The Role of Carbon Deposition from CO Dissociation on Platinum Crystal Surfaces during Catalytic CO Oxidation: Effects on Turnover Rate, Ignition Temperature, and Vibrational Spectra

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Experiments were performed to understand the process of ignition during platinum catalyzed CO oxidation using sum frequency generation (SFG) vibrational spectroscopy, Auger electron spectroscopy (AES), gas chromatography (GC), and temperature programmed desorption (TPD). Both CO dissociation and CO oxidation ignition studies on the (100), stepped (557), and (111) surfaces of platinum are presented. Rapid CO dissociation on the Pt(100), Pt(557), and Pt(111) occurred in narrow temperature ranges (± 10 K) at 500, 548, and 673 K, respectively. The CO ignition temperature at a pressure of 40 Torr of CO and 100 Torr of O_2 is lower on Pt(100) than on Pt(111) and Pt(557). Thus, both CO dissociation and the ignition of CO oxidation are structure sensitive. An in depth study of CO oxidation on Pt(557) was performed on both initially clean and initially carbon covered platinum surfaces to investigate the role of carbon obtained from CO dissociation in CO oxidation. Under excess O_2 and excess CO conditions, a clean platinum surface will remain carbon free below and above ignition. However, a carbon oxide species was formed on initially carbon covered platinum surfaces once oxygen was added at a high temperature (548 K). This carbon oxide species results in a large SFG background signal, allowing us to measure the formation and reactivity of this species during oxidation reactions. The carbon oxide species also formed on initially clean platinum below the ignition temperature when the Pt crystal was exposed to equal partial pressures of CO and O₂. The turnover rates on the carbon oxide covered platinum surfaces were higher than on the initially clean surfaces below ignition. The ignition temperature on the carbon covered surface (648 K) was lower than on the clean platinum (700 K) surface at equal pressures of CO and O_2 . All of this evidence indicates the surface carbon oxide species is better at oxidizing CO than platinum under certain pressure and temperature conditions. CO dissociation is an important step during the onset of ignition, when surface carbon oxidation provides a new exothermic reaction channel in addition to the Pt surface catalyzed oxidation of molecular CO.

Introduction

The oxidation of carbon monoxide (CO) on catalyst surfaces is one of the most studied heterogeneous catalytic reactions. At certain pressures of CO and O₂ (10^{-6} to 760 Torr), the reaction proceeds under two different kinetic regimes separated by an ignition temperature. Below the ignition temperature, the reaction rate is governed by surface reaction kinetics.^{1,2} In this regime, the CO oxidation reaction mechanism follows Langmuir–Hinshelwood kinetics, and the surface is primarily CO covered.³⁻¹⁰

$$CO(a) + O(a) \rightarrow CO_2(g)$$

This reaction is positive first order in O_2 and negative first order in CO pressure.^{10,11} These results agree for both lowpressure and high-pressure studies on platinum single crystals.⁷ The activation energy for this reaction was found to be between $30^{10,12}$ and 42 kcal/mol.⁷ In a narrow temperature range, a transition occurs where the surface, once both CO and atomic oxygen covered, becomes exclusively oxygen covered.⁶ The rate of CO₂ production becomes high, causing a rapid increase in temperature usually called ignition. Ignition occurs when the heat losses in the system can no longer keep pace with the amount of chemical energy evolved by the exothermic surface reaction.^{1,2,13,14} Experimentally, the ignition temperature is recognized by the observation of a spontaneous temperature increase.^{1,2} Above the ignition temperature, a new, mass transport controlled steady state reaction rate is established.^{1,2,13}

Using platinum wires, Rinnemo and co-workers showed the ignition temperature is dependent on the CO and O₂ partial pressure.⁵ As the CO/O₂ ratio increases, the ignition temperature increases. Ignition temperatures on Pt single crystals range from 500 to 600 K.^{5,7} Above ignition, the surface is oxygen covered, and the reaction is mass transport limited by either CO approaching or CO₂ leaving the surface.

$$CO(g) + O(a) \rightarrow CO_2(g)$$

The rate of reaction above ignition is extremely high with turnover rates well above 1000 (molecules/site)/s on Pt single crystals. Su and co-workers found the activation energy to be 14 kcal/mol on Pt(111) at a pressure of 40 Torr of CO and 100 Torr of O_2 ,⁷ similar to the activation energy found using molecular beams on an oxygen covered Pt(111) surface (11.7 kcal/mol).¹⁵ For both CO and O_2 , a positive half-order dependence in partial pressure was observed under high-pressure conditions.⁷

In this paper we report on studies of the surface structure sensitivity of CO dissociation and ignition temperatures over platinum single crystal surfaces. Sum frequency generation

(SFG) surface vibrational spectroscopy and Auger electron spectroscopy (AES) were used to monitor the effect of exposing platinum single crystals to high pressures of CO at high temperatures. Monitoring the shift of the CO top-site peak by SFG as a function of temperature allowed us to determine when CO dissociation occurs. We define the CO dissociation temperature as the temperature where we can detect significant amounts of carbon on our platinum surface using AES. This temperature coincides with a dramatic change in the CO spectral feature as monitored by SFG. The dissociation of CO at a pressure of 40 Torr of CO has been studied on three different crystal faces of platinum: the (100), the stepped (557), and the (111) orientation surfaces. Carbon deposition occurs at different temperatures depending on the surface structure of the platinum crystals as they are heated at constant CO pressure: 500 K for the (100) surface orientation of platinum, 548 K for Pt(557), and 673 K for Pt(111). Thus, CO dissociation is surface structure sensitive, and its mechanism is related to roughening of the metal surfaces by platinum carbonyl formation, leading to the Boudouard reaction.

$$2CO \rightarrow C + CO_2$$

The dramatic decrease of the CO vibrational frequency to 2054 $\rm cm^{-1}$ just before dissociation takes place, as detected by SFG, led us to this conclusion.

