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COMMUNICATIONS

# CO Oxidation over AuPd(100) from Ultrahigh Vacuum to Near-Atmospheric Pressures: The Critical Role of Contiguous Pd Atoms

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The pioneering work by Haruta et al.[1,2] on low-temperature CO oxidation catalyzed by supported Au nanoparticles has stimulated numerous studies in this area during the past 20 years.[3] A number of factors such as the Au particle size, the support, and the preparation methods affect the performance of these catalysts. Among these factors, particle dimension appears to be a key, noting that the highest reactivity is exhibited by particles of certain sizes (typically 1−5 nm) while smaller and larger particles show much lower activity.[4,5] Supported Au films of two-layer thickness have also been found to be more reactive than thinner and thicker films.[6] The inertness of large Au particles is consistent with the fact that bulk gold (for instance single crystals) is completely inactive toward CO oxidation using CO + $O_2$ as reactants. However, Au single crystal surfaces predosed with atomic oxygen catalyze CO oxidation facilely even at liquid nitrogen temperature.[7,8] For a Langmuir−Hinshelwood-type reaction, coadsorption of both CO and active oxygen is essential for CO oxidation.[9] Large Au particles as well as bulk Au indeed adsorb CO under reaction conditions; however, large Au particles as well as bulk Au do not activate dioxygen since no oxidation is observed between molecular CO and molecular $O_2$ on these surfaces. In fact, no study has reported any significant $O_2$ activation or dissociation to form oxygen adatoms on any gold substrate, including stepped or polycrystalline surfaces between 200 and 500 K.[8] Previous studies have also shown that even for a Au layer electronically perturbed by a TiO substrate, there is no dissociation of $O_2$.[10] This suggests then that adding a second element, capable of dissociating $O_2$, to a bulk gold surface might facilitate the dissociation of $O_2$. The as-formed $O_{(ads)}$ might then "spill over" to gold sites where reaction could occur with CO. Here we employ a AuPd(100) single crystal to test this possibility. A AuPd alloy is a good choice since Pd is known to dissociate $O_2$ as low as ∼150 K[9] while pure Pd catalyzes CO oxidation at much higher temperatures (≥400 K) under steady-state conditions.[11,12] We employ polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) and reaction kinetics measurements, methods described in detail recently.[11,12]

Figure 1 presents typical temperature-dependent PM-IRAS spectra acquired at CO pressures of $1 \times 10^{-3}$ and 10 Torr on a AuPd(100) sample annealed at 800 K for 30 min prior to CO adsorption. This treatment leads to a surface with ∼10% Pd and ∼90% Au where the Pd atoms are completely isolated by Au.[13] CO vibrational features can be assigned accurately based on previous studies: $\nu_{CO}$ at >2100 cm$^{-1}$ corresponds to atop CO on Au sites; $\nu_{CO}$ at 2060−2085 cm$^{-1}$, to atop CO on isolated Pd sites; and $\nu_{CO}$ between 1900 and 2000 cm$^{-1}$, to bridging CO on contiguous Pd sites.[14−16] The key information addressed by Figure 1 is that gas-phase CO pressures higher than $1 \times 10^{-3}$ Torr are required to segregate a sufficient amount of Pd to the surface to form contiguous Pd sites. To be more precise, a CO pressure of ∼0.1 Torr is required for the formation of a significant population of contiguous Pd sites at the surface (supporting data 1).

