Carbon Monoxide Oxidation on Single-Crystal Platinum:
Oscillatory Kinetics from Adsorbate-Induced Surface Structural Transformation

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A. Background

Understanding the mechanisms of chemical reactions is crucial in improving industrial productivity as well as enriching the fundamental scientific knowledge in chemistry. Catalysts, such as platinum and palladium, can speed up chemical reactions. Reactions that make use of catalysts often take place far from thermodynamic equilibrium and display nonlinear behavior. Under certain conditions, many reactions have been found to proceed in oscillatory manners, as listed in Table 1.

reaction	catalyst	catalyst type	orientation	p-range [mbar]
		CO Oxidation		
$CO + O_2$	Ir,[24] Pd[24–26]	poly		mbar to atm[a]
	Pt,[30–43] Rh[44,45]	poly		mbar to atm
	CuO[46]	poly		mbar to atm
	Pd	SC[b]	(110),[47–54] (111)[55]	10^{-3}–1
	Pt	SC	(100),[56–72] (110)[13,73–93]	10^{-6}–10^{-3}
	Pt	SC	(210)[94,95]	10^{-4}–10^{-1}
	Pt	SC[c]	[001] zone[96,97]	10^{-6}–10^{-4}
	Pt	SC	(111), (1311)[98]	atm
	Pt	SC	FET[42,99,100]	10^{-6}–10^{-4}
		Other Oxidation Reactions with O_2		
$H_2 + O_2$	Ni,[101–104] Pd[105]	poly		atm
	Pt,[106–108] Rh[109]	poly		atm
	Pt	SC	FET[110,111]	10^{-4}
$NH_3 + O_2$	Pt[112–114]	poly		mbar to atm
$C_nH_m + O_2$	Ag,[115,116] Pd,[117] Pt[118–120]	poly		atm
	Rh,[44] CuO,[121]	poly		atm
	zeolites[122]	poly		atm
oxidative CH_4 coupling	La_2O_3–BaO–MgO[123]	poly		atm
$C_nH_mOH + O_2$	Pd,[124–126] Pt[127]	poly		atm
	V_2O_5,[128] zeolites[129]	poly		atm
		NO Reduction		
$NO + CO$	Pd,[62] Pt[42,130]	poly		10^{-4} to atm
	Pt	SC	(100),[131–143] [001] zone[136,144]	10^{-9}–10^{-5}
	Rh	SC	(110)[145]	10^{-6}
$NO + H_2$	Pt	SC	(100),[146–151] FET[152]	10^{-7}–10^{-5}
	Rh	SC	(110),[153,154] FET[11,155]	10^{-7}–10^{-5}
$NO + NH_3$	Pt[156,157]	poly		1 to atm
	Pt	SC	(100)[151,158–160]	10^{-6}
	Rh	SC	FET[11,155,161]	10^{-6}
NO + propene	Pt[162]	poly		atm
		Hydrogenation		
$CO + H_2$	Fe,[163,164] Pd[165]	poly		atm
$C_2H_4 + H_2$	Ni,[166] Pd,[167] Pt[168]	poly		atm
$PhNO_2 + H_2$	Cu,[169] Ni[169]	poly		atm
methanol to gasoline conversion	zeolite[170]	poly		atm
		Decomposition Reactions		
CH_3NH_2	Ir,[171] Pt,[171,172] Rh[171]	poly		1 to atm
		Field-Induced Reactions		
$H_2 + H_2O$	Pt	SC	FET[173]	10^{-6}

[a] Atmospheric pressure. [b] Single crystal. [c] Cylindrical Pt single crystal with axis parallel to [001]. [d] Field emitter tip.

Table 1. List of oscillatory catalytic reactions [1]

One of the most studied oscillatory catalytic reactions is the oxidation of carbon monoxide (CO) on single-crystal (SC) platinum. In this reaction, CO combines with oxygen (O_2) to form carbon dioxide (CO_2) in the steps shown in Figure A1. Essentially, CO and O_2 adsorb ("stick") to the

platinum surface, and they then combine and desorb ("fly way") from the catalyst surface as CO_2. gas. These steps are collective called the Langmuir-Hinshelwood mechanism. The chemical species and mechanism are rather simple, and thus the modeling of this reaction is quite accessible. Moreover, this oxidation reaction of CO has some practical uses because CO is poisonous; catalytic converters in automobiles actually utilize platinum catalysts to convert harmful CO emission to nontoxic CO_2.

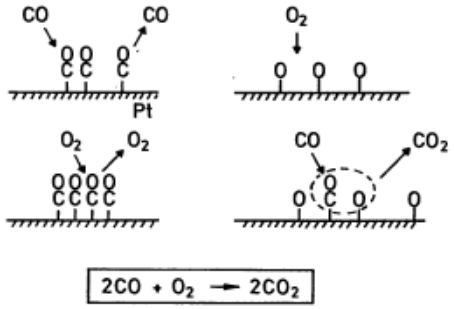

Figure A1. Graphical representation of CO oxidation on platinum. [2]

The reaction steps are shown below. The symbol [*] denotes an empty site on the platinum catalyst, and [CO-*] and [O-*] denote adsorbed CO and oxygen, respectively.

Adsorption of CO (forward rate = k_1, reverse rate = k_{-1})

$CO + [*] \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [CO\text{-}*]$

Adsorption of O_2 (forward rate = k_2)

$O_2 + [*] \xrightarrow{k_2} 2[O\text{-}*]$

Combination of adsorbed CO and O & production of CO_2 (forward rate = k_3)

$[CO\text{-}*] + [O\text{-}*] \xrightarrow{k_3} CO_2 + 2[*]$

Overall reaction

$CO + O_2 \rightarrow CO$

B. Simple Kinetic Modeling and Bistability

Given the above reaction mechanism, two governing differential equations with two variables – degrees of coverage of CO and oxygen on the catalyst surface (θ_{CO} and θ_O, respectively) – can be established [1]*. The variables θ_{CO} and θ_O theoretically range from 0 (clean catalytic surface) to 1 (fully covered catalytic surface).

