STUDIES ON SELF-SUSTAINED REACTION-RATE OSCILLATIONS

I. Real-time surface infrared measurements during oscillatory oxidation of carbon monoxide on platinum

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Time-resolved infrared absorption features in the $1800-2400 \text{ cm}^{-1}$ region during a typical cycle in the oscillatory oxidation of CO over a platinum foil were obtained by Fourier transform infrared reflection absorption spectroscopy. Pretreatment of the foil in an oxidizing environment at high temperatures was found to be necessary to induce large-amplitude, stable oscillations. The oscillations are approximately square-wave in shape, with a high and a low reaction-rate branch. The level of chemisorbed CO in the high reaction-rate branch is typically below the noise level, while in the low reaction-rate branch substantial surface coverages of CO can be observed. No evidence for CO bridge-bonded to the platinum substrate or chemisorbed in the presence of a subsurface Pt oxide could be found at any time during the oscillation cycle. Evidence is presented for the existence of CO islands in the low reaction-rate branch. It is also shown that the low reaction rate realized in this branch is not due to blocking of the surface by chemisorbed CO.

1. Introduction

Self-sustained reaction-rate oscillations for metal-catalyzed oxidations have been documented in the literature since the observations of oscillations during CO oxidation over Pt mesh by Hugo in 1970 [1]. Recent reviews by Sheintuch and Schmitz [2] and Slin'ko and Slin'ko [3] describe many such studies of oscillating systems. Reaction-rate oscillations have been observed during the oxidation of propylene [4], ethylene [5,6], NO and NH₃ [7], NO and CO [8], cyclohexene [9], and CO and butene [10] over Pt, during the oxidation of H₂ over Pt [11], Ni [12–15], and Pd [16], and during the oxidation of CO over Rh [17], Ir [18], Pd [18], and Pt [19–28].

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Early measurements made on oscillating systems focused on bulk quantities, such as CO and CO₂ partial pressures, gas and catalyst temperatures, and gas flow rates. It is now believed that the reaction-rate oscillations result from surface rate processes rather than from interactions between bulk transport and chemical rate processes [14,15]. Whether the underlying surface rate processes giving rise to the observed oscillations are the same for all the systems is not clear at this time. Only recently have surface sensitive techniques such as solid electrolyte potentiometry [5,6,26], contact potential difference measurement [15], transmission infrared spectroscopy [22,23,27], video LEED and work-function measurements [24,25] been applied to investigate the state of the catalyst surface as reaction oscillations are occurring. None of these studies, however, has conclusively demonstrated which mechanism is responsible for these complex oscillatory behaviors.

The aim of this work is to assess in a quantitative manner the potential of real-time surface infrared spectroscopy for resolving some fundamental questions about oscillations. Such questions include the roles that adsorbates such as CO, O, and possible impurities (Si, C,...) and that oxides in the near surface region (SiO₂, PtO₂,...) play on the time variation of CO oxidation rate over a Pt foil. Many of these questions have arisen from a number of widely different proposed theoretical models which have not been thoroughly tested experimentally. In order to yield useful data, any experimental technique applied to the system must be able to probe the reaction on all relevant timescales, and must provide unambiguous support or disproof of specific proposed mechanisms.

The experimental technique of infrared reflection absorption spectroscopy (IR-RAS) has found wide use in the study of adsorbates on low surface area substrates, in particular on single-crystal surfaces in UHV environment [29]. The development of Fourier transform interferometers has added higher energy throughput, broader spectral range, and time resolution to the technique. For this experimental system the question is whether the technique covers a wide enough frequency range to measure all relevant adsorbates, and whether the time resolution available can probe the surface on all relevant timescales.

We have addressed some of these questions by studying with FTIR-RAS the CO adsorbed on a Pt foil under oscillating conditions. To do so we first designed a reaction cell and sample holder which maximizes the infrared signal-to-noise ratio (S/N) while maintaining a precise control of the average sample temperature, as described in section 2. This design yields S/N among the best ever achieved with IR-RAS, and permits quantitative spectroscopy of adsorbates on a subsecond timescale. Next, it was necessary to develop a specific sample preparation procedure in order to yield reproducible oscillations (section 3). In contrast to UHV studies, cleaning procedures for studies near atmospheric pressure are not well established, let alone understood,

although they are a determining factor in the oscillatory behavior of a sample. This has led at least one group to propose that surface impurities must be present in large quantity for oscillations to occur [28]. Through correlation of surface preparation with surface IR data, we have obtained a reliable characterization of the surface and have established criteria for oscillations (section 3.1).

