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# Geometrical Structure of the Au-Fe<sub>2</sub>O<sub>3</sub> Interfacial Perimeter for CO Oxidation

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Dedication ((optional))

Abstract: The geometrical structure of the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeter, which is generally considered as the active sites for low-temperature oxidation of CO, was examined. It was found that the activity of the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts not only depends on the number of the gold atoms at the interfacial perimeter but also strongly depends on the geometrical structure of these gold atoms, which is determined by the size of the gold particle. Aberration-corrected scanning transmission electron microscopy images unambiguously suggested that the gold particles, transformed from a twodimensional flat shape to a well-faceted truncated octahedron when the size slightly enlarged from 2.2 to 3.5 nm. Such a size-induced shape evolution altered the chemical bonding environments of the gold atoms at the interfacial perimeters and consequently their catalytic activity. For Au particles with a mean size of 2.2 nm, the interfacial perimeter gold atoms possessed a higher degree of unsaturatedly coordinated environment while for Au particles with a mean size of 3.5 nm the perimeter gold atoms mainly followed the atomic arrangements of Au {111} and {100} facets. Kinetic study, with respect to the reaction rate and the turnover frequency on the interfacial perimeter gold atom, found that the low-coordinated perimeter gold atoms were intrinsically more active for CO oxidation. <sup>18</sup>O isotopic titration and Infrared spectroscopy experiments verified that CO oxidation at room temperature occurred at the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeter, involving the participation of the lattice oxygen of  $Fe_2O_3$  for activating  $O_2$ and the gold atoms for CO adsorption and activation.

Gold nanoparticles (NPs), dispersed on reducible metal oxides, are reported to be highly active for low-temperature oxidation of CO, showing a prominent size effect. Au NPs < 3 nm are highly active but Au NPs > 5 nm are nearly inert.<sup>[1]</sup> Meanwhile, the oxide-supports that possess redox characteristics, such as TiO<sub>2</sub>, CeO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>, play an crucial role in enhancing the catalytic activity: they not only disperse and stabilize the Au NPs but also control the gold-oxide interface structure through strong metal-support interactions <sup>[1d,1e,2]</sup>. The dominant reaction pathway involves the participation of surface lattice oxygen on the oxide-support for activating O<sub>2</sub> and the Au NP for adsorbing CO.<sup>[1d,2d,2e,2g,2h]</sup> In this context, Au/Fe<sub>2</sub>O<sub>3</sub> catalysts provide a typical example: the activity for low-temperature oxidation of CO is intimately related to both

the size of the Au NPs and the surface properties of Fe<sub>2</sub>O<sub>3</sub>.<sup>[1b,2i,3]</sup> Extensive studies have continuously focused on the origin of the size effect of Fe<sub>2</sub>O<sub>3</sub>-supported Au NPs in CO oxidation, but identification of the active sites remains controversial and inconclusive. To date, low-coordinated Au atoms, [1a,1b,3b] bilayer Au clusters,<sup>[3c]</sup> positively-charged Au species,<sup>[4]</sup> and Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeters<sup>[1d,2i,5]</sup> were all proposed to be the potential active sites. The experimentally observed high activity on smaller Au NPs in the size range of 2-5 nm was traditionally attributed to the gold atoms located at edges, corners, kinks, and steps.[1a-c] However, aberration-corrected scanning transmission electron microscopy (ac-STEM) study on Au/Fe<sub>2</sub>O<sub>3</sub> catalysts evidenced the wide size distribution of Au NPs on Fe<sub>2</sub>O<sub>3</sub>, consisting of faceted particles (2-15 nm), bilayer clusters (~0.5 nm), and even highly isolated atoms.[3c] The observed activity was ascribed to the Au bilayer clusters, instead of the faceted Au NPs even if their sizes were smaller than 5 nm. Deposition of Au colloids with a relatively uniform size of ~2 nm onto Fe<sub>2</sub>O<sub>3</sub> ruled out the presence of isolated Au atoms, monolayers or bilayers in the catalyst, and the catalytic activity of such systems was thus straightforwardly attributed to the faceted gold NPs.[3d,3f] A ac-STEM study on the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial structures found that the activity for CO oxidation was proportional to the total length of the perimeters of Au particles on the oxide-support.<sup>[2i]</sup> In most cases, much attention has been given to the primary sizes of the Au NPs or the goldoxide interfacial perimeters, but examination of the impact of the geometrical structure of the Au NPs on the catalytic activity is rare. Here, we report detailed investigations on the atomic arrangement of the perimeter gold atoms by tuning the size of Au NPs in the range of 2-5 nm; the reaction rate for CO oxidation at room temperature was correlated not only to the total length of the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeter but also more dominantly with the geometrical arrangements of the perimeter gold atoms.

