CO OXIDATION ON Pd/Al₂O₃. TRANSIENT RESPONSE AND RATE ENHANCEMENT THROUGH FORCED CONCENTRATION CYCLING

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(Received 19 November 1984)

Abstract—Catalytic oxidation of CO over Pd/Al₂O₃ was studied with a novel monolithic reactor, with inside the reactor detection of reactants and products. Periodic switching of the feed between CO/N₂ and O₂/N₂ resulted in time-averaged rates which were more than 40 times the maximum achievable steady-state rate. To our knowledge, these enhancement factors are the highest ever observed for any reaction-catalyst system. Mapping the time-averaged reaction rates in the cycle time–CO duty fraction plane resulted in a unique global maximum at each temperature and flow rate. The ratio of optimum periodic operation rate to steady-state rate does not increase monotonically with decreasing temperature but exhibits a maximum. Transient response experiments show the presence of more than one type of surface species of CO and oxygen taking part in the reaction. While the transient responses for CO and oxygen pretreated catalysts are similar in appearance, step-up and step-down responses to and from the steady state are not. The implications of these observations in terms of the possible surface processes are discussed.

INTRODUCTION

Deliberate periodic operation of chemical reactors for improvements in performance and/or selectivity was discussed by Douglas (1967, 1972) and extensively studied and reviewed by Bailey (1973, 1977). Initially most of the papers on periodic operation were theoretical but in recent years the number of experimental papers has increased considerably. Dennis and Kabel (1970) studied the periodic operation of a vapour phase ethanol dehydrogenation reactor. Oxidation of SO₂ was investigated by Unni et al. (1973) and rate improvements of 30% were achieved. Renken (1974, 1976) found the periodic operation of a tubular ethylene oxidation reactor to be superior to steady-state operation in terms of selectivity and temperature control. Improvements in selectivity or yield in butadiene hydrogenation were reported by Al-Taie and Kershenbaum (1978). Billimoira and Bailey (1978) obtained improvements both in ethane and ethylene yields in the hydrogenation of acetylene by periodic feed switching. Rinker and Wilson (1982) and Jain et al. (1983) investigated the periodic operation of ammonia synthesis reactors with improvements of 30–50% compared to steady-state operation.

Cutlip (1979) has studied the periodic operation of a CO oxidation reactor extensively in a gradientless reactor and showed that with a Pt/Al₂O₃ catalyst the rate of reaction can be increased by a factor of 20 compared to the steady state by periodically switching the feed between CO and O₂ streams. Barshad and Gulari (1985a) investigated rate enhancements in CO oxidation over Pt/Al₂O₃ in a tubular reactor using much shorter cycling times. They observed rate enhancements of as much as a factor of 18 over that of the maximum possible steady-state rate at the same temperature. This work demonstrated that the increased rates were not due to the reactor switching between two isothermal steady states or increased surface coverage by oxygen. In a later study, Barshad et al. (1986) determined that during periodic operation the time-average surface concentrations of the various species of absorbed CO were significantly different from that of the steady state even though the total amount of CO on the catalyst surface was the same. Increased oxidation rates were correlated with the appearance of a "reactive" CO species which existed in significant amounts only during periodic operation.

Periodic operation of chemical reactors has also become a reality on a very large scale during the last few years. All of the 1982 and later models of GM cars have a periodically operated catalytic converter. The feed is switched at a frequency of 2 Hz between oxygen-rich and CO rich streams (Herz, 1982). On the homogeneous reaction side, a new furnace developed by DOE-funded research operating on a pulsed combustion principle is being marketed by Lennox Inc. under the model name of "Pulse Furnace". The efficiency of this furnace is 96% of the theoretical maximum, resulting in 40% improvement over conventional furnaces.

The first goal of this study was to find out whether forced concentration cycling leads to increased CO oxidation rates with a different catalyst from the platinum group metals, Pd/Al₂O₃. Unlike platinum, supported palladium crystallites are not easily oxidized at low temperatures, thus the state of the catalyst is better defined. The second goal was to obtain transient response data to help in our understanding of the kinetics of CO oxidation over palladium. While there is a large amount of single-crystal work on this system, atmospheric work with polycrystalline supported catalysts is lacking.