A newly identified phenomenon of rapid reaction level (spike) which demands the ultimate time resolution achievable with our system is documented in section 3.2. Next, a discussion of the data is presented in view of previous work (section 4). The implications of our measurements of CO adsorption for some previously proposed models are then outlined. Several models are shown to be inconsistent with our observations. Suggestions for other measurements extending the range of the infrared work are proposed. These measurements are more difficult than the detection of CO on the surface and will require extensive effort. Although the present work cannot completely solve this intricate problem, several conclusions about the mechanisms of oscillation can be drawn (section 5). Care is taken, however, not to mislead the reader by proposing an ill-tested model, but instead to carefully summarize and interpret the measured data.

2. Experimental system

The experimental system consists of a Pt foil catalyst sample, a constant-resistance controller to monitor and control the average temperature across the foil sample, a gas handling system to supply CO, O_2 or a reaction mixture of CO and O_2 in He at a desired flow rate and a reaction cell placed in a Nicolet 6000 FTIR spectrometer for surface infrared analysis.

The reaction cell is constructed of stainless-steel, UHV-compatible components and has an internal volume of about 8.5×10^{-4} m³. The small external dimensions allow the cell to be mounted directly onto the FTIR spectrometer bench. Electrical, thermocouple and gas flow feedthroughs, and a pressure gauge are mounted on the cell. A view port permits visual examination of the sample and temperature calibration at high temperature by means of a pyrometer. Infrared windows (CaF₂ or KBr) are mounted at both ends of the cell and are sealed with Viton O-rings. The windows have a viewing diameter of 38 mm. Under static conditions, the base pressure of the cell (10^{-2} Pa) is limited by the long path to a turbomolecular pump. This base pressure is adequate, however, since the normal working pressure of the cell during flow experiments is in the 10^3 Pa range.

The Pt samples used in this study are foils of dimensions 90 mm \times 13 mm \times 0.0127 mm or 0.0254 mm (Johnson-Matthey, purity > 99.99%). A novel sample holder was developed to hold the foil sample optically flat, even after high-temperature flashing and annealing, to have a negligible contact resis-

tance ($< 5 \times 10^{-3} \Omega$), and to allow precise adjustment of the sample position. These factors were critical in achieving our very good infrared S/N.

The pre-mixed reaction gas used in the present study contains 0.52% CO (99.5% purity) and 49.2% O₂ (99.6% purity), and the balance is He (99.995% purity). This gives an effective $P_{\rm CO}/P_{\rm O_2}$ ratio of 0.011, well within the concentration range of oscillations over Pt described by Turner et al. [20].

It is well documented that during nonisothermal reaction-rate oscillations, large catalyst temperature excursions occur [18,20,27]. In addition, spatial temperature variations have been reported during oscillations over supported catalysts [27]. As surface rate processes depend strongly on temperature it would be desirable (from the point of view of modelling efforts) to maintain the catalyst temperature constant during the reaction rate oscillations. To heat our sample to reaction temperature, a dc current is applied. We have devised a temperature measurement and control system based on a constant-resistance controller [30]. The sample temperature is estimated from the measured resistance, with an absolute accuracy of ± 15 K. However, relative changes of ± 1 K are detectable. The resistance of the sample is controlled through a DC feedback loop.

Since the sample resistance is very low ($\approx 0.02 \ \Omega$ at 298 K), high currents (> 10 A) are necessary to heat the sample to 575 K or more. The resistance control system is capable of delivering up to 20 A current to the sample, controlling the sample resistance to within an equivalent of ± 1 K in average temperature with a response time of 5 ms, and providing a means to monitor the progress of the reaction.

