CO oxidation trends on Pt-group metals from ultrahigh vacuum to near atmospheric pressures: A combined in situ PM-IRAS and reaction kinetics study


Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842-3012, United States

**Abstract**

The CO oxidation reaction on Pt-group metals (Pt, Rh, and Pd) has been investigated at low (<10^{-3} Torr) and near atmospheric (1–10^2 Torr) pressures in a batch reactor under steady-state conditions and at various gaseous reactant compositions using PM-IRAS and kinetic measurements. The results indicate that Langmuir–Hinshelwood kinetics adequately provides a general description of the kinetic trends over a wide range of pressures provided that mass transfer effects are considered. At high pressures, the reaction kinetics fall into three regimes: a CO-inhibited low temperature regime where the reaction rate is determined by CO desorption; a mass transfer limited regime at high temperatures; and a transient, high-rate regime which lies in between the other two regimes. The data show that the most reactive surface phase, at both low and high pressures, is a CO-uninhibited phase. This surface phase is not an oxide phase, but a surface phase that contains primarily chemisorbed atomic oxygen and a low coverage of CO.

© 2008 Elsevier B.V. All rights reserved.

**1. Introduction**

CO oxidation on Pt-group metals is one of the most extensively investigated surface reactions. The reaction mechanism is generally accepted to follow a Langmuir–Hinshelwood (LH) mechanism where a surface reaction occurs between chemisorbed CO and atomic oxygen, with CO2 leaving the surface immediately upon formation [1]. This reaction generally displays two regimes: a low reaction rate regime on CO-rich surfaces and a higher reactivity regime on CO-uninhibited surfaces. Additionally, traditional ultra-high vacuum (UHV) studies have also revealed that bulk oxides of Pt-group metals are relatively inactive for catalyzing CO oxidation [2]. This conclusion is well-supported by CO titration experiments performed at low pressures where the reactivity of different Pd–O species follows the order: chemisorbed oxygen > surface oxide > bulk oxide [3]. Although, the kinetics of the CO oxidation reaction is well-understood at low pressures, due to the inapplicability at high pressures of most surface-sensitive techniques, a detailed understanding of this reaction at pressures near one atmosphere together with a correlation between the low and high pressure kinetics, are still wanting. Trends observed at low pressures may not extrapolate to high pressures given the high level of complexity of transient phases that can exist at the conditions of working catalysts.

In recent years surface-sensitive techniques applicable at high pressures (e.g., scanning tunneling microscopy (STM) and sum-frequency generation spectroscopy (SFG)) have provided fundamental insights and prompted new questions regarding CO oxidation under realistic reaction conditions. For example, using SFG, Su et al. [4] found that on Pt(111) near atmospheric conditions the reaction rate is linearly proportional to the surface coverage of CO adsorbed at nonregistry or defect (or distorted) surface sites. These results led the authors to conclude that these special sites are the sites onto which the active CO species is bonded. This proposal, however, has been controversial since these “new” CO species have been suggested to arise from water contamination [5]. Frenken and coworkers used in situ STM coupled with a high-pressure flow reactor to investigate CO oxidation on Pt(110) and Pd(100) surfaces at atmospheric pressures [6,7]. These authors proposed that the formation of a surface oxide (based on topographic change of the sample surface during reaction) has a dramatic and beneficial effect on the CO2 production rate. Accordingly these researchers concluded that an oxide surface exhibits a superior reactivity for CO oxidation compared with a reduced surface. The authors further proposed that the reaction no longer obeys the LH mechanism at high pressures but instead follows the so-called Mars–Van Krevelen redox mechanism. More recently, surface X-ray diffraction (SXRD) has been used by the same authors to confirm the formation of oxide phases at high CO2 formation rate conditions [8,9]. Very recently, Gustafson et al. studied high-pressure CO oxidation over Rh(111) and (100) with identical approaches, i.e. SXRD coupled with reaction kinetics measurements, and found that at high O2/CO ratio conditions, a high CO2 formation rate occurs concurrently with the appearance of a surface oxide species [10]. Collectively these studies have challenged our understanding of CO oxidation.
We have found recently that within the high reaction rate regime at high pressures, under appropriate reaction conditions, the reaction rate can reach several thousand CO\textsubscript{2} molecules per second on model Pd and Pt catalysts [11]. These so-called “hyperactive” surfaces contain a relatively high (>0.1 ML) oxygen coverage and a relatively low (<0.1 ML) CO coverage. These recent studies under realistic conditions have raised questions that we hope to help clarify in the present studies. First, can Langmuir–Hinshelwood kinetics adequately describe CO oxidation kinetics at low and high pressures? Secondly, what is the nature of the most reactive oxygen phase at high pressures, chemisorbed oxygen or an oxide?

