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## Applied Catalysis A: General

Selective CO oxidation with nano gold particles-based catalysts over Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>Nielson F.P. Ribeiro<sup>a</sup>, Fabiana M.T. Mendes<sup>c</sup>, Carlos A.C. Perez<sup>a</sup>, Mariana M.V.M. Souza<sup>b,a</sup>, Martin Schmal<sup>a,\*</sup><sup>a</sup> NUCAT/COPPE/UFRJ, Centro de Tecnologia, Bloco G, sala 128, CEP 21945-970 Rio de Janeiro/RJ, Brazil<sup>b</sup> Escola de Química, Universidade Federal do Rio de Janeiro, Centro de Tecnologia, Bloco E, sala 206, CEP 21940-900 Rio de Janeiro/RJ, Brazil<sup>c</sup> INMETRO-DIMAT – Divisão de Materiais, Divisão de Metrologia de Materiais Av. Nossa Senhora das Graças, 50, Prédio 3 CEP 25250-020 Xerém, Duque de Caxias, RJ, Brazil

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## ABSTRACT

We present the preparation, characterization and catalytic evaluation of gold-based catalysts over Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and 10% ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in selective CO oxidation. Oxidation and reduction pretreatments were evaluated using in situ X-ray diffraction, and the size of gold particles was determined. All catalysts contained gold particles in the range of 2–5 nm, with as-prepared samples containing a mixture of gold species (Au<sup>3+</sup> and Au<sup>0</sup>). The catalytic tests showed complete CO oxidation at temperatures lower than 100 °C, with Au/ZrO<sub>2</sub> sample presenting the best performance. Both the support and pretreatment conditions were found to cause changes to gold species. In situ X-ray diffraction patterns indicated the presence of different gold phases and of nanometer-scale crystallites of gold, which was confirmed by transmission electron microscopy results. It was also found that cationic gold improved the activity of Au/ZrO<sub>2</sub>. Concerning stability, time on stream tests showed that all samples were stable to coke deposition and sintering.

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## 1. Introduction

One of the challenges of recent catalytic research has been to develop catalysts that are capable of eliminating residual CO at the end of the hydrogen production process. Achieving this goal is essential for good operation of proton exchange membrane fuel cells (PEMFCs), because CO at concentrations higher than 10 ppm poisons the anode catalyst, which decreases the efficiency of PEMFCs [1]. The selective CO oxidation reaction (SELOX) is the most economically and technologically promising process for cleaning this residual CO, as compared to other processes [2–5].

It is well known that bulk gold catalyst has low activity, which is mainly attributed to its low chemisorption strength as well as its electronic configuration [6–8]. However, when gold is highly dispersed on a metallic oxide, its surface chemistry drastically changes, producing a new material that is highly active and selective to the oxidation reaction [9]. Gold-based catalysts also offer advantages over traditional platinum-based catalysts. Among these advantages are high activity at low temperatures and a relatively stable price [9,10].

The synthesis of gold-based catalysts with ultra-fine particles has usually been carried out by deposition/precipitation. However, chemical vapor deposition [11], co-sputtering [12], co-precipitation [9], and adsorption of gold colloids [13] have also been successfully used. The utilization of incipient wetness or wet impregnation will hardly provide high metallic dispersion, mainly because of the low melting point of gold (1063 °C) and large amount of residual chlorine [11]. Another important factor that has a strong influence on activity and reaction mechanism is the choice of the support, which can fall into the following categories: (a) supports that are active in reaction, acting as a source of oxygen for the reaction, such as TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>; and (b) supports that are inert in reaction, such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, MgO [14].

Although studies on gold supported catalysts have been widely reported in the literature, the use of mixed oxides to combine the chemical properties of reducible oxides with the physical properties of traditional oxides, such as Al<sub>2</sub>O<sub>3</sub>, has been little studied. To our knowledge, the literature reports only on the work of Gluhoi et al. [15] and Centeno et al. [16], both on Au/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and that of Radwan et al. [17], on Au/Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>.

The zirconia support is a reducible oxide in the presence of a metal; however, the surface area of this material is relatively low. In order to increase the surface area and the dispersion of the oxide, ZrO<sub>2</sub> was anchored over alumina by Souza et al. [18], where

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