The experimental cell was mounted directly onto the optical bench of a Nicolet 6000 FTIR spectrometer. The focusing mirrors were adjusted to bring the incident IR beam at an angle of $85^{\circ} \pm 2^{\circ}$. A gold wire grid on AgBr polarizer (Perkin-Elmer), mounted on an externally controlled, motor-driven stage was placed between the reaction cell and the detector. During data collection, the position of the polarizer was fixed to yield either p polarization or s polarization. Either an InSb or a HgCdTe, liquid-nitrogen-cooled photodetector was used.

Unless stated otherwise, all spectra have been collected using the InSb detector, at a mirror velocity of 0.2 m/s, with 4096 data points per interferogram (2048 points per spectrum at a resolution of 4 cm⁻¹). Under these conditions, the noise level ($\Delta R/R$) is 0.2% for each 0.6 s scan, making it possible to detect 5% of a monolayer of CO with this time resolution. Since the full spectral range of the detector (2200 cm⁻¹ for InSb in this system) is measured in this time, gas-phase CO₂ concentrations, as well as adsorbed CO coverages are monitored at the same time. As will be shown in section 3, reaction transitions can occur with durations of less than 5 s, making the rapid-scan capability of the infrared system particularly valuable for these experiments.

3. Experimental procedure and results

3.1. Sample pretreatment and surface reactivity

As no oscillations could be induced on a nominally clean sample, we investigated the surface IR spectrum over the range 2000 to 2300 cm⁻¹ as various pretreatments were performed. In particular, we looked for CO adsorbed upon exposure to CO/O_2 mixture, after annealing the sample at progressively higher temperatures in flowing O_2 . The spectra obtained are shown in fig. 1. It is clear from this figure that increasingly severe oxygen treatment led to higher surface coverages of CO on the Pt foil. It was also found that increasingly severe oxygen treatment increased the ability of the catalyst sample to sustain reaction-rate oscillations. Fig. 2 shows voltage traces of reaction-rate oscillations after the three treatment levels described in fig. 1. The oscillations were found to be larger in magnitude and more uniform after the harsher treatments.

The above observations were quite reproducible and allowed successful initiation of oscillatory behavior on *new* samples. The surface infrared results



Fig. 1. Infrared spectra of adsorbed CO as a function of Pt sample pretreatment. All spectra were measured at 4×10^3 Pa of flowing reaction mixture at room temperature: (a) with no pretreatment; (b) after 60 s at 535 K in 4×10^3 Pa flowing reaction mixture; (c) after 60 min at 775 K in 10^{-2} Pa flowing O₂ and cooling in O₂, followed by 60 s at 535 K in 4×10^{-3} Pa of flowing mixture; (d) after 60 min at 1075 K in 10^{-2} Pa flowing O₂ and cooling in O₂ followed by 10 s at 535 K in 4×10^{-3} Pa of flowing mixture; (e) as in (d), followed by 60 additional seconds at 535 K in mixture; (f) as in (e), followed by 3 additional minutes at 535 K in mixture.



Fig. 2. Oscillation results as a function of pretreatment. Oscillations obtained in 4×10^{-3} Pa of flowing reaction mixture, shown as sample potential drop $(-V_m)$ versus time, with sample resistance held constant: (a) no pretreatment in oxygen, new sample heated to 535 K; (b) after O₂ treatment at 775 K; (c) after O₂ treatment at 1075 K.

suggest that the cause of the increasing CO adsorption and the more pronounced reaction-rate oscillations with increasingly severe oxygen treatment is likely to be the increasing cleanliness of the platinum surface after these treatments.

3.2. Inducing oscillations

The conditions under which oscillations are initiated can provide important information as to the oscillation mechanism. Discussed below is a reliable method to induce oscillations on any new foil sample, based on spectroscopic results.

Before each oscillation experiment, the sample was heated for 3 min in 4×10^3 Pa of flowing reaction mixture at ≈ 775 K. Baseline spectra were then collected using p and s polarizations in flowing mixture at room temperature. The CO coverage obtained from these spectra was used as a qualitative measure of the cleanliness of the surface and the reproducibility of the starting surface. The gas pressure in the reaction cell was then set at the desired value (typically 4×10^3 Pa).

When the average temperature of the sample was around 525 K, a small increase in the programmed sample resistance would result in a sharp decline



Fig. 3. Detail of spike in reaction rate, shown as sample potential drop $(-V_m)$ versus time. Sample resistance, i.e. temperature, is held constant by controlling the current through the sample to compensate for changes in reaction rate. Thus, a decrease in V_m corresponds to an increase in reaction rate.