2. Experimental section

The experimental apparatus used for the polarization-modulated infrared absorbance spectroscopy (PM-IRAS) and reaction kinetics measurements has been described in detail previously [11]. Briefly, the apparatus consists of: (1) a UHV section equipped with Auger spectroscopy (AES), low energy electron diffraction (LEED), and UTI 100 mass spectrometer (for low pressure kinetic measurements), and (2) a high pressure reaction cell for high pressure kinetic/PM-IRAS measurements. Low pressure kinetic measurements ($P < 10^{-3}$ Torr) were carried out under steady state conditions by backfilling the UHV chamber with the desired gas mixture and monitoring the CO\textsubscript{2} and CO mass spectrometer signals (correcting for fragmentation). High pressure kinetic measurements ($10^{-3} - 10^{2}$ Torr) were conducted in a batch reactor mode using a method described previously [11]. In this study, reaction rates were calculated from the pressure change of the gas phase as measured with a Baratron gauge (based on loss of gas volume following a stoichiometric reaction). Uncertainties associated with the pressure change measurements (and hence the calculated TOF values) are estimated to be approximately ±5%. Single crystal samples (Pt, Pd, and Rh) were cleaned with standard procedures, and their cleanliness verified by AES. PM-IRAS allows for infrared measurements during reaction across the low to high pressure regimes studied.

3. Results and discussion

3.1. Low pressure and high pressure–low temperature regime

In Fig. 1a the reaction rates of O\textsubscript{2}/CO (1/2) mixtures on a Pd(100) surface over a wide CO pressure range ($P_{CO} = 10^{-8} - 8$ Torr) are displayed as Arrhenius plots. Similar data and trends were observed on Pt [12] and Rh [13] surfaces; hence, Pd will provide a suitable example for a broader discussion of the three Pt-group metals studied. The CO flux (the horizontal dashed lines) for each pressure was calculated using the Hertz–Knudsen equation [14]. Several trends become apparent upon examination of Fig. 1a. 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 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 [15,16]. These data are consistent with behavior observed in previous studies [15,16] and show that, under these conditions, the surface is dominated by CO, with a correspondingly low oxygen coverage due to adsorption/dissociation of O\textsubscript{2}. Similar behavior has been observed recently in our laboratory for Rh/SiO\textsubscript{2} supported model catalysts, which show a CO-inhibited regime ($E_a \sim 110$ kJ/mol) at elevated pressures and under similar O\textsubscript{2}/CO conditions [17]. At lower pressures, the reaction activation energies within the CO-inhibited regime deviate slightly from 110 kJ/mol, indicating a subtle CO\textsubscript{ads} and O\textsubscript{ads} interaction, which has been observed previously in low pressure studies [2]. Nonetheless, the surface reaction on Pd under these conditions is inhibited by CO as has been observed on Pt [12] and Rh [13] single crystal surfaces.

