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Oscillating reactions in heterogeneous catalysis: What new information can be obtained about reaction mechanisms?

M.M. Slinko

Institute of Chemical Physics, Russian Academy of Science, Kosygina Str. 4, Moscow 119334, Russia

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ABSTRACT

This paper demonstrates through a few selected examples including CO oxidation and methane oxidation over metallic catalysts the knowledge that may be obtained from the study of the oscillatory behaviour over supported and massive catalysts under atmospheric pressure conditions. The information about reaction mechanisms that can be obtained from the waveforms of reaction rate oscillations, from the phase shifts between oscillations of different products concentrations, and from visual observations of surface spatiotemporal behaviour is discussed.

1. Introduction

Oscillating reactions are key phenomena in dealing with the formation of structures ordered in space and/or time in physical and chemical systems. Heterogeneous catalytic reactions are highly non-linear, multilevel chemical systems, operated far from thermodynamic equilibrium. Temporal and spatiotemporal structures can originate at various levels of a heterogeneous catalytic system. The first level would be an element on a single crystal surface with oscillatory behaviour which can be described by a kinetic point model. The second level is represented by a spatially extended single crystal surface commonly including spatial inhomogeneities or by a single metal cluster bounded by differently indexed planes. The third level for massive catalysts may be considered as a whole polycrystalline metallic surface and for supported catalysts as a pellet. Finally the fourth level for supported catalysts is represented by a catalyst bed. From the second level up always an array of local oscillators has to be considered and the observed more or less synchronised behaviour not only depends upon the properties of local oscillators but also on the strength and the nature of the coupling between them. If periodic oscillatory behaviour of the global reaction rate is observed, then there is complete synchronisation of the local oscillators at each level of the heterogeneous catalytic system. Coupling between the local oscillators may occur through surface diffusion, diffusion through the gas phase, and by heat transfer. The dominant mechanism of synchronisation will depend upon the nature of the local oscillators and the experimental conditions used [1–3].

Ben Nieuwenhuys demonstrated for the first time (see Ref. [4]) that oscillatory reactions could be followed at the sharp tips (10^3 Å) with near atomic resolution (~10 Å) by using field emission microscopy (FEM). He reported a number of very important results. First of all it was demonstrated that the reaction of nitric oxide with hydrogen on a rhodium field emitter tip was structure sensitive. Not all planes of the different crystallographic orientations simultaneously exposed to the reaction mixture showed oscillating behaviour. Secondly, it was found that the dynamic behaviour of the integrated emission intensity of several planes of the rhodium emitter was closely connected with the properties of travelling reaction fronts. It was shown that, at the relatively low temperature of 430 K, the four quadrants of a [1 0 0]-oriented rhodium tip oscillated independently of each other. At higher temperature the reaction waves started at the (5 3 3) and (3 2 1) planes and travelled around the tip parallel to step edges. The maximum amplitude of the emission current oscillations occurred when the propagating front spread across a large part of the tip. The minimum amplitude was observed when the reaction wave covered only one quadrant of the tip. The results clearly demonstrated the importance of surface diffusion for the synchronisation of the local oscillations.

At the next level up in size, the meso scale represented by extended single crystal surfaces, real-time visualization of surface structures during oscillatory behaviour was first achieved by Ertl in 1989, using the photoemission electron microscope (PEEM) [5]. A fascinating variety of spatiotemporal phenomena were observed, including "target" patterns, spiral waves, standing waves and cellular structures [3]. It was shown that two mechanism of coupling via surface diffusion and diffusion via the gas phase operated over single crystal surfaces (surface area of ca. 1 cm^2) at pressures in the 10^{-5} mbar range. However, in contrast to the very fine metal tips

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E-mail addresses: slinko@polymer.chph.ras.ru, mmslinko@mail.ru.

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used by Nieuwenhuys (~1000 Å in radius), gas phase coupling was the major driver of synchronisation under these conditions.

The study of oscillatory behaviour at the macro-level (cm-scale), namely on extended polycrystalline surfaces and under atmospheric pressure conditions, is complicated by several factors. These include gradients of concentration and temperature which can originate both in the reactor and within the catalyst particles. In addition, massive and supported metallic catalysts are highly sensitive to impurities as well as to defects in surface morphology. Most surface science methods are limited to the study of reactions over single crystal surfaces under ultra high vacuum (UHV) conditions, and only a small number of experimental techniques can be used for the monitoring of the catalyst surface under atmospheric pressure conditions. However in spite of these difficulties, the study of the oscillatory behaviour of heterogeneous catalytic reactions under atmospheric pressure conditions can produce important information about the reaction mechanism. The goal of the present paper is to demonstrate with a few selected examples what kind of knowledge can be obtained through the study of oscillatory behaviour over supported and massive catalysts at the macro-scale and at atmospheric pressure. The study of oscillations with different waveforms (regular periodic, irregular, chaotic oscillations), the phase shift between oscillations of different products concentrations and the spatiotemporal behaviour via imaging of the colour variation of a catalyst surface will be analysed.

2. An analysis of the waveforms of reaction rate oscillations

Different types of oscillations can arise under atmospheric pressure conditions including kinetic oscillations, complicated thermokinetic oscillations and pure thermokinetic oscillations [2]. The most informative phenomena are the kinetic oscillations. Their properties and the causes of their appearance are closely connected with the details of the reaction mechanism and do not depend upon mass and heat transfer processes. Kinetic oscillations under atmospheric pressure conditions were discovered in the early 1970s for carbon monoxide oxidation over a platinum catalyst [6] and hydrogen oxidation over a nickel catalyst [7]. Since then, different types of oscillatory behaviour have been observed in more than 65 heterogeneous catalytic systems. A list of known oscillating reactions can be found in Ref. [8]. The majority are oxidation processes occurring on metal catalysts in various forms, for example wires, foils, powders, gauzes or metals supported on a variety of inert materials. The reactions have been studied in various types of reactors, including continuously stirred tank reactors (CSTR), flow reactors and reactors designed as infrared (IR) or solid electrolyte potentiometric (SEP) cells. In most studies only the integral signal of reaction rate oscillations has been measured. At atmospheric pressure the waveform of reaction rate oscillations is usually aperiodic in character. Regular periodic oscillations have been observed only in a small number of studies, where special attention was paid to the elimination of temperature and concentration gradients [9].

