Small sub-nm metal clusters: the key missing point in many catalytic processes?.

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The discovery of Haruta et al. (T. Hayashi, et al. J. Catal. 1998,178, 566) showing the catalytic activity of oxide-supported gold nanoparticles opened a very exciting field of research in nanocatalysis. Since then much effort was devoted to the understanding of such surprising catalytic activity (see e.g. M. M. Schubert et al. J. Catal. 2001, 197, 113). But, it was not until recently that it was recognized that most of the activity of catalysts synthesized by standard chemical procedures (deposition-precipitation, impregnation, etc.) can be attributed to the presence of small gold clusters containing only a few atoms, with large nm-sized particles being mostly spectators (A. A. Herzing et al. Science, 2008, 321, 1331).

Small metal clusters, are considered to be one of the most exciting areas in the next generation of catalysts (H.Häkkinen et al. Angew.Chem.Int.Ed.2003, 42,1297). However, although different experimental and theoretical results seem to support this idea, there are until now no conclusive evidences for this claim. The main reason for this uncertainty is the difficulty to prepare such tiny entities, which depend very much on the type of preparation, the functional groups attached to them and the supporting material. In the last years we have developed several soft wet-chemical techniques to control the growth of very small sub-nm metal clusters of different materials (Pt,Au,Ag,Cu,..) down to 2-3 atoms (Guillén-Villafuerte et al. Angew.Chem.Int.Ed. 2006, 45, 4266 ; Ledo-Suárez et al. Angew.Chem. Int.Ed. 2007, 46, 8823; Rodríguez-Vázquez et al. Langmuir, 2008, 24, 12690; Selva at al. J.Am.Chem.Soc. 2010, in press). These methods allow, in a simple way, to select and scale up the production of clusters (M.A. López Quintela and J. Rivas. Stable Atomic Quantum Clusters, Production Method Thereof and Use of Same. Patent Applications PCT/ES2006/070121, 2006; WO2007017550A1, 2007), without using strong-binding ligands, like thiols, phosphines, etc, which may inhibit, in some cases, their catalytic properties. In this talk we will summarize the catalytic properties of small metal clusters (< 10-13 atoms) mainly focused on two specific areas: their electrocatalytic properties and also their ability to catalyze and direct the growth of anisotropic structures (rods, prisms,…).