The Au/Fe<sub>2</sub>O<sub>3</sub> catalysts were prepared by aqueous-phase deposition-precipitation of gold species onto a rod-shaped Fe<sub>2</sub>O<sub>3</sub> support. To control Au NPs in the size range of 2-5 nm, the solid precursor was calcined at 573, 673 and 723 K in air, respectively; the resulting catalysts were labeled as Au-T, where T refers to the temperature of calcination. Aberration-corrected environmental TEM examination on the evolution of the Au NPs during the calcination process, focusing on the growing pattern of Au NPs on a single  $Fe_2O_3$  rod (Figure 1), confirmed the occurrence of particle coalescence. Upon heating in air, Au NPs did not detach from the surface of the Fe<sub>2</sub>O<sub>3</sub> rod up to 573 K. Oswald ripening, however, may have occurred at this stage. Appreciable migration of small Au NPs started to occur at 673 K. A small Au particle at the rod edge (marked as ①) almost disappeared and another Au particle of ~2 nm (marked as 2) moved from the edge to the flat surface of the Fe<sub>2</sub>O<sub>3</sub> rod. Two neighboring clusters/particles

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(labeled as (6)) combined into a faceted larger particle, showing a typical character of particle coalescence. Upon further heating to 743 K, another Au particle (marked as (3)) moved from the edge to the flat surface of the Fe<sub>2</sub>O<sub>3</sub> rod, far away from its original location; the other two particles (labeled as (1) and (4)) entirely vanished, probably combining with nearby particles to form larger ones ((2)<sup>°</sup> and (5)<sup>°</sup>). In fact, the migration and coalescence of Au nanoparticles at this stage were observed to occur within seconds (Figure S1). Thus, the growth of Au nanoparticles, during the process of calcination in air, followed mainly the coalescence mechanism.



Figure 1. Environmental TEM images of gold particles under air atmosphere (0.8 Torr) and at 573 K for 100 min (a), 673 K for 46 min (b), and 743 K for 47 min (c), showing the growing pattern of Au particles/clusters on a single  $Fe_2O_3$  rod as increasing the temperature.

Aberration-corrected STEM has been successfully applied to determine the atomic structures of Au NPs, clusters and singleatoms supported on reducible oxides, and the importance of the metal-support interfaces for catalysis have been demonstrated a convincing fashion.<sup>[3c,3d,6]</sup> Detailed analyses of ac-STEM images of the Au-T catalysts confirmed that the mean size of the Au NPs increased with the temperature of calcination: 2.2 nm for Au-573, 3.5 nm for Au-673, and 5.4 nm on Au-723 (Figure S2). Simultaneously, the shape of the Au NPs evolved from a twodimensional oblate type to a hemispherical truncated octahedron. On the Au-573 sample, both Au clusters (0.5-1.5 nm) and NPs (1.5-2.5 nm) were observed; the two-dimensional flat Au clusters tightly attached to the Fe<sub>2</sub>O<sub>3</sub> surface while the Au NPs possessed a shape of quasi-truncated octahedron. The Au clusters (0.5-1.5 nm) tended to show lattice fringes of crystalline materials, but they did not form well-defined facets (Figure 2a and Figure S3); the Au atoms in the clusters possessed an atomic distance slightly greater than those on the regular facets of Au NPs, indicating the stronger effect of metal-support interactions. The Au atoms at the interfacial perimeter tightly bonded to the Fe<sub>2</sub>O<sub>3</sub> rod and had a less ordered arrangement (with respect to the center Au cluster), suggesting a highly unsaturatedly coordinated environment. Such wetting behavior of Au clusters on the Fe<sub>2</sub>O<sub>3</sub> surfaces manifests the strong metal-support interaction. The Au NPs (1.5-2.5 nm), on the other hand, evolved toward truncted-octahedron with prominant Au {100} and {111} facets. Epitaxial nucleation and growth of Au NPs on Fe<sub>2</sub>O<sub>3</sub> surfaces were occasionally observed as well (Figure S3). However, the Au atoms at the interfacial perimeters seemed to be relatively disordered (Figure 2b). Quantitative measurement of Au clusters and NPs in the Au-573 sample revealed that the mean diameter was 2.2 nm while the height of the Au islands was ~0.69 nm, approximately three layers of Au atoms (Figure 2c).



