FEM AND FIM STUDY OF REACTION ZONES ON PLATINUM

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Dedicated to Dr Karel Mach on the occasion of his 60th birthday.

The initial shape of the reaction zones for the interaction of hydrogen and oxygen on the surfaces of the single crystals of platinum in FEM and FIM devices is discussed in connection with the effect of temperature and surface anisotropy. Interaction of the (H_2 + O_2) mixture has been studied at room temperature and the results were confronted with the interaction of hydrogen and preadsorbed oxygen at low temperature and with the anisotropy of the low-temperature field-corrosion of platinum.

Key words: Surface reaction zone; Platinum surface; Field corrosion.

Location and characterization of active sites on catalyst surfaces represent fundamental problems for understanding of the detailed microscopic mechanism of the given catalytic process. This knowledge can then serve as one of the guide lines for the "construction" of new catalysts.

FEM (field emission microscope) and FIM (field ion microscope) techniques with their unique magnification and resolution can supply useful experimental information for solving these problems[1]. The mentioned techniques have been frequently used for studies of the reaction zones for various reaction systems on single-component catalysts including (H_2 + O_2) reaction on platinum single crystals (see *e.g.* refs[1–4]).

This study is devoted to the comparison of three basic types of surface interactions: (i) reaction of a (H_2 + O_2) mixture *on* the platinum surface *at the room temperature*; (ii) reaction of gaseous hydrogen *at a low temperature* with oxygen, preadsorbed *on* the platinum surface; and finally (iii) interaction of nitrogen *at a low temperature with* the platinum surface (field corrosion). The shapes of the reaction zones in these cases were confronted with each other. This study is a part of a more extensive investigation of the time development of reaction zones and of oscillation phenomena[5]. Additionally, it will be extended to more realistic models of metal catalysts supported by oxides[6,7] which might enable to investigate also the role of the frontier-regions between the metallic islands and oxidic support surface in these interactions.

EXPERIMENTAL

The experimental equipment and techniques used in this study – ($H_2 + O_2$) reaction on a platinum single crystal surface in FIM – has been described elsewhere[7]. The reaction mixture (in proportion $H_2 : O_2 \approx 1 : 1$, total pressure $p = 6 \ . \ 10^{-2}$ Pa) has been prepared separately in an all-glass apparatus connected to the UHV metal system *via* a sapphire leak-valve. The proportion between hydrogen and oxygen in contact with the sample surfaces has not been known exactly since the getter-ion and sublimation pumps (switched off during the experiment) could not be separated from the measuring volume, and the whole system was thus operated under dynamic conditions. As a result an unknown part of reactants could be trapped in the mentioned pumps. Nevertheless, a sufficient number of oxygen and hydrogen molecules obviously reached the platinum surfaces, since the reaction-diffusion zone could not be otherwise observed in these experiments where the higher ionization yield of the product molecules (H_3O^+) has been exploited for its imaging, similarly as in refs[2–4]. The ($H_2 + O_2$) reaction has been investigated at room temperature only.

RESULTS AND DISCUSSION

Figure 1 shows initial shape of the reaction zone (Fig. 1c) together with the crystallographic orientation of the platinum single crystal (see clean Pt surface on a FEM image in Fig. 1a). The indexing of the individual crystallographic planes was transferred from Fig. 1a onto Figs 1b, 1c and 1d which were obtained in the reaction mixture (in the field ionization regime). The approximate indexing of planes is based on the FEM image because the study of the shape (and possible crystallographic anisotropy) of the reaction zone necessitated to use platinum tips with a large end-diameter. On such surfaces besides the central region, also many other crystallographic planes (approximating the large “hemispherical” apex of the tip) can be investigated. In contrast to FEM the voltage needed for FIM imaging of such a blunt tip would exceed 25 kV which is a limiting value used in ordinary FIM laboratories for the work without special safety precautions.

As already mentioned, the field ionization yield is higher within the reaction zone, because besides oxygen (imaging gas in Fig. 1b) also product molecules contribute to imaging of this region. This part of the surface thus appears as a bright region on the FIM image (Figs 1c and 1d). Since the surface imaging is performed at room temperature and with large imaging molecules (H_2O, O_2), the atomic resolution (obtained in ordinary FIM experiments with He or Ne imaging at $T \leq 78$ K), is not attained and only more or less bright regions are observed (Figs 1b–1d). The reaction zone did not show any notable anisotropy, either in the initial state (Fig. 1c) or after its spreading over a larger portion of the sample surface (Fig. 1d). The zone exhibits a roughly circular shape centered between the (001) and (113) planes in a good agreement with literature[2,4]. During the time evolution of this “circle” also its effective center moves. The bright region, when attaining the shank, becomes less bright and indistinguishable from the background (compare Figs 1c and 1d). This effect is due to the increased radius of curvature at the shank leading to a lower intensity of the electric field in this region.

