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Activation of Oxygen by Metallic Gold in Au/TiO_2 Catalysts

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Supported Au catalysts have shown a remarkable activity in a variety of low-temperature oxidation reactions, such as the oxidation of CO.[1,2] Despite extensive investigations of powder[1−10] and model[11,12] catalysts, the mechanism by which molecular oxygen is activated in these reactions is not understood.[13] Gold single crystals are inactive toward oxygen unless energy is provided to break the O−O double bond.[14] Activation of O_2 on the gold particles has been observed for Au/TiO_2 and Au/Al_2O_3.[15,16] On the other hand, for reducible supports (such as TiO_2) it has been suggested that this step proceeds on the support, which then provides active oxygen to the gold cluster.[2,5,17−20] This view is supported by the low reactivity of bulk gold toward O_2.[21] Density functional theory (DFT) calculations[22,23] predict two oxygen activation pathways for gold supported on oxides: (i) an activation on the gold cluster and (ii) activation on the support oxide. However, experimental data elucidating O_2 activation over these catalysts is scarce.[24,25] The measurements reported here provide strong evidence for activated gold−oxygen complexes formed by gold supported on a reducible oxide (TiO_2). Fully reduced gold particles appear to take part in the activation of molecular oxygen.

Au/TiO_2 catalysts with two different nominal metal loadings (4 wt % and 1 wt %; AAS indicated actual loadings of 3.2 wt % and 1.0 wt %, respectively) were prepared via deposition−precipitation with urea.[3,4] Catalytic reaction rates (plug-flow, 1% CO, 2% O_2, balance He, total flow 230 mL/min) were 0.35 (1 wt %) and 0.29 (4 wt %) $mol_{CO}\ s^{-1}\ mol_{Au}^{-1}$. TEM images of the reduced catalysts (see Supporting Information) revealed small average particle sizes of approximately 1.7 nm (Table 1). After reduction (20 mL/min 5% H_2/He, 373 K, 1 h), the catalysts were consecutively exposed to O_2, a CO/O_2 mixture and CO at 298 K (Table 1), while Au L_3-edge X-ray absorption spectra were measured in transmission[26] (station 9.3, SRS, Daresbury, U.K.). The main features of the X-ray absorption near-edge structure (XANES) at the Au L_3-edge are determined by dipole-allowed, intra-atomic electronic transitions from a $2p_{3/2}$ core level state to unoccupied d-states in the Au valence region. In compounds containing cationic gold there is an intense near-edge resonance ("white line") that arises from unoccupied d-states, as for example for $AuCl_3$ (Figure 1). The antibonding component of chemisorptive adsorbate/cluster interactions also leads to d-band depletion in the same spectral region.[16,27,28]

Immediately after reduction of the 4 wt % Au catalyst the Au L_3-near-edge (in He) essentially resembles that of Au foil, indicating that all gold resides in metallic clusters. There is no evidence for the presence of cationic gold species. Subsequent exposure to O_2 leads to an increase of the intensity in the d-band region, as evident from the magnified difference spectrum, $\mu(O_2) - \mu(He)$, at the bottom of Figure 1. The resonance at 11920 eV clearly indicates that exposure to O_2 decreases the d-band occupancy, that is, an interaction of Au with adsorbed oxygen. The decrease was even more pronounced for the 1 wt % catalyst (Table 1), indicating that the fraction of Au atoms in contact with oxygen was larger. TEM images suggested identical average particle sizes for both catalysts, but the EXAFS (higher Au−Au coordination number, Supporting information) and a lower catalytic reaction rate also indicate that Au in the 4 wt % sample is overall less disperse than in the 1 wt % catalyst.

Table 1. Particle Sizes, Au−Au Coordination Numbers (CN), and Relative Amount of d-Band Depletion (Determined by Integration of the XANES Resonances Shown in Figure 2) of Au/TiO_2 Catalysts under Various Gas Atmospheres[a]

	d-band depletion (au)						CN_{Au-Au}
	O_2[b]	CO/O_2[b]	CO[b]	CO/O_2[c]	O_2[c]	d_{Avg} (Nm)	(in He)
Au/TiO_2 (1 wt %)	0.16	0.30	0.32	0.36	0.21	1.7	6.8
Au/TiO_2 (4 wt %)	0.08	0.06	0.09	0.06	0.05	1.7	8.1
Au/Al_2O_3 (0.3 wt %)[29]	n/a	n/a	0.31	n/a	n/a	1.5	5.7

[a] Conditions: 298 K, 20 mL/min, 100 kPa total pressure, 10 kPa reactive gas mixture (pure O_2, 1:1 CO/O_2 or pure CO), balance He. n/a = not available. [b] First exposure cycle. [c] Second exposure cycle.