Figure 2. STEM images and structural illustrations of the representative Au NPs with mean sizes of 2.2 nm (a-c), 3.5 nm (d-f), and 5.4 nm (g-i) in the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts. The insets in (c), (f) and (i) illustrate the proposed geometrical arrangements of the gold atoms located at the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeter positions.

On the Au-673 catalyst, the Au NPs were crystallized and showed well-developed polyhedra (Figure 2d-f and Figure S4). The majority of the Au NPs were in the size range of 2.5-4.0 nm, with a mean diameter of ~3.5 nm and a typical height of ~2.1 nm (~9 layers of Au atoms). The Au NPs had a shape of truncated octahedron orientated close to the [011] direction. The lattice spacings of 0.23 and 0.21 nm, forming an angle of 54.7°, corresponded to the Au {111} and {002} planes, respectively. The {111} truncations of Au NPs were more frequently observed than those of the {100} planes, a consequence of the equilibrium shape of fcc metals.<sup>[7]</sup> The Au {111} surfaces interact with Fe<sub>2</sub>O<sub>3</sub> with an orientation relationship of Au(111)//Fe<sub>2</sub>O<sub>3</sub>(110). The interfical perimeter Au atoms bonded to the surface Fe atoms directly with a Au-Fe distance of 0.35 nm, and were also regulated by being part of the Au{111} facets (Figure S4). In the case of the Au-723 sample, well-faceted Au NPs with sizes of 2.0-7.0 nm were clearly seen (Figure 2g-i). The Au NPs displayed a truncated octahedral shape with an average diameter of ~5.4 nm and an average height of ~3.2 nm (~14 layers of Au atoms). Well-developed Au {111} and {100} facets were identified on the polyhedral particles; their orientation relationships with Fe<sub>2</sub>O<sub>3</sub> (110) were clearly identified (Figure S5). These ac-STEM observations confirm that the shape of the Au NPs, upon increasing size, transformed from an oblate form in Au-573 to a truncated octahedron consisting primarily of Au {111} and {100} facets in Au-673, and then to a hemispherical truncated octahedron in Au-723. Because of this shape evolution, the geometrical structure of the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeters changed significantly: from an almost disordered circle for smaller Au clusters to a large polygon with straight sides corresponding to the Au {111} and {100} facets for larger Au NPs (Figure 2c,2f,2i). In principle, the geometrical structure of the Au-Fe<sub>2</sub>O<sub>3</sub> interface is governed by the relative bonding strengths between the Au NPs and the Fe<sub>2</sub>O<sub>3</sub> surfaces. With smaller Au NPs and clusters the strong Au-Fe<sub>2</sub>O<sub>3</sub> interaction dominates and thus the Au atoms wet the Fe<sub>2</sub>O<sub>3</sub> surface; for larger Au particles the interfacial Au atoms are strongly influenced by the Au-Au bonding and thus the interfacial atoms maintain their

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positions of the equilibrium shape of the *fcc* metals. The adhesion energies for Au NPs on Fe<sub>2</sub>O<sub>3</sub>, derived from the Wulff construction, <sup>[7]</sup> were 2.52 J m<sup>-2</sup> for 2.2 nm, 1.09 J m<sup>-2</sup> for 3.5 nm, and 1.03 J m<sup>-2</sup> for 5.4 nm (Table S1). The sharp drop in adhesion energy with the slight increase in size from 2.2 to 3.5 nm reflects a significant shape transformation of the Au NPs. Therefore, the strong Au-Fe<sub>2</sub>O<sub>3</sub> interaction transformed the shape of Au clusters and small Au NPs and consequently the geometric structure of their interfacial perimeters.



Figure 3. CO–TPR profiles (a) and XPS of Au4f (b) of the Au/Fe $_2O_3$  catalysts containing Au NPs with mean sizes of 2.2, 3.5 and 5.4 nm, respectively.

