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1989 J. Phys.: Condens. Matter 1 SB1

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A photoemission microscopy study of Pt surfaces during the catalytic oxidation of CO

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Received 20 April 1989

Abstract. The transition from the high- to low-rate branches of the CO oxidation reaction has been observed on the grain surfaces of a Pt foil using photoemission electron microscopy. Dark areas of the image (high work function) distinguish the oxygen-rich adlayer of the high-rate regime from the light areas (low work function) characteristic of the low-rate regime. Not all grains exhibit the transition; grain boundaries and surface imperfections act as nucleation centres. Preliminary data for the Pt(100) surface show surface corrugations on approximately the $0.5\ \mu\text{m}$ scale that serve as channels for C combustion during oxidation cycles and may relate to the activity of this surface for the CO oxidation reaction.

1. Introduction

Oscillatory heterogeneous reactions are known to occur both on supported catalysts (see, e.g., [1]) and on metal single-crystal surfaces [2]. Particular attention has been paid to the oxidation of CO to CO₂ over Pt [3]. It is generally agreed that this reaction proceeds via the Langmuir–Hinshelwood mechanism, i.e. coadsorbed atomic O and CO react to form CO₂. The CO and O₂ molecules together need three sites to adsorb, and subsequent desorption of the product in turn frees two adsorption sites. Since CO blocks O adsorption, but O does not block CO adsorption, the reaction rate is strongly dependent on the supply of CO. In a simplified picture, the reaction can be divided into three regimes [3] when the O₂ pressure and temperature are kept constant. As the CO pressure is increased from zero, the rate of CO₂ production increases linearly with increasing supply of adsorbed CO. At too high a CO pressure, the rate decreases because CO blocks the dissociative adsorption of O₂ molecules and thus the supply of adsorbed O. In an intermediate region, the CO₂ production rate can oscillate between the two extremes, known as the high- and low-reaction-rate branches.

While most investigators agree that a temporary limitation on the supply of a reactant causes the oscillatory behaviour, the nature of the blocking or hinderance, the mechanism for reactivation of the blocked site and the organisation of the blocking on a macroscopic scale is still the subject of discussion. In [2, 3] it was suggested that surface reconstruction of faceting alter the sticking coefficient of O on the reconstructed surface, so that a reduction in the number of appropriate sites rather than a site blocking regulates the reaction rate. A second model [4] suggests that C blocks adsorption sites, and only samples with sufficient C reserves will show oscillatory reaction rates. Si and Pt oxides

have also been suggested as blocking agents [5]. A difficulty in understanding the reaction rate in the unstable region where kinetic oscillations occur and in finding a suitable mechanism is the observation of oscillatory behaviour on many materials in several forms: single crystals, wires, foil and supported catalysts.

We have used a newly constructed electron microscope based on the prototype in [6] to investigate the Pt surface during the catalytic oxidation of CO. Preliminary results for both polycrystalline Pt foil and the single-crystal Pt(100) surface are presented. Photoemission electron microscopy (PEEM) [7–9] and low-energy electron microscopy (LEEM) provide a real-space image of the sample surface under controlled conditions in ultra-high vacuum or in a reactive gas mixture. Such techniques provide a unique opportunity of studying both the surface morphology and the geometrical distribution of adsorbed reactants during a heterogeneous reaction. Previous electron microscopy studies of this sort have invariably been *ex situ*, e.g. the scanning electron microscopy study of Pt wire used for CO oxidation reported in [10].

2. Experimental details

A description of the microscope used may be found in [6]. An Osram HBO 100 high-pressure mercury lamp was used for PEEM. The lateral resolution in PEEM was about 100 nm for the operating conditions used to record the images in figure 1. The instrument is in principle capable of 20 nm resolution. The Pt surfaces were cleaned with extended cycles of Ar ion sputtering and electron bombardment heating (with an enclosed filament from behind) in O₂. Although the foil was regularly heated to higher than 1300 K, subsequent etching of the foil after removal from the microscope showed that several grain orientations were present [11].

