Chemical Reaction Fronts on Platinum Surfaces

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In many chemical reactions catalysed on platinum surfaces it is necessary that two reactants be adsorbed simultaneously. Often one reactant is so strongly adsorbed that it blocks the adsorption of the second; such a reaction is said to be self-poisoned. An example is the oxidation of carbon monoxide, where carbon monoxide forms a strongly adsorbed monolayer which effectively blocks the adsorption and decomposition of oxygen. Photoelectron microscopy shows, however, that oxygen can penetrate the carbon monoxide film at special defect sites, typically inclusions or microdust particles, on the platinum. From these special adsorption sites the oxygen rapidly reacts with neighbouring adsorbed carbon monoxide. Reaction fronts initiate at these sites and rapidly propagate across the surface. A second type of self-poisoning occurs in decomposition reactions for which vacant surface sites are necessary; for instance, the decomposition of nitric oxide in the presence of hydrogen. A monolayer film of nitric oxide poisons the reaction not by blocking the adsorption of hydrogen, but rather by preventing the dissociation of nitric oxide which requires a neighbouring unoccupied surface site. Empty sites are provided on impurity particles which weakly adsorb nitric oxide and initiate reaction fronts. Impurity sites also initiate reaction fronts when graphite is removed from platinum by oxidation. In order to avoid self-poisoning in catalytic reactions, these studies suggest that special adsorption sites should be introduced artificially to provide vacant sites by adsorbing only weakly the reactants causing self-poisoning.

A chemical reaction front forms a boundary between unreacted material and an area which has undergone chemical reaction. A flame moving through a combustible medium is an example of a chemical reaction front. In unmixed systems reactants must diffuse together. They react in what are called reaction-diffusion fronts (1).

If the reaction at the front involves a chain-reaction or autocatalytic step, in which formation of product accelerates the reaction, the front may travel many orders of magnitude faster than diffusion alone would permit (1). Fronts occur in a very large variety of chemical reactions, and are extensively studied in the relatively new science of synergetics, which considers dynamic systems which are far from equilibrium (2).

Chemical reaction fronts also occur in monolayer films adsorbed on platinum during many catalytic reactions. The possibility of reaction fronts on platinum and the need for vacant surface sites was considered by Langmuir in 1921 (3). Fronts were detected by many indirect means (4), but can now be observed directly on platinum single-crystal or polycrystalline surfaces using photoelectron microscopy (5).

Photoelectron Microscopy

In the photoelectron process, electrons are emitted from a sample exposed to light. For solids, the energy of the light must exceed the

energy necessary to eject an electron into the vacuum. This minimum energy is called the work function. For most surfaces, this requires ultra violet light. Photoelectron emission is sensitive to a single adsorbed monolayer on a surface. Because of this it is possible to observe single monolayer films by photoelectron microscopy.

Images of surfaces are obtained by simply focusing photoelectrons onto a viewing screen. This is accomplished by using an electron lens similar to those used in conventional electron microscopy. Figure 1 is a schematic diagram showing the basic features of a simple photoelectron microscope with an electromagnetic lens. In practice, however, more complicated arrangements with multiple lenses are used (6,7). The contrast in a photoelectron image depends upon the relative photoelectron yield. Areas with different work functions release different numbers of photoelectrons, which, in turn, produce a different intensity on a viewing screen.

Although atomic resolution has not been achieved in photoelectron microscopy, the great advantage of this technique is its ability to observe dynamic events in real time, such as reaction fronts (5) and chemical kinetic oscillations (8–10) in single monolayer adsorbed films. These can be recorded at ordinary video rates (0.04 s per frame) or photographed directly from the viewing screen. Still photographs, however, only poorly portray the dynamics occurring during catalytic reactions on surfaces. The studies reported here were performed on single crystal platinum surfaces under ultra high vacuum.

