPR, XAFS)

## RESULTS AND DISCUSSION

In our recent work [5], kinetic measurements and operando ATR pointed out a significant support effect in the selectivity towards cyclohexanone and cyclohexanone, as well as a pronounced cluster modification towards bulk during the reaction was observed depending on size ( $Au_{25}$  vs  $Au_{144}$ ) and support ( $TiO_2$  vs.  $SiO_2$ ) by HERFD-XAS (Fig. 2). Therefore, introduced the Pd doping aiming for higher structure stability during the reaction and enhanced catalytic behaviour. Preliminary STEM-HAADF analysis of the supported  $PdAu_{24}$  clusters revealed that the particle size is preserved during the catalytic

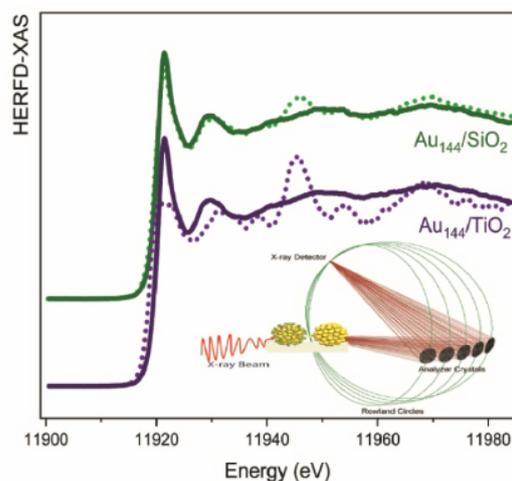


Figure 2. HERFD-XAS spectra before and after reaction

oxidation of cyclohexane reaction. The kinetics test show an enhancement in activity and selectivity to the desired products.

## **CONCLUSION**

The application of supported thiolate protected gold clusters for catalysis is an emerging field. However, to date it was mostly assumed that the clusters remained intact during the catalytic reaction. The current work represents one of the first cluster structure studies, revealing how size, support, composition and reaction environments affect stability, which may help to further develop catalysis by thiolate metal nanoclusters.

## **REFERENCES**

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