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Dynamics of catalytic reactions and reactors

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Abstract

Heterogeneous catalytic reactions and catalytic reactors are known to exhibit complex dynamic behavior and significant progress has been made, in the past two decades, in understanding this complexity using the tools of nonlinear dynamics and advanced experimental methods. This article presents an overview of complex dynamic behavior in heterogeneous catalysis and points out their intriguing nature along with practical implications. The issues discussed are the source of oscillatory behavior, classification of complex motions, transitions to chaotic solutions and spatiotemporal patterns in reactors of various geometries.

Keywords: Reaction dynamics; Catalytic reactor

1. Introduction

Nonlinear dynamics is currently one of the fastest growing scientific fields. Progress in this field allows us to classify, understand and sometimes predict complex temporal and spatiotemporal patterns. This field also has changed our perception of order and disorder. Heterogeneous catalytic reactions and catalytic reactors are known to exhibit complex dynamic behavior and significant progress has been made, in the past two decades, in understanding this complexity using the tools of nonlinear dynamics and advanced experimental methods. There is a growing class of oscillatory reactions and elucidating their mechanism has been a subject of intensive research (see Refs. [7,14–17,34,39,40,45]). While order in temporal signals has been associated with a steady or periodic motion and disorder implied random behavior or noise, nonlinear dynamic theory showed that there exists a whole spectrum of intermediate motions in the form of chaotic solutions: these are sustained transient aperiodic motions that can be predicted by a deterministic system (i.e., by a set of ordinary or partial differential equations) as are most models of catalytic systems. Chaotic solutions emerge, upon changing a parameter, from periodic solutions and the two can be lumped together as oscillatory behaviors. Characterizing the motion in catalytic systems is further complicated by the distributed nature of such systems: the catalyst state (temperature, adsorbate concentration) is not always homogeneous and may vary across the catalyst (wire, disk, foil or a bed). When that happens we may find complex spatiotemporal patterns on the surface [43].

This article tries to present an overview of complex dynamic behavior in heterogeneous catalytic reactions and catalytic reactors, and to point out their intriguing nature along with practical implications. This work does not intend to review the published literature in

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this field (the relevant reviews are cited), and most of the examples that will be presented are taken from the author's own work; rather, this work tries to bridge the knowledge obtained by various groups, and to assess the importance of this information for practical purposes of catalyst and reactor design. Specifically, we try to bridge the knowledge obtained by low-pressure vs. high-pressure studies, by single-crystal vs. polycrystalline surfaces and between simple geometries like a catalytic wire or pellet and the packed-bed or monolithic reactor. We will resort to qualitative arguments and geometric representation and avoid, as much as possible, the representation in terms of mathematical models.

2. Oscillatory behavior

Intensive research into catalytic oscillations in the last two decades has revealed a fascinating array of phenomena, including chaos and pattern formation, in a large class of oxidation reactions and over many forms of catalyst materials. Oscillatory behavior has been observed during the oxidation of carbon monoxide, hydrogen, ammonia, hydrocarbons, alcohols, ethers and formic acid, as well as during nitrogen-monoxide reduction by ammonia or carbon monoxide and the hydrogenation of carbon monoxide or ethylene (see the foregoing reviews for citations of these oscillators). This line of research is of great academic interest because experimental results conform with basic ideas and theories of nonlinear dynamics that have been emerging since the 1970s. This research may also be of significant commercial importance since the class of oscillatory reactions is of importance in pollution abatement processes (the catalytic convertor or the selective catalytic reduction) and in several partial oxidation processes.

