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Oscillatory behaviour of the reduction of NO by H_2 over Rh

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The NO reduction by H_2 on Rh has been studied by field emission microscopy (FEM). It has been observed that this reduction shows oscillatory behaviour at 460 K and $P_{NO} = -1.5 \times 10^{-7}$ Torr and $P_{H_2} = 1 \times 10^{-6}$ Torr. Unique features of FEM are the very high spatial resolution and the presence of, in principle, an indefinite number of different crystal planes. The oscillatory behaviour is reflected by periodic changes in the emission current and in the images observed. The communication between different surfaces present on the field emitter is shown on a fluorescent screen. Diffusion and gas phase coupling seem to play a role. Many of the features reported earlier for the oscillatory behaviour of the NO–H_2 and NO–NH_3 reactions over Pt(100) are observed on Rh as well, including the surface explosion. The vacancy model proposed earlier for the oscillations over Pt(100), can be applied to the reactions described in this paper as well.

Keywords: Oscillatory behaviour; rate oscillations; NO reduction; Rh

1. Introduction

Oscillating reactions in heterogeneous catalysis have attracted much attention during the last years [1]. Until quite recently, the CO oxidation over Pt was studied most often, but other reactions like the CO–NO reaction and, lately, also the NO–H_2 and NO–NH_3 reactions over Pt were studied in more detail in this respect. Most of the recent findings of the latter reactions have been presented and summarized in several papers by our group [2–5]. It was shown that a vacancy model involving periodic coverage changes of NO, oxygen and the hydrogen source was able to explain the oscillations observed during these DeNOx-reactions over Pt(100), and that it should also be applicable to Pt surfaces in general [4,5]. It was suggested that the surface reconstruction between the (1×1) and (5×20) phases of Pt(100) did take place during oscillating behaviour, but that they were not the cause of the behaviour observed. Of course more information is needed on this subject at this stage. The latest research efforts have therefore been focussed on the observation of oscillations on a variety of surfaces and on various metals, for example the NO–CO reaction on Rh(110) [6] and the CO–O_2 reaction on Pd(110) [7].

In this paper the high resolution power of field emission microscopy is used to study the NO–H_2 reaction over the many crystal planes present on a Rh field emitter. This paper describes how to obtain the oscillations reported and summarizes the first results for the NO–H_2 reaction. In the course of our experiments we became aware of similar FEM observations for the CO–O_2 reaction on a Pt tip [8].

2. Experimental

The experiments were performed using the digital field emission microscope (DigiFEM) on which we reported earlier [9,10], but now used mainly in the conventional mode. Images observed on a fluorescent screen were recorded real-time using a CCD video camera.

Special care was taken in cleaning the (100)-oriented Rh field emitters. The base pressure of the UHV system was better than 2×10^{-10} Torr. High-purity gases were used because it was found that the use of high-purity gases is essential for long-lasting oscillatory behaviour. All gas pressures mentioned are corrected for ion gauge sensitivity. For H_2 the correction factor was assumed to be 0.5. For NO and NH_3 the factor used was 1.3.

3. The procedure followed to observe oscillations

Oscillations can be found easily for the NO–H_2 reaction over Rh, once some basic parameters are known. We reported earlier the oscillations observed during the NO–H_2 and NO–NH_3 reactions on Pt(100) [2–5], and a detailed reaction mechanism for these DeNOx-reactions over Pt was derived, involving the important role of vacancies. From the fact that it was found that the surface reconstruction of Pt(100) is most likely not necessary for the observation of rate oscillations, the vacancy model should be applicable to many more reactions on many different metals and over a variety of crystallographic orientations. From the conditions necessary for the observation of oscillations on Pt, it should thus be possible to deduce the conditions under which the same reactions could show oscillatory behaviour on Rh, keeping in mind the differences in heats of adsorption of NO and H_2 between Rh and Pt, and also the large strength of the Rh–N and Rh–O bonds when compared to their Pt equivalent. The dissociation of NO on Rh is thus energetically favoured in comparison with Pt. To remove the N- and O-atoms from Rh a relatively high partial pressure of the reducing agent, in this case H_2, will be required.

