1. Experiments

The experiments were carried out in a combined elevated-pressure reactor-ultrahigh vacuum (UHV) system with a base pressure of $2 \times 10^{10}$ Torr equipped with a single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), a low-energy electron diffraction (LEED), a quadrupole mass analyzer, and a high-resolution electron energy loss spectroscopy (HREELS). After preparation and characterization in the UHV chamber, the gold film sample was transferred \textit{in-situ} into the reaction chamber through a double-stage, differentially pumped Teflon sliding seal. The Mo(112) sample was cleaned by repeated cycles of oxidation at 1200 K followed by a flash to 2100 ~ 2200 K, and characterized using AES and LEED. The substrate temperature was measured via a (W/5 wt%Re)/(W/26 wt%Re) thermocouple spot-welded to the back sample surface. A liquid-nitrogen cryostat and an electron beam heater allowed control of the sample temperature between 90 and 2300 K. The silica films were prepared by evaporating Si onto the Mo(112) surface from a tantalum filament in UHV at room temperature (1). Titanium and gold were evaporated from a Ti wire and a gold wire wrapped around a Ta filament that was heated resistively. Ti amount was estimated from AES ratio, where an AES breakpoint corresponding to a monolayer was observed in the plot of Ti/Mo ratio versus deposition time by depositing Ti onto the Mo(112) surface following a subsequent oxidation at 600K. The Au flux was calibrated from the well-order film and AES break points in the present study. The Au coverage is reported in monolayers (ML) with respect to the top layer Mo atom density in Mo(112). Research-grade CO was further purified by cooling to liquid N$_2$ temperature, then transferred to a glass bulb; O$_2$ was use as received. A CO:O$_2$ (2:1) mixture was used for the kinetic studies. The CO$_2$ product was analyzed by mass spectrometry and cross-checked by trapping and measuring the product partial pressure; both methods yielded identical results. The energy resolution of the HREELS measurements was between 8 ~ 12 meV (64 and 96 cm$^{-1}$) as determined by the full width at half-maximum (FWHM) of the elastic peak; a primary energy ($E_p$) of $\sim$5 eV was used.

2. Supporting figures (Figs. S2-S7)

Fig. S1. M.-S. Chen, D. W. Goodman, unpublished data.

Left panel: HREEL spectra of a well-ordered Mo(112)-c(2x2)-[SiO₄] surface subsequent to deposition of 1.5 ML Ti followed by oxidization at 600 K and an anneal at 1150 and 1400 K, respectively, to form a (8x2)-TiOₓ film.

Right panel: HREEL spectra subsequent to deposition of Au on a Mo(112)-(8x2)-TiOₓ surface at room temperature; note the blue-shift of the Ti-O phonon feature.
Fig. S2. C.-W. Yi, K. Luo, D. W. Goodman, unpublished data.


Right panel: Temperature-programmed desorption (TPD) spectra for Au on the Mo(112)-(8x2)-TiO$_x$ surface. Before each TPD, the sample was annealed at 900 K in 5x10$^{-9}$ Torr O$_2$ for 10 min.
Fig. S3. W. T. Wallace, K. K. Gath, D. W. Goodman, unpublished data.

Left panel: STM image (25 nm x 25 nm) of Mo(112)-(8x2)-TiO$_x$

Right panel: STM image (25 nm x 25 nm) of 0.4 ML Au/ Mo(112)-(8x2)-TiO$_x$
Fig. S4.  Z. Yan, M.-S. Chen, D. W. Goodman, unpublished data.

Left panel: a) AES spectrum of 1 ML Au deposited on a clean Mo(112) surface at room temperature that exhibits a (1x1) low-energy electron diffraction (LEED) pattern; b) After annealing a) at 900 K in 5 x 10⁻⁹ Torr O₂ for 10 min to form a poorly ordered (1x3) LEED pattern. Note that an anneal of Au/Mo(112) in oxygen induces a marked decrease of the Au/Mo AES ratio due to oxidation of the Mo(112) substrate which Au does not wet.

Right panel: Au/Mo AES ratio as a function of Au deposition time on the Mo(112) surface at room temperature. A break point is apparent at 0.7, the ratio corresponding to one monolayer Au on Mo(112).
Fig. S5. M.-S. Chen, D. W. Goodman, unpublished data.

HREEL spectra of various amounts of CO (saturated at 0.4 L) adsorbed on a well-ordered Mo(112)-(1x1)-(Au,TiO\textsubscript{x}) surface at 90 K, then warmed to 150 and 160 K.
Fig. S6. M.-S. Chen, D. W. Goodman, unpublished data.

HREEL spectra of a (8x2)-TiO_x surface subsequent to the deposition of 1ML Au followed by an anneal to the indicated temperatures.
Fig. S7. M.-S. Chen, D. W. Goodman, unpublished data.

Left panel: HREEL spectra subsequent to the deposition of Pd onto a Mo(112)-(8x2)-TiO$_x$ surface and an anneal to 900 K; a single phonon peak at 70 meV, assigned to Ti$^{2+}$-O-Pd$^{5+}$, appears concurrently with the appearance of a (5x2) LEED pattern.

Right panel: HREEL spectra subsequent to the deposition of 1 ML Au onto a well-ordered Mo(112)-(5x2)-(Pd,TiO$_x$) surface at room temperature followed by an anneal to 900 K that shows the Ti-O phonon shift induced by Au.