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Previous work with single crystals by Engel and Ertl (1978) has indicated that even under high vacuum and single-crystal conditions there were three different surface species contributing to the CO$_2$ production. CO oxidation on platinum group metals is believed to proceed through the following steps:

\[
\begin{align*}
\text{CO}_{(g)} + S & \rightleftharpoons \text{CO} \cdot S \quad (1) \\
\text{O}_2(g) + 2S & \rightleftharpoons 2\text{O} \cdot S \quad (2) \\
\text{O} \cdot S + \text{CO} \cdot S & \rightleftharpoons \text{CO}_2(g) + 2S \quad (LH) \quad (3) \\
\text{CO}_2(g) + \text{O} \cdot S & \rightleftharpoons \text{CO}_2(g) + \text{S} \quad (ER). \quad (4)
\end{align*}
\]

The third step is the Langmuir–Hinshelwood (LH) step, indicating that the reaction occurs between the two surface species. In the Eley–Rideal (ER) mechanism, the reaction is believed to occur between the adsorbed oxygen atom and a gas phase CO molecule, step (4). Despite the apparent simplicity of the overall reaction, one of the points yet to be conclusively resolved is whether the LH or ER mechanism is the main mechanism. One of our goals was to obtain evidence to decide between the two mechanisms.

EXPERIMENTAL

(A) The reactor system

The automated reactor system used in this investigation is shown in Fig. 1. The details of the reactor system have been discussed elsewhere (Barshad and Gulari, 1986). For the purposes of this paper it is important to note that two different detection methods were used to follow conversion and transient responses. FTIR based inside the reactor detection was used to follow the transients with a time resolution of 0.15–0.6 s. Since the IR beam samples the whole reactor it gives a length-average response. Under differential reactor conditions, the total signal from this detector is proportional to half the outlet concentration. Overall conversion was measured with in-line NDIR detectors. Reactant flow rates were measured individually with Kurz Instruments mass flow meters with an accuracy of 2% of the reading.

(B) The catalyst

A cylindrical piece 34 mm long and 32 mm in diameter was core-drilled from an Engelhard xj7 monolith. A washcoat of alumina (20 wt %) was applied and calcined. Pd was loaded by successive dipping into a solution of PdCl$_2$ containing a known amount of Pd and drying to obtain 1% by wt Pd on the surface. After drying, the monolith was calcined in air at 673 K and reduced in situ in flowing hydrogen. The physical properties are given in Table 1.

The Reynolds number in the channels ranged from 1 to 2 corresponding to flow rates of 0.5 and 1 dm$^3$ min$^{-1}$. Approximately 94–96% of the total length of the reactor is in the fully developed regime. Average residence time in the reactor was 2 s or less.

RESULTS AND DISCUSSION

Two types of experiments were carried out to characterize the performance of the Pd/Al$_2$O$_3$ catalyst: transient response to step changes in the inlet

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**Table 1. Physical properties of the catalyst**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel dimension (rectangular)</td>
<td>1.3 mm</td>
</tr>
<tr>
<td>Channel density</td>
<td>50.5 Ch. cm$^{-2}$</td>
</tr>
<tr>
<td>Wall thickness</td>
<td>0.3 mm</td>
</tr>
<tr>
<td>Open area</td>
<td>64.0%</td>
</tr>
<tr>
<td>Geometric area</td>
<td>24.5 cm$^2$/cm$^3$</td>
</tr>
<tr>
<td>Apparent density</td>
<td>0.8 g/cm$^{-3}$</td>
</tr>
<tr>
<td>BET surface area (apparent)</td>
<td>15.3 m$^2$/g$^{-1}$</td>
</tr>
<tr>
<td>Dispersion</td>
<td>21.3%</td>
</tr>
</tbody>
</table>

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Fig. 1. Schematic drawing of the reactor system used in this study.
concentration, and continuous operation with periodic feed switching. The flow rates in all the step-up experiments were kept constant at 0.5 dm$^3$ min$^{-1}$ and a short purge with nitrogen preceded the step up in concentration. The details of our findings are as follows.

(A) Transient response experiments

Figure 2 shows the CO and CO$_2$ transient responses of a CO pretreated catalyst to a step up of oxygen in nitrogen. In Fig. 2 we see an interesting phenomenon, observable with only inside the reactor detection. Upon entering the reactor, oxygen displaces some weakly held CO. Even though the desorbed CO transient lasted for approximately 0.3 min (18 s) or more than eight residence times, its presence could not be detected by the outside detector. This apparent contradiction is easily resolved if one takes into account the fact that about 90% of our IR signal comes from gas-phase molecules within one mean free path of the catalyst surface and that a gas phase molecule entering any one of the channels of the monolith will collide with the walls a minimum of 10 times before leaving the reactor. With an adsorption probability very close to one, the displaced CO becomes re-adsorbed in the close vicinity of the desorption site. Thus even though there were detectable amounts of CO inside the channels of the monolith, the concentration of CO in the product stream was much lower and could not be detected by the in-line NDIR detector monitoring the product stream.

