Support Effects on Electronic Behaviors of Gold Nanoparticles Studied by X-Ray Absorption Fine Structure

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Abstract. The electronic properties of gold nanoparticles supported on different supports were studied with X-ray absorption fine structure (XAFS). It was found that the tunability of the d-electron distribution in the nano-sized Au clusters can be realized by selective supporting. The Au atoms in the clusters gain 5d electrons when supported on SiO₂, and lose 5d electrons when loaded over MgO, Al₂O₃, and TiO₂. Contractions in bond lengths of between 0.5 and 1.6% from bulk metal values were observed from EXAFS data. This work demonstrates that the important role of the different supports in the 5d-charge distribution of Au nanoparticles and usefulness of XAFS in probing the electronic behavior of noble metal nanoparticles.

Keywords: Au, metal-support interaction, XAFS.

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INTRODUCTION

In contrast to the inert nature of the bulk metal, nano-sized Au particles often demonstrate high and unusual catalytic activities due to “nanosize effect” [1]. The d electrons play an important role in determining the electronic, magnetic and catalytic behavior of transition metals. When metal atoms are confined in a nanoscale space, factors affecting the electronic structure will become more complex [2]. Further, due to larger fraction of metal atoms located on the surface, the optimization of surface energy and the metal-substrate or metal-adsorbate interaction will influence the electronic structure of the transition metal nanoparticles. Thus one can modify the electronic behavior of nanoparticles by carefully controlling their surface environments.

The tendency of nanoparticles to aggregate provides a challenge to the performance of Au nanoparticle catalysts. A simple approach to solve this problem is realized by choosing appropriate support; Au nano-sized clusters can be stabilized via the intersurface interaction with support. However, the interaction between support and Au cluster can change the interplay of structure and electronic properties of nanostructures. A fundamental understanding of the metal/support surface is important in designing efficient catalyst systems.

EXPERIMENTAL

Nano-sized Au catalyst samples were prepared by incipient wetness impregnation of AuCl₃ onto TiO₂, SiO₂, Al₂O₃ and MgO powder (120-150 mesh, calcined at 500 K before use), respectively. The gold loading was 1 wt% in all these samples. Au L-edge XAFS spectra were measured in transmission mode and fluorescence yield mode on the superconducting-wiggler based beamline of U7C at National Synchrotron Radiation Laboratory (NSRL, 0.8 GeV with I_max=300 mA). The fixed-exit Si(111) flat double crystals were used as monochromator. The samples were reduced in an in situ cell with 4% H₂/He at 500 K until the intensity of the white line remained unchanged, then sample was cool down to liquid nitrogen temperature in H₂ and XAFS spectra were taken. EXAFS analysis was performed by following standard procedure. For the curve fitting analysis, the empirical phase shift and amplitude functions for Au–O and Au–Au were calculated with FEFF code [3]. The analysis of EXAFS data was performed using the NSRLXAFS software package [4].
RESULTS
EXAFS Analysis

The Fourier transform intensities of the k-weighted EXAFS functions \(k \chi(k)\) are shown in Figure 1 for the Au samples supported over MgO, Al\(_2\)O\(_3\), SiO\(_2\), and TiO\(_2\) calcined at 500 K, and that of Au foil is also included for comparison. Except Au/MgO, all other samples demonstrate similar higher-shell features to gold foil, indicating the existence of clustered gold atoms, consistent with an fcc-structure retained in the Au nano-particles.

![Figure 1](image)

FIGURE 1. (a) Experimental raw EXAFS data for gold nanoparticles supported on TiO\(_2\), SiO\(_2\), Al\(_2\)O\(_3\) and MgO along with that of Au foil. (b) Corresponding Fourier transforms (k, \(\Delta k = 3–14.3 \text{ Å}^{-1}\)). (the samples are indicated with the same line type).

In the EXAFS analysis the finite nanoparticle size is reflected in the reduced average coordination number resulting from their considerable surface-area-to-volume ratio. As shown Table 1, the Au clusters in the supported samples have a reduction of Au-Au coordination number in the order of Au foil (12) > TiO\(_2\) (9.6) > SiO\(_2\) (7.9) > Al\(_2\)O\(_3\) (6.5).

The relative first nearest Au-Au length contraction and the Debye–Waller factor change as a function of the inverse Au-cluster diameter. It should be noted that the bond lengths obtained from EXAFS results are average. The noticeable decrease in lattice constants in supported Au cluster can be understood in terms of a simple liquid drop model[5] where enhanced surface energy is a main reason for the contracted lattice (nanosize effect). In response to the compressive tension, the atomic positions of the surface atoms should shift away from ideal sites and toward the cluster’s core. Therefore these surface atoms should have shorter the first Au-Au coordination distance [6]. Enhanced disorder in the first coordination bond distance should be correlated with the influences that result from cluster-support interactions, since one of the most plausible explanations for the static disorder found in the nanosized clusters is the relaxation of the bond lengths exhibited by surface atoms, a process driven by the substantial surface tension of a high radius of curvature solid. The increased disorder in the nano-clusters might be predominantly located at their surface. These results point out that the metal-support interactions in nano-Au/TiO\(_2\) and Au/SiO\(_2\) are much weaker than in Au/Al\(_2\)O\(_3\).