(spike) in the potential drop across the sample followed by a slow recovery (see fig. 3). The potential drop across the sample before the spike was larger than that following the spike. This transition was accompanied by a substantial increase in the gas-phase CO₂ level, indicating that the catalytic oxidation had ignited. The adsorbed CO band disappeared after the spike. Any further increase in the average temperature of the sample (above $T_0 \approx 535$ K) brought about a mild increase in the reaction rate and no additional sharp transitions were observed.

If the average temperature of the sample was decreased below T_0 the catalytic oxidation remained ignited until about 10–20 K below T_0 at which point a quenching of the reaction rate would occur. This transition, occurring over a duration of several seconds was indicated by an increase in the potential drop across the sample, and a decrease in gas-phase CO₂, and slowly increasing adsorbed CO.

Reaction-rate oscillations occurred in the temperature region just above and somewhat below T_0 . The precise position of the lower limit for the oscillatory region was difficult to define, as the period of oscillation increased with decreasing average sample temperature to well over 60 min and became difficult to monitor. An estimate of the lower limit is 15 K below T_0 , and that of the upper limit is 5 K above T_0 , so that the region of oscillations is approximately 20 K around T_0 .

3.3. Time-resolved data during oscillations

With oscillations well-established, detailed IR studies were performed during the entire oscillation cycle. The primary goal of these studies was to assess the value of FTIR-RAS for this specific problem. The data presented here on CO adsorption on Pt shows that quantitative information can be obtained for al the important timescales of the oscillations. It further provides a tool for the evaluation of proposed models, as well as new insights into the phenomenon, as will be discussed in section 4.

Fig. 4 shows a trace of the potential drop across the sample, during a single period of the reaction-rate oscillations for a 0.0127 mm thick Pt foil. Important features of a cycle are the high and low reaction states, the large, sharp ignition transient, or spike, and the small minicycles, similar in shape to the main cycle. These features have appeared in all oscillations observed with our system. The voltage trace shown in fig. 4 is exerpted from a 36 h run, during which the oscillations were sustained with < 10% change in period or amplitude.

Reaction-rate oscillations were observed under constant-current (variabletemperature) mode of operation as well. Qualitative features of the oscillations under constant-current mode were very similar to those observed under the constant-resistance mode. In addition, qualitative features of the oscillations remain unchanged over a wide range of total gas pressure in the cell $(5 \times 10^2$ to 5×10^4 Pa) and average sample temperatures in the 475 to 550 K range.

During the oscillation cycle shown in fig. 4, 200 infrared spectra were collected, each spectrum signal-averaged from 10 scans (requiring 12.5 s per spectrum with a 60% duty cycle, i.e. 7.5 s of measurement). Individual spectra corresponding to the six points marked in fig. 4 are shown in fig. 5. During the early part of the ignited branch in the main cycle (before the minicycles begin



Fig. 4. Single oscillation period, shown as sample potential drop $(-V_m)$ versus time. Sample was maintained at 540 K in 4×10^3 Pa of flowing reaction mixture. 200 spectra were collected during the time shown; letters a-f refer to individual spectra shown in fig. 5.



Fig. 5. Individual spectra collected during single oscillation period shown in fig. 4: (a) just after transition (spike) to high reaction-rate branch; (b) during dip in minicycle; (c) after dip in minicycle, but before transition to low reaction-rate branch; (d) early in low reaction-rate branch; (e) later in low reaction-rate branch; (f) just before transition (spike) to high reaction-rate branch. Collection time is 12.5 s per spectrum.

to appear), the adsorbed CO is below the noise level, i.e. the coverage of CO is less than 5% of a monolayer (see curve a of fig. 5). Once minicycles begin to appear, small amounts of adsorbed CO can be detected during the partially quenched segment of the minicycles (curve b). CO could not be detected during the high side of the minicycles (curve c). In the quenched segment of the main cycle, the absorption due to adsorbed CO rises rapidly at first, then continues to increase slowly, reaching a maximum just before the ignition occurs (curves d to f).