The CO$_2$ response given in Fig. 2 shows two very sharp peaks. The first peak starts shortly after oxygen enters the reactor, reaching a maximum and then decreasing. However, approximately 20 s after the introduction of oxygen, a second maximum occurs in CO$_2$ production. The second peak is also very sharp and contributes about 30% of the total CO$_2$ production. Within 40 s the CO$_2$ response is down to zero again. Figure 3 shows the CO and CO$_2$ responses of the oxygen-pretreated catalyst to a CO step up. The CO$_2$ response shown in Fig. 3 is similar to that in Fig. 2. The characteristic rise and decay times of the first peak are comparable to those of the first peak of Fig. 2. However, the second peak of Fig. 3 is much broader and contributes as much CO$_2$ as the first peak. CO$_2$ production continues at a very low level for several minutes after the introduction of the CO step.

One plausible explanation for the double peaks observed in the CO$_2$ transients is a thermal shock propagating behind the reaction front and causing an increased rate of reaction. Kaul and Wolf (1984) reported significant local temperature excursions using a pellet designed for transmission IR studies. Their later work (Kaul and Wolf, 1985) showed that increased gas velocities past the pellet surface decrease the magnitude of the local temperature excursions. While we could not directly rule out the possibility of significant local temperature excursions, the double peaks are characteristic of the palladium catalyst. Under similar conditions, platinum gave only single peaked transients. Changing the diluent gas from nitrogen to helium to increase the heat-transfer coefficient did not change the shape of the transient. There are several factors that make the conditions more favourable for the case of CO oxidation: (a) the heat of reaction for CO oxidation is less than half that of ethylene oxidation used by Kaul and Wolf; (b) it has been observed that the CO$_2$ molecules formed by the reaction between adsorbed CO and oxygen on platinum are extremely energetic (Becker et al., 1977; Egner et al., 1984; Mantell et al., 1981) and take into the gas phase a large fraction of the heat of reaction in their vibrational modes. This last point is important because it shows that only a fraction of the total energy is left on the active site to be dissipated. If the CO$_2$ molecules can escape without colliding with the support too many times they will carry part of their energy into the gas phase. To some extent this is possible with the monolithic support in that the thickness of the wash...
coat is on the order of 1 μm or less. Even if the CO₂ molecules lost all of their energy in colliding with the pore walls of the support, this mechanism distributes the heat of reaction much more uniformly and eliminates hot spots.

If one assumes that there is no heat transfer from the catalyst to the gas phase or to the core of the monolith it is possible to have adiabatic temperature increases of close to 50–60 K on the catalyst surface. However, the characteristic times associated with dissipation of this energy are much shorter than the time interval between the first and second peaks in the CO₂ transient, and if the energy is dissipated into the support the temperature rise of the catalyst is of the order of 1 K (Herz and Shinouskis, 1984). Thus the majority of the evidence is against a thermal origin for the second peak. Another possible reason for the double peaks in the CO₂ transients may be the different reaction rates on the two thermodynamically stable planes of Pd, the (111) and (100) planes. Perhaps the most likely reason for the double peaks in the CO₂ transients is the fact that initially CO adsorbs onto the catalyst in a homogeneous two-dimensional fluid-like fashion without any distinct structure (Engel and Ertl, 1979). We think the fluid-like structure reorganizes with time into a more ordered form. Thus the two peaks are due to different reactivities of the fluid-like and ordered reactants on the catalyst surface. As indirect evidence for this hypothesis, increasing the purge time between the surface pretreatment and introduction of the second reactant decreased the separation time between the two peaks and finally merged them into one (Zhou and Gulari, 1985). The purge time needed was a strong function of temperature, again indicating a kinetic origin.

The total amount of CO₂ produced during the CO step up is almost exactly twice the amount produced during the oxygen step at 70°C. As the temperature is increased, this ratio decreases slowly. This is to be expected since on palladium essentially all the adsorbed CO molecules are bridge-bonded and at higher temperatures thermal desorption changes the ratio of adsorbed CO to oxygen. We should also note that in Fig. 3 the maximum in the CO₂ production occurs exactly when the CO signal reaches half its maximum. The fact that the CO₂ peak is leading the CO peak is positive evidence for a Langmuir–Hinselwood type (reaction between adsorbed CO and O) mechanism, in agreement with the findings of Engel and Ertl (1978). If an Eley–Rideal type (reaction between adsorbed oxygen and gas phase CO) mechanism contributed significantly to CO₂ production, the CO and CO₂ signals would be in phase.

