Electrocatalysis

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Enhanced Activity for Electrocatalytic Oxidation of Carbon Monoxide on Titania-Supported Gold Nanoparticles**

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Since a paper by Haruta et al.[1] in 1989 highlighted the critical role of both dispersion and support on the catalytic activity of Au for the gas-phase oxidation of CO, much attention has focused on the optimization of the catalyst structure as well as understanding the reasons for the observed enhanced catalytic activity. The field has been reviewed by several authors[2–7] and there is a general agreement that the Au nanoparticles dispersed on certain metal oxide substrates are much more effective catalysts than the bulk metal for several gas-phase oxidations. Titanium dioxide is a preferred substrate and several authors have investigated the influence of the size of the Au particles on the rate of CO oxidation[8–11] by using this substrate; recent work concludes that there is a maximum in activity when the mean diameter is approximately 3 nm. It has also been shown that moisture increases substantially the rate of CO oxidation.[12,13] There have, however, been no previous reports demonstrating similar promoted catalysis by supported nanoparticles in electrocatalysis.

The application of nanoparticle Au catalysts within fuel cell systems is of considerable interest.[14] There have, however, been no reports of studies of the anodic oxidation of CO on Au nanoparticle catalysts. We have recently described a high-throughput approach to the study of particle-size effects and the influence of the substrate on the performance of supported electrocatalysts.[15,16] It is based on the physical vapor deposition of the catalyst using a unique system that employs source shutters to achieve a controlled gradient of depositing elements across a substrate or an array of pads that are appropriate for combinatorial screening of new materials.[17] The use of 10 × 10 arrays of electrodes combined with instrumentation that allows the simultaneous measurement of voltammetric responses at each of the electrodes[18,19] allows the rapid accumulation of a large number of data points. The application of rotating disc electrodes fabricated in similar ways allows checks on the reliability of the data to be performed.[15,16] These procedures have now been applied to the definition of the influence of supported metal particle size on the oxidation of CO on Au supported on slightly reduced titania and carbon substrates. Baeck et al.[20] have recently described a combinatorial approach to the determination of the influence of Au particle size on the activity of anodic CO oxidation, but their particles were substantially larger than those obtained in the synthetic procedure used herein. The oxidation of CO on polycrystalline Au in acid solution gives simple voltammetry with well-formed waves/peaks negative to potentials where Au oxide is formed on the surface.[21,22] Although it is clear that, at a rotating disc electrode, these waves have mass-transport-controlled plateaux and also that adsorption of CO at polycrystalline Au is weak, the mechanism remains uncertain. Moreover, CO oxidation has also been studied at single-crystal and other Au surfaces and although the voltammetric response remains similar, there is evidence that the extent of CO adsorption (as determined by stripping voltammetry and IR spectroscopy) varies strongly with the nature of the Au surface.[23–25]

Figure 1 shows voltammograms for solutions of 0.5 M $HClO_4$ saturated with CO over the potential range from 0.0 V to +0.7 V versus a reversible hydrogen electrode (RHE) at disc electrodes rotated at 900 rpm. Curve (a) is recorded at a surface prepared as Au nanoparticles with a mean diameter of 2.8 nm on TiO_x ($x \approx 1.96$). Curve (b) is for a Au disc and curve (c) is for an uncoated TiO_x surface. With all three electrodes, no significant current was found over the potential range shown when the CO was removed by passing a stream of argon through the solution. It can immediately be seen that the Au nanoparticles are effective catalysts for CO oxidation. There is a substantial potential range in which oxidation of CO occurs at the nanoparticles, but not at bulk Au or unmodified TiO_x. Moreover, the current densities for CO oxidation at the Au-nanoparticle-covered surface are substantial; at +0.5 V, the current density is approximately

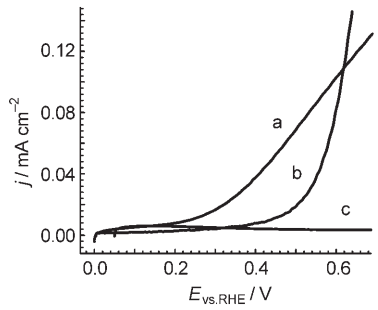

Figure 1. Voltammograms for disc electrodes in CO-saturated 0.5 M $HClO_4$, a temperature of 298 K, a rotation rate of 900 rpm, and a potential scan rate 20 mV s^{-1}. a) Au nanoparticles (mean diameter 2.8 nm) on TiO_x, b) polycrystalline Au, and c) TiO_x. j = current density (with respect to geometric area).

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25% of the estimated mass-transport-controlled value. Of course, as reported in the literature,[21–25] anodic oxidation of CO occurs at the more-positive potential. However, there are no previous reports of CO oxidation at potentials as low as +0.2 V versus the RHE.

