



A combined XPS and PA study of gold nanoparticles deposition on ceria/zirconia mixed oxides

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Abstract – The gold nanoparticles are promises in numerous fields of science and technology, including electronics, catalysis and bioanalysis. Gold-catalysts have been reported as effective catalysts for CO oxidation, CH₄ oxidation, NO_x reduction and water-gas shift reaction. The role of Au particle size and the oxidation state of gold has received great attention is related to the high catalytic activity in the CO oxidation.

In the last few years the gold nanostructured catalysts have attracted rapidly growing attention, due to their potential applicability to various reactions of industrial and environmental interest. It is, due to the various factors, especially electronic (quantum size effect, oxidation state) and optical effects, nature of the support material (state and structure) and the preparation method. My researches focus on the interaction between gold nanoparticles and different support materials, among then cerium and zirconium oxides [1].

In this work, the supported gold nanoparticles were prepared by impregnating the calcined commercial supports (ZrO₂, CeO₂, Ce_{0.58}Zr_{0.42}O₂ and Ce_{0.70}Zr_{0.30}O₂) with an aqueous solution (0.025 mol.L⁻¹) of hydrogen tetrachloroaurate (III)trihydrate (HAuCl₄.3H₂O) for 1 h. The process was carried out in a sand bath to assure the temperature uniformity of the impregnating solution. Samples were gently stirred with a glass stick, filtered and washed with ultra-pure hot water, about 50 °C, to remove chloride ions. Then, the samples were dried at 120 °C, during 12 h. After that period, the system was heated until reaching 600 °C at heating rate of 5 °C.min⁻¹ under air flow (30 mL.min⁻¹), being kept at this temperature for 2 h. The solids were characterized by XDR, SEM, XPS and PA techniques.

The XRD patterns of the samples (Fig.1) showed weak diffraction lines of gold at $2\theta = 38.3^\circ$ and 44.4° corresponding to Au (111). As shows in the PA spectra (Fig.2), the plasmon band at 500-600 nm corresponds to gold spherical nanoparticles, in good agreement with SEM results. Comparison the spectra of the samples, was observed a red shift with decreasing particle size of the 520 nm for the bigger particles to 570 nm for the smaller ones. The increased in the Au content does not contributed for increase the homogenous distribution of Au on surface of the support. The particle size distributions of gold in these two samples are broad, in the range of 20-30 nm. XPS analysis in terms of Ce 3d_{5/2}, bindings energies revealed both Ce⁴⁺ and Ce³⁺ existed on the surface of the samples. The Au 4f_{7/2} core level is slightly shifted, in all samples, towards a lower binding energy (83.0 eV) than that of bulk Au⁰ (84.0 eV). This is attributed to a charge transfer from the supports to the gold particles, as it exceeds the extent of the surface core level shift (-0.4 eV) that could be expected from the nanometric size of the gold particles. These could be explained by the differences in the metal-support interactions in all materials.

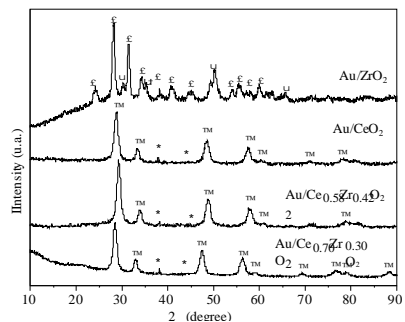


Figure 1: XDR patterns of the Au/CeO₂, Au/ZrO₂ e Au/Ce_xZr_{1-x}O₂ catalysts calcined in air at 600 °C. () cubic-type structure of CeO₂; () monoclinic and () structure of ZrO₂; and (*) gold.

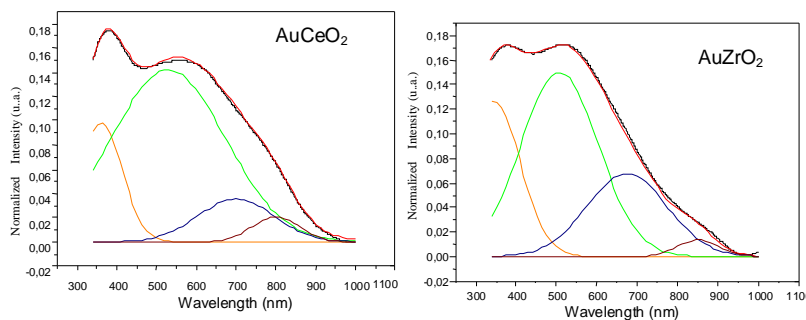


Figure 2: Infrared photoacoustic spectroscopy (PA) spectra of the catalysts. (a) AuCeO₂; (b) AuZrO₂

[1] I. Tuzovskava, N. Bogdanchikova, A. Simakov, V. Gurin, A. Pestryakov, M. Avalos and M. H. Farias. Chem. Phys. 338, 23 (2007).