Supplementary Information

The dynamic behavior of dilute metallic alloy Pd$_x$Au$_{1-x}$/SiO$_2$ raspberry colloid templated catalysts under CO oxidation

Authors: Amanda Filie,[a] Tanya Shirman,[a] Michael Aizenberg,[a] Joanna Aizenberg,[a,b] Cynthia M. Friend,[a,b] and Robert J. Madix[a]*

[a] John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138, USA.
[b] Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138, USA.
*corresponding author: rmadix@seas.harvard.edu

S.1 Quantification of CO$_2$ Production Using a GC-TCD

The calibration curve for quantifying the production of CO$_2$ was generated using a gas tank containing CO$_2$ diluted in He with a known analytic precision (Airgas, 5% ± 0.05% CO$_2$, balance He; referred to hereafter as the CO$_2$/He mixture). The CO$_2$/He mixture was sent directly to the combined gas chromatograph-thermal conductivity detector (GC-TCD) via a mass flow controller at a total flow rate of 25.0 sccm. The response factor (m, Eq. 1) was determined by dividing the known concentration of CO$_2$ in the calibration mixture ($x_{CO_2,cal}$) by the average area under the response curve of the TCD corresponding to the elution of CO$_2$ from the GC column ($A_{TCD,cal}$). The uncertainty of the response factor ($U(m)$, Eq. 2) was calculated by error propagation; the error of the response factor was found to be two orders of magnitude lower than the factor itself.

$$m = \frac{x_{CO_2,cal}}{A_{TCD,cal}} \qquad \text{Eq. 1}$$

$$U(m) = m \cdot \sqrt{\left(\frac{U(x_{CO_2,\,cal})}{x_{CO_2,\,cal}}\right)^2 + \left(\frac{U(A_{TCD,\,cal})}{A_{TCD,cal}}\right)^2} \qquad \text{Eq. 2}$$

The rate of CO$_2$ formation ($\dot{r}_{CO_2,volumetric}$, Eq. 3) was calculated by multiplying the total volumetric flow rate of the reactor feed ($\dot{Q}_{tot,in}$) and the concentration of CO$_2$ in the reactor effluent ($x_{CO_2,\,out}$). The latter quantity was the product of the average area of the CO$_2$ elution peak of several chromatograms under steady state activity, and the response factor, essentially a re-arrangement of Eq. 1.

$$\dot{r}_{CO_2,volumetric} = \dot{Q}_{tot,in} \cdot x_{CO_2,\,out} = \dot{Q}_{tot,in} \cdot A_{TCD} \cdot m \qquad \text{Eq. 3}$$

The rate of CO_2 produced normalized by the total mass of metal ($\dot{r}_{CO_2,mass\ normalized}$, Eq. 4), was calculated using the ideal gas law to convert standard cubic centimeters per minute to micromoles of CO_2 produced per second normalized by the mass of precious metal in the catalyst.

$$\dot{r}_{CO_2,mass\ normalized} = \dot{r}_{CO_2,volumetric} \times \frac{P}{R \cdot T} \times \frac{1}{w_{met} \cdot w_{Pd}}$$

Eq. 4

where P is atmospheric pressure (101325 Pa),

R is the ideal gas constant (8.314 J/(mol $\cdot$ K)),

T is the standard temperature (298 K),

w_{met} is the total loading of precious metal on the silica support (weight %), and

w_{Pd} is the average Pd composition of the bimetallic nanoparticles (weight %).