Secondly, 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, i.e. as the reactant CO pressure is increased, a higher temperature is required to lower the CO surface coverage to achieve a reactive, CO-uninhibi-
ingly low, over the entire pressure range (10^{-8} - 10^{-3} Torr) during the CO oxidation reaction. Shown in Fig. 2b are CO reaction probabilities estimated from the kinetic data; these reaction probabilities were calculated by dividing the measured TOF by the CO flux to the sample at the specific pressure. Taken together these data illustrate several key points. For a given reactant pressure, as the CO PM-IRAS integrated intensity decreases, the CO reaction probability increases for all pressure ranges shown; in other words, CO inhibits CO_2 formation. Also apparent from the data is that higher temperatures are required to remove CO from the surface at higher pressures, i.e. higher temperatures are required to achieve a reactive, CO-uninhibited surface. Finally, these data reveal that the highest reaction rate (peak rollover point) is achieved at that point where the CO IRAS signal becomes exeedingly low, over the entire pressure range (10^{-8} - 10^{-3} Torr). In an ideal Langmuir–Hinshelwood case, a simple reaction rate law of the form \( r = kC_OC_O \), in principle, can be used to describe the reaction kinetics. This simplified rate law predicts a maximum rate at that point at which the CO and O coverages are approximately equal. However, for Pd and Pt surfaces, other researchers [18,19] and we [20] have found that the actual surface condition for optimum CO oxidation is not as ideally predicted. The CO_2 formation maximum \( (R_{\text{max}}) \) typically occurs at that point where the CO coverage is very low. The same behavior is also found for Rh surfaces at very low pressures [21,22]. Our low pressure findings then are consistent with previous studies in the literature. Low CO coverages allow for facile O_2 adsorption and dissociation which, in turn, facilitate reaction. Fig. 3 displays CO PM-IRAS data for a O_2/CO mixture of 0.5 as a function of temperature, for four of the reaction pressures used in Figs. 1 and 2. The PM-IRAS data illustrate that as the temperature is increased and the rollover point approached, the CO coverage decreases with a concomitant red-shift in the CO stretching frequency. Further, as the CO integrated area approaches zero (and hence approaches the most reactive surface), no vibrational frequencies associated with CO near O adatoms are observed (for Pd, \( \nu_{\text{CO}} > 2087 \text{ cm}^{-1} \), i.e. there is no evidence for a large surface concentration of O atoms. This key point, i.e. the surface with the highest reactivity is one with a negligible CO coverage, will be revisited during further discussion of the high pressure data. Note that similar trends have been observed for Pt [12] and Rh [13] surfaces.

Finally, for the low pressure measurements, Fig. 4 presents data which highlights the CO oxidation kinetic behavior as a function of temperature. Displayed in Fig. 4 are reactivity measurements (on a per surface area basis) on Pd, Rh, and Pt surfaces for a O_2/CO (1/1) mixture at P_{CO} \sim 10^{-6} Torr. These data illustrate that as the reaction temperature is increased, the steady-state reaction rate over the different metal surfaces first peaks then slowly decreases; this peak temperature is different for the various metals (Rh < Pd < Pt). As discussed above, the peaks in the reactivity correspond to rollover points where the reaction conditions produce low CO coverages on the surface. These data show, however, that CO inhibition occurs on the different metal surfaces at different temperatures. Since the CO binding energy is similar on Pt, Pd, and Rh surfaces [2], this reaction inhibition is attributed to oxygen inhibition on the surfaces, as has been observed previously on Rh at low pressure [23] and in CO titration measurements on Rh [24]. Furthermore, this argument is readily extended to unsupported [3] and supported [25] Pd model catalysts. Subsequently we will show that this behavior can also be extended to high pressures and that the order of the inhibition effect correlates with the oxygen adsorption energies on each of the catalytic surfaces.

### 3.2. High pressure–high temperature regime

Having discussed the general reaction behavior at low pressures and within the CO inhibited regime at high pressures, we now focus on the reactivity data at high pressures and temperatures. As the data in Fig. 1a demonstrate, as the pressure is increased from low to high (P_{CO} = 8 Torr), the rollover points in the kinetic data appear to “flatten” at TOF’s exceeding \sim 100, becoming invariant with temperature at high temperatures and pressures. This behavior is common to the Pt-group metals (Pt, Rh, and Pd) [12,13]. In addition, the CO reaction probability (the ratio of the TOF to the CO flux at a given pressure) decreases with an increase in the pressure. This is most evident in Fig. 1b, which shows the CO reaction probabilities taken from Fig. 1a for several temperatures as a function of the total pressure. For each temperature, it is clear that as the pressure is increased above \( P \sim 10^{-6} \text{ Torr} \) at temperatures \( >550 \text{ K} \), the CO reaction probability begins to decrease with increasing pressure. The CO reaction probabilities drop from a value of \sim 40\% at \( P_{CO} < 10^{-4} \text{ Torr} \) to \sim 1\% at \( P_{CO} > 1 \text{ Torr} \). This effect is due primarily to mass transfer limitations which become important at elevated pressures, i.e. \( P_{T} = 10^{-3} \text{ Torr} \). As the mean free path of the reactants becomes progressively smaller with an increase in the pressure, the resistance to gas-phase transport increases. Note that the onset of this effect is apparent in Fig. 2, i.e. the CO reaction probabilities at \( P_{CO} = 10^{-3} \text{ Torr} \) are noticeably lower than the corresponding values at \( P_{CO} \leq 10^{-4} \text{ Torr} \). Thus, mass transfer effects, a phenomenon which unfortunately has been neglected in many previous kinetic studies at elevated pressures, can become an important factor in defining the kinetic behavior at high pressures and temperatures.