Fig. 1. Aperiodic oscillations observed during carbon monoxide oxidation over a 20 mg sample of a NaX zeolite catalyst containing 4.4% palladium (Ø of zeolite crystallites is 50 μm, Ø of Pd clusters is 10 nm). Initial catalyst temperature $T_0 = 453$ K. Feed CO concentration is 0.4 vol.%. [10].

One of the most interesting model oscillating systems is CO oxidation over a palladium–zeolite catalyst. A NaX faujasite (Si/Al = 1.25) was used as a matrix. Special catalyst preparation procedures produced a narrow distribution of palladium particle sizes of 4 nm or 10 nm, which are located within the channels and cages of the zeolite matrix [10]. Experimental studies and mathematical modelling of the observed oscillatory behaviour demonstrated that the origin of oscillations was similar to the mechanism of oscillations detected during CO oxidation over a Pd(1 1 0) single crystal surface under UHV conditions. In both cases the mechanism of kinetic oscillations involved a periodic switching of the surface between states of low and high activity by periodic variation in the concentration of the subsurface oxygen, which could be converted into chemisorbed oxygen as it segregated to the surface and vice versa [2,3]. Therefore the reaction of CO oxidation over palladium catalysts can be considered to be structure insensitive. The main difference between the single crystal and the zeolite supported catalysts is that much more complicated waveforms of oscillations were observed over the Pd–zeolite catalysts. Regular periodic, irregular, mixed-mode and chaotic oscillations could all be observed over Pd–zeolite catalysts by varying the temperature and the carbon monoxide/oxygen ratio.

Typical irregular oscillations over Pd–zeolite catalysts are shown in Fig. 1. Similar complicated waveforms were observed for the samples with large zeolite crystallites (50 μm) and high concentrations of palladium (2.5–14%). Regular periodic oscillations of the type shown in Fig. 2 were observed only for catalysts containing 10 nm palladium clusters within small zeolite crystallites (5 μm) and low palladium loadings (0.01–0.05% Pd).

The reaction of CO oxidation over palladium catalysts represents a very complicated multilevel system. Oscillatory behaviour may arise at the lowest level, which is a single crystal plane. Palladium clusters of 10 nm diameter can be considered as the second level of the system, followed by a zeolite crystallite of 5 μm in diameter, which is in many ways similar to a typical pellet of a supported catalyst. At 0.05% palladium loading the zeolite crystallite contains ca. 7×10^3 Pd clusters. A catalyst bed of 60 mg contains 2.5×10^8 zeolite crystallites with 1.75×10^{12} Pd clusters, which have to be synchronised.

Usually it is very difficult to establish the prevailing mechanism of synchronisation under atmospheric pressure conditions, where all three mechanisms of coupling can operate. However for

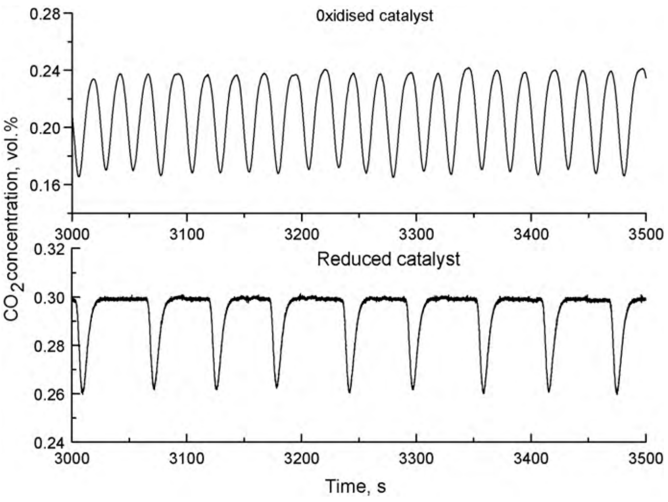

Fig. 2. Oscillatory waveform observed at 503 K following different pre-treatments of a 0.05% Pd–NaX zeolite catalyst (Ø of zeolite crystallites is 5 μm, Ø of Pd cluster is 10 nm): (a) pre-oxidised in a flow of O_2 at 503 K; (b) pre-oxidised, but followed by exposure to a reactant mixture containing 1% carbon monoxide for 30 min at 503 K [12].

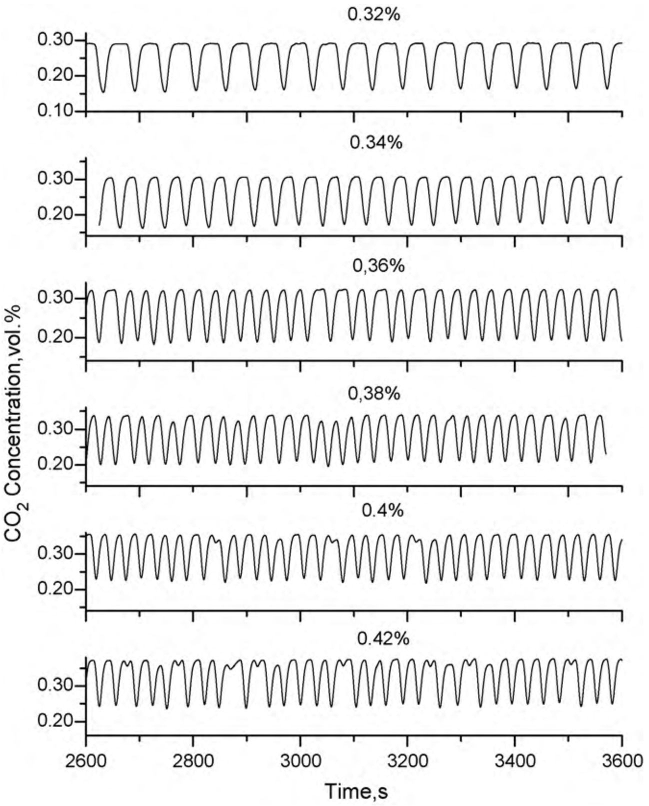

Fig. 3. The intermittency-I route to chaos, observed during the stepwise increase of feed CO concentration over a 0.05% Pd–zeolite catalyst at 503 K [12].