The ignition temperatures for CO oxidation on the three platinum crystal faces also show structure sensitivity. The ignition of CO oxidation, when the combustion reaction evolves more heat than the system can dissipate, is correlated with carbon deposition from CO dissociation by our experimental findings. The oxidation of surface carbon to CO_2 represents a new exothermic reaction channel, increasing the amount of chemical energy evolved by the oxidation reaction.

The role of carbon deposited by CO dissociation during catalytic CO oxidation over platinum was investigated on Pt-(557). The discovery of a new SFG signature, indicating the presence of both carbon and oxygen on a platinum surface, gives insight into the role of carbon during combustion. When carbon is deposited on a Pt single crystal during reaction at high temperatures (>500 K), it reacts immediately with oxygen to produce a surface carbon oxide species. This carbon oxide species increases the level of the SFG background, and this background is dependent on the surface carbon-to-oxygen ratio. This allows us to detect carbon deposition on an initially carbon free surface during the oxidation reaction. Carbon cannot be detected on the platinum surface when combustion is carried out at high pressures (40-100 Torr) either in excess oxygen or in excess CO. The metal surface remains carbon free both below and above the ignition temperature in these circumstances. However, both carbon and oxygen are detectable on the platinum surface when it is exposed to equal partial pressures of CO and O₂, indicating the formation of a carbon oxide species.

The ignition temperature on the initially carbon covered Pt-(557) surface is lower than on the clean platinum surface at equal partial pressures of CO and O₂. This is additional evidence that carbon deposition by CO dissociation is an important step for the onset of ignition, and the carbon oxide covered platinum surface is a better CO oxidation catalyst than platinum. The rapid gasification of surface carbon

$$C + O_2 \rightarrow CO_2$$

must be the reason for the absence of surface carbon on platinum

under most experimental conditions of CO oxidation, resulting in an oxygen covered metal surface.

Experimental Section

Sum Frequency Generation. SFG is a powerful technique for studying high-pressure catalytic reactions on single crystal surfaces because it is surface specific, nondestructive, and highly sensitive with good spectral resolution. SFG has been described in detail elsewhere,^{16–20} so only a brief discussion will be given here. During an SFG experiment, two laser beams are overlapped in time and space on a single crystal surface. The first beam is a fixed visible 532 nm green beam (ω_{vis}), and the second beam is a tunable infrared (IR) beam (ω_{IR}) in the wavelength range between 2 and 10 μ m (1000–4000 cm⁻¹). The visible and IR beams mix on the surface to drive an oscillating dipole, emitting a coherent beam of photons at the sum of the visible and IR frequencies ($\omega_{SFG} = \omega_{vis} + \omega_{IR}$). This beam is easily detected.

Under the electric dipole approximation, the intensity of the sum frequency signal is proportional to the square of the second-order nonlinear surface susceptibility $(I \propto |\chi^{(2)}|^2)$. The susceptibility is described by

$$\chi^{(2)} = A_{\rm NR} + \sum_{\rm R} \frac{A_{\rm R}}{(\omega_{\rm IR} - \omega_0 - i\gamma)}$$

where $A_{\rm NR}$ is the nonresonant contribution, γ is the line width, $\omega_{\rm o}$ is the resonant vibrational frequency, and $\omega_{\rm IR}$ is the IR frequency. The resonant strength, $A_{\rm R}$, is proportional to the number and orientational average of molecules on the surface and the IR and Raman transition moments. As observed in this equation, when $\omega_{\rm IR}$ is equal to $\omega_{\rm o}$, $\chi^{(2)}$ is maximized and so a surface vibrational spectrum can be obtained by scanning $\omega_{\rm IR}$ through a frequency range of interest.

Because A_R is proportional to the IR and Raman transition moments, the selection rules for both IR and Raman spectroscopy must be obeyed. Hence, media must be both IR and Raman active to generate SFG. Only media lacking inversion symmetry will satisfy this requirement, as shown by group theory. Usually, bulk materials are centrosymmetric and do not generate SFG. Isotropic gases and liquids also do not generate SFG. Only at surfaces or interfaces where the centrosymmetry is broken can SFG be produced. This is the reason SFG is surface specific. Thus, the technique can be used to probe any interface as long as the media the laser beams pass through do not interfere with the light.

The visible and tunable IR laser beams were generated using a Nd:YAG laser to pump a commercial optical parametric generation/amplification (OPG/OPA) system provided by LaserVision. This system utilized the fundamental output of the Nd:YAG laser of 1064 nm to pump a KTP crystal to generate a visible beam of 532 nm. This beam was split, with one portion being sent to the experiment and the second portion being sent to a pair of KTP crystals to generate a beam in the near-IR (710-880 nm). This near-IR beam was then difference frequency mixed with a 1064 nm beam through two KTA nonlinear crystals, generating a tunable IR beam between 1950 and 4000 cm⁻¹.

The p-polarized IR and visible beams are both spatially and temporally overlapped on a single crystal mounted in an ultrahigh vacuum (UHV) chamber. The visible beam makes an angle of 50° with respect to surface normal, whereas the IR beam is at 55° with respect to surface normal. The SFG beam

is sent through a monochromator, and the signal intensity is detected by a photomultiplier tube and integrated by a gated integrator.

Ultrahigh Vacuum/High-Pressure Reaction Chamber. A UHV system with a base pressure below 1×10^{-10} Torr was used to perform the experiments.²¹ The system was equipped with a rearview retarding field analyzer (RFA) for AES and low-energy electron diffraction (LEED) studies. A quadrupole mass spectrometer monitored the background gas composition in the system under vacuum. For high-pressure experiments, the bell jar was separated from the vacuum pumps, and gases were introduced through a manifold system. Through a recirculation loop attached to the chamber, the gas composition under high-pressure catalytic conditions could be monitored by gas chromatography (GC), allowing us to calculate reaction kinetics. After a high-pressure experiment, the chamber was pumped down to UHV. At that time, the surface composition of the platinum crystal was analyzed using AES and, in certain cases, temperature programmed desorption (TPD) studies were performed.

