Catalysis Letters 27 (1994) 27–32

Gas-phase coupling in the CO oxidation reaction on polycrystalline platinum

J. Lauterbach and H.H. Rotermund

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin, Germany

Received 22 April 1994; accepted 5 May 1994

We report on self-sustained rate oscillations during the catalytic CO oxidation reaction on polycrystalline platinum. The photoelectron emission microscope enabled us to distinguish between three different types of grains. We found that the (110)- and the (100)-type grains are responsible for the development of rate oscillations while the (111)-type grains remain in a steady state. Gas-phase coupling is the dominant mechanism leading to a synchronisation of the different oscillating grains over macroscopic distances.

Keywords: catalytic CO oxidation; kinetic oscillations; polycrystalline platinum; pattern formation

Self-sustained rate oscillations in open systems far from equilibrium have first been investigated systematically in the famous Belousov–Zhabotinskii reaction [1]. The discovery of oscillating reactions in the field of heterogeneous catalysis then launched many investigations in the past two decades. One reaction in this field is the CO oxidation on platinum, for which oscillations on various types of catalysts like supported catalysts, wires or foils have been reported [2]. Many of these experiments have been performed close to atmospheric pressures. In this case, individual parts of the catalyst are synchronised by heat conductance either through the catalyst itself, through the supporting material or through the surrounding gas phase. Studies on well defined single crystal surfaces at low pressures using UHV techniques provided crucial insight into the underlying microscopic pressures [3,4]. Rate oscillations on single crystal surfaces under low pressure conditions ($p < 1 \times 10^{-3}$ mbar) were first reported by Ertl and co-workers [5] for Pt(100) and since then many systems have been investigated. In this isothermal case, the dominant coupling mechanism can be propagating reaction diffusion fronts (diffusion coupling) or pressure variations caused by different rates of consumption of the reactants (gas-phase coupling).

The development of an easy to operate UHV-compatible photoelectron emission microscope (PEEM) [6] first enabled the in situ observation of spatio-temporal pattern forming during the reaction [7]. On Pt(110), for example, rate oscillations at sample temperatures around 550 K could be linked to the formation of a standing wave pattern. In this case, large areas of the surface are oscillating in phase [8]. The Pt(100) surface also showed irregular rate oscillations caused by the transformation of the surface between a high reactive, predominantly oxygen-covered state and a low reactive, CO-covered state [9]. The transition between these two states occurs via propagating reaction–diffusion fronts.

Recent investigations performed in our group with polycrystalline platinum foils showed that these samples consist of three different types of grains [10]. The PEEM experiments revealed a wide variety of characteristic reaction–diffusion patterns on the different grain types comparable to the well studied behaviour of the single crystal surfaces Pt(100), Pt(110) and Pt(111). With these polycrystalline samples we could also establish self-sustained rate oscillations and monitor the pattern formation on the different grains and hence investigate their individual contributions to the CO_2-rate for the first time. The observed results will be discussed in this short communication.

The experiments were performed with a standard UHV-system equipped with facilities for surface cleaning and characterisation. The CO_2-signal could be monitored in situ during the reaction through a differentially pumped quadrupole mass spectrometer. A feedback-controlled gas inlet system ensured a high stability of the partial pressures of the reactants. The reaction–diffusion patterns were observed by a PEEM, which image reflects the local work function of the surface with a spatial resolution of 0.2 μm and a temporal resolution of 20 ms. In the PEEM images, regions with a lower work function appear brighter due to their higher photoelectron yield and vice versa. So the oxygen covered parts of the surface appear dark due to their higher work function while the CO-covered areas with their lower work function appear grey in the PEEM. The single grains can be distinguished using their different values of the work function in the clean and adsorbate covered state. The polycrystalline sample consisted of a 11×11 mm^2 platinum foil with 0.5 mm thickness. For recrystallisation the foil was heated up to 1300 K in air for 2 h and subsequently mechanically polished and electropolished. After transfer into the UHV-system the sample surface was cleaned by repeated cycles of oxidation at 800 K, Ar^+-ion sputtering and annealing up to 1000 K. Further properties can be found in ref. [10].

