Using Three Dimensions in Catalytic Mesoporous Nanoarchitectures

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ABSTRACT

Gold–titania (Au–TiO2) composite aerogels were synthesized, characterized, and tested as ambient-temperature oxidation catalysts for carbon monoxide. Adding alkanethiolate-monolayer-protected gold clusters (with ~2-nm Au cores) directly to titania sol before gelation yields uniformly dispersed guests in the composite aerogel. The Au guests aggregate to ~6 nm upon calcination to remove the alkanethiolate and crystallize amorphous titania to anatase. The resulting composite aerogel exhibits high catalytic activity toward CO oxidation at room temperature at Au particle sizes that are essentially inactive in prior Au–TiO2 catalysts. Transmission electron microscopy illustrates the three-dimensional nature of the catalytic nanoarchitecture in which the Au guests contact multiple anatase nanocrystallites.

An extensive literature describes the ability of nanometer-sized gold supported on titania (Au/TiO2) to catalyze the low-temperature oxidation of carbon monoxide.1–11 The mechanism of oxidation (in particular the individual roles of the gold and titania) is still being elucidated. Agreement exists that oxygen is activated at either titania or the gold–titania interface, while carbon monoxide undergoes weak, reversible adsorption at the surface of the gold nanoparticle.1,2 The surface diffusion of adsorbed CO on the gold to the activated oxygen sites at the interface, with possible spillover of activated oxygen to the gold, enhances oxidative turnover.

Studies by Haruta and co-workers6 show that 3-nm gold particles supported on titania optimize the effectiveness of catalytic oxidation of carbon monoxide. Gold sized at 3 nm appears to balance the need for a large ratio of perimeter-to-bulk (i.e., high catalyst dispersion), while still presenting enough surface area for carbon monoxide adsorption and surface diffusion. Smaller particles are thought to be partially buried in the titania support, while larger particles are thought to lose carbon monoxide to desorption before diffusion to the active perimeter permits oxidation.6,9,11,13 Although 12-nm Au supported on iron oxide remains active for CO oxidation,14 which argues for a less size-dependent mechanism such as spillover involving reactive atomic oxygen, titania-supported catalysts with Au particles larger than 5 nm are reported to be less active for CO oxidation.12

The typical Au/TiO2 catalyst derives from nanocrystalline or commercial nanocrystalline titania7 and deposition of organogold complexes on as-precipitated metal hydroxides.3,4

Haruta et al. report high catalytic activity for oxidation of carbon monoxide at 8 wt % Au/TiO2 by using a high-surface-area titania precursor (100 m2 g−1 titanium hydroxide) and calcining at 300 °C to form well-dispersed 3-nm gold.15 A key distinction between this preparation and others is that fully crystalline TiO2 is not used as the starting support. Other variations to prepare Au/TiO2 catalysts include chemical vapor deposition of organogold complexes on amorphous or commercial nanocrystalline titania7 and deposition of gold–phosphine complexes on as-prepared metal hydroxides.3,4

Surface chemistry plays a pivotal role in the final distribution of the titania-supported gold and the ultimate activity of Au/TiO2 for catalytic oxidation of carbon monoxide. Even after calcination to form the crystalline oxide, the gold is more highly dispersed when initially adsorbed to hydroxylated support precursors and yields a much more active composite catalyst. An increase in the number of nucleation sites, made possible by the physicochemical nature of disordered or amorphous supports, is thought to promote greater dispersion relative to the same deposition chemistry carried out on highly crystalline titania.3,7,13

We now report the synthesis, characterization, and catalytic efficacy of gold–titania composite aerogels (Au–TiO2) as ambient-temperature oxidation catalysts for carbon monoxide. The composite aerogel offers a catalytic architecture in which a network of nanoscopic titania serves as the host and alkanethiolate monolayer-protected gold clusters (Au-MPCs) are guests. We previously showed that about-to-gel silica sol will nanoglue solid guests into the gel’s nanostructure to create materials that retain molecular access to the guest and add the properties of the guest to the composite.16–18
Aerogels are nanoscopic pore-solid architectures with high surface area (150—1000 m² g⁻¹) and a continuous mesoporous network.¹⁹ The high surface area makes aerogels particularly attractive for catalysis²⁰ and should allow for deposition of large effective concentrations of gold nanoparticles while maintaining a well-dispersed population of particles. The three-dimensional (3-D) continuous mesoporous network facilitates rapid diffusion of reactants to active sites in the aerogel, such that mass transport occurs on the order of open-medium diffusion rates.²¹ As mass transport must be factored into the kinetics of any catalyst, the continuous mesoporous structure of aerogels will be critical to their performance as composite, nanostructured catalysts.