Equation 1. $$\frac{d\theta_{CO}}{dt} = k_1 p_{CO}\left[1-\left(\frac{\theta_{CO}}{\theta_{CO,Sat}}\right)^3\right] - k_{-1}\theta_{CO} - k_3\theta_{CO}\theta_O$$

Equation 2. $$\frac{d\theta_O}{dt} = s_{O_2} k_2 p_{O_2}\left[1-\frac{\theta_{CO}}{\theta_{CO,Sat}}-\frac{\theta_O}{\theta_{O,Sat}}\right]^2 - k_3\theta_{CO}\theta_O$$

**In this paper, only one specific type of single-crystal platinum surface, Pt(110), is investigated as the catalyst. The label (110) refers to a certain crystographic orientation of bulk platinum with a regular lattice structure. Detailed information can be found in any introductory materials science or solid state physics books.*

Equation 1 shows the rate of change in CO coverage (θ_{CO}) on the platinum surface. The first term contributes to an increase in θ_{CO}; that is, it represents the adsorption of CO. The first two factors are quite straight-forward: The forward rate of CO adsorption (k_1) and the partial pressure of CO (p_{CO}) – which is equivalent to the amount of CO gas input – are positively related to CO coverage. The third factor ($1- [\theta_{CO}/\theta_{CO,Sat}]^r$) indicates how much space for CO adsorption is remaining on the catalyst. In other words, if the level of CO coverage is saturated ($\theta_{CO} = \theta_{CO,Sat}$), then the third term goes to zero and no more increase in θ_{CO} takes place. The *r*-th power on the ratio $\theta_{CO}/\theta_{CO,Sat}$ shows the effect of the "precursor" adsorption of CO in decreasing the adsorption rate of CO, as pre-existing CO molecules on the platinum surface block reaction sites. In most papers, *r* is set to 3. The second and third terms ($k_{-1}\theta_{CO}$ and $k_3\theta_{CO}\theta_O$) both contribute to a decrease in θ_{CO}, as $k_{-1}\theta_{CO}$ represents the reverse process of CO adsorption and $k_3\theta_{CO}\theta_O$ represents CO_2 desorption (product formation).

Similarly, Equation 2 describes the rate of change in oxygen coverage (θ_O). The first term represents oxygen adsorption and therefore contributes to an increase in θ_O. Again, the forward rate of adsorption (k_2) and partial pressure of oxygen (p_{O2}) are positively related to oxygen adsorption. The factor s_{O2} is the "sticking coefficient" of oxygen on the platinum surface, where the greater the sticking coefficient, the greater the likelihood of an oxygen molecule adsorbing. The remaining factor ($[1- \theta_{CO}/\theta_{CO,Sat} - \theta_O/\theta_{O,Sat}]^2$) again shows the availability of oxygen adsorption sites on the catalyst. Here, both the degree saturation of CO coverage and oxygen coverage affect the adsorption site availability for oxygen, since CO can block oxygen attempting to adsorb (see Figure 1). The last term ($k_3\theta_{CO}\theta_O$) again contributes to a decrease in θ_O as CO_2 is produced from adsorbed oxygen.

The desorption rate constants k_{-1} and k_3 are dependent on temperature [3]. They can be represented in the form of the Arrhenius equation:

$$k_i = k_i^O \exp(-E_i / RT)$$

where k_i^O is a constant unique to the reaction, E_i is the activation energy of the reaction, R is the universal gas constant, and T is the temperature. The reaction rate is therefore very sensitive to any change in the temperature, which affects the rate constant in an exponential manner. On the other hand, the adsorption rate constants k_1 and k_2 are dependent on the partial pressures of CO and O_2. In Equations 1 and 2, the temperature T, CO partial pressure p_{CO}, and oxygen partial pressure p_{O2} are parameters.

C. Oscillatory Kinetics

Equations 1 and 2 by themselves do not predict oscillatory behavior. Yet, for the oxidation of CO on the Pt(110) catalyst, oscillatory reaction rates have been observed for a certain range of parameters (see Table 2). There must be an additional mechanism at work to trigger such oscillatory behavior in this simple reaction.

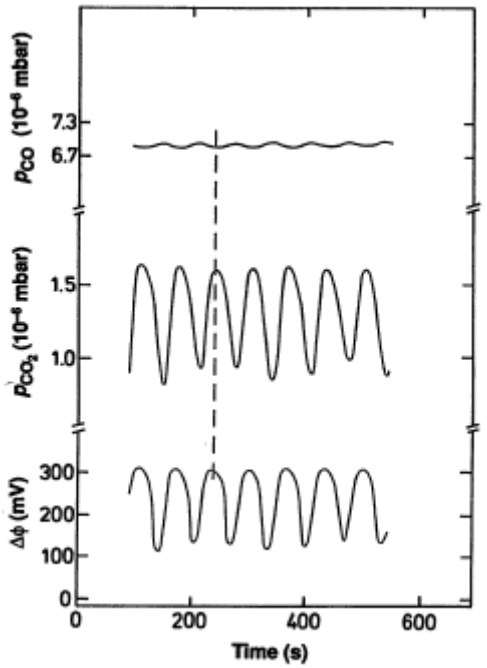

Figure C1. Oscillating reaction rate of the oxidation of CO on Pt(110). The partial pressure of CO_2 pCO2 is proportional to the reaction rate. The quantity $\Delta\Phi$ (work function) is proportional to the oxygen coverage (θ_O), which is also proportional to the reaction rate. [2]

The answer lies in the change in the structure of the platinum surface. A clean Pt(110) surface has a "reconstructed" 1x2 surface to minimize the free energy. In other words, the 1x2 phase is thermodynamically more stable than the 1x1 phase*. However, when CO is adsorbed, the platinum surface tends to have the 1x1 phase because this configuration is more thermodynamically favorable when CO is adsorbed. Furthermore, the sticking coefficient of oxygen is greater for platinum in the 1x1 phase.

