Gold Atoms Stabilized on Various Supports Catalyze the Water–Gas Shift Reaction

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CONSPECTUS

For important chemical reactions that are catalyzed by single-site metal centers, such as the water–gas shift (WGS) reaction that converts carbon monoxide and water to hydrogen and carbon dioxide, atomically dispersed supported metal catalysts offer maximum atom efficiency. Researchers have found that for platinum metal supported on ceria and doped ceria in the automobile exhaust catalyst, atomic $Pt-O_x-Ce$ species are the active WGS reaction sites. More recently, preparations of gold at the nanoscale have shown that this relatively "new material" is an active and often more selective catalyst than platinum for a variety of reactions, including the WGS reaction. The activity of gold is typically attributed to a size effect, while the interface of gold with the support has also been reported as important for oxidation reactions, but exactly how this comes about has not been probed satisfactorily. Typical supported metal catalysts prepared by traditional techniques have a heterogeneous population of particles, nanoclusters, subnanometer species, and isolated atoms/ions on the support surfaces, making the identification of the active sites difficult. Both we and other researchers have clearly shown that gold nanoparticles are spectator species in the WGS reaction. Evidence has now amassed that the gold active site for the WGS reaction is atomic, that is, $Au-O_x$ species catalyze the reaction, similar to $Pt-O_x$.

In this Account, we review the relevant literature to conclude that the intrinsic activity of the $Au-O_x(OH)-S$ site, where S is a support, is the same for any S. The support effect is indirect, through its carrying (or binding) capacity for the active sites. Destabilization of the gold under reducing conditions through the formation of clusters and nanoparticles is accompanied by a measurable activity loss. Therefore, it is necessary to investigate the destabilizing effect of different reaction gas mixtures on the gold atom sites and to consider regeneration methods that effectively redisperse the gold clusters into atoms.

For gold catalysts, we can remove weakly bound clusters and nanoparticles from certain supports by leaching techniques. Because of this, we can prepare a uniform dispersion of gold atoms/ions strongly bound to the support surface by this two-step (loading followed by leaching) approach. Presently, one-step preparation methods to maximize the number of the single atom sites on various supports need to be developed, specific to the type of the selected support. Often, it will be beneficial to alter the surface properties of the support to enhance metal ion anchoring, for example, by shape and size control of the support or by the use of light-assisted deposition and anchoring of the metal on photoresponsive supports. Because of their importance for practical catalyst development, synthesis methods are discussed at some length in this Account.
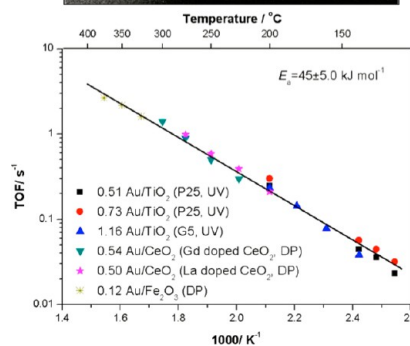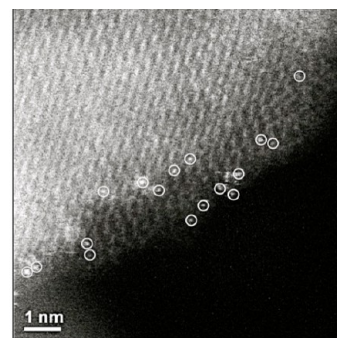
Introduction

It is now recognized that atomically dispersed metals on various supports provide the catalytic centers for certain reactions.[1] Incorporation of a metal atom on a zeolite or oxide almost always implies that it is cationic and thus not in the form most commonly encountered in supported metal catalysts. For practical applications, methods for the synthesis and stabilization of atomic sites on supports are

needed to maximize the efficiency of precious metal use, if a precious metal is selected, and to minimize the cost.[2,3] The support must offer many anchoring sites to stably bind the metal ions through $-O$ linkages. Because of their crystallinity and uniform structure, zeolites have been studied more extensively as "ligands" binding the metal cations.[1,2] Open oxide supports lack the uniformity of anchoring sites and must be carefully prepared to meet the challenge of active site stability. In this Account, only a cursory reference to zeolites is made, the emphasis being on atomically dispersed gold on open oxide supports, prepared and evaluated as catalysts for the low-temperature water−gas shift (WGS) reaction.

The WGS reaction, $(CO + H_2O \rightarrow H_2 + CO_2)$, which is important in upgrading H_2-rich fuel gas streams for fuel cells and other applications, has been studied on various supported metal catalysts.[4] For the low-temperature range (200−350 °C), catalysts based on the Pt-group metals are of interest as alternatives to the low-stability Cu/ZnO catalysts.[4−6] Supports such as ceria and zirconia-doped ceria are preferred because they can anchor and stabilize metal atoms on their surfaces. Much of our knowledge derives from the use of doped ceria in the automotive exhaust three-way catalyst (TWC), where $Pt-O_x-Ce$ species have been identified as the active sites for the WGS reaction.[7,8] Novel catalyst designs that maximize the number of such sites have been actively investigated. Doping with zirconia or certain rare earth oxides suppresses the grain growth of ceria at high temperatures and increases its oxygen storage capacity.[9−12] Nanocrystalline ceria with a high concentration of Ce^{3+} and oxygen vacancies[13] is a preferred support for the Pt-group metals,[8,9,14−16] as well as for $Cu^{17,18}$ and $Au^{15,19,20}$ catalysts.

Historically, gold was realized as an active catalyst much later than platinum. Its superior catalytic oxidation activity at the nanoscale was first reported by Haruta for the CO oxidation reaction in 1987.[21] The high activity of nanoscale gold on TiO_2, α-Fe_2O_3, and Co_3O_4 was theorized to derive from the interaction of gold nanoparticles at the interface with the support.

The water−gas shift reaction was one of the many reactions found to be catalyzed by gold in the years following Haruta's discovery. The Andreeva group in 1996[22] and the Flytzani-Stephanopoulos group in 2001[19] first reported the low-temperature WGS activity of nanostructured gold supported on Fe_2O_3 and CeO_2, respectively. Both groups identified an important role of the support but did not specify at first whether the support played a direct or indirect role in

the catalysis by gold. Au/CeO_2 was found to be superior to gold supported on other oxides, whether prepared by coprecipitation or deposition/precipitation,[15,19] the latter promoted as the preferred method for Au/TiO_2.[23] A flurry of research activity followed using many oxide supports and various methods of preparation and characterization. A detailed account can be found in a recently published review.[24] However, the key question of whether the choice of support affects the mechanism of the water−gas shift reaction at low-temperatures is still being debated.

It is a main objective of this Account to show that the effect of the support is indirect. Thus, we make the case that partially oxidized gold species, $Au-O-(OH)_x-S$, are the active sites, with S being a support atom in the vicinity of the gold atom that activates water and supplies $-OH$ groups. Accordingly, gold and platinum, two very different metals electronically, have similar active sites for the WGS reaction, the support stabilizing these active Au (or Pt) sites through $-O$ bonds.

