

## In-situ XAS Characterization of Low Gold Content Au/TiO<sub>2</sub> and Au/CeO<sub>2</sub> Catalysts during Preferential CO Oxidation in Hydrogen

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### Introduction

Although gold is a highly unreactive metal, gold finely dispersed on the surfaces of metal oxides is catalytically active for a number of reactions, including CO oxidation and the preferential CO oxidation in hydrogen. The hypotheses that have been postulated to explain the catalytic activity of supported gold for CO oxidation are varied and contradictory [1]. Some views point towards zerovalent gold nanoparticles as the responsible for the remarkable low-temperature activity of supported gold [2], but the presence of cationic gold species in working supported gold catalysts has been proposed too [3–6]. Recently, a small fraction of the supported gold in WGS catalysts was shown to be cationic and responsible for the catalytic activity [5]. However, under some experimental conditions, it has been claimed that Au<sup>δ+</sup> species are reduced to metallic gold due to an interaction with the support and/or the reactive gases under typical reaction conditions for PROX of CO in H<sub>2</sub> or WGS [6]. Furthermore, the strong interaction of the gold species and the different supports increases the difficulty in the analysis.

In this work, we report the in-situ X-ray absorption spectroscopy (XAS) investigation of the structure and oxidation state(s) of low content CeO<sub>2</sub>- and TiO<sub>2</sub>-supported gold catalysts under both working CO oxidation and PROX of CO in H<sub>2</sub> conditions.

### Materials and Methods

The catalysts were prepared by a modified deposition-precipitation method using small amount of HAuCl<sub>4</sub> as gold precursor to allow low-gold content (0.25–2 Au wt %) deposition and the corresponding metal oxide support (TiO<sub>2</sub> or CeO<sub>2</sub>). The fresh supported gold samples were washed and rinsed several times and checked for gold content by ICP. The samples were characterized by XRD, TEM, N<sub>2</sub>-adsorption, and UV-vis spectroscopy. In-situ XAS characterization was performed with an in-situ XAS cell at the Laboratorio Nacional de Luz Sincrotron (LNLS) in Campinas, Brazil at beamlines D06A-DXAS and D04B-XAFS1.

### Results and Discussion

Under similar preparation procedures and loadings, CeO<sub>2</sub> and TiO<sub>2</sub>-supported gold samples show widely different Au species distribution. TiO<sub>2</sub>-supported samples have only detectable zerovalent gold signals by XANES, consistent with previous results [7]. However, we can not rule out the presence of cationic gold. CeO<sub>2</sub>-supported gold samples clearly show

the white-line associated with cationic Au, which is dependent on the gold content. These results are shown in Figure 1. An EXAFS analysis indicates that the structure of the catalysts changes with the percentage of gold in the samples.

An analysis of the reaction results indicates that in the case of PROX, the oxidation of CO depends on the zerovalent and cationic gold ratio that increases with gold content on CeO<sub>2</sub>-supported samples. Light-off temperatures, conversions and selectivity of both CO and H<sub>2</sub> oxidations depends also on the ratio of zerovalent and cationic gold.

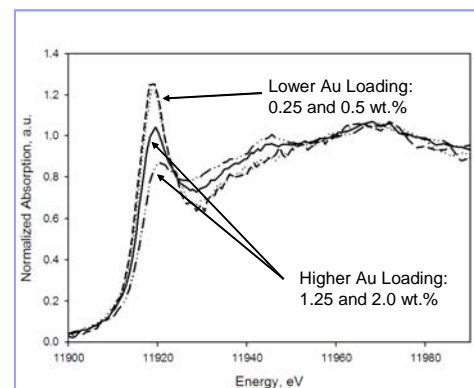


Figure 1. XANES data characterizing Au/CeO<sub>2</sub> catalysts with different Au loadings.

### Significance

This work contributes to the fundamental understanding of supported gold catalysts by the identification of the gold active species under working conditions for PROX of CO in H<sub>2</sub>, a relevant reaction for fuel-cells technology and a H<sub>2</sub>-fuel economy.

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