The Oxidation of Carbon Monoxide on Pt{100}

Under certain reaction conditions, fronts are seen during the catalytic oxidation of carbon monoxide on platinum. The conditions necessary are shown schematically in Figure 2. This reaction is self-poisoned by carbon monoxide. At lower temperatures and high partial pressure of carbon monoxide, the carbon monoxide effectively forms an impenetrable
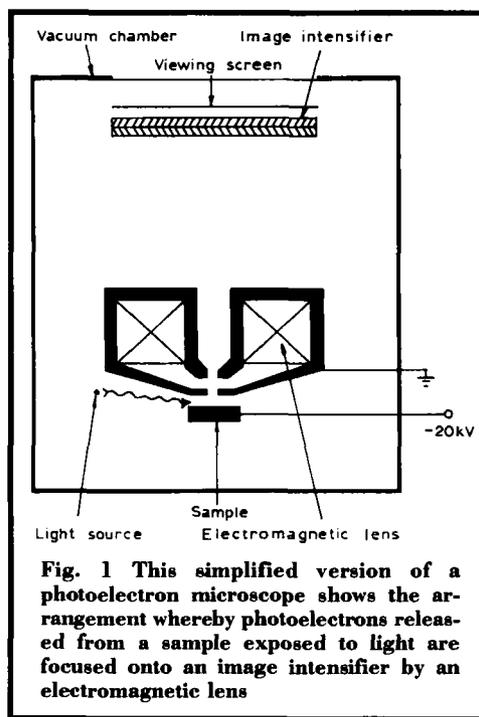

Fig. 1 This simplified version of a photoelectron microscope shows the arrangement whereby photoelectrons released from a sample exposed to light are focused onto an image intensifier by an electromagnetic lens

monolayer film on platinum which blocks the adsorption and dissociation of oxygen, and stops the reaction. This is represented in Figure 2(a). In order for the reaction to proceed, a hole must be formed in the carbon monoxide film to allow the adsorption of oxygen. One way to produce holes in the film is to increase the temperature to 500 K and thermally desorb some of the carbon monoxide Figure 2(b). On an ideal defect-free surface this would occur randomly throughout the film and no fronts would be formed. A second method to produce holes in the carbon monoxide film is to provide impurity sites on the platinum which do not adsorb carbon monoxide, but which adsorb oxygen.

Oxygen adsorbed on such sites can react with the side of the carbon monoxide film, which is vulnerable to attack, although the top of the film remains inert. This is shown schematically in Figure 2(c) and (d). Once initiated at an impurity site, the reaction front propagates out into the carbon monoxide film, removing it by forming carbon dioxide, which
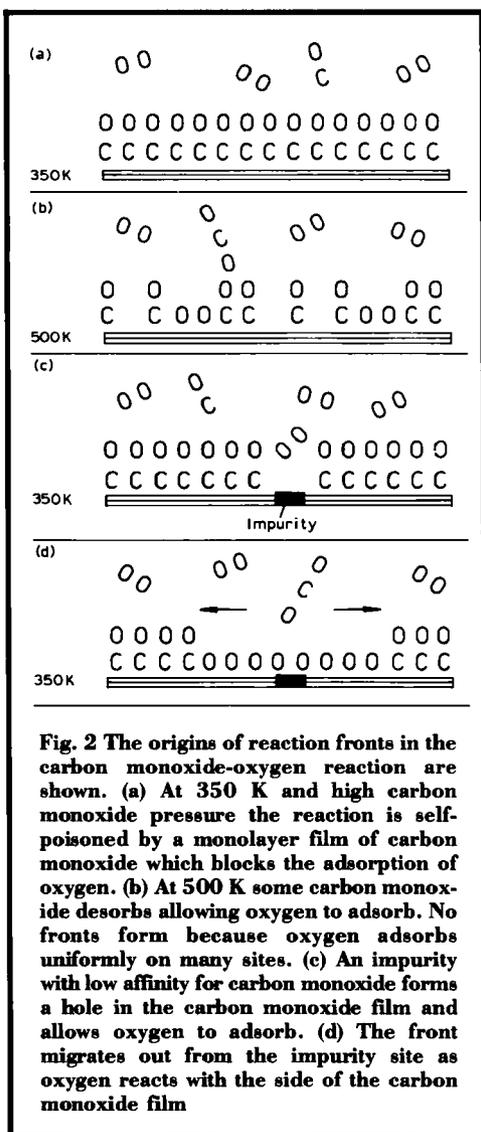
Fig. 2 The origins of reaction fronts in the carbon monoxide-oxygen reaction are shown. (a) At 350 K and high carbon monoxide pressure the reaction is self-poisoned by a monolayer film of carbon monoxide which blocks the adsorption of oxygen. (b) At 500 K some carbon monoxide desorbs allowing oxygen to adsorb. No fronts form because oxygen adsorbs uniformly on many sites. (c) An impurity with low affinity for carbon monoxide forms a hole in the carbon monoxide film and allows oxygen to adsorb. (d) The front migrates out from the impurity site as oxygen reacts with the side of the carbon monoxide film

