

High-Pressure CO Oxidation on Pt(111) Monitored with Infrared–Visible Sum Frequency Generation (SFG)

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Abstract: Catalytic CO oxidation on Pt(111) to CO₂ was studied under atmospheric pressures of CO and O₂ and at various temperatures. Surface vibrational spectroscopy by sum frequency generation was used to probe the surface species, while the reaction rate and gas composition were simultaneously monitored by gas chromatography. Correlation between the turnover rates and the surface coverage of various CO species were utilized to identify the active CO species in the reaction. Ignition, above which the reaction becomes self-sustained, divides the reaction into two reactivity regimes. Below ignition, atop bonded CO appears as the major species on the surface, but the reaction rate is inversely proportional to the surface coverage of this species, indicating that it is not the active species but rather an inhibitor. The observed activation energy for the reaction in this regime suggests that desorption of atop CO is the rate-limiting step in the reaction. Above ignition, the atop CO becomes hardly detectable and the activation energy reduces to the one directly associated with the reaction energy barrier between adsorbed CO and O on Pt. In all cases, the reaction rate is linearly proportional to the surface coverage of CO adsorbed at non-registry sites or defect (or distorted) surface sites. They are therefore identified as the active CO species in this surface catalytic reaction.

Introduction

The catalytic oxidation of carbon monoxide to carbon dioxide over platinum group metals has been one of the most widely studied surface reactions since the classic work by Langmuir.¹ This reaction is important for automobile emission control.² The relative simplicity of the process has made it a subject of extensive theoretical and experimental investigation.^{3–6} Many features of this reaction have already been revealed. It has been shown that the reaction proceeds via a Langmuir–Hinshelwood mechanism⁷ (reaction following adsorption of reactants). Under certain conditions, the reaction shows oscillatory behavior, hysteresis, and formation of CO₂ with excess translational and vibrational energy.^{8–11} The metal catalyst surface exhibits structure rearrangements in some range of temperature and reactant pressure.¹²

Ultrahigh vacuum (UHV) studies revealed that thermal excitation of the adsorbed oxygen initiated the reaction.¹³ Different CO₂ desorption peaks were found depending on the adsorption states of the oxygen species. The mobile oxygen atoms on the surface that approach and react with CO molecules are supposedly responsible for the CO₂ production. Infrared (IR) spectroscopic studies showed that atop CO was the major carbon monoxide species present on the surface during the catalytic formation of CO₂ in UHV. Mieher et al.¹⁴ reported that CO₂ production could be induced from coadsorbed CO and O₂ at low temperature (<100 K) by photon irradiation. They suggested that it was due to excited oxygen atoms reacting with adsorbed CO. Campbell et al.⁷ showed that the activation energy of this reaction changed dramatically with change of oxygen coverage. They attributed the change to weakly bonded CO existing above the oxygen adlayer as a reaction precursor.

The same reaction has been studied at higher CO pressures. In situ infrared spectroscopic studies at elevated pressures of 10⁻⁵ Torr found a CO–O complex formed at the perimeter of CO clusters with a size of ~10 Å being an intermediate for CO₂ production in the high-reactivity branch, while CO islands dominated the surface in the low-reactivity branch.¹⁵ Kinetics studies of CO oxidation on Pt(100) were carried out by Berlowitz et al.¹⁶ at elevated pressure between 0.1 and 600 Torr. It was found that the reaction mechanism changed around 500 K, and its dependence on CO pressure changed from 0 to -0.9 order as the temperature increased from 450 to 650 K. Infrared spectroscopic work on supported platinum catalysts at high-pressures¹⁷ revealed that the density of atop CO species oscillated out of phase with the reaction rates.

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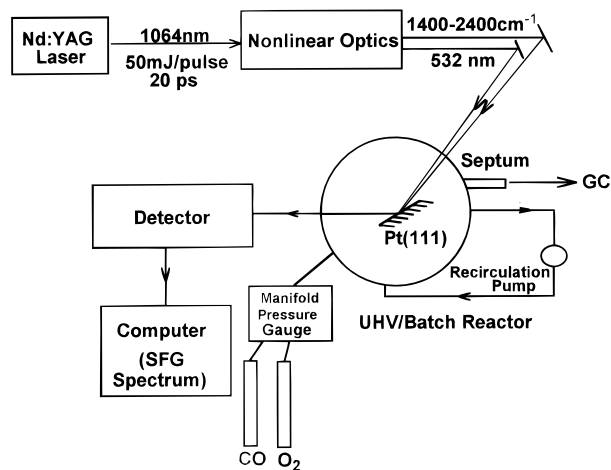


Figure 1. Schematic diagram of the experimental setup for high-pressure surface catalysis studies.

Despite such extensive studies, the picture for the mechanistic steps of this catalytic reaction is still not complete. Especially, the identity and characteristics of the active CO species on the catalyst surface that is converted to CO₂ still remain unclear.

We note that most of the above-cited work was carried out at very low ambient pressures or under UHV. Yet, what is of practical importance is the CO oxidation process under a real atmospheric pressure. To understand the high-pressure catalytic process, it is of great importance to identify surface species present during catalysis under high-pressure. In general, the results of low-pressure studies cannot be extrapolated to high-pressures, and it is difficult for conventional surface techniques to detect surface species under high-pressures. Recently, sum frequency generation (SFG) spectroscopy has been developed as a probe for interfacial studies, especially for studies of interfaces between dense media. It can therefore be readily adopted to overcome the pressure gap and study high-pressure catalytic reactions.

