

# Nanostructured Au/CeO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> catalysts for the CO oxidation and the water-gas shift reactions

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## Introduction

Au-CeO<sub>2</sub> and Au-Fe<sub>2</sub>O<sub>3</sub> are very active catalysts reported to date for the catalytic oxidation of carbon monoxide by various oxidants, such as oxygen in low-temperature dry CO oxidation [1, 2], and the PROX reaction in the presence of large amount of hydrogen and water [3, 4]; and water in low-temperature WGS reaction [5-7]. There is conflicting information in the literature about the oxidation state of gold during the dry CO oxidation reaction. In this work, fundamental studies of the interactions of gold/ cerium oxide and gold/ iron oxide with CO are reported to shed light on the activity/stability of various structures in oxygen and water. We compare the activity of nanostructured Au-CeO<sub>2</sub> and Au-Fe<sub>2</sub>O<sub>3</sub> catalysts for both the low temperature CO oxidation and the WGS reactions and try to identify the common or distinct structures of gold responsible for the activity on these two different supports.

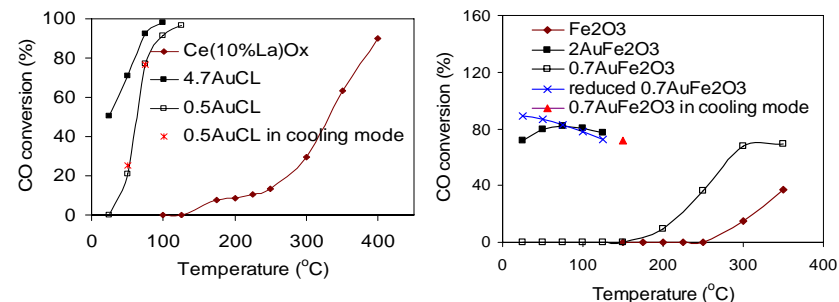
## Materials and Methods

High-content (~5at.%) gold-ceria catalysts were prepared by deposition precipitation on nanocrystalline ceria and low-content (0.5at.%) gold-ceria catalysts prepared by leaching weakly bound gold from ceria [5]. The 2 at.% gold-iron oxide was purchased from World Gold Council (WGC) and its leached derivative 0.7at.%gold-iron oxide was prepared by NaCN leaching of the parent. Low temperature CO oxidation and WGS reaction light-off tests and kinetic measurements were conducted at atmospheric pressure with the catalyst in powder form in a packed-bed flow reactor. The gas streams were analyzed by a HP-6890 gas chromatograph equipped with a thermal conductivity detector. Several techniques such as FTIR, XANES, XPS, TPR and UV-VIS were used to characterize the catalysts.

## Results and Discussion

High-content gold-ceria and gold-iron oxide catalysts contain both Au<sup>0</sup> nanoparticles and oxidized gold clusters. Gold species weakly bound to ceria or iron oxide can be removed by sodium cyanide at pH ≥12. The leached materials only retain the strongly bound oxidized gold species. The activity of the leached gold-iron oxide catalyst in CO oxidation is approximately two orders of magnitude lower than that of the parent material. CO adsorption study on gold-cerium oxide by FTIR showed that the CO-Au<sup>+</sup> bond on the oxidized Au clusters is much stronger than on metallic Au nanoparticles on cerium oxide [8]. Catalytic study shows that the dry CO oxidation reaction is much more facile on Au<sup>0</sup> than on oxidized gold clusters, as found here for both Au-CeO<sub>2</sub> and Au-Fe<sub>2</sub>O<sub>3</sub> catalysts. In Figure 1, CO oxidation light off temperatures for the Au<sup>0</sup> containing catalysts are much lower than those for catalysts contain only oxidized gold species. XANES, XPS, TPR and UV-VIS analyses show that reduction of the leached samples containing only oxidized gold is needed to activate the catalyst. This can be accomplished by pre-reduction in hydrogen or by long exposure to the CO/O<sub>2</sub> reaction gas mixture at temperatures above 120 °C for AuCeO<sub>2</sub> or 350 °C for AuFe<sub>2</sub>O<sub>3</sub>.

Well dispersed metallic gold nanoparticles provide the active sites for the low temperature CO oxidation reaction on both CeO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. On the other hand, the WGS reaction lights off above 100°C, similarly for samples containing gold nanoparticles and oxidized gold species strongly bound with the support (parent) or their derivatives prepared by leaching out the weakly bound gold, and containing only the strongly bound oxidized gold species. The WGS reaction activation energy is the same over both the Au-CeO<sub>2</sub> and Au-Fe<sub>2</sub>O<sub>3</sub>, 49±7 kJ/mol. This points to activation of -OH from the oxide support and the strongly bound CO on Au<sup>δ+</sup> as a plausible mechanism for this reaction.



**Figure 1.** CO conversion in the CO oxidation over gold-ceria and gold-iron oxide catalysts. Gas mixture: 2%CO-1%O<sub>2</sub>-balance He; space velocity: 100,000/h.

## Significance

In the literature, most of the catalysts incorporating Au<sup>0</sup> also contain cationic gold and it is very difficult to separate the function of each. In this paper, we report new data on the catalytic activity and structure of nanoscale Au/Fe<sub>2</sub>O<sub>3</sub> and Au/CeO<sub>2</sub> in low-temperature CO oxidation and the WGS reactions. Low-content gold catalysts with only oxidized gold species present help to distinguish the reaction activity of oxidized gold from the metallic gold nanoparticles.

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