desorbs, and replacing it by adsorbed oxygen. An adsorbed monolayer of oxygen does not poison the reaction. By artificially adding such impurity sites on the platinum, the reaction can be made to proceed more efficiently at lower temperatures, or at higher partial pressures of carbon monoxide. In practice, such sites are often present in the form of impurity inclusions or dust particles.

A reaction front propagating through a monolayer of carbon monoxide adsorbed on

Pt{100} at 350 K is shown as a photoelectron image in Figure 3. The front initiated at an impurity inclusion, seen in the centre of each frame. The monolayer film of oxygen, which forms behind the reaction front, appears dark relative to the carbon monoxide because it has a higher work function, 6.46 eV (11), compared to 6.11 eV of carbon monoxide (11). A deuterium lamp, which has a maximum photon energy of ~6.9 eV (180 nm), was used as the light source.

To initiate the front, oxygen at a pressure of 1.0×10^{-2} Pa was added to the vacuum chamber of the microscope. This is near to the maximum pressure at which observations can be made. The partial pressure of carbon monoxide was increased until the platinum surface was saturated with a monolayer of carbon monoxide. This required a partial pressure of carbon monoxide of only 2.4×10^{-3} Pa. Impurity sites were also saturated with adsorbed carbon monoxide under these conditions, and the reaction was self-poisoned. When the partial pressure of carbon monoxide was lowered reaction fronts initiated at dust particles and inclusions.

The carbon monoxide, which is relatively weakly adsorbed on some impurities, is displaced by competitive adsorption of oxygen. Oxygen adsorbed on the impurity sites then reacts with the side of the neighbouring carbon monoxide film.

The reaction-diffusion fronts illustrated in Figure 3 show an anisotropy. This is caused by step bunches on the surface which hinder diffusion. Step bunches, which are groups of atomic steps, are often observed on platinum surfaces after sputtering (12), thermal etching or catalytic etching (13). They also arise from glide lamellae or slip bands (14) which form on platinum when it is thermally stressed. Figure 4 shows step bunches on a Pt{100} single crystal surface. To make them visible in the photoelectron image, they were decorated with carbon (15). This was removed before the catalytic reaction, by heating in oxygen. The directions of the step bunches varied in different areas of the crystal.
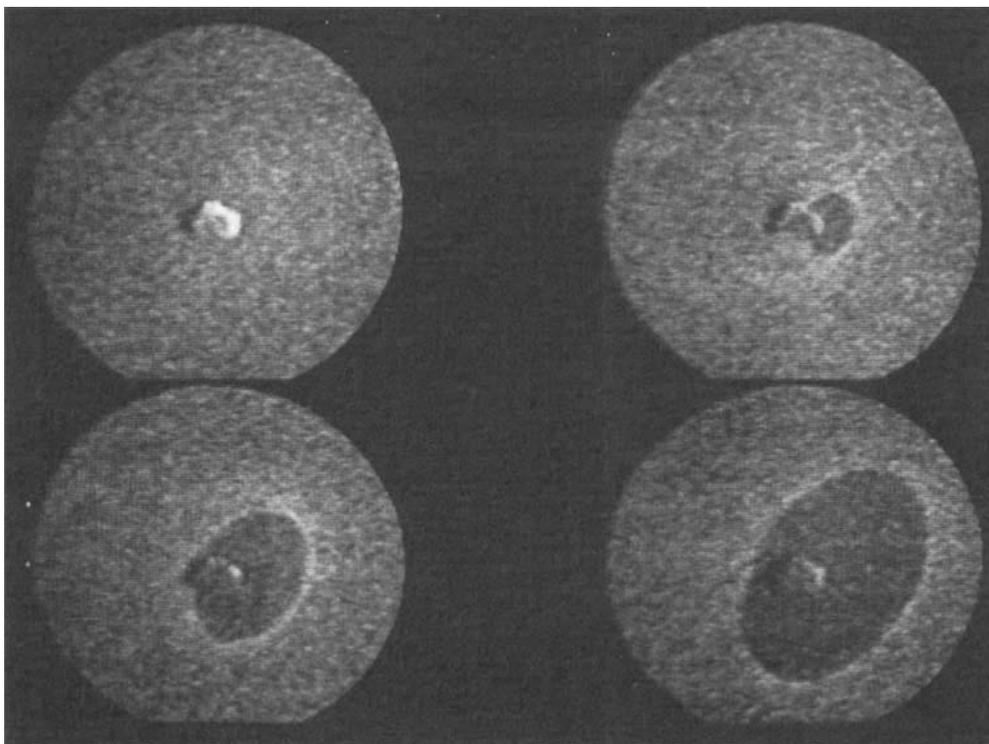
Fig. 3 A reaction front during the oxidation of a monolayer of carbon monoxide adsorbed on Pt{100} is shown at 0, 15, 18 and 25s. Bright areas on the photoelectron image are monolayers of carbon monoxide, dark areas are monolayers of oxygen. The impurity inclusion initiates a front at 350 K. Diameter: 230 μm