Research into catalytic oscillations have been pursued along two main avenues without much interaction between them. Research at high (atmospheric and above) pressures typically employed polycrystalline catalysts, either in the form of supported catalysts or as foils and wires, in various types of catalytic reactors. This research was aimed at demonstrating the phenomena, mapping its behavior in the temperature-concentration plane and assessing its significance for reactor design purposes. Only limited success was achieved at elucidating the underlying kinetic mechanisms, due to the difficulty in in-situ surface probing under these conditions and masking of kinetics by thermal effects as well as by heat- and mass-transfer resistances. Certain conclusive results have been achieved by surface potential measurements, surface IR-absorption, ellipsometry and X-ray diffraction (see references later). The other avenue of research used surface science methodology to study the surface processes that occur under well-defined conditions using several surface probing techniques like low-energy electron diffraction (LEED) and photoemission electron microscopy (PEEM). Surface science researchers have used high-vacuum conditions (under which thermal and transport effects are negligible) and single-crystal catalysts. This research was very successful in elucidating the kinetics, and several models have been written and tested for well-defined conditions. Still, these results cannot be translated into design models because of the gap in the conditions employed in the two avenues described here. Future research should bridge the gap between the information obtained by these two groups of investigators; the key differences between surface science and catalytic studies are in the range of pressures employed, the catalysts' shape, whether polycrystalline or single crystal, and in thermal effects and the resistances to heat and mass transfer at high pressures.

We now describe the qualitative nature of an oscillatory mechanism. A necessary condition for the occurrence of oscillatory behavior is the existence of an autocatalytic step, where a species inhibits the rate of its reaction or accelerates the rate of its production. Such steps are common to the self-inhibitory exothermic oxidation reactions either due to kinetics, as evident by negative order, or due to thermal acceleration. Such kinetics may produce steady-state multiplicity (also termed bistability). Another necessary condition for periodic behavior is the coupling between two or more variables; this is typically realized by the incorporation of a slow step that leads to catalyst deactivation on the active branch and its activation on the low-activity branch. If the system cannot reach a steady solution on either branch then it will continuously oscillate between these two branches.

Both low- and high-pressure studies suggest that in most systems oscillations are caused by the self-inhibitory nature of catalytic reactions coupled with a slow process that changes the surface activity. Thermal effects are important only at high pressures. Whereas in several low-pressure studies the slow process has been uniquely determined, the nature of this step at high pressures is still debatable. There is a significant evidence suggesting that surface oxidation is a slow process in most high-pressure studies. Surface oxidation is not significant under low pressures due to small oxygen pressures (for an extensive review of the chemistry of catalytic oscillators, see Refs. [39,45]). The rates of oxidation and reduction of the catalyst are of the orders of magnitude lower than the rates of surface reactions (typically 1 s^{-1}), which explains the long oscillation periods and the time-scale separation.

A few techniques are available for surface probing at high pressures: Contact potential difference (CPD) was used by Kurtanjek et al. [20] to monitor oscillations in surface state along with measurements of effluent oxygen concentration during the oxidation of hydrogen over a nickel plate in a continuous-flow reactor. Oscillatory states were observed over a wide range of temperatures (160–400°C) for mixtures containing excess of hydrogen. CPD measurements indicate that the system oscillates between a state in which oxygen is chemisorbed on a reduced surface and an oxidized surface state. Periodic oscillations were observed when either significant mass or heat transfer limitations existed. One such state, presented in Fig. 1(left), shows relaxation oscillations composed of slow motion along the two branches and rapid jumps between them. CPD oscillations were accompanied in this case by relatively large oscillations in oxygen (52–88% of conversion) and in temperature (5°C), assuring synchronization of surface oscillations. Aperiodic oscillations emerged when the transport resistances were small: the aperiodic trace in Fig. 1(right) was obtained under similar operating conditions to those of Fig. 1(left), but under a tenfold increase in flow rates. The fluctuations were rapid, with an almost constant frequency, but the amplitude of both CPD and oxygen concentration changed in similar but irregular fashion. Small surface temperature oscillations with an amplitude of <0.20°C were detected. Oscillations persisted even at large flow rates, indicating that the coupling between transport and chemical rate processes is not the cause of oscillations.