Pd–zeolite catalysts coupling via heat transfer can be excluded due to the low thermal conductivity of the zeolite matrix. Moreover the coupling of distant palladium clusters via diffusion on the surface of the zeolite support can be also neglected because the surface diffusion coefficients of the reactants are very small. Specific experimental studies demonstrated that in this system the coupling through the gas phase diffusion was the dominant mechanism for the synchronisation of the local oscillators at different levels of the system [11,12]. Therefore gas phase gradients due to external and/or internal diffusion limitations could lead to the appearance of complex, aperiodic oscillations. The results presented in Ref. [12] clearly demonstrate that coupling through the gas phase on the scale of a catalyst bed is so strong, that when Pd–zeolite catalysts with different natural frequencies were placed together into the same reactor, they could easily be synchronised. The experimental results showed that the loss of synchronisation occurred on the level of a zeolite crystallite. The appearance of CO concentration gradient within the zeolite crystallite, caused by internal diffusional limitations, resulted in the breakdown of synchronisation of palladium clusters situated at various distances from the centre of the zeolite crystallite. Fig. 3 shows the variation of the waveform of oscillations caused by increasing the carbon monoxide inlet concentration in very small steps (0.02– 0.04%). The calculated positive values of the largest Lyapunov exponents together with the finite dimension of the strange attractor indicated that the reaction dynamics was already chaotic for CO inlet concentration larger than 0.4%. However in addition to establishing the existence of deterministic chaos in a dynamical system it is also important to identify a route to chaos, which the system undergoes with the variation of the control parameter. The identification of the route to chaos may be very helpful in the discrimination of various models producing an oscillatory behaviour used for the simulation of the experimental data. Corresponding to various bifurcations which lead to the loss of stability of the limit cycle and the appearance of chaotic behaviour three main routes of transition to chaos in dynamical systems can be identified: via period-doubling bifurcations (Feigenbaum scenario), via the breaking of a torus (Ruelle and Takens scenario) and via intermittency (Pomeau-Manneville scenario) [13]. The variation of the Fourier spectrum and the Poincare section as a function of the CO concentration in the feed allowed the identification of the intermittency-I route to chaos for the experimental data shown in Fig. 3 [14]. This is the first qualitative evidence for such a transition during reaction rate kinetic oscillations on supported catalysts under atmospheric pressure conditions.

The increase of the inlet CO concentration from 0.3% to 1.1% caused the increase of the Pd activity and the appearance of the CO concentration gradient inside the zeolite crystallite. The results of the simulations presented in Ref. [15] demonstrated, that the increase of the gradient of the CO concentration within the zeolite crystallite may cause the breakdown of the synchronisation of Pd clusters situated at various distances from the centre of the zeolite crystallite and results in chaotic behaviour. The analysis of the observed time series indicated the conditions of the experiment, when internal diffusion limitations originated and had to be considered—the information, which is very important for the kinetic study of many reactions.

While many time series reported in the literature for heterogeneous catalytic reactions appear to be complex, the distinction made between periodic and chaotic oscillations was often based only on a visual inspection of the time series. It is essential that deterministic chaos is properly identified, and distinguished from random noise and quasiperiodic behaviour, or mixed-mode oscillations [2]. Important information about the mechanism of a reaction can be obtained from chaotic experimental time series by constructing a strange attractor representing the geometrical image of the chaotic movement. The embedding dimension (d_E) of the reconstructed attractor indicates an upper limit of state variables necessary to model the system [16]. Calculation of the embedding dimension for the time series shown in Fig. 3 gave a value d_E greater than or equal to 10. This is much larger than values which were obtained by Razon et al. [17] ($d_E = 4$) for chaotic oscillations during carbon monoxide oxidation over a massive platinum foil, or over a Pt(1 1 0) single crystal surface by Eiswirth et al. [18] ($d_E = 5$). The large value of the embedding dimension observed during carbon monoxide oxidation over Pd–zeolite catalysts indicates the occurrence of the so-called “diffusional chaos” in a distributed system, and supports the idea that internal diffusion limitations play a crucial role in the origin of the chaotic behaviour.

Useful information about reaction mechanisms is not limited to chaotic oscillations. Regular periodic oscillations of the global reaction rate are the result of complete synchronisation of local oscillators at all levels of the system, and so can give information about the catalytic processes which occur on a single metal cluster. Fig. 2 shows that the waveforms of regular oscillations of the carbon monoxide oxidation rate over Pd–zeolite catalysts are sensitive to the preliminary pre-treatment of the catalyst. For a catalyst subject to severe reduction conditions the period of the oscillations increased and the catalyst spent longer time in the high activity state. Simulation of the regular oscillations over Pd–zeolite catalysts using the “oxide” model showed that the waveform of oscillations was very sensitive to the oxidation state of palladium [12]. An oxidised catalyst spends more time in the low activity state, with a high carbon monoxide coverage which results in a slow reduction of the subsurface oxygen. When the concentration of the subsurface oxygen falls down a critical value, the catalyst reaches a high activity state in which the palladium surface is mainly covered by oxygen. Rapid formation of subsurface oxygen causes a transition to the low activity state after a short time.