The reaction-diffusion fronts travel more slowly over the steps compared to travel along them. Surface steps can strongly bind reactants and form activation barriers for diffusion over them (16, 17). Diffusion over steps is impeded and therefore reaction-diffusion fronts travel with a lower velocity in directions over steps, relative to directions parallel to steps.

The Nitric Oxide + Hydrogen Reaction on Pt{100}

In excess hydrogen, platinum readily catalyses the formation of ammonia from NO (18). This is an unwanted side reaction in automobile air pollution control catalysts, on which nitric oxide in the presence of hydrogen is preferentially converted into nitrogen and water (18). In fact, according to Shelef the un-wanted production of ammonia was one of the most difficult problems to overcome in the
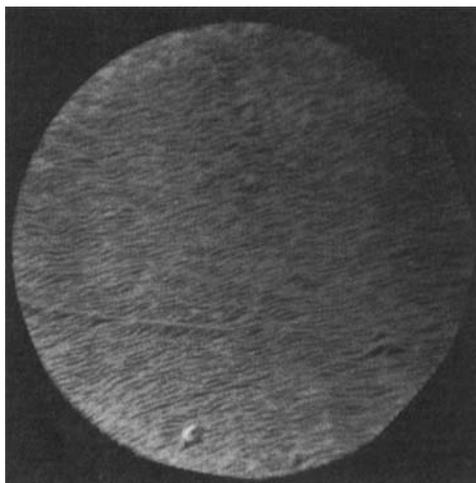

Fig. 4 The step structure on Pt{100} is shown. Reaction-diffusion fronts migrate more rapidly along steps than over them, because of diffusion barriers at the steps. Steps are decorated with carbon. Diameter: 230 μm
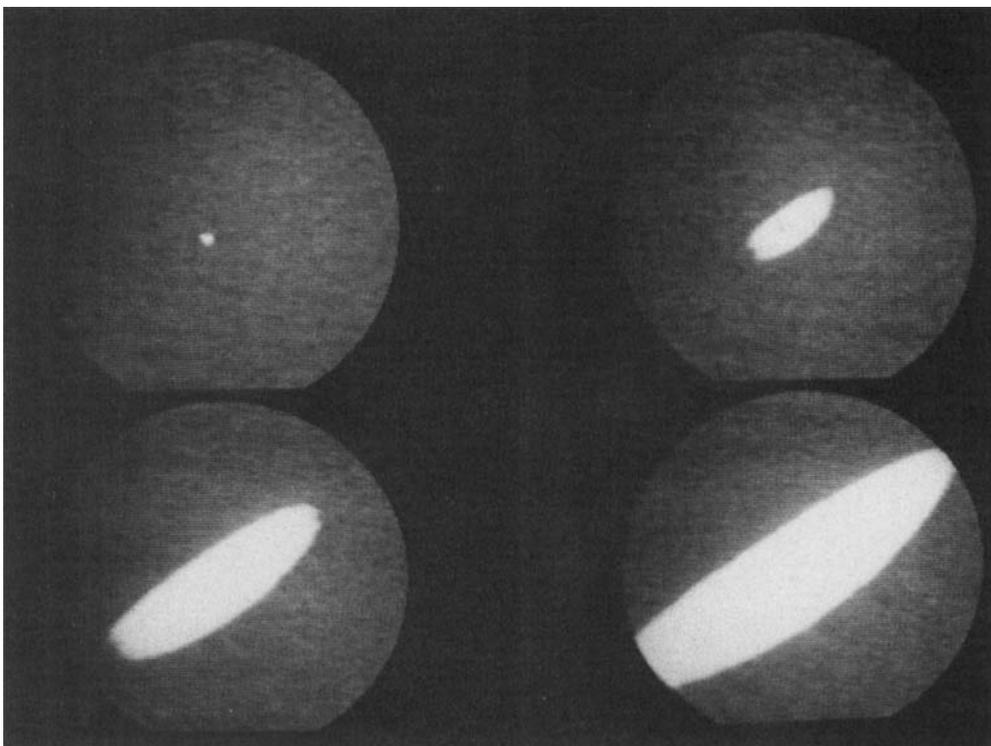
Fig. 5 A front initiated at a dust particle in the reaction between nitric oxide and hydrogen on Pt{100} is shown at 0, 5, 10 and 12 s. The dark areas are monolayer nitric oxide, and the bright areas are ammonia. Temperature = 415 K. Diameter: 230 μm