Fig. 1 shows a typical example for self-sustained rate oscillations observed at a sample temperature of 472 K. In this case the control parameters were kept constant after the establishment of the rate oscillations. One oscillation period starting at minimum reaction rate consists first of a smaller maximum followed by another rate minimum and finally by an even higher peak. The time difference between the large peaks was determined to range between 270 and 340 s, which is also the corresponding value for one oscillation period.

The first 10 min of fig. 1 are expanded in fig. 2. The numbers indicated on the curve correspond to the six PEEM pictures shown in fig. 3. There a part of the poly-

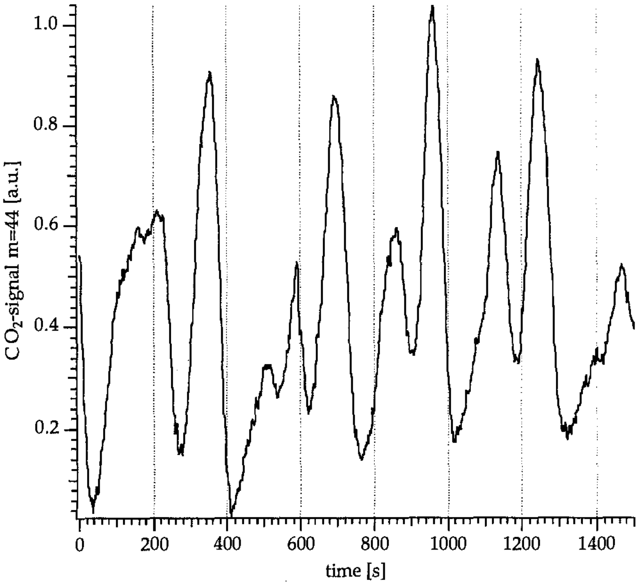

Fig. 1. CO_2-rate oscillations under steady state conditions on polycrystalline platinum; $T = 472$ K; $p_{O_2} = 4.0 \times 10^{-4}$ mbar, $p_{CO} = 7.8 \times 10^{-5}$ mbar.

crystalline surface, demonstrating the different behaviour of the single grains during one complete oscillation period, is imaged. In frame 1 the reaction rate is low because all the grains are in the CO-poisoned state. In this case the dissociative adsorption of oxygen on the surface is blocked and therefore the CO_2-production

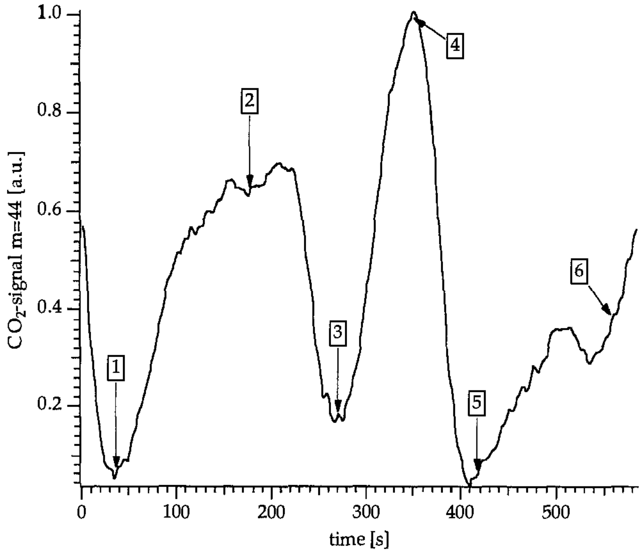

Fig. 2. Enlargement of the first 10 min from fig. 1.