S.2 Conditioning of $Pd_{0.02}Au_{0.98}$ RCT-SiO$_2$

The observed activation energy, when increasing from 523 K to 563 K in the initial temperature ramp, agrees with the previous light-off study (Fig. S1). The activation energy of sequential thermal treatments approaches ~ 80 kJ per mole (Table S1) indicating the catalyst reached a conditioned state.
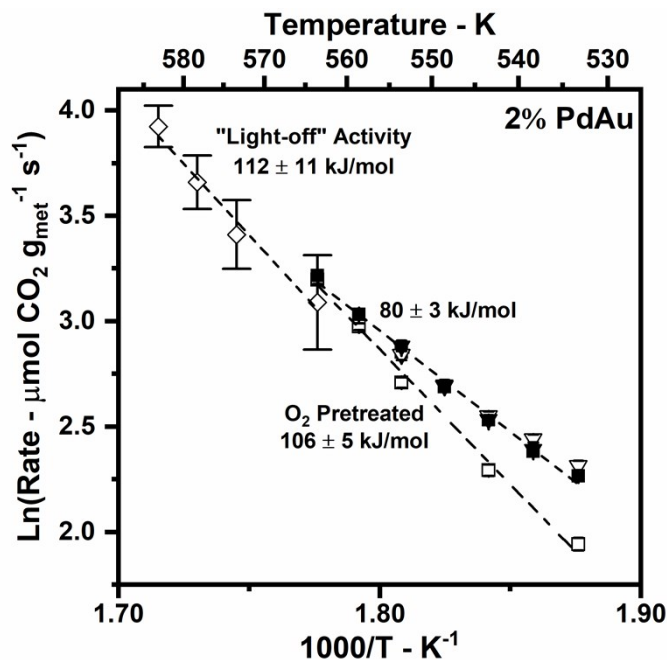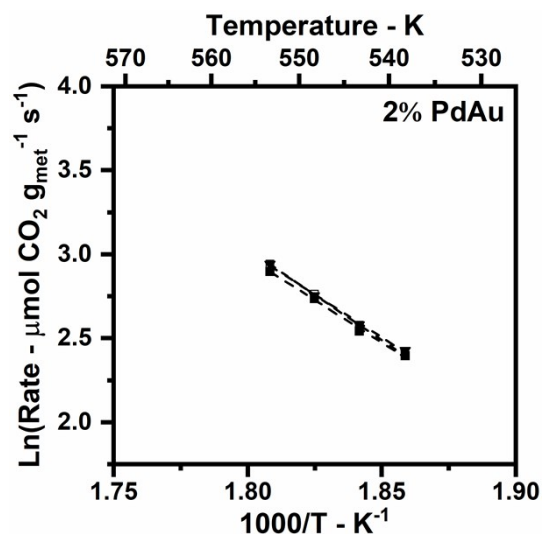

Figure S1. Sequential temperature ramps between 538 K and 553 K revealed the initial activity of the O$_2$-pretreated 2% PdAu catalyst agreed with the observed "light-off" activity and ultimately converged to a "conditioned state" where the activity at each temperature is reproduced. The previously reported "light-off" activity (112 ± 11 kJ mol^{-1}) of the "as-prepared" 2% PdAu catalyst (◇) was similar to the initial apparent activation energy (106 ± 6 kJ mol^{-1}) of the O$_2$-pretreated 2% PdAu catalyst (□). Retracing the temperature downwards (■) showed activity was enhanced, resulting in a significantly lower activation energy (80 ± 3 kJ mol^{-1}). Repeating this thermal treatment (increasing and decreasing temperature, ▽ and ▼, respectively) showed this activity was reproducible and resulted in an activation energy of 81 ± 4 kJ per mole. Data for the "as-prepared catalyst" taken from reference 1. Reaction conditions: 523 K ≤ temperature ≤ 563 K; 5% CO, 10% O$_2$, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalysts: m_{cat}"Light-off" Activity = 40.0 mg, m_{cat} O$_2$ Pretreated = 36.0 mg of $Pd_{0.02}Au_{0.98}$ RCT-SiO$_2$, metal loading = 11.6 wt%.

Table S1. The activation energy over sequential temperature ramps over the O_2-pretreated 2% PdAu for the oxidation of CO, corresponding to the Arrhenius plot in Fig. S1. Reaction conditions: 523 K ≤ temperature ≤ 563 K; 5% CO, 10% O_2, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalyst: m_{cat} O_2 Pretreated = 36.0 mg of $Pd_{0.02}Au_{0.98}$ RCT-SiO_2, metal loading = 11.6 wt%.

Temperature Ramp	Activation Energy (kJ mol^{-1})
Increasing	106 ± 5
Decreasing	80 ± 3
Increasing	63 ± 3
Decreasing	81 ± 4

The activation energies for sequential thermal treatments of the O_2-pretreated 2% PdAu catalyst stabilized under reaction conditions at 553 K (Fig. S2) approaches an activation energy of ~85 kJ per mole (Table S2).

