Cyclohexene is produced by the hydrogenation of.

Under standard conditions, 1-methylcyclohexene was produced to 6-oxohexanoic acid (9) in 59% yield. Oxidation of cyclopentene (100 g) with 30% H2O2 (736 g), Na2WO4·2H2O (4.84 g), and [CH4·(n-C8H17)3N]HSO4 (6.84 g) at 70–90°C for 13 hours produced crystalline glutaric acid (10) in 175 g in 90% yield. Oxidative cleavage of the C(9)–C(10) bond of [CH4·(n-C8H17)3N]HSO4 and 552 g (4.868 mol) of aqueous 30% H2O2. After the mixture was stirred for 12 hours, the resulting white precipitate was separated by filtration and washed with 20 ml of cold water. The product was dried in a vacuum to produce 138 g (78% yield) of 2 as a white solid (with a melting point of 151.0-152.0°C). A satisfactory elemental analysis was obtained without further purification. Concentration of the mother liquor produced 23 g of pure 2; the yield determined by GC (OV-1 column, 0.25 mm by 50 m, GL Sciences, Tokyo) was 93%. The identified byproducts were 1,2-cyclohexanediol (2% yield) and glutaric acid (4% yield). In the second run, a 2-liter round-bottomed flask was charged with the water phase of the first run, which contained the W catalyst, 5.67 g (12.2 mmol) of [CH4·(n-C8H17)3N]HSO4 and 552 g (4.868 mol) of aqueous 30% H2O2. After the mixture was vigorously stirred at room temperature for 10 min and then 100 g (1.217 mol) of 1 was added. The biphasic mixture was heated successively at 75°C for 30 min, at 80°C for 30 min, at 85°C for 30 min, and at 90°C for 6.5 hours, with stirring at 1000 rpm. The homogenous solution was allowed to stand at 0°C for 12 hours, and the resulting white precipitate was separated by filtration and washed with 20 ml of cold water. The product was dried in a vacuum to produce 138 g (78% yield) of 2 as a white solid (with a melting point of 151.0-152.0°C). A satisfactory elemental analysis was obtained without further purification. Concentration of the mother liquor produced 23 g of pure 2; the yield determined by GC (OV-1 column, 0.25 mm by 50 m, GL Sciences, Tokyo) was 93%. The identified byproducts were 1,2-cyclohexanediol (2% yield) and glutaric acid (4% yield). In the second run, a 2-liter round-bottomed flask was charged with the water phase of the first run, which contained the W catalyst, 5.67 g (12.2 mmol) of [CH4·(n-C8H17)3N]HSO4 and 552 g (4.868 mol) of aqueous 30% H2O2. After the mixture was vigorously stirred at room temperature for 10 min and then 100 g (1.217 mol) of 1 was added. The biphasic mixture was heated successively at 75°C for 30 min, at 80°C for 30 min, at 85°C for 30 min, and at 90°C for 6.5 hours, with stirring at 1000 rpm. The homogeneous solution was allowed to stand at 0°C for 12 hours. The resulting white precipitate was separated, washed, and dried in a vacuum to produce 138 g (78% yield) of analytically pure 2 as a white solid.

Under the standard conditions of alcohol oxidation, Baeyer-Villiger ring enlargement of simple cyclohexanones is negligible (8). A separate experiment showed that 1,2-cyclohexanediol is not a reaction intermediate.


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Onset of Catalytic Activity of Gold Clusters on Titania with the Appearance of Nonmetallic Properties

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Gold clusters ranging in diameter from 1 to 6 nanometers have been prepared on single crystalline surfaces of titania in ultrahigh vacuum to investigate the unusual size dependence of the low-temperature catalytic oxidation of carbon monoxide. Scanning tunneling microscopy/spectroscopy (STM/STS) and elevated pressure reaction kinetics measurements show that the structure sensitivity of this reaction on gold clusters supported on titania is related to a quantum size effect with respect to the thickness of the gold islands; islands with two layers of gold are most effective for catalyzing the oxidation of carbon monoxide. These results suggest that supported clusters, in general, may have unusual catalytic properties as one dimension of the cluster becomes smaller than three atomic spacings.

