

## Metallic Corner Atoms in Gold Clusters Supported on Rutile Are the Dominant Active Site during Water–Gas Shift Catalysis

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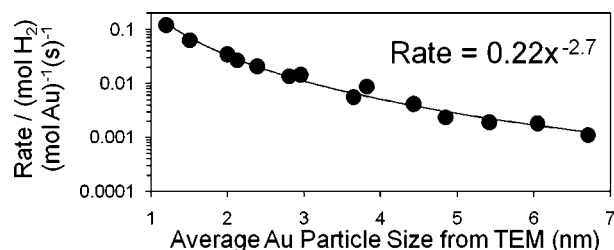
**Abstract:** Au/TiO<sub>2</sub> catalysts used in the water–gas shift (WGS) reaction at 120 °C, 7% CO, 22% H<sub>2</sub>O, 9% CO<sub>2</sub>, and 37% H<sub>2</sub> had rates up to 0.1 moles of CO converted per mole of Au per second. However, the rate per mole of Au depends strongly on the Au particle size. The use of a nonporous, model support allowed for imaging of the active catalyst and a precise determination of the gold size distribution using transmission electron microscopy (TEM) because all the gold is exposed on the surface. A physical model of Au/TiO<sub>2</sub> is used to show that corner atoms with fewer than seven neighboring gold atoms are the dominant active sites. The number of corner sites does not vary as particle size increases above 1 nm, giving the surprising result that the rate per gold cluster is independent of size.

The catalytic reactivity of nanoparticles has been attributed to causes which originate either from differences in their electronic structure or from the different geometry of nanoparticles versus bulk surfaces. The inert nature of bulk gold as compared to gold nanoparticles makes gold catalysts ideal to study the origin of the activity of nanoparticles. In literature concerning gold catalysis, perimeter sites,<sup>1</sup> low coordinated corner sites,<sup>2</sup> cationic gold,<sup>3</sup> and bilayers<sup>4,5</sup> of gold have been proposed as the active species. The many types of sites present on supported catalysts increase the difficulty of identifying a dominant site. Here, the use of a model nonporous support enhances the ability to characterize the gold nanoparticles.<sup>6</sup> The characterization is sufficient to allow correlation between the differences in turnover rate (TOR) that exist between nanogold and bulk gold and to understand why nanogold is catalytically active in several different reactions. In particular, gold nanoparticles on reducible oxides have been shown to have similar low temperature water–gas shift (WGS) rates per gram of catalyst to industrial type Cu–ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>7</sup> However, debate remains concerning the properties that control the activity of supported gold catalysts for the WGS reaction.

It has been shown experimentally and theoretically that gold atoms with lower gold–gold coordination generally exhibit stronger heats of adsorption and higher TORs than are observed for a bulk Au(111) surface or Au atoms with high Au–Au coordination.<sup>2,8</sup> There is also a well-known support effect for the WGS reaction.<sup>9</sup>

These findings have led several researchers to emphasize the contact between small metallic Au clusters and the support as the active site.<sup>9,10</sup> However, a thorough study relating Au particle size and rate per active Au species has not been performed previously for the WGS reaction. Thus, this system represents an opportunity to explore the important general question of how catalytic sites are defined in cases where coordinative unsaturation can greatly alter catalytic function.

Au deposited on nonporous rutile TiO<sub>2</sub> was prepared to investigate the active sites for Au nanoparticles. The activity of the catalysts was measured using a plug flow reactor apparatus (see Supporting Information), and the particle sizes were evaluated using transmission electron microscopy (TEM). The results in Figure 1 show a clear trend that catalysts with a smaller average Au particle size have larger rates per mole of Au. The difference in rate between the largest (6.7 nm) and smallest (1.2 nm) average particle size samples was over 2 orders of magnitude. In WGS studies over transition metals such as Pd, Pt, or Cu, the rate is generally normalized by the total amount of surface metal to give a TOR, and it has been concluded that the WGS TOR of Pt catalysts is independent of weight loading and particle size.<sup>11</sup> Au catalysts do not exhibit this trend because the rate normalized by the amount of surface Au (calculated from the total amount of Au multiplied by dispersion) varies with particle size. For regular shapes that have volumes proportional to the diameter cubed, dispersion is equal to a constant divided by particle diameter  $d$ .<sup>2,12</sup> Consequently, the rate per total mole of Au should vary approximately as  $d^{-1}$  for the TOR to remain constant with changes in particle size. Rather than a  $d^{-1}$  dependence, we found that the rate per total mole of Au varied with particle diameter as  $d^{-2.7\pm 0.1}$ , which means that the rate per surface Au atom varied roughly as  $d^{-1.7}$ . Thus, all of the atoms on the surface of each particle cannot be considered the active sites if it is assumed that each site has a similar rate independent of Au particle size.



**Figure 1.** Rate per total mole of Au calculated at 120 °C, 6.8% CO, 21.9% H<sub>2</sub>O, 8.5% CO<sub>2</sub>, and 37.4% H<sub>2</sub> versus average Au particle size.