Figure S2. Sequential temperature ramps of the O_2-pretreated 2% PdAu stabilized at 553 K under reaction conditions for ~ 3 h revealed the catalyst reached a "conditioned state," where the activity at each temperature was reproduced regardless of direction of temperature change. The activation energy measured when the reaction temperature was decreased from 553 K to 538 K after stabilizing the catalyst (▪) was found to be 83 ± 3 kJ per mole. Retracing the temperatures upward (▪) and then downward (▪) resulted in the same activity within error suggesting the catalyst reached a "conditioned" state. Reaction conditions: 538 K ≤ temperature ≤ 553 K; 5% CO, 10% O_2, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalyst: m_{cat} = 36.0 mg of $Pd_{0.02}Au_{0.98}$ RCT-SiO_2, metal loading = 11.6 wt%.

Table S2. The activation energy over sequential temperature ramps over the O_2-pretreated 2% PdAu stabilized at 553 K under reaction conditions, corresponding to the Arrhenius plot in Fig. S2. Reaction conditions: 538 K ≤ temperature ≤ 553 K; 5% CO, 10% O_2, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalyst: m_{cat} = 36.0 mg of $Pd_{0.02}Au_{0.98}$ RCT-SiO_2, metal loading = 11.6 wt%.

Temperature Ramp	Activation Energy (kJ mol^{-1})
Decreasing	83 ± 3
Increasing	90 ± 1
Decreasing	85 ± 4

S.3 Conditioning of Au RCT-SiO$_2$ Compared to Pd$_{0.02}$Au$_{0.98}$ RCT-SiO$_2$

The steady state activity of the Au RCT-SiO$_2$ catalyst at 553 K after the thermal treatment (Fig. S3) was lower than that of the Pd$_{0.02}$Au$_{0.98}$ RCT-SiO$_2$ (Fig. S2). Furthermore, the activation
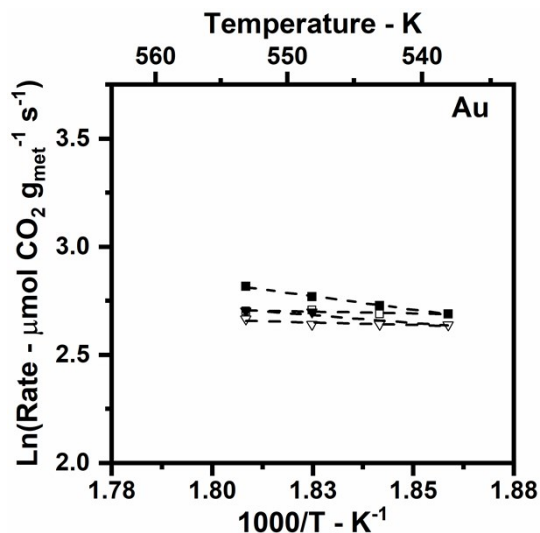
Figure S3. The activity of the O$_2$-pretreated Au catalyst exposed to reaction conditions at 553 K for ~ 3 h declined gradually with thermal treatment. The activation energy measured when the reaction temperature was decreased from 553 K to 538 K after attempting to stabilize the catalyst (■) was found to be 21 ± 2 kJ per mole. Retracing the temperatures upward (■), then downward (■), and finally upward (■) showed a decrease in catalyst activity, approaching a conditioned state insensitive to changes in temperatures. Reaction conditions: 538 K ≤ temperature ≤ 553 K; 5% CO, 10% O$_2$, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalyst: m$_{cat}$ = 40.8 mg of Au RCT-SiO$_2$, metal loading = 9.2 wt%.

Table S3. The activation energy over sequential temperature ramps over the O$_2$ pretreated Au RCT-SiO$_2$ stabilized at 553 K under reaction conditions, corresponding to the Arrhenius plot in Fig. S3. Reaction conditions: 538 K ≤ temperature ≤ 553 K; 5% CO, 10% O$_2$, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalyst: m$_{cat}$ = 40.8 mg of Au RCT-SiO$_2$, metal loading = 9.2 wt%.