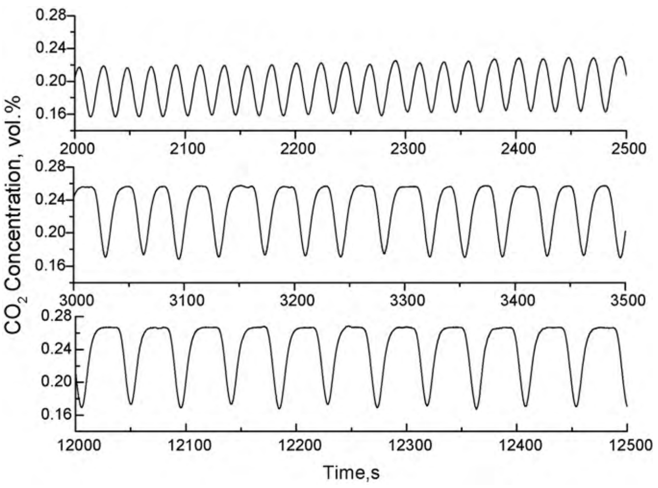

Fig. 4. The evolution of the oscillations during CO oxidation with time over a 0.05% Pd–zeolite catalyst (Ø of zeolite crystallites is 5 μm, Ø of Pd cluster is 10 nm) at 503 K and 0.3% inlet concentration [12].

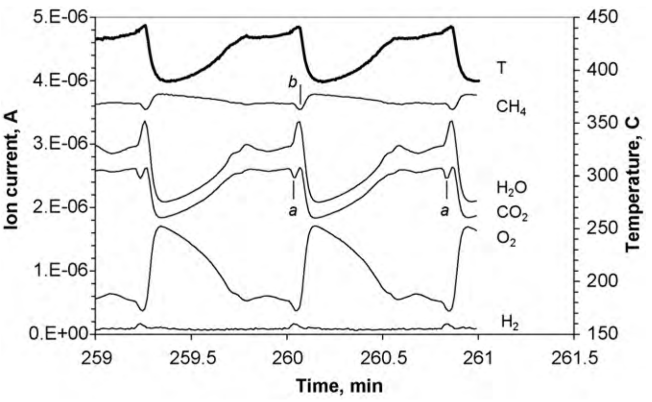

Fig. 5. Oscillatory behaviour observed during methane oxidation over a palladium foil catalyst (3 mm × 3 mm × 0.35 mm) at 648 K. The feed rate is 20 ml/min with gases in the ratios CH_4:O_2:Ar = 82:14:4. Concentration signals for different gases have been vertically offset by the factors shown below to avoid overlapping: H_2 (100×, -1.8×10^{-6}), O_2, CO_2 ($+1.6 \times 10^{-6}$), H_2O ($+1.8 \times 10^{-6}$), CH_4 (-2.3×10^{-6}) [26].

A different situation is observed for the reduced catalyst. Here the system spends more time in the high activity state, where the surface coverages are small, the concentration of adsorbed oxygen dominates and the formation of the subsurface oxygen proceeds relatively slowly. There is a short downturn, or spike in the rate, which corresponds to blocking of the surface by carbon monoxide, which occurs at a next critical concentration of the subsurface oxygen. At high carbon monoxide coverages, reduction of the subsurface oxygen proceeds quickly and so the system returns to the high activity state after a short time. These are common trends in studies of carbon monoxide oxidation which show oscillating behaviour. They have been observed in many studies, for example in Ref. [19], where the oscillatory patterns looked like spikes "up" for an oxidised catalyst and spikes "down" for a reduced catalyst. These patterns allow conclusions to be drawn about the state of the catalyst during long runs or during variation of the experimental conditions. Fig. 4 shows the evolution of regular oscillations over a 0.05% Pd–zeolite catalyst at 503 K. It can be seen that, with increasing activity of the catalyst, the system spends more time in the high activity state, when the waveform of the oscillations tends to approach that of a reduced catalyst. Variations of the waveform of regular oscillations can thus clearly indicate variations in the state of the catalyst.

3. An analysis of phase shifts between oscillations of different products concentrations

The first studies focused on the analysis of the phase shift between oscillations of various product concentrations were performed in Ben Nieuwenhuys's group. They studied NO + H_2 reactions over platinum group metals. In addition to the importance of these reactions in automotive catalysis, they are of interest since three nitrogen containing species can be formed [21], viz.:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{1}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{2}$$

$$2NO + H_2 \rightarrow N_2O + H_2O \tag{3}$$

It was shown that over Pt(1 0 0) the rates of production of nitrogen and ammonia oscillated in phase but were in an antiphase relationship to the nitrous oxide formation rate [20]. Quite another picture was observed over Rh(5 3 3) and the other Rh(1 1 1)-like single crystal surfaces, where nitrogen production was almost in antiphase to ammonia synthesis, and the formation of nitrous oxide was not observed under oscillatory conditions [22,23]. The causes of the different behaviour of rhodium and platinum catalysts have been analysed. On Rh(1 1 1)-like surfaces the origin of oscillations can be related to periodic transitions between nitrogen-rich and oxygen-rich surfaces, with adsorbed oxygen destabilising the nitrogen adlayer and causing an acceleration in the rate of nitrogen production. However at the Pt(1 0 0) surface the important step involved the autocatalytic creation of vacant sites required for nitric oxide dissociation—the so-called "surface explosion" phenomenon [22,23]. Mathematical modelling of the oscillations in the NO + H_2 reaction over Rh(5 3 3) [24] and Pt(1 0 0) [25] has demonstrated that various types of lateral interactions between the species adsorbed on the surface cause the different phase shifts between oscillations of products concentrations in these systems.

Recently it was demonstrated that the new information concerning the reaction mechanism can be obtained from an analysis of phase shifts between oscillations of different products concentrations during methane oxidation over Pd catalysts [26]. Oscillatory behaviour in this reaction was observed in the presence of excess methane, when only the products of complete oxidation, viz. carbon dioxide and water, were detected [27–29]. Zhang et al. were the first to observe the phase shift between oscillations of carbon dioxide and water signals during methane oxidation over a palladium foil [29]. The authors proposed that the reason for such unusual dynamic behaviour was the accumulation of hydrogen in the bulk of the palladium catalyst and the delay in its reactivity towards oxygen. However, the results of a study of the oscillatory behaviour over a palladium foil reported in Ref. [26] demonstrated that high hydrogen solubility in palladium was detected only at temperatures lower than 373 K. Dissolved hydrogen was completely removed from the catalyst at temperatures higher than 413 K, and so could not play an essential role at temperatures of 573–758 K, where the oscillations were observed. Fig. 5 shows the oscillatory behaviour during methane oxidation over a palladium foil at 648 K [26]. It can be seen that the water signal does not follow the carbon dioxide signal for part of the oscillatory cycle. Moreover, at point *a* both methane and carbon dioxide concentrations decrease, while water and hydrogen concentrations rise. Visual observations of the palladium foil surface showed that at point *a*, a colour wave quickly spread from the downstream part of the foil to the top of the foil. The colour of the catalyst changed from dark grey to light grey. The spreading of the colour wave was accompanied by an increase of the catalyst temperature. All these experimental data indicate that at point *a* reduction of palladium oxide to metallic palladium occurred.

