

Kinetic Oscillations in the Platinum-Catalyzed Oxidation of Co

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Oscillations of the steady-state rate of catalytic CO oxidation on clean Pt surfaces were observed under low-pressure conditions and are related to the adsorption properties of the reactants. Evidence is presented for a model in which the reversible $(5 \times 20) \rightleftharpoons (1 \times 1)$ phase transition of the Pt(100) surface (which is associated with a marked variation of the oxygen sticking coefficient) is responsible for the oscillations.

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During recent years numerous reports have appeared in the literature on the observation of temporal oscillations in the steady-state rate of heterogeneously catalyzed reactions, among which the oxidation of carbon monoxide on platinum surfaces was the most extensively studied.¹ An equally large number of theoretical models were developed which are able to simulate the occurrence of such oscillations.^{2,3} However, all experimental studies so far were performed with poorly defined surfaces and (with one exception⁴) at fairly high pressures (≥ 1 Torr); no direct additional information supporting the origin of the oscillations has been available. The present work is the first report on sustained kinetic oscillations of a catalytic reaction performed with clean surfaces (polycrystalline and single crystalline Pt) under UHV conditions. The results are interpreted in terms of a novel mechanism based on the adsorbate-induced and reversible phase transition of the surface structure of the Pt(100) surface.

The experiments were performed in a stainless-steel UHV flow system equipped with a differentially pumped quadrupole mass spectrometer and with facilities for Auger-electron spectroscopy (AES) using a retarding-field energy analyzer. Either a polycrystalline Pt wire or Pt(111) and Pt(100) single-crystal samples were used. The Pt(111) surface was slightly misoriented and contained about 5% of defect sites as evident from previous O₂ and CO adsorption experiments performed with the same sample.⁵ The Pt(100) sample was oriented within 0.5° of the (100) plane and had been previously studied by Rutherford backscattering and low-energy electron diffraction.⁶ Cleaning of the surfaces was performed by repeated oxidation/reduction cycles until no impurities could be detected by AES. A Kelvin probe could be placed in front of the surfaces in order to continuously monitor the variation of the work function during the reaction.

The mechanism of this reaction is now well

established^{7,8} and proceeds through the following schematic steps:



Here, * denotes a free adsorption site. It has to be pointed out that preadsorbed oxygen has no noticeable inhibiting effect on CO adsorption. If, on the other hand, the surface concentration of CO exceeds a critical value the uptake of oxygen will be inhibited. Desorption of CO takes place in the temperature range of interest (450–530 K) while oxygen desorption can be neglected under these conditions. Under the chosen experimental conditions no evidence was ever found (by AES or $\Delta\phi$) for the formation of a more tightly bound (and less reactive) subsurface oxygen species.⁹ The mechanism proposed by Sales *et al.*³ for the origin of the oscillations based on slow formation and reduction of this species can clearly be ruled out in the present context; nevertheless it can come into play at higher pressures, particularly if surface impurities such as Si or Ca (Ref. 10) are involved.

If, at constant temperature and O₂ pressure, the steady-state rate, r , of CO₂ formation is recorded as a function of CO pressure, it at first increases continuously with increasing p_{CO} , then reaches a plateau, and finally decreases again. The explanation is straightforward: At first θ_{CO} and thereby $r = k\theta_{\text{O}}\theta_{\text{CO}}$ increase with increasing p_{CO} (θ_{O} and θ_{CO} are, respectively, the adsorbed CO and O coverages). Simultaneously θ_{O} decreases [since its rate of formation through Reaction (2) is constant if p_{O_2} is kept constant] until the plateau is reached, where θ has become very small and oxygen adsorption is now rate limiting, i.e., $r = s(\text{O}_2)p_{\text{O}_2}$ where $s(\text{O}_2)$ is the (dissociative) sticking coefficient for oxygen. Further increase of p_{CO} then causes the buildup of an appreciable

CO coverage which inhibits oxygen adsorption; that means that $s(\text{O}_2)$ and therefore r decrease. These aspects are crucial for the interpretation of the oscillations: These were observed at temperatures between 450 and 530 K under conditions where the steady-state rate r had just passed the above-mentioned plateau.

A typical set of data obtained with the polycrystalline wire is reproduced in Fig. 1. The periodic variation of the CO_2 partial pressure (= reaction rate) is also reflected in a corresponding modulation of the work function $\Delta\varphi$. For the work with the single-crystal surfaces this latter quantity was therefore used to characterize the oscillations, thereby eliminating effects from the rear or edges of the samples.