In this paper, we present results on high-pressure catalytic CO oxidation on Pt(111) under near atmospheric pressures and at high temperatures (500–1300 K). The surface species were monitored by SFG spectroscopy while the reaction turnover rate was measured by gas chromatography (GC). Correlations between concentrations of surface species and the production rate of carbon dioxide were found. We showed that the active CO surface species mainly responsible for the CO₂ production both above and below the ignition temperature is not the one adsorbed at atop sites, but those adsorbed at incommensurate or defect sites.

Experimental Section

The experiments were carried out over a Pt(111) single crystal situated in a UHV-batch reactor system, which has been described elsewhere.¹⁹ The schematic diagram of the experimental arrangement is shown in Figure 1. The UHV chamber was pumped by a turbomolecular pump and an ion pump and had a base pressure lower than 1×10^{-10} Torr. The platinum(111) single crystal was cut, oriented, and polished by the normal procedures. It was mounted on a manipulator and could be resistively heated to 1400 K or cooled by flowing liquid nitrogen down to 120 K. The chamber was equipped with a number of surface tools: an ion gun that can be used to sputter-clean the crystal, a mass spectrometer, and a retarding field analyzer

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(RFA) for Auger and LEED. It also had two CaF₂ windows that allow tunable infrared and visible light into the chamber to overlap on the Pt(111) and the SF output to exit.

A passive-active mode locked Nd:YAG laser with a 20 ps pulse width was used as the laser source. A portion of its 1064-nm fundamental beam was frequency-doubled to 532 nm, which was used as the visible input in SFG. The rest of the fundamental beam was sent to pump an optical parametric system that generates an infrared beam tunable between 1100 cm⁻¹–2400 cm⁻¹.¹⁸ The SF output from the Pt crystal was collected by a photonmultiplier and a gated integrator.

The SFG technique has been described in detail previously.^{20–22} Briefly, SFG is a second order nonlinear optical process in which a tunable infrared beam is mixed with a visible beam to generate a sum frequency output. This process is only allowed in the electric dipole approximation in a medium without centrosymmetry. As a result, in the present case of a gas/Pt system, the SFG signal is dominated by contribution from the Pt(111) surface, where inversion symmetry is necessarily broken. Both the surface platinum atoms and the adsorbed molecules should contribute to the SFG output. However, for the CO/Pt(111) case, the signal from the surface platinum atoms is much weaker than that from CO in the CO stretch region.

High-pressure catalysis studies were carried out in a batch reactor, which was converted from the UHV chamber by simply blocking the turbomolecular pump and the ion pump via a gate valve. Gas pressure was measured by a Baratron gauge that can monitor pressure between 100 mTorr and 1000 Torr. The reactant gas mixture was continuously circulated in the system by a recirculation pump, and a septum was used as a sampling port. An HP-5890 series II gas chromatograph (GC) with a column that can separate CO₂ from CO was employed to monitor the gas-phase kinetics.

The platinum sample was cleaned with cycles of argon ion bombardment. The cleanness was checked routinely by Auger analysis. The CO gas was purified by passing it through a liquid-nitrogen-cooled molecular sieve to remove traces of carbonyl contaminants. We have not detected the presence of carbonyls of other transition metals (i.e., Fe or Ni) under any conditions of the experiment reported here. The sample was isolated from the pumps before high-pressure gases were introduced into the reactor; the sample was then resistively heated to a temperature between 500 and 1300 K, at which the turnover rate was high enough for GC measurement at all stages, and the surface SFG spectrum could be taken to probe the surface species present.

Results

(a) High-Pressure CO Chemisorption on Pt(111). High-pressure chemisorption of CO on Pt(111) at 295 K was studied by SFG surface vibrational spectroscopy. The spectra are presented in Figure 2. Under UHV conditions, two CO species were present, giving rise to peaks at 1845 and 2100 cm⁻¹ that can be attributed to CO adsorbed at bridge sites and atop sites, respectively.^{23–26} As expected, the peak at 1845 cm⁻¹ is weak compared to the one at 2100 cm⁻¹, because of the small IR and Raman cross sections and the broad peak width at room temperature for CO at bridge sites.²⁷

Upon raising the CO pressure to 1 Torr, the bridge-bonded CO was no longer observable and the frequency of atop species shifted to 2105 cm⁻¹. This result has also been observed with high CO coverage on Pt(111) in UHV studies.²³ The absence of bridge-bonded CO was now partly due to the lower CO occupancy of the bridge sites and partly due to the weak re-

