

Imbihl and Mikhailov Reply: The central idea of our Letter was that the principal mechanism responsible for the onset of chaotic oscillations in catalytic surface reactions consists in delays in the response of a population of reactive islands to the global reaction rate [1]. To test this hypothesis, we have considered a strongly simplified model which neglects some of the known details which were incorporated in previous modeling.

The model is not based on the concept of homogeneous nucleation of new islands, as is wrongly assumed in the preceding Comment [2]. Instead, we consider heterogeneous nucleation at structural defects produced by the reaction. Scanning tunneling microscopy experiments which showed that 1×1 -CO islands develop preferentially near step edges gave a clear indication towards heterogeneous nucleation [3]. We assume that the number of temporary defects which are generated by the reaction exceeds by far the number of permanent defects such as steps and therefore we take only the former ones into account. Accordingly, the total nucleation rate w is set proportional to the reaction rate kpq in our model [see Eq. 4 in [1]].

At present, no measurements of the island nucleation rate under reaction conditions have been performed. In the experiments by King *et al.* on Pt(100)/CO only the exponent for the growth rate of the total 1×1 area has been determined [4,5] (we regret that the volume and the page number of Ref. [4] was incorrectly cited). These experiments were conducted (i) in absence of a reaction, (ii) only for CO and not for NO, and (iii) the surface was a well-annealed hex (hex-R) phase whereas the NO + CO reaction took place on a hex surface roughened by the reaction. Moreover, the temperature only varied between 380 and 410 K while the chaotic oscillations are found at a larger temperature of $T = 480$ K. In these measurements performed at 380, 390, 400, and 410 K the exponents 3.9, 4.7, 5.4, and 5.8, respectively, were determined yielding an average value $\nu = 4.5 \pm 0.4$. By a linear extrapolation of this sequence to $T = 480$ K, we have obtained the exponent $\nu = 9$ which yields the value $r = \nu + 1 = 10$ used in our simulations. In a private correspondence, which we acknowledge here, King pointed out that the scatter of the experimental data is too large to deduce a T dependence of the exponent, but, on the other hand, the assumption of such a dependence is also not in contradiction to the experimental data. In any case, we refer to the experiments by King and co-workers only in the sense that they provide an indication of strong sensitivity of the island nucleation and growth processes on the adsorbate coverage [4,5].

The interpretation of the growth exponent suggested by King is that to 4 to 5 CO molecules have to come together in order to restructure the surface in a concerted reaction step [4,5]. This concerted reaction step could be either the formation of a critical nucleus at a structural defect in which case the nucleation rate would be rate limiting for the growth of the 1×1 area, or, 4 to 5 CO molecules

would be required to allow for the further growth of an already existing supercritical 1×1 -CO island. In contrast to the former case the exponent for the nucleation growth would be unknown then. Since the experimental data did not allow us to distinguish between the two possibilities we chose the first one for our model.

What we neglect is only the coverage dependence for the growth of the supercritical islands, which have passed the critical size. Such a dependence may in principle lead to a competition between the growing islands, as described by the Lifshitz-Slyozov theory. If such a competition were present, it would have led to a nonlinear dependence of the growth rate of the total 1×1 area. Such a dependence is, however, in contradiction to the experiments by King and co-workers who found that the exponent is almost independent of the size of the already existing 1×1 area [4]. Even if such a dependence were present, we see no convincing arguments that it would suppress chaos.

The conversion of a growing island to the reactive state occurs as "surface explosion" inside the island is ignited [6]. The ignition can be triggered by fluctuations, structural defects, and coverage gradients between the edge and the interior of the island. The critical age of an island, used in our model, represents a characteristic waiting time for the surface explosion in a growing island. Though this critical age may depend on the coverage, no experimental data or analytical theory is available that would allow us to deduce this dependence. To avoid unnecessary speculations, we have used in our simple model the assumption of a constant critical age.

R. Imbihl

Institut für Physikalische Chemie und Elektrochemie
Universität Hannover
Callinstrasse 3-3a
30167 Hannover, Germany

A. S. Mikhailov

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

Received 5 April 1996

[S0031-9007(97)03203-1]

PACS numbers: 82.65.Jv, 05.70.Ln

- [1] N. Khurstova, G. Vesper, A. Mikhailov, and R. Imbihl, *Phys. Rev. Lett.* **75**, 3564 (1995).
- [2] V. P. Zhdanov, preceding Comment, *Phys. Rev. Lett.* **78**, 4303 (1997).
- [3] A. Borg, A.-M. Hilmen, and E. Bergene, *Surf. Sci.* **306**, 10 (1994).
- [4] A. Hopkinson, X.-C. Guo, J. M. Bradley, and D. A. King, *J. Chem. Phys.* **99**, 8262 (1993).
- [5] A. Hopkinson, J. M. Bradley, X.-C. Guo, and D. A. King, *Phys. Rev. Lett.* **71**, 1597 (1993).
- [6] T. Fink, J.-P. Dath, R. Imbihl, and G. Ertl, *J. Chem. Phys.* **95**, 2109 (1991).