The amplitude of the periodic work-function variation, $\delta\Delta\varphi$, turned out to be very small for the Pt(111) sample. Much larger effects were observed with the Pt(100) surface, while the values for the polycrystalline Pt wire were between these two limiting cases (Fig. 2). Since the Pt(111) surface contained defects (see above) and the $\Delta\varphi$ amplitude increased if the Kelvin probe was shifted from the center of the sample to its edges, it is concluded that a perfect (111) plane would exhibit no oscillations at all. For the conditions underlying Fig. 2 the frequency of

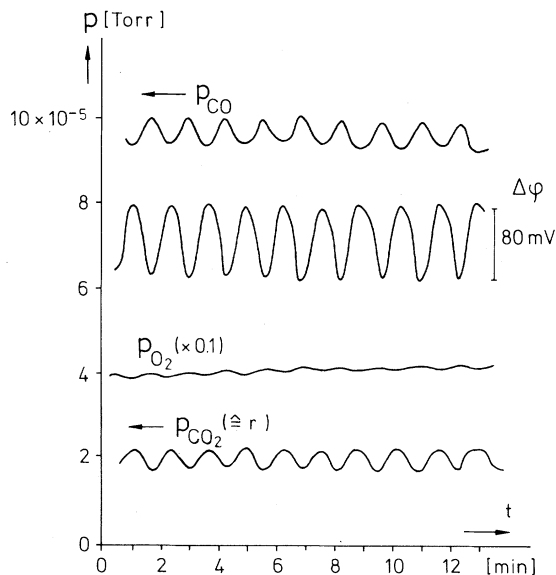


FIG. 1. Typical recorder traces of oscillatory kinetics on polycrystalline Pt: p_{CO} , p_{O_2} , and p_{CO_2} (= rate of CO_2 formation), as well as $\Delta\varphi$ as a function of time. $T = 502$ K, $p_{\text{O}_2} = 4 \times 10^{-4}$ Torr, and $p_{\text{CO, av}} = 1 \times 10^{-4}$ Torr.

the oscillations increases with temperature from $\sim 0.005 \text{ sec}^{-1}$ at 450 K to $\sim 0.1 \text{ sec}^{-1}$ at 520 K for all three samples in a quite similar manner. This suggests the operation of the same microscopic mechanism; the variation of the fraction of the surface area involved results in a corresponding variation of the $\Delta\varphi$ amplitude. The low-temperature cutoff of the oscillations (~ 450 K) coincides approximately with the temperature below which the CO coverage (even at low CO pressures) becomes rather high. The extinction of the oscillations at ~ 530 K coincides, on the other hand, with the temperature at which the rate of CO desorption from Pt(100), as well as from the defects on Pt(111), reaches its maximum; i.e., above this temperature θ_{CO} is very small unless the CO partial pressure is enormously increased.

For a given O_2 pressure (4×10^{-4} Torr) and fixed temperature the oscillations were restricted to a rather narrow range of CO pressures. These CO pressures are plotted in Fig. 3 for Pt(100) as a function of temperature in the form $\log p_{\text{CO}}$ vs $1/T$ (circles).

The Pt(100) surface is known to be stable in a quasihexagonal (5×20) structure¹¹ when it is clean, but to undergo a phase transition into the unreconstructed (1×1) structure if the coverage of an adsorbate exceeds a critical value.⁶ This transformation under the influence of CO was studied recently in detail by using a fast video-low-energy electron-diffraction system.¹² Adsorbed CO forms patches of the (1×1) surface

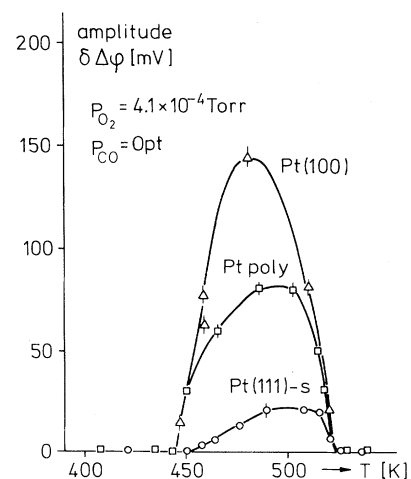


FIG. 2. Amplitude of the oscillations as reflected in the work-function modulation as a function of temperature for three different Pt surfaces.

covered with a $c(2 \times 2)$ overlayer at a (local) critical coverage $\theta_{CO,loc} = 0.5$. If, on the other hand, θ_{CO} is lowered again, the surface transforms back into the (5×20) structure. The squares in Fig. 3 denote the conditions for which upon continuously increasing the temperature at constant p_{CO} (i.e., continuous decrease of the CO coverage) the (5×20) structure just starts to develop.¹² These data points coincide well with the conditions for which the kinetic oscillations are observed, which strongly suggests that both effects are related to each other. Further support is obtained by the observation that the time scales for both processes are similar.¹³