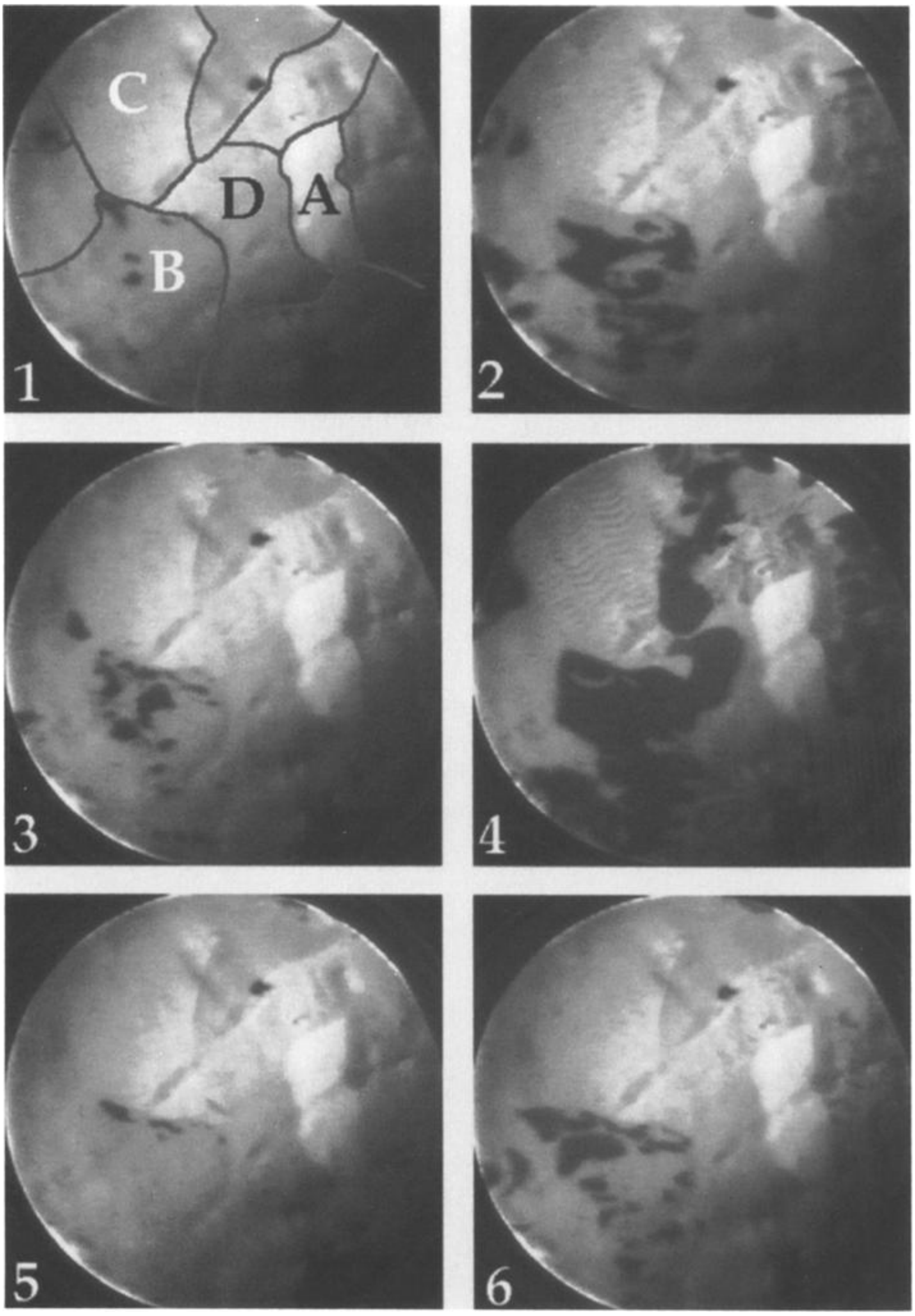

Fig. 3. PEEM images from the polycrystalline surface showing different grains under reaction conditions. The diameter of the frames is 600 μm. $T = 472$ K; $p_{O_2} = 4.0 \times 10^{-4}$ mbar, $p_{CO} = 7.8 \times 10^{-5}$ mbar.

rate is low. Note that the bright grain marked A on the right-hand side always stays in the CO-covered state. It belongs to the (111)-type of grains, which, similar to the Pt(111) single crystal surface, only exhibit bistable behaviour and therefore do not contribute to the oscillations at all. With increasing reaction rate both the grains of the (100)-type (i.e. the grain marked B) and the (110)-type (i.e. grain marked C) show an increase in the coverage of oxygen and are transformed into a more reactive state. Some of the (100)-type grains reach a state where they are almost totally covered with oxygen (i.e. grain marked B in frame 2). Irregular CO-fronts develop on this oxygen phase. This characteristic pattern formation has also been observed on a Pt(100) single crystal sample under similar conditions [9]. The (110)-type grains, on the other hand, show oxygen wave trains with a much smaller wavelength on the otherwise CO-covered surface. These fronts disappear again when the system passes through the rate-minimum in frame 3. The strong rate maximum (frame 4) corresponds to the highest overall coverage of oxygen on the surface. In this case even the grain marked with D, which could be classified as (100)-type, is covered with oxygen and on the (110)-type grain (marked C) in the upper left once more narrow oxygen fronts appear. In the following rate minimum a large fraction of the surface is covered with CO again (see frame 5).