Absence of any significant anisotropy in the shape of the reaction zone even at the "initial" stage is probably caused by mobility of the surface platinum atoms at room temperature. Experimental evidence of such a mobility has been obtained under similar conditions with platinum clusters deposited onto a WO_x layer[8]. Obviously, the effect of the trapping-sites distribution onto the initial shape of the reaction zone is suppressed in this case, in contrast to the low temperature experiments, where this effect of the anisotropic distribution prevails[1].

Figure 2 reproduces the FEM image of anisotropy of the initial shape of the reaction zone around the Pt (111) plane for the reaction of preadsorbed oxygen with hydrogen. The reaction proceeded at $T = 115$ K in the presence of gaseous hydrogen. Adsorbed oxygen increased the work function of the platinum surface by about 1 eV. The surface regions covered by unreacted oxygen therefore appeared as a dark region on the FEM image. Water molecules produced by the reaction desorbed and condensed on the wall kept at $T = 78$ K. The resulting bare platinum surface was immediately covered by

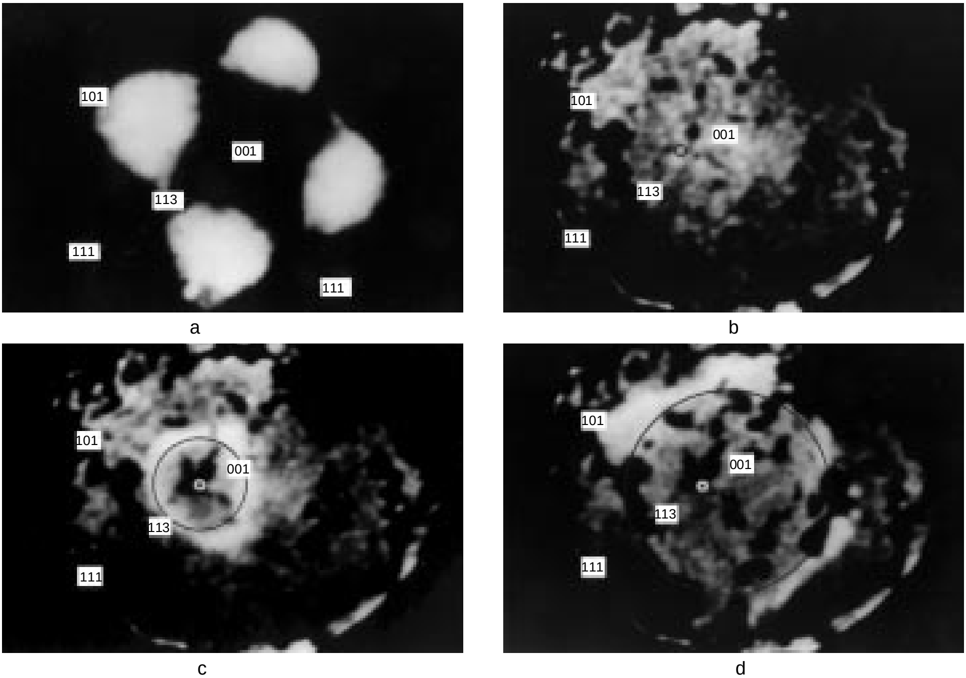

FIG. 1

Interaction of the reaction mixture ($H_2 + O_2$) on a platinum surface at room temperature. Pressure 6.5 . 10^{-2} Pa, $H_2 : O_2 \approx 1$. a FEM image of the clean platinum surface (imaging voltage $U \approx 4.4$ kV); b field ion image of the surface a in the reaction mixture, $U \approx 16$ kV; c continuation 1/7 s after b, reaction zone approximated by a circle visible as a bright circular strip; d continuation 2/7 s after b, reaction zone again approximated by a circle (small white circle shows center of the reaction zone *sub* b hydrogen trapped from the gas phase. However, since the adsorbed hydrogen increases the work-function of platinum by about 0.3 eV only, and the field emission of electrons depends exponentially on the negative value of the work-function, the reaction zone appears on the FEM image as a bright region. The initial anisotropy of the reaction zone at low temperature can be understood in terms of the anisotropic distribution of trapping sites for hydrogen molecules in the vicinity of (111) plane of platinum[1,9].