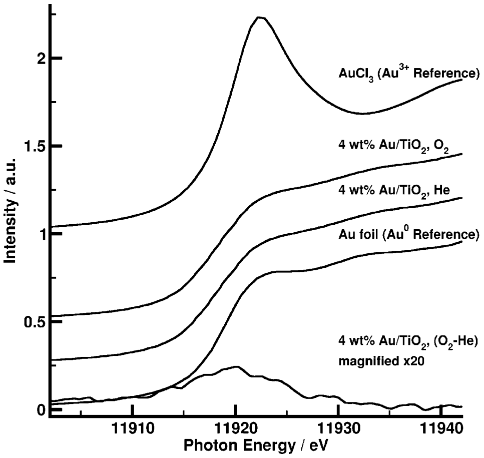

Figure 1. Au L_3 XANES of 4 wt % Au/TiO_2 catalyst exposed to O_2 and He; also shown are Au^{3+} ($AuCl_3$) and Au metal references. The bottom spectrum is the difference between the two catalyst spectra.

Further differential XANES spectra in Figure 2 reveal that d-band depletion is also caused by exposure to the CO/O_2 mixture and to CO only. The variations in the amount of the d-band depletion

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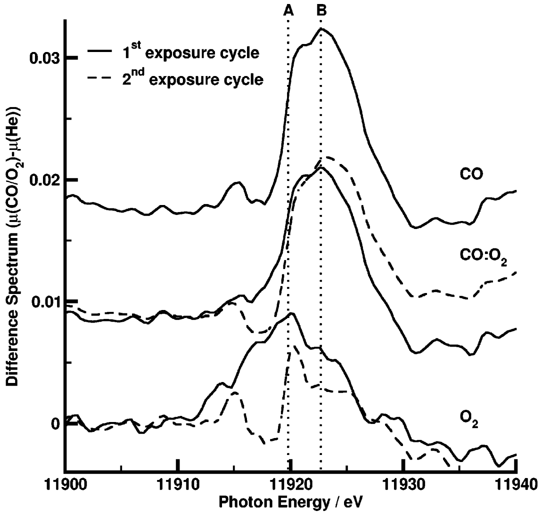

Figure 2. XANES difference spectra, μ(reactive atmosphere) − μ(He), for 4 wt % Au/TiO_2. The position of the XANES resonance differs in pure O_2 (A) and pure CO (B). Dashed lines denote a second exposure cycle.

(Table 1) and energy positions of the corresponding XANES resonances allow a more detailed analysis of the interaction between the gas phase and the gold clusters. The observation of a resonance in the presence of O_2 indicates that an activated Au−O complex similar to that recently observed on a nonreducible support can be formed.[16] In pure CO, a similar XANES feature at slightly higher photon energy (11923 eV) is visible. For the 1 wt % Au/TiO_2 catalyst the intensity of this CO-induced XANES feature (Table 1) is comparable to the resonance observed for a Au/Al_2O_3 catalyst, even though one support is more easily reducible than the other.[29] Ab initio XANES simulations[30] for a geometry-optimized Au_{10}−CO cluster using full multiple-scattering calculations suggest that the features observed in CO-rich gas environments may be due to back-bonding from the Au d-band to the $2\pi^*$ molecular orbitals of CO. Similar calculations have been carried out to predict the interaction between O_2 and Au.[16] They show that the energy difference of the near-edge resonances observed in O_2 and CO (A and B in Figure 2) can be attributed to changes in the d-projected density of states.

The XANES of the samples in a CO/O_2 mixture is very similar to the one observed in pure CO, confirming the expectation[31−34] that CO dominates the interaction with the gold component. A second exposure cycle produces changes comparable to those of the first (Figure 2), indicating that the activated Au−O complex is re-formed after the sample was also exposed to CO. The intensities of the changes (Table 1) are stronger for the 1 wt % catalyst, in which Au is probably more disperse (vide supra).

Our results suggest that metallic gold particles on a reducible support (TiO_2) form activated gold−oxygen complexes, which might play a role in the mechanism of O_2 activation and hence CO oxidation. This conclusion agrees with those derived from model catalysts,[35] for which it was shown that reduced gold is the active component in the oxidation of CO. It has previously also been suggested that cationic[36] or anionic gold[37] species are active in CO oxidation. Our data suggest a different view, namely that chemisorption of CO and O_2 on the catalyst both cause a significantly depleted Au d-band in otherwise essentially metallic gold clusters. This view supports a recent in situ XPS study of a similar Au/TiO_2 catalyst, which favored an interpretation of core-level binding energy shifts in terms of final-state screening variations (either relaxation and/or Coulomb effects) during the photoemission from metallic gold clusters.[31]

More experiments are necessary to elucidate the nature of the active gold−oxygen complex, and detailed kinetic measurements are required to determine its role in the reaction mechanism. Although we cannot distinguish whether O_2 is activated on the gold clusters only or at the cluster-support interface,[22,23] the formation of similar activated Au−O complexes on reducible (TiO_2)[15,31,this study] and on nonreducible (Al_2O_3)[15,16] supports suggests that the modified electronic structure of Au nanoclusters contributes to the high catalytic activity of these materials.

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Supporting Information Available: TEM micrographs; EXAFS analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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