3. Results and discussion

Image contrast in PEEM is a sensitive function of the sample work function. The highest-energy UV light emitted by the lamp is just sufficient to allow observation of some low work-function Pt facets [8]. Adsorption of O raises the work function of the surface beyond the photoemission threshold. Thus dark areas can be used as indicators of an O-rich adlayer. At the beginning of a typical reaction cycle (the high-rate branch) the entire Pt surface is 'black'; only low-work-function dust particles can be observed and used for focusing. The very light areas typical of the completed cycle (low-rate or completely inactive branch) actually consist of several different regions of differing work functions. These can be identified as predominantly CO covered with varying amounts of C. Areas covered with CO were determined to have work functions greater than 4.4 eV using an edge filter (280 nm) and could easily be converted to 'dark' areas by mild heating in O₂. Other regions of still lower work function (4.4 eV) remained light after heating to about 900 K in O₂. These are most probably due to C adsorption on the Pt surface [12] which results from cracking of CO at surface imperfections [13].

A typical sequence of PEEM images of a polycrystalline Pt foil in a 5:1 O₂-CO gas mixture at 5×10^{-5} Torr is shown in the photographs in figure 1. The vertical striations are marks left on the foil by the rolling process. The foil was heated to about 900 K in the gas mixture and observed for the complete cooling cycle until the entire surface had become 'bright' in PEEM. This simulates the two extremes in the oscillatory reaction; at