*The 1x1 phase is the configuration that platinum atoms take in the bulk (non-surface) state.

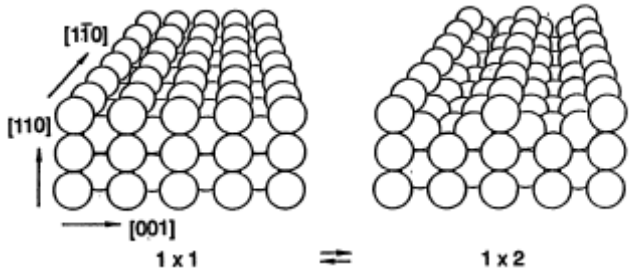

Figure C2. Oscillation of the configuration of the Pt(110) surface. [2]

Oscillatory reaction rates emerge as follows:

(1) A mostly clean catalyst surface ($\theta_{CO} < 0.2$) has the 1x2 reconstructed surface configuration. At this stage, the reaction is slow because not much CO and O_2 are bound to the catalyst.

(2) As more CO molecules become adsorbed ($0.2 < \theta_{CO} < 0.5$), the surface transitions from the 1x2 reconstructed configuration to the 1x1 configuration.

(3) When large CO coverage ($\theta_{CO} > 0.5$) is attained, the surface configuration is mostly in the 1x1 phase. Here, the reaction rate is high because oxygen molecules become more easily adsorbed to the 1x1 platinum surface.
(4) Since CO_2 is produced at a high rate, θ_{CO} decreases. When θ_{CO} reaches the threshold of 0.5, the transition from the 1x1 configuration to the 1x2 configuration takes place. Once θ_{CO} is below 0.2, the reaction is back to Step (1); the cycle is repeated.

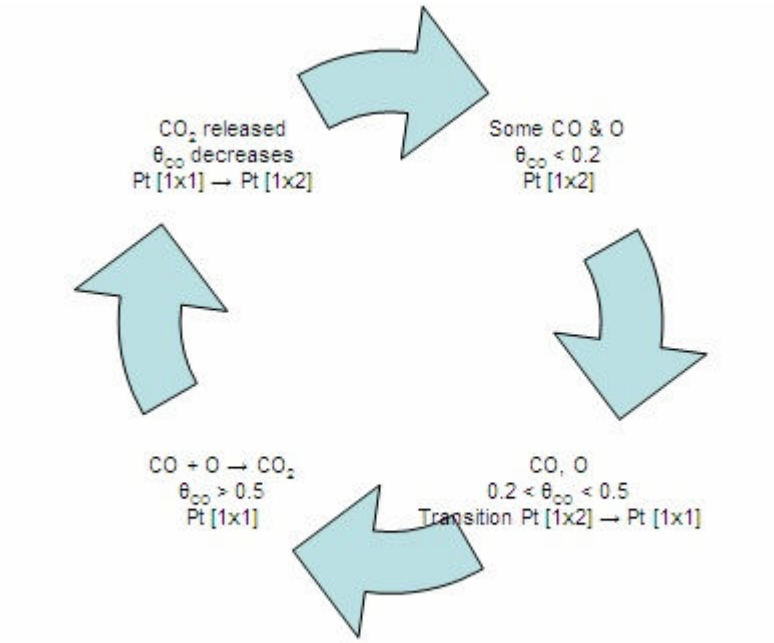

Figure C3. Oscillatory kinetics of CO oxidation on Pt(110).

In order for this cyclic behavior to occur, the parameters (T, pCO, and pO2) must be in a specific range (see Table 2). For instance, if pCO is too low, the CO coverage will never exceed the threshold of 0.2. If pCO is too high, a high CO coverage inhibits the adsorption of oxygen, thereby slowing down the reaction and preventing θ_{CO} from dropping below 0.5. Moreover, a low temperature results in a high CO coverage, while a high temperature results in a low CO coverage.

Pressure Range (torr)	Ratio of Partial Pressures	Temperature Range (K)
10^{-5}-10^{-3}	$1 < p_{O2}/ p_{CO} < 24$	$440 < T < 590$

Table 2. Conditions for which oscillating reaction rates of CO oxidation on Pt(110) have been observed [4]

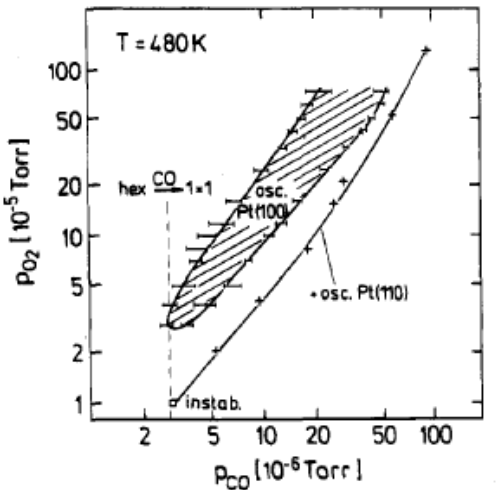

Figure C4. Existence diagram for the occurence of oscillating CO oxidation reaction rates on Pt(100) and Pt(110) at a fixed temperature of 480K. Pt(100) has a wider existence region for oscillatory behavior because the sticking coefficients of oxygen on the two surface configurations are significantly different. [1]

To model the oscillatory behavior, a third variable θ_{1x1} expresses the fraction of the platinum surface present in the 1x1 configuration. The following three differential equations can now encompass the oscillatory CO oxidation reaction on Pt(110).

