Summary Abstract: Oxidation of carbon monoxide over Ag (111) by preadsorbed active oxygen studied by XPS and UPS

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Recently, the oxidation of adsorbed carbon monoxide has attracted attention as a simple surface chemical reaction amenable to various surface-sensitive techniques. For example, CO oxidation over Ir(111),1-3 Ir(110),4 Pt,5,6 Rh,7,8 Ag(110),9 Pd,10-12 and Cu (110)13 have been studied, usually by mass spectrometry,2-11 but also by XPS,1,3 molecular beams,12 LEED,10 and work function and ellipsometry measurements.13 In the present work, the kinetics of CO oxidation over Ag(111) was studied by monitoring XPS intensities. The electronic structure is revealed by XPS and UPS and is presented elsewhere in a more comprehensive paper.14

The VG ESCA-3 hemispherical electron spectrometer, with UV and x-ray (1486.6) sources,1 calibration, sample preparation, in situ cleaning by Ar+ bombardment, annealing, and temperature control have all been described previously.15

Oxygen adsorbs on Ag(111) at 300 K provided a hot (1500 K) Pt filament is nearby. The filament was a 9 cm length of 0.5 mm diameter very high purity wire that was tightly coiled and placed “line of sight,” 3.5 cm from the front face of the Ag(111) sample. The adsorbed oxygen exhibits an asymmetrical 0 ls line at 528.5 eV with a full width at half maximum of approximately 1.6 eV and valence levels at 1.8 and approximately 5 eV, and is denoted active oxygen because it reacts readily with incident CO molecules. Probably the hot Pt excites, e.g. triplet → singlet rather than dissociates the oxygen. Apparently, the excited (unlike the ground state) molecule adsorbs with a high sticking coefficient, S, on Ag(111), where it dissociatively adsorbs. With the filament off, S ~ 0. On Ag(110), Wachs and Madix16 observed a similar, but much less dramatic effect due either to pronounced
crystallographic specificity, or inadvertent excitation by other hot filaments or the Vacon pump. All filaments were off and oil diffusion pumps were employed in the present work.

Transient kinetics measured in the spectrometer during exposure of Ag(111)/O to CO at an estimated $10^{-7}$ Torr (1.33 X 10^{-5} Pa) are shown in Fig. 1 for various substrate temperatures, $T$, between 180 and 400 K. The ordinate is the 0 1s intensity of active oxygen at 528.5 eV, scaled according to the absolute coverage determination of Zhdan et al. Evidently, [O], the active oxygen coverage is depleted by impinging CO, either by conversion to another adsorbed state with different O 1s binding energy, or by removal by chemical reaction. Supplemental XPS experiments rule out the former and we assume the removal product to be CO$_2$(g). The removal rate increases with decreasing $T$, but it is always at least three times smaller than the incident rate of CO impingement.

Since supplemental experiments also showed no significant carbon 1s intensity, clearly a second CO removal mechanism dominates over CO$_2$(g) production by at least a factor of two. The simplest is, of course, first order CO desorption. Thus, the mass balance equation (assuming $S = 1$ for CO) is

$$\frac{d[P_{CO}]}{dt} = \nu_{CO}[CO] \exp(-E_{CO}/kT). \quad (1)$$

For our coverage regime, the Langmuir–Hinshelwood mechanism is a reasonable starting point:

$$\frac{-d[O]}{dt} = \nu_{CO2}[CO][O] \exp(-E_{CO2}/kT) = \text{Rate of CO}_2 \text{formation} \quad \text{formation}, \quad (2)$$

where the prime indicates rate constants for the rate limiting reaction step—CO$_2$ desorption being undoubtedly instantaneous at these temperatures. Substituting Eq. (2) into Eq. (1) and rearranging, gives

$$\frac{-d[O]}{dt} = \frac{P_{CO}}{\sqrt{2\pi kT M}} \nu[O] \exp(-E/kT) + 1, \quad (3)$$

where $\nu = \nu_{CO2}/\nu_{CO}$ and $E = E_{CO2} - E_{CO}$.

Since the incident rate of CO impingement is at least three times smaller than the rate of CO$_2$ formation, the latter is less than half the rate of CO desorption. Therefore, their ratio (the first term in the denominator) is small compared to unity and Eq. (3) then becomes

$$T = -\ln \left( \frac{\sqrt{2\pi kT M}}{P_{CO}} \cdot \frac{d[O]}{dt} \right) = \frac{E}{kT} - \ln[O]\nu, \quad (4)$$

which is plotted in Fig. 2 for $t = 0$, along with a straight line least squares fit wherein $E = -1.4$ kcal/mole and $\nu = 10^{-17}$ cm$^2$. The linearity of Fig. 2 further corroborates that Eq. (4) is a suitable approximation to Eq. (3). A recent study by Bowker et al. for CO oxidation over Ag(111) gives these values to be $-1.1$ kcal/mole and $1.5 \times 10^{-17}$ cm$^2$. Note that $E$ is known to a greater accuracy ($\sim 0.1$ kcal/mole) than is possible for either of the difference terms defining it. The negative sign for $E$ indicates CO$_2$ formation is energetically favored over CO desorption. Nevertheless, CO desorption is kinetically favored, i.e. more frequent because CO$_2$(g) production depends on $[CO]$ which is small since 180 K exceeds the CO desorption temperature, $T_d$. In other words, since the CO is weakly chemisorbed, the residence time at the relatively warm temperatures employed here ($\geq 180$ K) is too small to allow for significant reaction with adsorbed oxygen.

For a sufficiently low temperature, however, the first term in the denominator of Eq. (3) dominates so that the rate of CO incidence flux is equal to that of CO$_2$(g) production. In this regime $T = 0$, a horizontal line through the origin in Fig. 2. The intersection with Eq. (4), at 137 K, is a crude measure of $T_d$ and agrees with values obtained by TDMS for similar systems. In particular, for W(100)/Xe, $T_d = 145$ K, and $E_{Xe} = 3 \times 10^{14}$ s$^{-1}$ and $E_{Xe} = 9.3$ kcal/mole. If these values are appropriate to CO/Ag(111), we estimate $\nu_{CO2} = 3 \times 10^{-3}$ cm$^2$/s (typical for second order) and $E_{CO2} = 7.9$ kcal/mole. Alternatively, by employing isosteric measurements of the adsorption of CO on Ag(111) which do not yield the pre-exponential a$^2$ where the heat of adsorption was found
to be 6.5 kcal/mole, we estimate $E_{\text{CO}_2} = 5.1$ kcal/mole, in agreement with Bowker's study 5.2 kcal/mole$^9$ employing the same $E_{\text{CO}}$. Since the rate parameters $v$ and $E$ for CO oxidation over the Ag(111) surface (present study) are very similar indeed to those over Ag(110)$^9$ we conclude that similar reaction mechanisms are involved.

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18The frequency factor ratio is obtained from their intercept of 0.002 seconds$^{-1}$ upon division by $F = 3 \times 10^{14}$ molecules/cm$^2$s, (their calibration for the gas flux from their doser) and multiplication by ln 10.

