

## Dynamic transformations of gold species supported on nanostructured alumina, ceria and ceria-zirconia mixed oxides prepared by sol-gel

Andrey Simakov<sup>1,\*</sup>, Elena Smolentseva<sup>1</sup>, Felipe Castillon<sup>1</sup>, Miguel Estrada<sup>2</sup>, Eunice Vargas<sup>3</sup>, Ricardo Rangel<sup>4</sup>, Brenda Acosta<sup>4</sup>, Sergio Fuentes<sup>1</sup>, Vladimir Sobolev<sup>5</sup>, R. Kenzhin<sup>5</sup>

<sup>1</sup>Centro de Nanociencias y Nanotecnología, UNAM, Ensenada, B.C., 22800 (México)

<sup>2</sup>Posgrado en Física de Materiales, CICESE, Ensenada, B.C., 22800 (México)

<sup>3</sup>Posgrado en Nanomateriales, UABC, Ensenada, B.C., 22800 (México)

<sup>4</sup>Departamento de Posgrado, Facultad de Ingeniería Química, UMSNH, C.P. 58060, Morelia, Michoacán (México).

<sup>5</sup>Boriskov Institute of Catalysis, Novosibirsk, 630090 (Russia)

\*andrey@cnyun.unam.mx

### Introduction

While gold has been demonstrated to be chemically most inactive among noble metals due to its electronic configuration [1], matrix-trapped finely dispersed gold species are known to be highly reactive for CO oxidation even at low temperature [2], particular those supported on nano crystalline ceria [3,4]. The number of structural defects of ceria could be controlled by size of ceria crystals and also by partial replacement of Ce atoms with Zr atoms [5].

The present paper is devoted to study the dynamic transformations of gold species supported on nanostructured ceria pure or stabilized in alumina as pure oxide or as that doped with Zr in time of sample pretreatments and CO oxidation in dynamic regime.

### Materials and Methods

The supports based on nano crystalline pure alumina, pure ceria, alumina doped by ceria (10 and 30%), massive CeZrO<sub>2</sub>, alumina doped with CeZrO<sub>2</sub> (10 and 30%) have been prepared by sol gel technique described elsewhere [6] using organic precursors. The samples of nanostructured ceria were prepared by high temperature treatment at high pressure of ceria obtained by sol-gel technique. Gold (3wt.%) catalysts were prepared by DP technique using urea and HAuCl<sub>4</sub> salt as a gold precursor.

The prepared samples were tested by different techniques such as UV-Vis spectroscopy *in situ* based on fiber optics, XPS, TEM, XRD, FTIR of CO adsorbed, transient analysis of CO oxidation using mass-spectroscopy, TPR, TPD and TPO, by pulses of hydrogen and oxygen isotopic exchange analysis.

### Results and Discussion

The continuous monitoring of gold species under treatments of freshly prepared samples in different gases (O<sub>2</sub>, H<sub>2</sub> or He) by UV-vis and FTIR *in situ* revealed that the process of surface species transformation could be divided conditionally into two steps. There are Au(OH)<sub>3</sub> species formed due to precursor hydrolysis and finely dispersed ones obtained by chemisorption of gold precursor molecules. Under the samples heating at temperature range 25-200°C it was detected thermal decomposition of gold precursor with slight change of its structure accompanying with water and CO<sub>2</sub> desorption.

The formation of reduced gold species proceeds within temperature range 200-350°C accompanied with consumption of hydrogen or oxygen from the gas phase and desorption of ammonia and products of its oxidation. Application of liquid phase reducing agent effective at room temperature (formaldehyde) reveals presence of two types of metal gold species formed by reduction of gold complexes stabilized on the support surface and Au(OH)<sub>3</sub> nanoparticles, respectively.

Ceria based samples characterized with different mobility of surface oxygen species due to their difference in structure are highly effective to stabilize finely dispersed gold nanospecies-clusters which manifest reversible red-ox transformations even at room temperature at CO oxidation or at sample expose to air.

The measurements of catalytic activity at room temperature reveal high affectivity of finely dispersed gold nanospecies-clusters in prepared catalysts in CO oxidation with TOF within range 1-0.3 mol CO/mol Au/s. By means of transient analysis and spectroscopic measurements *en operando* it was proved directly that reduced gold species are less active in CO oxidation than those partly oxidized.

### Significance

The present work summarizes experience in the monitoring of gold species supported on differently prepared nanostructured ceria based supports characterizing with high catalytic activity in CO oxidation. The development of new nano structured materials is quite promising for the design of new effective catalysts.

### Acknowledgements

The authors acknowledge E.Flores, I.Gradilla, J. A. Díaz, P. Casillas, M. Sainz, F. Ruiz, E. Aparicio and J. A. Peralta for their technical support. This research project was supported by DGAPA-PAPIIT (UNAM, Mexico) through Grants No. IN 120706-3, IN110208 and CONACyT research grant 50547-Q.

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