Equation 1. $$\frac{d\theta_{CO}}{dt} = k_1 p_{CO}\left[1-\left(\frac{\theta_{CO}}{\theta_{CO,Sat}}\right)^r\right] - k_{-1}\theta_{CO} - k_3\theta_{CO}\theta_O$$

Equation 2. $$\frac{d\theta_O}{dt} = s_{O_2} k_2 p_{O_2}\left[1-\frac{\theta_{CO}}{\theta_{CO,Sat}}-\frac{\theta_O}{\theta_{O,Sat}}\right]^2 - k_3\theta_{CO}\theta_O$$

Equation 3. $$\frac{d\theta_{1x1}}{dt} = \begin{Bmatrix} -k_4\theta_{1x1} & for\ \theta_{CO} \le 0.2 \\ k_4\left(\sum_{i=0}^{3} q_i {\theta_{CO}}^i - \theta_{1x1}\right) & for\ 0.2 \le \theta_{CO} \le 0.5 \\ k_4\left(1-\theta_{1x1}\right) & for\ \theta_{CO} \ge 0.5 \end{Bmatrix}$$

Equation 3 takes into account the oscillating nature of the platinum surface. Thus, it consists of three different parts to describe the three stages of the oscillation – the predominantly 1x1 stage, the transition stage, and the predominantly 1x2 stage – which are related to the degree of CO coverage. The coefficients q_i in the polynomial expression here are chosen to make the function continuous and consistent with experimental results.

Furthermore, to model the different sticking coefficients of oxygen for the two surface configurations, the following equation is used:

Equation 4. $$s_O = \theta_{1x1} s_{O1} + \left(1-\theta_{1x1}\right) s_{Or}$$

where $s_{O1} = 0.6$ is the oxygen sticking coefficient on the 1x1 surface and $s_{Or} = 0.4$ is the oxygen coefficient on the 1x2 reconstructed surface.

The numerical integration of the three differential equations above produced the time series below (Figure C5). There is a good qualitative agreement between this theoretical model and the observed result (Figure C1). The time scales of the two figures are different because of the difference in temperatures, which has an exponential effect on the rate constants.

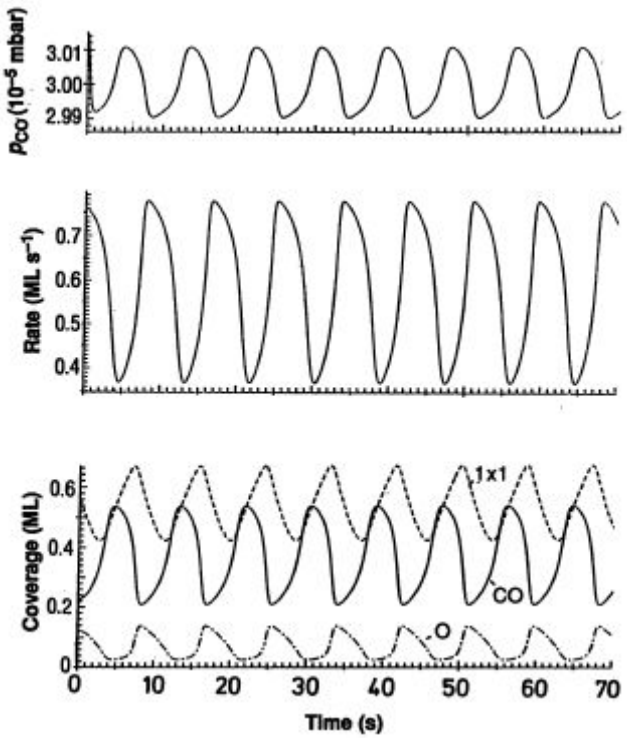

Figure C5. Time series resulting from numerical integration of the three differential equations modeling the kinetics of CO oxidation on Pt(110). The parameters were set at: T = 540 K, pO2 = 6.7×10^{-5} mbar, and pCO = 3.0×10^{-5} mbar. [2]

Also, a bifurcation diagram in the pO2 versus pCO parameter plane (Figure C6) was generated from the three equations [3]. Oscillations are observed only within the narrow shaded regions. Figure C7, though not drawn to scale, is a better bifurcation diagram showing different limit sets [3]. Regions 6 and 7 exhibit stable limit cycles and therefore stand for oscillatory behavior. In contrast, Region 1, which is outside of the area bounded by the saddle-node bifurcation curves, has only one fixed point; this stable node represents either a high reaction rate (high pO2 and low pCO) or a low reaction rate (low pO2 and high pCO). Region 2, with two stable nodes, represent bistability. Regions 3 and 5 exhibit limit cycles, but they are unstable. Region 4 is representative of a situation that is close to being oscillatory.

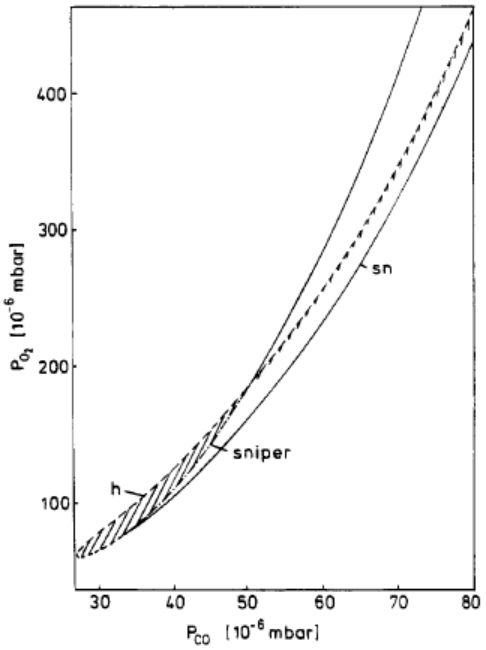

Figure C6. Bifurcation diagram in p_{O2} vs. p_{CO} plane. [3]