development of automotive catalytic converters, and rhodium was eventually substituted for some of the platinum (18).

Reaction-diffusion fronts are seen in the reaction between nitric oxide and hydrogen on Pt{100} under certain reaction conditions, see Figures 5–7. The dark areas in these are covered with a single monolayer of nitric oxide, work function 5.82 eV (19). The bright areas are believed to be ammonia or a precursor of ammonia (that is NH or NH_2) based upon its work function (5 eV). This work function rules out the bright areas being pure hydrogen. The

production of ammonia was also detected in the gas phase by mass spectroscopy, in agreement with studies by Madden and Imbihl (20).
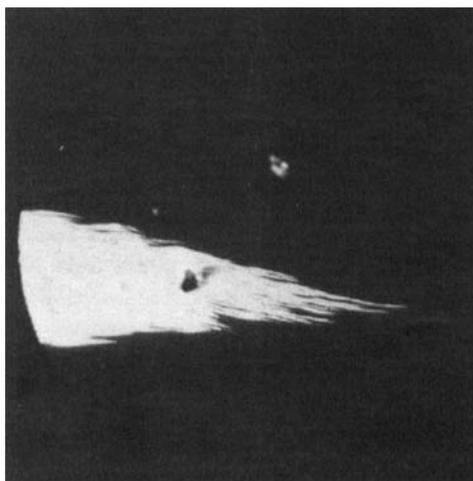