Kinetic oscillations in catalytic CO oxidation on Pt surfaces have been the subject of a large number of studies. Oscillations have been observed with various forms of catalysts over a wide range of conditions [7,8,16,39]. The mechanism of oscillations at low pressures ($p < 10^{-3}$ mbar), under isothermal conditions on single-crystal surfaces, has undoubtedly been identified as a reconstruction mechanism. A number of observations suggest that even on Pt single-crystal surfaces at low pressures, the reconstruction mechanism is not the only factor controlling oscillatory behavior. According to the reconstruction mechanism no oscillations should occur on Pt(111) but already the

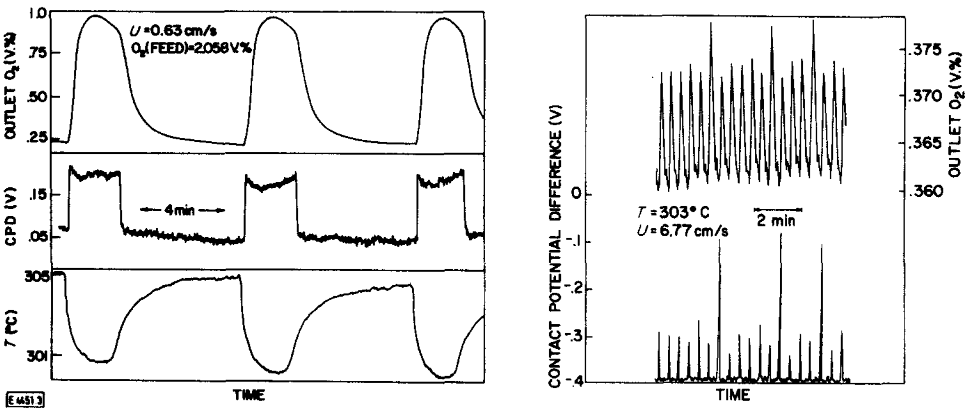

Fig. 1. (Left) Periodic and (Right) aperiodic behavior observed during hydrogen oxidation on a Ni plate under similar operating conditions and different flow rates [20].

first study by Ertl et al. [6] showed that oscillations can occur at 10^{-4} mbar on a Pt(111) surface with a large defect concentration. High-pressure experiments at 1 atm by Yeates et al. [49] demonstrated that under these conditions oscillatory behavior can be found with flat and stepped Pt(111) single-crystal surfaces. Studies with open Pt surfaces such as Pt(110) and high-index planes of Pt demonstrated that a reaction-induced faceting may occur and that the faceting can be associated with the formation of a more tightly bound oxygen species [9,18]. Experiments by Vishnevskii and Savachenko [47] conducted with a Pt(110) surface at 10^{-4} mbar showed that extended exposure of the surface to oscillatory conditions leads to the formation of an oxide species characterized by XPS. Recent investigations with photoemission electron microscopy of catalytic CO oxidation on Pt(100) and Pt(110) revealed that a subsurface oxygen species may result, being characterized by a strong lowering of the work function [22,35].

The mechanism of oscillations at higher pressures remains unsolved but oxide formation, during CO oxidation on Pt, was inferred from the in-situ IR study [27] and from solid electrolyte potentiometry experiments [46]. Recently, Hartmann et al. [13] using in-situ X-ray, showed that silica-supported Pt-clusters catalyzing CO oxidation underwent reversible oxidation to PtO/Pt_3O_4. The smaller clusters were oxidized more readily. This may explain the observation that the existence of oscillations on supported catalyst depends on the particle size [38].

