MoO₃ is widely used as a catalyst, sensor, electrochemical device, and display material. It is considered that surface defect sites play a key role in most of catalytic applications, either as active centers or as anchoring sites for supported particles. The evolution of defect sites is a typical process upon reducing the fully oxidized MoO₃, and has been extensively studied in the past decades. These studies, which mainly focus on identifying crystalline phases employing X-ray radiation or electron emission as detection techniques, provide complex information including both the surface and bulk phase. In fact, the chemistry of several outermost layers of MoO₃, which is still a challenging task, is more meaningful for catalytic reactions that usually take place on a surface. Calculations have proposed models of surface defect sites, and have suggested that electrons left behind after oxygen removal could be confined or be localized in defect sites or oxygen vacancy sites. We have employed probe reactions to investigate the surface properties of oxide catalysts, and have obtained precise surface information, such as acidity and basicity, at the identical level of contacted adsorbates, reactants, or sensing gas. Inspired by this work, we endeavored to develop new strategies to detect and measure surface electrons, and to establish a structure–activity relationship. It turns out that confined electrons on the surface of reduced MoO₃ are transferrable to the pertinent environment, and such electron transfer greatly depends on the reduction degree of MoO₃ and the electron affinity of acceptors. Based on above results, we prepared negatively charged gold nanoparticles by depositing gold colloids on MoO₃, and we evaluated their catalytic performance. We demonstrate herein that a profound knowledge of the state of electrons in surface defect sites is necessary to successfully understand catalysis mechanisms, and is in turn helpful in directing catalyst design.

The fully oxidized MoO₃ was prepared by calcining ammonium heptamolybdate in oxygen, and it was used as starting material. Reduction of MoO₃ was conducted in an atmosphere of 5% H₂ balanced with Ar gas at temperatures ranging from 200°C to 480°C. The numbers in the sample names, for example M390, indicate the reduction temperature, in this case 390°C. Reactions between molybdenum oxides and electron acceptors were carried out in acetonitrile solution and were monitored by ultraviolet/visible (UV/Vis) spectroscopy.

We employed tetracyanoethylene (TCNE) as a probe molecule. The molecule has four cyano groups conjugated to the central C=C double bond with low-energy π* orbitals. The addition of an electron to TCNE produces an electron–TCNE complex (TCNE⁻), the color of which is blue and can be quantitatively measured by UV/Vis spectroscopy. The absorption peak at about 330 nm signifying the formation of the blue anion radical of TCNE⁻ is evidence of an electron-transfer reaction. Both the fresh TCNE acetonitrile solution (Figure 1a) and the suspension solution with the fully oxidized MoO₃ (Figure 1b) did not show the absorption peak. When a partially reduced MoO₃ (M390) was tested, the acetonitrile solution instantaneously changed color to blue. The maximum absorption peak was observed at 328 nm (Figure 1c), and was assigned to be TCNE⁻⁺ indicating that the electron-transfer reaction had occurred. The sample reduced at 450°C (M450) did not result in the absorption peak of TCNE⁻⁺, indicating that no electron is transferred to the TCNE molecule (Figure 1d).