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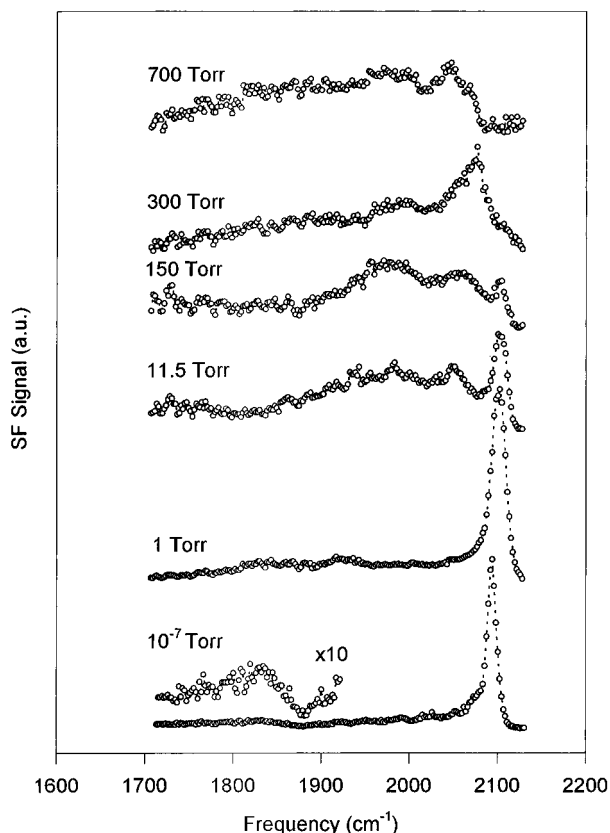


Figure 2. Pressure dependence of SFG spectra of CO on Pt(111) at 295 K under various CO pressure.

sponse of SFG spectroscopy to this species.³³ The frequency shift was the result of enhancement of dipole coupling between adsorbed CO molecules as increasing CO coverage increased their packing density,²⁸ thereby weakening their bonds to the metal.

Further increase of the CO pressure resulted in a decrease of the intensity of the atop CO without further frequency shift or broadening. At the same time, a new peak at 2045 cm^{-1} together with a broad background became visible. At 700 Torr of CO, the spectrum was completely dominated by the new feature and the broad background extended to 1700 cm^{-1} . The spectra were reversible and reproducible with variation of the gas pressure. The reversibility is demonstrated in Figure 3, in which the spectra taken after exposing a clean Pt(111) sample to 10^{-7} Torr of CO, then to 700 Torr, and finally back to 10^{-7} Torr, are presented. The dramatic change of the SFG spectrum with an increase of CO indicated a change in the bonding of the CO surface species. The spectrum can be explained by the reversible formation of an incommensurate overlayer of CO and perhaps also some terminally bonded CO at distorted or defect sites.³⁰ The latter could be multiply bonded carbonyl cluster-like species ($\text{Pt}(\text{CO})_n$, $n > 1$) judging from the similarity of their vibration spectrum to that of platinum carbonyls.³⁵

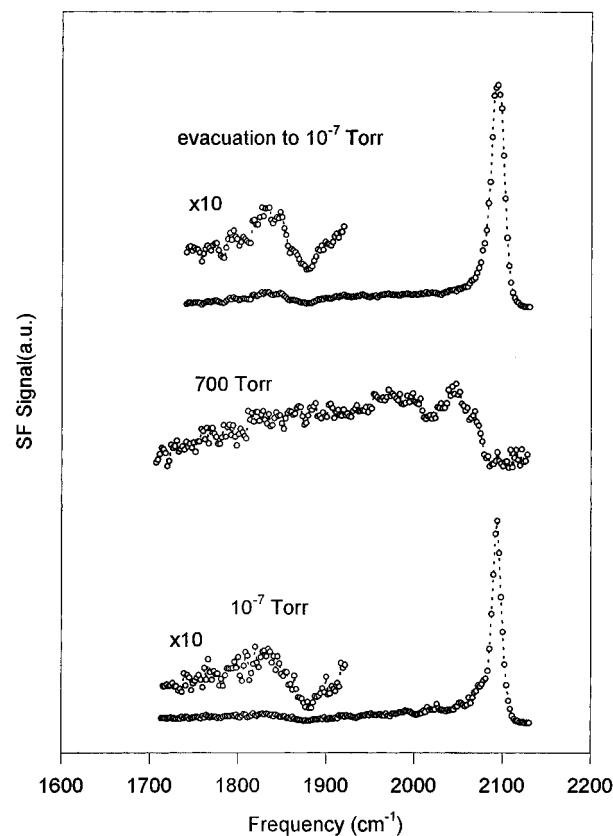


Figure 3. SFG spectra showing the reversibility of CO adsorption on Pt(111).

(b) Temperature Dependence of the SFG Spectrum during High-Pressure CO Oxidation on Pt(111) with Excess CO.

CO oxidation experiments were carried out with reactant gases at a total pressure of a few hundred torr and different compositions of carbon monoxide and oxygen. The gases were mixed in the reactor and the total pressure of the reactor was brought up to 1 atm by adding helium gas. The order in which CO and O_2 were introduced did not influence the results. CO pressure was varied from tens to hundreds of torr. The partial pressure of CO at a given total pressure was an important factor; therefore, the chemistry of the reaction was explored by varying the CO/ O_2 ratios at a given total pressure. The helium gas serves the purpose of regulating the platinum sample temperature during the reaction.