The redox property of the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts was investigated by temperature-programmed reductions with CO and H<sub>2</sub> (Figure 3a and Figure S6). Compared to the reduction behavior of the rodshaped Fe<sub>2</sub>O<sub>3</sub> support, the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> in the Au /Fe<sub>2</sub>O<sub>3</sub> catalysts occurred at much lower temperatures. This demonstrates that Au NPs promoted the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> in the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts, which was more pronounced on the Au-573 sample with smaller Au NPs. This is primarily because the smaller gold particles interact more strongly with Fe<sub>2</sub>O<sub>3</sub> and more effectively adsorb and activate H<sub>2</sub> or CO molecules.<sup>[8]</sup> The binding energies at 83.8-83.9 eV in the XPS of Au4f in the Au-T catalysts verified the metallic Au<sup>0</sup> species (Figure 3b), regardless of the particle size. The XPS of O1s suggested the presence of two types of oxygen species: lattice oxygen and surface oxygen.<sup>[9]</sup> Interestingly, the amount of surface oxygen species, which might be removable during the redox cycles, varied with the size of Au NPs: 27% on Au-573, 20% on Au-673 and 17% on Au-723 (Table S2). These surface oxygen species might be located at the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeters and actively participated in the strong metal-support interactions.<sup>[2h,8a]</sup>

CO oxidation on the Au/Fe<sub>2</sub>O<sub>3</sub> catalysts was tested at room temperature; the size of the Au NPs affected the activity dramatically (Figure S7). The conversion of CO approached ~100% on Au-573, sharply lowered to 30% on Au-673 and further declined to 6.5% on Au-723. The most outstanding activity obtained over the Au-573 catalyst, containing Au NPs with a mean size of 2.2 nm, supports the previous results that Au NPs < 3 nm are often highly active.<sup>[1]</sup> STEM analysis on the used catalysts

after CO oxidation for 12 hours confirmed that there were no apparent changes in the size and shape of Au NPs (Figure S8). To verify the reaction mechanism of CO oxidation on the Au-573 catalyst, pulse experiments with an initial CO titration and a subsequent <sup>18</sup>O<sub>2</sub> injection were performed at room temperature (Figure 4a). Once the sample was exposed to CO, CO<sub>2</sub> was immediately formed, evidencing that the Fe<sub>2</sub>O<sub>3</sub> support supplied active oxygen species, probably the surface oxygen species at the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeters, to oxidize the CO adsorbed on the Au NPs to CO<sub>2</sub>. The consumption of <sup>18</sup>O<sub>2</sub> at the subsequent pulse indicated the replenishment of isotopic oxygen species to the oxide-support. During the sequential alternating injections of CO and <sup>18</sup>O<sub>2</sub>, the production of C<sup>16</sup>O<sup>18</sup>O verified that <sup>18</sup>O atoms, which had been incorporated into the Fe<sub>2</sub>O<sub>3</sub> support for restoring the stoichiometry, participated in the reaction cycles. This result confirmed that CO oxidation occurred at the Au-Fe<sub>2</sub>O<sub>3</sub> interfacial perimeter via a redox mechanism: CO is adsorbed on the Au NP while  $O_2$  is activated on the  $Fe_2O_3$  around the interfacacial perimetric sites.<sup>[2i,10]</sup> IR spectra of CO adsroption on the Au-T catalysts also supported such a reaction route (Figure S9). Upon exposure of the Au-573 sample to CO at room temperature, two intense bands, bridge-bonded and linearly -bonded CO on Au, appeared at 2046 and 2106 cm<sup>-1</sup> in the carbonyl region.<sup>[11]</sup> Simultaneously, bicarbonate species with typical bands at the carbonate region (1200-1700 cm<sup>-1</sup>) were detected, indicating that the adsorbed CO rapidly reacted with the oxygen species on Fe<sub>2</sub>O<sub>3</sub> surface to form carbonates. When O<sub>2</sub> was supplied to compensate for the consumed surface oxygen species, the bands for CO adsorption on Au NPs almost vanished while the bands of carbonate species intensified significantly because of the reaction between adsorbed CO on Au and surface oxygen species on Fe<sub>2</sub>O<sub>3</sub> at the interfcial perimeters.



**Figure 4.** Mass spectra (a) during alternating sequential CO and  ${}^{18}O_2$  pulses over the Au–573 catalyst at 300 K and the proposed redox cycle of Fe<sub>2</sub>O<sub>3</sub>; reaction rates (b) of CO oxidation over the Au-T catalysts at room temperature.