Temperature Ramp	Activation Energy (kJ mol^{-1})
Increasing	21 ± 2
Decreasing	3 ± 2
Increasing	12 ± 3
Decreasing	4 ± 2

energy for CO oxidation over the Au RCT-SiO$_2$ approached zero (Table S3), which is different from the case of Pd$_{0.02}$Au$_{0.98}$ RCT-SiO$_2$ that approached 85 kJ per mole (Table S2).

S.4 Au RCT-SiO$_2$ Insensitivity to Temperature: Steady State Activity at 553 K

The conditioned state of the monometallic Au catalyst was reached by initiating reaction conditions at 553 K and cycling the reaction temperature. Although the monometallic Au seemed to approach a steady state activity after 3 h at 553 K (Fig. S4A), catalyst activity gradually declined over time, during which 3 consecutive temperature ramps were conducted. The conditioned state of the Au catalyst exhibited a residual activity that was independent of reaction
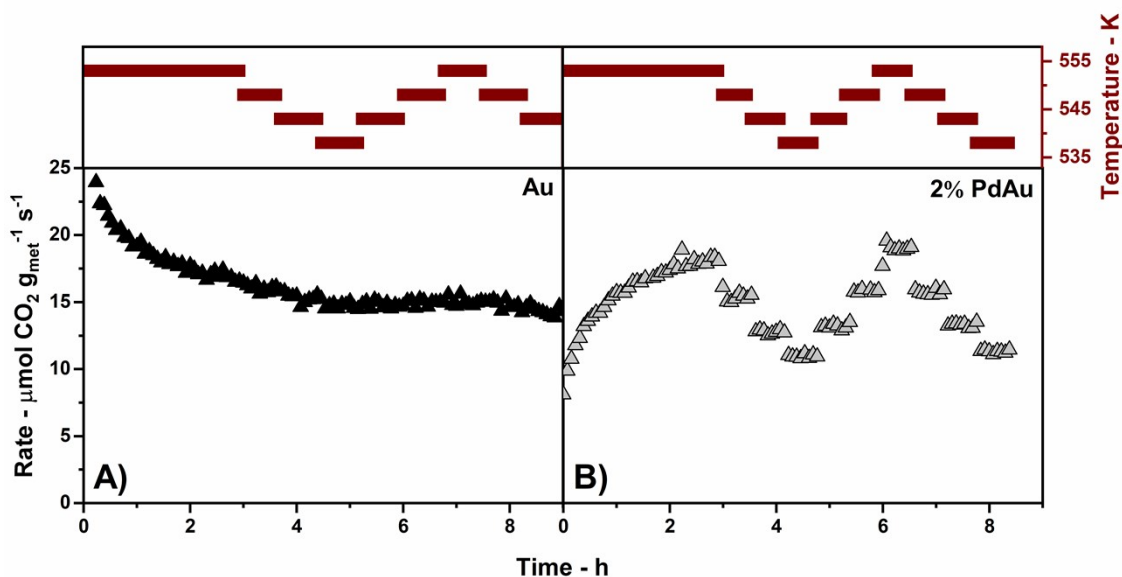
Figure S4. The activity of the Au catalyst showed a gradual decline over reaction conditions while that of the 2% PdAu catalyst dependended significantly on temperature. (A) The rate of CO$_2$ formation over the O$_2$-pretreated Au catalyst declined steadily at 553 K over 3 h, and further declined over time despites changes in temperature. (B) The rate of CO$_2$ formation over the O$_2$-pretreated 2% PdAu catalyst steadily increased at 553 K over 3 h at 553 K and its activity responded to temperature ramps. Reaction conditions: 538 K $\leq$ temperature $\leq$ 563 K; 5% CO, 10% O$_2$, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalysts: m$_{cat}$ = 40.8 mg of Au RCT-SiO$_2$, metal loading = 9.2 wt%; m$_{cat}$ = 36.0 mg Pd$_{0.02}$Au$_{0.98}$ RCT-SiO$_2$, metal loading = 11.6 wt%.
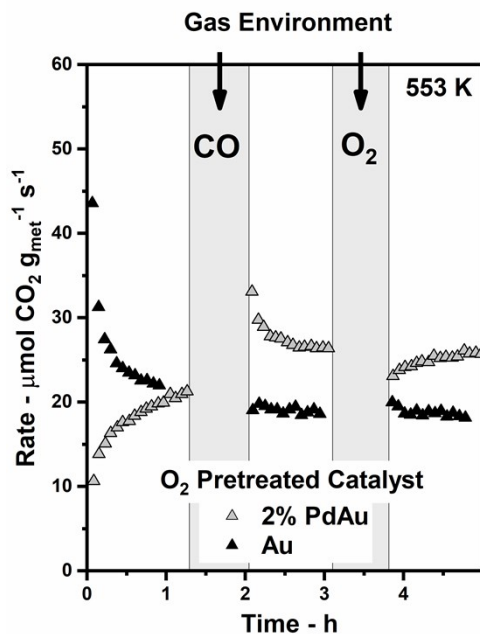
temperature, unlike the activity of the 2% PdAu that depended on temperature (Fig. S4B).