The *in situ* SFG spectra during reaction with 100 Torr of CO/40 Torr of O_2 /600 Torr of He (i.e. CO in excess) at various temperatures are shown in Figure 4. Co-adsorption of CO and O_2 below ~ 750 K suppressed the formation of CO species observed under high-pressure CO chemisorption on Pt(111) discussed in the last section. Only atop bonded CO at about 2090 cm^{-1} and a low-frequency shoulder representing the incommensurate CO overlayer formation are now present in the SFG vibrational spectrum (Figure 4). The atop CO was present on the surface even at a sample temperature of ~ 750 K. The reaction turnover rate increased by about one order of magnitude in the 590–750 K temperature range with increasing temperature. However, the intensity of the atop CO in the SFG spectrum, which directly relates to atop CO coverage, decreased with increasing temperature, while the SFG intensity for the incommensurate CO overlayer went up. Above 760 K, the reaction became self-sustained, proceeding at a constant high temperature without the need of heating because of the high exothermicity of this reaction. The onset temperature at which the reaction becomes self-sustained is defined as the ignition

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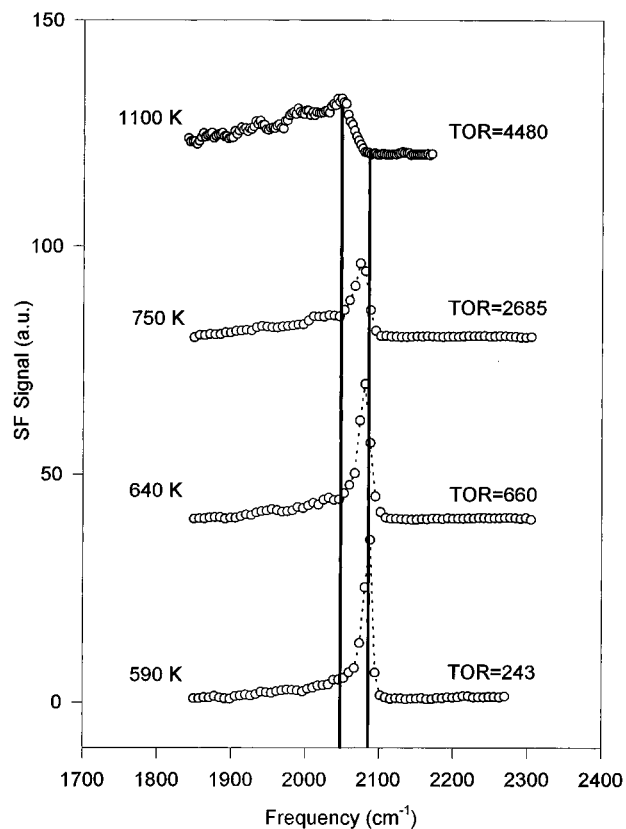


Figure 4. Temperature dependence of SFG spectra of high-pressure CO oxidation on Pt(111) under 40 Torr of O₂/100 Torr of CO/600 Torr of He. The CO₂ turnover rate (TOR) for each temperature is also indicated.

temperature. A typical temperature variation versus time around the ignition point is shown in Figure 5a. This temperature is a function of the experimental conditions and depends on heat transfer processes in the reactor. The ignition temperature as a function of CO partial pressure in our experiment is depicted in Figure 5b. The surface SFG vibrational spectra above and below the ignition temperature were completely different as seen in Figure 4. The spectrum at 1100 K was dominated by a low-frequency broad band and a peak at 2045 cm⁻¹. These features have been assigned to incommensurate CO and CO adsorbed at defect sites.³⁰ The reaction rate was found to increase with an increase of the intensity of this band.

(c) Temperature Dependence of the SFG Spectrum during High-Pressure CO Oxidation on Pt(111) with Excess O₂. The CO oxidation reaction was also investigated with the relative partial pressure of CO/O₂ greater than unity. The SFG spectra obtained during CO oxidation at various temperatures with 100 Torr of O₂, 40 Torr of CO, and 600 Torr of He are shown in Figure 6. The reaction rate was low when the sample temperature was low and the SFG spectrum was dominated by the atop CO species as in the case with excess CO. At 540 K, a reaction rate of 28 molecules of CO₂ per platinum surface site per second was obtained. With increasing temperature, the atop CO peak intensity decreased but the reaction rate increased. Above 600 K, the system reached the high reactivity regime and the reaction became self-sustained.

As presented in Figure 6, the SFG spectra obtained at temperatures above the ignition temperature again are dramatically different from those obtained below the ignition temperature. The atop CO peak that was the dominant feature at low temperatures disappeared completely above the ignition temperature, while three new broad bands centered at 2045, 2130, and 2240 cm⁻¹ showed up as the turnover rate increased to 2238