**Figure 1.** UV/Vis absorption spectra of TCNE solution. a) TCNE (1 g L⁻¹) in acetonitrile, b), c), d) Spectra of the solution in (a) after incubating the fully oxidized MoO₃, M390, and M450, respectively, for 10 min.
The above-mentioned results indicate that reduction condition is very important. When the reduction was conducted in the range of 350–410°C, the solution color of TCNE changed to blue (Supporting Information, Figure S1). The maximum amount of transferable electrons was detected at 390°C (M390; Figure 2). We believe that the temperature range of 350–410°C is critical to remove oxygen from MoO₃ and to maintain the bulk phase in an unreduced state. Upon reduction, the confined electron in the oxygen vacancy site is metastable, and therefore transferable once it contacts with adsorbed TCNE molecule. When the reduction temperature is increased to 410°C, the confined electrons occupying the oxygen vacancy site redistribute (delocalize) to a neighboring Mo site because of the decrease in the Fermi level, resulting in Mo⁵⁺ or Mo⁶⁺. As a result, the bulk phase is reduced, generating bulk oxygen vacancy sites and forming Mo suboxides or Magneli phases.[9] In our study, no evidence was observed at 400°C (M390; see the Supporting Information, Figure S2d,e). At temperature less than 300°C, no reduction of MoO₃ is observed, and the prolongation of reduction time (isothermal time) also does not lead to further reduction; that is, no amount of transferable electrons is shown in Figure 3. We employed a series of electron acceptors with electron affinities ranging from 1.0 eV to 2.8 eV (Figure 3). The results show that an electron can be abstracted by acceptors with larger electron affinity. The threshold value of electron affinity is about 2.0 eV, which can be viewed as the critical energy of exciting electrons from HOMO orbitals of oxygen vacancy sites (the Fermi level). Consequently, the stability of the reduced samples under ambient conditions is understandable because the electron affinity of molecular oxygen and water is 0.46 eV and 1.3 eV, respectively, which are too weak to form O₂⁻ or hydrated electron (H₂O⁻) species.[10] In this study, TCNE (2.3 eV) is an ideal probe molecule for studying surface defect sites. Although TCNQ has a larger electron affinity value (2.8 eV) than TCNE, the geometric hindrance probably restricts its adsorption on oxide surface, and hinders the electron-transfer process.

Electron transfer from MoO₃ to electron acceptors attracted our interest in catalytic applications. It has been reported that an electron-rich environment, and especially organic ligands, such as nitrogen-containing polymers, is advantageous for selective oxidation reactions.[14,15] There-
fore, MoO$_3$ could be regarded as a group of electron-rich inorganic ligands, and could be good candidate for a catalyst support. We prepared several gold catalysts using the same source of gold colloid as impregnation solution on the as-prepared MoO$_3$ according to previous work,$^{[16]}$ and thus the size affect on different catalysts is eliminated. The gold colloid containing a uniform size of nanoparticles (ca. 3 nm) was prepared by reducing chloroauric acid with NaBH$_4$ (Supporting Information, Figure S4a,b). The study allows us to evaluate pure support effects on catalytic activity.

We studied the charge state of Au nanoparticles using XPS. The binding energy was corrected for surface charging by taking the C1s peak of contaminant carbon as a reference at 285.0 eV.$^{[17]}$ Figure 4a shows the XP spectra of Au/MoO$_3$, Au/M$_{390}$, and Au/M$_{450}$. The Au 4f$_{7/2}$ binding energies of these samples are 83.8, 83.7, and 82.9 eV, respectively. The Au 4f$_{7/2}$ binding energy of Au/M$_{390}$ is significantly smaller (82.9 eV) than that of the bulk gold film (84.0 eV). The $\Delta$1.1 eV negative shift of the binding energy of Au 4f$_{7/2}$ suggests that negative charges are deposited on Au, which is the result of electron transfer from oxygen vacancy sites. The $\Delta$0.3 eV negative shift of the binding energies of Au 4f$_{7/2}$ was reported for other supported Au particles and was explained in a similar manner.$^{[14,16,19]}$ The reason for electron transfer from oxide to gold nanoparticles is explained as follows. Electron affinity of neutral gold particle is size-dependent.$^{[20]}$ When the size is remarkably decreased to less than about 5 nm, surface Au atoms on the nanoparticle behave more like a single Au atom, are highly active, and easily anionically ionized. The electron affinity of a single Au atom is 2.3 eV,$^{[20]}$ which is larger than the threshold value of electron transfer. The driving force for electron transfer from the oxide surface to Au atoms originates from surface conjugation and the differential Fermi energy level. It takes some charge to equalize the Fermi levels.$^{[20,21]}$