Fig. 5 shows additional kinetic data for probing deeper into the kinetics at elevated pressures. Shown in Fig. 5 are kinetic data
obtained from Pt(110) and Pd(100) surfaces at various O2/CO ratios (10–0.5) and at \( P_{\text{CO}} = 8 \) Torr. Similar data and general trends were observed on Rh surfaces\[13\], so that the following Pt(110) and Pd(100) discussion is consistent with all surfaces studied.

The data show three primary regimes for reaction at higher pressures: first, at lower temperatures, there is a CO-inhibited regime which increases with temperature. This is the regime discussed in Section 3.1, whose activation energy is \( E_a = 110 \) kJ/mol (CO binding energy) on the Pt, Pd, and Rh surfaces. As the temperature is increased in this regime, the TOF increases until a short lived, "jump" in reactivity is observed (denoted by the arrows in the reactivity data of Fig. 5). This "jump" in reactivity has been described in a recent study in our laboratory\[11\], and is a transient reaction regime where the TOF can reach values of several thousand CO2 molecules per site per second. CO PM-IRAS spectra near the jump show a rapid decrease in the CO IRAS stretching feature before and after the jump point. However, this transient reactive phase is short lived, as it is limited by mass transfer of the reactants within the boundary layer above the sample surface. If the mass transfer limit can be circumvented, then this transient phase should be more protracted, behavior which indeed has been experimentally observed (not shown here). For example, high pressure

\[ P_{\text{CO}} = 1 \times 10^{-5} \text{ Torr} \]

\[ P_{\text{CO}} = 1 \times 10^{-6} \text{ Torr} \]

\[ P_{\text{CO}} = 1 \times 10^{-7} \text{ Torr} \]

\[ P_{\text{CO}} = 8 \text{ Torr} \]

Fig. 3. CO PM-IRAS as a function of reaction temperature for O2/CO (1/2) mixtures at various CO pressures over Pd(100).

Fig. 4. CO2 formation rate over Rh(111) (■), Pd(100) (●), Pd(111) (▲), Pd(110) (▼), and Pt(110) (★) as a function of reaction temperature. Reactant is an O2/CO (1/1) mixture at CO pressure of \( 1 \times 10^{-6} \) Torr.
experiments conducted over Pd(100) using the entire chamber (UHV section (~61.6 L) plus the high pressure cell (~0.6 L) show identical kinetics below the jump point compared with the kinetics observed in experiments using the high pressure cell volume alone. However, at the jump point the transient regime in the (UHV section plus the high pressure cell) experiment is sustained for a much longer period of time due to the increased volume of the reactants and enhanced reactant stirring due to thermal convection. Similar results have been observed by Su et. al. over Pt(1 1 1) [4]. Thus, this “jump” is likely associated with a highly reactive surface which rapidly consumes reactants in the near surface region of the catalyst, thereby causing limitation of reactivity to the transport of reactants to the surface from the bulk gas phase. Under highly oxidizing conditions (O2/CO > 5), Rh and Pd surfaces begin to show decreases in reactivity at higher temperatures, likely due to reaction inhibition due to the formation of bulk oxide. At these points, reactivity over the oxide surface is decreased below the mass transfer limit due to sample oxidation. At low pressures, it has generally been shown that an oxide displays much lower reactivity for CO oxidation [2,3]. At elevated pressures, lower reactivity has also been observed on oxide and oxygen-rich Pt-group metal surfaces in previous kinetic studies [15,16]. Similar deactivation has also been observed in our laboratories in recent kinetic measurements on Rh/SiO2 model catalyst samples, which show rapid deactivation at high temperatures and high O2/CO ratios, presumably due to particle oxidation effects [17].