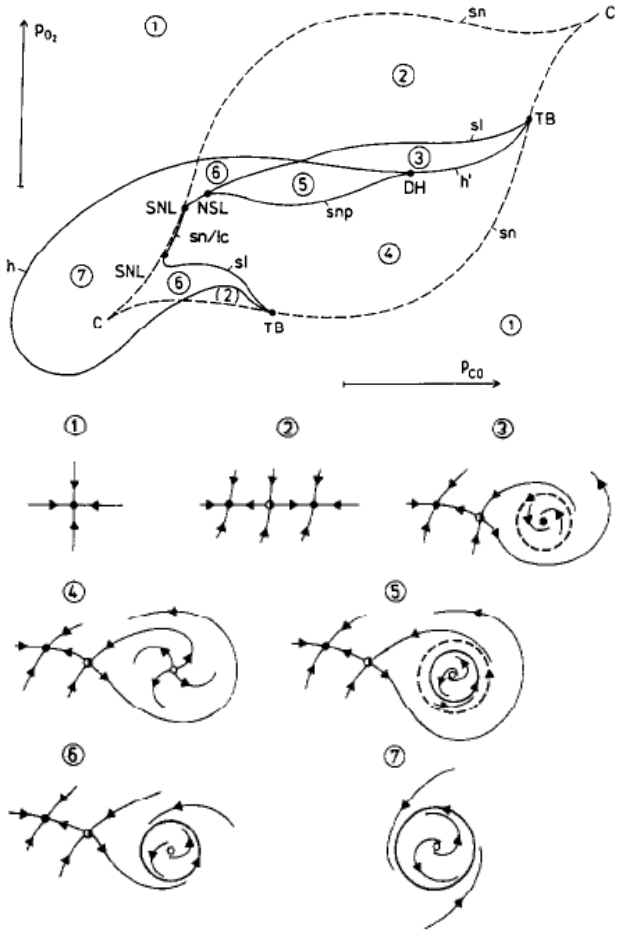

Figure C7. Close-up of different stability regions and seven types of stability behavior. [3]

D. Mathematical Experimentation to Obtain Oscillatory Behavior from ODEs

To elucidate the mathematics that leads to oscillatory behavior, a system of ordinary differential equations (Equations 1-3) were simulated with MATLAB.

Equation 1. $$\frac{d\theta_{CO}}{dt} = k_1 p_{CO}\left[1-\left(\frac{\theta_{CO}}{\theta_{CO,Sat}}\right)^r\right] - k_{-1}\theta_{CO} - k_3\theta_{CO}\theta_O$$

Equation 2. $$\frac{d\theta_O}{dt} = s_{O_2} k_2 p_{O_2}\left[1-\frac{\theta_{CO}}{\theta_{CO,Sat}}-\frac{\theta_O}{\theta_{O,Sat}}\right]^2 - k_3\theta_{CO}\theta_O$$

Equation 3. $$\frac{d\theta_{1x1}}{dt} = \begin{Bmatrix} -k_4\theta_{1x1} & for\ \theta_{CO} \le 0.2 \\ k_4\left(\sum_{i=0}^{3} q_i {\theta_{CO}}^i - \theta_{1x1}\right) & for\ 0.2 \le \theta_{CO} \le 0.5 \\ k_4\left(1-\theta_{1x1}\right) & for\ \theta_{CO} \ge 0.5 \end{Bmatrix}$$

In all simulations, the initial condition was set to a "clean surface" – that is, $\theta_{CO} = 0$, $\theta_O = 0$, and $\theta_{1x1} = 0$. The code for the simulation is attached at the end of the paper.

The simulations showed that oscillating behavior is attained for a very narrow range of parameters. For instance, at $p_{CO} = 30.5\times10^{-6}$ Torr and $p_O = 90.0\times10^{-6}$ Torr, oscillatory kinetics was obtained at a temperature of 540 K as shown in Figure D1. However, when the temperature was varied by only 10 K, oscillatory behavior was no longer observed as shown in Figure D2. Any change in temperature has an exponential effect on rates, since rate constants are determined by the Arrhenius equation, $k_i = k_i^O\, exp(-E_i / RT)$. Similarly, slight changes in the partial pressure of CO also eradicated oscillatory as the dynamics of the differential equations is altered (Figure D3). From these simulations, it could be concluded that oscillatory behavior disappears for the CO-Pt(110) catalyst system with only a small change in physical parameters. Whenever oscillatory behavior is not attained, each value tends to stability. The caption under each figure justifies its dynamics from the physical standpoint.

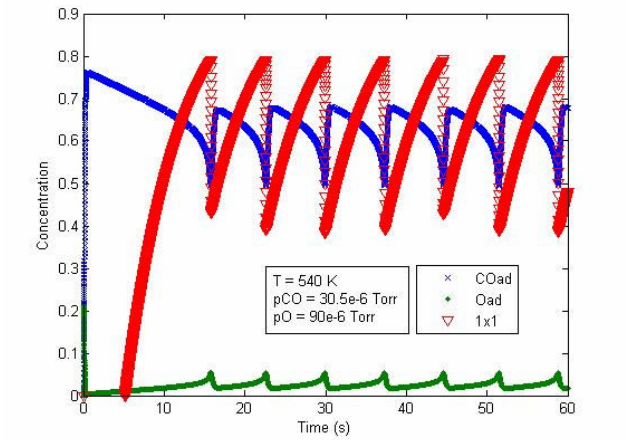

Figure D1. Oscillatory behavior observed. The parameters are within the oscillatory regime specified by the bifurcation curve from Section C.