Identifying the Active Gold Sites on Various Supports

Supported metal catalysts typically comprise a nonuniform collection of structures, including nanoparticles, subnanometer structures, and atoms, the latter being TEM-invisible and traditionally ignored, especially in the early literature, due to the lack of high-resolution instrumentation. It is now possible to image sub-nanometer clusters and individual atoms and ions with subangstrom resolution using aberration-corrected annular dark field scanning transmission electron microscopy (ac-ADF/STEM), see Figure 2a,b. This has enabled imaging single atoms of gold in zeolites[25] and on open supports, for example, MgO,[26] FeO_x,[27,28] and TiO_2.[29] Model catalysts prepared by atomic gold deposition on single crystal surfaces and imaged with atomic-resolution scanning tunneling microscopy (STM), provide useful complementary information.[30] Of course, before atomic-resolution imaging became available, spectroscopic methods, such as EXAFS, were used to demonstrate the presence of isolated cations and follow their evolution in situ, pioneered by Gates and co-workers.[26,31] For some reactions, like ethylene hydrogenation, isolated gold cations on MgO are the exclusive active sites.[26] For other reactions, like the CO oxidation, a more complex picture has emerged whereby the coexistence of gold cations and clusters increases the activity.[1] Despite being considered more complex than dry CO oxidation,[24] the WGS reaction involving the activation of water, rather than dioxygen, seems to converge to a simpler structural picture of an active site.[1]

There are two issues to contend with in clarifying the actual structure of a gold active site: (i) Are gold cations active for the WGS reaction, and if so are they the exclusive active sites? (ii) Are all supports similar, assuming of course that the support can stabilize the active gold cations effectively through oxygen linkages and provide the −OH groups in the vicinity of the gold cation? If issue ii holds true, a kinetic evaluation should find the same apparent activation energy for all gold catalysts under similar reaction conditions. We address these issues below.

Activity of Gold Cations for the WGS Reaction. The Ichikawa group first reported on the WGS reaction activity of gold loaded in zeolites.[32] Using $AuCl_3$ as precursor, and without further treatment, they found evidence for Au^+ as the active site on several zeolites, all examined at 50 °C. Identification of surface species was made by *in situ* FTIR. Isolated mononuclear gold complexes on open supports can be carefully prepared, as shown by Gates and co-workers on MgO, starting from an organometallic precursor of gold.[26] The stability of the active gold sites in zeolites and on MgO in realistic WGS fuel gas streams and temperatures has not been evaluated.

Open supports like CeO_2, can stabilize active gold sites on their surfaces at realistic gas compositions and temperatures as high as 350 °C.[12,15,19,20] How does this stabilization come about? It has been known since the 1980s that the interaction of Pt metals with ceria greatly increases the surface reducibility of the latter,[33] which is crucial to improving the lightoff temperature of the automotive TWC. This is a surface effect, also holding true for gold;[15,19,34,35] that is, the bulk reducibility of ceria is not affected. Thus, it may be incorrect to view the metal ion as a bulk dopant, substituting for a Ce^{4+} ion in the lattice. We note that in coprecipitated $Au-CeO_x$ materials, the presence of gold suppresses the grain growth of ceria during calcination.[19] The smaller the particle size of ceria below ~10 nm, the higher the concentration of Ce^{3+} and oxygen vacancies.[13] The bridged Au−O−Ce species, however, can be extra-lattice, similar to metal ions bound to the extra-framework oxygen of zeolites. A single gold atom adsorbed atop a $CeO_2(111)$ oxygen was found active for the WGS reaction by DFT.[36] In recent computations, Zhang et al. have shown that on the stoichiometric $CeO_2(111)$ surface, the most stable adsorption site of Au is on a bridge-like site in which the Au binds to two O atoms.[37] On nonstoichiometric CeO_{2-x}, both oxygen and cerium ion vacancies are probable loci for gold atom adsorption.[37]

Fu et al.[15] used NaCN solutions to effectively remove all metallic gold nanoparticles and other weakly bound gold species from ceria. Multiple washes and heat treatment in air followed to remove any cyanide species from the surface. The residual gold species were mainly Au^{1+}, as shown by XPS,[15] and isolated gold cations were initially present, as found by XANES/EXAFS.[38] The leached and parent materials exhibited identical WGS activity, which demonstrates the residual cationic gold species, strongly bound to ceria, as the active sites for the WGS reaction.

The interaction of gold atoms with single crystal surfaces of ceria prepared by hydrothermal techniques as rods, cubes, and polyhedra at the nanoscale was reported first by Si and Flytzani-Stephanopoulos in 2008.[39] In that work, gold (1 wt %) was loaded on the ceria nanoshapes by deposition−precipitation (DP), and after calcination, cyanide leaching was used to leave only the strongly bound gold on the surface. The parent catalysts showed a strong shape effect, namely, weakly bound gold nanoparticles on the ceria nanocubes ({100} surfaces) and strongly bound, TEM-invisible gold on the ceria nanorods ({110} and {100} surfaces). Oxygen vacancies are easier to form on the {110} than the {100} surfaces of ceria,[40] and this may explain the higher fraction of strongly bound gold on the former. Figure 1 shows the state of gold on the various ceria shapes, and the corresponding WGS activity. The parent and leached gold catalysts had the same total activity (expressed as mol $CO_2/(g_{total} \cdot s)$ or $CO_2/(m_{total}^2 \cdot s)$); but it was now possible to rank order the shape effect. Thus, after leaching, almost 0.6 wt % Au remained bound to the {110} planes (of ceria rods), while only 0.03 wt % Au was left on the {100} surfaces (of the cubes). The specific activity of these residual gold atoms on either surface was the same, as was the apparent activation energy (E_{app}) of the reaction. Hence the shape effect of ceria is indirect,[41] simply manifesting the different ability of each ceria surface to bind gold, but ceria does not alter the mechanism of the reaction. Hensen's group have recently reproduced the shape effect of ceria on the stabilization of different gold structures, which they examined for the WGS and other reactions.[42]