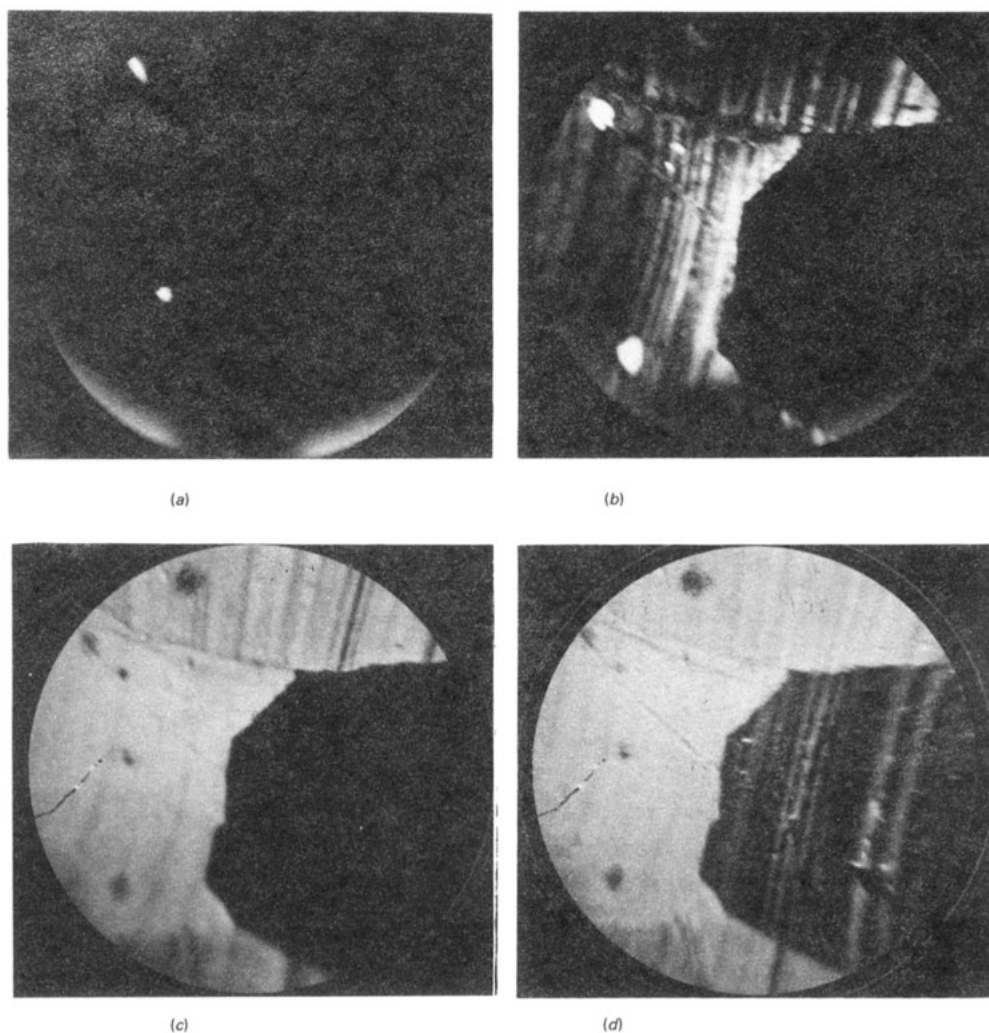


Figure 1. PEEM images of a Pt foil in a 5:1 O₂-CO mixture at 5×10^{-5} Torr total pressure: (a) high-rate branch, about 500 K; (b) 4 min later, no change in the right-hand grain; (c) 8 min after (a), a few light areas in the right-hand grain appear; (d) 9 min after (a), the right-hand grain has become partially light, with CO beginning to block the CO oxidation reaction, $T \approx 400$ K. The complete field of view is about 100 μm in all the photographs.

the higher temperature there is an O-rich adlayer but, as the temperature is lowered, some adsorbed CO reacts with adsorbed O to form CO₂. Subsequently, the continued adsorption of CO at a temperature insufficient for the formation of CO₂ blocks the adsorption of O and eventually halts the reaction completely. Usually the full cycle lasted about 20 min. The CO₂ partial pressure was qualitatively observed to drop from a 'high' value to a 'low' value (a difference of 20%) during the time span (about 10 min) covered in figure 1. The sample geometry does not allow for precise partial pressure analysis during PEEM; the measurements of CO₂ in the chamber is further hindered by a large signal produced by the UV lamp and desorption from high-voltage insulators.

The average cooling rate during this period was approximately 10 K min^{-1} . Heating in vacuum, or in either CO or O₂ alone did not produce the transition shown in figure 1.

The photographs shown in figure 1 are excerpts from a video tape film of the entire cooling process, which allows a more detailed analysis of events. While the entire surface was 'dark' initially, the grains on the left-hand side of the field of view began to lighten uniformly from the grain boundaries inwards. The right-hand grain, however, remains dark, i.e. covered with O and probably some CO, for several minutes before lightening in a relatively fast transition that begins at nucleation points in the *centre* of the grain. Each of the grains shows considerable structure due to the manufacturing process. In spite of these large-scale structures that serve as nucleation centres, it is clear that different grain surfaces behave differently with respect to the CO oxidation reaction. The qualitative correlation of the CO₂ partial pressure and the temperature with the transition of the right-hand grain in figure 1 suggests that only certain grain orientations, the presence of which was verified by subsequent etching, provide the active surfaces. At a later stage in these investigations, we hope to be able to identify the active grain orientations using LEEM. Steady state oscillations could not be produced at the pressures attainable in our microscope, so that no further conclusions as to the reactivation of blocked sites could be made.

We have recently begun the investigation of CO oxidation on Pt(100) since this surface is known to show oscillatory behaviour during CO oxidation at total pressures accessible in our microscope [2, 3]. So far, stable oscillations on Pt(100) could not be produced although the transition analogous to that on the Pt foil is observed. Large-scale surface structures ($0.5\text{--}1.0 \mu\text{m}$) serve as nucleation centres. Figure 2(a) shows the Pt(100) surface undergoing the same transitions as the Pt foil in figure 1. The experimental conditions were the same. For reasons of space we show only one picture in the sequence, corresponding roughly to figure 1(d). The crystal has a long history of successfully sustained oscillations in other experiments and is considered to be exceptionally clean. Thus, it can be heated in O₂ at pressures up to 10^{-4} Torr without detectable oxidation products. Ridges which are clearly visible in images of the clean surface are highlighted by CO adsorption at the ridge crests or ledges (bright lines) in the upper portion of the figure. The ridges are extended in one direction with a separation of about $0.5 \mu\text{m}$. A grain boundary, where the ridges meet at an angle of about 45° , is also shown. The lower portion of the photograph is still dark, indicating different reactivities for different 'grains', even on single-crystal Pt.