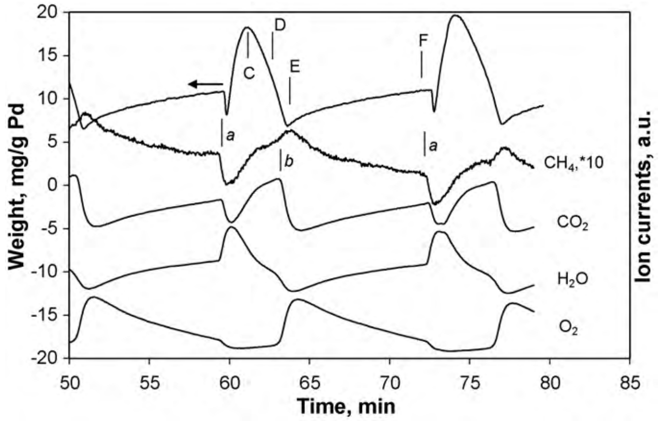

Fig. 6. Oscillatory behaviour observed during methane oxidation over a palladium powder catalyst (Ø = 1.05 μm) at 573 K. The feed rate is 20 ml/min with gases in the ratios CH_4:O_2:Ar = 82:14:4. Concentration signals for different gases have been vertically offset by the factors shown below to avoid overlapping: (O_2 (-1.0×10^{-6}), CO_2 ($+1.5 \times 10^{-6}$), H_2O ($+0.6 \times 10^{-6}$), CH_4 ($10\times$, -5.97×10^{-5})) [26].

The decomposition of methane over reduced palladium leads to the formation of carbon and hydrogen species. Hydrogen interacts with adsorbed oxygen, and a significant increase in the water production rate can be detected at point *a*, together with methane consumption from the gas phase. In contrast, at point *b* the peak of carbon dioxide concentration is observed, while there are no methane or water maxima coinciding with the increase in the production rate of carbon dioxide. Evidently surface carbon species resulting from methane decomposition accumulated after point *a*, and they oxidised at point *b*, producing peak of carbon dioxide evolution.

To reveal the causes of such interesting behaviour, thermogravimetric analysis (TGA) was combined with on-line mass-spectrometry of the effluent gas mixture, and temperature-programmed oxidation (TPO), in experiments using palladium powder. Fig. 6 shows the self-sustained weight oscillations observed by TGA and the corresponding oscillations of the mass spectrometric ion currents related to all the gas phase components. The same character of oscillations displaying carbon accumulation at point *a* and carbon oxidation at point *b* can be detected also in Fig. 6 in experiments using Pd powder. The weight variations may correspond to changes in the amounts of carbon and/or oxygen both in the bulk and at the surface of the catalyst. To reveal the state of the palladium catalyst during oscillatory behaviour, experiments were performed in which there were interruptions of the reaction at various stages of an oscillatory cycle, followed by temperature-programmed reaction (TPR) or temperature-programmed desorption (TPD). At the points in the oscillatory cycle marked in Fig. 6 as *a*, C, D, E and F, the furnace power and the reactants feed were both switched off and followed by fast evacuation the reaction mixture. After cooling to room temperature, the sample was heated in a 5%O_2–He flow up to 973 K and carbon dioxide evolution was measured [full details of the experiment can be found in Ref. [26]]. It was shown that the weight rises and falls during the transitions *a* → C → D → E were mainly due to carbon deposition and removal respectively. The amount of carbon in the catalyst was nearly constant during the stage E → F. Additional TPD experiments demonstrated that the weight increase during the time interval between points E and F was caused by oxidation of the catalyst.

Interesting information about the mechanism of methane oxidation over the palladium catalyst was provided by correlations of the observations about the state and the activity of the catalyst. In the first place it became clear that, depending on the phase of the oscillatory cycle, three states of reduced palladium exist with different reactivities. At point *a* (see Fig. 6), the newly reduced palladium exhibited the highest extent of methane conversion. However, this very active state of reduced palladium was very quickly modified by carbon (point C in Fig. 6). The reduced palladium surface modified by carbon displayed an intermediate degree of methane conversion and was active in both water and carbon dioxide production. The final state of reduced palladium was reached at point E. Here, the least active state of the reduced palladium was obtained—the lower activity resulting from blocking of the active sites by adsorbed oxygen. It can be seen that the oxidised state PdO (point F in Fig. 6) is more active than the reduced state blocked by oxygen (point E) and is less active than the newly formed reduced state without carbon (point *a*).

The oxidation state of the palladium, which is more active is widely debated in the literature [30]. Some researchers [31,32] reported that the metal phase was more active, while other studies demonstrated that PdO was the main active phase [33,34]. This confusion could arise, because it was not realized up to now that various states of the metallic Pd with different activities (larger and smaller than activity of PdO) could exist under the reaction conditions. Various authors could obtain a variety of states of the reduced Pd during methane oxidation at different temperatures and compositions of a reactant mixture and could make completely different conclusions from the comparison of Pd and PdO activities.

Secondly, in Ref. [26] Bychkov et al. demonstrated that accumulation of carbon in their palladium powder catalyst was the reason for the antiphase oscillations of the reaction products carbon dioxide and water. Unexpectedly, accumulating carbon did not poison methane oxidation at some stage of the oscillatory cycle (stage *a* → C in Fig. 6). It is believed that there is migration of the surface carbon into the bulk, leaving the catalyst surface essentially clean. This conclusion is in agreement with recent experimental results of Bowker et al. [35], who demonstrated that the surface carbon present on a Pd(1 1 0) surface above 450 K appeared not to poison the reactions of ethane, acetaldehyde and acetic acid decomposition. It was shown that the Pd surface appeared to act as a “sponge” for carbon atoms. In our study of oscillatory behaviour it was shown that hundreds of carbon monolayers could be periodically accumulated in the palladium powder catalyst and removed from it during one oscillatory cycle.

