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Atomically Dispersed Au–(OH)_x Species Bound on Titania Catalyze the Low-Temperature Water-Gas Shift Reaction

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S Supporting Information

ABSTRACT: We report a new method for stabilizing appreciable loadings (~1 wt %) of isolated gold atoms on titania and show that these catalyze the low-temperature water-gas shift reaction. The method combines a typical gold deposition/precipitation method with UV irradiation of the titania support suspended in ethanol. Dissociation of H₂O on the thus-created Au–O–TiO_x sites is facile. At higher gold loadings, nanoparticles are formed, but they were shown to add no further activity to the atomically bound gold on titania. Removal of this “excess” gold by sodium cyanide leaching leaves the activity intact and the atomically dispersed gold still bound on titania. The new materials may catalyze a number of other reactions that require oxidized active metal sites.

Atomically dispersed supported metal catalysts offer new prospects for low-cost, sustainable energy and chemicals production, as discussed in a recent review.¹ The water-gas shift (WGS) reaction, which is important in upgrading H₂-rich fuel gas streams for fuel cell and other applications, has been shown to occur on atomically dispersed metals on oxide supports. Thus, novel catalyst designs that maximize the number of such sites have been actively investigated. Along with improved Cu/ZnO catalyst designs,² the Pt-group metals^{3–7} are promising catalysts, as is gold when highly dispersed on a support such as ceria^{8–15} or iron oxide.^{12,15–18} Gold supported on titania has not been examined extensively for the WGS reaction. Of course, this was one of the first catalysts reported by Haruta and co-workers as an extremely active catalyst for ambient-temperature oxidation of carbon monoxide.^{19,20} Au/TiO₂ prepared by a deposition/precipitation (DP) technique was recently investigated for the WGS reaction.^{21,22} On the basis of kinetic data and geometric arguments, it was proposed that the corner atoms on the gold cuboctahedral nanoparticles with fewer than seven neighboring gold atoms are the dominant active sites and that the total rate is proportional to the number of gold particles but does not depend on their size. Gold nanoclusters and isolated gold atoms on titania were not included in the counting of active gold species in that work.²² However, recent atomic-resolution imaging studies via aberration-corrected scanning transmission electron microscopy (ac-STEM) clearly showed that even a minor amount of atomically dispersed gold on the titania surface benefits the CO oxidation reaction²³ as well as various dehydrogenation reactions.²⁴ These gold species are also very active for the

WGS reaction on ceria and doped ceria,^{8–15,25} iron oxide,^{12,15–18} zirconia,^{26,27} and lanthana.²⁸ Indeed, for WGS-active gold supported on the above oxides, gold nanoparticles can be leached out by alkali cyanide solutions, and the residual gold (a small fraction of the original amount) on these supports was found to catalyze the reaction equally well.^{8–10,12,28}

Cyanide leaching allows for isolated gold species to be imaged and their reactivities be followed by various techniques in the absence of particles that would distort the data (e.g., in IR, XANES, XPS, and other “averaging” techniques). For the Au/Fe₂O₃ WGS catalysts, Allard and co-workers^{17,18} showed that atomic gold species are strongly bound even after redox heat treatments and after exposure to the WGS reaction gas mixture up to 673 K. In work with Au/Fe₃O₄(111) single crystals, gold atoms bound over the uncapped O atoms were shown to be stable to 773 K.^{29,30} Thus, renewed effort should be spent on properly characterizing the atomically dispersed Au–O_x oxide sites, even though they are not visible by regular TEM. Qiao et al.³¹ showed that a single Pt atom place-exchanged in an FeO_x surface has excellent CO oxidation activity in the preferential CO oxidation reaction.

As reported by Fu and co-workers,^{8,10} the sodium cyanide leaching of the gold must be done only after oxidative heat treatment of the fresh material when the DP technique is used to add the gold. This allows for strong Au–O(OH)_x–Ce association to take place first, which resists cyanide complexation. Otherwise, almost all of the deposited gold is leached out even from the ceria surfaces. To date, it has been challenging to retain the atomically dispersed Au–O_x species on TiO₂. For titania supports, a different energy stimulation must be used to create stable anchoring sites for gold. For example, using a model Au/TiO₂ film, Lahiri et al.³² showed that UV irradiation enabled the stabilization of the semiconductor–metal interface through the accumulation of gold cations, presumably at surface defect sites. Recent computational work by Laursen and Linic^{33,34} has shown that oxygen vacancies are not needed to stabilize cationic gold on titania, and the electron-rich defects are energetically unfavorable and would be healed rapidly in H₂O or O₂ environments. This was corroborated by scanning tunneling microscopy studies,³⁵ which revealed that the image features earlier attributed to oxygen vacancies on well-annealed TiO₂ single crystals are actually protons atop bridging oxygen or –OH groups bound to Ti through atoms. In the present work, we have extended the UV irradiation technique to titania