Another question to be addressed is whether the data from single-crystal studies can be applied to polycrystalline surfaces. While the mechanism and kinetics of CO oxidation on Pt have been determined at low pressure for several crystal planes, these results cannot be averaged over a polycrystalline catalyst, even if the distribution of planes is known. This is due to the interaction between planes: while certain planes do not support oscillatory behavior, they may be excitable and may be driven by other oscillatory planes [10]. Also, the surface rearranges over a slow time scale so that crystal-planes distribution varies, usually in favor of certain planes that are more stable. Furthermore, supported polycrystalline catalysts include a large number of small crystallites (of size 50–500 Å or typically 20–200 atoms). Many of the reactions found to be oscillatory are also structure sensitive, i.e., their specific reaction rate varies with crystallite size, probably due to edge and corner effects.

3. Aperiodic behavior

Oscillatory behavior at high-pressure catalytic systems is typically complex and aperiodic rather than simple and periodic like the one shown in Fig. 1(a). Typical complex patterns include multipeak periodic motions, quasiperiodic behavior which are bound by a periodic envelope, chaotic aperiodic solutions and highly random behavior. Models of 'higher degree of complexity' require a larger number of variables for their description and random processes require, strictly speaking, an infinite number of such variables.

Research into aperiodic solutions addressed the following issues:

3.1. *The source of aperiodic behavior*

Complex behaviors require at least three dynamic variables for their predictions (i.e., three ordinary differential equations) and a large number of models that can admit chaotic solutions have been suggested in the literature. Most of them incorporate complex kinetics, or the interaction of autocatalytic kinetics and thermal effects. Catalytic chaos is mathematically no different from chaos in any other open dynamic system, but there are several features which uniquely characterize catalytic systems:

3.1.1. *Spatial distribution*

Almost all catalytic systems are distributed in space. Chaos can emerge in distributed two-variable systems due to insufficient coupling. There is a growing evidence that this is the case in many catalytic systems. The verification of this conjecture requires direct distributed probing of the surface, a task that is still too complex in most systems. The foregoing discussion on periodic patterns emphasized the role of synchronization and communication on the oscillatory patterns, and this issue is addressed further on.

3.1.2. *Nonuniform properties*

Many catalytic systems are nonuniform in their activity. A distributed and nonuniform system is

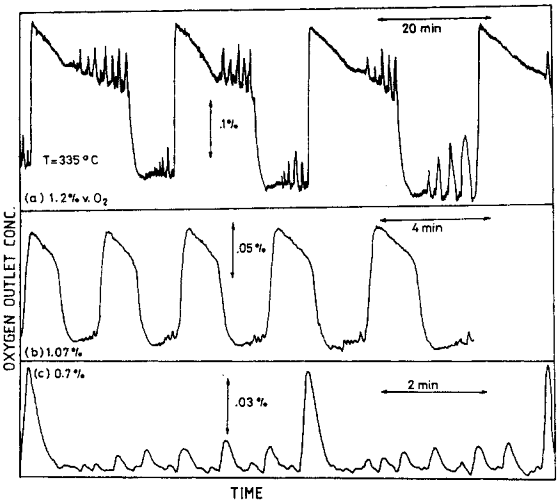

Fig. 2. Complex behavior observed during hydrogen oxidation on a Ni plate at three different inlet oxygen concentrations [20].

similar to the interaction of many different oscillators, a situation that is known to induce complex behavior.

Spatial distribution and nonuniform properties increase the complexity of behavior, so that chaos can be produced even with a simple (two-variables) kinetic model. There is no systematic methodology to reconstruct models that account for complex behavior, and there is no test that discriminates between chaos due to kinetics or spatial distribution.

3.2. *Characterization of the motion*

While multipeak periodic motion can be identified by simple inspection, the discrimination between the other three types of motions is more involved and require special tools. Complex motions can sometimes be described as a combination of other motions, in a way that aids the modeling of this behavior. Fig. 2 presents three time traces of oxygen outlet concentration that were recorded during hydrogen oxidation on Ni [20]. The upper trace (1.2% in feed) resembles superposition of high-frequency oscillations on long-period relaxation oscillations. As already stated, relaxation oscillations require wide separation of time scales, and this trace, therefore, suggests the existence of three widely different time scales. The superimposed oscillations vanish at 1% in feed and the trace is quite periodic. The lower trace (0.7% in feed) exhibits a mixture of high-amplitude low-frequency oscillations with low-amplitude high-frequency behavior.