4. An analysis of the spatiotemporal behaviour

It is now well recognised that a catalyst surface may represent an array of local oscillators coupled by transport processes and temperature variations. If the coupling between different oscillators is sufficient, all elements oscillate in phase and homogeneous behaviour in space is observed. When the size of the system is significant and/or the rate of the coupling is not strong enough, spatiotemporal structures appear. At pressures below 10^{-4} mbar, spatiotemporal phenomena have been explored in depth using PEEM, and a fascinating variety of different dynamical patterns were discovered for reactions on single crystal surfaces [3,5]. However, only a very few experimental techniques can provide information about spatiotemporal surface structures under high-pressure conditions which are characteristic of many catalytic reactions. Some steps towards bridging the pressure gap between UHV and atmospheric pressure studies have been taken in the last 10 years through the development of two new methods, “Ellipso Microscopy for Surface Imaging” (EMSI) and “Reflection Anisotropy Microscopy” (RAM). However, up to now these methods had been used to image spatiotemporal behaviour only at pressures in the mbar range [36]. The only technique with relatively high spatial resolution which has been used to observe spatial patterns in catalytic reactions at atmospheric pressure is infrared (IR) thermography [37]. The variations in the temperature of the catalyst are visualized by imaging the blackbody radiation emitted from the surface. This method was used to observe spatiotemporal patterns at atmospheric pressure during hydrogen oxidation on platinum [38], nickel [39], and oxidation of carbon monoxide and ethylene over supported rhodium catalysts [40]. However all of these studies have focused on highly nonisothermal regimes under conditions where external transport limitations could significantly influence the reaction rate and its dynamic behaviour. Large amplitude temperature oscillations (45–236 K) were mainly of a thermokinetic nature. Kinetic oscillations with small-amplitude temperature oscillations of 0.2–8 K (i.e. under approximately isothermal conditions) have been studied using IR thermography only during carbon monoxide oxidation over thin-film platinum catalysts [9].

There is, however, a group of reactions during which one can observe and record the surface spatial structures without any expensive imaging techniques. Recently it was demonstrated that periodic variations of colour could be observed during oscillating behaviour of methane and ethane oxidation over nickel and cobalt catalysts [41,42]. Nonisothermal oscillations in these systems arise through an oxidation–reduction mechanism. Periodic transitions of the catalyst surface from an oxidised state (dark colour) to a reduced state (light colour) occurred, together with variations of the catalyst temperature. Visual observations of the colour of the catalyst surface provided important information about the variation of the activity and the selectivity during oscillations. Simultaneous measurements of gas phase concentrations revealed that mostly carbon dioxide was produced over the oxidised state, while carbon monoxide and hydrogen production rates reached their maxima over the completely reduced surface. Moreover, variations of spatial patterns were detected over nickel foil and especially over cobalt foil catalysts [41]. It was shown that in most cases regular reaction rate oscillations were associated with periodic movements of reduction–oxidation waves. During methane oxidation over a cobalt foil, transitions from the low reactivity, oxidised state to the high reactivity, reduced state occurred through the propagation of a wave of the reduced state, without visible pattern formation. However, the reverse transition to the low reactivity state, which occurred via fronts of the oxidised state, was much slower. During the movement of the oxidation front the area of the oxidised catalyst expanded and contracted continuously revealing some kind of a so-called "a breathing motion". During an oscillatory cycle the system remained longer in the low reactive state, where the surface was predominantly but never completely oxidised, and some kind of surface turbulence could be detected on the downstream part of the catalyst surface. Here areas of reduced and oxidised surface appeared and disappeared in a chaotic manner. No macroscopic reaction rate oscillations were detected during this turbulent regime, and the system was in the low activity state. A movie demonstrating this spatiotemporal behaviour can be viewed via the Internet, on the homepage of the Institute of Chemical Physics RAS [43].

More intricate variations of the colour of the cobalt foil could be observed during studies of oscillatory ethane oxidation [44]. The oscillations of methane oxidation were observed at temperatures 1023–1073 K – higher than the temperature of Co_3O_4 decomposition to CoO – and during the oscillatory behaviour the catalyst surface colour changed periodically between dark (CoO) and light (metallic cobalt). Oscillations during ethane oxidation over the cobalt foil were detected at temperatures of 823–873 K, under the conditions where Co_3O_4, which has a grey colour, may exist. This grey colour was detected during oscillations of ethane oxidation, indicating the deeper oxidation of the catalyst in this case compared to methane oxidation. The results were supported by TGA analysis combined with on-line mass-spectrometry and TPO experiments.

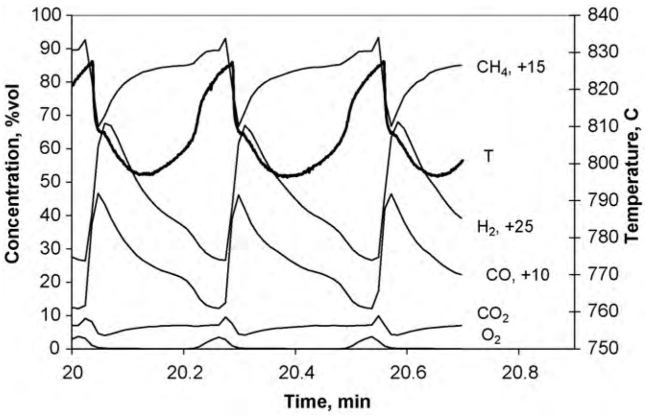

Fig. 7. A sequence of images of a cobalt foil surface recorded during ethane oxidation at the following time points: 0.00 s, (b) 0.32 s, (c) 1.52 s, (d) 1.64 s, (e) 1.80 s, (f) 2.80 s, (g) 4.40 s, (h) 4.68 s. A reaction mixture comprising C_2H_6:O_2 = 7:3 was supplied at the flow rate of 28 ml/min at temperature 873 K [44].

