Microscopic and spectroscopic techniques at near-atmospheric pressures have been used in recent years to investigate CO oxidation over Pt-group metals. New insights have been obtained that allow broadening of the understanding of this reaction beyond the ultrahigh vacuum regime where it is well-understood. However, new issues also have arisen that need clarification. In this paper, we review recent work in our laboratory, using polarization modulation infrared reflection absorption spectroscopy (PM-IRAS) and reaction kinetics measurements from ultrahigh vacuum to near-atmospheric pressures. These studies reveal a continuity of this reaction with respect to pressure over Pt, Pd, and Rh; that is, Langmuir–Hinshelwood kinetics is exhibited over a wide pressure range with no apparent “pressure gap”. The difference between Ru(0001) and other noble metals is well-understood with respect to higher oxygen binding energies and reduced CO inhibition. It is concluded that for all Pt-group metals the most active phase is one saturated with chemisorbed oxygen and with low CO coverages. The significance of oxide phases under most industrially relevant catalytic conditions suggested recently in the literature is not consistent with the experimental data.

### 1. Introduction

CO oxidation reaction over transition metal is generally accepted to follow the Langmuir–Hinshelwood mechanism described as follows:  

\[
\begin{align*}
\text{CO}_g & \rightarrow \text{CO}(a) & k_1 (1) \\
\text{CO}(a) & \rightarrow \text{CO}_g & k_2 (2) \\
\text{O}_2(g) & \rightarrow 2\text{O}(a) & k_3 (3) \\
\text{O}(a) + \text{CO}_g & \rightarrow \text{CO}_2 & k_4 (4)
\end{align*}
\]

The significance of this reaction is twofold. From an applied perspective, this reaction is important in industrial and automobile emissions upgrading as well as in the generation of CO-free hydrogen for fuel cells. From a fundamental scientific point of view, this is one of the most extensively studied model reactions in heterogeneous catalysis since it is relatively simple yet comprises all the basic steps of a heterogeneous process, that is, adsorption, diffusion, dissociation, reaction, and desorption. This reaction is rather well-understood under (near) ultrahigh vacuum (UHV) conditions where typical surface analytical probes are applicable. Under elevated pressures (Torr level and above), it is less well-understood, due at least partially to the inapplicability of most surface-sensitive probes. From a kinetic point of view, this reaction operates at both steady-stateand non-steady-state conditions. Steady-state behavior is easier to understand, while non-steady-state phenomena (e.g., oscillation) are more difficult to follow.

In the past decade or so, new efforts have been made to investigate the reaction with surface-sensitive probes available to elevated pressures. These include sum frequency generation (SFG), polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), high pressure scanning tunneling microscopy (HP-STM), surface X-ray diffraction (SRXD), and high pressure X-ray photoelectron spectroscopy (HP-XPS). Some new insights indeed have been obtained in the past decade or so, new efforts have been made to investigate the reaction with surface-sensitive probes available to elevated pressures. These include sum frequency generation (SFG), polarization modulation infrared reflection absorption spectroscopy (PM-IRAS), high pressure scanning tunneling microscopy (HP-STM), surface X-ray diffraction (SRXD), and high pressure X-ray photoelectron spectroscopy (HP-XPS). Some new insights indeed have been obtained.
made by these new studies; however, new debates have arisen. It is noteworthy that the Langmuir–Hinshelwood mechanism that adequately describes most experimental findings at low pressures has been questioned at elevated pressures.\textsuperscript{21–23} Moreover, the nature of the active surface phases as a function of pressure, for example, whether there is a so-called pressure gap or not, has been debated. In this Article, we present results of recent studies using single crystal model catalysts coupled with reaction kinetics measurements and in situ PM-IRAS, aiming to shed some new light and clarify the recent debates in CO oxidation at elevated pressures.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{(a) Steady-state CO$_2$ formation rate (TOF) as a function of time at various temperatures over Pd(100). O$_2$/CO (1/1) mixture at $P_{CO} = 1 \times 10^{-6}$ Torr as the reactant. (b) Corresponding PM-IRAS spectra as a function of temperature. Sample temperatures are marked adjacent to each spectrum. Note that no surface CO species is detectable at 500 K and above. Data from ref 19.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{(a) Steady-state CO$_2$ formation rate (TOF) as a function of time at various temperatures over Rh(111). O$_2$/CO (1/1) mixture at $P_{CO} = 1 \times 10^{-6}$ Torr as the reactant. (b) Corresponding PM-IRAS spectra as a function of temperature. Sample temperatures are marked adjacent to each spectrum. Note that surface CO species is still detectable at the highest reaction rate. Data from ref 18.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|}
\hline
Frequency / cm$^{-1}$ & PM-IRAS Signal Intensity / a.u. \\
\hline
2200 & 1978 \\
1900 & 1956 \\
1700 & 1947 \\
1500 & 1942 \\
1300 & 1933 \\
1100 & 1925 \\
900 & 1920 \\
700 & 1915 \\
500 & 1920 \\
\hline
\end{tabular}
\caption{PM-IRAS Signal Intensities at Various Frequencies.}
\end{table}