Another way to characterize the motion is to determine the minimal number of variables that are necessary to describe the motion. At least three variables are required to describe chaotic motion, and a higher number of variables imply a more complex mechanism or a highly distributed system. This characterization does not identify the source of complexity. The characterization of motion also requires excellent reproducibility. Many catalytic systems are affected by a slow deactivation process that change the nature of oscillations.

3.3. *Transitions (bifurcations) of periodic to aperiodic motions*

There are three major routes for bifurcations to chaos, upon changing a parameter, and all have been observed in catalytic or electrochemical systems.

In the period-doubling transition a single-peak cycle changes into a double-peak (period-doubling), with slightly different amplitude of the two peaks and then again into a four-peak, and the process repeats itself over parameter intervals that become shorter at every doubling, and eventually it ends in a chaotic solution. This transition was observed during anodic dissolution of a Ni foil in sulfuric acid [24] under galvanostatic (constant total current) conditions. Fig. 3 presents the time traces and the reconstructed phase plane (see explanation in the following) of (a) the single-peak, (b) double-peak, (c) four-peak and (d) chaotic oscillations for four successive currents. The identification of the period-doubling scenario is evident from the time traces or from the phase-plane trajectories. Since we typically measure only one signal ($x(t)$, the potential in this case), and cannot plot the trajectory in the space of state variables (phase space), it is customary to plot a time-delayed phase plane by plotting $x(t)$ vs. $x(t+\tau)$, where τ is a certain time delay (this is similar to plotting $x(t)$ vs. its derivative, dx/dt, while avoiding the noise of numerical derivation). This phase plane will exhibit the qualitative nature of the original trajectory in the phase plane: a simple oscillatory state will exhibit a closed loop (Fig. 3a), an n-peak cycle will be translated into n

loops (Fig. 3b,c) while a chaotic state will fill the plane (Fig. 3d). The latter state indicates that a higher dimension space is required for its description. The dimension of the trajectory can be reduced by recording the x value at the Nth intersection of the trajectory with a certain arbitrary plane (this is referred as a Poincare section, denoted by $x(N)$). This procedure is similar to recording the x value at the Nth peak. Plotting now $x(N{+}1)$ vs. $x(N)$ may yield a simple curve with a single maxima (Fig. 4). The intersection of this curve with the diagonal, $x(N+1) = x(N)$, is a simple periodic solution in which all successive peaks are identical. But the construction of the sequence of $x(1)$, $x(2)$,..., $x(N)$, starting from any $x(0)$, does not converge to this solution but rather exhibits a chaotic sequence (see inset in Fig. 4). The parabolic nature of the return map corresponds to one of the most studied model of chaotic solution. The logistic map, $x(N+1) = 4bx(N)(1 - x(N))$, is a difference rather than a differential equation, which exhibits many of

