

Catalytic Gold Nanoparticles on an Iron Oxide Surface: A Scanning Tunneling Microscopy/Spectroscopy Study

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Introduction

Gold, initially regarded as a catalytically inert precious metal, has been studied intensively for the past few decades ever since the discovery that ultrafine gold particles (<10nm) dispersed on metal oxides show surprisingly high catalytic activity for H₂ and CO oxidation. [1] Multiple hypotheses have been proposed to explain the catalytic activity of supported gold, in particular for the water-gas shift (WGS) reaction and the oxidation of CO on oxides. The complex nature of the geometric and electronic structures of gold nanoparticles dispersed on high surface area supports contributes significantly to the difficulty of identifying the role of gold in Au-oxide catalytic systems. However, charged gold nanoparticles in the recent investigation of the low-temperature WGS reaction on Au/ceria catalysts by Flytzani-Stephanopoulos and co-workers, have been observed to be active sites for the reaction while neutral Au nanoparticles are simply spectators. [2] To elucidate the nature of the enhanced reactivity of gold in these oxide systems, we have prepared a model catalyst system consisting of vapor deposited gold on a single crystal iron oxide surface in ultrahigh vacuum. This sample has been used to investigate the site specific adsorption of Au nanoparticles and adatoms on the oxide and the relationship between the size of the formed Au nanoparticles and their oxidation state using Scanning Tunneling Microscopy and Spectroscopy. The observation of adsorption sites and electronic structures of Au species on this iron oxide support provides strong evidence that atomic gold adatoms are likely positively charged and responsible for CO adsorption at low temperature.

Materials and Methods

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a VT STM (Omicron GmbH). A natural single crystal α -Fe₂O₃(0001) sample was cleaned *in situ* by repeated cycles of Ar⁺ ion sputtering and annealing in vacuum at $T = 1000$ K. Approximately once in every 10 cycles, the sample was annealed with 1×10^{-6} torr of oxygen at $T = 1000$ K in order to achieve the desired surface structure, 2×2 Fe₃O₄ (111), and to efficiently remove carbon. Multiple cycles of sample preparation reduce the bulk Fe₂O₃(0001) sufficiently to develop a conducting thin layer of Fe₃O₄(111). This 2×2 Fe₃O₄(111) surface film was used as the supporting oxide for the gold in this study. After obtaining a clean and well-ordered 2×2 Fe₃O₄ (111) surface, gold was evaporated onto the Fe₃O₄ (111) surface from a homemade Au evaporator attached to the UHV chamber's loadlock. The flux of gold particles was monitored

with a quartz crystal microbalance. The Au/Fe₃O₄ was imaged at room temperature and carbon monoxide adsorption on the Au/Fe₃O₄ was investigated at low temperature.

Results and Discussion

Gold forms two electrically distinct types of nanoparticles on an iron oxide surface upon annealing a multilayer Au/Fe₃O₄(111) at 500°C: large nanoparticles (~8nm) and adatoms. The signatures of site-specific adsorption (see Figure 1) and quantum confinement of electrons for Au adatoms (see the red curve in Figure 2) are readily apparent in the present data when compared to a previous study of pristine iron oxide. [3] STS measurements show that large nanoparticles (~8nm) are metallic (the green curve of Figure 2) while single gold adatoms appear to be bonded to the oxygen sites on the Fe₃O₄(111) surface (the red curve of Figure 2). Site-specific adsorption at oxygen surface atoms and the size sensitive nature of the electronic structure (Coulomb blockade) suggest that Au adatoms are positively charged. When this Au/Fe₃O₄(111) catalyst system is dosed with CO at 260K, there is evidence for CO adsorption at gold adatom sites. These observations are consistent with the proposal that nonmetallic, positively charged, “invisible” Au particles are the catalytically active species for the water gas-shift reaction on Au/metal oxide surfaces.

Significance

Au adatoms on a reduced Fe₃O₄(111) surface are strongly adsorbed on oxygen sites, likely positively charged, and responsible for CO adsorption.

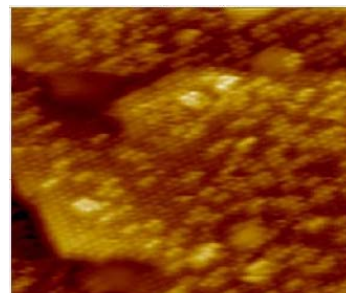


Figure 1. An STM image of CO/Au/Fe₃O₄ (111) at 260K after dosing 0.1L of CO on the annealed Au/Fe₃O₄(111)

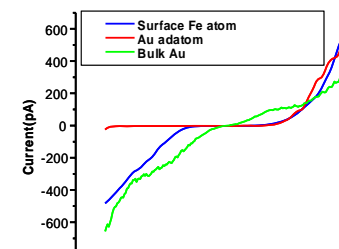


Figure 2. I(V) curves on surface Fe atoms (blue), Au adatoms (red), and large Au nanoparticles (green)

References

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