\subsection*{2. Experimental Section}

PM-IRAS and reaction kinetics measurements were the primary methods used in our studies. The experimental apparatus has been described in detail previously.\textsuperscript{16–20} Briefly, the apparatus consists of (1) an ultrahigh vacuum (UHV) section equipped with Auger spectroscopy (AES), low energy electron diffraction (LEED), and an UTI 100 quadrupole mass spectrometer (QMS) and (2) a high pressure infrared/reaction cell. The infrared cell can be isolated from the UHV section with differentially pumped Teflon sliding seals and can be pressured to atmospheric pressure without compromising the vacuum of the UHV section. In certain cases where a large volume reactor is required, the infrared cell and the main chamber can be directly coupled (the sliding seals removed).

Several single crystal samples were used in these studies, namely, Pd(111), (100), and (110), Rh(111), Pt(110), and Ru-(0001). The cleaning of these samples follows common steps: argon ion sputtering, oxidation in $\sim 1 \times 10^{-7}$ Torr of O$_2$ to remove carbon impurities, and annealing in UHV. PM-IRAS measurements were carried out using a Bruker Equinox 55 FTIR
spectrometer coupled with a polarization modulator to subtract infrared signals arising from gas-phase absorption. This method allows in situ measurements of surface species over a wide range of pressures from UHV to atmospheric. Two methods were used to study CO oxidation kinetics: (1) low pressure kinetic measurements ($P_{\text{CO}} \leq 1 \times 10^{-3}$ Torr) were carried out under steady-state flow conditions by backfilling the infrared cell ($\sim 1.0$ L, where the sample is located) with the desired gas mixture and monitoring the CO$_2$ (44 amu) and CO (28 amu) mass spectrometer signals (correcting for fragmentation and sensitivity at these two masses). In this case, the infrared cell and the main chamber were coupled, since the QMS was located in the main chamber; and (2) high pressure kinetic measurements ($P_{\text{CO}} \geq 0.1$ Torr) were conducted using the infrared cell as a batch reactor where the cell was decoupled from the UHV chamber. When a large volume reactor was required, the infrared cell and the main chamber were directly coupled (total volume $\sim 61.6$ L). Reaction rates were derived by postreaction analysis of the gas phase composition using the QMS or, alternatively, by measuring the pressure change of the gas phase in situ with a precise pressure gauge. CO conversion, unless otherwise specified, was kept below 10% to ensure the acquisition of differential reaction rates.

C.P. grade CO (>99.5%, Matheson Tri-Gas) was further purified by passing through a 4A molecule sieve and liquid-nitrogen-cooled trap to remove metal carbonyl impurities. Ultra-high purity O$_2$ (Matheson Tri-Gas) was used as received.

3. Results and Discussion

3.1. Low Pressure Kinetics and PM-IRAS. Figure 1a shows a plot of the CO$_2$ formation rate (turnover frequency, TOF, CO$_2$ molecule s$^{-1}$ cm$^{-2}$) at various reaction temperatures using an O$_2$/CO mixture (1/1) at $P_{\text{CO}} = 1 \times 10^{-6}$ Torr over Pd(100). The details for calculating the reaction rates are described elsewhere.$^{18}$ Figure 1b shows the corresponding PM-IRAS spectra at various temperatures. Under such reaction conditions, only bridging CO features, which red-shift with increasing temperature, are detected on Pd(100). There are several salient points to mention regarding these data. First, the reaction can be divided into two regimes: a low-rate regime on a CO-dominant surface and a high-rate regime where the surface CO coverage is below the detection limit of IRAS, that is, below $\sim 0.01$ monolayer. These two regimes are termed as the CO-inhibited regime and the CO-uninhibited regime, respectively, in the following discussion. Second, the reaction rate remains extremely constant with time at any given temperature, indicating no accumulation of inhibitory species with time. It is noteworthy that such steady-state behavior is retained for $P_{\text{CO}} \leq 1 \times 10^{-3}$ Torr over a wide range of O$_2$/CO ratios from net reducing to net oxidizing.$^{19}$

Figure 2 displays identical measurements performed on Rh(111), where Figure 2a shows the reaction kinetics and Figure 2b the corresponding PM-IRAS spectra. Compared with Pd(100), two differences need to be addressed. First, the reaction runs steadily below $\sim 485$ K (i.e., in the CO-inhibited regime), demonstrated by the constant rate with time at a given temperature; at
485 K and higher (i.e., in the CO-uninhibited regime), the reaction rate decreases with time at any given temperature, demonstrating oxygen inhibition. Second, the CO coverage is nonzero where the reaction rate maximizes (at 485 K). Note that, on both Pd and Pt surfaces, the CO signal always becomes undetectable at the reaction rate maximum.\textsuperscript{19}