From the spectra collected during the oscillation cycle shown in fig. 4, the peak frequency, the FWHM and the integrated absorbance of CO linearly bonded to platinum, and the integrated absorbance of gas-phase CO_2 were calculated and are shown in fig. 6.

In order to investigate the events occurring on the catalyst surface during the ignition period (spike), infrared spectra with only one scan per spectrum were collected. These are shown in fig. 7 from which it is clear that the adsorbed CO is removed within a few seconds, approximately the same length of time it takes for the voltage trace to settle down in the ignited branch (fig. 3).



Fig. 6. Spectral features as a function of time for the oscillation cycle shown in fig. 4: (a) Integrated intensity of absorption from gas phase CO_2 ; (b) integrated intensity of absorption from adsorbed CO (note that minicycles appear toward the end of the low reaction-rate branch); (c) bandwidth of absorption from adsorbed CO; (d) frequency of absorption from adsorbed CO.

4. Discussion

In this section, we first discuss the infrared observations in the context of previous work. While the main features of the data are in agreement with previous work, new features such as the ignition spike help to provide more insight into the reaction mechanism. We then review the major oscillation models, and critically apply our data to support or dismiss specific points when possible.

4.1. Reaction regimes

At a fixed feed gas composition and flow rate, as the sample temperature is raised slowly, at least three regimes can be identified. At low temperatures, the sample is predominantly covered with CO and a very low reaction-rate obtains (regime III). At some critical temperature T_0 (dependent on the gas-phase composition, pressure and flow rate), ignition occurs. At temperatures well above T_0 , a high reaction rate obtains and the surface coverage of CO is typically below the noise level for infrared measurement in our system (regime I). In a small temperature range around T_0 , an oscillatory oxidation of CO obtains (regime II). This pattern is in agreement with the results reported by Turner et al. [18,20] and Okamoto et al. [26].

The voltage trace obtained during the oscillations can be viewed as ap-



Fig. 7. Spectra collected during reaction ignition (spike). The time resolution is 0.6 s per spectrum. Ignition began after spectrum (b) was collected. Adsorbed CO is below the noise level by the time spectrum (g) was collected, 3.0 s later. The voltage trace of a spike lasts approximately 5 s.

proximately square-wave in shape, except near the transitions. The square-wave contains a low reaction-rate branch and a high reaction-rate branch. Our infrared results indicate substantial CO coverages during the low reaction-rate branch. In the high reaction-rate branch, however, the surface coverage of CO is typically below the noise level, except in the partially quenched segment of the minicycles where a small surface coverage of CO is detected (see fig. 5, curve b). On the basis of the typical levels of adsorbed CO (fig. 6b) and gas-phase CO_2 in the reactor (fig. 6a), it is consistent to identify the low and the high reaction-rate branches as representative of regimes III and I respectively, in agreement with the conclusions of previous researchers [18,20,26].

4.2. High reaction-rate branch

As the level of adsorbed CO in the high reaction-rate branch is typically below the noise level (except in the partially quenched segment of the minicycles), our infrared results do not reveal much information concerning the state of the surface during this branch. We believe that the fraction of the surface occupied by oxygen (chemisorbed or otherwise) is increasing slowly in this branch and that shortly before the transition from the high to the low reaction-rate branch of the main cycle, there is a densely packed layer of oxygen on the surface. Such a densely packed layer of oxygen could inhibit chemisorption of CO, resulting in a slow decay in the reaction-rate branch to the low reaction-rate branch of the main cycle.

4.3. Low reaction-rate branch

The voltage trace obtained during the oscillation cycle shows that the transition from the high to the low reaction-rate branch occurs over several seconds duration (fig. 4). This is supported by the gas-phase CO_2 concentration measurements (fig. 6a). The surface coverage of CO increases rapidly during the transition period and at a much slower rate during the low reaction-rate branch. Even though the timescale for increase in CO coverage during the transition period is rapid compared to the period of the oscillation, it is still very long compared to typical timescales for chemisorption of CO. It is difficult to rationalize such a long timescale for the adsorption of CO purely on the basis of variation in its sticking probability alone. We therefore suggest that a densely packed layer of oxygen is present on the surface shortly before the transition from the high to the low reaction-rate branch.