The procedure to observe oscillating behaviour is now easy and as follows:

Step 1: H_2 is introduced into the system to the desired pressure at 300 K.

Step 2: NO is introduced.

Step 3: The pressure is given time to stabilize. The equipment is used in the flow mode.

Step 4: An image is produced on the fluorescent screen. In our case an emission current of about 2 nA is used most of the time.

Step 5: The tip is heated slowly with applied field from room temperature to the temperature at which a surface explosion occurs. This surface explosion results in a very bright image caused by an explosion in emission current due to NO desorption, dissociation and reaction, which lowers the work function of the system. The applied field can now be lowered in order to prevent field effects and tip damage.

Step 6: The temperature is lowered very slowly until NO adsorption occurs, as judged from a lowering of the emission intensity.

Step 7: Oscillations are observed. Both emission current and all processes displayed on the fluorescent screen are recorded.

4. Results

After introduction of a mixture of 1.5×10^{-7} Torr NO and 1×10^{-6} Torr H_2, the tip was heated slowly to 530 K, where a surface explosion was observed. The series of images obtained during this explosion is shown in fig. 1. Fig. 1A shows the image obtained just before the surface explosion occurs. The reaction between NO and H_2 starts on the rough planes on (321) and surroundings (fig. 1B). In fig. 1C the reaction is seen to spread into the direction of (311) and (320). In fig. 1D, almost the entire surface experiences a surface explosion. In fig. 1E the surface explosion has reached its peak. In figs. 1F and 1G the surface becomes occupied with nitrogen atoms, as is judged from the characteristic N-image. The entire surface explosion took about 0.5 s and was also characterised by a tremendous increase in emission intensity. All images shown in fig. 1 were recorded with a constant applied potential.

After the observation of the surface explosion, the temperature was lowered slowly until oscillations were observed at 460 K. Just before the oscillations started a characteristic "fence-like" image was observed (fig. 2A). The appearance of this image is taken as $t = 0$. Fig. 2B was recorded at $t = 1$ s and was characterised by a brightening of part of the emission pattern. The cycle starts around the (321) surface again. Fig. 2C at $t = 2.9$ s, or 1.9 s after the start of the oscillations, shows that the travelling wave spreads across the surface, also in the direction of (310). Our preliminary results do not show yet whether the travel-