Although a complete analysis has to wait for the mathematical solution of the model to be proposed, its qualitative features can easily be outlined: As mentioned above, the reaction rate may be expressed as

$$r = k_r \theta_O \theta_{CO} = s(O_2) p_{O_2}. \quad (4)$$

If now "steady-state" conditions are assumed, the CO coverage under reaction conditions, θ_{CO} ,

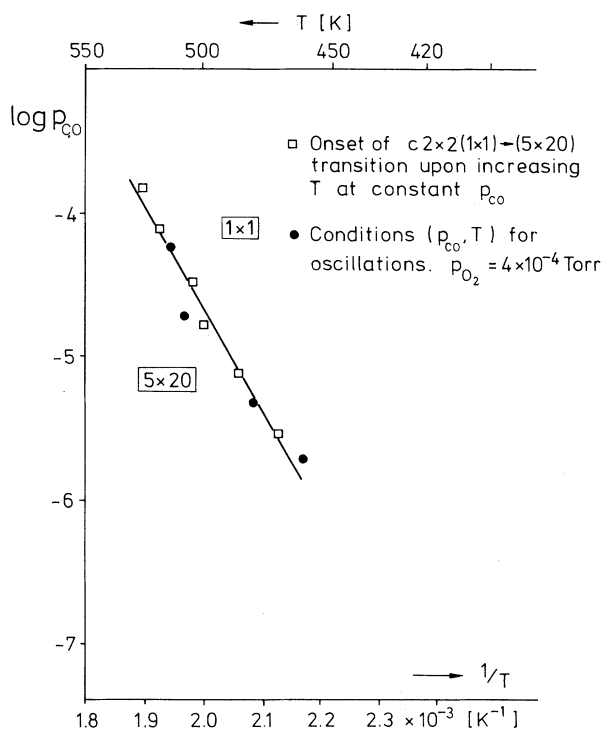


FIG. 3. $\log p_{CO}$ vs $1/T$ for Pt(100): Circles characterize the conditions for oscillatory kinetics at $p_{O_2} = 4 \times 10^{-4}$ Torr. Squares mark the onset of the $c(2 \times 2)$ - (1×1) - (5×20) phase transition induced by thermal CO desorption (Ref. 12).

can simply be related to that which would be established without reaction, ${}^0\theta_{CO}$, through

$$\theta_{CO} = \frac{{}^0\theta_{CO}}{1 + k_r \theta_O / k_d(CO)} = {}^0\theta_{CO} - \frac{s(O_2) p_{O_2}}{k_d(CO)}, \quad (5)$$

where $k_d(CO)$ is the rate constant for CO desorption. The essential point is that the sticking coefficient for dissociative oxygen adsorption, $s(O_2)$, is strongly structure dependent: It is of the order of 10^{-3} to 10^{-4} for Pt(100)- (5×20) ,¹⁴ but at least two orders of magnitude larger for the (1×1) phase,¹⁵ even if the latter is covered with CO up to $\theta_{CO} = 0.5$ [giving rise to a $c(2 \times 2)$ -overlayer structure].⁸ If one starts with a CO coverage ${}^0\theta_{CO}$ (without reaction) which is just above the critical value below which the $(1 \times 1) \rightarrow (5 \times 20)$ transformation occurs, $s(O_2)$ as well as r [Eq. (4)] will be large. According to Eq. (5) θ_{CO} will then be lowered and eventually drop below its critical value, so that the surface will relax into the (5×20) structure. (Note that the oxygen coverage will always be very small since the effects are only observed under conditions where oxygen adsorption is rate limiting. So θ_O will be without any noticeable effect on the surface phase transformation.) Now $s(O_2)$ and r will be small, and according to Eq. (5) θ_{CO} will again approach the value ${}^0\theta_{CO}$. Then the surface switches back into the (1×1) structure, r again becomes large, and one cycle of the oscillations is completed. It is evident that with this model the coverage ${}^0\theta_{CO}$ is crucial and should just be at the borderline for the $(1 \times 1) \rightarrow (5 \times 20)$ transformation. This conclusion is nicely confirmed by the two sets of data points in Fig. 3. Also the temperature limits observed can easily be explained in terms of Eq. (2) and this model: Below ~ 450 K the CO coverage will always be so high (even at very low p_{CO}) that under reaction conditions it will not drop below the critical value for restoration of the (5×20) phase. Above ~ 530 K, on the other hand, the rate of CO desorption will become so fast that considerably higher CO pressures are needed in order to increase ${}^0\theta_{CO}$ above its critical value, and in addition the modulation of θ_{CO} through the second term of Eq. (2) decreases with increasing $k_d(CO)$ (i.e., increasing temperature).

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