During the low reaction-rate branch, the changes in the peak frequency at which the infrared radiation is absorbed by chemisorbed CO (fig. 6d) and the frequency width at half-maximum (fig. 6c) are quite small. These observations, along with fig. 6b suggest that the local adsorption environment for the CO

does not change substantially during the low reaction-rate branch, while the amount of chemisorbed CO increases steadily, i.e. the CO molecules reside on the surface in islands. The growth of CO islands would occur at the expense of oxygen islands which are slowly removed by reaction at the island boundaries.

It can be seen from fig. 6a that the CO_2 content in the gas phase increases slowly in the low reaction-rate branch. This implies that the rate of the oxidation reaction increases slowly in this branch. The surface coverage of CO is also increasing slowly in this branch (fig. 6b). It then follows that the low reaction rate obtained in this branch is not solely due to a simple blocking of the surface by chemisorbed CO. Oxygen, for example, adsorbed or otherwise, may play an important role in suppressing the reaction rate.

4.4. The ignition period

As the average temperature of the sample remains constant during the oscillations, the energy dissipation from the sample to the gas phase and to the sample holder through conduction, convection and radiation is approximately constant at all times. A portion of the energy dissipated by the sample is supplied by resistive heating while the remainder comes from the chemical reaction. Treating the low reaction-rate branch as the baseline, it is a straightforward calculation to determine from the voltage trace during ignition (spike) the excess thermal energy given to the sample by the reaction occurring on it during the ignition process. If it is assumed that the heat of reaction is completely transferred to the sample before the product CO_2 desorbs from the surface, a lower bound for the number of CO molecules that must have reacted during this period can be calculated. Assuming that 7.2×10^{14} CO molecules are adsorbed at saturation coverage [40] we obtain that at least 100 monolayers of CO must have reacted during the spike shown in fig. 3. The actual number of CO molecules that will have reacted on the surface during the spike will be, in general, larger than this estimate, as it has been established that only a fraction of the heat of reaction is transferred to the sample before the product CO₂ desorbs from the surface [41]. It therefore follows that the spike is not simply the "burning-off" of a single monolayer of CO. This is in agreement with the spectra shown in fig. 7. Here it can be seen that once the ignition starts, the CO coverage drops below the noise level in less than 3 s, while the spike itself lasts nearly 5 s (fig. 3). It can be seen from fig. 7 that the peak frequency remains approximately constant during the spike, while the integrated absorption of the peak decreases. This suggests that during the spike, the chemisorbed CO originally present on the surface in the low reaction-rate branch is being reacted away at island boundaries. Kaul and Wolf [42] propose that the ignition represents a temporary increase in the efficiency of energy transfer from "hot" CO₂ molecules to the catalyst surface. The energy calculation discussed above does not support this proposal.

4.5. Various hypotheses for the occurrence of oscillations

The experimental results show two distinct features, namely, the minicycles and the main cycle. It follows from simple mathematical arguments that any lumped parameter model describing these results must contain at least three dependent variables. The period of the minicycles observed in our experiments is in the range of 30 to 90 s, while the residence time of the gases in the reactor is in the range of 10 to 30 s. It therefore appears reasonable to argue that one of the three key dependent variables is the partial pressure of CO in the reactor and that the period of the minicycles is related in some fashion to the residence time of the gases in the reactor. The other two key dependent variables must reflect conditions at the catalyst surface (for example, the coverages of the adsorbates). In order to explain the long period of the main cycle it is essential that there be a kinetic rate process taking place on the catalyst surface with a characteristic time comparable to the period of the main cycle. Identifying this kinetic rate process has been the goal of every experimental study on this topic. Several hypotheses for this slow rate process have been proposed in the literature.

Experiments performed with a HgCdTe detector failed to reveal any bridge-bonded CO on the surface at any time during the oscillation cycle. It is therefore unlikely that the oscillations are caused by a slow reversible process in which the chemisorbed CO goes from a linearly-bonded state to a bridge-bonded state cyclically, as has been speculated in the past [2]. Several other studies dealing with oscillatory oxidation of CO over supported platinum catalysts have led to a similar conclusion [22,23].

