

Size-dependent dynamic structures of supported gold nanoparticles in CO oxidation reaction condition

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Gold (Au) catalysts exhibit a significant size effect, but its origin has been puzzling for a long time. It is generally believed that supported Au clusters are more or less rigid in working condition, which inevitably leads to the general speculation that the active sites are immobile. Here, by using atomic resolution in situ environmental transmission electron microscopy, we report size-dependent structure dynamics of single Au nanoparticles on ceria (CeO₂) in CO oxidation reaction condition at room temperature. While large Au nanoparticles remain rigid in the catalytic working condition, ultrasmall Au clusters lose their intrinsic structures and become disordered, featuring vigorous structural rearrangements and formation of dynamic low-coordinated atoms on surface. Ab initio molecular-dynamics simulations reveal that the interaction between ultrasmall Au cluster and CO molecules leads to the dynamic structural responses, demonstrating that the shape of the catalytic particle under the working condition may totally differ from the shape under the static condition. The present observation provides insight on the origin of superior catalytic properties of ultrasmall gold clusters.

gold catalysis | size effect | adsorbate-induced disorder | dynamic low-coordinated atoms

The discovery of catalytic properties of gold (Au) is a landmark in catalysis science (1, 2). The observation of supported Au nanoparticles (NPs) of ~2–5 nm possessing robust catalytic properties (3, 4) has triggered extensive studies of Au heterogeneous catalysts (5–9). Consequently, it has been generally realized that only nanosized Au particles are active (1, 7, 8), and their reactivities are highly size dependent (8, 10). However, the origin of such a significant size effect and the associated catalytic mechanism remain as the biggest puzzle (8, 9). It was suggested that the atoms on the metal-support interface were the active sites (5), and hence the size dependence would be directly related to the ratio of the perimeter sites to the particle size. However, this picture relies on the contention that, under the working condition, the Au NP is more or less rigid, such that the atoms at the interior of the particle would hardly participate in the reactions or remain inactive (11–14). However, in situ studies in recent years have revealed otherwise, that the surface structures of supported metallic NPs (15–18), including the noblest gold metal (19), are not rigid. Takeda and coworkers (20, 21) explored Au NP catalyst supported on TiO₂ and CeO₂ under various gas conditions and found that the Au NPs with a size of 2–5 nm remain as face-centered cubic (FCC) structure but undergo surface restructuring under high O₂/CO ratio or upon adsorption of CO molecules on Au surface. Other in situ experimental studies also revealed that CO can etch the surface of bulk Au by relocating the atoms to form clusters (11, 13). As Au particle sizes further decrease, the ratio of surface atoms dramatically increases; and hence the ultrasmall cluster may completely lose its structure stability due to the interaction between the surface atoms and CO molecules. Nonetheless, in situ study

on ultrasmall (<2-nm) supported Au clusters in reaction condition is still lacking to date, which is critical in unveiling the origin of size effect in ultrasmall Au catalysis.

Here, through state-of-the-art aberration-corrected environmental transmission electron microscopy (ETEM) and a unique in situ experiment setup (see *Methods* and *SI Appendix, Fig. S1A*, for details), we directly captured the structure evolution of individual Au NPs [supported on CeO₂(111) surface] under catalytic working condition. The sizes of Au NPs range from ~2-nm-sized hexagonal single layers (in which all atoms are literally on surface) to NPs of 4–5 nm in diameter. We find that, upon exposing to reactant gases (CO + O₂) at room temperature, the structures of ultrasmall Au clusters were dramatically changed, featuring a transition from FCC structure to dynamic disordered structure and with Au (presumably Au/CO) atoms dynamically stretching out of the particle surface to form dynamic low-coordinated atoms (DLCAs). In contrast, large Au NPs remained rigid in FCC structure with typical surface reconstruction. The size-dependent dynamic structural changes and generation