Figure 3 compares the reactivity of various surfaces under identical reaction conditions, that is, O\textsubscript{2}/CO mixture of 1/1 at $P_{\text{CO}} = 1 \times 10^{-6}$ Torr. CO\textsubscript{2} formation rates are reported as CO\textsubscript{2} molecule per area per second in this case for direct comparisons. These data illustrate that, with an increase in the reaction temperature, all samples display the two regimes discussed above separated by a sharp peak in the rate; this peak temperature varies for the various metals (Rh < Pd < Pt). These data indicate that the CO inhibited regime occurs on the different metal surfaces at different temperatures. However, the similarities of CO binding energy on Pt, Pd, and Rh surfaces\textsuperscript{10} suggest a similar extent of CO inhibition for all three metals. Thus, this reactivity difference then likely arise due to differences in the reactivities of the catalyst surfaces toward O\textsubscript{2}. Furthermore, the reactivity loss at temperatures higher than the peak points (i.e., in the CO-uninhibited regime) is best described by a decrease in the sticking probability of the reactants. This effect is, on the one hand, caused by the high sample temperatures and, on the other hand, formation of a less reactive oxygen species (i.e., oxygen inhibition) on the surfaces. The drastic reactivity loss above ~485 K for Rh(111) is due largely to oxygen inhibition, and this notion has been realized previously on Rh at low pressure\textsuperscript{28} and in CO titration measurements on Rh.\textsuperscript{29} In contrast, oxygen inhibition is much less pronounced for Pd and Pt surfaces.

It is difficult to quantify the detailed reaction kinetics under all reaction conditions. However, under certain conditions, the kinetics can be simplified substantially. At low-temperature steady-state conditions, that is, on CO-saturated surfaces, solving C and O conservation equations gives \( R_{CO} = \frac{2k_3}{k_1} k_2(T) \frac{P_{O_2}}{P_{CO}} \) \( \theta_C \) (5)

This expression is fully consistent with the data shown in Figure 3 for the CO-inhibited regime. Especially, if the extent of CO inhibition is assumed to be the same for these surfaces, \( O_2 \) dissociation should largely represent the \( CO_2 \) formation rate. Indeed, the close-packed \( Pd(111) \) maximizes at slightly higher temperatures than does the more open \( Pd(100) \) and \( (110) \) surfaces, and the peak temperature order (\( Rh < Pd < Pt \)) relates directly to the oxygen adsorption energies of these metals.16

With increasing reaction temperature, the steady-state CO coverage will eventually drop to zero (see e.g., Figure 1b) while the surface remains metallic. In this maximum reactivity state, the reaction rate can be simplified as

\[ R_{CO_2} = k_3 P_{O_2} (1 - \theta_O) \]  \( \theta_O \)  \( \theta_C \) (6)

This rate expression predicts drastic rate loss when the oxygen coverage exceeds a threshold value if the Langmuir–Hinshelwood mechanism always holds. This can be rationalized by the decrease in the surface residence time of both CO and \( O_2 \) as well as the decrease in the \( O_2 \) dissociation probability. It is also inferred from Figure 3 that the threshold oxygen coverage does not necessarily remain the same for different metals and different surface orientations.

3.2. Elevated Pressure Kinetics and PM-IRAS over Rh-(111). At near-atmospheric pressures, the study of CO oxidation over Pt-group metals can present technical difficulties; for example, beyond the CO-inhibited regime, the reaction rate can be limited by mass and heat transfer.17–19 Note that these limitations do not exist at low pressures and thus make correlations between low- and high-pressure regimes difficult. Compared with supported high surface area catalysts, planar samples are far more advantageous yet still do not eliminate these mass transfer difficulties. Accordingly, we have applied reduced-sized samples, large-volume reactors, and gas circulation devices to limit mass and heat transfer limitation to the degree possible.16–19