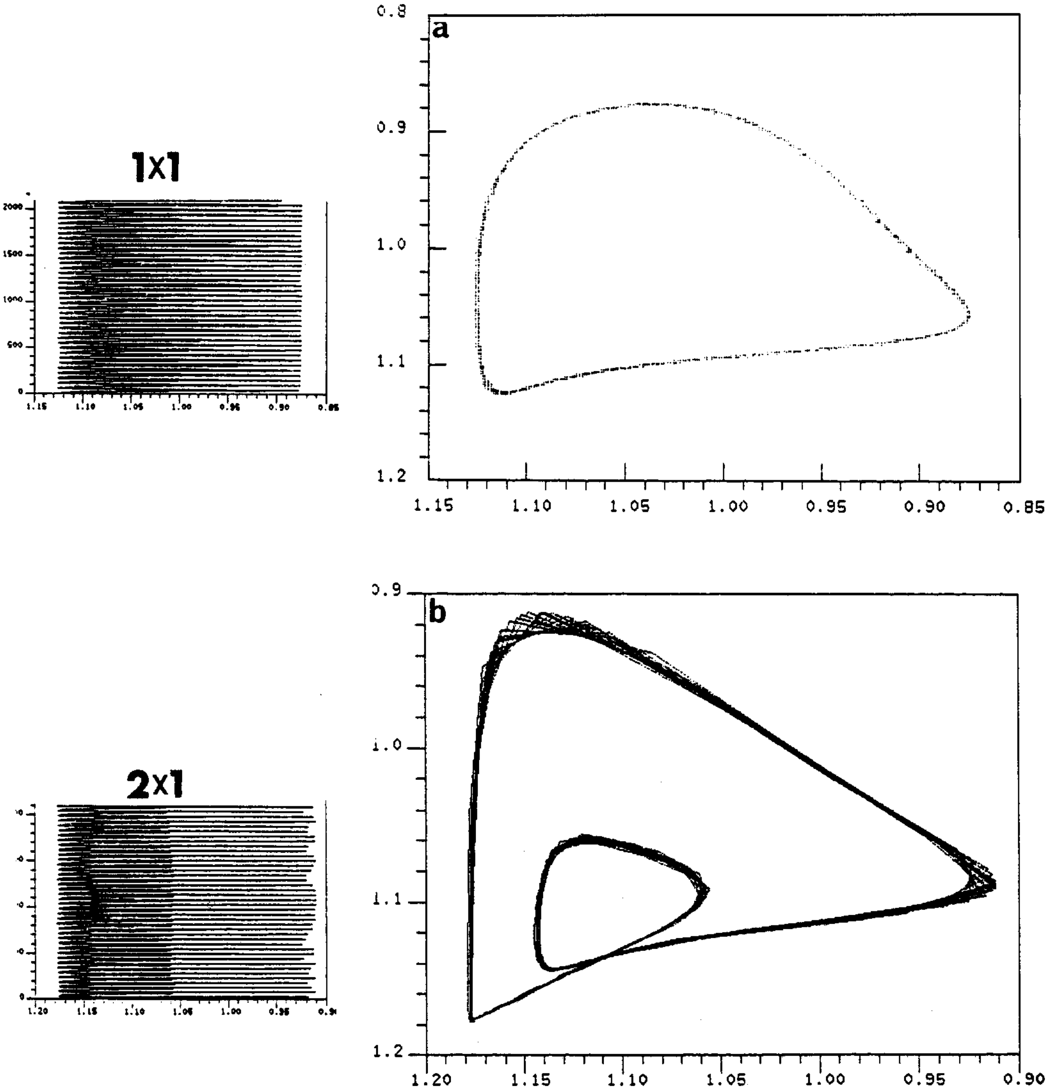

Fig. 3. Period doubling transition to chaos, observed during anodic dissolution of Ni, at four different currents. The small diagrams are the potential–time traces (ordinate is time) while the large ones are the time-delayed phase planes [23].