An atomic-level understanding of structure-activity relations in surface-catalyzed reactions is one of the most important goals of chemical science today. Department of Chemistry, Texas A&M University, College Station, TX 77842–3012, USA.

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References and Notes
including STM and STS.

We have used such model catalysts to study the unusual and as yet unexplained catalytic properties of nanosize Au clusters. STM, STS, and elevated pressure reaction kinetics measurements demonstrate that the structure sensitivity of the CO oxidation reaction on Au clusters supported on TiO$_2$ is related to a quantum size effect with respect to the thickness of the Au clusters; clusters with a two-layer thickness of Au, which exhibit a band gap uncharacteristic of bulk metals, are shown to be particularly suited for catalyzing the oxidation of CO.

Gold has long been known as being catalytically far less active than other transition metals. Quite recently, however, it was found that when dispersed as ultrafine particles and supported on metal oxides such as TiO$_2$, Au exhibits an extraordinary high activity for low-temperature catalytic combustion, partial oxidation of hydrocarbons, hydrogenation of low-temperature catalytic combustion, partial oxidation of CO on supported Au clusters, and reduction of nitrogen oxides ($\text{unsaturated hydrocarbons}$, and reduction of oxidation of hydrocarbons) ($\text{hydrogenation}$ of low-temperature catalytic combustion, partial oxidation on supported Au clusters, and reduction of oxidation of nitrogen oxides ($\text{unsaturated hydrocarbons}$). For example, Au clusters can promote the reaction between CO and O$_2$ to form CO$_2$ at temperatures as low as 40 K; clusters of varying size supported on TiO$_2(110)-(1 \times 1)$ surface. The Au clusters are imaged as bright protrusions with a relatively narrow size distribution. The clusters, with an average size of about 2.6 nm in diameter and about 0.7 nm in height (two to three atomic layers), preferentially nucleate on the step edges of the TiO$_2(110)-(1 \times 1)$ substrate.

The reaction studies of this surface indeed show a marked size effect of the catalytic activity of the supported Au clusters for the CO oxidation reaction, with Au clusters in the range of 3.5 nm exhibiting the maximum reactivity (Fig. 3A).

The $I$-$V$ characteristics obtained from several

![Fig. 1. CO oxidation turnover frequencies (TOFs) at 300 K as a function of the average size of the Au clusters supported on a high surface area TiO$_2$ support (7). The Au/TiO$_2$ catalysts were prepared by deposition-precipitation method, and the average cluster diameters were measured by TEM. The solid line serves merely to guide the eye.](image1)

![Fig. 2. A CCT STM image of Au/TiO$_2(110)-(1 \times 1)$ as prepared before a CO$_2$ reaction. The Au coverage is 0.25 ML, and the sample was annealed at 850 K for 2 min. The size of the images is 50 nm by 50 nm. (B) STS data acquired for Au clusters of varying sizes on the TiO$_2(110)-(1 \times 1)$ surface. For reference, the STS of the TiO$_2(110)-(1 \times 1)$ substrate is also shown.](image2)

![Fig. 3. (A) The activity for CO oxidation at 350 K as a function of the Au cluster size supported on TiO$_2(110)-(1 \times 1)$ assuming total dispersion of the Au. The CO$_2$ mixture was 1:5 at a total pressure of 40 Torr. Activity is expressed as (product molecules) × (total Au atoms)$^{-1}$s$^{-1}$. (B) Cluster band gap measured by STS as a function of the Au cluster size supported on TiO$_2(110)-(1 \times 1)$. The band gaps were obtained while the corresponding topographic scan was acquired on various Au coverages ranging from 0.2 to 4.0 ML. (C) Relative population of the Au clusters (two atom layers in height) and great-}
eral Au clusters supported on TiO$_2$(110)-(1×1) for various Au coverages from 0.2 to 4.0 ML are shown in Fig. 3B in terms of their band gaps as a function of the Au cluster size. A metal-to-nonmetal transition occurs as the cluster size is decreased below 3.5 by 1.0 nm$^2$ (3.5 nm in diameter and 1.0 nm in height, ~300 atoms per cluster). This result is similar to that of Pd/TiO$_2$(110) for which the metal-to-nonmetal transition occurs at a cluster size of 3.0 nm by 1.1 nm (~300 atoms per cluster) (9).