The Pt(557) single crystal used for this study was mounted in the UHV chamber. A Pt(557) surface is prepared by cutting a platinum single crystal 9.5° relative to the (111) orientation.4,22,23 This prepares a stepped surface with six atom wide terraces of (111) orientation and single atom high steps. Prior to each experiment, the single crystal was cleaned by two cycles of argon ion bombardment followed by annealing in 5×10^{-7} Torr of oxygen at 1123 K for 2 min. The oxygen was pumped out, and the crystal was annealed at a pressure below 2×10^{-9} Torr at 1133 K for 1 min. Once the crystal was shown by AES to be clean, the sample was exposed to high pressures of CO (Scott Specialty 99.99%) and O₂. The CO was further purified by flowing it through a liquid nitrogen trap before introducing it to the sample. When catalytic experiments were performed, the chamber acted as a batch reactor. For SFG experiments, the chamber was equipped with a CaF_2 window at the end of an inverted flange to allow the IR light to reach the sample with minimal gas phase absorption. The path length from the window to the crystal is approximately 4 cm. To normalize for any gas phase absorbance of the IR beam, an IR cell was attached to the sample loop to allow for the acquisition of gas phase IR transmission spectra of gas mixtures.

Carbon can be deposited on Pt(557) by heating to 548 K in high-pressure CO.²¹ In this work, CO oxidation was performed on both initially clean and initially carbon covered surfaces. The initially carbon covered surfaces were prepared by heating the crystal in the desired pressure of CO before introducing O₂.

Results

Surface Structure Sensitivity of CO Dissociation on Pt-(**557**), **Pt(111**), **and Pt(100**). In this section, the results for experiments that explore the properties of Pt single crystals under high-pressure CO and high temperatures are discussed.²¹ The pressure of CO used in these experiments (40 Torr) is the same as that used during the CO oxidation reactions with excess oxygen. These high-pressure CO experiments are done to help understand the interaction of CO with platinum as a function of temperature and the mechanism of ignition under oxidation conditions. After a crystal was cleaned using the procedure described above, it was exposed to 40 Torr of CO. SFG spectra were acquired at 300 K. The samples were heated sequentially to higher temperatures, and at each temperature SFG scans were obtained and averaged. At a particular temperature for each crystal, the SFG spectra evolved with time. The sample was



Figure 1. Comparison of the adsorbed CO vibrational frequency as a function of temperature for Pt(111), Pt(557), and Pt(100) at a pressure of 40 Torr of CO. The Auger spectrum before and after heating Pt-(557) in the presence of 40 Torr of CO is included to show surface carbon can be detected after the experiment.

cooled to room temperature, and more SFG scans were acquired. For each surface, an irreversible process occurred where the peak position shifted to lower frequency. The chamber was quickly evacuated, and AES showed the surface was covered with carbon.

When the Pt(557) was exposed to 40 Torr of CO, a single CO peak was observed at 2100 cm⁻¹. As the sample was heated, the CO spectral feature shifted to lower frequencies. This occurred up to 523 K where the CO peak was observed at 2082 cm⁻¹. Once the sample was heated to 548 K, the peak shifted to 2077 cm⁻¹ and the intensity of this peak decreased over time. The crystal was cooled to 300 K. The post-heating cycle frequency of the CO peak was red-shifted to 2087 cm⁻¹, whereas the fitted amplitude remained essentially the same as before the heating cycle. The chamber was evacuated to 5×10^{-8} Torr, and an Auger spectrum was acquired. The spectrum was dominated by carbon, indicating CO decomposed at 548 K on Pt(557) at a pressure of 40 Torr of CO.

The same experiment was performed on the Pt(111) and Pt-(100) crystal faces, and CO dissociation was observed in both cases.²⁴ To summarize the results for CO dissociation on the three single crystal surfaces, Figure 1 shows the frequency as a function of temperature for these surfaces. The frequency of the CO spectral feature decreases until a critical temperature is reached where dissociation and carbon deposition occur. CO dissociation is obviously structure sensitive, because the dissociation temperatures for Pt(111), Pt(557), and Pt(100) are 673, 548, and 500 K respectively.

Surface Structure Sensitivity of CO Oxidation Ignition with Excess O₂ on Pt(557), Pt(111), and Pt(100). CO oxidation experiments with excess pressure of O₂ were performed on the (557), (111), and (100) faces of platinum. Only the results for Pt(557) will be discussed due to the qualitative similarities among all three crystal faces. After the Pt(557) single crystal surface was cleaned as described above, it was introduced to 40 Torr of CO, 100 Torr of O₂, and 630 Torr of He at 300 K. SFG spectra at different temperatures during the experiment are shown as a stacked plot in Figure 2. Each spectrum is the average of three consecutive scans. At 300 K, a single resonance is observed centered at 2094 cm⁻¹, due to a saturated coverage of top-site CO. The sample was heated to 473 K, and the CO peak red-shifted to 2085 cm⁻¹. The CO peak retained the same frequency and intensity as the temperature was increased to 623



Figure 2. SFG spectra of Pt(557) at a pressure of 40 Torr of CO and 100 Torr of O_2 as a function of temperature. The CO peak was absent once ignition was reached, indicating the surface was no longer CO covered above ignition.



Figure 3. SFG spectra of Pt(557) before and after CO oxidation at a pressure of 40 Torr of CO and 100 Torr of O_2 . Changes in the vibrational spectra are reversible, indicating the platinum surface is unchanged by this reaction.