CO-FTIR is a technique to probe charge state of supported Au particles.$^{[20,21]}$ Figure 4b shows the behavior of the CO adsorption band on Au/MoO$_3$, Au/M$_{390}$, and Au/M$_{450}$, respectively, in contact with 10 mbar of $^{12}$CO at RT. As for Au/M$_{390}$, the maximum $^{13}$CO band is quite broad and significantly red-shifted to 2067 cm$^{-1}$; whereas the values for Au/MoO$_3$ and Au/M$_{450}$ are 2095 cm$^{-1}$ and 2090 cm$^{-1}$, respectively. The maximum band related to $^{12}$CO is not far from the typical CO adsorption on neutral gold (2100 cm$^{-1}$). The spectroscopic features suggest that the adsorbing gold sites for Au/MoO$_3$ and Au/M$_{450}$ are neutral gold particles, and for Au/M$_{390}$ negatively charged gold particles. The red-shift of the CO band (2067 cm$^{-1}$) is due to the greater $\pi$ back-donation from the negatively charged Au. Theoretically, a red-shift of the CO stretching frequency of 25 to 80 cm$^{-1}$ depending on the charge on the gold clusters was predicted, which agrees rather well with our observed values.$^{[24]}$

We employed the aerobic oxidation of alcohols as model reactions to test activities of Au/MoO$_3$ catalysts. The fully oxidized MoO$_3$, M$_{390}$, and M$_{450}$ gave less than 15% conversion of benzyl alcohol (Table 1, entries 1–3). Doping the fully oxidized MoO$_3$ with gold particles gave 44% conversion of benzyl alcohol (Table 1, entry 4). An exceptional increase in the conversion of benzyl alcohol was observed over Au/M$_{390}$. Nearly 100% conversion of benzyl alcohol and the 94% yield of benzaldehyde were obtained (Table 1, entry 5). In comparison, the yield of benzaldehyde was 29% over Au/M$_{450}$ (Table 1, entry 6). The Au/M$_{390}$

![Figure 4. a) XPS and b) CO-FTIR spectra of the samples of (I) Au/MoO$_3$, (II) Au/M$_{450}$, and (III) Au/M$_{390}$.](Image 81x467 to 266x592)

Table 1: Aerobic oxidation of various alcohols.$^{[a]}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst$^{[b]}$</th>
<th>$S_{RT}$</th>
<th>Substrate</th>
<th>t</th>
<th>Conv.$^{[c]}$</th>
<th>Yield.$^{[d]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MoO$_3$</td>
<td>2.9</td>
<td>benzyl alcohol</td>
<td>10</td>
<td>11</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>M$_{390}$</td>
<td>14.2</td>
<td>benzyl alcohol</td>
<td>10</td>
<td>14</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>M$_{450}$</td>
<td>40.4</td>
<td>benzyl alcohol</td>
<td>10</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>Au/MoO$_3$</td>
<td>2.8</td>
<td>benzyl alcohol</td>
<td>10</td>
<td>44</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>benzyl alcohol</td>
<td>14</td>
<td>$&gt;99$</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>Au/M$_{450}$</td>
<td>39.0</td>
<td>benzyl alcohol</td>
<td>14</td>
<td>53</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>p-chlorobenzyl alcohol</td>
<td>14</td>
<td>$&gt;99$</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>cyclohexanol</td>
<td>10</td>
<td>$&gt;99$</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>2-phenylethanol</td>
<td>8</td>
<td>$&gt;99$</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>1-butanol</td>
<td>20</td>
<td>$&gt;99$</td>
<td>88</td>
</tr>
<tr>
<td>11</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>2-butanol</td>
<td>12</td>
<td>$&gt;99$</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>1-hexan</td>
<td>18</td>
<td>$&gt;99$</td>
<td>87</td>
</tr>
<tr>
<td>13</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>2-hexanol</td>
<td>18</td>
<td>$&gt;99$</td>
<td>85</td>
</tr>
<tr>
<td>14</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>1-octan</td>
<td>15</td>
<td>$&gt;99$</td>
<td>89</td>
</tr>
<tr>
<td>15</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>2-octan</td>
<td>15</td>
<td>$&gt;99$</td>
<td>90</td>
</tr>
<tr>
<td>16</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>benzyl alcohol</td>
<td>14</td>
<td>11</td>
<td>–</td>
</tr>
<tr>
<td>17</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>benzyl alcohol</td>
<td>14</td>
<td>$&gt;99$</td>
<td>93</td>
</tr>
<tr>
<td>18</td>
<td>Au/M$_{390}$</td>
<td>13.9</td>
<td>benzyl alcohol</td>
<td>14</td>
<td>$&gt;99$</td>
<td>92</td>
</tr>
</tbody>
</table>