The relative population of the Au clusters with a band gap of 0.2 to 0.6 V measured by STS from Au/TiO$_2$(110) is shown in Fig. 3C. This band gap is associated primarily with the size of the images is 50 nm by 50 nm.

The size of the images is 50 nm by 50 nm. Two CCT STM images of Au/TiO$_2$(110)-(1×1) as prepared in Fig. 2 (A) after 120 min of CO$_2$ exposure at 10 Torr, and (B) after 120 min of CO$_2$ (2:1) exposure at 10 Torr. The Au coverage was 0.25 ML, and the sample was annealed at 850 K for 2 min before the exposures. All of the exposures are given at 300 K. The image sizes are 50 nm by 50 nm.

In addition to the significant agglomeration of the Au clusters, extremely small, presumably TiO$_2$ clusters (~1.5 nm in diameter), were formed. X-ray photoemission spectra (XPS) before and after the CO exposure show no changes in the chemical composition of the Au/TiO$_2$(110)-(1×1) surface; however, the TiO$_2$(110) surface oxidized after the CO$_2$ and CO:O$_2$ were identical and because there were no detectable changes after exposure to CO, we conclude that the Au/TiO$_2$(110) surface exhibits an exceptionally high reactivity toward O$_2$ at 300 K that promotes the sintering of the Au nanocrystallites. The possible effect of thermal sintering can be excluded because of the anneal to 850 K before the adsorption experiments. Although O$_2$ adsorption on atomically flat metal single crystals of Au is a highly activated process with an extremely low sticking probability at 300 K (11), Au nanoclusters can activate O$_2$ and produce atomically adsorbed O atoms on Au clusters (12).

In the reaction kinetics studies (discussed above), the Au clusters exhibited a very high activity toward CO oxidation; however, the surface was effectively deactivated after reaction for 120 min. This deactivation is believed to be caused by O$_2$-induced agglomeration of the Au clusters as seen in Fig. 4B. The oxidation of the slightly oxygen-defi-
cient TiO₂ surface after the 120-min CO₂ exposure (Fig. 5) is likely lowering the activity of Au/TiO₂ even further, because the fully oxidized stoichiometric TiO₂ surface can no longer adsorb O₂ at 300 K (13). Oxidation of the TiO₂ surface during CO oxidation also provides direct evidence that the deactivation is not likely caused by encapsulation of Au clusters by reduced Ti suboxides as, for example, in the case of Pt/TiO₂ (110) (14).

In order to better understand the role of O₂ in CO oxidation and in various O₂ pretreatments that are commonly applied to Au/TiO₂ catalysts to improve their activity (15), the clean TiO₂(110) surface (Fig. 6A) was exposed to O₂ at 2 × 10⁻⁸ Torr. After O₂ treatment, small islands randomly nucleated on TiO₂(110) and finally covered the entire surface (Fig. 6B). Low-energy electron diffraction (LEED) showed a (1×1) pattern indicating that the islands are growing pseudomorphically. XPS measurements of this rough TiO₂ surface after the O₂ treatment indicated that the surface is not significantly changed in chemical composition and thus is still slightly O-deficient. Recently, it was suggested that partially reduced Ti⁴⁺ (n ≤ 3) ions can be formed in a vacuum-annealed and Ar⁺-bombarded TiO₂(110) surface by annealing at 800 K and reoxidizing to TiO₂(110)-(1×1) terraces in an O₂ ambient of 7.5 × 10⁻⁸ Torr (7). A similar kind of oxidation of the reduced Ti⁺⁺ ions may occur during the O₂ treatment used here.