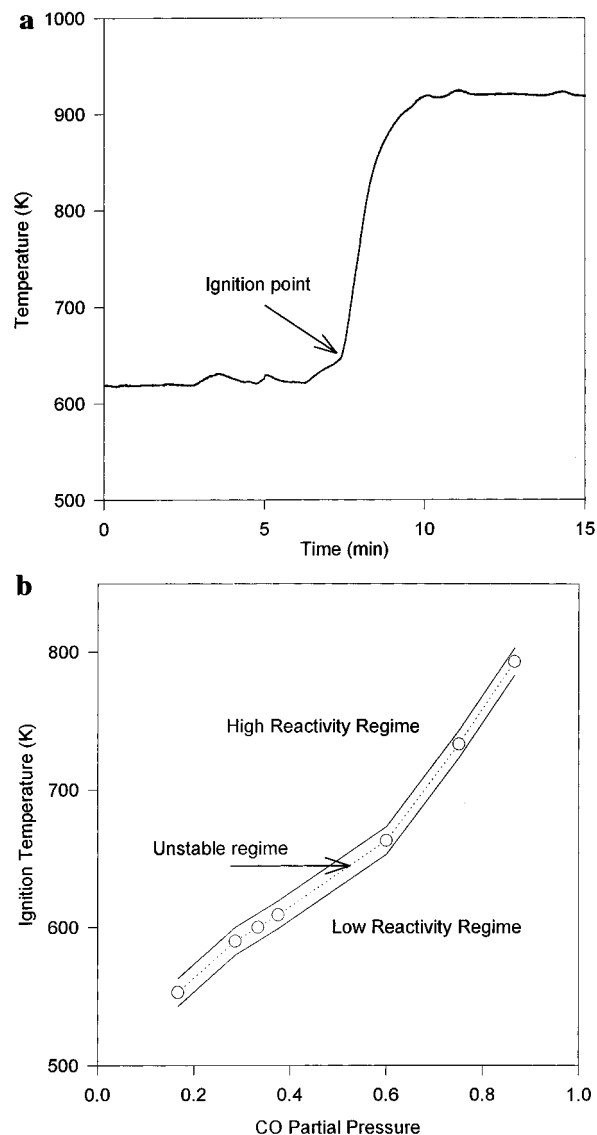


Figure 5. (a) A typical surface temperature variation as a function of time around the ignition point of the reaction. (b) Dependence of the ignition temperature on the CO partial pressure for CO oxidation on Pt(111). The total pressure of CO and O₂ is 140 Torr.

molecules per platinum site per second at 740 K. The 2130-cm⁻¹ peak can be attributed to the stretch mode of CO adsorbed at oxidized platinum sites, which has previously been shown not to be important in CO oxidation.³¹ The broad feature centered at 2045 cm⁻¹ again can be assigned to the incommensurate CO overlayer together with the terminally bonded CO at defect or distorted Pt sites. This band appeared even below the ignition temperature as a shoulder next to the atop CO feature (see the spectrum at 590 K in Figure 6).

The assignment of the 2240-cm⁻¹ feature is more difficult. The peak is blue-shifted by 100 cm⁻¹ from the stretch mode of free CO and red-shifted by 100 cm⁻¹ from the stretch mode of free CO₂. There are reports that platinum carbonyl cations ([Pt-(CO)₄]²⁺) in solutions show such high CO stretch vibrational frequencies³⁷. By analogy, the 2240-cm⁻¹ feature in our case may correspond to the stretch mode of CO multiply bonded to Pt on an oxidized surface. On the other hand, considering the possible presence of nascent CO₂ species on the surface, one may also assign this feature to a CO₂-related surface species. The 1630-cm⁻¹ peak form a CO-O complex observed by Richardson¹⁵ at 10⁻⁵ Torr on Pt(100), however, was not observed in our experiment at all temperatures.

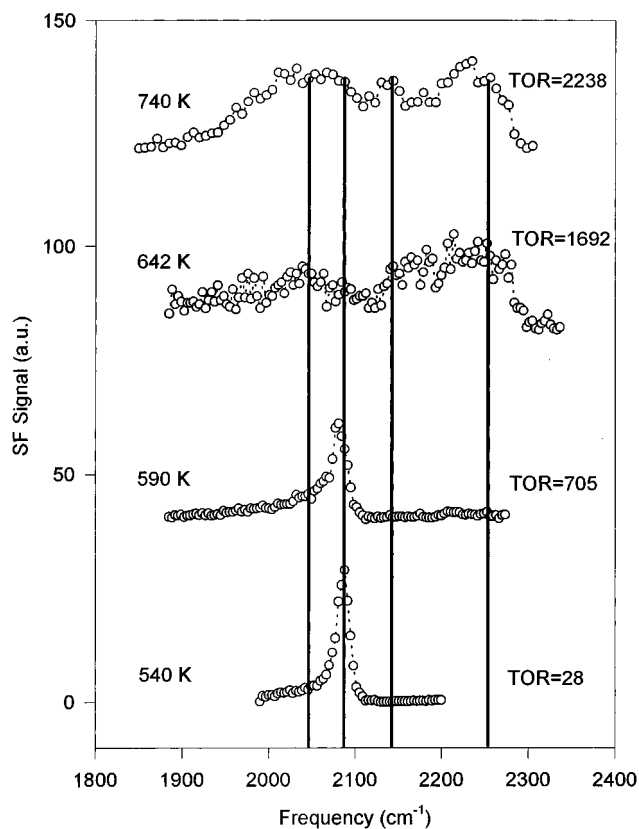


Figure 6. Temperature dependence of SFG spectra of CO oxidation on Pt(111) under 40 Torr of CO/100 Torr of O₂/600 Torr of He.

The correlations between the reaction turnover rate and the coverages of two different surface CO species above and below the ignition temperature are displayed in Figure 7a–c. The CO coverages were altered by changing the CO/O₂ relative partial pressure, while the sample temperature was kept constant. Figure 7a shows the turnover rate versus the atop CO coverage at 590 K, which is below the ignition temperature. The same plots for CO species adsorbed at incommensurate or distorted platinum sites at 720 K (above the ignition temperature) and 590 K are presented in Figure 7, parts b and c, respectively.