Figure 4 displays a typical example of a reaction cycle using an \( O_2/CO \) (1/1) mixture at an initial CO pressure of 8 Torr over Rh(111). The combined volume of the UHV chamber and the infrared cell (61.6 L) is used as the reactor to allow extended reaction time while maintaining low CO conversions. The Rh-(111) sample was heated stepwise from 325 to 710 K, after which the sample was cooled to 560 K and then heated again to 585 K. Finally, the sample was cooled to 460 K. All temperature changes are displayed in the bottom panel. Concurrently, the pressure of the gas phase was monitored and the resulting pressure change (shown in the upper panel) was used to calculate the reaction rates. From the pressure—time curve, one observes three reaction regimes: (1) a low reaction rate regime below 560 K (the CO-inhibited regime, determined with PM-IRAS shown below), (2) a high reaction rate regime above 560 K (the mass transfer limited regime, as indicated by the invariant rate or pressure drop versus temperature), and (3) a transient state with a much higher rate in between (the hyperactive state). In this latter state, heat generated by the reaction caused a transient sample temperature jump of \( \sim 25 \) K (marked with solid circles). However, cooling from 710 to 560 K and then increasing the temperature to 585 K, the hyperactive state was not observed (marked with dashed circles) either because there is insufficient reactant in the near surface region, or because the less-reactive surface oxide survives these processes. Only when the sample was cooled to 460 K or below to reduce the surface oxide and to replenish the near surface region CO and annealed again is this behavior reproducible (data not shown).

It is of great importance to determine whether the hyperactive state is equivalent to the CO-uninhibited state at low pressures. This will determine whether (1) there is indeed a pressure gap and (2) the Langmuir–Hinshelwood mechanism is maintained over the entire pressure range. It is not straightforward to use PM-IRAS to determine this issue with \( Pd \) and Pt samples, since in both the hyperactive and mass transfer limited regimes CO is undetectable on these surfaces.19 In contrast, a Rh(111) sample is more advantageous in this regard since the surface states are better resolved with chemisorbed CO species.18

Figure 5 summarizes the reaction kinetics data over Rh(111) in Arrhenius plots under various \( O_2/CO \) ratios from 1/2 to 10/1 where the initial CO pressure was maintained at 8 Torr. As is apparent, the behavior for the \( O_2/CO \leq 2/1 \) mixtures is very similar where the reaction rate increases linearly with temperature in an Arrhenius plot until the transient hyperactive state, after which the reaction rate remains essentially constant indicative of the mass transfer limited regime. The situation for the 5/1 and 10/1 mixtures is quite the same prior to the rollover temperature; however, a dramatic change occurs at temperatures higher than the rollover point. In this case, particularly for the 10/1 mixture, the reaction rate drops to a value much lower than that predicted by mass transfer limitation considerations.

Figure 6 displays the corresponding PM-IRAS spectra. Note that the CO coverages below \( \sim 450 \) K are between 0.5 and 0.75 ML for all \( O_2/CO \) ratios indicated by the coexistence of both atop and...
threefold hollow CO species. At such CO coverages, the CO₂ formation rate is too low to be measured reliably with gas pressure changes but nevertheless demonstrates that CO inhibition is significant in affecting CO₂ formation. Importantly, surface CO species are still clearly visible in the hyperactive state, making oxygen coverage estimation possible based on the CO band intensity and vibrational frequencies. For stoichiometric to mildly oxidizing reactants (O₂/CO₂), a weak CO band is found at ~2069 cm⁻¹ in the hyperactive regime, indicating an oxygen coverage of ~0.5 ML. It is important to point out that the surface oxygen coverage never exceeds 0.5 ML during the low pressure steady-state reaction conditions. This consistency of the CO and O coverages at both low and high pressures strongly suggests that from UHV to near-atmospheric pressures the surface reactant conditions at the high reaction rates are the same, i.e. a CO-uninhibited surface covered with a rather dense layer of chemisorbed oxygen.

For net oxidizing reactants (O₂/CO ≥ 5), a new CO feature appears at 2084 cm⁻¹ immediately after the temperature at which the rate rolls over. This new feature was not detected under any conditions at low pressures, that is, between 10⁻⁸ and 10⁻⁴ Torr at any O₂/CO ratio, and not at elevated pressures, that is, between 10⁻³ and 10 Torr, with O₂/CO ratios of ≤ 2. By oxidizing Rh(111) with low pressure O₂ and determining the oxygen coverage using X-ray photoelectron spectroscopy (XPS), followed by CO titration monitored with IRAS, the appearance of the 2084 cm⁻¹ CO feature indicates a surface O coverage of ~0.9 ML. While this oxygen coverage indicates some oxygen has entered into the third layer to form a surface oxide, its formation yields a lower CO₂ formation rate than that resulting from mass transfer limitation.

3.3. Elevated Pressure Kinetics and PM-IRAS over Pd(100). Figure 7 displays Arrhenius plots of a series of reactions carried out over Pd(100) with reactants of various O₂/CO ratios while maintaining the CO pressure at 8 Torr. In all cases, the reaction can be divided into the three regimes described above: (i) a CO-inhibited low-temperature regime; (ii) a high-temperature regime; and (ii) a transient, hyperactive regime between (i) and (iii). It is noteworthy that the high-temperature regime may or may not be mass transfer limited. For net oxidizing mixtures (O₂/CO ≥ 5), the reaction rate decreases first to values below the mass transfer limiting rate with increasing temperature and, as the reaction temperature is further increased to 650—700 K, the reaction rate increases again.