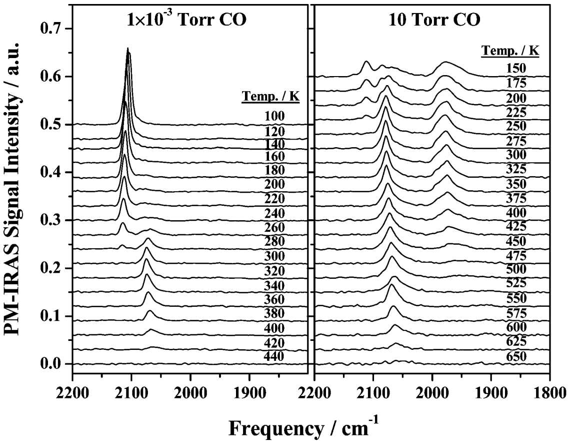

***Figure 1.*** (Left) Temperature-dependent PM-IRAS spectra of $1 \times 10^{-3}$ Torr of CO on a AuPd(100) surface well-annealed at 800 K for 30 min. (Right) Temperature-dependent PM-IRAS spectra of 10 Torr of CO.

The reactivity for CO oxidation at low pressures (≤$10^{-3}$ Torr) was probed using a stoichiometric CO + $O_2$ mixture in a steady-state flow mode.[11,12] The reactants were leaked into the chamber where the unreacted reactants and $CO_2$ product were monitored simultaneously with a quadrupole mass spectrometer (QMS). For a well-annealed AuPd(100) surface without contiguous Pd sites, the 44 amu ($CO_2$) QMS signal intensity never becomes higher than the background, i.e., no $CO_2$ formation is found for any reaction conditions. In contrast, for a freshly ion-sputtered surface (without annealing), $CO_2$ formation is detected as low as ∼160 K. The ion-sputtered sample indeed shows contiguous Pd sites determined with CO titration (supporting data 2). These experiments provide convincing evidence that neither Au nor isolated Pd sites are capable of dissociating $O_2$. Only when contiguous Pd sites are available can $O_2$ dissociation and CO oxidation occur. For pure Pd, steady-state $CO_2$ formation only becomes detectable above ∼400 K[12] suggesting that, on AuPd(100), $O_{(ads)}$ "spillover" to Au sites does indeed occur since $CO_2$ formation takes place at temperatures much lower than 400 K.

At CO pressures higher than ∼0.1 Torr, Pd segregates to the surface to form contiguous sites, suggesting that a well-annealed AuPd(100) sample exposed to high pressure reactants should facilely catalyze low-temperature CO oxidation. This reactivity was demonstrated in a batch mode, and the representative data are shown in Figure 2. Figure 2a shows a plot of the $CO_2$ formation rate (turnover frequency, $CO_2$ molecule per surface site per second) with a stoichiometric $CO/O_2$ (2/1) mixture at various pressures at a reaction temperature of 400 K. $CO_2$ formation was monitored with a quadrupole mass spectrometer. Figure 2b presents the corresponding CO PM-IRAS spectra acquired during reaction.

The results shown in Figure 2 reveal two key points. (1) Higher CO pressures enhance the segregation of Pd to the surface, as

10.1021/ja9008437 CCC: $40.75

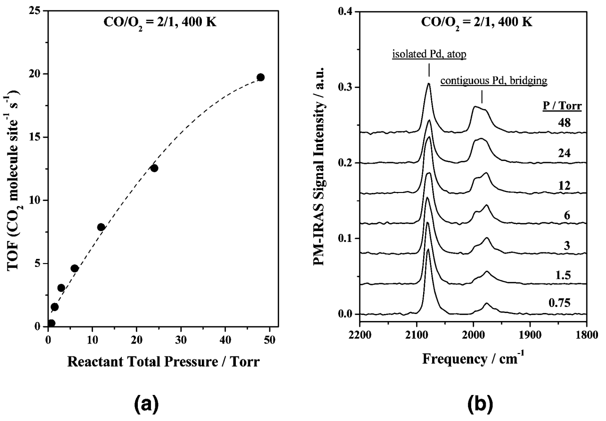

***Figure 2.*** (a) CO$_2$ formation rate (TOF) as a function of reaction temperature on an AuPd(100) surface annealed at 800 K for 30 min. Reactants are CO/O$_2$ (2/1) mixtures at various pressures. Reactions are carried out at 400 K in a batch mode using a high-pressure cell (~1.0 L) as the reactor. (b) The corresponding PM-IRAS spectra at various reactant pressures.