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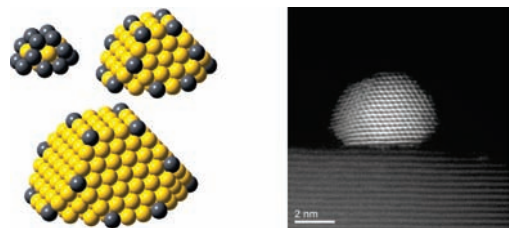
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The samples were further characterized to understand the effects of nanoparticle size. In agreement with literature,<sup>13</sup> diffuse reflectance infrared Fourier transform spectroscopy results showed that the rate per gram of catalyst was proportional to the 2100  $\text{cm}^{-1}$  peak area of CO adsorbed on  $\text{Au}^0$  (Figures S3–S4) but the 2050  $\text{cm}^{-1}$  peak area as well as CO adsorbed on  $\text{Au}^{\delta+}$  do not correlate with the rate. To determine if only subnanometer Au clusters were the active site, high-resolution aberration-corrected scanning transmission electron microscopy (STEM) experiments were performed on four different Au/rutile catalysts. With the assumption that subnanometer clusters are the active sites, a rate per mole of Au was calculated from the rate per gram of catalyst and the estimated surface coverage of subnanometer clusters. This rate is larger than the calculated rate of collision of energetic CO molecules on the same clusters, thus ruling out subnanometer clusters as the dominant active sites. This finding agrees with other results which show that CO oxidation rate per Au cluster is significantly decreased for Au clusters below a certain size range of approximately 8 atoms or below 0.8 nm in size.<sup>14,15</sup>

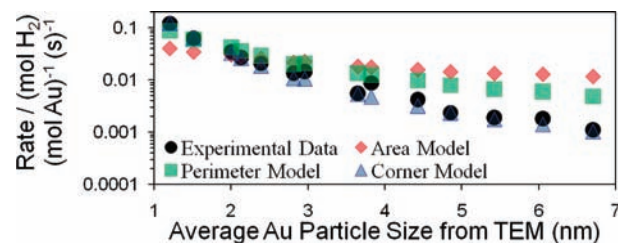
To further distinguish the active sites for Au/TiO<sub>2</sub>, a physical model of various Au clusters was created to determine how the frequency of different types of sites varies with particle size. The TEM studies indicate that the Au particle morphology was best described by a truncated cubo-octahedron. A model was then constructed to calculate the rates for each sample, assuming that different sites are active. This model uses particle size distributions determined from TEM in conjunction with information regarding the number of sites for clusters of a particular size determined from the truncated cubo-octahedra model shown in Figure 2.



**Figure 2.** (Left) Physical models of corner type sites on truncated cubo-octahedral Au clusters with 25, 119, and 331 atoms based on a (right) typical high-angle annular dark-field STEM image of the Au particles.

The model is based on the assumption that the rate of the active sites on the Au clusters (i.e., the true TOR) does not depend on particle size. This assumption is based on density functional calculations from which it is suggested that the most important factor affecting the adsorption and reaction properties of Au atoms is their coordination with other atoms.<sup>16</sup> A rate for each sample was calculated from the following equation: Rate per mole of Au =  $[\sum c_{\text{site}} s(d)]/[\sum t(d)]$ , where  $s(d)$  is the number of atoms for a cluster of diameter  $d$  that correspond to the site of interest,  $t(d)$  is the total number of atoms for that cluster, and the summation was carried out over all the Au clusters identified from the TEM image of that catalyst. In other words, the full particle size distribution was used for each sample. The constant  $c_{\text{site}}$  was calculated from a best fit of the model with the experimental rate data over the full range of average particle sizes represented by all 14 samples studied. The use of the model rutile support was critical for this study because the TEM images provided a precise measure of the particle size distribution needed for this analysis.

The data are compared to the results of the model in Figure 3. The rate per mole of Au varies as  $d^{-1.71}$  if atoms on the perimeter in contact with the support are the active sites and as  $d^{-2.82}$  if corner



**Figure 3.** Best fits of model rates to experimental data.

atoms are the active sites. We note that the particle size dependence of the experimental data is between that of the corner atom model and the perimeter model and that allowing for multiple sites to contribute to the rate will improve the fit to the data. However, the experimental rate is clearly best fit by the corner model. A corner model has been used to explain the size effect observed for Au catalysts in the oxidative environment of CO oxidation.<sup>2,12</sup> It is surprising that the model can also be used to explain the particle size dependence in the highly reducing atmosphere present during WGS.

Here a “corner” site is a specific type of site that does not change in absolute number with a change in particle diameter and exhibits a Au–Au coordination number less than 7. It has been argued that Au atoms in contact with the support will be inactive due to the increased coordination provided by the support.<sup>17</sup> As shown in Figure 2, the corner sites that have contact with the support have a Au coordination number of 4, but those without support contact have a Au coordination number of 6. Although there are differences between these two types of sites, it is clear that a lack of coordination of the Au atoms in the clusters provides the dominant sites.

The conclusion that corner atoms are dominant sites implies that the rate on each cluster larger than approximately 1 nm in size is the same and that the total rate of a given sample is proportional only to the number of clusters, but not their size. To create more stable WGS catalysts with higher rates per mole of Au, it is necessary to maintain small average gold particle sizes to maximize the number of clusters for the weight loading of gold used. The presence of the corner atoms with low Au–Au coordination is caused by the geometry of the nanoparticles. Thus, it is possible to explain the high rate per mole of Au of the nanoparticles without invoking explanations involving changes to the electronic nature of the nanoparticles with size. A question of interest for future work is how the corner sites, implicated by the unusual diameter dependence of the rate per mole of gold found in this work, participate in the dual functionality of WGS catalysts which results from the nature of both the metal and the support.

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**Supporting Information Available:** Materials, calculation details, experimental methods, Table S1, and Figures S1–S4. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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