As seen in Figure 7a, the reaction rate increases significantly with a decrease of the atop CO coverage. This clearly indicates that atop CO is not an active participant in CO oxidation. Its presence on the surface actually inhibits the reaction. However, as described in Figure 7, parts b and c, the reaction rate is proportional to the concentration of the incommensurate CO surface species that shows a broad band around 2045 cm⁻¹ both above and below the ignition temperature. Therefore, this species must be directly responsible for CO oxidation at all temperatures.

The kinetics of CO oxidation changed dramatically at the ignition temperature with excess oxygen. Different apparent activation energies were observed above and below the ignition temperature. The results are presented in Figure 8. An activation energy of 42 kcal/mol was obtained below the ignition temperature, which is close to the CO desorption energy in UHV. Above the ignition temperature where the reaction is self-sustained, a value of 14 kcal/mol was observed, which is close to the activation energy of the reaction on Pt(111) with high oxygen coverages (11.7 kcal/mol) obtained in molecular beam studies.⁷

Approximately a half-order dependence on both oxygen and carbon monoxide was found above the ignition temperature.

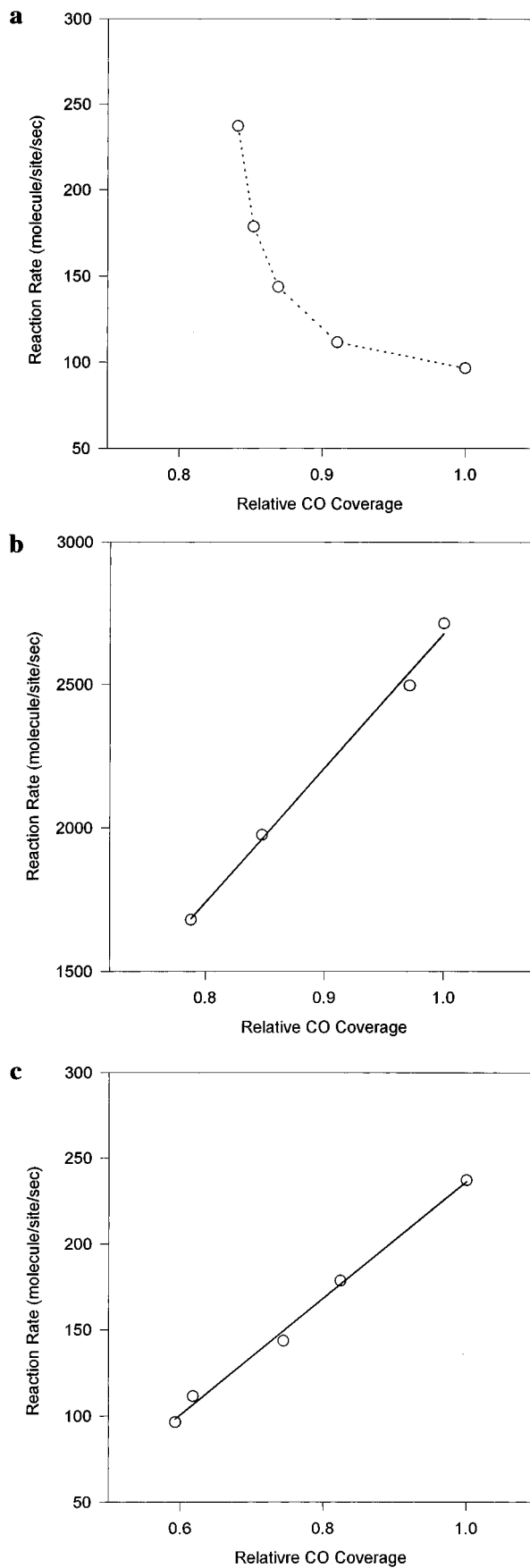


Figure 7. (a) Reaction rate versus atop CO coverage at 590 K. (b) Reaction rate versus surface coverage of incommensurate CO (or CO adsorbed at distorted platinum sites) at 720 K. (c) Reaction rate versus surface coverage of incommensurate CO at 590 K.

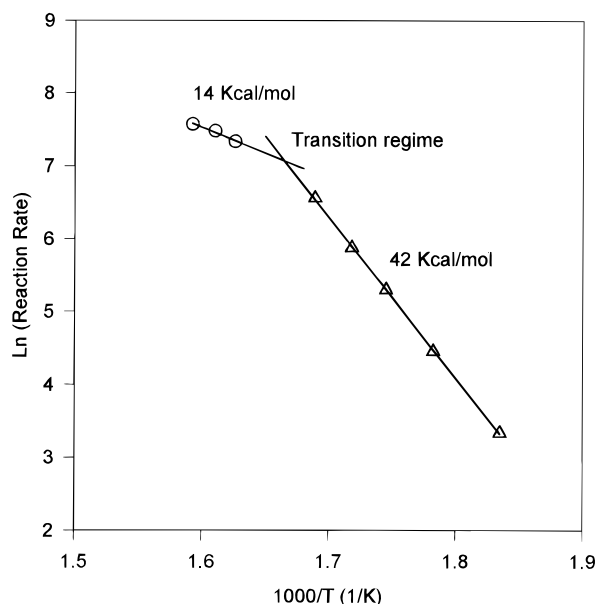


Figure 8. Arrhenius plot for the rate of CO oxidation on Pt(111) at 100 Torr of O₂/40 Torr of CO. Two different activation energies can be deduced from the data for reaction below and above the ignition temperature.