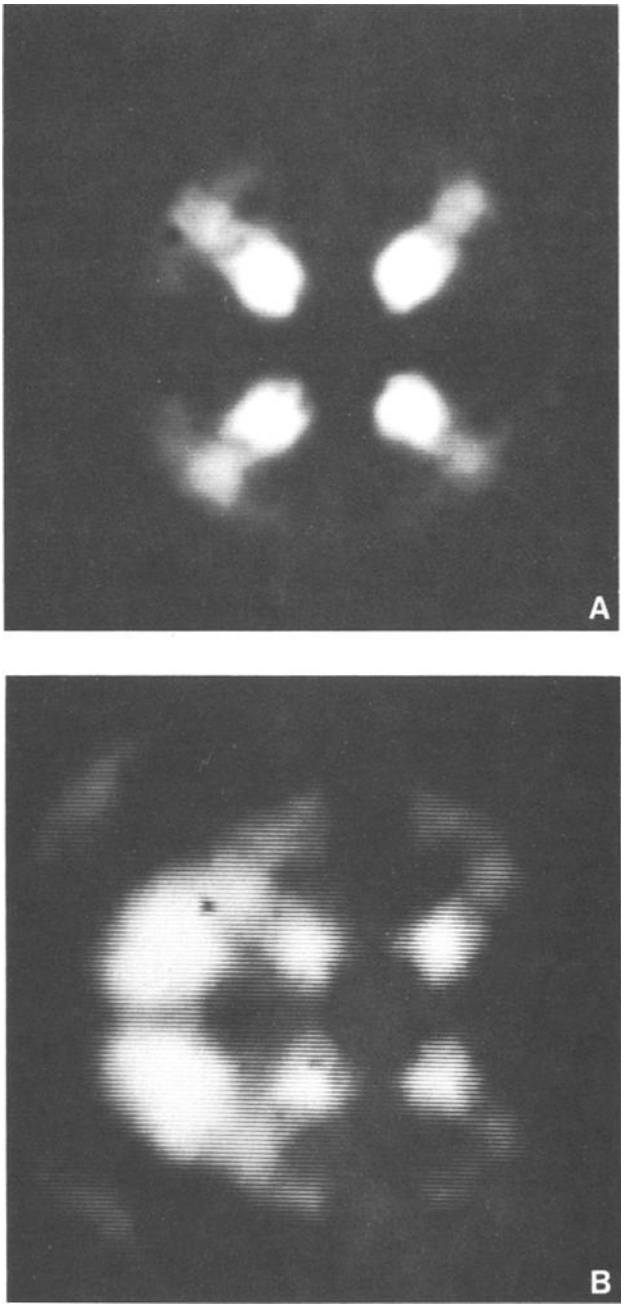


Fig. 1. Images observed during a surface explosion. Conditions: $P_{NO} = 1.5 \times 10^{-7}$ Torr, $P_{H_2} = 1 \times 10^{-6}$ Torr, $T = 530$ K, $t_{total} = 0.5$ s. (A) Just before the start of a surface explosion; (B) the start of the surface explosion; (C–E) the spread of the surface explosion across the surface; (F and G) the surface is covered by nitrogen atoms following the surface explosion.