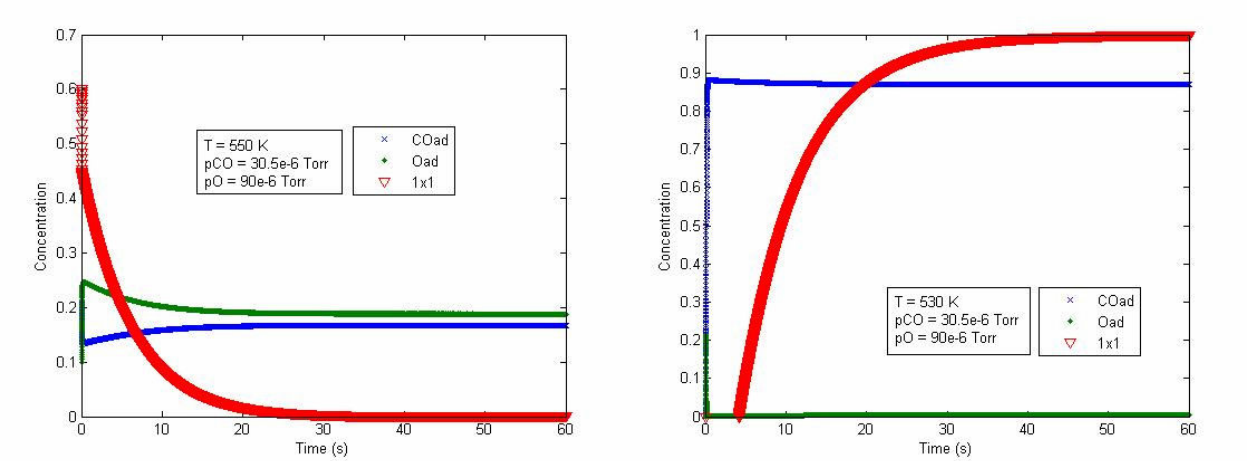

Figure D2. Disappearance of oscillation (temperature change). The higher temperature (left) causes the concentration of adsorbed CO to decrease, therefore driving the surface phase to 1x2. The lower temperature (right) allows the CO concentration to remain high, driving the surface phase to 1x1 and preventing oxygen adsorption.

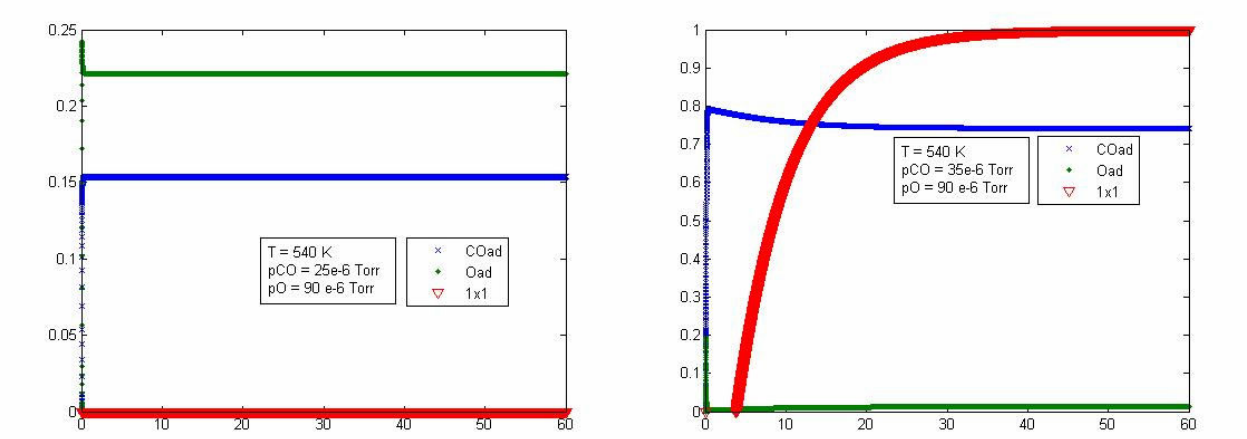

Figure D3. Disappearance of oscillation (p_{CO} change). The lower p_{CO} (left) causes the platinum surface to remain in the 1x2 phase, instead of the 1x1 phase, thus prohibiting oscillatory kinetics. The higher p_{CO} causes the platinum surface to be entirely 1x1, again preventing oscillatory behavior.

Other values in the equations can be altered to produce different outcomes. For instance, in Equation 1, the *r*-th power on the ratio $\theta_{CO}/\theta_{CO,Sat}$ can be changed. Figures D4a and D4b were generated with the same set of physical parameters as shown in Figure D1 (which displays oscillatory behavior) while changing the *r* value to 2 (D4a) and 4 (D4b) from the default value of 3. The behavior in Figure D4a is oscillatory, but the fraction of the 1x1 phase is negative, which is physically nonsensical. The behavior in Figure D4b is non-oscillatory.

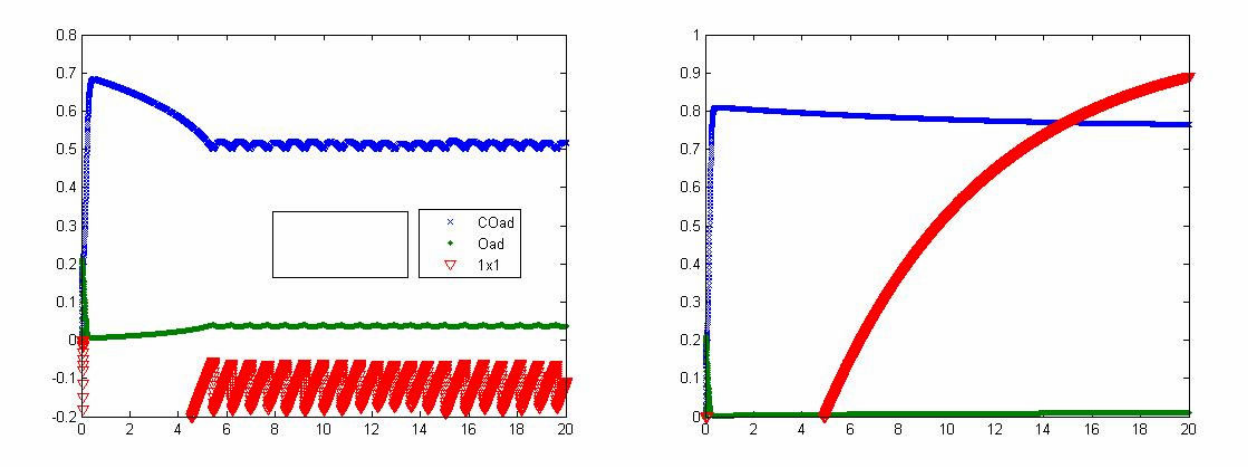

Figure D4a. (left). r = 2; **Figure D4b.** (right) r = 4.