Received: January 3, 2013

Published: February 25, 2013

powders with the addition of ethanol as a charge scavenger, where gold donates the separated electrons to $-OH$ groups. The method was optimized to bind and stabilize a large number of atomically dispersed gold species on the titania [see the Supporting Information (SI)].

Temperature-programmed surface reaction (TPSR) profiles of selected samples (designations are explained in Table S1 in the SI), with steady-state holds of 4 h at each target temperature, are shown in Figure 1. The catalytic activity of

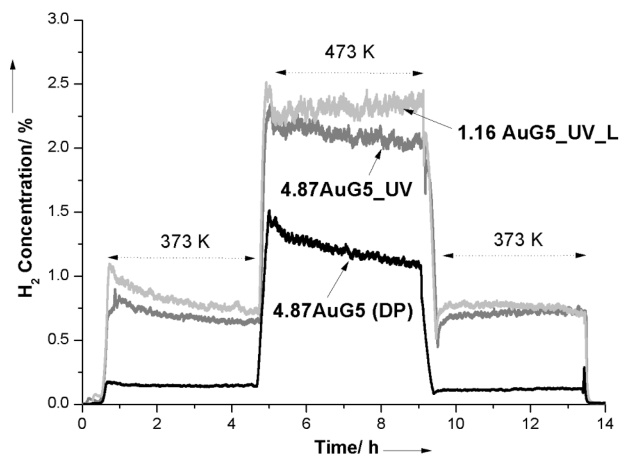


Figure 1. Low-temperature WGS TPSR profiles with steady-state holds of 4 h at 373 and 473 K (heating rate: 5 K/min; 10% CO/3% H_2O in He, 30 mL/min; 100 mg sample). Shown is the H_2 produced as a function of time. The consumption of CO and the production of CO_2 and H_2 fit the stoichiometry of the WGS reaction.

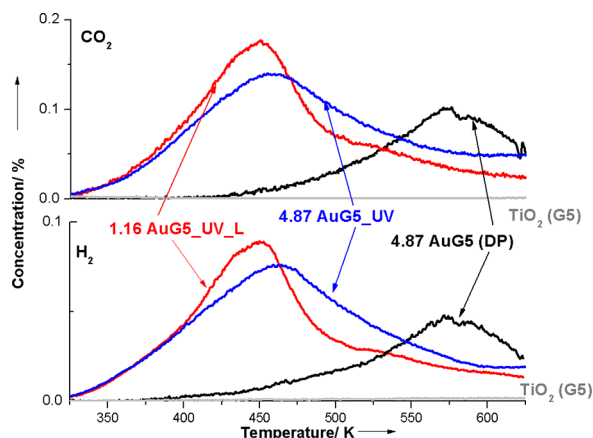


Figure 2. CO TPR profiles (10% CO in He, 30 mL/min; heating rate: 10 K/min; 100 mg sample) for the parent and leached Au/TiO₂ catalysts. Each sample was purged with 30 mL/min He at 373 K for 20 min and then cooled to 323 K in He. Before being heated from 323 to 623 K, the sample was stabilized in 10% CO in He for 20 min.

the UV-treated samples was significantly enhanced, as shown by comparison of the 4.87 AuG5 (DP) and 4.87 AuG5_UV irradiated samples. The reason is that a large fraction of the gold in the UV-irradiated sample is atomically dispersed and stable, as proven by sodium cyanide leaching, which left more than 20% of the gold intact on the surface. The resulting leached sample (1.16 AuG5_UV_L) had activity similar to that of the parent. The slightly better activity of the UV-irradiated sample after leaching is attributed to the removal of gold particles, which uncovers additional anchored gold atoms from