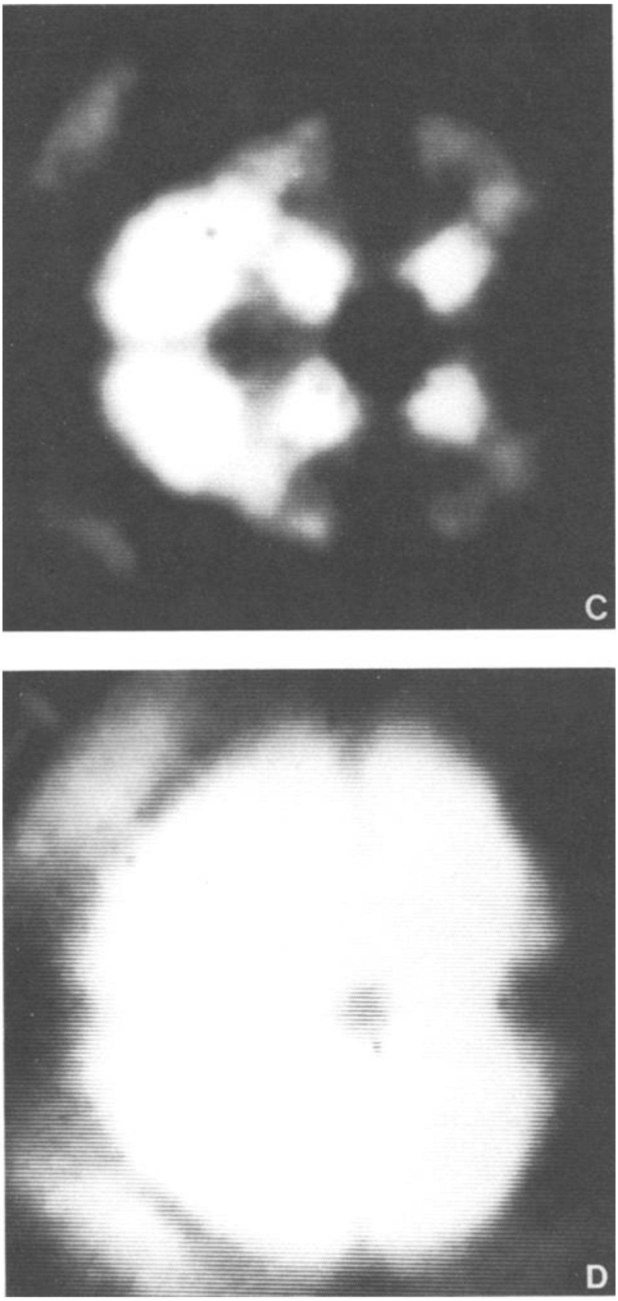
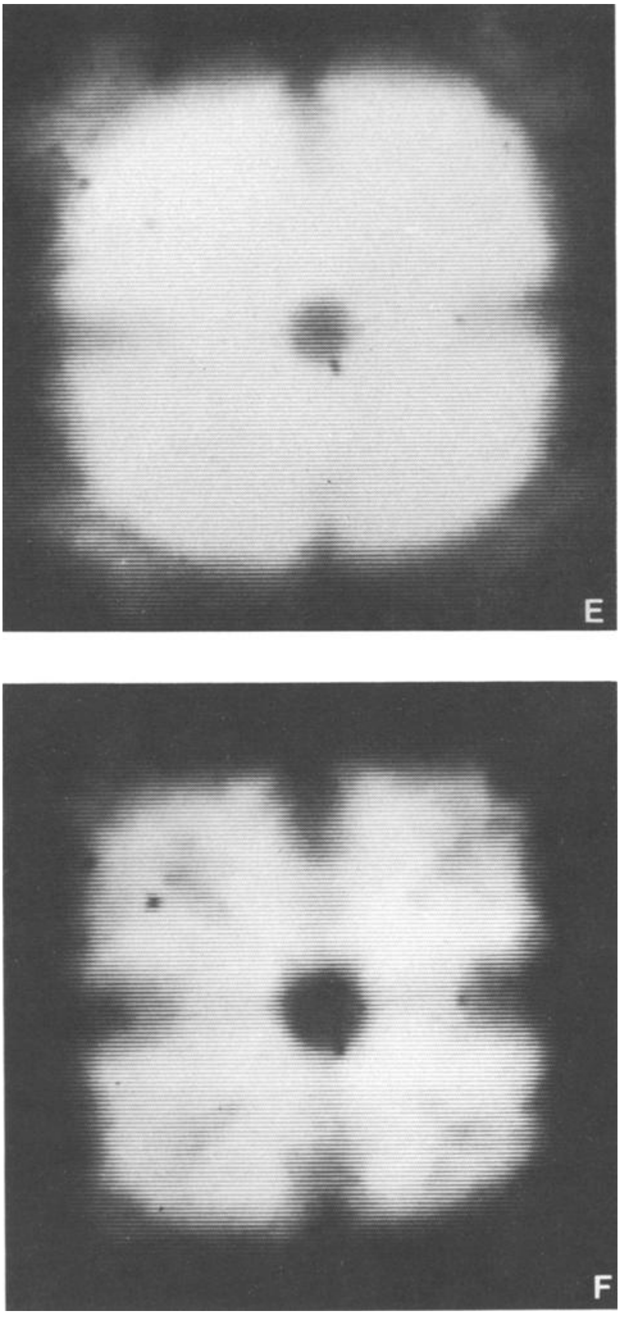


Fig. 1 (continued).



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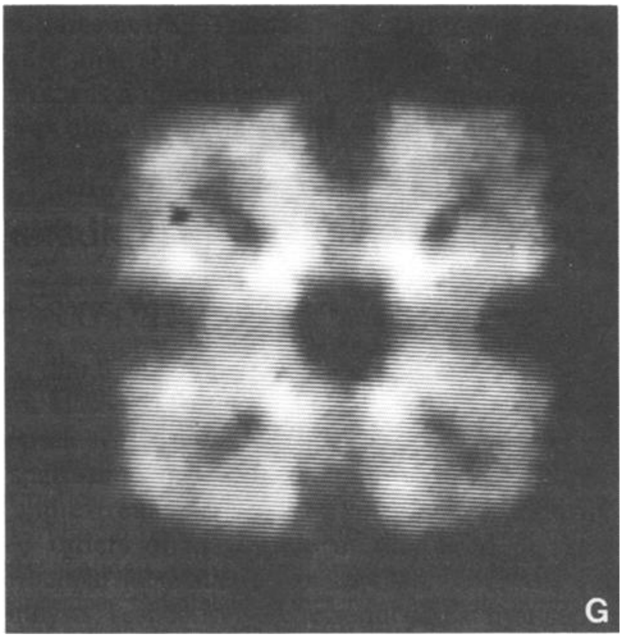