Figure 8. PM-IRAS spectra as a function of reaction temperature over Pd(100) for various O₂/CO mixtures at initial CO pressure of 8 Torr. O₂/CO ratios are displayed within the top part of each panel, and sample temperatures are marked adjacent of each spectrum. Data from ref 19.

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Figure 8 presents the corresponding PM-IRAS spectra acquired during the experiments shown in Figure 7. In all cases, the spectra acquired prior to the rollover points show ν\textsubscript{CO} with frequencies higher than ∼1960 cm\textsuperscript{-1} consistent with the CO coverages being higher than ∼0.6 ML\textsuperscript{10}. Under such reaction conditions, the CO\textsubscript{2} formation rate is determined entirely by CO desorption. Indeed, the activation energy for the reaction measured in this regime is very close to the CO desorption energy. Spectra acquired immediately after the rollover points, however, depend critically on the O\textsubscript{2}/CO ratio. For reactants with O\textsubscript{2}/CO ratios \textlesssim 2, no CO species are detected after the rollover points. For reactants with O\textsubscript{2}/CO ratios \textgtrsim 5, however, following the rollover of the rate, CO species appear with vibrational frequencies at 2142 and 2087 cm\textsuperscript{-1}. For 10/1 mixtures, the 2142 cm\textsuperscript{-1} feature blue-shifts slightly at 550 and 575 K. It is noteworthy that the appearance of these new CO species shows that the Pd surface has been oxidized. Moreover, the CO\textsubscript{2} formation rate decreases to a value below the mass transfer limiting rate in the temperature range where the oxides are formed and increases back to the mass transfer limiting rate at higher temperatures where these oxides dissociate. Identical experiments were also performed over Pd(111) and Pd(110) surfaces and the results obtained were essentially identical; in particular, the 2142 and 2087 cm\textsuperscript{-1} features also form at high O\textsubscript{2}/CO ratios, demonstrating that a common oxide surface is involved.

During the high pressure experiments described above, it was difficult to spectroscopically monitor the CO surface species within the hyperactive regime primarily because this regime only exists transiently. In order to monitor the rather short duration of this regime, continuous infrared scans were carried out near the rollover point with each spectrum acquired by superimposing only five scans (total collection time ∼5.3 s) over a Pd(100) sample exposed to an O\textsubscript{2}/CO (10/1) mixture at 500 K. This is the shortest acquisition time that can provide a spectrum with reasonable quality. Figure 9a displays a portion of the spectra near the hyperactive state which clearly shows three distinct regimes: (A), (B), and (C). Figure 9b plots the integrated CO peak areas and are presented the reaction rates (TOF) in each regime is displayed. Data from ref 19.

Figure 9. (a) PM-IRAS spectra around the hyperactive region and (b) areas of CO PM-IRAS signals at 1980 (■), 2087 (●), and 2140 (▲) cm\textsuperscript{-1} as a function of reaction time. Initial reactant is an O\textsubscript{2}/CO (10/1) mixture at P\textsubscript{CO} = 2 Torr and reaction is carried out at 500 K. The reaction is divided into three regimes (see text), and the reaction rate (TOF) in each regime is displayed. Data from ref 19.

Figure 10. Arrhenius plots of CO\textsubscript{2} formation of 1/2 (■), 1/1 (●), 2/1 (▲), 5/1 (▼), and 10/1 (●) O\textsubscript{2}/CO mixtures over Pt(110) at initial CO pressure of 8 Torr. The transient reaction rate jump is highlighted with arrows. Data from ref 19.

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regime at low pressures where the CO coverage is close to zero while the surface oxygen remains chemisorbed; and (2) an oxidized sample has much lower reactivity than a CO-uninhibited metallic sample.

### 3.4. Elevated Pressure Kinetics and PM-IRAS over Pt(110)

Similar high pressure experiments were also carried out on Pt(110). Figure 10 displays Arrhenius plots of reactions carried out with gas reactants of various O₂/CO ratios with an initial CO pressure of 8 Torr. As seen previously, three reaction regimes are evident. However, for Pt(110), there is no apparent variation of the CO₂ formation rate within the mass transfer limited regime. Figure 11 plots the corresponding PM-IRAS spectra. Clearly, the surfaces are CO-covered within the low-temperature regime, while no CO species are found within the second and third regimes. In other words, the PM-IRAS data provide no evidence for the oxidation of Pt; that is, no CO species associated with Pt oxides are detected. Finally, experiments were carried out using reactants with an O₂/CO ratio equal to ~35/1 and an O₂ pressure of ~0.5 bar, conditions very similar to those used by Frenken and Hendriksen. At a reaction temperature of 425 K, the temperature at which the authors claimed to discover the “superior oxide reactivity”, our results show that the Pt(110) sample is fully covered by CO and the reaction rate is barely measurable. This reaction condition could be maintained for hours of operation. Only when the sample is carefully heated to 480 K do the second and third reaction regimes appear (Figure 12). Because the CO component is so dilute in the reactant mixture, only ~1 K increase of the sample temperature during the second regime is evident, and the reaction rate is only slightly higher than the third regime, that is, the mass transfer limited regime. Moreover, during the second and third regimes, no surface CO species is detectable; that is, there is no evidence for oxidation of Pt under these conditions.