Significance

Gold is the noblest metal. However, when the size decreases to nanoscale and is supported on reducible oxides, the gold nanoparticle shows exceptionally high catalytic performance even at low temperatures. Here, through state-of-the-art in situ aberration-corrected environmental transmission electron microscopy and ab initio molecular-dynamic simulations, we discovered that, upon exposing to reactant gas (carbon monoxide and oxygen), ultrasmall gold clusters on ceria show a size-dependent order-to-disorder transformation with generation of dynamic low-coordinated atoms, which presumably can effectively boost the oxidation reaction of carbon monoxide. The findings provide much-needed insights on the origin of size-dependent catalytic properties of supported gold and demonstrate a size effect in adsorbent-particle interactions that may widely exist and play an essential role in heterogeneous catalysts.

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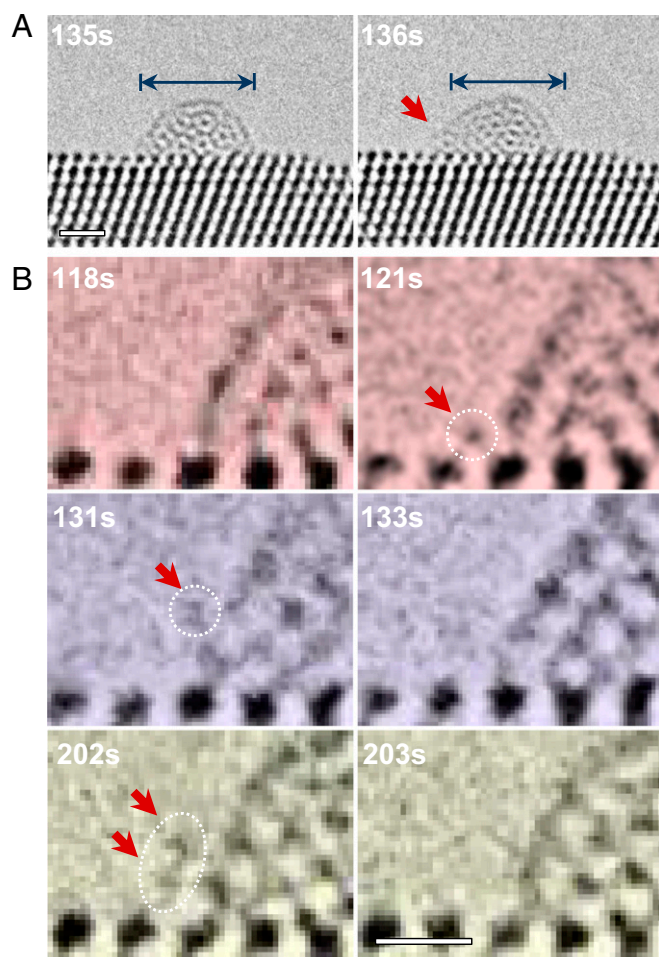


Fig. 2. Dynamic structure changes of the <2-nm Au NP under reaction condition. (A) Continuous structural changes of the Au NP (the double arrow serves as a reference to indicate the liquid-like flow of atoms within 1 s). (B) Enlarged HRTEM images showing that Au atoms in the vicinity of Au/CeO₂ contact were dynamically stretched out forming dynamic low-coordinated atoms (DLCAs) (indicated by red arrows and dashed circles) on Au surface and Au/CeO₂ perimeter. (Scale bars: A, 1 nm; B, 500 pm.)

observation (10, 12, 22), but has never been directly observed previously.