Thus the visual observations of the catalyst surface during oscillations showed that, due to the greater reducing ability of ethane, shown in Ref. [44] even Co_3O_4 could be reduced during oscillatory behaviour. This is the reason for the significant decrease of the temperature range of the oscillations during ethane oxidation over cobalt, in comparison to that of the oscillations during methane oxidation.

The existence of three states of a cobalt surface with different degrees of oxidation may be the reason why more complicated spatiotemporal surface structures are observed during ethane oxidation by the cobalt foil compared to the nickel foil. Fig. 7 shows a sequence of images of the catalyst surface which were recorded during the oscillatory behaviour of ethane oxidation over a large cobalt foil sample (7 mm × 3 mm × 0.75 mm). The corresponding movie can again be viewed via the Internet [45]. Fig. 7a shows the initially reduced surface of the sample. The propagation of the oxidation front is depicted in Fig. 7b and c. It can be seen that the oxidation wave does not spread across the whole surface, but stops with the formation of a clear boundary between the oxidised (dark) and reduced (light) parts of the surface. Fig. 7d–f shows the backward motion of the oxidation front. However, the upstream (previously oxidised) area, and the downstream reduced part of the catalyst are still separated by a noticeable boundary, as can be seen in Fig. 7f. Only after some seconds the dark, newly reduced surface becomes light coloured. Fig. 7g and h demonstrates that several boundary lines exist after some oscillatory cycles. It is suggested that diffusion of oxygen from the oxidised surface into the bulk of the cobalt foil can occur on the oxidised area of the catalyst. The existence of a noticeable boundary after the backward motion of the oxidation front may represent a situation where the upper surface layers of cobalt were already reduced, but not all of the oxygen incorporated into the bulk has been removed.

The spatially homogeneous oscillations could be observed only for the case, when a cobalt foil of a smaller size (4 mm × 4 mm × 0.16 mm) was studied in a CSTR reactor. Under these conditions, for which all gradients in the gas phase concentrations were eliminated and at sufficiently high temperatures the rates of propagation of oxidation and reduction fronts were so large that they could synchronise the whole surface of the cobalt foil.

Propagating waves of oxidation and reduction can carry information about the reaction mechanism, and especially about the mechanism of coupling between local oscillators. Fig. 8 shows the oscillatory behaviour during methane oxidation over a nickel catalyst in the form of a capillary (diameter 2 mm) with one end welded closed. A chromel–alumel thermocouple was inserted inside the

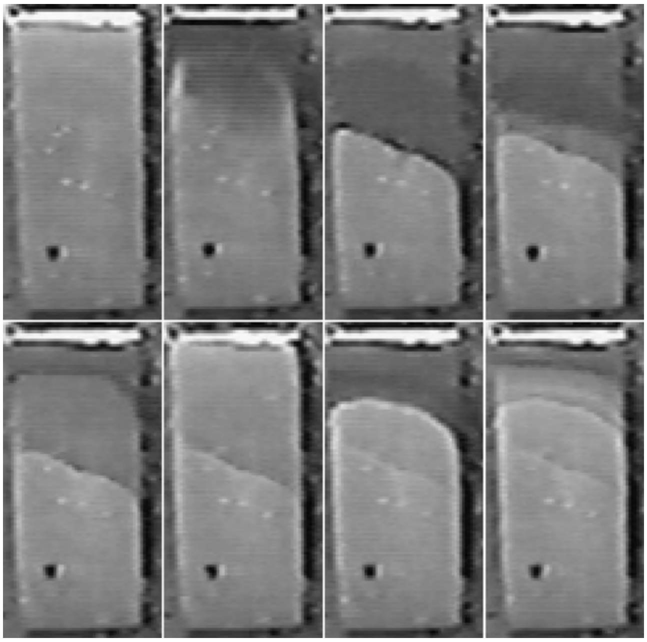

Fig. 8. Oscillatory behaviour during methane oxidation over a nickel capillary catalyst (Ø = 2 mm). The feed rate is 20 ml/min with gases in the ratios CH_4:O_2 = 20:5. Initial temperature is 1073 K [43].

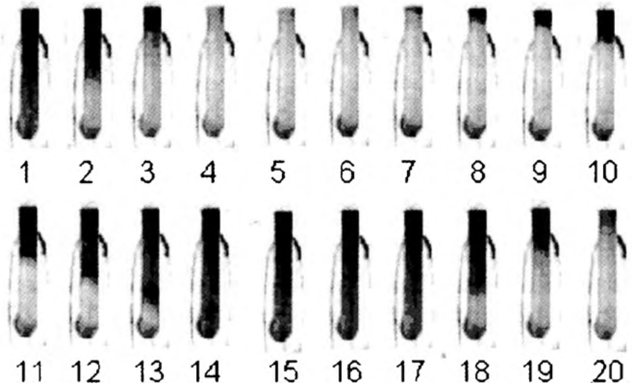

Fig. 9. A sequence of images of a nickel capillary recorded by a video camera during one oscillatory cycle of methane oxidation. Images 1–4 and 17–20 show reduction process while images 7–14 show oxidation. The feed rate is 13 ml/min with gases in the ratios CH_4:O_2 = 20:5. Initial temperature is 1073 K.

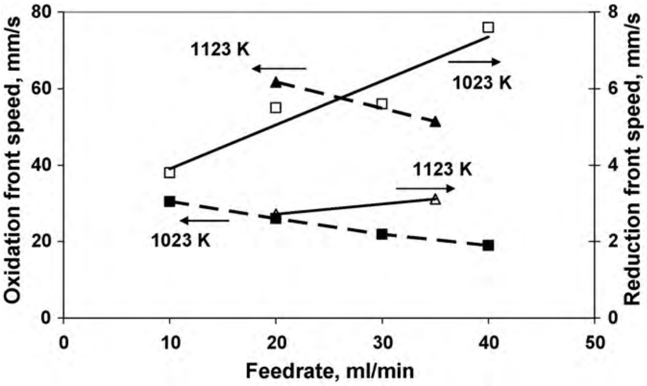

Fig. 10. The speed of oxidation fronts (solid line) and reduction fronts (dotted line) as a function of feed rate at 1023 K and 1123 K in the reaction of methane oxidation over a nickel capillary.