In situ examination of the catalyst structure during the WGS reaction can be made by EXAFS. However, the catalysts originally examined were ceria or ceria−zirconia loaded with 2−5 wt % Au,[43,44] that is, with much more gold than either support could bind atomically. In the presence of the metallic gold nanoparticles and clusters, it is impossible to separate out and follow the minority structure on the surface, that is, the $Au-O_x-Ce$ species. To overcome this difficulty, Deng et al. examined leached Au/CeO_x catalysts.[38] Starting from a fully dispersed gold state, for which no
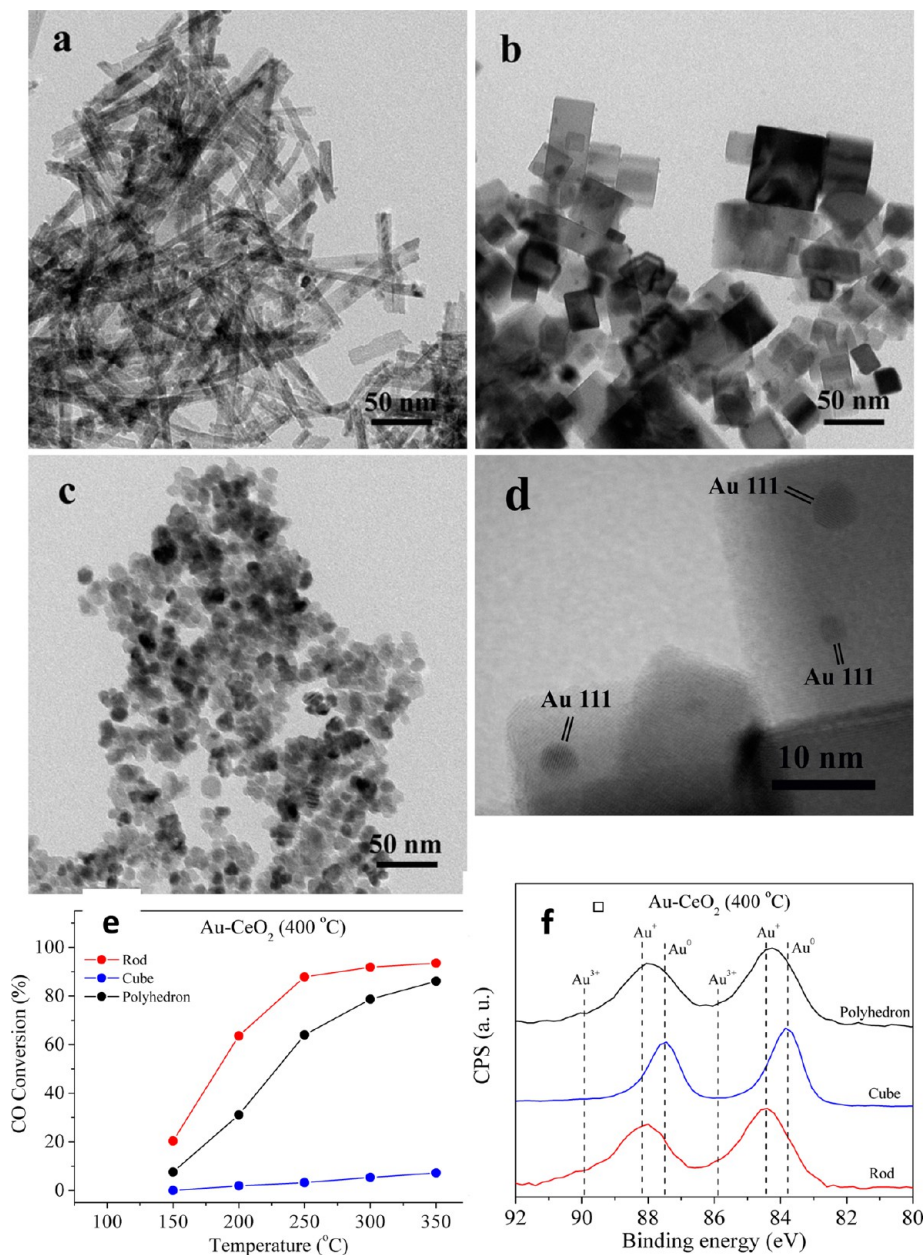
FIGURE 1. TEM (a−c) and HREM (d) images of the 1% Au on CeO_2 nanorods (a), cubes (b, d), and polyhedra (c), "shape effect" on the WGS reaction profiles (e), and Au 4f XP spectra on CeO_2 nanorods, cubes, and polyhedra (f). Reproduced with permission from ref 39. Copyright 2008 WILEY-VCH GmbH & Co. KGaA.

Au−Au contributions were found, they followed the evolution of the gold structure under reaction conditions. The redox potential of the reaction gas mixture controlled the extent of oxidation of the gold species. As the number of oxidized gold species dropped and gold aggregation took place, a partial loss of catalytic activity occurred. This is attributable to gold destabilization from the Au−O_x−Ce active site.[38] Gold destabilization was reversible, that is, redispersion of atomic gold was possible by oxidation at 400 °C, accompanied by an increase of the surface oxygen

and recovery of the catalytic activity.[38] In a similar EXAFS study of leached Au/CeO_{2-x} nanorods, Guan et al. also found gold cluster formation, but how much of the gold remained in the active Au−O_x−Ce state was not possible to determine due to the "averaging" inherent to this technique.[42]

The Role of the Support Oxide. Having found the ceria shape-independent specific activity of gold species,[41] it is natural to wonder whether other supports may similarly stabilize active Au−O_x species, and whether there is a real
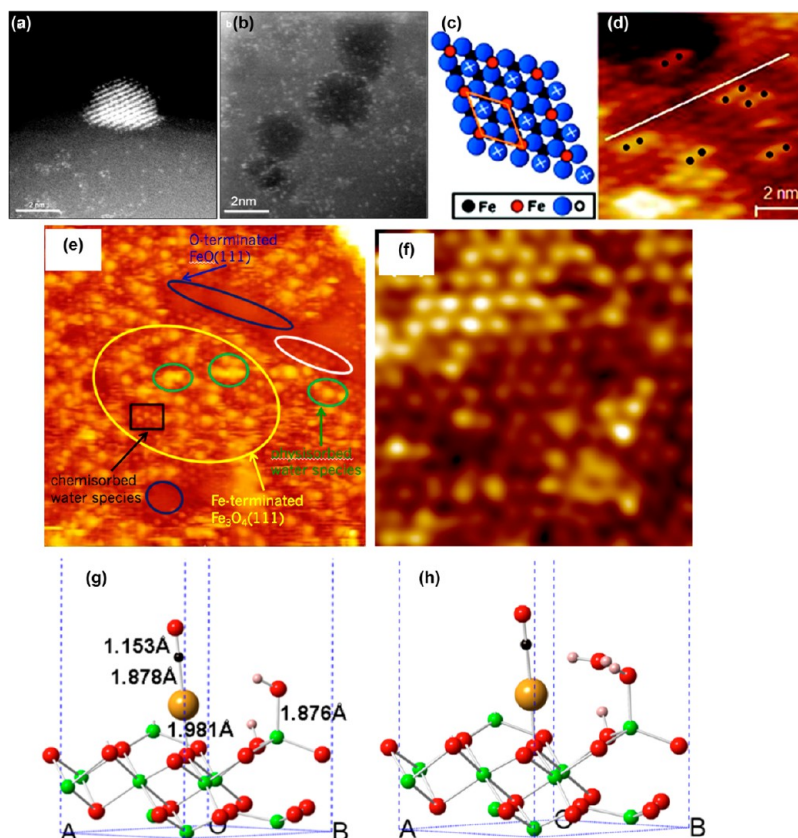
FIGURE 2. HAADF/STEM images of powder Au−Fe$_2$O$_3$ catalysts: (a) A typical area of the parent 2 atom % Au/Fe$_2$O$_3$ catalyst (World Gold Council) showing both nanoparticles and atomic gold; (b) the 0.7 atom % Au−Fe$_2$O$_3$ sample (leached from the parent with a 2 wt % NaCN aqueous solution) shows isolated gold atoms in bright contrast (panels a and b reproduced with permission from ref 27. Copyright 2009 Japanese Society of Electron Microscopy). (c) A model of the Fe(III)-terminated Fe$_3$O$_4$(111) surface; Au atoms are bonded atop uncapped oxygen sites labeled by ×, which correspond to the black dots in panel d; (d) the bright features labeled in the STM image by black dots are Au adatoms that are aligned with the 3-fold hollow sites of the hexagonal 2 × 2 structure, one direction of which is indicated by the white line (panels c and d reproduced from ref 30. Copyright 2009 American Chemical Society). (e) Topographic STM image of an iron oxide surface after dosing 0.15 L of water at 235 K (reproduced from ref 51. Copyright 2012 American Chemical Society). (f) The STM image at 245 K shows only hydroxyl groups (bright features) on the Fe-terminated Fe$_3$O$_4$(111) surface (reproduced from ref 51. Copyright 2012 American Chemical Society). DFT-computed optimized H$_2$O and CO adsorption on an Au-doped Fe$_3$O$_4$ (111) surface: (g) dissociative water adsorption; (h) two H$_2$O molecule adsorption (red, O atoms; green, Fe atoms; black, C atom; orange, Au atom; pink, H atoms) (panels g and h reproduced from ref 51. Copyright 2012 American Chemical Society).