The atomic-scale mechanisms that underpin the observed size-dependent structural dynamics of Au NP in reaction condition were provided by our first-principles DFT calculations combined with AIMD simulations. In doing so, we chose both Au SLs and Au NPs that are represented by those shown in Fig. 1. We selected Au₁₉ SL with 12 adsorbed CO molecules supported on CeO₂(111) surface as the initial structure for AIMD simulations (Fig. 3A). Note that a surface oxygen vacancy was used to stabilize the Au₁₉ SL (23, 24). After ~25-ps evolution, the original SL lost its hexagonal configuration and transformed to 3D clusters, which is primarily caused by extraction and motion of Au atoms in the form of Au'CO species (Fig. 3B), while isolated Au₁₉ or supported CO-free Au₁₉ SLs maintained hexagonal SL configuration within the simulation time span at 300 K (*SI Appendix, Figs. S4 and S5*). This single layer-to-3D cluster transition was further confirmed by the calculation of distance distribution of Au atoms relative to the mass center of the cluster (Fig. 3C), where both supported and unsupported Au₁₉ maintained hexagonal SL structures as manifested by three well-defined peaks (at 2.8, 4.9, and 5.6 Å for three kinds of Au atoms), while these three peaks all disappeared in Au₁₉ with CO adsorption, suggesting

a collapse of the SL and formation of disordered structure as shown in the *Movies S4 and S5* (12). The AIMD simulation on the behavior of Au SL is fairly consistent with our experimental observations in Fig. 1.

Moreover, the dynamic behavior of the supported Au cluster mainly involves breaking and formation of Au–Au bonds, while the stronger Au–CO bonds are relatively stable (Fig. 3B), indicating that the transport of CO on Au cluster is based on Au'CO species. The diffusion barrier for Au'CO species on Au cluster is estimated to be ~0.07 eV, by the potential of mean force $V(r) = -k_B T \ln(g(r))$, where $g(r)$ is the radial distribution function (Fig. 3D). This barrier is significantly lower than the reported barrier (~0.6 eV) for the diffusion of CO on FCC Au (22) but is well consistent with the barrier of Au'CO diffusion on Au(111) surface or supported Au SL (*SI Appendix, Fig. S6*). This facile transport of Au'CO species was also evidenced by the fact that Au'CO species was stretched out of the Au cluster and migrated to the surface oxygen site to form O_{surf}–Au–CO (Fig. 3B, green ball), which is a thermodynamically favorable process. The agile Au'CO species agree well with our experimental observations on formation of DLCAs in Fig. 2.

Since CO adsorption-induced Au'CO extraction plays an essential role for the observed order-to-disorder transformation and is likely responsible for formation of DLCA, we further evaluated the size dependence of the energies and barriers for this process (Fig. 3E). Compared with that on the edge of bulk Au, formation energies of Au'CO (or DLCA) at the edges of supported Au nanorod and SL are much lower, even with negative values (*SI Appendix, Fig. S6*). When two COs adsorb on adjacent Au sites, the energy barriers for Au'CO extraction on supported Au nanorod and SL are 0.04 and 0.29 eV, respectively; whereas the barrier for the same process on bulk Au(111)/(111) edge is much higher (~0.92 eV), manifesting that smaller Au NPs are more susceptible to Au'CO extraction.

Furthermore, the calculated coverage-dependent adsorption energy per CO molecule on Au NPs linearly decreases with increasing particle size, leading to a considerable decrease of CO coverage with increasing Au particle size (*SI Appendix, Fig. S7*). The low coverage of large NPs can be attributed to the decrease of edges and apexes sites where CO is more likely to adsorb (25–27). Mpourmpakis and coworkers (28) recently reported that the average binding energy of CO on Au increases exponentially with decreasing Au NP diameter, which has similar tendency with catalytic activity for CO oxidation. Moreover, the size-dependent order-to-disorder transformation of supported Au NPs is also partially rooted in the decreasing cohesive energy of the particle as the particle size decreases (*SI Appendix, Figs. S7 and S8*). Above all, the size dependences of CO adsorption energy, Au'CO extraction barrier, and Au cohesive energies give rise to the size dependence in structural responses of supported Au NPs.