It has been suggested that exposure of platinum to oxygen at high temperatures may lead to the formation of a subsurface oxide [18,20,31-36]. Once formed, this subsurface oxygen would be difficult to remove at lower temperatures as a result of low diffusity of oxygen in bulk platinum at these temperatures [34]. It has also been suggested in the literature that the oscillations are caused by a slow reversible formation and reduction of such an oxide [5,6,18,20,31] and a model based on such a hypothesis has been shown to reproduce experimental data quite well [31]. Several studies [37-39] have reported that chemisorption of CO on a supported platinum catalyst following a high-temperature oxygen treatment gives rise to an infrared absorption feature at ≈ 2120 cm⁻¹. This absorption feature has been attributed to the C=O stretch from CO chemisorbed on platinum oxide. However, an infrared absorption feature at $\approx 2120 \text{ cm}^{-1}$ was not detected at any time during the oscillation cycle. Our results do not, therefore, provide a direct support for the cyclic formation and removal of an oxide as an explanation for the observed oscillations.

On the basis of their solid electrolyte potentiometry and transmission infrared spectroscopy studies, Okamoto et al. [26] argue that the oscillations are caused by a slow rate process that has an activation energy of 54 kJ/mol. They further argue that the most plausible rate process responsible for the oscillations is the mobility of chemisorbed CO molecules. Even though the inherent ability of the CO molecules to migrate on the catalyst surface is quite high at these temperatures, their movement on the surface is likely to be severely restricted by the very high total surface coverages present at all times during the oscillations. As already discussed, our results strongly suggest that nonuniform distributions of carbon monoxide and oxygen (in the form of separate islands) exist on the catalyst surface. It is, however, far from obvious at this stage whether these nonuniform distributions are the cause or the effect of the observed oscillations. Several researchers have attempted to incorporate the presence of nonuniform distributions in kinetic models in an effort to understand their role in explaining the oscillations [43,44]. No clear picture has emerged yet.

Ertl and co-workers [25,26], on the basis of their video-LEED data and work-function measurements, argue that the oscillations are caused by a reversible reconstruction of the (100) surface of platinum. Our results cannot be used to critically evaluate this hypothesis. Clearly, substantial work, both experimental and theoretical, remains to be done before this issue can be resolved completely.

5. Conclusions

In this paper we have shown that FTIR-RAS can be used advantageously to study non-steady-state surface reactions, in particular the oscillatory oxidation of CO over Pt. The response time of the instrument used is adequate to study all important timescales in the oscillations. Extending the frequency range so as to probe all forms of oxygen associated with the surface is clearly important, although difficult. The study of the CO vibration alone has allowed us to critically evaluate various theoretical models.

Though no self-contained explanation of the mechanism is available at this time, our present results establish several points which we now summarize. The pretreatment in oxidizing atmosphere results in a marked uptake of CO upon exposure, indicating that some as yet unidentified surface contamination is removed. On the now reactive surface, close to 1 monolayer of CO is adsorbed linearly in the low reaction-rate branch of the oscillation. There is no evidence for bridge bonding. Since the level of CO in the high reaction-rate branch is below the noise level (except in the partially quenched segments of the minicycles), it is likely that the fraction of surface occupied by oxygen (chemisorbed or otherwise) increases in the high reaction-rate branch and that there must be a densely packed layer of oxygen on the surface shortly before the transition from the high to the low reaction-rate branch of the cycle. In the low reaction-rate branch the CO molecules appear to reside on the surface by forming islands. The growth of these islands is presumed to occur at the expense of oxygen islands, which are slowly removed by reaction at the island boundaries. In the low reaction-rate branch, the surface coverage of CO increases slowly and so does the reaction rate. This indicates that the low rate of reaction in this branch cannot be due only to a simple blocking of the surface by chemisorbed CO. The transition from the low to the high reaction-rate branch occurs very rapidly. During the ignition process, the chemisorbed CO originally present on the surface is being reacted away at island boundaries. The ignition process, however, is not simply the "burning-off" of a single monolayer of CO.

It should be stressed that there is so far no unambiguous evidence for the presence of oxide on the surface during oscillations, although a mechanism based on oxide formation has been widely investigated. Clearly adsorbed oxygen is a key element in the oscillation mechanism. A direct probe of this oxygen is critical. Our results with CO and the experimental insights gained from this study will help considerably in the study of the interaction of oxygen (and possibly impurities) at the Pt surface. Such a work is under way.

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