K. The turnover rate for the production of CO₂ at 623 K was 20 (molecules/site)/s. Once the sample was heated to the ignition temperature, 640 \pm 20 K, the temperature jumped to 723 K. The turnover rate was calculated to be 1400 (molecules/site)/s, and the SFG spectrum was featureless. If the sample was cooled below the ignition point, the reaction was quenched and the CO resonant peak recovered to the same frequency and intensity observed before ignition, as shown in Figure 3.

For all three surfaces, the qualitative features of the SFG spectra are essentially the same. Below the ignition temperature, the CO peak slowly shifts as a function of temperature until the ignition temperature is reached. At the ignition temperature, the crystal temperature increases rapidly, and the CO peak decreases rapidly. Once above the ignition temperature, no spectral feature is observed for these pressure conditions.



Figure 4. SFG spectrum of a clean platinum surface at a pressure of 40 Torr of CO is compared to the SFG spectrum of the surface at 300 K after the oxidation reaction at a pressure of 40 Torr of CO and 100 Torr of O_2 . The oxidation reaction took place on an initially carbon covered Pt(557) surface. The large SFG background indicates the surface is carbon oxide covered. The SFG background from a clean platinum crystal is given as a reference.

 TABLE 1: Temperature Ranges (K) for the Onset of Rapid

 CO Dissociation and the Transition from Surface Reaction

 Controlled Kinetics to Mass Transport Controlled Kinetics (Ignition)

	Pt(100)	Pt(557)	Pt(111)
CO dissociation temp	500 ± 10	550 ± 10	673 ± 10
(40 Torr CO)			
oxidation ignition temp	500 ± 20	640 ± 20	620 ± 20
(40 Torr CO, 100 Torr O ₂)			

Even though the SFG spectra were very similar for all three crystal faces during CO oxidation at these pressure conditions, the ignition temperature was considerably different for the Pt-(100) surface as compared with the Pt(111) and Pt(557) surfaces. Table 1 compares the CO dissociation and the CO oxidation ignition temperatures for the three surfaces. As evident from the table, a similar trend for the structure sensitivity of both CO dissociation occur at a higher temperature for the (111) surface than Pt(100). The CO ignition temperature for Pt(111) and Pt-(557) are very similar to each other within experimental error, indicating CO oxidation occurs mainly on the (111) terraces. This agrees with other studies, which indicated the (111) terrace sites are more important for CO oxidation than step sites.^{4,25,26}

To determine how carbon affects the reaction under excess O_2 , a carbon covered Pt(557) surface was prepared as described above, and the reaction was performed. As soon as 100 Torr of O_2 was added at 548 K, any residual CO peak disappeared, and the SFG background increased significantly. The implication of this large background will be discussed below. Once the ignition temperature was reached (640 ± 20 K), the background increased as the sample was cooled back to room temperature. The CO peak does not recover when the sample is cooled to room temperature under these pressure conditions, as shown in Figure 4. The



Figure 5. Temperature profile and SFG signal as a function of time for Pt(557) at a pressure of 40 Torr of CO and 100 Torr of O₂. The temperature and SFG signal were monitored as the crystal temperature was raised to the ignition temperature. (A) On initially clean platinum, the CO peak was monitored at 2085 cm⁻¹. The temperature of the crystal was slowly ramped to the ignition temperature as we monitored the CO top site peak at 2085 cm⁻¹. Once the ignition temperature was reached, the intensity of the CO peak immediately decreased. As the temperature of the crystal was cooled below the ignition temperature, the intensity of the CO peak immediately recovered. The SFG background did not change during the experiment, indicating the platinum surface remained clean. (B) On initially carbon covered platinum, the SFG background was monitored at 2075 cm⁻¹. The SFG background increased as ignition occurred, indicating the presence of carbon oxide on the platinum surface under these reaction conditions.

turnover rates below (548 K) and above ignition (723 K) were 20 and 1280 (molecules/site)/s, respectively. Figure 5 shows the temperature and SFG intensity traces as a function of time for both the initially clean (A) and initially carbon covered (B) surface under excess O_2 . As shown in (A), the CO peak disappears immediately upon ignition and no change in the SFG background is observed. On an initially carbon covered surface (B), the SFG background increases dramatically upon ignition and stays large as the reaction proceeds.

Auger spectra of both the initially clean and initially carbon covered platinum surfaces were acquired after CO oxidation. The spectrum of the initially clean surface after CO oxidation revealed a small carbon peak in addition to the platinum peaks. This is attributed to electron beam dissociation of CO. The spectrum of the initially carbon covered platinum surface after



Figure 6. SFG spectra of Pt(557) at a pressure of 100 Torr of CO and 40 Torr of O_2 as a function of temperature. The CO top site peak redshifted in frequency as the temperature was raised. No distinct ignition temperature is seen in this case. Instead, a smooth change in temperature is observed at all temperatures. Thus, the system was able to change from surface reaction controlled kinetics to mass transport controlled kinetics without experiencing the instability associated with ignition.

reaction reveals both a large carbon peak and a large oxygen peak. Thus, the SFG background originates from an oxidized carbon species.

CO Oxidation with Excess CO on Pt(557). After the Pt-(557) crystal was determined by AES to be clean, 100 Torr of CO, 40 Torr of O₂, and 630 Torr of He were introduced to the chamber. At 300 K, a single SFG peak at 2100 cm⁻¹ was observed. The crystal was heated gradually to 1023 K. As the crystal was heated, the SFG peak slowly shifted to 2040 cm⁻¹ at 1048 K, as shown in Figure 6. Detectable CO₂ production began at 673 K, although the turnover rate did not become high (990 (molecules/site)/s) until 723 K. The crystal was allowed to cool, and the post-reaction SFG spectrum was identical to the pre-reaction spectrum. As previously reported, the ignition temperature is dependent on the CO to O₂ ratio.⁵ As the ratio increases, the ignition temperature increases. No distinct ignition temperature is seen in the excess CO case. Instead, a smooth change in temperature is observed at all temperatures. Thus, the system was able to change from surface reaction controlled kinetics to mass transport controlled kinetics without experiencing the instability associated with ignition.¹