This report also introduces Au-MPCs into the preparation of Au/TiO₂ catalysts. These compounds, first synthesized by Brust et al.,²² consist of 2–3-nm gold cores (containing anywhere from a few dozen to a few hundred gold atoms, depending on preparation conditions²³) that are protected from aggregation by alkanethiolate monolayers (containing 4–16 methylene units). The ω-termini of the ligands may consist of a methyl group or any number of reactive functional groups,²⁴–²⁶ A mixed monolayer can be created by synthesizing Au-MPCs in the presence of mixed ligands, or by making permethyl-terminated MPCs and then stoichiometrically exchanging with the ligands of choice.

Using Au-MPCs in the preparation of nanoparticle-on-oxide catalysts is desirable because one starts with Au(0) particles with a relatively well-controlled size distribution. Gold-MPCs can be isolated and are stable as “dry” compounds, thus providing chemical and processing flexibility when designing and preparing nanocomposites. Judicious choice of protecting ligands leads to particles that dissolve readily in the solvents suitable for sol–gel chemistry. Finally, the protecting ligand may also be chosen such that it specifically attaches to hydroxyls on the metal oxide colloids in the about-to-gel sol, giving good dispersion of the metal particles in the final gel.

Gold-MPCs in an ethanolic solution, added directly to the Ti(IV) precursor solution during the sol–gel chemistry, remain uniformly dispersed in the composite aerogel, as seen by transmission electron microscopy (TEM) for an uncalcined 6 wt % Au-MPC–TiO₂ composite aerogel (Figure 1). The alkanethiolate capping layer is a 1:1 (mol/mol) mixed monolayer of 11-mercaptoundecanoic acid (MUA) and decanethiol (DT). The Au-MUA:DT particles have an average diameter of 2.3 nm and appear to be partially encased in amorphous titania. The Au clusters are well dispersed throughout the entire volume of the aerogel, unlike a recent report of an aerogel composite made by exposing a wet silica gel to Au-MPCs in which the Au particles clustered at the boundary of the gel.²⁷

After calcination to crystallize amorphous titania to anatase TiO₂ and to burn off the alkanethiolate ligands, the ~2-nm Au particles in the Au–TiO₂ composite aerogels segregate to the surfaces of the titania nanocrystals and aggregate to average diameters of 5–10 nm. This calcination-induced growth can be seen by high-resolution TEM, whether mixed-monolayer (Au-MUA:DT) or single-ligand monolayers of 11-mercaptoundecanol (Au-MU) protect the Au clusters (Figure 2A,B, respectively). The calcined composite aerogels have primary TiO₂ particle sizes of 10–12 nm, which is comparable to the average Au particle size. This size comparability allows individual Au particles to make contact with multiple titania particles, in contrast to morphologies in which the titania particle size greatly exceeds the Au particle size (as an example of the greater than 10-fold size discrepancy in standard Au/TiO₂ catalysts, see Figure 5 in ref 1).

The crystallinity of titania in the postcalcination composite aerogels is evident by the pervasive lattice fringes seen in Figure 2A. Phase identification as anatase was verified by electron and X-ray diffraction for composites derived from both Au-MPC guests. The Raman spectrum of MPC-derived Au–TiO₂ composite aerogel (1 wt % Au) has peaks characteristic of anatase TiO₂ at 405, 520 and 630 cm⁻¹.