Fig. 1 (continued).

ling wave over the surface is caused by (a) the removal of a work function increasing reactant or reaction intermediate like NO or N (reaction front), or (b) by diffusion of an electropositive reaction product or reaction intermediate, like NH_x (diffusion front). As we have some indications in favour of the reaction front this will be used in this paper.

In figs. 2D–2G it can be seen that the reaction fronts move symmetrically from two sides across the surface until, at $t = 14$ s, the front has covered the entire surface. Note that the (210) planes and areas around (211) do not seem to contribute to the oscillations under these conditions. This was also shown using the DigiFEM in the digital mode.

Image 2H was recorded at $t = 15$ s, so 1 s after the maximum intensity was observed. The emission intensity of the crystal planes decreases, starting on the smoother planes around (100) and between (100) and (111). After a while the image is again that of fig. 2A and the reaction front appears again. The oscillations are very stable for many hours because of the character of the reaction, which apparently does not contain any oscillation-inhibiting component, the good base pressure of the UHV-system and the use of high-purity gases. The oscillations are not influenced noticebly by the applied field: increasing and decreasing of the field strength during oscillations, or switching on and off of the applied field did not influence the oscillations to a measurable extent. This was also observed earlier during a surface explosion observed when heating in hydrogen of a Rh tip precovered with NO at 78 K [11].