CO oxidation under excess CO was also performed on an initially carbon covered platinum surface by first heating the Pt(557) single crystal in 100 Torr of CO at 573 K. After 20 min of heating, 40 Torr of O2 and 630 Torr of He were introduced into the chamber. Immediately, any residual CO peak vanished, and the SFG background increased substantially. The SFG background was monitored as a function of temperature, as shown in Figure 7. A high turnover rate for CO₂ production began at 673 K, 50 deg lower than observed on the initially clean surface. As the sample temperature was increased to 723 K, the SFG background increased substantially. A small SFG peak at 2070 cm⁻¹ was also observed in addition to the large background at 723 K. With a continuing increase of the temperature above 723 K, the SFG background began to decrease, and the small peak decreased in frequency as well. By 1023 K, the SFG spectrum was flat without any features or large background. The spectrum at 300 K after the crystal was heated to 1023 K is very similar to the spectrum at 300 K before dissociating CO, which indicates the surface is free of the carbon oxide species.

100 Torr CO, 40 Torr O₂ on carbon covered Pt



Figure 7. SFG spectra of an initially carbon covered Pt(557) surface at a pressure of 100 Torr of CO and 40 Torr of O_2 . A large SFG background, due to carbon oxide on the surface, was seen at temperatures as low as 573 K. As the surface was heated, the SFG background intensity went through a maximum at 723 K. The SFG background intensity then decreased as the temperature was raised even further. At 1023 K, we observed a flat, featureless spectrum very similar to the spectrum of clean platinum (shown in Figure 4). This indicates the carbon oxide species responsible for the large SFG background can be removed from the surface at high enough temperatures at these reaction conditions.



Figure 8. Comparison of the turnover rates for both initially clean and initially carbon covered Pt(557) as a function of temperature at a pressure of 100 Torr of CO and 40 Torr of O_2 . The carbon oxide covered Pt surface had a higher turnover rate at low temperatures, indicating the carbon oxide covered Pt surface is a better CO oxidation catalyst than the initially clean Pt surface at these pressures and at temperatures below 873 K.

Figure 8 compares the turnover rates versus temperature for the initially clean and initially carbon covered platinum surfaces under excess CO. The turnover rate on the initially carbon covered surface is much higher at low temperatures than on the initially clean surface. Around 873 K, the turnover rates become essentially the same. The rates converge for the two different surfaces when the SFG background decreases for the initially carbon covered surface, indicating any residual carbon oxide is being gasified away. Figure 9 shows the temperature and SFG intensity traces as a function of time for both the initially clean (A) and initially carbon covered (B) surfaces. The temperature was ramped linearly and no sudden jump to indicate ignition occurred. On the initially clean surface (A), the spectral feature decreases in intensity linearly (although peak position does red-shift) and no appreciable change in the background is observed. The initially carbon covered surface (B) shows the background reaches a maximum around 723 K and then decreases until the background is negligible around 1023 K, indicating the surface is free of the carbon oxide species.

CO Oxidation with Equal Pressures of CO and O₂ on Pt-(557). The Pt(557) crystal was cleaned as described above and introduced to 70 Torr of CO, 70 Torr of O2, and 630 Torr of He at 300 K. The sample was gradually heated to just below the ignition temperature. Interestingly, the SFG background began to increase around 623 K, unlike the other two pressure regimes where the SFG background does not increase under oxidation conditions for an initially clean crystal. As the sample is heated higher, the background increases. As stated previously, the background is due to a carbon oxide species on the surface. Because carbon was not deposited before the reaction began, CO is actually dissociating under these oxidizing conditions. The reaction rate at 673 K, which is below the ignition temperature for these conditions, is 900 (molecules/site)/s. The ignition temperature was 700 K, and upon ignition the temperature increased to 790 K. The turnover rate at 790 K was 4300 (molecules/site)/s. After the reaction, the sample was cooled, and the SFG spectrum revealed an irreversible change happened during reaction (Figure 10). The peak position for both spectra is 2100 cm⁻¹, although CO is adsorbed on a modified platinum surface after ignition. The modified surface has a carbon oxide species coadsorbed with CO, which explains the increased background.



Figure 9. Temperature and SFG signal as a function of time for Pt-(557) at a pressure of 100 Torr of CO and 40 Torr of O_2 . (A) On an initially clean surface, the temperature is ramped linearly, and we do not observe a distinct ignition temperature. The CO peak decreases linearly, and the SFG background remains negligible, indicating carbon deposition is not occurring under these conditions. (B) On an initially carbon covered surface, a distinct ignition temperature is not observed. The SFG background reaches a maximum at 723 K before decreasing. At 1023 K, the SFG background resembles that of clean platinum, indicating the carbon oxide surface species gasifies above 723 K.

The same pressures of CO and O2 were also explored on an initially carbon covered Pt(557) crystal. After the crystal was cleaned, 70 Torr of CO was introduced into the chamber, and the sample was heated to 573 K. After 20 min, 70 Torr of O₂ was added along with 630 Torr of He. Immediately, any residual CO peak disappeared and the SFG background increased. At 623 K, below the ignition temperature, the turnover rate was 800 (molecules/site)/s. This rate is substantially higher than that observed on the initially clean Pt surface under the same conditions at 623 K. The sample was gradually heated and ignition was observed at 648 K. This ignition at 648 K is 50 deg lower than that observed for the initially clean crystal. The SFG background increased as a function of temperature below ignition but did not increase appreciably after ignition, indicating the relative concentrations of carbon and oxygen on the surface were not changing. Above ignition, at 790 K, the rate was 4400



Figure 10. SFG spectra of Pt(557) at a pressure of 70 Torr of CO and 70 Torr of O₂ before and after reaction. Although the frequency of the top site CO peak is the same in both spectra, the peak is superimposed upon a large SFG background in the post-reaction spectrum. This indicates the platinum surface was modified during the oxidation reaction and now contains a carbon oxide species.