The CO₂ transient responses to a CO or an oxygen step up when the other reactant was present in the gas phase provided no additional information. For the oxygen step, CO₂ production increased slowly to its steady-state value without any overshoots.

Figure 4 gives the CO and CO₂ responses to a CO step down from steady-state operation while the gas-phase oxygen concentration was kept constant. We see that as soon as the gas-phase CO concentration is almost zero, the CO₂ production rate increases very sharply, reaching a maximum and then decaying slowly. The decay side shows the presence of a strong shoulder in exactly the same point in time as the second peak observed in Fig. 2. The opposite experiment, step down of oxygen from the steady state, resulted in a monotonic decrease to zero in the CO₂ signal.

The complex transients shown in Figs 2–4 indicate that the mechanism of CO oxidation may be much more complex than a simple reaction between two adsorbed reactants. IR spectroscopic work shows that there are at least three types of CO adsorbed on supported palladium (Sheppard and Nguyen, 1976): two bridge-bonded and one linearly bonded species. On the basis of high-vacuum single-crystal work, Engel and Ertl (1979) concluded that even on the Pd(111) surface there are three different types of CO species. Transient IR work done in our laboratory (Zhou and Gulari, 1985) showed that at least during the CO step-up experiments the rate of reaction is linearly correlated with the presence of an active surface CO species, believed to be CO molecules adsorbed in the middle of oxygen islands. The surface structure containing these species can form only if the surface is oxygen-pretreated (Engel and Ertl, 1979).

### (B) Periodic operation results

When compared to the steady-state reaction rates, the peak reaction rates observed in the transient response experiments show the possibility of obtaining high time-averaged reaction rates by operating the reactor at unsteady state. This possibility was quantitatively tested by cyclic feed switching between 10% CO in N₂ and 15% O₂ in N₂. Time-averaged reaction rates were measured as a function of CO duty fraction (fraction of the cycle time CO feed is on) and cycle time at constant temperature. Figure 5 shows a typical start up of periodic operation from the steady state. We see that within one cycle time the time-averaged rate of reaction increases dramatically.

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**Fig. 4. CO and CO₂ transient responses to a CO step down in the feed after steady-state operation with 10% CO, 10% O₂ and 80% N₂ for 10 min. Note that the second peak observed in the CO₂ transient shown in Fig. 2 is seen as only a shoulder at the same point in time. Conditions: 376 K, 10% CO, 15% O₂ in N₂, atmospheric pressure, flow rate 0.5 dm³ min⁻¹. Same detector system as in Fig. 2.**
In Fig. 6 we show the effect of changing duty fraction on the reaction rate. When the length of the CO pulse is short, the reaction rate increases in phase with the CO pulse, it reaches a maximum and then starts to decrease. As soon as the CO feed is off, the rate increases sharply again and then decreases to zero. Essentially all of the CO$_2$ is produced during the first 25 s of the cycle time. At a duty fraction of 0.5, it is clear that both peaks have complicated structures, each one having at least two components. As soon as the CO feed is turned off, a very sharp rise is observed in the CO$_2$ signal. The height of this peak is more than that of the first peak. Increasing the duty fraction to 0.7 does not result in additional features. Figure 7 shows the effect of temperature on the CO$_2$ transient response at constant duty fraction and cycle time. At 93°C the rate of reaction increases sharply after the CO concentration in the gas phase drops to zero, or about 10 s after the CO feed is switched off and O$_2$ feed is on. The sharp rise is followed by a slow decrease to a minimum and then there is another increase to a maximum. Turning the CO on at this point decreases the reaction rate sharply at first to a minimum followed by a fast increase to a maximum. This "CO on" response peak is higher and broader than the "CO off" peaks and the area under it is approximately twice the area of the "CO off" peaks. Increasing the temperature makes the "CO off" peak sharper with a maximum reaction rate that is more than twice the maximum rate at 93°C. The second maximum also disappears and becomes a shoulder on the sharp peak. The "CO on" peak becomes broader with increasing temperature.