The reaction rate of CO oxidation on the Au-T catalysts was measured at room temperature; it was 0.193 mmol<sub>CO</sub>  $g_{Au}^{-1} s^{-1}$  on Au-573, dramtically droped to 0.0257 mmol<sub>CO</sub>  $g_{Au}^{-1} s^{-1}$  on Au-673, and further declined to 0.0087 mmol<sub>CO</sub>  $g_{Au}^{-1} s^{-1}$  on Au-723 (Figure 4b). Since CO oxidation occurred at the interfacial perimeters, the reaction rates were normalized with the total number of the perimeter Au atoms, estimated from the mean size of the Au NPs in the respective Au-T catalysts. The turnover frequency (TOF) on the perimeter Au atom was 0.173 s<sup>-1</sup> for Au-573, 0.105 s<sup>-1</sup> for Au-673 and 0.104 s<sup>-1</sup> for Au-723 (Table S3). This suggests that the

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intrinsic activity of the perimeter Au atoms is higher for the Au NPs with an average size of 2.2 nm than those of the Au NPs with mean sizes of 3.5 and 5.4 nm. This suggests that the total number of perimeter Au atoms is a good meaure of the activity of relatively larger Au NPs. However, other factors may also influence the experimentally observed TOF of Au clusters or smaller Au NPs. According to the dependence of the the geometrical models of the Au NPs on their sizes, derived from the ac-STEM images (Figure 2 and Table S1), the coordination environment of the perimeter gold atoms in the Au-573 catalyst differs significantly from those in the Au-673 and Au-723 catalysts, originating from the stronger Au-Fe<sub>2</sub>O<sub>3</sub> interaction for smaller Au NPs and clusters. For Au NPs of 3.5 and 5.4 nm, they possess a shape of well-faceted truncated octahedron with Au {111} and {100} facets predominantly; the perimeter Au atoms in these well-faceted Au NPs have a coordination number of 7; they are chemically bonded with the Fe<sub>2</sub>O<sub>3</sub> support but are also more strongly coordinated with the neighboring Au atoms on the Au {111} and {100} facets. In contrast, the perimeter gold atoms on the Au clusters or the less crystallized smaller Au NPs in the Au-573 catalyst, strongly interacted with the Fe<sub>2</sub>O<sub>3</sub> surfaces but relatively weakly coordinated with the neighboring Au atoms since the average height of these small Au particles is only three atomic layers. Therefore, the coordination number of the perimeter gold atoms in these oblate clusters or smaller Au NPs can be appreciably less than 7. Such a change in the chemical bonding environment of the perimeter Au atoms significantly modified their adsorption strength of CO, as being evidenced by the TPR and IR data (Figure 3a and Figure S9). Consequently, the low-coordinated perimeter Au atoms on the smaller Au NPs are intrinsically more active, yielding a higher TOF in CO oxidation than those on the well-faceted Au NPs.

In summary, our experimental data, analyses and discussions clearly demonstrate that the activity for CO oxidation of  $Au/Fe_2O_3$  catalysts primarily depends on the total number of the perimeter Au atoms for larger Au NPs. For smaller Au NPs and Au clusters not only the total number of the Au perimeter atoms but also the geometrical arrangement of the perimeter Au atoms become important. The chemical environment of the low-coordinated perimeter Au atoms, determined by the size of the Au NPs and the metal-support interactions, may play the most important role in achieving high activity for low-temperature oxidation of CO on supported Au catalysts.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

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# COMMUNICATION

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Layout 1:

### COMMUNICATION

Interface Geometry. The variation in activity for CO oxidation on Au/Fe<sub>2</sub>O<sub>3</sub> catalysts, as increasing the size of gold particles in the range of 2-5 nm, is intimately associated with the geometrical structure of the interfacial perimeter Au atoms. For smaller gold particles, the perimeter gold atoms possess a low-coordinated environment and thus show a much higher intrinsic activity.

2.6 nm Au 1.8 nm Au Perimeter Geometry  $\delta_{0000}^{000000}$ 2 nm Xuejiao Wei, Bin Shao, Yan Zhou, Yong Li, Chuanchuan Jin, Jingyue Liu, Wenjie Shen

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Geometrical Structure of the Active Au-Fe<sub>2</sub>O<sub>3</sub> Interfacial Perimeter for CO Oxidation