(molecules/site)/s. Because the SFG background was still considerable, the carbon was not oxidized away as in the case with excess CO. Figure 11 shows the temperature and SFG intensity traces as a function of time for both the initially clean (11A) and initially carbon covered (11B) surfaces. On the initially clean surface, the background is observed to increase as a function of temperature and reaches a maximum shortly after ignition. Also, the CO peak disappears immediately upon ignition.

Increased SFG Background Signal from a Carbon and Oxygen Containing Surface Species. In addition to SFG signal enhancement when the IR beam is at the same frequency as a vibrational mode, there can also be SFG enhancement when the visible beam is near an electronic resonance of a surface species. If this is the case, the SFG background increases and is considerably higher than the normal SFG nonresonant background. In this study, under certain conditions, the SFG background was found to increase. To determine the cause of this background, control experiments were performed.

The sample was heated in pure CO or pure O_2 to high temperatures to determine whether either one of these species was responsible for the observed background. When the Pt-(557) crystal was heated in high pressures of CO, CO dissociated and deposited carbidic carbon, as determined by AES.²¹ The addition of this carbon species did not contribute to the SFG background, as seen in previous studies. When a clean prepared platinum surface is heated in a high pressure of O_2 , the SFG background remains at the same level as the nonresonant background for clean platinum. AES reveals a clean platinum surface, and no evidence of atomic oxygen on the surface is observed in the spectrum. This result is expected because platinum does not easily oxidize under these conditions, unlike other transition metals.

Because the SFG background increased in the presence of both CO and O_2 , an experiment was performed where the sample



Figure 11. Temperature and SFG signal as a function of time for Pt-(557) at a pressure of 70 Torr of CO and 70 Torr of O₂. The temperature and SFG signal were monitored as the crystal temperature was raised to the ignition temperature. (A) On an initially clean surface, a sharp jump in temperature is observed at 700 K, and the CO peak immediately decreased. The SFG background is observed to increase beginning at 573 K and reaches a maximum just after ignition. This indicates carbon is being deposited under oxidation conditions and a carbon/oxygen species is being formed. (B) On an initially carbon covered surface, the ignition temperature was observed at 648 K, 50 deg lower than on the clean Pt surface under these conditions.

was heated first in 40 Torr of CO to deposit carbon onto the surface. Once the carbon was deposited, the system was evacuated. AES revealed a carbon covered platinum surface. The carbon covered surface was then titrated with 5×10^{-7} Torr of O₂ as a function of temperature starting at 300 K. After being heated at various temperatures, the crystal was cooled and three SFG spectra were acquired and averaged. Figure 12A shows the absolute intensity SFG spectra of Pt(557) under vacuum after titration in O₂, and Figure 12B shows the corresponding Auger spectra. It is important to note that Figure 12A is not a stacked plot. There is a direct correlation between the intensity of the SFG background and Auger oxygen-to-carbon ratio, as shown in Figure 12C. Clearly, as the O/C ratio increases, the SFG background increases. The species giving rise to the large SFG background is an oxidized carbon species.



Figure 12. (A) Change in SFG spectra from an initially carbon covered Pt(557) surface as the crystal was heated in 5×10^{-7} Torr of O₂. The SFG background increased as the temperature was increased, indicating we were forming a carbon oxide species on the surface. Please note this is an absolute intensity plot and not a stacked plot. (B) Auger spectra of carbon covered Pt(557) as a function of temperature as it was heated in 5×10^{-7} Torr of O₂. (C) SFG background at 2140 cm⁻¹ plotted against the corresponding oxygen to carbon Auger peak ratio. The intensity of the SFG background was found to increase as the oxygen/ carbon Auger peak ratio increased.

Various carbon oxides exist on activated carbon. These species have been characterized using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and TPD experiments.^{27–29} Depending on the surface preparation, different oxide species of carbon can form. A TPD experiment was performed on the carbon oxide species found on Pt(557). CO and CO₂ were monitored by mass spectrometry as a function of temperature to determine the decomposition temperature of this unknown species. Both CO and CO₂ evolved between 1000 and 1100 K with similar pressures, indicating a single type of species was decomposing. Because the pressures were similar, the carbon oxide is likely a carboxylic anhydride species (-(CO)O(CO)-).

Discussion

Both CO dissociation and CO oxidation ignition are structure sensitive.²⁴ Pt(100) showed the lowest dissociation and ignition temperatures (500 K), whereas Pt(111) exhibited the highest dissociation and ignition temperatures (>620 K). Thus, CO dissociation is an important step for ignition.

Much is known about the rates of CO oxidation above and below ignition, but what remains unclear is the mechanism causing the sudden transition from a CO and O covered surface to an atomic oxygen covered surface. One explanation describes the ignition as the point where CO coverage decreases below a critical coverage, no longer inhibiting oxygen adsorption.⁶ In this view, the CO coverage can decrease either by desorption or reaction. Using molecular beams on Pd(110), Bowker and co-workers showed a surface under CO oxidation conditions is already covered with oxygen to about one-fourth of the saturation value even below ignition.⁶ Ignition would only occur when the CO coverage decreased to below 0.4 monolayer.

In addition to this observation about the onset of ignition, CO dissociation induced carbon deposition must also contribute to the decrease in CO coverage at the ignition temperature. The ignition temperature trend for CO oxidation on the three platinum crystal faces correlates with the CO dissociation temperature trend. The ignition of CO oxidation is controlled by carbon deposition from CO dissociation and is surface structure sensitive.

