

## Direct Evidence of Oxidized Gold on Supported Gold Catalysts

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Supported gold catalysts have drawn worldwide interest due to the novel properties and potential applications in industries. However, the origin of the catalytic activity in gold nanoparticles is still not well understood. In this study, time-of-flight secondary ion mass spectroscopy (TOF-SIMS) has been applied to investigate the nature of gold in Au (1.3 wt %)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au (2.8 wt %)/TiO<sub>2</sub> catalysts prepared by the deposition–precipitation method. The SIMS spectrum of the supported gold catalysts presented AuO<sup>+</sup>, AuO<sub>2</sub><sup>+</sup>, and AuOH<sup>+</sup> ion clusters. These measurements show direct evidence for oxidized gold on supported gold catalysts and may be helpful to gaining better understanding of the origin of the catalytic activity.

Bulk gold is typically regarded as catalytically inert as compared to platinum group metals. However, it has been found that there is a remarkable change in its catalytic activity when gold is deposited on metal oxides such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and Co<sub>3</sub>O<sub>4</sub><sup>1–3</sup> with the particle size down to several nanometers. For example, highly dispersed gold nanoparticles on metal oxides are extremely active for reactions such as partial oxidation of hydrocarbons, reduction of nitric oxides, low-temperature CO oxidation, and propene epoxidation.<sup>2</sup> There is now worldwide interest aroused by such catalytic properties of supported gold nanoparticles.<sup>4–6,9–11</sup>

The activity of gold catalysts in the oxidation reactions is somewhat surprising, because dissociatively adsorbed oxygen is generally thought to be the active oxidant in related reactions on other noble metals.<sup>7</sup> Molecular oxygen is known not to dissociatively adsorb on bulk gold at pressures as high as 1400 Torr and temperatures between 300 and 500 K.<sup>8</sup> The origin of the catalytic activity in supported gold nanoparticles is still not well understood, with many questions remaining about the site of the reaction and the nature of the interaction between gold nanoparticles and the support.

Another unresolved issue is the oxidation state of the Au active site. Some researchers claim the ionic Au as the active species.<sup>12,13</sup> One model proposed is an ensemble consisting of metallic Au and Au–OH species.<sup>10,14</sup> In contrast, other researchers proposal that the active site is metallic Au, which is based on the fact that the only detectable species is metallic Au on an active catalyst. The spectroscopic techniques used to

arrive at this conclusion includes XPS,<sup>15,16</sup> Au<sup>197</sup> Mössbauer<sup>17</sup> and XANES.<sup>18</sup> Recently, oxygen was proposed to be chemisorbed on gold nanoparticles on the basis of the density functional theory (DFT) calculations or upon indirect experimental evidence.<sup>19–24</sup> The oxidized gold species was further considered to be the active sites on the basis of relative catalytic activities after different treatments (calcination and reduction) of the samples.<sup>25–28</sup> However, unsupported gold nanoparticles also exhibit CO oxidation at room temperature, although the bulk gold surface never catalyzes the reaction.<sup>29</sup> In short, so far, few experiments have presented direct evidence for oxidized gold on supported gold catalysts.

Our approach is to employ a sensitive surface analytical technique, Time-of-flight secondary ion mass spectroscopy (TOF-SIMS), which can identify not only the elemental composition but also the molecular species with high sensitivity (order of ppm). We report, for the first time, the use of TOF-SIMS to investigate the nature of gold in Au(1.3 wt %)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au(2.8 wt %)/TiO<sub>2</sub> catalysts. These measurements show a direct evidence for oxidized gold on supported gold catalysts.

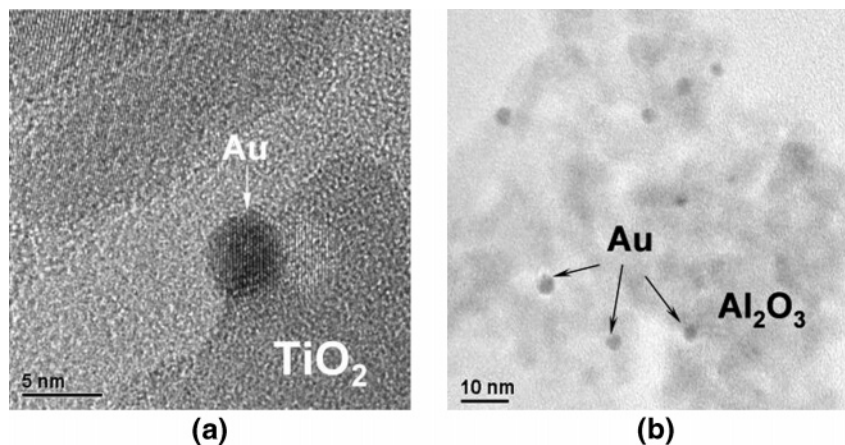
Supported gold catalysts of Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> were prepared by a deposition-precipitation method (DP) which is described elsewhere.<sup>1,14</sup> The catalysts were calcined at 350 °C. Gold loading of Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> in weight was 1.3% and 2.8%, respectively, as determined by inductively coupled plasma spectroscopy (ICP) examination. Gold particle size, measured by a Hitachi HF-2000 cold field emission gun (cFEG) transmission electron microscope (TEM), was rather uniform between 2 and 5 nm (Figure 1). The particles were dispersed very well. XPS measurements show only metallic gold in both samples. Catalytic tests for 45 min on stream showed that both the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Au/TiO<sub>2</sub> catalysts were highly active at room-temperature oxidation of carbon monoxide, 3.2 mol of CO/(min mol of Au) and 10.8 of CO/(min mol of Au), respectively.