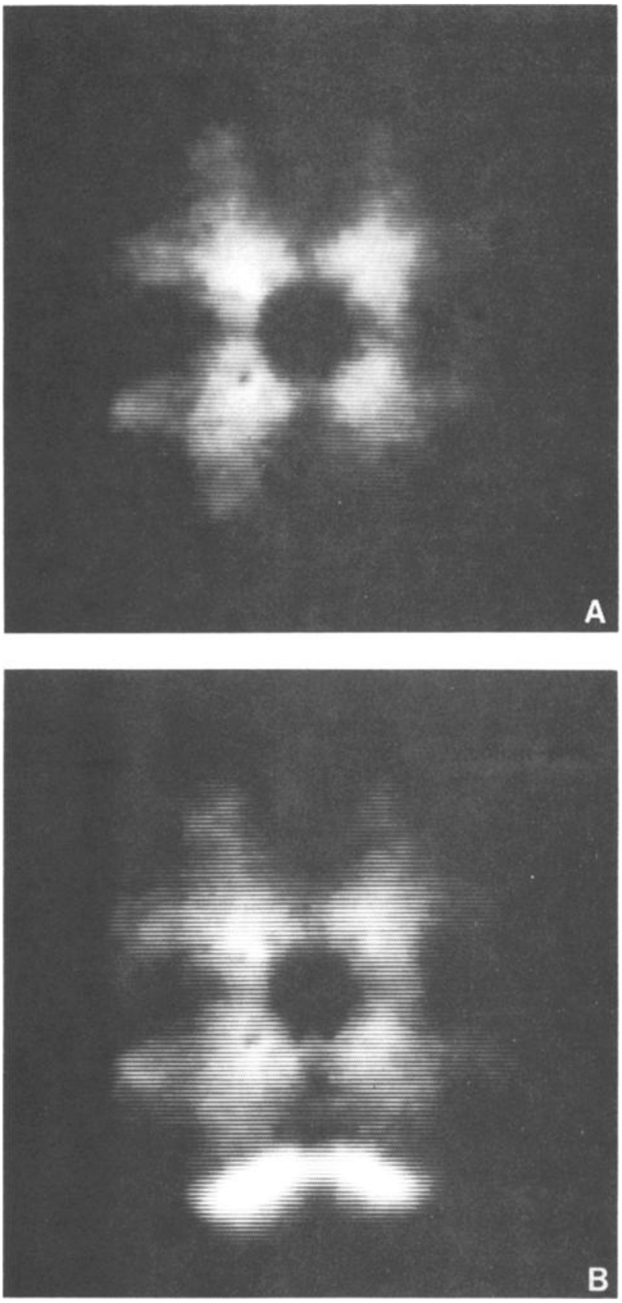


Fig. 2. The images recorded during an oscillation. (A) Characteristic "fence-like" image recorded just before the start of an oscillation. $T = 460$ K, further conditions as in fig. 1. This image is taken as $t = 0$. (B) $t = 1$ s. (C) $t = 2.9$ s. (D–G) Reaction fronts move symmetrically from two sides across the surface. (G) is recorded at $t = 14$ s, at the point of maximum emission intensity. (H) $t = 15$ s. The emission intensity of the crystal planes decreases, starting on the smoother planes around (100), and between (100) and (111).

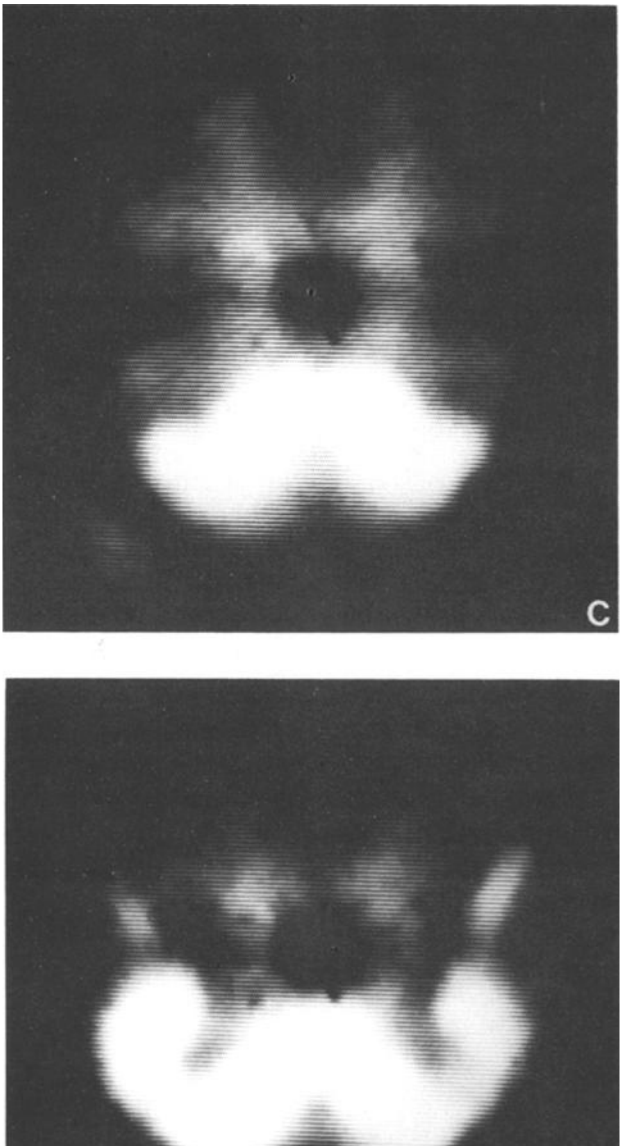
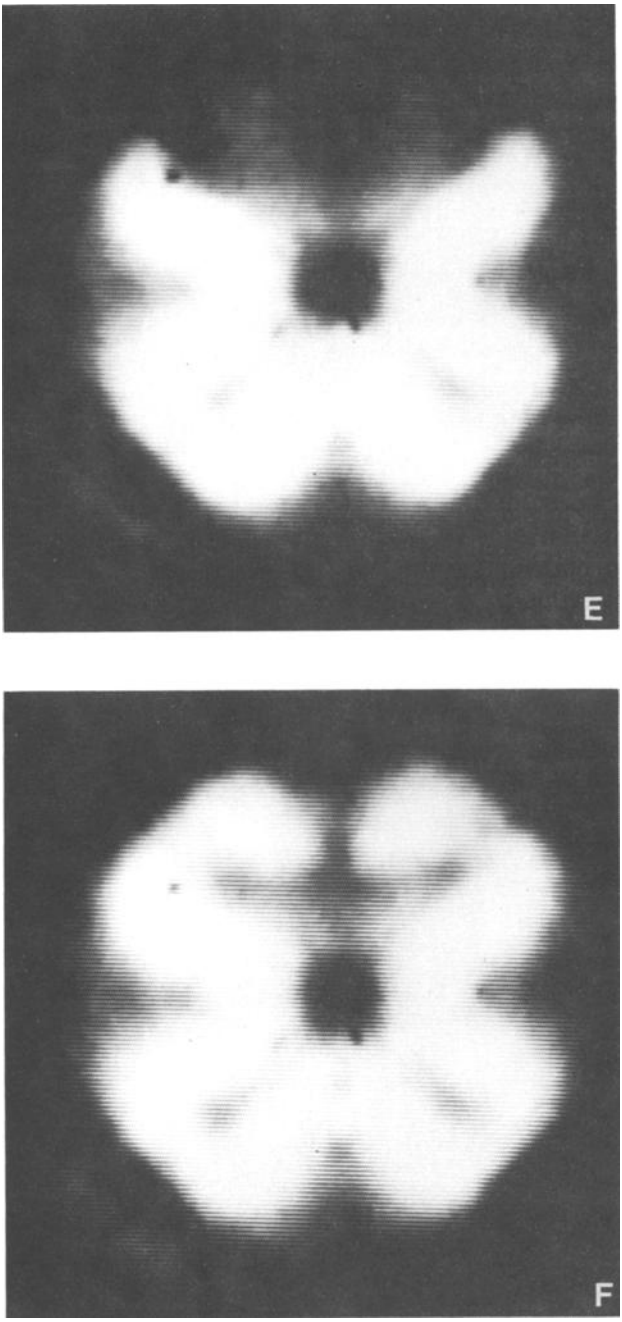