Effect of Surface Carbon on CO Oxidation and Ignition. CO oxidation experiments were performed and turnover rates were measured on both initially clean and initially carbon covered Pt(557) above and below the ignition temperature. The reaction on an initially clean Pt surface under excess O_2 is well-known. On the basis of previous studies, the reaction follows Langmuir–Hinshelwood kinetics below ignition, and CO₂ is produced by the reaction of adsorbed CO and adsorbed atomic oxygen.^{5,6,10} Above ignition, mass transport kinetics control the reaction.^{1,2,13}

When CO oxidation is performed on an initially carbon covered Pt(557) surface under excess oxygen, the reaction kinetics are the same as those on the initially clean Pt(557) surface. However, the SFG background increases under these reaction conditions. This large SFG background is due to a surface carbon oxide species. On the basis of our kinetic data, this species is as active for O_2 dissociation as the initially clean Pt.

When the reaction was performed on an initially carbon covered Pt(557) surface under excess CO, the rate of CO_2 production below ignition is significantly higher than on an initially clean platinum surface. The surface oxide species, believed to be carboxylic anhydride (Figure 13), appears to be better at oxidizing CO than an initially clean Pt surface. The amount of the carbon oxide surface species is proportional to



Figure 13. Proposed structure for carboxylic anhydride on the surface.²⁷ This species is thought to be responsible for the large SFG background seen under certain pressure and temperature conditions.

the intensity of the SFG background. The rate of CO_2 production through the reaction of CO and oxygen on the carboxylic anhydride covered platinum surface is faster than the rate of production of CO_2 from the reaction of adsorbed CO and O on platinum.

Once above 723 K, the SFG background begins to decrease as a function of temperature, indicating the carboxylic anhydride species is gasifying at these temperatures. By 900 K, the background is essentially gone, and the rate is the same as observed on an initially clean Pt(557) surface, indicating the surface carbon oxide was completely gasified. At these temperatures, the reaction kinetics are mass transport controlled.

When CO oxidation was performed at equal pressures of CO and O_2 , we found evidence for CO dissociation on an initially clean Pt surface under oxidation conditions. Also, the ignition temperature in this pressure regime is 50 deg lower for the initially carbon covered Pt surface than the initially clean surface. CO dissociation is an important mechanistic step for the ignition of CO oxidation, as supported by the above evidence.

Carbon and Oxygen Surface Species. When CO is dissociated, carbidic carbon islands are formed on the surface. When the initially carbon covered platinum surface is heated in the presence of O_2 , the carbon islands become terminated with oxygen, which give rise to the SFG background and also allow oxygen detection in the Auger spectrum. The background is due to an electronic resonance of the 532 nm beam with the carbon oxide species, and the size of the carbon islands will determine the amount of oxygen observed in the Auger spectrum. The intensity of the SFG background is also dependent on the concentration of carbon and oxygen on the surface. As the carbon-to-oxygen ratio decreases, the SFG background increases.

Activated carbon is a common support used in catalysis. There have been many studies on activated carbon surfaces.^{27–29} When activated carbon is introduced to oxidizing conditions, it becomes oxygen terminated, and many techniques have been used to identify the types of carbon oxide species. One such technique is TPD. Otake and co-workers oxidized an active carbon either by heating in air or by exposing the carbon to concentrated nitric acid.²⁷ When the carbon was heated in air, they found the surface began to oxidize significantly at 573 K, and upon further heating, the amount of oxidation became much more considerable. These temperatures are similar to those used in this study where the large SFG background is observed to grow under oxidizing conditions.

Once the carbon was oxidized, Otake and co-workers performed TPD experiments on the system.²⁷ The amounts of CO and CO₂ and temperatures at which they are evolved classify the oxide species present on the surface. They observed two CO peaks at 900 and 1175 K. One CO₂ peak at 900 K was also observed. Otake and co-workers determined this surface oxide to be carboxylic anhydride. When this species decomposes, both

CO and CO₂ evolve simultaneously in equal concentrations. The 900 K temperature is very similar to the temperature of CO and CO₂ evolution in our TPD experiments and also of the gasification of the carbon oxide species under oxidation conditions during catalytic experiments. The concentrations of CO and CO₂ evolved in our experiments are essentially equal. Thus, an important carbon oxide species on the Pt surface must be carboxylic anhydride.

The electronic resonance with the 532 nm beam may be due to a metal complex involving platinum atoms and the anhydride species similar to what is seen for d-d transitions in organometallic clusters.³⁰ Calculations modeling the system are currently being performed and will be published at a later date. After the carbidic carbon has been deposited through the dissociation of CO, carbon islands are formed. When these carbon islands are exposed to O₂ near 600 K, the carboxylic anhydride species forms from the reaction of surface oxygen and carbon.

Conclusions

There is a similar trend for CO dissociation and CO oxidation ignition temperatures for the (111), (557), and (100) crystal faces of platinum, indicating both processes are structure sensitive. CO dissociation at 40 Torr of CO was observed on Pt(100), Pt(557), and Pt(111) at 500, 548, and 673 K, respectively. The ignition of CO oxidation at 40 Torr of CO and 100 Torr of O_2 on the three crystal faces was observed at 500, 640, and 620 K, respectively. The similarity in the ignition temperatures for the (557) and (111) crystal faces implies the terrace sites on the (557) crystal are more important for the onset of ignition than the step sites. CO dissociation is important for the chemical energy evolved by the reaction.

The rate of reaction below ignition was considerably higher on the initially carbon covered Pt surface when the reaction was performed in excess CO or equal pressures of CO and O2. For the excess O₂ condition, ignition was very close to the start of CO₂ production and so pre-ignition kinetics could not be studied as in depth as in the other two cases. In addition to the higher turnover rates on the initially carbon covered surface, the SFG background was significantly larger than observed on the initially clean surface. The background was due to the presence of a carbon oxide surface species with an electronic resonance in the visible region near 532 nm, the frequency of the visible beam used in these SFG experiments. The magnitude of the SFG background has been correlated with the amount of carbon oxide on the Pt surface. Because of the higher turnover rate and the existence of the carbon oxide species, this surface is better at oxidizing CO than initially clean Pt. The carbon oxide species is proposed to be a carboxylic anhydride, as observed in studies on activated carbons. This species decomposes near 900 K with similar concentrations of both CO and CO₂. Additionally, it gasifies near this temperature under oxidation conditions.