Fig. 6 The anisotropy of fronts is shown during the reaction between nitric oxide and hydrogen at 375 K. Fronts migrate faster along steps. Diameter: 230 μm
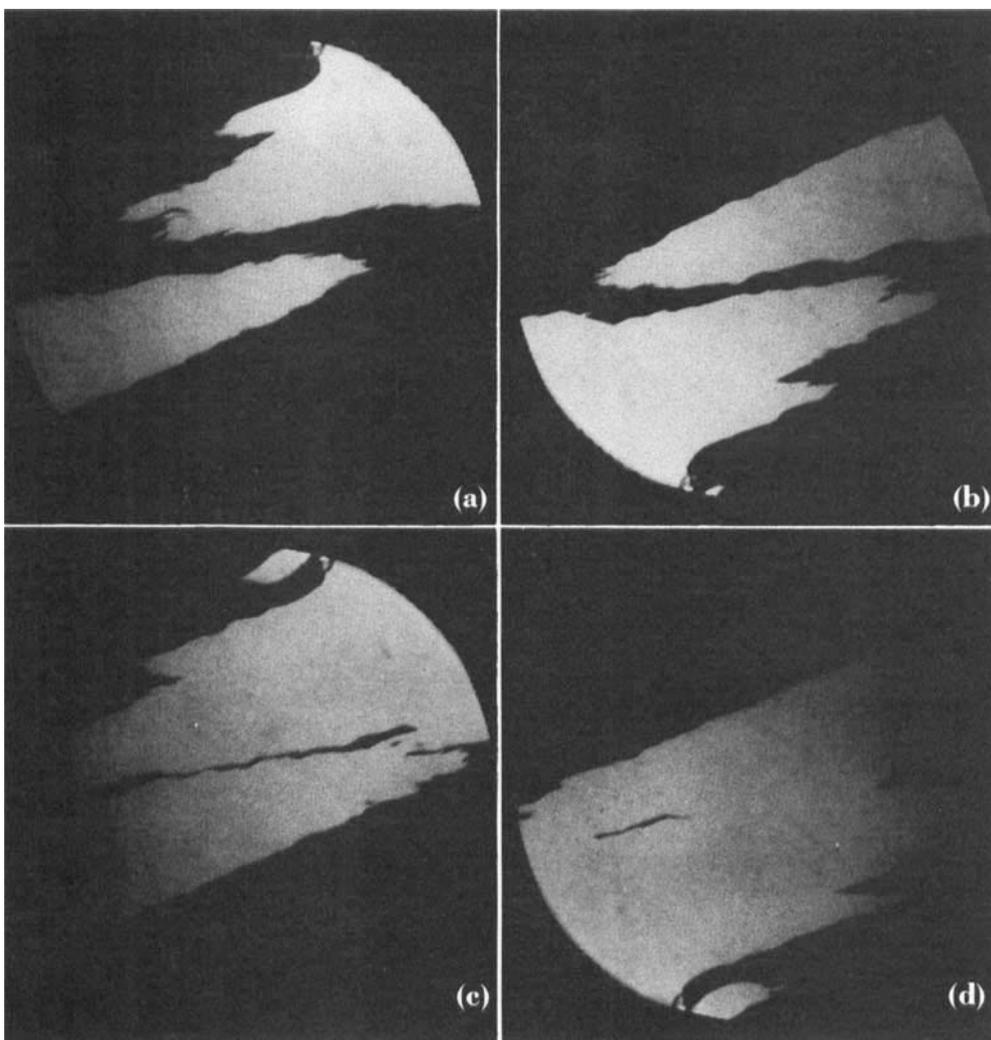
Fig. 7 The collision of fronts during the reaction between nitric oxide and hydrogen at 380 K is shown. Diameter: 230 µm

The fronts of Figure 5 were initiated as follows: The sample was kept at 415 K and the hydrogen pressure adjusted to 1.7×10^{-5} Pa. The surface was then saturated with nitric oxide by increasing its partial pressure to 1×10^{-2} Pa. Upon reducing the partial pressure of nitric oxide to 1×10^{-4} Pa, the fronts initiated at dust particles after an induction time of a few seconds. The fronts propagated out into the nitric oxide monolayer at a speed of 9 µm/s in directions along steps and about one third as fast across steps.

Anisotropy of the fronts is more pronounced at lower temperatures. Figure 6 shows a front initiated at a dust particle at 410 K and then cooled to 375 K. The long streamers follow step bunches. Anisotropy increased at lower temperatures because diffusion over the steps becomes more difficult.

The collision of two fronts is shown in Figure 7; each initiated at a dust particle at 410 K. The sample was cooled to 380 K to reduce the speed of the fronts and to allow still photography. The impurity particles apparently initiate the
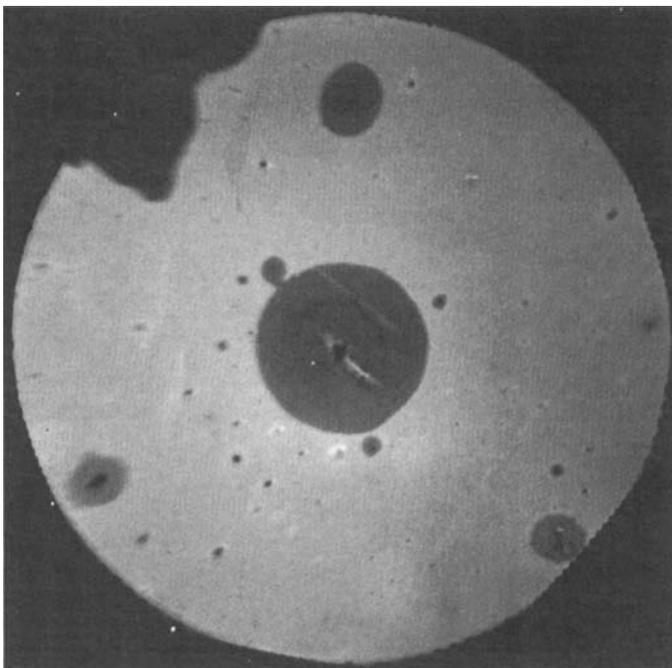
Fig. 8 Reaction fronts are shown during the oxidation of graphite on Pt{100}. Dark areas are covered with adsorbed oxygen and show where graphite was removed. Fronts initiate at impurity particles. Diameter: **230 μm**

reaction by providing empty sites which are necessary for nitric oxide to decompose.