7

## S.5 Au RCT-SiO$_2$ Insensitivity to Effects of Reaction Conditions at 553 K

The activity of the monometallic Au catalyst showed no sensitivity to temporary exposures to a CO/He or O$_2$/He environment, unlike the 2% PdAu catalyst (Fig. S5).

Figure S5. The O$_2$-pretreated Au and 2% PdAu catalysts showed very different behavior when subjected to a CO environment. The CO/He environment had no effect on the activity of the Au, whereas a transient enhancing effect was observed for the 2% PdAu catalyst. Reaction conditions: temperature = 553 K; 5% CO, 10% O$_2$, balanced with He; total flow rate = 25.0 sccm; gas hourly space velocity = 2000 hr^{-1}. Catalysts: m$_{cat}$ = 40.8 mg of Au RCT-SiO$_2$, metal loading 9.2 wt%; m$_{cat}$ = 40 mg of Pd$_{0.02}$Au$_{0.98}$ RCT-SiO$_2$, metal loading = 11.6 wt%.

S.6 Au RCT-SiO$_2$ Kinetic Orders on CO and O$_2$

The reaction orders over the monometallic Au catalyst showed a positive fractional order dependence on both CO (Fig. S6A) and O$_2$ (Fig. S6B).
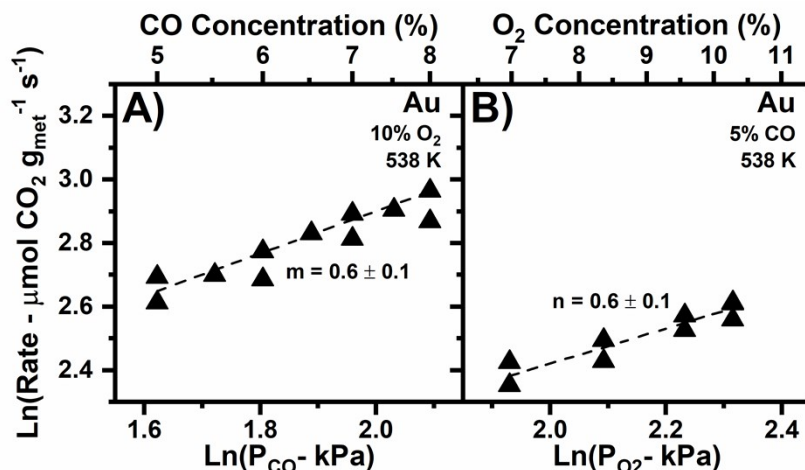
Figure S6. The reaction order dependence of Au on CO and O$_2$ were both positive, fractional orders. (A) The reaction order of CO and (B) O$_2$ were determined by changes in the rate of CO$_2$ production per mass of metal in Au as the inlet partial pressure of carbon monoxide and oxygen were varied, respectively, at 538 K. Reaction conditions: kinetic studies on CO, 5 - 8% CO, 10% O$_2$, balanced with He; kinetic studies on O$_2$, 5% CO, 7 - 10% O$_2$, balanced with He. Total flow rate of 25.0 sccm; m_{cat} = 40.8 mg of Au RCT-SiO$_2$, metal loading 9.2 wt%.

References

1   M. Luneau, T. Shirman, A. Filie, J. Timoshenko, W. Chen, A. Trimpalis, M. Flytzani-Stephanopoulos, E. Kaxiras, A. I. Frenkel, J. Aizenberg, C. M. Friend and R. J. Madix, *Chem. Mater.*, 2019, **31**, 5759–5768.