The size-dependent dynamic structure of supported Au NPs under reaction condition could contribute significantly to the catalytic process. It is well known that, in heterogeneous Au catalysts, the adsorption sites of reactants such as CO and O₂ are spatially different: O₂ easily adsorbs on the CeO₂ surface defects at the perimeter of Au and CeO₂ contact (29–31), whereas CO adsorbs on Au surface but not on CeO₂ surface (30, 32, 33). DFT calculations indicate a high energy barrier for CO migration on the surface of an FCC-structured gold, which does not favor low-temperature CO transport toward the absorbed O₂ (22). As such, traditional rigid models suggested that only the low-coordinated atoms on the perimeter contribute to the catalytic activity (5, 34). However, our observation clearly revealed a scenario in which ultrasmall Au nanostructures were not rigid but vigorously evolving under reaction condition, and DLCAs can be generated via CO chemisorption, which, as manifested by our simulations, enable the facile transport of CO molecules (through Au'CO) to

has a base pressure of $\sim 10^{-8}$ mbar. Reactant gases (stoichiometric CO + O₂) were mixed and leaked into the ETEM chamber with pressure controlled at 10^{-4} to $\sim 10^{-3}$ mbar. Gas mixing and pressure control were accomplished by a laboratory-developed auxiliary system, which is a computer-controlled system and therefore warrants a precise control of desired gas mixture and pressure. The gas composition was confirmed via a residual gas analyzer with sensitivity down to 10^{-11} mbar (near the sample area). All of the experiments were performed at room temperature.

HRTEM Image Simulation. To confirm the HRTEM contrast of the dynamically generated single Au atom, we used the DFT-calculated structure model as input to simulate the HRTEM images and compared the simulated images with the experimentally captured ones (*SI Appendix, Fig. S2*). The HRTEM image simulation of the Au NP was carried out using the multislicing method, which is integrated into the code “simulate,” as is described in ref. 37. The parameters for the image simulation were chosen as follows: accelerating voltage of 300 kV and a spherical aberration coefficient of the objective lens of 2 μm .

Circumventing the (Imaging) Electron-Beam Effects. One of the major concerns regarding the in situ TEM observation is the electron beam effect. Kuwauchi et al. (20) have systematically studied electron beam effects on the intrinsic structure of Au NPs supported on TiO₂ and found that irreversible structure changes could happen for Au/TiO₂ by increasing total dose or/and electron current density. A safety zone, where the intrinsic structure of Au/TiO₂ is well preserved, has been identified to be a total dose of $< 1,000 \text{ A}\cdot\text{s}\cdot\text{cm}^{-2}$ and an electron current density $\phi < 20 \text{ A}\cdot\text{cm}^{-2}$ (20). They also found that CeO₂ is more stable than TiO₂ upon exposure to electron irradiation. Based on these results, we strictly control the electron current density to $\phi < 4 \text{ A}\cdot\text{cm}^{-2}$ to minimize the beam effect. A quantitative analysis of beam dose rate effect on the dynamics of Au is provided in *SI Appendix*. Furthermore, we also carry out beam-blank experiments, as described in *SI Appendix, Fig. S3A*, which confirm what we observed is not dominated by electron-beam effects.

It would be generally expected that electron beam could have a detrimental effect for the adsorption of CO/O₂ on the surface of Au NP through direct knock-on mechanism and/or desorption by energy transfer from electrons. With these two factors in mind, Yoshida et al. (21) have discussed the desorption rate of CO molecule from Au NPs under beam illumination. Following their method, we estimate the maximum adsorption rate of CO molecules per surface Au atom to be $\sim 5 \times 10^1 \text{ s}^{-1}$ in our working gas condition (CO: O₂ = 2:1 at 10^{-3} mbar at room temperature). The desorption rate was estimated to be 10^{-2} s^{-1} (21); thus, the adsorption rate is two orders of magnitude higher than that of desorption, indicating that dynamic adsorption of CO and structural change induced by CO can be observed in our ETEM experiments.