To quantify the effect further and to define the influence of the size of the Au nanoparticles, a series of potential step experiments were carried out by using 10×10 arrays of electrodes with different amounts of deposited Au on both TiO_x and carbon as the substrate; the mean diameters of the Au nanoparticles as a function of the position of the electrode within the array were determined by TEM as previously described.[15] The potential of the electrodes were stepped in 100 mV intervals, each step 90 s duration, and the current response was recorded again by using an electrolyte consisting of 0.5 M perchloric acid saturated with CO. Examples of such experiments are shown in Figure 2. With the Au/TiO_x electrode, the rate of CO oxidation clearly increases as the potential is made more positive and it can be seen that the activity is maintained throughout the 90 s hold at each potential. In contrast, no oxidation is observed within the potential range investigated for the Au/C electrode. The responses of five 10×10 arrays with Au/TiO_x electrodes were analyzed to determine the influence of Au particle size. In Figure 3, the results are illustrated for two potentials and the data are presented as plots of current density (based on the total Au/electrolyte interface as calculated from TEM images and assuming that the Au centers are hemispherical[15,16]) versus the mean nanoparticle diameter. The conclusions are clear and striking. Nanoparticles with diameters below a critical size (≈1.5 nm) are inactive but above this critical diameter, the specific activity increases steeply and then passes through a maximum. This maximum occurs with a nanoparticle diameter close to 3 nm. As expected, the specific activity also increases as the potential is made more positive. The number of data points achieved in five experiments by using single 10×10 electrode arrays should also be emphasized.

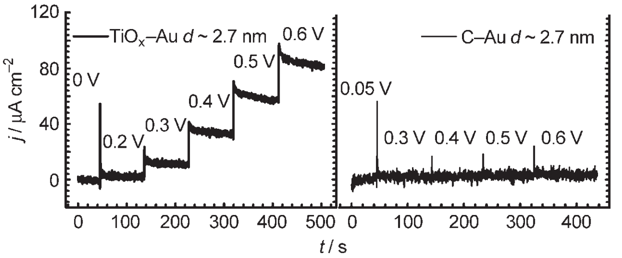

Figure 2. Current density (geometric) versus time response to potential steps on TiO_x- (left) and C-supported (right) Au nanoparticles (mean diameter 2.7 nm) in CO saturated 0.5 M $HClO_4$. Measurements were made in 0.5 M $HClO_4$ at 298 K.

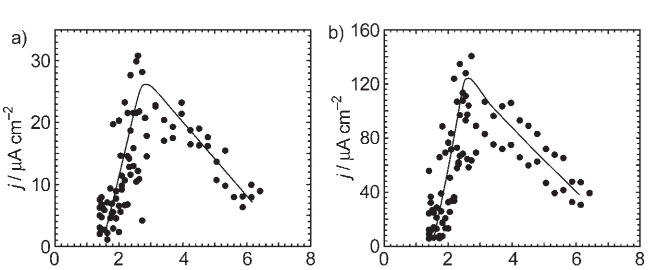

Figure 3. Dependence of the specific activity (mean diameters of the Au nanoparticles as a function of the position of the electrode within the array were determined by TEM) of anodic CO oxidation on the mean nanoparticle diameter of TiO_x-supported Au. a) 0.3 V, b) 0.5 V versus the RHE. Measurements were made in 0.5 M $HClO_4$ at 298 K. d = mean particle diameter.

We reemphasize that activity for the anodic oxidation of CO over the potential range +0.2 to +0.5 V versus the RHE is not observed for polycrystalline Au or carbon-supported nanoparticles in the same size range. In the case of the heterogeneous catalysis of CO oxidation, the promoting supports are metal oxides, most notably titania,[1–13] and the specific activity also shows a maximum with nanoparticles that have a mean diameter of 3 nm.[8–11] This close analogy leads us to suggest that the mechanism for the induced activity in the electrocatalytic and gas-phase systems have common origins despite the fact that the oxidant in the electrochemical case is provided through the activation of water (rather than oxygen) in the provision of the surface oxidant of a Langmuir–Hinshelwood reaction. Of the mechanisms proposed to account for this activity, the results here suggest that a mechanism based on the reaction of a substrate-accommodated oxidant diffusing and reacting at the perimeter of the nanoparticles[8,26] is unlikely; there is no evidence that titania can activate water to produce such an oxidant (OH) at these low potentials. One alternative is that structural factors, and the availability of low coordinate Au atoms, on small Au nanoparticles on titania make them optimal for CO adsorption or water activation. This is analogous to the suggestion that these sites stabilize CO or oxygen.[10,27–29] Indeed, there is strong evidence of a surface structural dependence in CO electrocatalytic oxidation on Au.[25] It is also apparent that structural and electronic modifications associated with substrate-induced strain in the Au particle[30,31] or charge transfer[32] can to some extent contribute to the modification of Au nanoparticles on titania substrates. The alternative is that a quantum size effect is responsible for the Au activity in this size regime at two-dimensional Au particles,[9] and the high CO oxidation activity for continuous Au bilayer structures on titania has been cited as evidence that the role of edge effects and direct mediation of the underlying titania is less important.[33] Although the origin of the support-induced activity and particle-size dependence in Au heterogeneous catalysis continues to be debated,[34] we show herein that the models developed must also be able to account for the similar behavior we have described herein in electrocatalytic oxidation of CO. Although there appears to be an important role played by water in heterogeneous oxidation of CO[12,13,35] and it may be tempting to make comparison with the electrochemical interface, it is not evident at present how the proposed mechanisms for water-induced promotion of the reaction may be pertinent to the electrocatalytic process. Similarly it is not evident that there is any relationship between CO electrocatalytic oxidation and the promotion of the water–gas shift reaction on supported Au particles,[36] which appears to be promoted by defect stabilized cationic Au.[37]

In summary, we suggest that the particle size and substrate-dependent activity observed here for the electrochemical oxidation of Au provides an opportunity to consider the origin of the unique activity of supported Au nanoparticles in a new light. These results also demonstrate that manipulation of catalytic activity by particle size and support in electrocatalysis provides an important tool for the future optimization of electrocatalysts.

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