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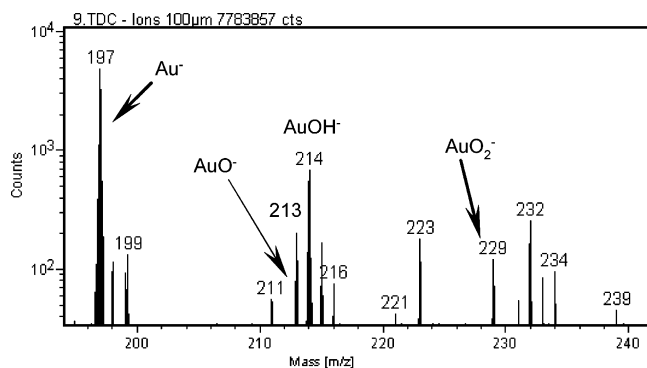
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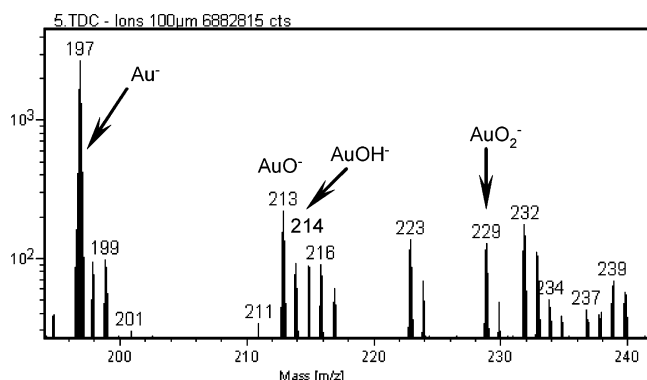
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**Figure 1.** TEM images of gold nanoparticles on oxide supports: (a)  $\text{TiO}_2$ ; (b)  $\text{Al}_2\text{O}_3$ .



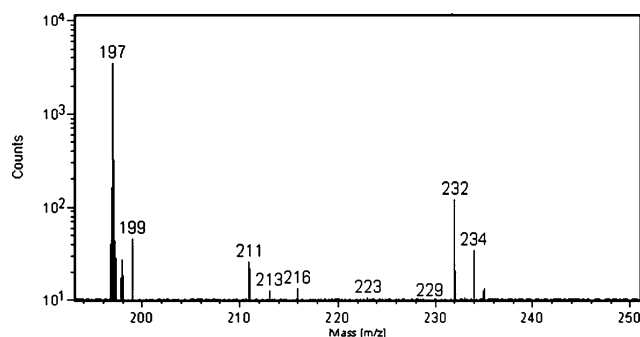
**Figure 2.** Negative ion mode SIMS spectrum of  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$ .



**Figure 3.** Negative ion mode SIMS spectrum of  $\text{Au}/\text{TiO}_2$ .

TOF-SIMS was performed with a Physical Electronics PHI TRIFT III, which is equipped with a pulsed  $\text{Ga}^+$  liquid ion gun operated at 15 kV. The ion source was operated with a current of 600 pA. Figures 2 and 3 shows the negative-ion mode SIMS spectra obtained from  $\text{Au}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Au}/\text{TiO}_2$  catalysts, respectively. A series of ion clusters related to gold were found. The peak with  $m/z$  of 197 was assigned to  $\text{Au}^-$ . Peaks of 213, 214, and 229 were ascribed to ion fragments  $\text{AuO}^-$ ,  $\text{AuOH}^-$ , and  $\text{AuO}_2^-$ , respectively. For comparison, SIMS measurements were also performed on gold foil (purity 99.99%) purchased from Aldrich (Figure 4), yielding only the characteristic peak of gold ( $m/z = 197$ ). The peaks associated with  $\text{AuO}^-$ ,  $\text{AuOH}^-$ , and  $\text{AuO}_2^-$ , such as 213, 214, and 229, were not found.