The fact that some aggregation occurs during crystallization of the TiO₂ aerogel into its anatase habit is not surprising given the physical changes that the aerogel domains undergo. The specific surface area of uncalcined titania aerogel is ~500 m²/g, while calcined TiO₂ aerogel contracts to 150–200 m² g⁻¹. The postcalcination particle size of the Au guests in Au–TiO₂ composite aerogels does depend on the nature of the capping ligand: 5.5 nm for Au-MUA:DT and 8.1 nm for Au-MU. Carboxylates are known to bind well to surface titanos,²⁹ so the carboxylic acids on Au-MUA:DT termini may create “surface-sited” particles that are more highly dispersed in the uncalkined gel than the hydroxyl-terminated Au-MU, thereby restricting the ultimate degree of growth.

The nature of the original Au-MPC, and its weight loading in the composite gel, also affects the physical data derived for the various Au–TiO₂ composite aerogels. It is not atypical for added metals or metal ions to change the final morphology of calcined porous oxides, often through inhibition of crystallization and preservation of the higher-surface-area amorphous phase.⁴,¹⁵ In our composite aerogels, how-
ever, lower specific surface areas and higher average pore diameters are consistently observed with higher gold loadings; see Table 1. We propose that the Au-MPCs, particularly those with carboxylate monolayer termini mixed into the monolayer (Au-MUA:DT), may preferentially nucleate where there are high concentrations of surface titanols (at the mouths of micropores and small mesopores and within the necked regions between titania domains) and block the smaller pores. The net result is lower specific surface area (because less microporous volume is accessible to nitrogen) but a higher average pore size, as shown in Figure 3 (because the mesopores remain relatively unobstructed).

Table 1. Surface Area and Porosimetry of Au–TiO2 Composite Aerogels

<table>
<thead>
<tr>
<th>wt% of Au in Au–TiO2 aerogel</th>
<th>type of Au-MPC and amt used in 8 mL of TiO2 sol</th>
<th>BET surface area (m2 g−1)</th>
<th>BJH pore diameter; desorption [nm]</th>
<th>cumulative pore volume (mL g−1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.9–2.4% (XPS)</td>
<td>35 mg of Au-MU</td>
<td>204</td>
<td>7.0</td>
<td>0.44</td>
</tr>
<tr>
<td>5–7% (est)</td>
<td>60 mg of Au-MU</td>
<td>155</td>
<td>15.6</td>
<td>0.72</td>
</tr>
<tr>
<td>1% (est)</td>
<td>17 mg of Au-MUA:DT</td>
<td>179</td>
<td>8.7</td>
<td>0.48</td>
</tr>
<tr>
<td>3.6% Au (AAS)</td>
<td>40 mg of Au-MUA:DT</td>
<td>142</td>
<td>16.4</td>
<td>0.72</td>
</tr>
<tr>
<td>6.3% Au (AAS)</td>
<td>80 mg of Au-MUA:DT</td>
<td>148</td>
<td>11.3</td>
<td>0.56</td>
</tr>
<tr>
<td>10% Au (est)</td>
<td>120 mg of Au-MUA:DT</td>
<td>94</td>
<td>11.8</td>
<td>0.37</td>
</tr>
</tbody>
</table>

| a Estimated (est) weight loadings of Au in some samples are determined by comparing the amount of Au-MPC used in the preparation to that in similarly prepared Au–TiO2 composite aerogels whose compositions were determined by either X-ray photoelectron spectroscopy (XPS) or atomic absorption spectroscopy (AAS). The estimate involving Au-MU MPC is less accurate because it is difficult to separate the cluster from the excess of ligand used in its synthesis. b Alkanethiolate monolayers are either 100% 11-mercaptopoundecanol (MU) or a 1:1 (mol/mol) ratio of 11-mercaptopoundecanoic acid (MUA) and decanethiol (DT).

After calcination, Au–TiO2 composite aerogels range in color from red to deep purple. X-ray photoelectron spectroscopy reveals that the gold is metallic in character and that any sulfur groups remaining after calcination are present as sulfate. Electron paramagnetic resonance measurements at 77 K and room temperature show no measurable concentration of Ti3+ species in the deep purple composites, and both TiO2 aerogel films and Au–TiO2 composite aerogel films on conducting glass have identical band edges of 355 nm, or 3.5 eV, suggesting that the color is strictly due to Mie scattering by the included gold particles.