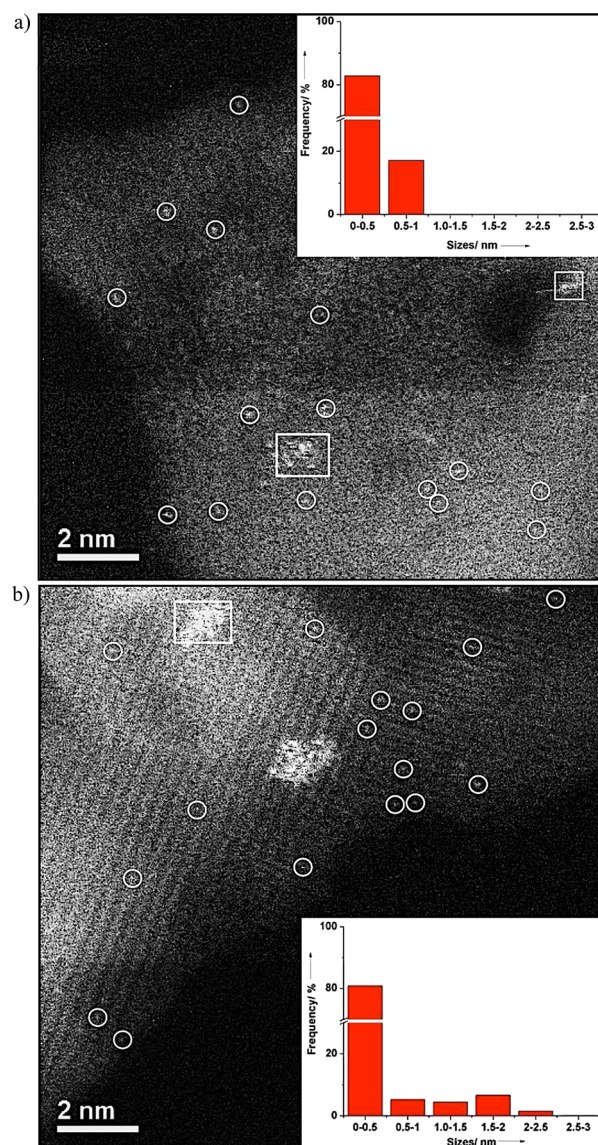


Figure 3. ac-HAADF/STEM images of (a) fresh 1.16 AuG5_UV_L and (b) used 1.16 AuG5_UV_L after reaction in TPSR mode to 373 K and held steady there for 4 h (Figure 1). Circles are drawn around isolated gold atoms and squares around few-atom gold nanoclusters. The size distributions (insets) are based on over 200 gold species counted from the high-magnification images (2 nm scale bar).

the basal planes of the particles.⁸ The same synthesis protocol worked well for both the G5 and P25 benchmark titania materials (Figures S1–S3 and Table S2) and was especially effective for the high-surface-area pure anatase G5-supported samples.

The CO TPR profiles shown in Figure 2 reveal the effects of the UV irradiation on the concentration of reducible oxygen and $-OH$ groups present on the surface of the corresponding samples. The activity of the parent 4.87 AuG5_UV was similar to that of its leached derivative, except for a slightly lower total amount of $-OH$ up to 473 K, in agreement with the steady-state conversion data in Figure 1. The oxygen species ($-OH$) were activated by CO at ~ 350 K, and production of CO_2 was accompanied by H_2 production. The H_2/CO_2 ratio was 1/2, in accordance with the $CO + -OH$ reaction stoichiometry. Bare TiO₂ did not provide any significant reducible species in the temperature range from 323 to 623 K. Therefore, $-OH$ groups

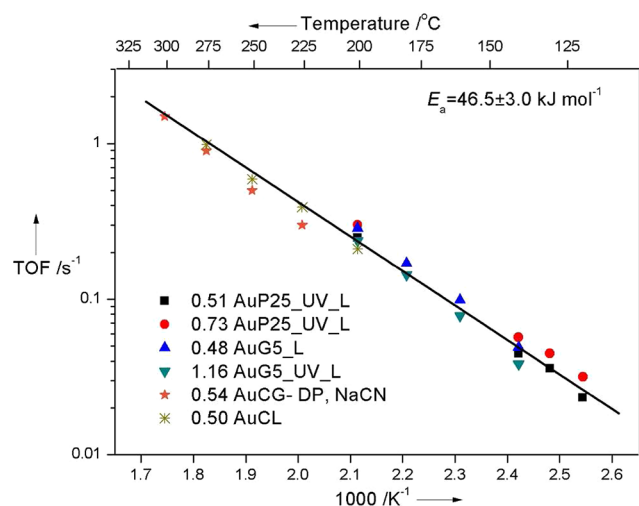


Figure 4. Arrhenius plot of TOFs for the WGS reaction over leached catalysts in a simulated reformat gas mixture (11% CO/26% H₂O/7% CO₂/26% H₂ in He). Data for Au/CeO₂ catalysts (AuCG and AuCL) were taken from refs 10 and 12.