Thus, in summary, these data demonstrate that at reactant pressures approaching one atmosphere, there exist three distinct phases for reaction: (1) a CO inhibited phase, where the reactivity is limited by CO desorption; (2) a highly reactive transient phase, which consists of a CO-uninhibited surface whose upper rate is limited by mass transfer (due to depletion of reactants in the boundary layer); and (3) a high temperature, mass transfer limited phase where reaction is limited by transport of reactants from the gas phase to the near surface region. This results in a temperature invariant reaction rate for mildly oxidizing conditions; however, for Rh and Pd surfaces, a decrease in reactivity for highly oxidizing conditions can result at high temperatures, likely due to oxidation induced deactivation of the sample.
3.3. Nature of the reactive surface near the jump point at high pressures and high temperatures

Finally, we turn our attention to the nature of the reactive surface near the jump point in the data of Fig. 5. As discussed in the low pressure data (Section 3.1), the most reactive surface at lower pressures is a surface with low to undetectable amounts of CO (as determined by PM-IRAS). However, the nature of the most reactive surface at higher pressures has been a subject of recent debate [6–11], with some researchers proposing that the most reactive surface corresponds to an oxide phase. Shown at the bottom of Fig. 5a and b are representative CO PM-IRAS spectra acquired before (T ~ 525 K) and after (T ~ 550 K) the jump point for the (5/1) O2/CO mixture over the Pt(110) and Pd(100) surfaces, respectively. As the data illustrate for Pt(110), the CO PM-IRAS signal attenuates rapidly from “before” to “after” the jump point, with no evidence for any oxygen-shifted CO PM-IRAS stretching features. Similar behavior is observed for PM-IRAS spectra obtained for all the jump points in the Pt(110) data. For Pd and Rh surfaces, similar results are observed for mildly oxidizing conditions (O2/CO < 2); i.e. before and after the jump point, the CO PM-IRAS signal rapidly falls to zero, with no evidence for IR stretching frequencies associated with CO near O atoms. For more oxidizing conditions, such as those shown at the bottom of Fig. 5b for Pd(100), (O2/CO > 5), the CO stretching frequencies (νCO > ~2087 cm⁻¹) associated with neighboring O species are observed after the jump, although CO stretching features typical of the reduced surface are observed prior to the jump. XPS studies conducted in our laboratory for Rh(111) (to be discussed in an upcoming publication [13]) demonstrate that the typical CO PM-IRAS stretching features observed near the jump point are associated with oxygen coverages no higher than ~0.5 ML, whereas higher νCO stretching frequencies are associated with oxygen coverages approaching ~1 ML. These data strongly suggest that similar to low pressures, the most reactive surfaces (surface approaching the jump point) at high pressures are those surfaces with low to undetectable CO coverage and O coverages below those characteristic of an oxide phase.

4. Conclusions

In summary, PM-IRAS and kinetic measurements of CO oxidation over Pt-group metals (Rh, Pt, and Pd) have been conducted over a wide pressure range (10⁻⁸–10⁻⁴ Torr). Overall these results suggest that Langmuir–Hinshelwood kinetics adequately provide a general description of kinetic trends over a wide range of pressures, as long as mass transfer effects are appropriately considered. Within the low and high pressure regimes, low temperature reactivity is CO-inhibited and dictated by CO desorption (E ~ 110 kJ/mol). At both low and high pressures, the data suggest that the most reactive surface phase is a CO-uninhibited phase (not an oxide phase) containing low to undetectable amounts of CO plus a chemisorbed oxygen phase. However at high pressures and high temperatures, mass transfer limitations become important and must be considered when interpreting kinetic data. At low pressures, reactivity at higher temperatures is affected by oxygen inhibition. At higher pressures, reactivity at higher temperatures can become inhibited by both oxygen inhibition (oxidation at sufficiently high O2/CO ratios) and mass transfer limitations.

Acknowledgments

We gratefully acknowledge the support for this work by the Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences under Grant No. DE-FG02-95ER14511 and the Robert A. Welch Foundation.

References