Undoubtedly, these peaks results from fragmentation of the surface of the particles, rather than recombination of species after ejection from the surface. Yu<sup>30</sup> has clearly demonstrated that negative ions are formed by direct lattice fragmentation for inorganic materials. Because the electronic affinity of negative charged ions is low, electron detachment is very



**Figure 4.** Negative ion mode SIMS spectrum of gold foil.

favorable, excluding the possibility of recombination of secondary negative ions. Thus static SIMS data give a direct identification of the chemical structure of the sample surface. This notion is further confirmed by the experiments by Aubriet et al.<sup>34</sup> They used the static SIMS technique to study the ternary oxides (e.g.,  $\text{FeCr}_2\text{O}_4$ ) and the mechanical mixture of binary oxides ( $\text{FeO}$  and  $\text{Cr}_2\text{O}_3$ ). Numerous metal–oxygen ions were obtained after bombardment with a  $^{69}\text{Ga}^+$  beam (15 kV, 600 pA). Recombination in gas phase did not take place between the emitted species. They suggested that the mechanism of ion formation, especially for oxide compounds, is direct ejection of species into vacuum under ion bombardment. Even if recombination was assumed to occur through collision in gas phase, the low amount of ejected species after bombardment of a primary beam may be considered as a limiting factor to these processes during static SIMS experiments. In our study, the SIMS spectrum of the catalyst samples exhibited the oxidized Au clusters of  $\text{AuO}^-$ ,  $\text{AuOH}^-$  and  $\text{AuO}_2^-$ . However, no oxidized Au clusters of  $\text{AuO}^-$ ,  $\text{AuOH}^-$  and  $\text{AuO}_2^-$  were found in the SIMS spectrum of the high-purity Au foil, although  $\text{Au}^-$  and  $\text{O}^-$  were still present in the spectrum. If secondary ion clusters were formed via the recombination mechanism, the ion cluster combined Au with O, such as  $\text{AuO}^-$  and  $\text{AuO}_2^-$ , would have been present in the in the SIMS spectrum of the high-purity Au foil.

The presence of  $\text{AuO}^-$  and  $\text{AuO}_2^-$  ion clusters in SIMS spectrum indicates the existence of oxidized gold in the catalyst, suggesting the chemisorbed oxygen on gold nanoparticles or partial oxidation of the gold. In the present work, XPS was also used to measure the chemical structure of gold. Only metallic gold was detected by XPS, and oxidized gold was not detected. This is because the amount of oxidized gold in the catalysts is too small to be detected by XPS, whereas TOF-SIMS has much higher detection sensitivity and suitable for detection of trace

elements and molecules. In addition, carbon-containing ion species ( $C_xH_y^-$ ) and chlorine ion ( $Cl^-$ ) were also detected in the catalyst due to common external contamination.  $AuOH^-$  is due to chemisorbed water on gold. For some metal oxides, the abundance of some hydrogenated ion clusters  $[M_xO_y(OH)_z]^-$  is often greater than that for the corresponding non-hydrogenated ion clusters.<sup>30,31</sup>

Au-associated species in the Au/oxide catalyst are derived from a solution of  $HAuCl_4$  in the deposition-precipitation process. As it has been reported, in a solution of  $HAuCl_4$  the predominant species at high pH are  $Au(OH)_3Cl$ ,<sup>31,32</sup> and the anionic gold complex is attracted to the positive charge on the oxide surface.<sup>33</sup> After subsequent calcination at 350 °C, the gold complex is reduced and metallic Au nanoparticles are formed. Bulk gold does not react directly with other high electronegative elements such as sulfur or oxygen. However, when the size of the gold particles is reduced, obviously, the fraction of atoms at the metal–support interface increases where cationic gold could be stabilized by the support. It is also possible that oxygen adsorbs readily on surface defects, the fraction of which also increases with decreasing Au particle size.

In conclusion, SIMS spectra of Au/ $\gamma$ - $Al_2O_3$  and Au/ $TiO_2$  catalysts exhibited oxidized Au clusters of  $AuO^-$ ,  $AuOH^-$  and  $AuO_2^-$ . Because these catalysts are highly active in room-temperature CO oxidation, the presence of the oxidic surface species may have implication in the nature of the active site of supported Au catalysts. Their presence is consistent with the possibility that the active site is an ensemble of Au–OH and metallic Au. This gives a direct evidence for oxidized gold in supported gold catalysts.

