Comment on ‘‘Delay-Induced Chaos in Catalytic Surface Reactions: NO Reduction on Pt(100)’’

Critical phenomena occurring in adsorbed overlayers at the conditions far from equilibrium are of high current interest [1]. To simulate such phenomena, one inevitably needs to employ a series of assumptions and simplifications, which should of course reflect the main properties of a system under consideration. The recent Letter by Khrustova, Veser, Mikhailov, and Imbihl [2], treating the chaotic kinetics of the NO-CO reaction on Pt(100), does not seem to satisfy the latter requirement.

The main idea employed in Ref. [2] is that the chaos results from an interplay between (i) adsorbate-induced surface reconstruction [the CO- and NO-induced (1×1) islands are formed in the domain of the “hex” phase], (ii) reaction on islands, and (iii) the feedback between the adsorbate coverages and the gas phase concentrations. The model contains three equations. Two of them, describing the kinetics of CO and NO adsorption on the hex phase and the feedback with the gas phase, are more or less standard. Equation (3) of [2], treating the variation in the (1×1) area, is represented as

$$dq/dt = -\mu q + w\,, \tag{1}$$

with

$$w(t) = Ac(t - \tau)^{\nu} p(t - \tau) q(t - \tau)\,, \tag{2}$$

where μ is the relaxation rate constant, $w(t)$ the rate of appearance of the new reactive (1×1) area, c the adsorbate coverage, p the pressure, and $\nu \simeq 10$ the exponent for the *nucleation* rate of the (1×1) islands. Since the adsorbate islands are assumed to become reactive only when they reach a critical size corresponding to a critical age τ, the rate $w(t)$ is considered to be proportional to the nucleation rate at the *delayed* time moment $t - \tau$.

Our comments on the equations above are as follows:

(1) Justifying Eq. (2), Khrustova *et al.* [2] refer to the results of measurements by King and coworkers [3,4]. The latter studies however *do not contain* detailed data for the *nucleation* rate. What King *et al.* [3,4] have really demonstrated is that the *island-growth* rate is proportional to c^{ν} with $\nu \simeq 4$. Taking into account that the measured growth rate is independent of the (1×1) area, they conclude [3,4] that (i) the (1×1) islands seem to be strongly anisotropic and (ii) nucleation is heterogeneous. This model, used by Hopkinson and King [5] to simulate the NO-CO reaction on Pt(100), is opposed to that proposed by Khrustova *et al.* [2]. King and coworkers [3,4] admit that one might treat their experimental data assuming that nucleation is homogeneous with the rate $\sim c^{\nu}$. They emphasize however (Ref. [4], p. 8277) that in the latter case each nucleation event should lead to very *rapid* phase transformation of a *limited area* of the hex phase. Physically, this condition can hardly be rationalized, but anyway it is not compatible with the model of Khrustova *et al.* [2]. In summary, we may conclude that the results of measurements by King and coworkers [3,4] cannot be used to justify Eq. (2).

(2) Inadequate citation of Refs. [3,4] by Khrustova *et al.* [2] might be considered as curious because, constructing the model, one can in principle ignore the growth law found by King *et al.* [3,4] (even if this finding looks reliable). The problem however is that, describing the island evolution, Khrustova *et al.* [2] ignore the coverage dependence of the growth rate *at all*. Meanwhile, such a dependence takes place even if the system is close to equilibrium (e.g., in the Lifshitz-Slyzov limit [6]). Including the coverage dependence of the growth rate into the model is expected to make its behavior more deterministic (the chaos might be suppressed).

(3) Khrustova *et al.* [2] *postulate* that the adsorbate islands become reactive only when they reach a critical size, which is treated simply as a free parameter. The physics behind this assumption is not clear. Why for example does not the critical size depend on adsorbate coverages?

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