The influence of the O₂-exposed, rough TiO₂ surface on the sintering of the Au clusters during CO oxidation at 300 K is shown in Fig. 6, C and D. If we compare a CCT STM image of 0.25 ML Au on TiO₂(110)-(1×1) after deposition of Au at 300 K, annealing at 850 K for 2 min, and a subsequent O₂ exposure of 2 × 10⁻⁸ Torr at 650 K for 10 min (Fig. 6C) with one for which no O₂ treatment was made (Fig. 2A), the only difference is the general disorder of the TiO₂ surface. The cluster density and size distribution of the Au clusters are identical for both surfaces. Upon exposure of the rough Au/TiO₂(110) surface to CO₂ at 120 min at a total pressure of 10 Torr at 300 K, the cluster density and size distribution of the Au clusters remain unchanged (Fig. 6D). The Au/TiO₂(110) surface was oxidized after the high-pressure CO₂ exposure (Fig. 4) and the cluster density of the TiO₂ clusters increased. The O₂-exposed, rough TiO₂ surface then prevents sintering of the Au clusters. Furthermore, a similar kind of atomically rough TiO₂ phase may be formed during the high-temperature reduction, calcination, and low-temperature reduction (HTRC/LTR) procedure used on high-surface area Au/TiO₂ catalysts (15). After this treatment Au/TiO₂ catalysts exhibit a higher degree of resistance toward sintering of the Au clusters during CO oxidation at low temperatures (15).

These results indicate that the pronounced structure sensitivity of CO oxidation on Au/TiO₂ originates from quantum size effects associated with the supported Au clusters. The observed tailoring of the properties of small metal clusters by altering the cluster size and its support could prove to be universal for a variety of metals and will likely be quite useful in the design of nanostructured materials for catalytic applications.

References and Notes
8. The experiments were carried out in a combined elevated-pressure reactor–ultrahigh vacuum (UHV) system with a base pressure of 5 × 10⁻¹¹ Torr equipped with a double-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES) and XPS measurements, a quadrupole mass analyzer, and a UHV-STM (Omicron) (R. A. Campbell and D. W. Goodman, Rev. Sci. Instrum. 63, 339 (1992)). After preparation and characterization in the UHV chamber, the Au/TiO₂(110) model catalyst was transferred in situ into the reaction chamber through a double-stage, differentially pumped Teflon sliding seal. This arrangement facilitates elevated-pressure adsorption studies in the pressure range of 1 × 10⁻⁸ to 1 × 10⁻¹ Torr. A TiO₂(110) single crystal [Commercial Crystal Laboratories], an n-type semiconductor after cycles of Ar⁺-ion bombardment and vacuum annealing at 700 to 1100 K, was found to be sufficiently conductive for electron spectroscopy and STM studies. This cleaning procedure produces a slightly oxygen-deficient surface with a well-ordered (1×1) surface as characterized by LEED and XPS measurements (J.-M. Pan, B. L. Maschhoff, U. Diebold, T. E. Maday, J. Vac. Sci. Technol. A 10, 2470 (1992); L. Zhang, R. Persaud, T. E. Maday, Phys. Rev. B 56, 10549 (1997)). Gold clusters were evaporated onto the TiO₂(110) surface from a source containing high-purity Au wire wrapped around a W filament that was heated resistively. The Au flux was calibrated with a Re(0001) substrate by using AES and STM as described (13). The Au coverage is reported in monolayers (ML), one ML corresponding to 1.387 × 10¹⁵ atoms per centimeter squared. After the Au deposition, the sample was annealed at 850 K for 2 min. The sample temperature was measured with a pyrometer (OMEGA OS3700), which was calibrated against a W-5% Re/W-26% Re thermocouple. Research-grade CO was further purified by storing at liquid N₂ temperatures; O₂ was used as received. The CO₂/Ar (2:1) mixture was prepared separately before the adsorption experiments.
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Long-Range Electrostatic Trapping of Single-Protein Molecules at a Liquid-Solid Interface
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The motion of single, dye-labeled protein molecules was monitored at various pH and ionic strengths within the 180-nanometer-thick evanescent-field layer at a fused-silica surface. Below the isoelectric point, molecules partitioning into the excitation region increased in number but maintained a random spatial distribution, implying that surface charge can influence the charged protein at distances beyond that of the electrical double-layer thickness. The residence times of the molecules in the interfacial layer also increased below the isoelectric point. However, immobilization on the solid surface for extended periods was not observed. Histograms of residence times exhibit nearly identical asymmetry as the corresponding elution peaks in capillary electrophoresis. These results are a direct verification of the statistical theory of chromatography at the single-molecule level, with the caveat that long-range trapping rather than adsorption is the dominant mechanism.

Insights into the detailed dynamics of adsorption and desorption at an interface are vital to designing new materials, elucidating biological processes at cell surfaces, studying electrochemical reactions, and understanding chromatographic mechanisms. For example,