associated with the gold–titania interface through facile H₂O dissociation initiate the WGS reaction at close to ambient temperatures. On the other hand, the 4.87 AuG5 (DP) sample was considerably less active, as shown by the activation of its –OH groups at >400 K. In cyclic CO TPR with intermittent surface rehydration under ambient conditions, similar results were obtained (Table S3 and Figure S4).

Atomic-resolution high-angle annular dark-field ac-STEM (ac-HAADF-STEM) was used to image the Au species in different structures, since sub-nanometer-scale clusters and atoms cannot be detected by regular TEM (Figure S5). As shown in Figure 3 and Figure S6, mostly (80%) gold atoms (0.2–0.3 nm) and some sub-nanometer (few-atom) gold clusters were present on the 1.16 AuG5_UV_L sample. The sub-nanometer clusters larger than 0.5 nm disappeared rapidly under WGS reaction conditions in favor of a few larger particles. A concomitant loss of activity (~30%) accompanied the formation of particles of much lower atomic efficiency (see the SI). After a second cyanide leaching to remove these particles, 0.43 wt % Au remained on this used sample as isolated atoms only (Figure S6c), and correspondingly, 41% of the original (fresh sample) activity remained (Table S4). Hence, the active gold sites are the isolated atoms stably anchored on the titania sites. These Au–(OH)_x species are held in a mildly oxidized state (Au^{δ+}) (Figures S7 and S8).

In a simulated reformat fuel gas mixture (Table S2), the new Au/TiO₂ catalysts performed even better than the active Au/CeO₂ catalysts investigated in prior work.^{8,10–12} With similar gold loadings and the same heat treatment, the catalysts evaluated in this work performed significantly better than commercial 1.0 wt % Au/TiO₂ (AUROLite) or the recently reported catalysts containing an abundance of gold nanoparticles (1–3 nm).²¹ The apparent activation energy of the reaction is similar to those reported for gold on titania, ceria, iron oxide, lanthana, and other supports,^{8,10,12,15,21,22,28} indicating that the support oxide itself does not participate directly in the WGS reaction (see the SI). We scaled the steady-state reaction rates by the amount of residual gold (after cyanide leaching) and cast them in terms of turnover frequency (TOF) in an Arrhenius plot (Figure 4). The similarity of the

TOFs over catalysts prepared with different compositions on different supports and subjected to very different treatment methods is noteworthy. Thus, an important analogy of Au/TiO₂ to other atomically dispersed supported gold catalysts is shown here for the first time.

This is the first demonstration of the application of UV treatment to activate Au/TiO₂ for the WGS reaction with or without subsequent cyanide leaching. The improved catalyst maintained excellent activity for the WGS reaction and showed good stability in long-time cool-down and startup operation up to 473 K. The present work provides new evidence that atomically dispersed gold species with surrounding extra surface –OH groups are the active sites for the WGS reaction on titania as well as on other oxide supports. The light stimulation of titania used in this work may be applied to the preparation of other catalysts, a worthwhile undertaking for future work.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Experimental section, optimization of sample preparation procedures, improved and stable catalyst activity, reducible Au–(OH)_x species, gold species detected in TEM and STEM images, and other characterizations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Support of this work by the U.S. Department of Energy (DOE) under Grant DE-FG02-05ER15730 is gratefully acknowledged. Microscopy research was partially conducted at the ShaRE User Facility at Oak Ridge National Laboratory, which is sponsored by the Division of Scientific User Facilities, Office of Basic Energy Sciences, DOE. M.Y. acknowledges partial support from AFOSR (MURI) Grant FA9550-08-1-0309 and thanks Dr. Sungsik Lee (Argonne National Laboratory) for assistance with the XANES work and Chongyang Wang (Tufts University) for help with the XAS data analysis.

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