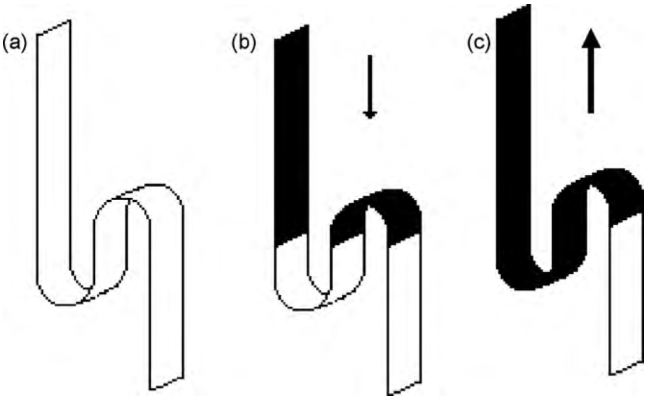

Fig. 11. (a) A schematic view of the bent nickel strip in methane oxidation. A schematic representation of the movement of the boundary between oxidised (black) and reduced (white) surface areas during the process of oxidation (b) and the process of reduction (c) [46].

nickel capillary close to the welded end, to avoid contact with the reactant mixture. Periodic colour changes were accompanied by temperature oscillations and oscillations of all concentrations. Visual observations of the surface revealed that during the oxidation process the temperature and the carbon dioxide concentration increased, while the reduction process was accompanied by a temperature decrease. Maxima in carbon monoxide and hydrogen production rates coincided with the reduced surface [46].

Fig. 9 displays the sequence of nickel capillary images recorded with a video camera during one oscillatory cycle. They demonstrate the movement of the dark boundary from the top to the bottom of the capillary in the direction of the gas flow in the reactor. The oxidation wave represents a transformation from metallic nickel (light colour) to nickel oxide NiO (dark colour) which takes 8 s (images 7–14). The reduction process occurs much more quickly, and so the capillary turns light completely during 0.8–1.1 s (images 1–4 and 17–20). In contrast to the oxidation process, the reduction of the oxidised nickel always starts at the bottom of the capillary. Here the gas phase oxygen concentration in a methane rich mixture is lowest due to a gradient of oxygen in the direction of the gas flow in the reactor. Movies demonstrating the periodic movement of oxidation and reduction waves can again be viewed via the Internet [47].

The way in which the speeds of the oxidation and reduction fronts depended on the feed rates was examined at various temperatures. It was found that the velocity of the reduction front exceeded that of the oxidation front. Moreover, as shown in Fig. 10, the velocity of the reduction front increased with temperature, while a decrease of the velocity of the oxidation front was observed at higher temperatures. To understand the origin of these differences in the temperature dependencies, methane oxidation has been studied over a sample manufactured from a bent nickel strip (see Fig. 11a). Fig. 11b and c presents schematic representations of the propagation of the boundary between oxidised and reduced surface areas during the processes of oxidation and reduction. It can be seen that the wave of the oxidation phase (dark surface area) moves strongly from the top to the bottom, in the direction of the gas flow. In contrast, the reduction of the oxidised nickel starts at the bottom of the strip and the reduced zone moves along the strip surface. These results demonstrate that the oxidation process is controlled by the gas phase composition, while reduction is mainly controlled by surface reactivity. The surface reactions become faster as the temperature increases and the speed of the reduction front also increases. By contrast, the nickel catalyst becomes more fully oxidised at higher temperatures but the speed of movement of the oxidation front decreases as the temperature increases.

5. Conclusions

The aim of this paper was to demonstrate that the study of the oscillatory behaviour in heterogeneous catalytic systems can reveal much more useful information in comparison with steady state kinetic measurements. The key points of the above discussion can be summarized as follows:

(1) The analysis of the character and the waveform of oscillations (regular periodic, quasiperiodic, self-similar mixed-mode and chaotic time series) can help to identify the strength of coupling of local oscillators on the various levels of a heterogeneous catalytic system. The most informative is the analysis of the chaotic oscillations. The value of the embedding dimension of a strange attractor can indicate the level on which deterministic chaos originates.
(2) In case of an oxidation–reduction mechanism the analysis of the waveform of the regular oscillations may give "in situ" information concerning the state of the catalyst.
(3) The observation of a phase shift between oscillations of the concentrations of the different reaction products indicates that the mechanism of oscillations is rather complicated and more than one feedback mechanisms operates in the system causing such an unusual dynamic behaviour. It may be the result of lateral interactions in the adlayer (as in the case of $NO + H_2$ reaction on Rh(1 1 1)-like surfaces) or carbon dissolution-removal (during methane oxidation over Pd catalysts).
(4) Visual observations of the colour of a catalyst surface together with simultaneous measurements of gas phase concentrations during spatiotemporal behaviour can provide important information about the correlation of the state of the catalyst surface with the activity and the selectivity of an oscillating reaction. In the case of methane oxidation over Co catalysts it was possible to follow the change of the activity and the selectivity during the cyclic variation of the Co valence (Co^0(bright colour) → CoO(black colour) → Co_3O_4(grey colour)).
(5) The analysis of the speeds of the oxidation and reduction fronts during methane oxidation over a Ni catalyst provided information about oxidation and reduction processes of the catalyst. It was demonstrated that the oxidation process was controlled by the gas phase composition, while reduction was mainly controlled by surface reactivity.

The examples of oscillatory behaviour for various reactions described in this paper demonstrate how the study of oscillatory behaviour is essential for understanding heterogeneous catalysis. I hope that this manuscript will stimulate many new interesting studies on this topic.

Finally I would like to finish the paper with a wise quotation from Ben Nieuwenhuys: "The mechanisms that cause non-linear behaviour are almost always present, and so in studying cases where they are predominant, the breadth of knowledge of these reactions can be refined" [48].

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