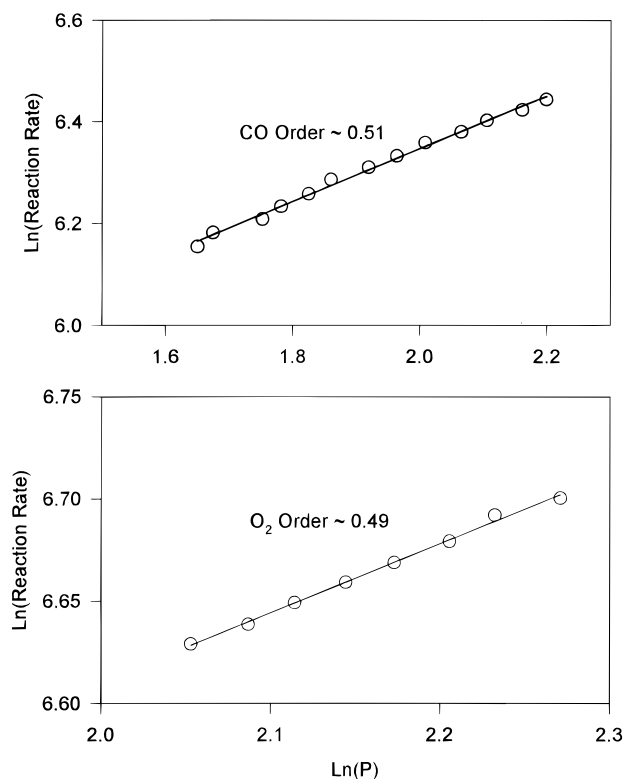


Figure 9. Reaction rate versus partial pressures of the reactants above the ignition temperature. Half-order dependence on the partial pressures of both reactants is obtained. The total pressure of CO and O₂ remains at 140 Torr.

The results are presented in Figure 9. Below the ignition temperature a negative-order dependence on CO and a positive-order dependence on O₂ over Pt(111) were observed, which is consistent with the results of previous studies.³²

Discussion

(a) High-Pressure CO Chemisorption on Pt(111). We have shown in Figure 2 that the surface vibrational spectrum of CO on Pt(111) under high CO pressure is very different from that

in UHV. Higher CO pressure should lead to a more compressed CO monolayer on the surface. This could lead to an incommensurate overlayer of CO molecules on Pt(111) as the adsorbed CO loses registry with the platinum surface atoms. The randomly adsorbed CO distribution explains the broad band between 1700 and 2100 cm⁻¹ in the CO stretch region of the SFG spectrum.

The peak at 2045 cm⁻¹ appears at high CO pressures. Its frequency is close to the terminally bonded CO stretch frequency of transition metal carbonyl clusters.³⁴ In our case, the peak could be associated with CO squeezed onto a Pt atom at the defect or distorted site, causing the CO stretch frequency to shift to the lower value. The high density of CO on the surface could also induce relocation of surface platinum atoms and roughen the surface. CO bonded to the protruded metal atoms could have a stretch frequency comparable to the vibrational frequency of terminally bonded CO in carbonyl molecules. It may even be possible that multiply bonded platinum carbonyl binary complexes Pt-(CO)_n (*n* > 1) are present on Pt(111) if local Pt surface structures are heavily reconstructed. This high-pressure CO-induced change of surface species microstructure has been observed by high-pressure STM in our group³⁶ although the details are yet to be worked out.

(b) High-Pressure CO Oxidation on Pt(111). High-pressure CO oxidation reactions appear to be very different above and below the ignition temperature with different surface species and different catalytic reaction kinetics. We discuss here the two different temperature regimes separately.

(1) Low-Temperature Regime. Even though the dominant surface species are the incommensurate overlayer and terminally bonded CO at distorted platinum sites in high-pressure CO adsorption on Pt(111), the atop CO appears to be the major CO species on Pt(111) in the high-pressure coadsorption of CO and O₂ below the ignition temperature. Oxygen must have suppressed the random adsorption occurring with CO only in the atmosphere (Figure 2). Presumably this is because oxygen competes with CO for adsorption at random sites and oxidized all CO species other than the atop one.

Although CO oxidation can be detected even at low temperature under UHV with coadsorption of CO and oxygen on Pt,^{7,13} only relatively high CO₂ production rates are measurable with GC in our experiment at high-pressures and at high temperatures. Because CO adsorption (of less than a full monolayer) at regular sites of Pt(111) has a much higher sticking coefficient than oxygen at lower temperatures, it hinders the dissociative chemisorption of oxygen on the surface and yields a low O coverage on the surface. It is known that CO oxidation proceeds via the L-H mechanism.⁷ Therefore, low O coverage results in a low reactivity. Higher surface temperature results in more CO desorption, as indicated by the decrease in the SFG intensity of the atop CO peak in Figures 4 and 6. Accordingly the oxygen coverage increases, and so does the reaction rate. This is true for the cases of excess O₂ and excess CO as shown in Figures 4 and 6, respectively.