Additional evidence for CO dissociation being important for the onset of ignition was found when CO oxidation reactions were performed at equal pressures of CO and O_2 . The SFG background increases when a carbon oxide species is on the surface. When CO oxidation was performed on an initially clean surface, the SFG background increased, indicating CO was dissociating. The deposited carbon reacted with oxygen to produce carboxylic anhydride. Thus, CO can dissociate under oxidizing conditions to deposit carbon. In addition, the ignition temperature was 50 deg lower for the initially carbon covered surface than the initially clean platinum surface. Hence, CO dissociation is important for ignition. The oxidation of surface carbon increases the amount of chemical energy evolved by the system, resulting in a decrease in the ignition temperature.

This observed carbon oxide species could be important in other oxidation processes such as methane oxidation. The concentration of this species is dependent on temperature, making it possible to control the amount of this species on the surface. Further experiments will be performed to gain a better understanding of this carbon oxide species. Experiments and calculations will be used to assign the electronic SFG resonance observed during the SFG experiments. A study correlating the intensity of the SFG background and the concentration of carbon and oxygen will also be performed using AES, so reaction kinetics can be related to the concentration of carbon and oxygen during reaction. This could greatly help us to understand the nature of combustion reactions.

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References and Notes

(1) Rinnemo, M.; Fassihi, M.; Kasemo, B. Chem. Phys. Lett. 1993, 211, 60.

(2) Fassihi, M.; Zhdanov, V. P.; Rinnemo, M.; Keck, K.-E.; Kasemo, B. J. Catal. **1993**, 141, 438.

(3) Hong, S.; Richardson, H. H. J. Phys. Chem. 1993, 97, 1258.

(4) Ohno, Y.; Sanchez, J. R.; Lesar, A.; Yamanaka, T.; Matsushima, T. Surf. Sci. 1997, 382, 221.

(5) Rinnemo, M.; Kulginov, D.; Johansson, S.; Wong, K. L.; Zhdanov, V. P.; Kasemo, B. *Surf. Sci.* **1997**, *376*, 297.

(6) Bowker, M.; Jones, I. Z.; Bennett, R. A.; Esch, F.; Baraldi, A.; Lizzit, S.; Comelli, G. *Catal. Lett.* **1998**, *51*, 187.

(7) Su, X.; Cremer, P. S.; Shen, Y. R.; Somorjai, G. A. J. Am. Chem. Soc. 1997, 119, 3994.

(8) Wartnaby, C. E.; Stuck, A.; Yeo, Y. Y.; King, D. A. J. Chem. Phys. **1995**, 102, 1855.

(9) Imbihl, R.; Cox, M. P.; Ertl, G. J. Chem. Phys. 1986, 84, 3519.
(10) Berlowitz, P. J.; Peden, C. H. F.; Goodman, D. W. J. Phys. Chem. 1988, 92, 5213.

(11) Zhdanov, V. P.; Kasemo, B. Appl. Surf. Sci. 1994, 74, 147.

(12) Langmuir, I. Trans. Faraday Soc. 1922, 17, 672.

(13) Kulginov, D.; Rinnemo, M.; Kasemo, B. J. Phys. Chem. B 1999, 103, 3170.

(14) Frank-Kamenetskii, D. A. *Diffusion and Heat Transfer in Chemical Kinetics*, 2nd ed.; Plenum: New York, 1969.

(15) Cambell, C. T.; Ertl, G.; Kuipers, H.; Segner, J. J. Chem. Phys. 1990, 73 (11), 5862.

(16) Shen, Y. R. Surf. Sci. 1994, 299/300, 551.

(17) Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. Phys. Rev. Lett. 1993, 70, 2313.

(18) Johal, M. S.; Ward, R. N.; Davies, P. B. J. Phys. Chem. 1996, 100, 274.

(19) Conboy, J. C.; Messmer, M. C.; Richmond, G. L. J. Phys. Chem. 1996, 100, 7617.

(20) Shen, Y. R. Nature 1989, 337, 519.

(21) McCrea, K. R.; Parker, J. S.; Chen, P.; Somorjai, G. A. Surf. Sci. 2001, 494 (3), 238.

(22) Lin, T. H.; Somorjai, G. A. Surf. Sci. 1981, 107, 573.

(23) Somorjai, G. A.; Joyner, R. W.; Lang, B. Proc. R. Soc. London A 1972, 331, 335.

(24) McCrea, K. R.; Parker, J. S.; Somorjai, G. A. Topics in Catal., in press.

(25) Szabó, A.; Henderson, M. A.; Yates, T., Jr. J. Chem. Phys. 1992, 96 (8), 6191.

(26) Akiyama, H.; Moise, C.; Yamanaka, T.; Jacobi, K.; Matsushima, T. Chem. Phys. Lett. **1997**, 272, 219.

(27) Otake, Y.; Jenkins, R. G. Carbon 1993, 31, 109.

(28) Dandekar, A.; Baker, R. T. K.; Vannice, M. A. Carbon 1998, 36, 1821.

(29) Haydar, S.; Moreno-Castilla, C.; Ferro-Garcia, M. A.; Carrasco-Marin, F.; Rivera-Utrilla, J.; Perrard, A.; Joly, J. P. *Carbon* **2000**, *38*, 1297.

(30) Shriver, D. F.; Atkins, P.; Langford, C. H. *Inorganic Chemistry*, 2nd ed.; W. H. Freeman and Co.: New York, 1994.