Fig. 2 (continued).



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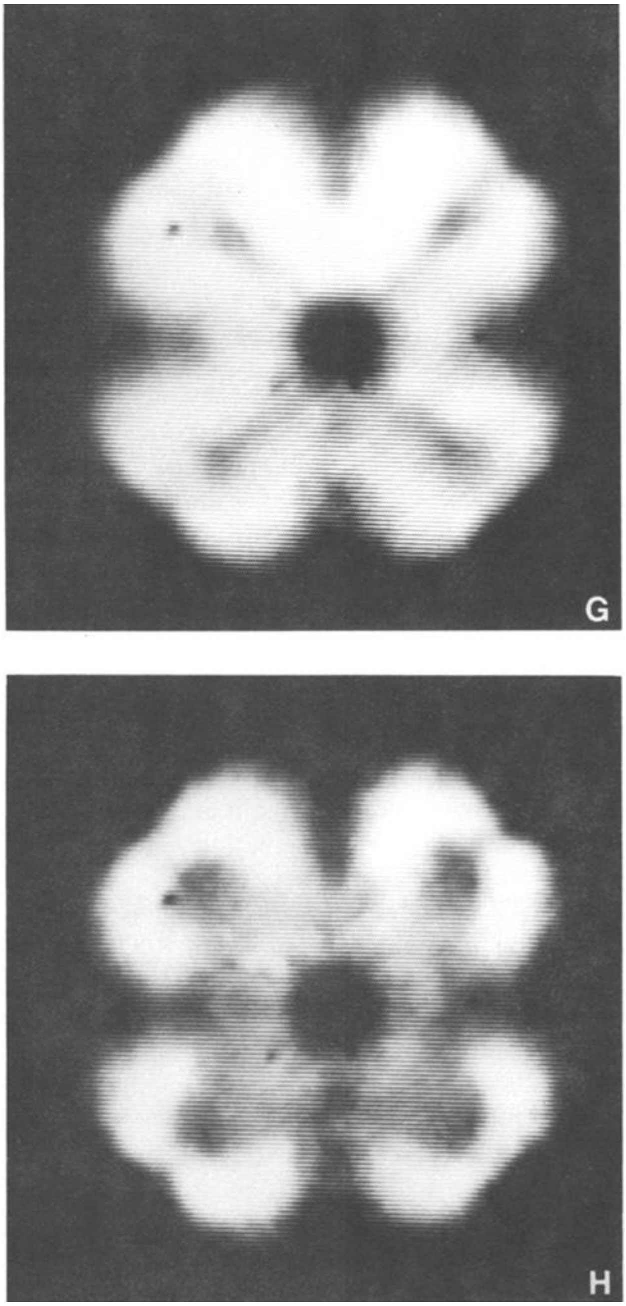