E. Transition to Chaos

As a parameter such as p_{CO} is varied, a transition from periodic oscillations to chaotic (aperiodic) behavior can be observed in the oxidation of CO [2]. As the partial pressure of CO is decremented, the time series of CO oxidation undergoes period doubling. The signal at time t is plotted against the same signal at some later time $t + \tau$, where τ is an arbitrary delay time. This plotting of f(t) versus $f(t + \tau)$ produces phase diagrams as shown next to the time series in Figure E1. From diagrams A to C, the Lyapounov exponents λ_i are still negative, and the trajectories in the phase diagrams converge; in these cases, the kinetics is periodic. However, when λ_i becomes positive, the behavior becomes aperiodic or chaotic, as the system becomes extremely sensitive to its initial condition.

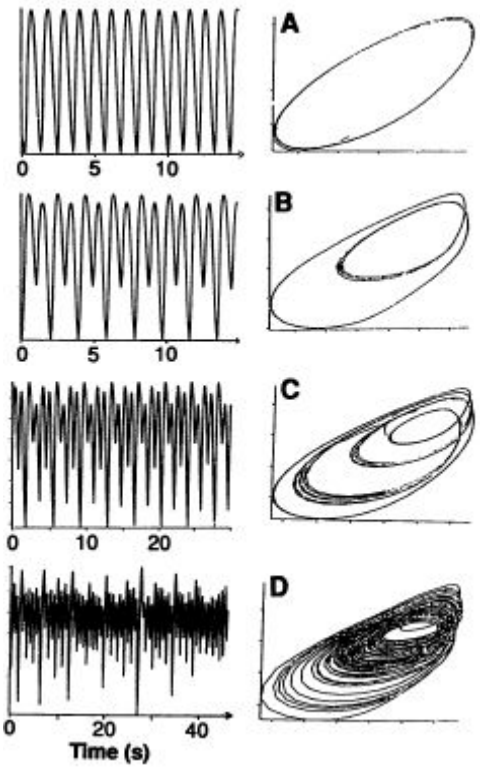

Figure E1. Transition from periodic to aperiodic behavior for the rate of CO oxidation. At T = 550 K and pO2 = 4.0×10^{-4} mbar, pCO is varied: (A) $p_{CO} = 1.65\times10^{-4}$ mbar, (B) $p_{CO} = 1.62\times10^{-4}$ mbar, (C) $p_{CO} = 1.60\times10^{-4}$ mbar, (D) $p_{CO} = 1.58\times10^{-4}$ mbar. [2]

F. Diffusion and Spatio-Temporal Patterns

The modeling so far has assumed that there the reaction rate and concentration depend only on time. In reality, these properties are also dependent on spatial position. Patterns ("chemical waves") as shown in Figures F1, F2, and F3 are observed using photoelectron emission microscopy (PEEM). Darker regions are covered with oxygen and therefore show high reactivity. Brighter regions are either bare platinum surfaces or covered with CO and therefore show low reactivity. Different patterns are observed depending on the parameters (T, p_{CO}, and p_{O2}).

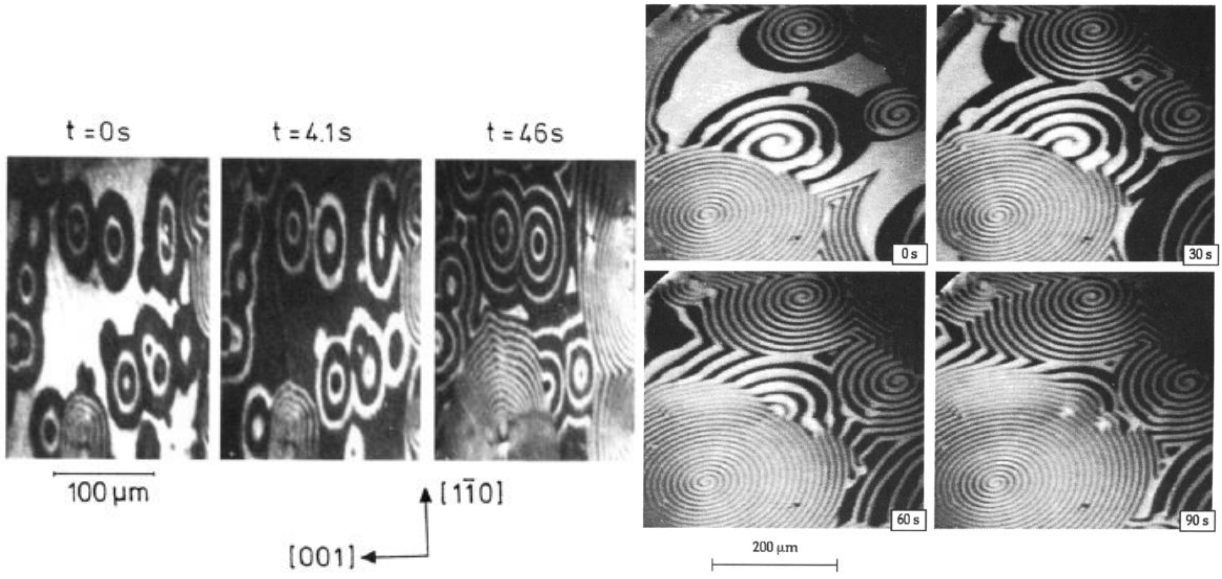

Figure F1. (left) PEEM images showing elliptic propagation of chemical waves from kinetic oscillations in CO oxidation on Pt(110). The experimental conditions are T = 427 K, p_{CO} = 3×10^{-5} mbar, and p_{O2}, = 3.2 $\times10^{-4}$ mbar. Dark areas in the image correspond to an oxygen covered; bright areas, to a CO covered or bare surface. [1]