The oxygen fronts forming on the (110)-type grains exhibit an interesting feature. Upon increase of the reaction rate the oxygen fronts appear homogeneously on the whole grain (see fig. 3, frames 2 and 4) but are not initiated at some defects, as could be expected from Pt(110) single crystal studies [11]. The fronts never seem to disappear totally but become so narrow that they are close to the resolution limit of the PEEM.

Regarding the two single crystal surfaces Pt(100) and Pt(110) held at a temperature of 480 K it has been observed that the partial pressures of the reactants under which oscillations occur mutually exclude each other [12]. However, on the polycrystalline sample the global rate oscillations are triggered by both the (100)-type and the (110)-type grains at the same time. Although the parameter range for pattern formation in the excitable state for the polycrystalline grains was found to be broader compared to the corresponding single crystal values, the parameter ranges for the (100)-type and the (110)-type grains still do not overlap at the control parameters used in this work. On a cylindrical Pt single crystal surface, Sander et al. [13] found a strong broadening of the oscillatory range around the (100)-orientation due to structural heterogeneity. However, at 480 K gas-phase coupling was only observed with the (110)-oriented parts of the cylinder, while for oscillations around the (100)-orientation this mechanism shows no significant influence. Ehsasi et al. [14] found evidence for gas-phase coupling with two separate Pd(110) single crystals mounted in an UHV-chamber. On microscopic length scale, diffusion coupling was dominant for the formation of rate oscillations on a Pt-field emitter tip [15]. On our polycrystalline sample, it is very rare to observe the propagation of reaction–diffusion fronts across the grain boundaries and it is non-existent in fig. 3. The grain boundaries apparently act as strong barriers for diffusion. Therefore gas-phase coupling must be the dominant information transfer mechanism which seems to be strong enough to induce oscillations on grain surfaces even when the control parameters are not ideal for the single crystal situation. We caution that the modelling of a "real" catalyst particle consisting of different crystal planes cannot be performed simply by the superposition of the contributions from the single elements, but that the different possible coupling mechanisms between the adjacent active parts have to be taken into account.

Acknowledgement

The authors are indebted to G. Ertl and G. Haas for fruitful collaboration in these studies.

References

[1] A.M. Zhabotinsky, Chaos 1 (1991) 379.
[2] F. Schüth, B.E. Henry and L.D. Schmidt, Adv. Catal. 39 (1993) 51.
[3] R. Imbihl, in: *Opt. Structures in Heterogeneous Reaction Systems*, ed. P.J. Plath (Springer, Berlin, 1989).
[4] G. Ertl, Adv. Catal. 37 (1990) 213.
[5] G. Ertl, P.R. Norton and J. Rüstig, Phys. Rev. Lett. 49 (1982) 177.
[6] W. Engel, M.E. Kordesch, H.H. Rotermund, S. Kubala and A. von Oertzen, Ultramic. 36 (1991) 148.
[7] H.H. Rotermund, W. Engel, M. Kordesch and G. Ertl, Nature 343 (1990) 355.
[8] S. Jakubith, H.H. Rotermund, W. Engel, A. von Oertzen and G. Ertl, Phys. Rev. Lett. 65 (1990) 3013.
[9] J. Lauterbach and H.H. Rotermund, Surf. Sci., in press (1994).
[10] J. Lauterbach, G. Haas, H.H. Rotermund and G. Ertl, Surf. Sci. 294 (1993) 116.
[11] S. Nettesheim, A. von Oertzen, H.H. Rotermund and G. Ertl, J. Chem. Phys. 98 (1992) 9977.
[12] M. Eiswirth, P. Möller, K. Wetzl, R. Imbihl and G. Ertl, J. Chem. Phys. 90 (1989) 510.
[13] M. Sander, M.R. Bassett, R. Imbihl and G. Ertl, Vacuum 41 (1990) 272.
[14] M. Ehsasi, O. Frank, J.H. Block and K. Christmann, Chem. Phys. Lett. 165 (1990) 115.
[15] V. Gorodetskii, J.H. Block, W. Drachsel and M. Ehsasi, Appl. Surf. Sci. 67 (1993) 198.