Fig. 2 (continued).

Presently, more research is devoted to investigate NO–H_2 oscillatory behaviour under different NO/H_2 ratios. In addition to the reaction fronts where, as in fig. 2, the entire surface is involved, oscillations taking place on only one quarter of the surface, a "quadrant", may occur. Under different conditions the four equivalent quadrants seem to be able to act more or less individually in a way that the period between succeeding oscillations on a quadrant is not identical for all quadrants. So one quadrant can show more oscillations in a given time than another. In this case the oscillations do not spread over the entire surface. This is especially observed at lower temperatures, probably indicating that not only gas-phase coupling but also diffusion rates can play an important role. This will need more investigation.

5. Discussion and conclusions

The NO–H_2 reaction shows oscillatory behaviour over Rh. Field emission microscopy is an excellent tool to determine the effect of surface structure on the oscillatory behaviour and the surface explosions. The method to obtain the oscillations described is presented. It was shown that reaction fronts move across the tip surface via (321) and (320) surfaces. Especially (210) and (310), and also (311), do not participate under these conditions. In our opinion, this is caused by the fact that the Rh–N bond strength on these planes is probably too strong and the reaction is inhibited by self-poisoning by Rh–N. The conditions under which oscillating behaviour is or can be observed on Rh, can be predicted assuming that the vacancy mechanism reported for these reactions on Pt(100) can be applied to Rh as well.

The unique features of FEM make it an excellent tool for the study of oscillating reactions: the resolution is very high and all processes can be studied real-time. The dynamical behaviour of oscillating reactions, like reaction fronts and the surface explosion, are displayed very clearly on a fluorescent screen and can be recorded by a CCD camera coupled to a video recorder. If desired the processes can be studied in minute detail using the DigiFEM in the digital mode.

The NO–H_2 reaction exhibited oscillatory behaviour under conveniently low pressures and low temperatures. Surface diffusion and gas phase communication seem to play a role. Their relative importance seems to depend on temperature as can be concluded from the first results obtained.

From the results collected here, it can be concluded that the need for a surface reconstruction to occur in order to be able to observe the oscillations reported seems rather unlikely. Many crystal planes participate in the surface explosion and the oscillatory behaviour, and for none of these planes reversible surface reconstructions, with a different reactivity of the surfaces towards one of the reaction components, have been reported for the reactants used here. The vacancy model, as was applied earlier to the NO–H_2 and NO–NH_3 reactions over Pt(100) and Pt in general, seems also applicable to Rh. On the basis of this vacancy model the conditions under which oscillations should be observable could be predicted well. Currently more research is in progress to study the oscillating reactions over Rh. FEM has proven to be an ideal technique for the study of these intriguing phenomena. The most recent results show that also the NO–NH_3 reaction over Rh shows oscillatory behaviour. These results will be published elsewhere.

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