

CONTROL OF THE METAL-OXIDE INTERFACE IN PRE-FORMED GOLD NANOPARTICLES ANCHORED TO INORGANIC OXIDES. IMPLICATIONS FOR CATALYSIS

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A key feature of nanoparticles acting as catalysts is that only a small part of their external surface provides the active sites where the reactions take place. The identification of catalytic active sites is a very vivid area of investigation encompassing a variety of disciplines, from basic research to applied engineering. However, the success is often limited by the nature of the catalysts themselves because the metal nanoparticles usually exhibit a wide range of sizes and facets, preventing accurate relationships between their properties and catalytic performance. Several approaches have been used to prepare nanoparticles on metal oxide supports including incipient wetness impregnation, co-precipitation, deposition-precipitation, ion exchange, gas-phase grafting, co-sputtering, organic capping, and dendrimer and micelle encapsulation [1]. Impregnation and precipitation methods are very simple and scalable, but normally suffer from precise particle size control. In contrast, organic capping and encapsulation methods produce size-controlled nanoparticles whose particle size is established before deposition on the metal oxide support [2-3]. Moreover, the coordinating ligands in the precursor solution and on the oxide surface prevent aggregation of the nanoparticles. In this work, we have prepared a variety of well-defined Au nanoparticles supported on TiO₂, TiO₂/SiO₂, and ZrO₂ from dodecanethiol-capped nanoparticles. When dispersed as fine particles of less than ~10 nm in dimension over selected metal oxides, gold exhibits exceptionally high activity in a variety of reactions. Samples have been characterized by high resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and temperature programmed reduction (TPR), and tested in several catalytic reactions, namely methane partial oxidation and epoxidation of propene for industrial purposes, and water gas shift and carbon monoxide preferential oxidation for fuel cell application. We have studied the contact structure between the Au nanoparticles and the oxide support following activation by cold oxygen plasma and calcination treatments and attempted to correlate it with catalytic activity in order to gain insight into the role of the metal-oxide interface and its effect on catalytic performance.

Our findings show that methane can be selectively oxidized into formic acid with O₂-H₂ mixtures under mild conditions over well-defined Au nanoparticles of about 3-4 nm in size treated under oxygen plasma. Catalytic activity is inhibited by surface stabilizing shells around Au nanoparticles or by thermal activation yielding Au nanoparticles larger than a critical diameter (see figure). In contrast, Au nanoparticles are stabilized following anchoring over inorganic oxide supports. High yields of propene oxide can be formed by epoxidation of propylene by N₂O over well-defined Au nanoparticles of about 5-6 nm supported on anatase and calcined at 673 K. For samples calcined at lower temperature or subjected to oxygen plasma treatment, the interaction between Au nanoparticles and TiO₂ is weak and poor catalytic performance is obtained, suggesting that the complex synergy created at the perimeter interface around Au nanoparticles appears essential for catalytic activity (see figure). The importance of the interaction between Au nanoparticles and the support is also evidenced in the water gas shift reaction by comparing the behavior of several ZrO₂-supported Au samples, with and without epitaxial growth. Finally, active Au catalysts for low-temperature CO preferential oxidation are designed with active metal-oxide interface, and their relevance for miniaturized fuel cell applications is discussed.

References:

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Figures:

