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Nonlinear dynamics on catalytic surfaces

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Abstract

Recent progress in nonlinear dynamics on surfaces is reviewed focusing on selected examples from single crystal studies. Complex patterns, fluctuations in small scale systems, and controlling catalytic reactions by microstructured heating or through local heating with a laser beam are some of the issues to be discussed.

Keywords: Nonlinear dynamics; Complex patterns; Catalytic reactions

1. Introduction

When the first experimental observation of rate oscillations in a catalytic reaction was reported by the group of Wicke in 1970 [1], this phenomenon almost immediately aroused the interest of scientists and numerous hypothetical mechanisms were proposed [2]. It soon became evident that the rate oscillations were the result of a selforganization process on the catalytic surface and that surface analytical tools and well-defined experiments and catalysts were required for understanding the mechanism behind the oscillatory kinetics [3–12]. Today the mechanistic aspect in these studies has almost completely vanished and the emphasis has shifted instead to controlling spatiotemporal pattern formation and to the development and application of spatially resolving in situ techniques that come close to atomic resolution. This situation reflects the enormous progress which has been made due to the concept of low pressure single crystal studies.

The purpose of this short review is not so much to give an overview of the individual reaction systems and the different subfields – this can be found in some older review articles [3–12] – but to demonstrate with a few selected topics the current status in the development of this field. Despite all the progress, which has been achieved in the detailed mechanistic understanding, there are still a number of questions, which are difficult to answer and which, to a certain degree, remain unsolved. This is first of all the question of the significance of the results in real catalysis. Secondly, the question whether and to what extent the results obtained in low pressure single crystal studies can be extrapolated to explain the oscillatory behavior at high pressure and with polycrystalline catalysts also remains difficult to ascertain. The classical pressure and material gap problem of heterogeneous catalysis is thus also present in the oscillation studies and its bridging remains a challenging task.

2. Mechanisms of oscillations and pattern formation

2.1. Basic requirements

Practically by definition heterogeneously catalyzed reactions are systems far from thermodynamical equilibrium. Kinetic oscillation and spatiotemporal pattern formation can develop in such systems and before they were investigated on catalytic surfaces these phenomena had already been extensively studied with liquid phase reaction systems, the most well known example being the Belousov-Zhabotinskii reaction [13,14]. The theoretical framework for understanding these phenomena have been developed in a branch of physics and mathematics, which is termed non-linear dynamics. The name reflects the fact that the underlying mathematical equations have to be non-linear in order to exhibit this type of behavior.

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Similar to liquid phase reactions the general structure of the mathematical equations describing spatiotemporal pattern formation on surfaces is that of a reaction–diffusion (RD) system. We can write such an RD system in the form

$$x_i = F_i(x_j, \lambda) + \Delta_i \nabla^2 x_i \qquad (1)$$

where x_i represents a variable, in our case the adsorbate coverage of species $i - \lambda$ stands for a set of parameters, e.g. partial pressure and temperature. The (non-linear) local reaction kinetics are contained in the expression F_i, while the second term represents the diffusion of species where, for simplicity, we have assumed simple Fickian diffusion. If the surface reacts spatially homogeneously the diffusion term vanishes and our system can be described by a set of ordinary differential equations (ODE's). If we therefore neglect the aspect of pattern formation, i.e. we assume a spatially uniformly oscillating surface, we discuss the mechanism in terms of a point model of ordinary differential equations (ODE's) representing the local reaction kinetics.

2.2. *Oscillation mechanisms*

In the review of oscillatory surface reactions by Schüth and Schmidt about 60 oscillatory reaction systems are listed [8]. Apparently, the mechanistic requirements for obtaining oscillatory behavior are not very restrictive and there has even been some speculation whether most, if not all, catalytic reactions exhibit oscillatory behavior in some parameter range. For most of the systems no detailed mechanistic investigations have been made. Detailed studies have been carried out for the reactions of the automotive catalytic converter, namely, catalytic CO oxidation and catalytic NO reduction, which are investigated on platinum, palladium, and rhodium surfaces. The mechanism may change depending on the reaction conditions. For the low pressure experiments of catalytic CO oxidation on platinum single crystal surface the phase transition model has been verified by experiment [15] while at high pressure ($p > 1$ mbar) an oxidation/reduction mechanism is supported by experimental data [16,17].

In the following a short overview of the mechanisms is given, which are well supported by experimental data and realistic mathematical modeling. For details the reader is referred to several review papers and references therein [5–10].

2.2.1. *Catalytic CO oxidation*

2.2.1.1. The surface phase transition model. The clean surfaces of Pt(1 0 0) and Pt(1 1 0) exhibit a reconstruction which can be reversibly lifted upon adsorption [6,7,10]. An adsorbate-induced surface phase transition between the clean reconstructed surface and the adsorbate-covered bulk-like (1 × 1) surface is thus constituted, which is controlled by a critical adsorbate coverage. Since oxygen adsorption on Pt surfaces is highly structure sensitive the phase transition is associated with a change in the oxygen sticking coefficient and thus with a change in catalytic activity.

The basic principle of the oscillation mechanism in catalytic CO oxidation on Pt(1 1 0) can be demonstrated with the help of Fig. 1. Starting with the CO-covered 1 × 1 surface the high reactivity will decrease the CO coverage until below a critical CO coverage the surface reconstructs into the less active 1 × 2 phase. On this phase CO adsorption dominates over O_2 adsorption and the CO coverage grows until beyond the critical CO coverage the active 1 × 1 is established again.

2.2.1.2. The oxidation–reduction model. Pd surfaces are insofar different from Pt as oxygen can more easily penetrate into the Pd bulk and oxide formation is facilitated. Moreover, the clean surfaces do not reconstruct. It has been demonstrated that even at low p ($p < 10^{-3}$ mbar) oxygen can penetrate reversibly into subsurface sites of Pd(1 1 0) thus lowering its catalytic activity [18]. This subsurface oxygen formation can give rise to oscillatory behavior because on the inactive CO covered surface the subsurface oxygen reservoir is depleted through segregation to the surface, followed by reaction with CO, thus restoring the catalytic activity of the Pd(1 1 0) surface. With the active

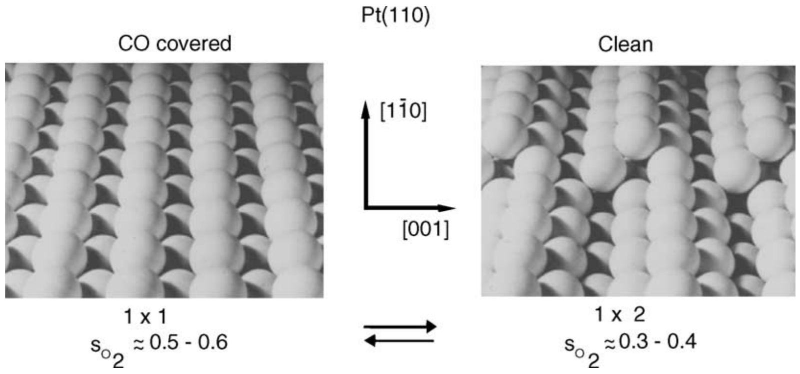

Fig. 1. Ball model illustrating the CO induced 1 × 1 ⇄ 1 × 2 surface phase transition of Pt(1 1 0). The different oxygen sticking coefficients, s_{O_2}'s, of the two phases are responsible for rate oscillations during catalytic CO oxidation. The model also demonstrates how the necessary mass transport of Pt atoms creates an atomic step on the surface.