<table>
<thead>
<tr>
<th>Support</th>
<th>Shell</th>
<th>(N)</th>
<th>(R(\text{Å}))</th>
<th>(\sigma^2(\text{Å}^2))</th>
<th>(\Delta E_0(\text{eV}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Au-O</td>
<td>1.4</td>
<td>1.972</td>
<td>0.0026</td>
<td>9.85</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>Au-Au</td>
<td>7.2</td>
<td>2.843</td>
<td>0.0058</td>
<td>2.09</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>Au-Au</td>
<td>8.7</td>
<td>2.856</td>
<td>0.0054</td>
<td>6.63</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>Au-Au</td>
<td>10.5</td>
<td>2.861</td>
<td>0.0045</td>
<td>3.08</td>
</tr>
<tr>
<td>Au foil</td>
<td>Au-Au</td>
<td>12</td>
<td>2.879</td>
<td>0.0027</td>
<td>7.94</td>
</tr>
</tbody>
</table>

The errors of data and fits are roughly estimated from the change of the residual factors to be 15% for \(N\), 0.25% for \(R\), 10% for \(\sigma^2\) and 4 eV for \(\Delta E_0\). No ambiguities of the theoretical standards are included.

In contrast to other supports, the \(r\) space of the MgO sample calcinated at 500 K demonstrates the first peak around \(r=1.6\) Å, which is not seen for gold foil. To fit low-\(r\) features, we considered O for first neighbor and Mg for second neighbor. The best fits yield an Au–O coordination, length and Debye–Waller factor of approximately \(N=1.37\), \(r=1.97\) Å and \(\sigma^2=0.0026\) Å\(^2\), respectively. Evidence of a weak contribution identified as Au-Mg was also found, but the uncertainty of the fitting makes this assignment only tentative. It is clear that the higher neighbor correlation for \(r=2.8\) Å almost vanishes, indicating that the structure is highly disordered. This is consistent with isolated Au atoms in the disordered MgO matrix.
Near Edge Analysis

![Near Edge Analysis Diagram](image)

FIGURE 2. Au L₃-edge XANES spectra of Au clusters supported over MgO, Al₂O₃, SiO₂, and TiO₂, compared with bulk Au. The inset expands the intensity changes of the "whiteline".

Figure 2 shows the normalized XANES spectra of the supported Au at the L₃ edges, which probes the unoccupied densities of d states (the whiteline of L₃ edge is mainly due to the 2p₃/2→5d dipolar transitions while the 2p₁/2→6s contribution is negligibly small). For the Al₂O₃, SiO₂, and TiO₂ supported samples, the XANES spectra exhibit similar three peak (b-d) patterns as bulk Au foil within the first 40 eV above the edge, which result from a multiple scattering process, are characteristic of an fcc structure in the nanoparticles. This result is consistent with that deduced from EXAFS data.

It is evident in Figure 2 that the SiO₂-supported Au nanoparticles exhibit a noticeable decrease in the white line intensity as compared to Au foil. One can deduce from this observation that Au atoms over SiO₂ gain 5d electrons, or lose 5d holes, relative to the bulk Au. Such d-charge-redistribution behavior has also been found in the XANES of porous-silicon-supported Au nanoparticles [7] and dendrimer-capped Au nanoparticles [8]. In the Au nanoparticles reported here, the nano-size effect plays a predominant role in modifying their electronic behavior. Stronger Au d-d interaction favors s-d rehybridization, increasing the d-electron count at the Au site in the nanoparticles [7]. In contrast to SiO₂-supported Au, the near edge spectra of Al₂O₃ and TiO₂ supported Au clusters exhibit a small but noticeable increase in the whiteline area (about 20 eV above the threshold) compared to Au foil. It indicates that more vacancies will be generated in the d-bands when Au clusters are supported on Al₂O₃ and TiO₂. On the MgO support calcinated at 500 K, the dramatic increase in the whiteline area was also observed with respect to that of Au foil. It clearly indicates that Au particles are in a higher oxidation state and can not be reduced with H₂ at 500 K, consistent with the single Au-O coordination peak at 1.7 Å in the radial distribution function.

The nature of the Au–support interaction involves a change in the electronic properties of the Au cluster, induced by and correlated with the electron richness of the support oxygen atoms and the ionic character of the cations in the oxide support [9]. With increase in electron richness of the support oxygen atoms the complete Au density of states shifts to higher energy (lower binding energy), and the location of the 6s,p bonding orbital (i.e., the interstitial bonding orbital) moves from the metal–support interface to the surface of the Au particles [10].

Additionally, the electronic properties of gold clusters also depend on their size. The STM measurements show a gradual development of the metallic character of the Au clusters with increasing particle size [11]. The insulator-to-metal transition is occurring at a cluster size of about 100 atoms (corresponding to coordination number of about 7.5). The defects on the surface of supports also need to be taken into account of the electronic properties change in these supported Au nanoparticles. A combination of work on MgO-supported Au clusters [12], and quantum chemical calculations [13] suggests that oxygen vacancy F-center defects at the metal-support interface facilitate electron transfer to the Au metal particle and activate it for catalysis. Considering all these effects, a systematic study based on density functional calculation for these supported Au nanoparticles is underway.

CONCLUSIONS

The electronic behavior of gold nano-clusters can be tailored through selective supports. The interaction of Au cluster with different supports also results in the various contractions in bond lengths. Generally Au/TiO₂ can be considered as pure Au nanoparticles, whereas Au/Al₂O₃ as nanoparticles partly capped with tightly binding ligands (oxygen atoms). Au atoms can be well embedded into disordered MgO matrix (which is calcined at 500K). The nature of the support and its defect structure may be important for the formation and stabilization of very small Au particles. In addition, it is demonstrated that XAFS can be a very powerful tool to evaluate the d-charge distribution in the gold clusters.

REFERENCES