### 3.5. General Trends from Low to near Atmospheric Pressures

Shown in Figures 13(a) and (b) are reaction rates of O₂/CO (1/2) mixtures over Pd(100) and O₂/CO (1/1) mixtures over Rh(111) plotted in Arrhenius form over a wide pressure range. CO fluxes (impinging CO molecules per surface site per second), shown as the horizontal dashed lines in the figures, were calculated using the Hertz-Knudsen equation. These lines represent the maximum CO₂ formation rate at a given CO pressure. Several trends become apparent upon examination of these figures. First, over the entire range of pressures, there exists a CO-inhibited regime at lower temperatures for each pressure. In the CO-inhibited regime at higher pressures, the reaction

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**Figure 11.** PM-IRAS spectra as a function of reaction temperature over Pt(110) for various O₂/CO mixtures at an initial CO pressure of 8 Torr. O₂/CO ratios are displayed within the top part of each panel, and sample temperatures are marked adjacent to each spectrum. Data from ref 19.
activation energy, $E_a$, at CO pressures of 1 Torr and above is $\sim 110$ kJ/mol, a value close to the desorption activation energy of CO, which under these conditions is rate limiting for reaction.1,33,34 These data are consistent with behavior observed in these previous studies and show that, under these conditions, the surface is dominated by CO, with a correspondingly low oxygen coverage due to adsorption/dissociation inhibition of O$_2$. Similar behavior has been observed recently in our laboratory for Rh/SiO$_2$ supported model catalysts, which show a CO-inhibited regime ($E_a \sim 110$ kJ/mol) at elevated pressures and under similar O$_2$/CO conditions.35,36 At lower pressures, the reaction activation energies within the CO-inhibited regime deviate slightly from 110 kJ/mol, indicating a subtle CO$_2$ and O$_2$ interaction, which has been observed previously in low pressure studies.10 Nonetheless, the surface reaction on Pd, Rh and Pt under these conditions is inhibited by CO and a general trend follows as the total pressure rises.

Second, the low pressure measurements show a pronounced rollover in the reactivity measurements at each pressure. For each catalyst studied, a higher reaction temperature is required to reach the rollover point with an increase in the total pressure. This rollover is related directly to CO inhibition of the reaction; that is, as the reactant CO pressure is increased, a higher temperature is required to lower the CO surface coverage to achieve a reactive, CO-uninhibited sample. In this latter regime, the reaction rate decreases with increasing temperature due to decreased residence times of the reactants. For Rh(111), O-inhibition is also pronounced. This general trend predicts that if mass and heat transfer limitations are successfully removed, elevated pressure kinetics in the CO-uninhibited regime follows an identical behavior; that is, the highest reaction rate occurs on a surface with low coverages of CO and high coverages of chemisorbed oxygen. Both an increase in the reaction temperature and oxide formation inhibits CO$_2$ formation.

Recently, Gustafson and co-workers37,38 studied CO oxidation at elevated pressures on Rh(100) and (111) surfaces using surface XRD and reaction rate measurements. In both studies, the authors discovered that an increase of the CO$_2$ production coincides with the formation of a thin RhO$_2$ surface oxide film, and argued that the trilayer oxide is highly active in CO oxidation. Based on the above discussion, this conclusion is invalid. In the present study, we show an almost identical behavior of Pt, Pd, and Rh in CO oxidation. It is also well-known that these three metals behave very differently toward oxidation. This suggests that an oxide phase is insignificant in CO$_2$ formation. The more logical explanation is simply that high CO$_2$ production results from the removal of CO-inhibition, rather than surface oxide formation. The metal surface, no longer “protected” by CO, is highly reactive such that the O$_2$/CO ratio near the surface quickly increases (i.e., CO becomes that mass transfer limited species) and the surface oxidizes. This trend is shown definitively in Figure 9. The

![Figure 12](image-url)

**Figure 12.** Gas pressure (upper panel) and sample temperature (bottom panel) versus reaction time over Pt(110). The initial O$_2$/CO ratio is $\sim 35/1$, and the total pressure is $\sim 403$ Torr. Note that there are three distinct regimes (see text) and the reaction rate (TOF) in each regime is displayed. Data from ref 19.

