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 \( \text{H}_2 \) and \( \text{CO} \) 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 \( \text{CO} \) 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-Stephanopoulou 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 \( \text{CO} \) 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-\( \text{Fe}_3\text{O}_4\)(0001) sample was cleaned in situ by repeated cycles of \( \text{Ar}^+ \) ion sputtering and annealing in vacuum at \( T = 1000 \text{ K} \). Approximately once in every 10 cycles, the sample was annealed with \( 1 \times 10^5 \text{ torr} \) of \( \text{O}_2 \) at \( T = 1000 \text{ K} \) in order to achieve the desired surface structure, \( 2 \times 2 \) \( \text{Fe}_3\text{O}_4 \) (111), and to efficiently remove carbon. Multiple cycles of sample preparation reduce the bulk \( \text{Fe}_3\text{O}_4 \) (0001) sufficiently to develop a conducting thin layer of \( \text{Fe}_3\text{O}_4 \) (111). This \( 2 \times 2 \) \( \text{Fe}_3\text{O}_4 \) (111) surface film was used as the supporting oxide for the gold in this study. After obtaining a clean and well-ordered \( 2 \times 2 \) \( \text{Fe}_3\text{O}_4 \) (111) surface, gold was evaporated onto the \( \text{Fe}_3\text{O}_4 \) (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/\( \text{Fe}_3\text{O}_4 \) was imaged at room temperature and carbon monoxide adsorption on the Au/\( \text{Fe}_3\text{O}_4 \) 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/\( \text{Fe}_3\text{O}_4 \)(111) at 500°C; large nanoparticles (~8nm) and adatoms. The signatures of site-specific adsorption (see Figure 1) and quantum confinement of electrons 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 \( \text{Fe}_3\text{O}_4 \)(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/\( \text{Fe}_3\text{O}_4 \)(111) catalyst system is dosed with \( \text{CO} \) at 260K, there is evidence for \( \text{CO} \) 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 \( \text{Fe}_3\text{O}_4 \)(111) surface are strongly adsorbed on oxygen sites, likely positively charged, and responsible for \( \text{CO} \) adsorption.

References