Periodic operation profiles can be understood with the help of the individual step response results. During the CO pulse, the catalyst surface becomes covered with CO. During the oxygen feeding portion of the cycle, after an induction time the surface CO reacts very rapidly with oxygen. After reacting with almost all of the adsorbed CO, chemisorbed oxygen covers a large fraction of the vacant sites. When the oxygen feed is turned off and the CO pulse is turned on, chemisorbed CO reacts with the preadsorbed oxygen. While the rise of the CO$_2$ concentration is rapid after the CO feed is on, the slow, almost exponential decay after the maximum is indicative of an oxygen-limited rate. It is also possible that chemisorbed oxygen is in the form of islands on the catalyst surface and that it does not

Fig. 6. CO$_2$ responses to varying the duty fraction (length) of the CO pulse for a fixed cycle period during periodic operation. Cycle period 60 s, temperature 384 K, flow rate 0.5 dm$^3$ min$^{-1}$. The arrows indicate when the CO feed is on (up arrow) and off (down arrow). FTIR inside the reactor detection was used.
diffuse on the surface, thus the reaction is restricted to the periphery of the oxygen islands. According to Engel and Ertl (1979), if the Pd(111) surface is oxygen-covered then introduction of CO first compresses the local surface coverage from $\Theta_0 = 0.25$ to $\Theta = 0.33$, forming active oxygen islands. During this phase, the reaction occurs at the periphery of oxygen islands between the rapidly diffusing CO molecules and the stationary oxygen atoms. Further increases in CO coverage lead to the formation of a mixed structure with $\Theta_0 = \Theta_m = 0.5$. As mentioned previously, our IR work shows a very good correlation between the absorbance due to CO adsorbed into these islands of mixed CO and oxygen and the rate of reaction. If the surface is CO-covered, introduction of oxygen leads to the formation of separate CO and oxygen islands (Engel and Ertl, 1979) and the reaction occurs only at the periphery of the oxygen islands.

It is of interest to note that during the individual step tests the CO$_2$ response contained double peaks for both CO- and O$_2$-pretreated catalysts. In the periodic operation case, only the lowest temperature transients exhibit double peaks. The second peak becomes a strong shoulder as the temperature is increased to $111^\circ$C. This difference is relatively easy to explain: during periodic operation, if the cycle time is not very long, there is not enough time for the reactants to form well-organized large islands covering all of the catalyst surface. IR work done in our laboratory (Zhou and Gulari, 1985) indicates that if the cycle time is in the high enhancement region the time-averaged surface coverage by CO is significantly less than the equivalent steady-state coverage.

(C) Iso-concentration contours and maximum time-averaged rate of reaction

Figure 8 shows a typical iso-concentration contour map, obtained by varying the cycle time and the duty fraction, and averaging the outlet concentration over many cycles to obtain time-averaged concentrations. The time-averaged concentration is proportional to the time-averaged reaction rate (the proportionality constant being the molar flow rate divided by the grams of catalyst). Perhaps the most striking piece of information available from this map is that at the optimum the time-averaged rate of reaction is about 44 times the steady-state rate! To our knowledge, this is the highest rate enhancement observed during periodic operation. We should note that at the optimum point approximately 70% of the CO feed has reacted. This indicates that the enhancement factor can be increased further by increasing the flow rate so that the reactor operates under differential conditions during the whole cycle. Table 2 shows the location of the optimum point of operation and the enhancement factors for several other operating temperatures and flow rates. The shapes of the iso-concentration contours are informative in that both at small and large duty fractions the dependence on the cycle time is very weak. This can be compared with those we obtained with a platinum catalyst (Barshad and Gulari, 1985), which exhibited a similar dependence at duty fractions lower than the optimum but for duty fractions higher than the optimum the iso-concentration contours showed a strong dependence on the duty fraction. We believe this is due to the fact that some of the platinum is oxidized during the reaction and the amount of platinum oxide formed is a strong function of the cycle time and duty fraction (Barshad et al. 1986). With