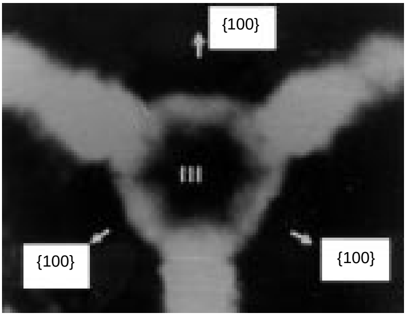

FIG. 2
FEM image of the initial shape of the reaction zone (bright area) around the Pt(111) plane for the reaction of H_2 with preadsorbed oxygen at 115 K (ref.[1])

The shape of the surface reaction zone is influenced by temperature of the experiment and by additional factors including: (i) the type of the surface interaction, and (ii) the nature of the interaction participants.

When the interaction of a gas *with* the platinum surface at a low temperature is investigated instead of the reaction between reactants *on* the surface, another type of anisotropy can be observed. For example, one can study anisotropy of the so-called field corrosion of platinum due to nitrogen. Figure 3b was obtained[10] with a platinum tip exposed for several seconds to about 10^{-2} Pa of nitrogen at T = 78 K in the presence of a high electric field corresponding to 60% of the evaporation field needed for obtain-

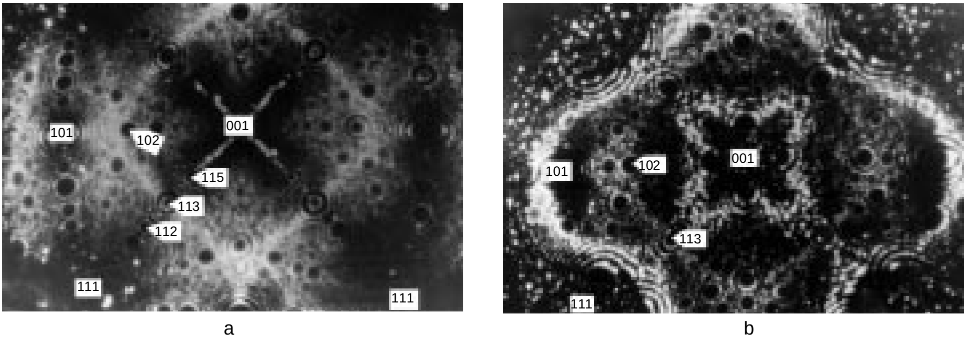

FIG. 3
Field corrosion of platinum by nitrogen[10]. a FIM image of platinum (imaging gas Ne, $T \approx 78$ K); b the same platinum tip after exposure for several seconds to about 10^{-2} Pa of nitrogen at the voltage corresponding to 60% of the evaporation voltage

ing the initial clean platinum-tip surface. In the presence of this high electric field nitrogen interacts with surface platinum atoms in certain regions only and surface complexes are formed there. As a result, bonds of these attacked surface platinum atoms to the rest of the crystal are weakened. Thus at the lower evaporation field, surface "corrosion" proceeds only in the above mentioned regions. This corrosion gives rise to "valleys" and "hollows" whose edges appear on the FIM image as bright strips, since small radius of curvature at these edges results in a higher intensity of the electric field. Inside the "etched region" a random structure is observed. As can be seen in Fig. 3, field corrosion starts both from the central (001) plane and from the outside shank along preferential directions (from (001) towards (111) *via* (113) plane and *vice versa*). It is interesting that this preferential direction of corrosive etching does not coincide with the active zones in the (H_2 + O_{ads}) reaction on the vicinal platinum (111) plane.

Summarizing the above, low-temperature experiments with platinum in FEM and FIM have proved the dominant effect of the trapping-sites distribution onto the shape of the surface reaction-zones for the (H_2 + O_2) reaction. On the other hand, at room temperature the shape of the reaction zone both at the initial stage and after spreading over a large portion of the platinum surface does not exhibit any significant anisotropy, probably due to the surface mobility of surface platinum atoms. A different anisotropy of the low-temperature field corrosion of platinum in the presence of nitrogen is probably due to some additional effect, *e.g.* the anisotropic weakening of bonds between Pt–N complexes and the rest of the platinum crystal on various crystallographic planes.

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