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The Role of F-Centers in Catalysis by Au Supported on MgO

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The discovery of the extraordinary activity exhibited by small gold clusters on certain oxide supports[1,2] has stimulated considerable research[3−11] to address the origin of this unusual behavior. We report, relevant to this question, a study of the oxidation of CO to CO_2 over Au clusters supported on MgO, annealed to temperatures between 900 and 1300 K prior to deposition of the Au cluster. Treating MgO at temperatures within this range has been shown previously to produce an F-center concentration within the surface region that is proportional to the anneal temperature. The results of Figure 1 show a direct correlation between the F-center concentration in the MgO support and the catalytic activity of the subsequently deposited Au, implying a critical role of surface F-centers in the activation of Au in Au/MgO catalysts.

The highly dispersed Au catalyst was prepared using the tetranuclear amidinate gold(I) complex $[Au_4(form)_4]$, form = [(*p*-tolyl)NCN(*p*-tolyl)].[12] Supported Au clusters were synthesized by grafting this complex to the MgO support (Fisher, Light) by dissolving the complex in tetrahydrofuran, followed by deposition onto the MgO support at 300 K to a nominal Au loading of 1 wt % with respect to the support. The MgO support was annealed to temperatures between 900 and 1300 K prior to deposition of the Au. The supported Au clusters, prior to reaction, were treated in flowing oxygen at 773 K for 3 h to remove any traces of the Au precursor ligands. Previous work[19] has shown that relevant surface defects, for example, F-centers, are stable below 1100 K, and therefore the process of depositing Au and the subsequent ligand removal should not alter the relevant defect concentration at the MgO surface. The subsequent Au cluster size was measured (Figure 2) with transmission electron microscopy and found to average 4.3 nm on the 1073 K annealed MgO support and 3.8 nm on the 1173 K annealed sample, consistent with an enhanced stability of Au clusters bound to a defect-rich MgO surface.[4]

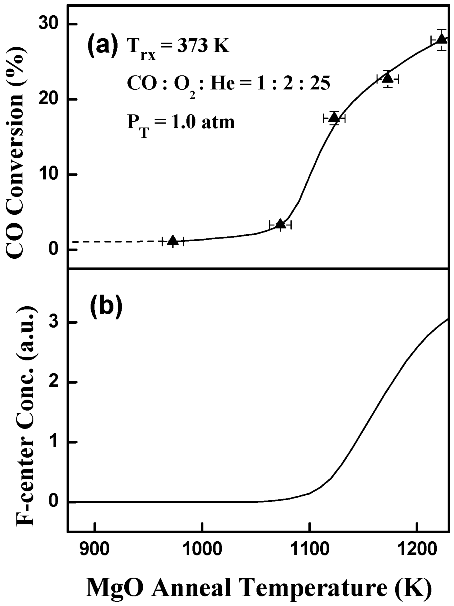

Figure 1. (a) Conversion of CO to CO_2 by Au/MgO as a function of the anneal temperature of the MgO support prior to deposition of the Au. The data were measured at 373 K in a mixture of $CO/O_2/He$ (1:2:25), maintaining a flow rate of 45 mL/min. (b) The relative concentration of F-centers in MgO as determined by electron energy loss spectroscopy as a function of the anneal temperature.[14] Figure 1b was adapted from ref 14.

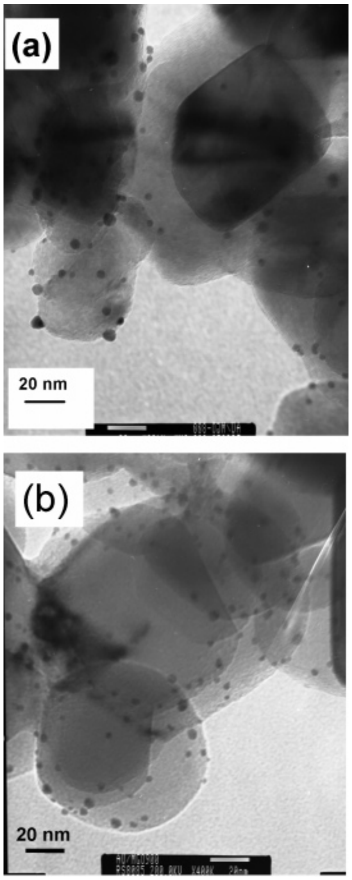

Figure 2. (a) Transmission electron micrograph of a Au/MgO catalyst where the MgO support was annealed to 1073 K prior to deposition of the Au. (b) Transmission electron micrograph of a Au/MgO catalyst where the MgO support was annealed to 1173 K prior to deposition of the Au.

The conversion of CO to CO_2 was monitored as the reaction temperature was varied between 298 and 573 K in a mixture of $CO/O_2/He$ (1:2:25), maintaining a flow rate of 45 mL/min. The conversion plotted in Figure 1a is that measured at 373 K and is uncorrected for the variation in the dispersion between the various cluster sizes of the catalyst. At higher anneal temperatures (>1273 K), the specific surface area of MgO dropped dramatically, with a corresponding increase in the Au cluster sizes and reduction in the CO catalytic oxidation activity.

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The data shown in Figure 1b, published previously,[13−16] were acquired for MgO thin films using electron loss spectroscopy (EELS) to characterize the electronic transitions associated with various defects in MgO. Specific defect assignments were determined by direct comparison with data acquired for bulk MgO. In Figure 1b, the normalized intensity of the EELS feature identified specifically as due to F-centers in or near the MgO surface is plotted as a function of the anneal temperature of the MgO support prior to deposition of the Au clusters. The correlation between the change in the catalytic activity of the subsequently deposited Au clusters and the change in the concentration of F-centers in the MgO support is consistent with F-centers playing a direct role in the activation of the Au clusters.[4] Recent theoretical results have shown that F-centers in MgO serve to anchor Au clusters and to control their charge state by partial transfer of charge from the substrate F-center to the Au cluster, thus promoting their catalytic activity.[4]

The results for the Au/MgO system are likely relevant to other oxide-supported Au systems, such as Au/TiO_2. Theoretical calculations have shown that F-centers on oxide surfaces can activate Au by transfer of electronic charge from the surface to the clusters (0.5 e for MgO[4] and 0.15 e for TiO_2[18a]). A recent model study of Au on a highly reduced TiO_x ordered film grown on Mo(112) has demonstrated that a highly reduced TiO_x support leads to strong bonding between Au and the reduced Ti atoms of the TiO_x support, yielding electron-rich Au.[17] These studies are entirely consistent with recent theoretical studies on the Au/TiO_2 system[18] that show the importance of reduced Ti defect sites at the boundary between Au clusters and a TiO_2 interface in determining the Au cluster shape and electronic properties.

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