Oxidation of Graphite on Pt{100}

Graphite and other carbonaceous materials are troublesome contaminants which block catalytic reactions on platinum. Often carbon must be removed periodically from platinum surfaces by combustion with oxygen. The reaction fronts formed during the oxidation of graphite on Pt{100} are shown in Figure 8. The light areas are covered with carbon, while the dark areas are covered with oxygen and show where the graphite was removed. The surface of graphite, which typically grows with its close-packed basal plane parallel to the platinum surface, can be quite inert towards oxygen and oxygen has difficulty in penetrating the graphite film. The graphite film was not a single monolayer, and can grow to become quite thick. Oxygen penetrates the film at dust particles and reacts with the side of the film. Once a hole is formed in the film, the graphite is rapidly removed as the reaction fronts propagate away from the initiation sites. The holes

in the graphite film are circular. Lack of anisotropy occurs because graphite does not diffuse. These studies suggest that graphite may be more efficiently removed from platinum surfaces if particles, which readily adsorb oxygen, are intentionally added to the surface.

Conclusions

Many catalytic reactions on platinum are limited by the availability of unoccupied surface sites. A key to the production of more efficient catalysts, for reactions which exhibit self-poisoning, appears to lie in the introduction of empty surface sites through the addition of impurities which only weakly adsorb the reactants that cause self-poisoning. Inert films which normally cause self-poisoning are removed by reaction fronts which initiate at holes in the film at impurity sites.

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Platinum Catalyses the Conversion of Methane to Higher Alkanes

A research group at the Université de Nancy and Laboratoire Maurice Letort, France, has found that the standard platinum catalyst EUROPT-1 promotes the conversion of methane to a range of saturated hydrocarbons up to C_6 or C_7.

A recent report (M. Belgued, P. Pareja, A. Amariglio, and H. Amariglio, *Nature*, 1991, **352**, (6338), 789–790) indicates that the reactions take place at moderate temperatures. The catalyst was reduced in a flow of hydrogen at 400°C, followed by a helium flush and cooling to the temperature of the experiment (150 to 280°C). The sample was then fed with a flow of pure methane. Transient evolutions of hydrogen and ethane were immediately observed. At 250°C and after an exposure to methane of 1 minute, the rate of ethane evolution passed through a maximum. Fast production of saturated hydrocarbons ranging from C_1 to C_6 or C_7 resulted from subsequently flushing the catalyst with hydrogen at the same temperature.

It was concluded from the results of a temperature-programmed desorption experiment carried out under the same conditions that the fraction of methane converted was 19.3 per cent. The authors have experimental evidence to support their hypothesis that the higher hydrocarbons are obtained via oligomerisation of CH_x species. They indicate two potential advantages of their method over the oxidative coupling for the conversion of methane into higher hydrocarbons: these being the much lower reaction temperatures and the fact that unconverted methane can be recycled. Low conversion efficiency is at present a limitation of this new process, however, and the possible inhibiting effects of deposited carbon on catalyst efficiency are currently being assessed. The technological progress implied by these results indicates that the use of a platinum catalyst, together with the choice of reaction temperatures and use of a flow reactor may have been significant factors.　　　　D.T.T.

Metal-Hydrogen Systems

A previous issue of this journal carried a selective report of the International Symposium on Metal-Hydrogen Systems, Fundamentals and Applications, held in Banff, Canada, September 2nd–7th, 1990, (R.-A. McN., *Platinum Metals Rev.*, 1991, **35**, (1), 24–27). The papers presented at that meeting, including those in the special sessions on hydrogen pairing in metals, have now been published in the *Journal of the Less-Common Metals*, 1991, **172–174**, Parts A and B.