Insights into nanocluster-surface interaction and reactivity

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Metal nanoclusters field is moving towards applications that involve the deposition of clusters on solid surfaces (oxides). We observed the flexibility and mobility of the cluster structure, once supported on surfaces and under reaction conditions by spectroscopic techniques [1]. The fate of the thiolates (ligands) during deposition of the clusters on an oxide support was never considered. This motivated us to study the evolution of the thiolate ligands upon supporting clusters on surfaces like CeO_2. S K-edge XAFS measurements revealed for the first time ligand migration from the gold clusters to the support, manifested by formation of unexpected oxidized sulfur species [2]. Deeper analysis at Au L_3-edge XAFS revealed the participation of the entire staple unit during the migration process.

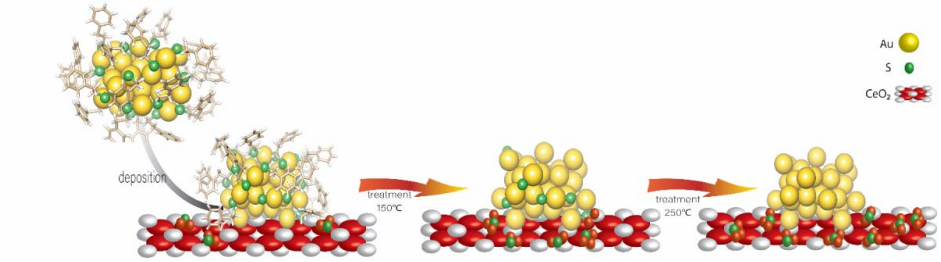

Fig.1 Scheme of ligand migration from $Au_{38}(SR)_{24}$ to CeO_2 during deposition and treatment

New functionalization can be introduced to the nanoclusters by ligand exchange. However, *are the new properties preserved when the cluster is immobilized on a surface?* We explore the extension of ligand engineering on supported $Au_{11}(PPh_3)_7Br_3$ nanoclusters. By several spectroscopic techniques, we could proof the first successful partial functionalization of nanoclusters immobilized on surfaces by ligand exchange, which will allow controlled nanocluster surfaces functionalization [3]

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[2] B. Zhang, A. Sels, G. Salassa, S. Pollitt, V. Truttmann, C. Rameshan, J. Llorca, W. Olszewski, G. Rupprechter, T. Bürgi, and N. Barrabés, *ChemCatChem*, **2018**. *10(23)* 5372-5376

[3] V. Truttmann, I. Illes, A. Limbeck, E. Pittenauer, M. Stöger-Pollach, G. Allmaier, T. Bürgi, N. Barrabés, G. Rupprechter, **2019**, submitted