INTRODUCTION
Nanoscience has recently revolutionized catalysis R&D, both at academic and industrial levels. To understand and control the catalytic performance of nanoparticles at molecular level is a major challenge and ultimately to bridge the gap between model and real catalysis. Metal clusters are well-defined nano-size systems that contain a precise number of atoms (few to 100) with specific elemental composition (e.g. Au, Ag, Pd,…). Advanced synthesis routed yield nanoclusters with high purity and homogeneity, with well-resolved and unique crystal structure. Their catalytic properties are often unexpected and remarkable, and differ strongly from those predicted by simple scaling laws, due to their quantized electronic and unique geometrical structure. Thiolate protected metal nanoclusters (M\(_n\)(SR)\(_m\)) open up new possibilities to create atomic precise catalytic active sites with resolved structures. A truly monodisperse catalytic surface provides ideal conditions for structure reactivity correlation studies. In our studies, we explore the design of catalytic active sites at atomic level with the monolayer protected metal clusters. Different metal combinations have been explored such as PdAu or PtAu.\(^1\) The interaction with different oxides supports and their properties evolution under different treatments have been studied by several techniques (FTIR, XAFS, XPS, HRTEM…).\(^2\) The final application for catalytic oxidation and photocatalytic reactions, in gas and liquid phase have been explored and analysed in situ operando techniques in order to correlate their catalytic properties with the structure and properties of the cluster catalysts.\(^3,4\)

EXPERIMENTAL
Monometallic and bimetallic thiolated metal clusters have been synthesized by optimized protocols based on Brust method.\(^1\)\(^-\)\(^4\) Their purification and isolation were obtained by SEC (size exclusion chromatography) and HPLC, and analysed by MALDI and UV-Vis. The physical-chemical properties, their structure and their reactivity, were investigated by X-ray Absorption Spectroscopy (XAFS) at several synchrotron sources (SLS, ALBA…), XPS, STEM, STM between others.

RESULTS AND DISCUSSION
The clusters significantly promote molecule activation by enhancing the adsorption energies of the reactant molecules on the catalyst surface. However, the stability under pretreatment and reaction conditions is strongly related with the nature of the support material. Several oxides have been
studied as support material for the Au clusters, among them, cerium oxide (CeO$_2$) turned out to be one of the best in our previous studies. The thiolate ligands around the gold core structure play an important role in the cluster stabilization and their catalytic activity. Once the clusters are supported, the ligands can be thermally removed in order to expose a larger gold surface area to the reactants. Depending on the degree of ligand removal, different catalytic activity and selectivity can be obtained for several oxidation reactions, due to changes in electronic configuration or available sites. In our previous studies, in situ EXAFS measurements indicated that the degree of thiolate ligand removal depend on the heating atmosphere and the support material. S K-edge measurements performed of fresh and used (after cyclohexane oxidation reaction) catalysts pre-treated at different temperatures were studied ex-situ. The results pointed out the different interaction of the thiol ligands depending of the support material after thermal treatment and also after reaction, observed for first time. XANES results at S K-edge show sulphur species at different oxidation states at the different stages. This could be related with the changes in catalytic/selectivity performance of the cluster catalysts in the different oxidation reactions. In the last study we focused on the structure stability of Au$_{38}$/CeO$_2$ under CO oxidation by operando Au L$_3$ edge XAFS. The results denoted the high stability of the Au$_{18}$ cluster structure during the reaction and the requirement of the pre-treatment in order to obtain such stability. In our latest studies, Au$_n$ clusters supported on TiO$_2$ have been studied in photocatalytic reactions. The comparison with the pair gold nanoparticles shows the clear enhancement of the gold nanoclusters in the photocatalytic performance.

CONCLUSION

Monolayer protected clusters have shown their outstanding performance in several catalytic reactions, allowing an unique homogenous and defined surface. Their stability under reaction conditions and their possibility of atomically level design will open a broad number of studies for not only catalytic applications.

REFERENCES