Figure F2. (right) A PEEM image at T = 448 K, p_{CO} = 4.3×10^{-5} mbar, and p_{O2}, = 4 $\times10^{-4}$ mbar. [1]

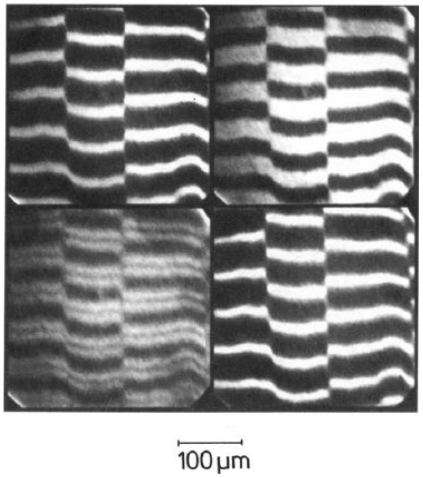

Figure F3. A PEEM image showing standing wave patterns at T = 550 K, p_{CO} = 1.75×10^{-4} mbar, and p_{O2}, = 4.1 $\times10^{-4}$ mbar. [1]

These chemical waves arise from diffusion, which is the transport of chemical species triggered by concentration differences between adjacent regions on the catalyst. The reaction and diffusion of the i-th chemical species is represented by the following equation:

$$\frac{\partial \theta_i}{\partial t} = F_i\left(\vec{\theta}, p, T\right) + D_i \frac{\partial^2 \theta_i}{\partial x^2}$$

where θ_i is the concentration of the i-th chemical species (equivalent to the fraction of the catalyst surface covered by the i-th speicies). The first term on the right hand side represents the change in θ_i due to reaction, which is a function of the concentration of each species present (represented collectively as a vector), partial pressures, and temperature. The second term represents diffusion in one direction (x-direction), with D_i being the diffusion coefficient. Since the surface of the platinum catalyst is anisotropic, another reaction-diffusion equation for the y-direction with a different diffusion coefficient is needed.

G. Future Studies

Catalysis is a process that can be applied to many chemical systems. Because of this there is an extensive amount of research that can be done beyond what has been studied for the carbon monoxide and platinum case. One of the easier extensions of this topic would be to study the behavior of the same gases with a different metal catalyst (such as palladium). In this case the steps of the reaction would be approximately the same. Experimental data would be used to determine the governing equations, whose stability could be analyzed and compared to that of the reaction on platinum. Any differences would provide a better understanding about the chemical differences of the two metals. A more difficult topic of study would be to use the same platinum catalyst, but to change the gas system. This requires much more research because the individual steps of the reaction must be determined experimentally even if the overall reaction is well known. The step by step process is what actually determines the governing equations, and this can only be found experimentally. Comparing this to the carbon monoxide and platinum case would provide useful information about what types of gas systems platinum best catalyses. The stability analysis of all of these systems will provide information about when these reactions proceed at their optimal rates, which is useful to efficiently use these reactions in industrial and other processes.

H. Conclusion

The oxidation of carbon monoxide on platinum is a good system to study for many reasons. The gases are simple enough that they may be easily modeled. The reaction is well understood so that the equations governing the reaction can be assumed accurate, and the experimental and calculated data are well matched. In addition, the behavior observed is interesting and can be characterized. The most notable behavior exists in a narrow region when the parameters are adjusted to specific conditions of pressure and temperature. The behavior in this region is of oscillatory nature and produces stability that includes stable and unstable nodes, saddle nodes, and limit cycles. When the parameters are varied further the system transitions from periodic oscillations to aperiodic chaotic conditions. The understanding of the stability of this reaction provides useful information for industrial processes as well as for general chemical knowledge.

I. References

[1] R. Imbihl and G. Ertl. "Oscillatory Kinetics in Heterogeneous Catalysis". *Chemical Review*. **95**, 697-733 (1995).

[2] G. Ertl. "Oscillatory Kinetics and Spatio-Temporal Self-Organization in Reactions at Solid Surfaces". *Science*. **254**, 1750-1755 (1991).

[3] K. Krischer, M. Eiswirth, and G. Ertl. "Bifurcation Analysis of an Oscillating Surface Reaction Model". *Surface Science*. **251/252**, 900-904 (1991).

[4] M. M. Slin'ko and N. I. Jaeger. *Oscillating Heterogenous Catalytic Systems*. Elsevier, 1994.

J. MATLAB Commands

*All values for the parameters were adopted from reference [3].

Function that simulates the three ODEs

```
function dy = eqnsKin(t, y)

T = 540; % default is 540
pO = 90e-6; %default is 90e-6
pCO = 30.5e-6; %default is 30.5e-6

k1 = 2e16*exp(-38000/(1.987*T));
k2 = 3e6*exp(-10000/(1.987*T));
k3 = 1e2*exp(-7000/(1.987*T));
r1 = 3; %default is 3
r2 = 2; % default is 2

dy = zeros(3,1);
dy(1) = pCO*4.18e5*(1 - y(1)^r1) - k1*y(1) - k2*y(1)*y(2);
dy(2) = pO*7.81e5*(y(3)*0.6 + (1 - y(3))*0.4)*(1 - y(1) - y(2)/0.8)^r2 -
k2*y(1)*y(2);
dy(3) = k3*phasetran(y(1), y(3));

end
```

Function that simulates phase transition

```
function f = phasetran(y1, y3)

if y1 <= 0.2
    f = -y3;
else
    if y1 > 0.2 & y1 < 0.5
        f = -1/0.0135*(1 - 1.05*y1 + 0.3*y1^2 - 0.026*y1^3) - y3;
    else
        f = 1 - y3;
    end
end

end
```

Command Window:

```
[T, Y] = ode45(@eqnsKin, [0, 60], [0.0, 0.0, 0.0]);
plot(T, Y(:, 1), 'x', T, Y(:, 2), '.', T, Y(:, 3), 'v');
```