evidenced by stronger bridging CO IRAS signals (Figure 2b). The enhanced surface Pd, in turn, leads to a higher CO$_2$ formation rate (Figure 2a). It is emphasized that this reaction rate increase is caused by enhanced surface Pd, rather than an increase in reactant pressure. This follows since if the surface composition is fixed, i.e., the surface Pd/Au ratio does not vary with reactant pressure, the CO$_2$ formation rate is also expected to be largely independent of the reactant pressure at a particular temperature. This is the case because the reaction is +1 order in O$_2$ pressure and −1 order in CO pressure and, therefore, zero order in total pressure over a wide reaction conditions.[12,17,18] (2) The number of contiguous Pd sites, although not straightforward to quantify, is proportional to the bridging CO peak area (supporting data 3). This allows the CO$_2$ formation rate to be normalized by dividing each TOF by the corresponding bridging CO peak area. From the results (supporting data 4), we conclude that as the surface contiguous Pd site density approaches zero, the CO$_2$ formation rate approaches zero.

A more detailed understanding of the growth of contiguous Pd sites can be obtained by analysis of the PM-IRAS spectra shown in Figure 2b. CO adsorbed on Pd bridge sites gives rise to spectral features at ~1970 and ~1990 cm$^{-1}$. The 1970 cm$^{-1}$ band dominates at lower pressures, while, with increasing pressure, the peak at ~1990 cm$^{-1}$ grows more significantly. Tentatively, the 1970 cm$^{-1}$ band is assigned to bridging CO without neighboring bridging CO, while the 1990 cm$^{-1}$ band is assigned to bridging CO with other CO molecules in neighboring bridging sites. In this case, coupling of CO molecules in the latter case causes movement to a higher frequency. A general picture, therefore, is the formation of Pd pairs at lower CO pressures with larger contiguous Pd patches forming at higher pressures.

The high-pressure reaction data confirm the importance of contiguous Pd sites in dissociating O$_2$. It must be emphasized that, at temperatures below ~400 K, the CO oxidation rate is exceedingly low on Pd single crystal surfaces due to CO inhibition.[12] This implies that contiguous Pd sites on a AuPd alloy surface, which exhibit no CO inhibition, do not behave as bulk Pd. The detailed reaction mechanism on these limited assemblies of Pd is likely to be quite complex with contiguous Pd sites providing O$_{(ads)}$ and surface Au and Pd sites, both contiguous and isolated, providing chemisorbed CO for the reaction. The fact that this reaction occurs on the mixed-metal surface at temperatures as low as ~160 K strongly supports the argument that CO adsorbed on Au sites must be involved in the reaction, at least at temperatures below 400 K. The same conclusion can also be drawn from a more detailed analysis of the data shown in Figure 2. As shown in Figure 2b, from a reactant pressure of 0.75 to 48 Torr, the bridging CO peak area (contiguous Pd sites) increases ~3 times. However, the kinetic data displayed in Figure 2a reveal that the CO$_2$ formation rate increases ~100 times over this pressure range. This can only be rationalized by the fact that higher gas pressures facilitate CO population on Au sites (where the CO binding energy is the lowest) and that these CO molecules, in turn, participate in the overall chemistry. This work implies that low-temperature CO oxidation should occur facilely on supported Au−Pd alloy particles and that particle size and support effects should be much less critical compared with supported, Au-only catalysts.

**Acknowledgment.** We gratefully acknowledge the support for this work by the Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences (DE-FG02-95ER-14511), and the Robert A. Welch Foundation.

**Supporting Information Available:** (1) PM-IRAS spectra at CO pressure of 0.1 Torr; (2) PM-IRAS spectra of well-annealed and sputtered samples; (3) Representative *in situ* PM-IRAS spectra as a function of reaction temperature; (4) CO$_2$ formation rate normalized with bridging CO peak area. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA9008437