"support effect" for the WGS reaction catalyzed by these gold species. Many reports of a support effect are found in the literature, for example, comparing reducible and nonreducible oxide supports,[45] M$_x$O$_y$ promoters of TiO$_2$-supported gold,[46] and preparation methods and dopants in ceria supports.[47] However, there is lack of systematic study of the support effect by identifying what species, if any, common to all active gold catalysts reside on the support. This issue remains confusing in the literature.

In their initial work with CeO$_2$ and FeO$_x$, the Flytzani-Stephanopoulos[19] and the Andreeva[24] groups, respectively, reported on the important role of the support for the WGS reaction. Over the following decade, these and other groups have noted the importance of specific surface oxygen sites on the support for an active catalyst. For example, FeO(OH)$_x$

surfaces were reported as essential for active Au/FeO$_x$ catalysts.[48] Elucidating the importance of −OH species in the vicinity of the gold ion centers is a new research focus, with examples spanning other oxide supports, such as LaO(OH)$_x$[49] and partially reduced TiO$_x$.[29] From the gathered evidence, the activity appears to be directly correlated with the number of surface −OH species that can be activated by CO at low temperatures, this number titrated by a simple CO-TPR experiment, as discussed below.

Deng et al.[50] have compared Au/CeO$_2$ and Au/FeO$_x$ and found the NaCN-leached derivatives of both catalysts equally active to the parent samples. The leached Au/FeO$_x$ catalyst after many hours of reaction in a reducing fuel gas mixture up to 350 °C still contained a large fraction of

isolated gold atoms along with sub-nanometer clusters, as shown by ac-HAADF/STEM.[27] Thus, similar to ceria, the iron oxide has good capacity to stabilize atomic gold species on its surface. The areal reaction rates are similar for the CeO_2- and FeO_x-supported gold catalysts and have similar apparent activation energies. Thus, the same active gold species are inferred on both supports.

We may visualize the active gold site as connected with $-O$ ligands to the support and $-OH$ groups adsorbed on the Ce or Fe atoms in the vicinity of the Au cation. This picture was recently probed by STM imaging of Au adatoms stabilized over the uncapped oxygen of Fe(III)-terminated $Fe_3O_4(111)$ single crystal surfaces[30] and by CO and H_2O adsorption on the gold-loaded[30] and on the gold-free surfaces.[51] A remarkable stability of gold adatoms to 500 °C was found. CO adsorbs linearly on the isolated gold adatoms,[30] while $-OH$ adsorbs on the three terminal iron atoms surrounding the gold adatom.[51] DFT work confirms these as the most energetically favored sites for the reaction of adsorbed CO and $-OH$.[51] Figure 2 depicts major findings from these reports. Diebold's group has recently shown a similar high stability of isolated gold adatoms on $Fe_3O_4(001)$.[52] Thus, we can prepare active and stable Au/FeO_x catalysts for the low-temperature WGS by maximizing the number of these strongly interacting $Au-O_x(OH)-Fe$ sites.

Au/TiO_2 catalysts are very interesting, because gold is known to bind weakly on TiO_2 if prepared by simple DP.[21] Thus, only a small fraction of gold is present as isolated atoms on titania, and the overall catalyst activity for WGS is inferior to Au/CeO_2.[19] Leaching of the gold from such surfaces leaves a very small amount of residual gold on the surface, which proves the point. However, in a recent paper, Yang et al. have shown how to overcome this barrier and demonstrated that UV-assisted gold deposition facilitates the anchoring of a large amount ($\sim$1 wt %) of gold atoms on the titania surfaces.[29] Figure 3 shows ac-HAADF/STEM images of a sample containing this high amount of gold in isolated atom state, stably anchored on the surface even after cyanide leaching, washing, and annealing to 200 °C in air. These sites appear to comprise Au^{1+} species bound over $Ti^{\delta+}$, based on XPS, XANES, and EPR analyses.[53] The $-OH$ groups on the surface more than double, as shown by CO-TPR. The leached and parent Au/TiO_x catalysts have similar activity, and the same number of low-temperature reducible $-OH$ species.[29] This is shown in Figure 4. Hence, the gold nanoparticles in the parent catalysts are determined to be a spectator species for the WGS reaction on Au/TiO_2. These results contradict the conclusions of a recent
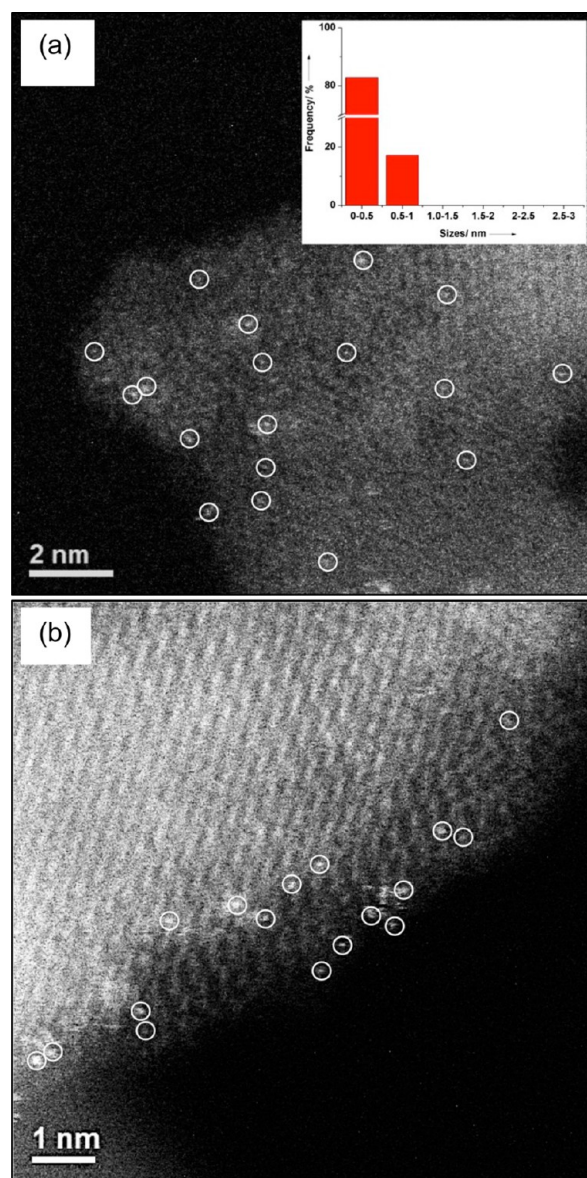