![Figure 13](image-url)

**Figure 13.** (a) CO$_2$ formation rate over Pd(100) from low ($10^{-8}$ Torr) to high (8 Torr) CO pressures as a function of reaction temperature. Reactant is an O$_2$/CO (1/2) gas mixture. Dashed lines represent CO flux at given pressure calculated using the Hertz–Knudsen equation. Data from ref 19. (b) CO$_2$ formation rate over Rh(111) from low ($10^{-8}$ Torr) to high (1 Torr) CO pressures as a function of reaction temperature. Reactant is an O$_2$/CO (1/1) gas mixture. Dashed lines represent CO flux at given pressure calculated using the Hertz–Knudsen equation. Data from ref 18.
formation of a surface oxide (rather than a bulk oxide) can be viewed as an indication of incomplete oxidation of the metal surface where the surface oxide coexists with the bare metal. This follows since O₂ adsorption and its dissociation probability in the CO-uninhibited regime cannot be higher on any oxide phase than on a metal surface (see eq 6).

3.6. Elevated Pressure Kinetics and PM-IRAS over Ru-(0001). Ru has long been known to be an exception of the Pt-group metals toward CO oxidation. Notably, Ru(0001) has been found to be the least reactive under UHV conditions, yet becomes highly active at near-atmospheric pressures and relatively low temperatures. This characteristic has long been referred to as an example of the “pressure gap” in heterogeneous catalysis. This behavior can be understood by the following reasoning. (1) The binding energy of CO with Ru is similar to that of other Pt-group metals so this property is not the main cause of the different reactivity behavior. (2) The binding energies of O with these surfaces, represented by the O₂ adsorption energies, do show a marked difference between Ru and the other noble metals, that is, Ru (334 kJ/mol) > Rh (234 kJ/mol) > Pd (230 kJ/mol) > Pt (180 kJ/mol). It is inferred from this trend that oxygen is the main cause of the reactivity differences. (3) The oxygen coverage must be high enough in order to decrease its binding energy. However, the oxygen coverage never exceeds 0.5 ML on Ru(0001) from dosing molecular oxygen at UHV conditions, consistent with the low reactivity of Ru(0001). In contrast, for a step-rich Ru(010) sample, the oxygen coverage does increase substantially at the step sites and such a surface does show reactivity at UHV conditions. (4) The oxygen coverage increases to ~1 ML on Ru(0001) at near-atmospheric pressures under typical CO oxidation conditions. It is important to note that this simultaneously causes (i) substantial reduction of the oxygen binding with the surface and (ii) the complete removal of CO-inhibition. In other words, a CO-uninhibited state is achieved at much lower temperatures on Ru than other Pt-group metals, rendering it “highly reactive” under certain reaction conditions while other metals are still completely inhibited by CO. It is noteworthy that Ru is not always more reactive than other Pt-group metals at elevated pressures. When other Pt-metals reach their CO-uninhibited states, they are much more reactive than Ru. In fact, under typical reaction conditions shown above, reaction on Rh, Pd, and Pt can become mass transfer limited (Figures 5, 7, and 10) while this has never been found on Ru. Again this is understood by the (still) higher oxygen binding energy and less availability of CO adsorption sites on Ru.

Figure 14. (a) CO₂ formation rate (TOF) as a function of reaction time over a preformed RuO₂(110) sample. CO (8 Torr) and O₂ (4 Torr) were used as the reactants. Reaction was carried out using the entire UHV chamber (61.6 L) as the reactor. Each rate point is the average of 10 min of reaction at each temperature, derived from the pressure change of the gas phase. The reaction was repeated five times using the same sample. Different symbols represent data obtained in different runs. RuO₂(110) was formed by reacting ~1.5 × 10⁻⁸ L of O₂ with Ru(0001) at 700 K. (b) Auger spectra of the as-formed RuO₂(110) sample (top), after the second run (middle), and after the fifth run (bottom). All spectra were taken after briefly annealing the sample to 600 K in UHV to remove volatile species. The corresponding oxygen coverage is marked adjacent to each spectrum. Data from ref 20.

In recent years, Over and co-workers have claimed to bridge the pressure gap by invoking RuO₂, most notably RuO₂(110) grown on Ru(0001), as the active phase under both UHV and elevated pressures. This, unfortunately, is not the case. First of all, there is ample evidence that this phase either cannot form or is not stable under many reaction conditions. Second, the CO binding energy on this phase is ~130 kJ/mol, very similar to the
CO binding energies on any other Pt-group metals. This implies that, even if this phase were stable, under conditions that other Pt-group metals are CO-inhibited, this phase will be equally CO-inhibited and cannot be “highly reactive”. However, one cannot generalize this behavior to oxides of other Pt-group metals. In the following experiments, these points are verified using a preformed RuO$_2$(110) sample.