$^{[a]}$ Typical reaction conditions: 5 mmol alcohol, 15 mmol K$_2$CO$_3$, 100 mg catalyst, 5 mL acetonitrile, 50 °C. Experiments were conducted in a quartz reactor. Pure oxygen gas (1 atm) was supplied by a balloon. Samples were withdrawn at intervals to track the reaction by TLC.

$^{[b]}$ M$_{390}$ and M$_{450}$ indicate that the catalyst supports were reduced in 5% H$_2$ balanced with Ar at 390 °C and 450 °C, respectively. The loading amount of Au was 1.1 wt% in all catalysts as analyzed by ICP-mass spectrometry.

$^{[c]}$ The conversion was determined by gas chromatography.

$^{[d]}$ Products were isolated on silica gel using hexane/ethyl acetate (2.5:1) as effluent solution. 

$^{[e]}$ In the absence of K$_2$CO$_3$.

$^{[f]}$ Air was used instead of pure oxygen.

$^{[g]}$ The result of the third reuse.
could catalyze the oxidation of other primary or secondary alcohols to the corresponding aldehydes or ketones in high yields (Table 1, entries 7–15). The reaction did not occur in the absence of base (Table 1, entry 16). The oxidation under 1 atm air proceeded in a comparable result to that under 1 atm of pure oxygen (Table 1, entry 17), indicating that the reaction was not controlled by an oxygen mass-transfer process. After reaction, the Au/M390 catalyst was filtered out, washed with solvent, and reused. Catalytic results were stable over three cycles (Supporting Information, Figure S5). The yields of benzoic aldehyde were more than 90% in all reuse tests (Table 1, entry 18). The inductively coupled plasma (ICP) mass analysis revealed that no Au species content was detected in the reaction mixture, indicating the strong interaction between Au and support. The hot filtration test was conducted. No further conversion of benzyl alcohol was observed after catalyst was filtered out, indicating that the catalyst was heterogeneous in nature (Supporting Information, Figure S6). The great difference of catalysis is majorly attributed to a support effect, because of which M390 is able to transfer electrons to the Au nanoparticles. It was reported by Tsunoyama et al. that the catalytic activity of Au for aerobic oxidations is enhanced by an increase in the amount of negative charge on the Au core.[14,25] The size effect on the cleavage of the C–H bond from alcohol to transfer electrons to the Au nanoparticles. It was reported by Tsunoyama et al. that the catalytic activity of Au for aerobic oxidations is enhanced by an increase in the amount of negative charge on the Au core.[14,25] The size effect on the cleavage of the C–H bond from alcohol to the corresponding aldehydes or ketones. The catalytic results of Au/MoO3 are likely relevant to other oxide-supported Au catalysts, such as Au/MgO, Au/TiO2 and Au/PVP.

In summary, we employed single electron oxidants as electron acceptors to investigate surface defect sites on partially reduced molybdenum oxides. We detected free electrons in surface defect sites and quantitatively measured the threshold value of electron transfer. Our studies show that partially reduced molybdenum oxides can transfer electrons to the pertinent environment. Such electron transfer deposits negative charges on the closely contacted Au nanoparticles, which explains high catalytic activities in the aerobic oxidation of alcohols. We believe that the study will greatly contribute to the knowledge of electron states of surface defect sites of oxides and their catalytic applications.

Received: August 22, 2011
Revised: January 9, 2012
Published online: March 13, 2012

**Keywords:** defect sites · electron transfer · heterogeneous catalysis · molybdenum oxides · oxidation

![Figure 5a](image) **Figure 5 a) Time-on-stream course of conversion.** PhCH2OH, PhCD2OH. C = conversion of benzyl alcohol. b) Arrhenius plot for the oxidation of PhCH2OH.