FIGURE 3. ac-HAADF/STEM images of (a) fresh 1.16 wt % Au/titania (anatase, G5-Millenium), catalyst prepared by UV-assisted DP, air calcination, and cyanide leaching of unbound gold and (b) the same sample after use (10% CO$-$3% H_2O-He, 30 mL/min 100 mg sample; held at 373 K for 4 h) and after a second 0.05 wt % NaCN leaching (0.43 wt % Au remained, all as isolated atoms). The circles are drawn around isolated gold atoms. Reproduced from ref 29. Copyright 2013 American Chemical Society.

report of a size-dependent gold activity in the >1 nm size range.[54] By not accounting for the sub-nanometer clusters and the omnipresent gold atoms in their samples, the authors have reached an improperly weighed rate. However, as stated above, it is very hard to keep many of these atoms bound to titania by the usual DP method of gold loading. The method used by Yang et al. is preferred, because it also leads to more stable, potentially practical catalysts.
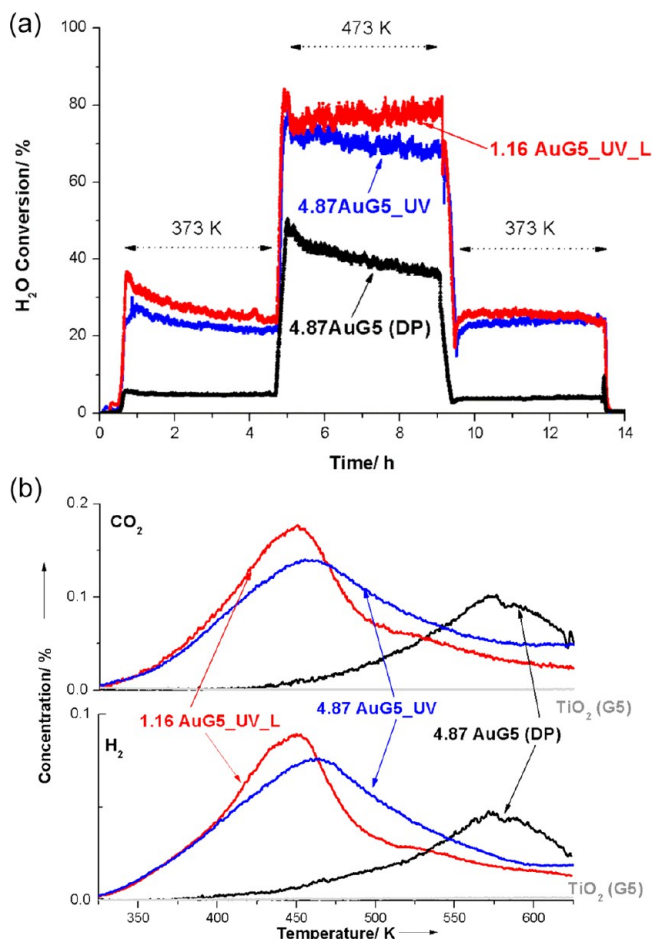
FIGURE 4. (a) Low-temperature WGS-TPSR with steady-state holds of 4 h at 373 and 473 K (heating rate, 5 K/min, 10% CO$-$3% $H_2O$$-$He, 30 mL/min; 100 mg sample). Shown is the H_2 produced. (b) CO-TPR profiles (10% CO$-$He, 30 mL/min, 100 mg) for the parent (AuG5) and cyanide leached (AuG5_L) Au/TiO$_2$ (anatase, G5-Millenium) catalysts. Samples were prepared by DP (deposition$-$precipitation) or UV (UV-assisted DP). Each sample was purged with 30 mL/min He at 373 K for 20 min, then cooled to 323 K in He, and stabilized in 10% CO$-$He for 20 min. Reproduced from ref 29. Copyright 2013 American Chemical Society.

An important mechanistic finding is that the E_{app} for the WGS reaction is the same for all the Au/TiO$_2$ samples, whether prepared by DP[29,54] or UV-assisted DP methods,[29] and it is the same for parent samples and their leached derivatives. Furthermore, the E_{app} is the same as for ceria-[15,20] and iron oxide-[50] supported gold. This confirms the same active species, Au$-$O$_x$$-(OH)-$, on any support. Casting the kinetic data from various sources in the form of an Arrhenius plot of TOF would be instructive for catalyst design. The question is what scaling factor to use to normalize the reaction rates. From our studies, we have concluded that the atomically dispersed gold, if properly counted, is that factor. This can be done for the leached catalysts that contain more than
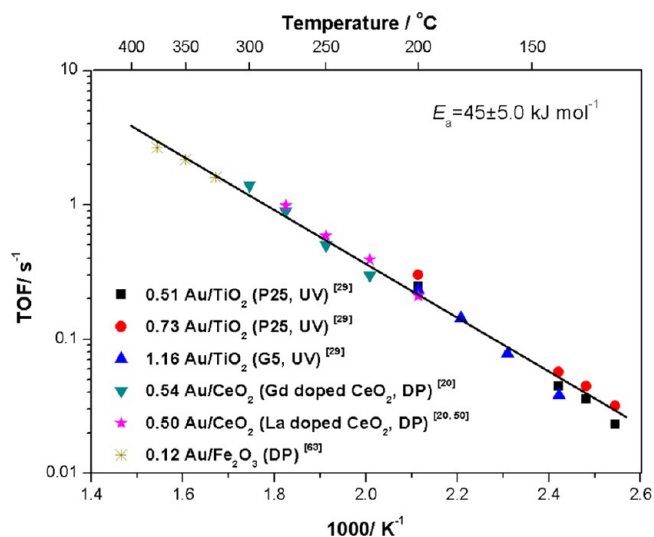
FIGURE 5. TOF plot for the WGS reaction over leached Au/CeO$_2$,[20,50] Au/Fe$_2$O$_3$,[63] and Au/TiO$_2$[29] catalysts in a simulated reformate gas mixture 11% CO$-$26% $H_2O$$-$7% $CO_2$$-$26% $H_2$$-$He. DP, deposition$-$precipitation; UV, UV-assisted DP. The numbers are the weight percentages of gold in each sample. P25, 30% rutile + 70% anatase from Degussa; G5,100% anatase from Millenium.

90% of their gold as isolated atoms on the surface. Figure 5 depicts a single TOF for atomic gold catalysts on various supports and constitutes the major conclusion of this Account.

An alternative scaling factor is the number of $-$OH species associated with the gold cation, which are found by integrating the CO-TPR plot up to the temperature of 350 °C, where the support oxide alone may be activated for the WGS reaction.[15,50] For this calculation, we consider the second (or later) cycle of a CO-TPR with intermittent rehydration, because the first cycle may also contain other adsorbed oxygen species that are irrelevant for the WGS reaction; that is, we count only the $-$OH species that react with CO to produce both CO_2 and H_2.[15,20,29,49,50,55] Since this method would give the same number of $-$OH on either the parent or leached gold catalysts, see Figure 4, it frees us from having to leach the catalyst to count the gold atoms. Such an example can be found in Boucher's thesis[55] for Au/ZnO nanoshapes from which gold cannot be leached by the usual cyanide method, because zinc oxide also partially dissolves. Hence, it is a more general method, useful for all supported gold catalysts and for other metal atoms catalyzing the WGS reaction, such as platinum.[56]

Rationalizing the Preparation Methods for Atomically Dispersed Supported Gold Catalyst Design