Figure 2. Transmission electron micrographs of Au–TiO2 aerogels calcined at 425 °C. The lattice fringes visible arise from anatase TiO2 nanocrystallites. (A) 3.6 wt % Au, prepared using Au-MUA:DT; average particle size in the calcined composite aerogel is 5.5 nm. Note: some Au nanoparticles appear to contact multiple anatase nanoparticles. (B) 4 wt % Au, prepared using Au-MU; average particle size in the calcined composite aerogel is 8.1 nm. Note: this sample is also well crystallized, but lattice fringes have been suppressed due to the choice of an objective aperture that increases the contrast between Au and titania.

Figure 3. Incremental pore volume as a function of pore size for Au–TiO2 aerogels calcined at 425 °C: (●) 1.0 wt % Au, prepared using Au-MUA:DT; (○) 3.6 wt % Au, prepared using Au-MUA:DT.
The activity of Au–TiO₂ composite aerogels for ambient-temperature oxidation of carbon monoxide was determined as a function of weight loading and/or average size of included gold; these data are summarized in Table 2. The oxidation rate of CO, measured in moles converted per second per gram of catalyst, rise monotonically with gold loading. The 3.6 wt % Au–TiO₂ aerogel composite derived from Au-MUA:DT performs very well, converting \( \sim 1 \times 10^{-5} \) mol s\(^{-1}\) of carbon monoxide to carbon dioxide per gram catalyst, despite doing so with 5.5-nm Au particles. A comparably loaded Au–TiO₂ aerogel with 8.1-nm Au particles (made using Au-MU) is also active, but 25 times less so.

Catalytic activity continues to rise for Au weight loadings > 3.6 wt %, with rates of 2 \times 10^{-5} \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1} for 10 wt % Au–TiO₂ composite aerogel. In our study, the gas flow rates were varied considerably from experiment to experiment (ranging from linear flow rates of 1-10 cm s\(^{-1}\)); yet, little or no measurable effect of flow conditions on measured rate constants was observed.

It is unlikely that CO oxidation at Au–TiO₂ composite aerogels involves a radically different chemical mechanism than at other Au/TiO₂ catalysts. We propose that Au–TiO₂ composite aerogel catalysts perform so well for particle sizes that offer minimal activity for more standard Au/TiO₂ catalysts because multiple Au/TiO₂ interfaces form at many of the Au particles as the TiO₂ aerogel densifies during crystallization and as the ∼2-nm gold cores aggregate. High-resolution TEM supports this supposition. Although in an individual TEM micrograph, contact between particles is difficult to distinguish from mere overlap in projection, the difference is clear in a through-focus series of micrographs. For the Au–TiO₂ composite aerogels shown in Figure 2, we observe that the Au particles contact multiple anatase nanoparticles.

The ability of the aerogel nanoarchitecture to create multiple points-of-contact of Au to TiO₂ contrasts with the single interfacial perimeter that forms when gold is deposited onto preformed TiO₂ or hydrous titanium oxide powders. Multiple Au/TiO₂ junctions shorten the average lateral diffusion distance of CO to the oxygen-active interface, as compared to the single-perimeter case. This multiplicity of contact between the Au guest and the TiO₂ host, which provides a three-dimensional control of the reaction zone, is depicted schematically in Figure 4. Particle size still matters in Au–TiO₂ composite aerogels, however, as catalytic performance diminishes as the size of the Au guests reaches 8.1 nm.

Haruta and co-workers proposed a similar “extended perimeter” hypothesis when comparing formation of particles from organogold complexes deposited by CVD on commercial nanocrystalline and amorphous TiO₂. The average particle size of Au deposited on the nanocrystalline support was 8 nm, yet modest rates of CO oxidation were still observed, in contrast to the sharp drop-off in activity for particles > ∼3 nm reported previously when using colloidal gold deposited on commercial nanocrystalline titania.