Figure 2(b) shows the oxidation and/or desorption of adsorbed CO and C on Pt(100) at the same grain boundary as figure 2(a), but after heating to about 900 K to simulate the low-to-high-reaction-rate transition in the oscillation reaction. The black areas are regions of adsorbed O (high work function). The oxygen islands (proposed in [14]) are elongated along the direction of the ridges, which are clearly resolved in the photograph. The remaining light areas are pure C at this temperature. The combustion of the surface C species on Pt(100) could be viewed in real time, and the spread of the O islands traced in the general direction along the ridges.

Because of the similarity of the 'light-dark' effects and a similarity in texturing of the Pt foil and Pt(100) surface, we speculate that the raised portions of both surfaces have a high activity for the adsorption of CO. CO dissociation is also expected [12] owing to the highly stepped slopes of the 'waves or ridges' on Pt(100) in the same way as at the rolling marks on the foil. It is likely that the requirements for cleaning the Pt (100) crystal—several tens of prolonged oxidation cycles at elevated temperatures—can lead to 'step bunching' [15, 16] or even facets that appear as smooth ridges in PEEM. We note

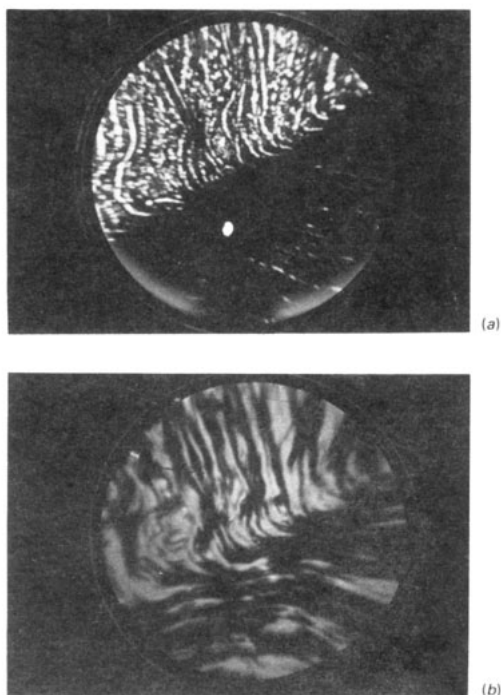


Figure 2. Pt(100) in the same gas mixture as figure 1. The field of view is about $100\ \mu\text{m}$. (a) A grain boundary runs from the lower left to the upper right of the figure. The ridges are highlighted by adsorbed CO in the upper half; in the lower half the ridges are not yet visible. The conditions are equivalent to figure 1(d). (b) The same position on the crystal, flashed to about 900 K in O₂, so that all the adsorbed CO but only a portion of the adsorbed C is removed. Note that the combustion of CO and C proceeds along the ridges.

that faceting is also observed to play a role in CO oxidation on Pt(110) [2]. It remains to be determined whether the roughness *or* cleanliness of the surface is the deciding factor. An unexpected but striking similarity of surface texturing on the single crystal and foil may be related to the observation of kinetic oscillations on these disparate surfaces.

4. Conclusions

PEEM can show in real time the adsorption processes occurring on Pt surfaces during the CO oxidation reaction. The image gives detailed information as to the reactivity of the grain surfaces and the type of nucleation centre. Surface structures on the fractional micrometre scale influence the surface reactivity and the geometrical distribution of reactants and products on the surface.

Acknowledgments

We would like to thank Professor E Bauer for his technical advice and cooperation during the construction of the microscope and Dr R Imbihl for the loan of the Pt(100) crystal.

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