The unified kinetics of gold on various oxide supports shown in Figure 5 clearly points to maximizing the number of gold

atoms stably bound on any support as the primary guiding principle for rational catalyst design. Accordingly, the choice of support and its properties are important. The "easiest" support to work with is ceria. To maximize oxygen defects, nanocrystalline ceria and zirconia- or rare earth oxide-doped ceria are recommended.[9,11,13,19] The urea gelation coprecipitation method is superior in preparing more uniform nanocrystalline ceria on which gold can be deposited by DP.[19] Properly controlled, single-step coprecipitation of gold and ceria may be preferred because it creates many $Au-O_x-Ce$ interacting species and suppresses the particle growth of ceria.[15,19] The gold "loading capacity" of the ceria surface is a function of its properties; and can be found by a simple leaching experiment. Of course, the ultimate number of stable $Au-O_x-Ce$ species on any support will be determined by the reaction conditions,[50] as in the TWC-Pt/CeO_x.[8]

The use of undoped ceria is problematic when realistic fuel gas streams are used and shutdown to ambient temperatures takes place in condensing water.[5,20,57] The reason is the formation of surface $Ce(OH)CO_3$ which inhibits the reaction upon restart and heating to the reaction temperature.[57] Treatment in air at 400 °C restores the activity. A remedy is to run the reaction with a small amount of molecular oxygen (0.5−1.0 mol %) in the gas, that is, under oxygen-assisted WGS conditions, which also stabilizes the active $Pt-O_x$ and $Au-O_x$ sites on ceria during reaction.[57] Alternatively, one can use suitably doped ceria or nonceria supports to solve this destabilization issue.

Identifying good preparation methods of nanogold catalysts has been the subject of many studies; albeit focusing primarily on how to prepare monodisperse gold nanoparticles on various supports. In an effort to see how the preparation methods affect the number of active sites for the WGS reaction, Hardacre and co-workers[58] used CO as a probe and showed that the Au−CO band areas detected by FT-IR correlate with the number of active gold sites on Au/$CeZrO_4$ samples prepared by changing the preparation parameters, including also the Zr content of ceria and sulfation of the $CeZrO_4$ support. It would be nice to include the leached derivatives of these samples to enable actual counting of the active gold sites, and establishing a common TOF, independent of the preparation parameters.

Nonreducible oxides with scant oxygen defects have few binding sites to atomically disperse metal ions. Zeolites are an exception due to their (varied) content of extra-framework oxygen. Some oxides may be prepared with many −OH groups by hydrothermal crystal growth in NaOH or other alkaline solutions. In a second step, the gold may be added by impregnation, deposition/precipitation, vapor deposition, and a number of other well established preparation techniques of supported metal catalysts.[59]

Often, ion adsorption by suitable control of the solution pH compared with the point-of-zero charge of the oxide surface is recommended for better metal dispersion.[60] Other strategies may be followed to maximize the metal ion anchoring sites on any support. These include template methods to create the required anchoring sites, for example, for lanthana[49] or even carbons.[61]

For the semiconductor titania, which interacts weakly with gold, a controlled UV-irradiation in an ethanol solution of a DP-prepared gold on titania works well to create many anchoring sites for atomic gold.[29] The titania "gold loading capacity" can thus be made to exceed ~1 wt %, better than that of some good nanoscale cerias (~0.5−0.8 wt %).[15]

Can we activate gold on any support, including earth-abundant, low-cost oxides, such as iron oxide, aluminosilicates, etc.? The answer is "yes" for the former, and this is a stable catalyst as discussed above; and also for the latter, potentially with the use of an alkali promoter. Alkali additives stabilize $Pt-O_x-(OH)_y-$(Na, K) species on silica,[56] alumina,[56] or even carbon nanotubes,[62] and these catalyze the WGS reaction. Evidently, the hydrophilic (Na, K) ions play a role similar to Ce or Fe-bound $Pt-O_x$. The E_{app} for the WGS reaction is the same (70 ± 5 kJ/mol) for Pt catalysts on any of these supports. Work on gold with alkali and alkaline earth additives is much less advanced when it comes to the WGS reaction. Gold on alumina can be rendered active with alkali and alkaline earth addition, but it is not very stable.[63,64] Gold on hydroxyapatite (Au/$Ca_{10}(PO_4)_6(OH)_2$) is an active WGS catalyst.[65] There may be new ways to prepare active gold compounds with alkali or alkaline earths containing −OH species that are stable. However, more work is needed to demonstrate the feasibility of this approach for gold.

Concluding Remarks

This Account is not a comprehensive review of the WGS reaction literature on gold catalysts. Rather, it is an attempt to put in perspective the evidence that has been accumulating over the past decade that the active sites for this reaction are not the metal nanoparticles. They are positively charged atoms of gold bound to a support with −O linkages and surrounded by a number of other oxygen species, including −OH groups, the latter participating in the reaction with CO adsorbed on the site. The $Au-O-(OH)_x-$ site has the same activity on any support, which frees the catalyst designer

from a particular support constraint. A few guidelines for maximizing the number of these gold sites were presented here, but it is left to the creativity of the researcher to realize such opportunities at the design stage, aided by advanced computational techniques, and by the powerful tools of atomic-resolution microscopy and spectroscopy. The advances in our understanding of the active gold site can now be used to guide the design of new gold catalysts and operating conditions, for example, oxygen-assisted WGS reaction to suppress the destabilization of $Au-O_x$ species and to prolong the catalyst lifetime.

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FOOTNOTES

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REFERENCES

1 Flytzani-Stephanopoulos, M.; Gates, B. C. Atomically dispersed supported metal catalysts. *Annu. Rev. Chem. Biomol. Eng.* **2012**, *3*, 545–574.

2 Thomas, J. M.; Saghi, Z.; Gai, P. L. Can a single atom serve as the active site in some heterogeneous catalysts? *Top. Catal.* **2011**, *54*, 588–594.

3 Yang, X.-F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-atom catalysts: A new frontier in heterogeneous catalysis. *Acc. Chem. Res.* **2013**, *46*, 1740–1748.

4 Ratnasamy, C.; Wagner, J. P. Water gas shift catalysts. *Catal. Rev. Sci. Eng.* **2009**, *51*, 325–440.

5 Liu, X. S.; Ruettinger, W.; Xu, X. M.; Farrauto, R. Deactivation of Pt/CeO$_2$ water-gas shift catalysts due to shutdown/startup modes for fuel cell applications. *Appl. Catal., B* **2005**, *56*, 69–75.

6 Tibiletti, D.; Meunier, F. C.; Goguet, A.; Reid, D.; Burch, R.; Boaro, M.; Vicario, M.; Trovarelli, A. An investigation of possible mechanisms for the water−gas shift reaction over a ZrO$_2$-supported Pt catalyst. *J. Catal.* **2006**, *244*, 183–191.

7 Murrell, L. L.; Tauster, S. J.; Anderson, D. R. Laser Raman characterization of surface phase precious metal oxides formed on CeO$_2$. *Stud. Surf. Sci. Catal.* **1991**, *71*, 275–289.

8 Hatanaka, M.; Takahashi, N.; Tanabe, T.; Nagai, Y.; Dohmae, K.; Aoki, Y.; Yoshida, T.; Shinjoh, H. Ideal Pt loading for a Pt/CeO$_2$-based catalyst stabilized by a Pt-O-Ce bond. *Appl. Catal., B* **2010**, *99*, 336–342.