With high activity Au–TiO₂ composite aerogels and low CO flow, conversions of ≥90% are typical, preventing the measurement of meaningful rate constants. To directly measure conversions of \( 10^{-5} \text{ mol s}^{-1} \text{ g}_{\text{cat}}^{-1} \) at room temperature, rather than extrapolate the activity to room temperature from measurements made at temperatures <0 °C as has been previously done, we diluted the Au–TiO₂ composite aerogel with TiO₂ aerogel. Dilution was accomplished by gentle grinding of the composite aerogel with anatase TiO₂ aerogel to distribute the catalyst throughout the sample bed. Measurements were done on several samples to average out any differences from sample-to-sample, but the variability induced by this dilution can be seen in Table 2.

Rate data are also reported in Table 2 in terms of moles of carbon monoxide converted per mole of Au in the various Au–TiO₂ composite aerogels. Composite aerogel catalysts derived from Au-MUA:DT exhibit comparable activity per
mole of Au at all weight loadings (1–10 wt %), which indicates that the aerogel-sited Au remains uniformly accessible to CO at all weight loadings.

The Au–TiO$_2$ composite aerogel catalyst derived from 1 wt % Au-MU performs at the same normalized activity as the Au-MUADT-derived Au–TiO$_2$ catalysts (see Table 2); however, at higher loadings, the activity plummets. These data support the micrographic evidence that the nature of the alkanethiolate ligand on the Au-MPC precursor influences the dispersion of gold in Au–TiO$_2$ aerogel, and thereby the normalized catalytic performance.

Several modifications to the aerogel-MPC method of making Au–TiO$_2$ catalysts can be proposed. In that the postcalcination structure has not been optimized to maintain the Au particle size at 2–3 nm (i.e., the size of the Au core in the as-synthesized Au-MPCs), activity could improve by controlling this parameter alone. Preventing aggregation could be achieved by preforming nanocrystalline titania aerogel and postmodifying the aerogel by soaking in Au-MPC solution.

With Au-MPC sizes predetermined and the final morphology of the oxide determined, we should eliminate the physical contraction of the support that appears to induce Au particle growth and aggregation. This approach might, however, eliminate the “multiple junction” advantage the current catalytic architecture exhibits. It would be worthwhile, however, to exploit the high surface area of aerogels directly, and compare Au–TiO$_2$ composite aerogels made by Au-MPC deposition to materials made by direct deposition of gold on materials with less surface area. Other approaches include calcining Au–TiO$_2$ composite aerogels at lower temperatures, yielding less dense gels with prospectively more highly dispersed gold, and direct deposition of Au-MPCs on amorphous TiO$_2$ aerogel, which can have specific surface areas of $\geq 500$ m$^2$ g$^{-1}$. Experiments along these directions are underway.

In summary, a new way to make highly active Au–TiO$_2$ catalysts has been described. Gold-MPCs can be tailored in terms of their surface characteristics and their core sizes, making them very attractive for molecular-level control of architecture in supported catalysts. Gold-MPCs allow introduction of the same type of metal particle at any step in the processing of nanocomposites, allowing one to optimize for a given application. Aerogel architectures provide important 3-D design and application flexibility through the bicontinuity of the nanoscopic networks of catalyst and mesopores.

The high porosity of aerogels and the synthetic flexibility of Au-MPC guests have allowed us to structure the titania support around nanoparticulate metal catalysts while retaining high activity for the included metal. The high surface area of aerogels may allow for deposition of unprecedented amounts of metal on the support. Activities for CO oxidation comparable to the best Au–TiO$_2$ catalysts described in the literature have been achieved, with few steps yet taken toward optimization.

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Supporting Information Available: Experimental section giving details of Au-PMCs and composite gels and aerogels. This information is available free of charge via the Internet at http://pubs.acs.org.

References

(30) We have noticed that at catalytic activities $\geq 10^{-6}$ mol s$^{-1}$ g$_{cat}$$^{-1}$, considerable heating of the composite aerogel catalyst occurs (which greatly raises the observed rate constant), unless the flow rates of carbon monoxide are kept low and those of oxygen are kept high. The titania in a self-heated Au–TiO$_2$ composite aerogel converts from anatase to rutile, which indicates that reaction temperatures increase from room temperature to $> 500^\circ$C. In the absence of self-heating, the size of the Au in postreaction Au–TiO$_2$ composite aerogels remains unchanged, as determined by high-resolution TEM.

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