Figure 14a displays the CO$_2$ formation rate at various temperatures over a preformed RuO$_2$(110) sample by reacting 1.5 × 10$^6$ L of O$_2$ with Ru(0001) at 700 K. During the experiment, RuO$_2$ is exposed to O$_2$/CO (1/2) mixture at $P_{CO} = 8$ Torr and then stepwise annealed from 400 to 650 K. The sample is kept at each reaction temperature for 10 min. The entire UHV chamber was used as the batch reactor, and the reactant was evacuated and replenished once the CO conversion reached ∼10%. The reaction was repeated five times using the same sample; that is, the sample was cooled to 400 K following the previous run to begin the next reaction. Between 400 and 600 K, the sample exhibits the lowest reactivity (TOF) during the first run. The reactivity increases considerably during the second run and further increases and stabilizes during subsequent runs. Above 600 K, a general trend is not found but the reactivity at 650 K during the first run is substantially higher than subsequent runs. Since the oxygen coverage is still above 1 ML, the surface consists of a nonstoichiometric surface oxide. Following the fifth run, the oxygen coverage has dropped to ∼0.84 ML, where the oxide species has disappeared and the sample is now covered with chemisorbed oxygen. These results reveal two important points for reactivity under stoichiometric reaction conditions between ∼400 and ∼600 K: (1) the chemisorbed oxygen phase displays higher reactivity than RuO$_2$ while a surface oxide has reactivity that lies in between; and (2) chemisorbed oxygen is the thermodynamically stable phase under these reaction conditions.

The reactivity difference between the chemisorbed oxygen and RuO$_2$ phases can be rationalized in terms of the CO binding strength of the two surfaces, obtained qualitatively by concurrent PM-IRAS measurements shown in Figure 15. As shown in the first run, the as-formed RuO$_2$ surface adsorbs CO to form two strong bands at 2130 and 2086 cm$^{-1}$. The signal intensity of these two features remains relatively unchanged up to 575 K. At higher temperatures, the 2130 cm$^{-1}$ feature disappears faster than the 2086 cm$^{-1}$ feature, with the latter being detectable as high as 650 K. Clearly, these spectra are consistent with the high binding energy of CO (∼130 kJ/mol) with an oxide surface. During the second and third runs, very similar spectra are obtained. However, at each specific temperature, the signal intensity is substantially reduced compared with the first run, indicating reduced CO binding with the surface. As has been shown in Figure 14b, by the end of the second run, the RuO$_2$ surface is already converted to a chemisorbed surface oxide. Conversion from a surface oxide to a chemisorbed oxygen phase must have occurred during the third run, since at the beginning of the fourth run a distinct CO feature appears at 2070 cm$^{-1}$. In the meanwhile, the 2024 cm$^{-1}$ signal, seen as a tail during previous runs, becomes better resolved. During the fifth run, the 2086 cm$^{-1}$ feature completely disappears. It is not possible to make precise assignments for the different CO bands. The 2130 cm$^{-1}$ band can be assigned to CO molecules adsorbed next to oxygen while the other lower-frequency features are assigned to CO molecules adsorbed farther away.
from surface oxygen. Nevertheless, the general picture shown in Figure 15 is that CO binds more weakly with the surface as the sample converts from bulk oxide to surface oxide to chemisorbed oxygen. This behavior, coupled with the reactivity data of Figure 14a, demonstrates that the CO binding energy plays a decisive role in CO₂ formation under these reaction conditions. Especially, these experiments demonstrate decisively that, under reaction conditions where other Pt-group metals are CO-inhibited, RuO₂ must also be CO-inhibited. In contrast, Ru surface covered with chemisorbed oxygen is CO-uninhibited and displays higher reactivity.

4. Summary

Recent investigations of CO oxidation at elevated pressures using high pressure surface-sensitive techniques have produced new insights and initiated new debates into this well-studied reaction. Recent results in our laboratory, conducted on Pt-group metals (Pd, Pt, Rh, Ru) from UHV to high pressures, suggest that Langmuir–Hinshelwood kinetics can adequately describe reaction kinetics across the pressure range, when mass transfer and oxidation effects are appropriately considered. The most highly active surface at low and high pressures is a CO uninhibited surface containing chemisorbed oxygen. In other words, there appears to be no “pressure gap” with respect to the active mechanism for CO oxidation on Pt-group metals. CO oxidation on Ru surfaces exhibits a more subtle kinetic picture. Under most relevant reaction conditions, a chemisorbed oxygen surface is the thermodynamically most stable phase and the most active phase for CO oxidation. These results indicate that the differences in Ru reactivity at high and low pressure can be understood in terms of CO and oxygen binding; thus, like Pd, Pt, and Rh, there exists no “pressure gap” for Ru surfaces.

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