9 Trovarelli, A. *Catalysis by Ceria and Related Materials*; Imperial Coll. Press: London, 2002.

10 Liu, W.; Flytzani-Stephanopoulos, M. Total oxidation of carbon monoxide and methane over transition metal-fluorite oxide composite metal catalysts: I. Catalyst composition and activity. *J. Catal.* **1995**, *153*, 304–316.

11 Kundakovic, L.; Flytzani-Stephanopoulos, M. Reduction characteristics of copper oxide in cerium and zirconium oxide systems. *Appl. Catal., A* **1998**, *171*, 13–29.

12 Fu, Q.; Kudriavtseva, S.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Gold-ceria catalysts for low temperature water-gas shift reaction. *Chem. Eng. J.* **2003**, *93*, 41–53.

13 Zhang, F.; Chan, S. W.; Spanier, J. E.; Apak, E.; Jin, Q.; Robinson, R. D.; Herman, I. P. Cerium oxide nanoparticles: Size-selective formation and structure analysis. *Appl. Phys. Lett.* **2002**, *80*, 127–129.

14 Bunluesin, T.; Gorte, R. J.; Graham, G. W. Studies of the water-gas shift reaction on ceria-supported Pt, Pd, and Rh: Implications for oxygen-storage properties. *Appl. Catal., B* **1998**, *15*, 107–114.

15 Fu, Q.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Active non-metallic Au and Pt species on ceria- based water-gas shift catalysts. *Science* **2003**, *301*, 935–938.

16 Pierre, D.; Deng, W.; Flytzani-Stephanopoulos, M. The importance of strongly bound Pt−CeOx species for the water-gas shift reaction: Catalyst activity and stability evaluation. *Top. Catal.* **2007**, *46*, 363–373.

17 Li, Y.; Fu, Q.; Flytzani-Stephanopoulos, M. Low-temperature water-gas shift reaction over Cu- and Ni-loaded cerium oxide catalysts. *Appl. Catal., B* **2000**, *27*, 179–191.

18 Si, R.; Raitano, J.; Yi, N.; Zhang, L.; Chan, S. W.; Flytzani-Stephanopoulos, M. Structure sensitivity of the low-temperature water-gas shift reaction on Cu-CeO$_2$ catalysts. *Catal. Today* **2012**, *180*, 68–80.

19 Fu, Q.; Weber, A.; Flytzani-Stephanopoulos, M. Nanostructured Au-CeO$_2$ catalysts for low-temperature water-gas shift. *Catal. Lett.* **2001**, *77*, 87–95.

20 Fu, Q.; Deng, W.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Activity and stability of low-content gold-ceria catalysts for the water-gas shift reaction. *Appl. Catal., B* **2005**, *56*, 57–68.

21 Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Novel gold catalysts for the oxidation of carbon monoxide at temperature far below 0 °C. *Chem. Lett.* **1987**, *2*, 405–408.

22 Andreeva, D.; Idakiev, V.; Tabakova, T.; Andreev, A. Low-temperature water-gas shift reaction over Au/α-Fe$_2$O$_3$. *J. Catal.* **1996**, *158*, 354–355.

23 Sakurai, H.; Ueda, A.; Kobayashi, T.; Haruta, M. Low-temperature water−gas shift reaction over gold deposited on TiO$_2$. *Chem. Commun.* **1997**, 271–272.

24 Tao, F.; Ma, Z. Water gas shift on gold catalysts: Catalyst systems and fundamental studies. *Phys. Chem. Chem. Phys.* **2013**, *15*, 15260–15270.

25 Lu, J.; Aydin, C.; Browning, N. D.; Gates, B. C. Imaging isolated gold atom catalytic sites in zeolite NaY. *Angew. Chem., Int. Ed.* **2012**, *51*, 5842–5846.

26 Guzman, J.; Gates, B. C. A mononuclear gold complex catalyst supported on MgO: Spectroscopic characterization during ethylene hydrogenation catalysis. *J. Catal.* **2004**, *226*, 111–119.

27 Allard, L. F.; Borisevich, A.; Deng, W.; Si, R.; Flytzani-Stephanopoulos, M.; Overbury, S. H. Evolution of gold structure during thermal treatment of Au/FeOx catalysts revealed by aberration-corrected electron microscopy. *J. Electron Microsc.* **2009**, *58*, 199–212.

28 Herzing, A. A.; Kiely, C. J.; Carley, A. F.; Landon, P.; Hutchings, G. J. Identification of active gold nanoclusters on iron oxide supports for CO oxidation. *Science* **2008**, *321*, 1331–1335.

29 Yang, M.; Allard, L. F.; Flytzani-Stephanopoulos, M. Atomically dispersed Au-(OH)$_x$ species bound on titania catalyze the low-temperature water-gas shift reaction. *J. Am. Chem. Soc.* **2013**, *135*, 3768–3771.

30 Rim, K. T.; Eom, D.; Liu, L.; Stolyarova, E.; Raitano, J. M.; Chan, S. W.; Flytzani-Stephanopoulos, M.; Flynn, G. W. Charging and chemical reactivity of gold nanoparticles and adatoms on the (111) surface of single-crystal magnetite: A scanning tunneling microscopy/spectroscopy study. *J. Phys. Chem. C* **2009**, *113*, 10198–10205.

31 Guzman, J.; Gates, B. C. Simultaneous presence of cationic and reduced gold in functioning MgO supported CO oxidation catalysts: evidence from x-ray absorption spectroscopy. *J. Phys. Chem. B* **2002**, *106*, 7659–7665.

32 Mohamed, M. M.; Ichikawa, M. Spectroscopic and kinetic studies of the reaction of CO+H$_2$O and CO+O$_2$ and decomposition of HCOOH on Au/H-mordenite catalysts. *J. Colloid Interface Sci.* **2000**, *232*, 381–388.

33 Yao, H. C.; Yu Yao, Y. F. Ceria in automotive exhaust catalysts I. Oxygen storage. *J. Catal.* **1984**, *86*, 254–265.

34 Zhou, Z.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Decoration with ceria nanoparticles activates inert gold island/film surfaces for the CO oxidation reaction. *J. Catal.* **2011**, *280*, 255–263.

35 Lee, Y.; He, G.; Akey, A. J.; Si, R.; Flytzani-Stephanopoulos, M.; Herman, I. P. Raman analysis of mode softening in nanoparticle CeO$_{2-\delta}$ and Au-CeO$_{2-\delta}$ during CO oxidation. *J. Am. Chem. Soc.* **2011**, *133*, 12952–12955.

36 Liu, Z. P.; Jenkins, S. J.; King, D. A. Origin and activity of oxidized gold in water-gas-shift catalysis. *Phys. Rev. Lett.* **2005**, *94*, No. 196102.

37 Zhang, C.; Michaelides, A.; King, D. A.; Jenkins, S. J. Structure of gold atoms on stoichiometric and defective ceria surfaces. *J. Chem. Phys.* **2008**, *129*, No. 194708.

38 Deng, W.; Frenkel, A. I.; Si, R.; Flytzani-Stephanopoulos, M. Reaction-relevant gold structures in the low temperature water-gas shift reaction on Au-CeO$_2$. *J. Phys. Chem. C* **2008**, *112*, 12834–12840.