With increasing surface temperature, eventually the atop CO peak in the spectrum disappeared or became undetectable. The temperature at which the atop CO peak disappeared was found to coincide with the ignition temperature (Figure 5). At a given surface temperature higher CO partial pressure led to higher CO coverage on the surface and therefore increased the ignition temperature. A similar onset temperature at which a new CO species at 2060 cm⁻¹ appeared while the atop CO attenuated was observed by Anderson³¹ in his studies of high-pressure CO

(36) John Jensen, In preparation.

oxidation on supported platinum catalyst; it also increased with an increase of CO partial pressure.

The relationship between surface concentration of atop CO and production rate of CO₂ has a strong negative power dependence (Figure 7a). This clearly indicated that atop CO cannot be the active species in this oxidation reaction. It also suggests that atop CO is not even a spectator; since a spectator only has the effect of blocking adsorption sites, one would expect a negative linear relation between the surface coverage of atop CO and the reaction rate, contradictory to our observation. We can therefore conclude that atop CO actually poisons rather than helps the reaction. The activation energy of 42 kcal/mol for the reaction below the ignition temperature is close to the CO desorption energy from the atop sites,⁷ indicating that desorption of CO in this temperature regime is indeed the rate-limiting step for this reaction. Consequently, the reaction showed a negative order dependence on CO partial pressure and a positive order dependence on O₂ in this temperature regime.

It should be noted that a small increase of CO desorption leads to a large increase in the reaction rate. Apparently, the empty atop sites left behind by CO desorption can accommodate oxygen dissociative adsorption. At the same time, the situation encourages incommensurate CO to adsorb randomly in the neighborhood. The latter is the active species responsible for the reaction. The linear relation (Figure 7c) between the coverage of incommensurate CO and the reaction rate strongly suggests that this is the case.

(2) High-Temperature Regime. Above the ignition temperature, the reaction becomes a self-sustaining process. The surface vibrational spectra for the case of excess CO and excess O₂ show some clear differences. With excess CO the SFG spectrum is relatively simple, namely, a broad band with a peak at 2045 cm⁻¹. It resembles that of CO on Pt(111) under high pressure of CO alone. As mentioned earlier, these are incommensurate CO species or CO adsorbed at distorted Pt sites. They are the species that appear active in the oxidation reaction. It suggests that in this case the surface structure and CO adsorption geometry are nearly the same as those under high-pressure CO alone.

With excess O₂, the SFG spectrum exhibits three broad bands. The atop CO peak is not clearly detectable. The one peak at 2045 cm⁻¹ is essentially the same as the spectrum observed with excess CO (discussed above). It represents the active CO species for the oxidation reaction on Pt. Figure 7b shows that the reaction rate is linearly proportional to the surface coverage of this species, again as in the case of excess CO, and the atop CO is not responsible for the catalytic reaction. Thus we can conclude that both above and below the ignition temperature, the CO species active in the reaction are the incommensurate ones or those adsorbed at defect or distorted sites of Pt.

The apparent activation energy of the reaction, deduced from Figure 8, exhibits a sudden change at the ignition temperature, indicating a change of the rate-limiting mechanism. As mentioned earlier, CO desorption at the atop sites is the rate-limiting step below the ignition temperature. Above ignition, the activation energy appears to be simply the energy barrier

of the surface-mediated reaction between the adsorbed CO and O. The absence of atop CO makes desorption of CO no longer the rate-limiting step. The observed half-order dependence on CO and O₂ partial pressures above the ignition temperature could be explained by postulating that CO and O form islands and the reaction occurs at the CO and O boundary lines.

The two other broad peaks at 2130 and 2240 cm⁻¹ are surface species found only with excess O₂. We can rule out the role of contaminants because only carbon and oxygen were found on the surface by Auger spectroscopy. The 2130-cm⁻¹ peak is related to CO adsorbed at oxidized Pt sites that has been shown to be unimportant in the CO oxidation process.³¹ The 2240-cm⁻¹ peak may be assigned to CO multiply bonded to oxidized platinum sites. In this case, the Pt atoms appear to be electron-deficient, and CO binding multiply to such atoms can have a CO stretch frequency higher than that of CO in the gas phase, as has been found in transition metal carbonyl cations in solution.^{37,38} The blue shift of the stretch frequency is due to strengthening of the chemical bond between C and O.^{29,39} This CO species associated with the 2240-cm⁻¹ peak is likely inactive in the reaction since it was not present with excess CO even when the reaction rate was comparable at a similar temperature above ignition. It could also happen that with excess O₂, nascent CO₂ may appear adsorbed on the surface during the reaction. The stretch frequency of CO₂ in the gas phase is known to be ~2350 cm⁻¹ and a red shift is expected for the adsorbed species.

Conclusion

High-pressure studies of CO oxidation on Pt(111) with use of SFG spectroscopy reveal that there are two different reaction regimes: below and above ignition. Below the ignition temperature, atop CO dominates the spectrum. The reaction has an apparent activation energy of 42 kcal/mol, which is close to the desorption energy of atop CO, indicating that desorption of atop CO is the rate-limiting step. The reaction rate is inversely proportional to the atop CO concentration, suggesting that atop CO plays the role of an inhibitor in the reaction. Above the ignition temperature, atop CO becomes hardly detectable and the activation energy reduces to 14 kcal/mol, which is basically the reaction energy barrier of the oxidation reaction of CO and O on Pt(111). In both cases, the active CO species in the reaction are identified as those adsorbed at non-registry sites or defect (or distorted) Pt surface sites. The reaction rate appears to increase linearly with the surface concentration of such species.

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