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**Table 2.** Experimentally determined periodic operation parameters for maximum time-averaged rate enhancement in catalytic oxidation of CO over Pd/Al$_2$O$_3$. The enhancement factor is the ratio of the maximum time-averaged rate achieved during periodic operation to the maximum steady-state rate possible at the same temperature.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Flow rate (dm$^3$ min$^{-1}$)</th>
<th>Concentration CO (vol%)</th>
<th>Concentration O$_2$ (vol%)</th>
<th>Cycle time (s)</th>
<th>CO duty fraction</th>
<th>Enhancement factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>344</td>
<td>0.50</td>
<td>10</td>
<td>10</td>
<td>150</td>
<td>0.2</td>
<td>14</td>
</tr>
<tr>
<td>363</td>
<td>0.50</td>
<td>12</td>
<td>10</td>
<td>90</td>
<td>0.2</td>
<td>18</td>
</tr>
<tr>
<td>375</td>
<td>0.50</td>
<td>12</td>
<td>10</td>
<td>40</td>
<td>0.3</td>
<td>22</td>
</tr>
<tr>
<td>384</td>
<td>0.50</td>
<td>12</td>
<td>10</td>
<td>20</td>
<td>0.3</td>
<td>24</td>
</tr>
<tr>
<td>366</td>
<td>0.70</td>
<td>15</td>
<td>10</td>
<td>20</td>
<td>0.3</td>
<td>44</td>
</tr>
</tbody>
</table>
palladium, a cycle time dependence becomes visible in the $T = 71$ and $93^\circ C$ iso-concentration contour maps. This is due to a trade off between the induction time required for oxygen to start reacting with the pre-adsorbed CO and the increased CO coverage at higher duty fractions. Figure 9 shows the $T = 71^\circ C$ iso-concentration contour map, which can be compared with that of Fig. 8. We should point out that the steady-state conversion given in Fig. 9 is essentially the minimum conversion that could be measured with our NDIR detector, and as such has a $\pm 30\%$ error.

An inspection of Table 2 reveals that for constant composition and flow rate the enhancement factor during periodic operation increases with temperature, going from 14 at $71^\circ C$ to 24 at $111^\circ C$. This behaviour is exactly opposite to that observed with platinum (Barshad and Gulari, 1985). Also, as the temperature increases, the optimum cycle time decreases sharply from 150 s at $71^\circ C$ down to 20 s at $111^\circ C$. This large decrease is certainly proof that the rate enhancement is related to the surface reaction kinetics and not to transport problems. The optimum duty fraction increases with temperature, going from 0.2 to 0.4.

One last point we want to comment on is the presence of an induction time or a minimum cycle time before significant rate enhancements can be observed. If we look at Fig. 8 (or Fig. 9) we see that the iso-concentration contours are very closely packed between the optimum cycle time and the two axes. We have found out that this is due to a minimum induction time that exists between the time CO is switched off (and oxygen switched on) and the time the sharp CO$_2$ production transient is detected. If the length of the oxygen pulse is at least this long during periodic operation, we have rate enhancement; if not, no rate enhancement is observed. Periodic operation tran-

sients show that as the temperature is decreased the CO$_2$ peak which corresponds to the “O$_2$ on” part of the cycle exhibits longer lag times. This may be due to the dual site requirement for oxygen adsorption.

During periodic operation, the surface temperature of the monolith was monitored with an IR thermometer having a spatial resolution of 3 mm and a thermal resolution of $\pm 1$ K. The magnitude of the temperature fluctuations did not exceed the thermometer resolution. Perhaps more importantly there was no visible correlation between the cycling frequency and temperature fluctuations.

A simplified schematic drawing of the catalyst surface shown in Fig. 10 is able to explain all of the experimental observations.

**CONCLUSIONS**

The results of this investigation show that concentration cycling can increase the rate of CO oxidation on palladium enormously. Rate enhancement is possible only if the surface is exposed to oxygen for a minimum time period without any CO being present in the gas phase.

Our results also show that CO oxidation on palladium has a complex mechanism which is of the Langmuir–Hinshelwood type, but there are several pathways leading to the formation of CO$_2$.

**NOTATION**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>vacant surface site</td>
</tr>
<tr>
<td>$CO\cdot S$</td>
<td>adsorbed CO</td>
</tr>
<tr>
<td>$O\cdot S$</td>
<td>adsorbed oxygen atom</td>
</tr>
<tr>
<td>$\Theta_{O}$</td>
<td>oxygen surface coverage</td>
</tr>
<tr>
<td>$\Theta_{CO}$</td>
<td>Carbon monoxide surface coverage</td>
</tr>
</tbody>
</table>

*Acknowledgements—*Acknowledgement is made to the Donors of The Petroleum Research Fund, administered by
the American Chemical Society, for partial support of this research. We are also grateful to the Department of Energy for grant DOE No. DE-FG-22-84PC70785 and the National Science Foundation grants CPE No. 8303850 and DMR No. 8100130 for partial support of this research.

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