39 Si, R.; Flytzani-Stephanopoulos, M. Shape and crystal-plane effects of nanoscale ceria on the activity of Au-CeO$_2$ catalysts for the water-gas shift reaction. *Angew. Chem., Int. Ed.* **2008**, *47*, 2884–2887.

40 Sayle, T. X. T.; Parker, S. C.; Sayle, D. C. Oxidising CO to CO$_2$ using ceria nanoparticles. *Phys. Chem. Chem. Phys.* **2005**, *7*, 2936–2941.

41 Yi, N.; Si, R.; Saltsburg, H.; Flytzani-Stephanopoulos, M. Active gold species on cerium oxide nanoshapes formethanol steam reforming and the water gas shift reactions. *Energy Environ. Sci.* **2010**, *3*, 831–837.

42 Guan, Y.; Michel Ligthart, D. A. J.; Pirgon-Galin, Ö; Pieterse, J. A. Z.; van Santen, R. A.; Hensen, E. J. M. Gold stabilized by nanostructured ceria supports: Nature of the active sites and catalytic performance. *Top. Catal.* **2011**, *54*, 424–438.

43 Tibiletti, D.; Fonseca, A. A.; Burch, R.; Chen, Y.; Fisher, J. M.; Goguet, A.; Hardacre, C.; Hu, P.; Thompsett, D. DFT and in situ EXAFS investigation of gold/ceria-zirconia low-temperature water gas shift catalysts: identification of the nature of the active form of gold. *J. Phys. Chem. B* **2005**, *109*, 22553–22559.

44 Wang, X.; Rodriguez, J. A.; Hanson, J. C.; Perez, M.; Evans, J. In situ time-resolved characterization of Au-CeO$_2$ and AuO$_x$-CeO$_2$ catalysts during the water-gas shift reaction: presence of Au and O vacancies in the active phase. *J. Chem. Phys.* **2005**, *123*, No. 221101.

45 Sandoval, A.; Gómez-Cortés, A.; Zanella, R.; Díaz, G.; Saniger, J. M. Gold nanoparticles: Support effects for the WGS reaction. *J. Mol. Catal. A: Chem.* **2007**, *278*, 200–208.

46 Ma, Z.; Yin, H. F.; Dai, S. Performance of Au/M$_x$O$_y$/TiO$_2$ catalysts in water-gas shift reaction. *Catal. Lett.* **2010**, *136*, 83–91.

47 Iheva, L. I.; Andreeva, D. H.; Andreev, A. A. TPR and TPD investigation of Au/α-Fe$_2$O$_3$. *Thermochim. Acta* **1997**, *292*, 169–174.

48 Tabakova, T.; Ilieva, L.; Ivanov, I.; Zanella, R.; Sobczak, J. W.; Lisowski, W.; Kaszkur, Z.; Andreeva, D. Influence of the preparation method and dopants nature on the WGS activity of gold catalysts supported on doped by transition metals ceria. *Appl. Catal., B* **2013**, *136*, 70–80.

49 Lessard, J. D.; Valsamakis, I.; Flytzani-Stephanopoulos, M. Novel Au/La$_2$O$_3$ and Au/La$_2$O$_2$SO$_4$ catalysts for the water—gas shift reaction prepared via an anion adsorption method. *Chem. Commun.* **2012**, *48*, 4857–4859.

50 Deng, W.; Carpenter, C.; Yi, N.; Flytzani-Stephanopoulos, M. Comparison of the activity of Au/CeO$_2$ and Au/Fe$_2$O$_3$ catalysts for the CO oxidation and the water-gas shift reactions. *Top. Catal.* **2007**, *44*, 199–208.

51 Rim, K. T.; Eom, D.; Chan, S. W.; Flytzani-Stephanopoulos, M.; Flynn, G. W.; Wen, X. D.; Batista, E. R. Scanning tunneling microscopy and theoretical study of water adsorption on Fe$_3$O$_4$: Implications for catalysis. *J. Am. Chem. Soc.* **2012**, *134*, 18979–18985.

52 Novotny, Z.; Argentero, G.; Wang, Z. M.; Schmid, M.; Diebold, U.; Parkinson, G. S. Ordered Array of Single Adatoms with Remarkable Thermal Stability: Au/Fe$_3$O$_4$(001). *Phys. Rev. Lett.* **2012**, *108*, No. 216103.

53 Yang, M. Doctoral thesis, Tufts University, Medford, MA, USA, in progress.

54 Shekhar, M.; Wang, J.; Lee, W. S.; Williams, W. D.; Kim, S. M.; Stach, E. A.; Miller, J. T.; Delgass, W. N.; Ribeiro, F. H. Size and support effects for the water—gas shift catalysis over gold nanoparticles supported on model Al$_2$O$_3$ and TiO$_2$. *J. Am. Chem. Soc.* **2012**, *134*, 4700–4708.

55 Boucher, M. B., PhD Dissertation, Tufts University, Medford, MA, U.S.A., 2013.

56 Zhai, Y. P.; Pierre, D.; Si, R.; Deng, W. L.; Ferrin, P.; Nilekar, A. U.; Peng, G.; Herron, J. A.; Bell, D. C.; Saltsburg, H.; Mavrikakis, M.; Flytzani-Stephanopoulos, M. Alkali-stabilized Pt-OH$_x$ species catalyze the low-temperature water-gas shift reactions. *Science* **2010**, *329*, 1633–1636.

57 Deng, W.; Flytzani-Stephanopoulos, M. On the issue of the deactivation of Au—ceria and Pt—ceria water-gas shift catalysts in practical fuel-cell applications. *Angew. Chem., Int. Ed.* **2006**, *45*, 2285–2289.

58 Pilasombat, R.; Daly, H.; Goguet, A.; Breen, J. P.; Burch, R.; Hardacre, C.; Thompsett, D. Investigation of the effect of the preparation method on the activity and stability of Au/CeZrO$_4$ catalysts for the low temperature water gas shift reaction. *Catal. Today* **2012**, *180*, 131–138.

59 Anderson, J. A.; Fernandez-Garcia, M. *Supported Metal in Catalysis;*. Imperial College Press: London, 2011.

60 Regalbuto, J. *Catalyst Preparation;* CRC Press: Boca Raton, FL, 2007.

61 Alves, L.; Ballesteros, B.; Boronat, M.; Cabrero-Antonino, J. R.; Concepción, P.; Corma, A.; Correa-Duarte, M. A.; Mendoza, E. Synthesis and stabilization of subnanometric gold oxide nanoparticles on multiwalled carbon nanotubes and their catalytic activity. *J. Am. Chem. Soc.* **2011**, *133*, 10251–10261.

62 Zugic, B.; Bell, D. C.; Flytzani-Stephanopoulos, M. Activation of carbon-supported platinum catalysts by sodium for the low-temperature water-gas shift reaction. *Appl. Catal., B* **2013**, DOI: 10.1016/j.apcatb.2013.07.013.

63 Zhai, Y., PhD Dissertation, Tufts University, Medford, MA, U.S.A., 2011.

64 Wang, Y. Master's Thesis, Tufts University, Medford, MA, U.S.A., 2012.

65 Venugopal, A.; Scurrell, M. S. Hydroxyapatite as a novel support for gold and ruthenium catalysts: Behaviour in the water gas shift reaction. *Appl. Catal., A* **2003**, *245*, 137.