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## References and Notes

- (1) Haruta, M.; Tsubota, S.; Kageyama, H.; Genet, M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
- (2) Haruta, M. *Catal. Today* **1997**, *36*, 153.
- (3) Hayashi, T.; Tanaka, K.; Haruta, M. *J. Catal.* **1998**, *178*, 566.
- (4) Abelson, P. H. *Science* **2000**, *288*, 269.
- (5) Haruta, M. *Chemical Record* **2003**, *75*, 3.
- (6) Bond, G. C. *Catal. Today* **2002**, *72*, 5.
- (7) Bondzie, V. A.; Parker, S. C.; Campbell, C. T. *J. Vac. Sci. Technol. A* **1999**, *17*, 1717.
- (8) Sault, A. G.; Madix, R. J.; Campbell, C. T. *Surf. Sci.* **1986**, *169*, 347.
- (9) Haruta, M. *CTATECH* **2002**, *6*, 102.
- (10) Bond, G. C.; Thompson, D. T. *Gold Bull.* **2000**, *41*, 33.
- (11) Valden, M.; Lai, X.; Goodman, D. W. *Science* **1998**, *1647*, 281.
- (12) Park, E. D.; J. S. Lee, J. S. *J. Catal.* **1999**, *186*, 1.
- (13) Finch, R. M.; Hodge, N. A.; Hutchings, G. J.; Meagher, A.; Pankhurst Q. A.; Siddiqui, M. R. H.; F. E. Wagner, F. E.; R. Whyman, R. *PhysChemChemPhys* **1999**, *1*, 485.
- (14) Costello, C. K.; Kung, M. C. Oh, H. S.; Y. Wang, Y.; Kung, H. H. *Appl. Catal. A: Gen.* **2002**, *232*, 159.
- (15) Lee, S. J.; Gavriilidis, A.; Pankhurst, Q. A.; Kyek, A.; Waner F. E.; Won, P. C. L.; Yeun, L. *J. Catal.* **2001**, *200*, 298.
- (16) Uczi, L.; Horvath, D.; Paszti, Z.; Toth, L.; Horvath, Z. E.; Karacs, A.; Peto, J. *Phys. Chem. B* **2000**, *104*, 3183.
- (17) Goossens, A.; Craje, M. W. J.; Van der Kraan, A. M.; Zwijnenbur, A.; Makkee, M.; Moulijn, J. A.; DeJongh L. J. *Catal. Today* **2002**, *72*, 95.
- (18) Haruta, M.; Tsubota, S.; Kobayashi, T.; Kageyama H.; M. J.; Delmon, B. *J. Catal.* **1993**, *144*, 175.
- (19) Okumura, M.; Kitagawa, Y.; Haruta, M.; Yamaguchi, K. *Chem. Phys. Lett.* **2001**, *346*, 163.
- (20) Wallace, W. T.; Wyrwas, R. B.; Whetten, R. L.; Mitric, R.; Bonacic-Koutecky, V. *J. Am. Chem. Soc.* **2003**, *125*, 8408.
- (21) Gottfried, J. M.; Elhobashi, N.; Schroeder, S. L. M.; Christmann, K. *Surf. Sci.* **2003**, *523*, 89.
- (22) Kim, Y. D.; Fischer, M.; Gantefor, G. *Chem. Phys. Lett.* **2003**, *377*, 170.
- (23) Franceschetti, A.; Pennycook, S. J.; Pantelides, S. T. *Chem. Phys. Lett.* **2003**, *372*, 471.
- (24) Berndt, H.; Pitsch, I.; Evert, S.; Struve, K.; Pohl, M. M.; Radnik, J.; Martin, A. *Appl. Catal. A* **2003**, *244*, 169.
- (25) Bond, G. C. *Catal. Rev.-Sci. Eng.* **1999**, *41*, 319.
- (26) Kang Y. M.; Wan, B. Z. *Catal. Today* **1995**, *26*, 59.
- (27) Gardner, S. D.; Hoflund, G. B.; Schryrer, D. R.; Schyer, J.; Upchurch, B. T.; Kirilin, E. J. *Langmuir* **1991**, *7*, 2135.
- (28) Visco, A. M.; Neri, F.; Neri, G.; Donato, A.; Milone, C.; Galvagno, S. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2869.
- (29) Iizuka, Y.; Tode, T.; Takao, T.; Yatsu, K.; Takeuchi, T.; Tsubota S.; Haruta, M. *J. Catal.* **1999**, *187*, 55.
- (30) M. L. Yu, *Phys. Rev. B* **1981**, *24*, 5625; *Appl. Surf. Sci.* **1982**, *11/12*, 196.
- (31) Haruta, M.; Ueda, A.; Tsubota, S.; Torres Sanchez, R. M. *Catal. Today* **1996**, *29*, 443.
- (32) Baes, C. F.; Mesmer, R. E. *The Hydrolysis of Cations*; John Wiley & Sons: New York, 1976; p 23.
- (33) Aubriet, F.; Poleunis, C.; Bertrand, P. *J. Mass Spectrom.* **2001**, *36*, 641.
- (34) Aubriet, F.; Poleunis, C.; Bertrand, P. *Appl. Surf. Sci.* **2003**, *203*, 114.