Computational Models. Supported Au SLs and NPs models on CeO₂(111) surface were built up to investigate their dynamic behavior under reaction condition. First, we constructed two single-layer structures that have 19 and 37 atoms, respectively, with hexagon dense-packed (111) plane of FCC Au, as shown in *SI Appendix, Fig. S4A*. The CeO₂(111)-p(5 × 5) and CeO₂(111)-p(6 × 6) surface slab models were used to support Au₁₉ and Au₃₇ SL, respectively, to avoid interaction between adjacent images. The slabs consisted of three O–Ce–O trilayers (nine atomic layers), where the bottom one O–Ce–O trilayer was frozen while the remaining layers were allowed to relax. All of the supercell slabs were repeated periodically with a 15-Å vacuum layer between the images in the direction perpendicular to the surface. Considering the extensive existence of oxygen vacancy on the CeO₂ surface, in both of the two models, we have removed one surface oxygen atom in the cell to model a partially reduced surface and located the SL above the vacancy as the initial structure of AIMD simulations.

The support effects were tested by investigating a series of supported Au nanorods on CeO₂(111)-p(3 × 5), which were used extensively to study the catalysis of supported Au NPs (22, 38). In this work, we built up Au nanorods with one and three atomic layers (*SI Appendix, Fig. S4B*). Note that, for three atomic layers of gold nanorod, all of the Au atoms were allowed to relax in the y and z directions, and for calculation of the Au/CO extraction process, the Au' atom and adjacent Au atoms were allowed to fully relax.

Two types of NPs were used to calculate the cohesive energies (E_b) and the dynamic properties with CO adsorption. Supported NPs with 7–370 atoms that mimic the shape observed from ETEM photographs are shown in *SI Appendix, Fig. S4C*, and unsupported NPs with 20–586 atoms, which were built up by Wulff construction, are shown in *SI Appendix, Fig. S4D*.

Details of DFT Calculations. All of the calculations reported herein were carried out by using the Quickstep module in the CP2K simulation package (39). The wavefunction was expanded by mixed Gaussian and plane-wave basis sets with an energy cutoff of 350 Ry for the plane wave (40–42). Molecularly optimized double- ζ valence plus polarization basis sets were used to minimize the basis set superposition errors (40). Geodecker–Teter–Hutter pseudopotentials were adopted to model the core electron with 11, 12, 6, and 4 valence electrons for Au, Ce, O, and C, respectively (43). The DFT+U method was utilized in our calculations to describe the Ce 4f electrons. The value of intraatomic coulomb term minus exchange term ($U - J$) was chosen to be 7.0 eV to reproduce the correct band gap, gap state location, and work function (12, 42). Reciprocal space mesh consisting of gamma point was used for Brillouin zone integration. The climbing-image nudged elastic band (CI-NEB) calculations were performed to locate the saddle points with convergence criterion for the maximum force of 2×10^{-3} atomic unit. Vibrational analysis was performed to test the imaginary frequency and vibration modes to confirm the CI-NEB results (44, 45). Adsorption energies E_{ads} were calculated according to the following equation:

$$E_{\text{ads}} = E_{(\text{slab}+\text{adsorbate})} - E_{(\text{slab})} - E_{(\text{adsorbate})}$$

where $E_{(\text{slab} + \text{adsorbate})}$, $E_{(\text{slab})}$, and $E_{(\text{adsorbate})}$ are the calculated electronic energy of species adsorbed on the slab, the bare surface, and the gas phase molecule, respectively. Reaction energies are defined as ΔE :

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

AIMD Parameters. To explore the geometry and morphology change of gold SL during reaction conditions, Born–Oppenheimer molecular dynamics (BOMD) simulations were carried out in the canonical (NVT) ensemble employing Nosé–Hoover thermostats (46, 47) with a time step of 1 fs at 300 K. Simulation of isolated Au₁₉ and Au₃₇ SLs were first carried out to test its stability in vacuum and reaction atmosphere. Then they were allowed to support on CeO₂(111) surface for at least 20 ps to compare the dynamic behaviors with or without CO molecules. In this work, Au₁₉/CeO_{2-x} and Au₁₉(CO)₁₂/CeO_{2-x} were investigated. To test larger Au SL, Au₃₇/CeO_{2-x} and Au₃₇(CO)₁₈/CeO_{2-x} were also simulated for at least 15 ps with time steps of 1 fs (*SI Appendix, Fig. S5*). Additionally, embedded-atom model (EAM) potential was used to do classical molecular-dynamics simulations for bare isolated NPs with a time step of 2 fs, and isolated NPs with adsorbed CO were also calculated by BOMD method with a time step of 2 fs (*SI Appendix, Fig. S8*).

Radial distribution function $g(r)$ is used to study the dynamic behavior of Au–Au and Au–C bonds, and the free energy diffusion barrier for Au/CO species on Au cluster is estimated by the potential of mean force:

$$g(r) = e^{-\beta\omega^{(2)}(r)},$$

where $g(r)$ is the radial distribution function, and $\omega^{(2)}(r)$ is the average work needed to bring the two particles from infinite separation to a distance r . Thus, the potential energy surface can be estimated by the following (48, 49):

$$V(r) = \omega^{(2)}(r) = -k_B T \ln(g(r)).$$

Coverage-dependent adsorption energy per CO molecule (E_{ads}) was evaluated on a series of isolated NPs. Inasmuch as CO molecules prefer adsorbing at DLCA sites than faces (25, 26, 50, 51), CO first adsorbs on apexes sites, then edges sites, then Au(100) surface, and last Au(111) surface.

To obtain a more direct description of the dynamic behavior of the NPs, we carried out AIMD simulations for isolated NPs under 1/2 CO coverage at room temperature for more than 20 ps. The final snapshot and radial distribution function $g_{\text{Au–Au}}(r)$ are shown in *SI Appendix, Fig. S8A and C*, respectively. To quantify the rigidity or plasticity of Au NPs with CO adsorption, we investigated the root-mean-squared bond length fluctuations (52):

$$\delta = \frac{2}{n(n-1)} \sum_{i < j} \frac{\sqrt{r_{ij}^2 - r_{ij}^2}}{r_{ij}}$$

Thermodynamic Calculations. For reactants at a given T and P , the corresponding coverage θ can be determined by the following:

$$E_{\text{dif}}(\theta) = d[\theta \times E_{\text{ads}}]/d\theta = \Delta\mu_{\text{CO}}(T, P),$$

where $E_{\text{dif}}(\theta)$ is the differential binding energy of reactants, and $\Delta\mu_{\text{CO}}(T, P)$ is the chemical potential of CO in gas phase. Dependence of E_{ads} on θ can be estimated from the linear fitting at various particle sizes (SI Appendix, Fig. S7B). At 300 K and standard pressure, $\Delta\mu_{\text{CO}}^{\circ}(T, P^{\circ})$ is then given by the following (53):

$$\begin{aligned}\Delta\mu_{\text{CO}}^{\circ}(T, P^{\circ}) &= [H(T, P^{\circ}, \text{CO}) - H(0 \text{ K}, P^{\circ}, \text{CO})] - T[S(T, P^{\circ}, \text{CO}) \\ &\quad - S(0 \text{ K}, P^{\circ}, \text{CO})] = [8.671 \text{ kJ} \cdot \text{mol}^{-1}] \\ &\quad - 298.15 \text{ K} [197.653 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}] = -0.52 \text{ eV}.\end{aligned}$$

When CO pressure is 10^{-4} bar:

$$\Delta\mu_{\text{CO}}(T, P) = \Delta\mu_{\text{CO}}^{\circ}(T, P^{\circ}) + kT \ln\left(\frac{P}{P^{\circ}}\right) = -0.52 + 0.0257 \ln(10^{-4}) = -0.76 \text{ eV}.$$

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