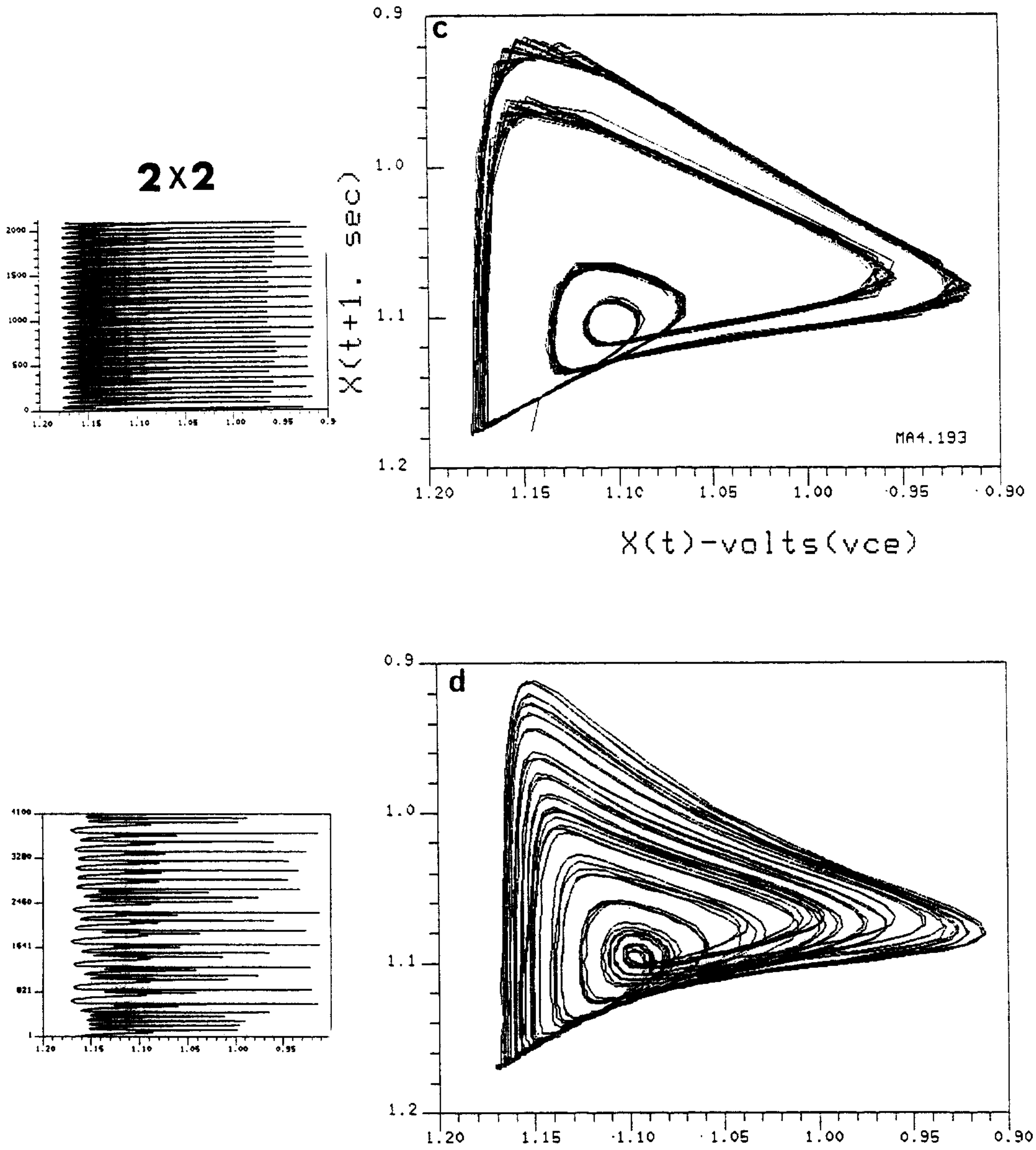

Fig. 3. (*Continued*).

the properties simulated for period-doubling transitions in differential equations.

Period-doubling was observed also during ammonia oxidation on a 7 cm long Pt wire, exposed to 1.0% oxygen and a similar concentration of ammonia diluted in nitrogen, and controlled to maintain an average preset temperature (160°C). Oscillations in this system were observed around the stoichiometric ratio of the reactants. A sequence of period-one, -two and -four states is shown in Fig. 5 (denoted as AM 95-93; [41]) but the adjacent chaos is missing. As the ammonia concentration is increased further the system exhibits period-five and period-two solutions before exhibiting aperiodic behavior (AM 90). Note that the oscillations base-line varies slowly in this catalytic system, and the phase-plane trajectories are not as

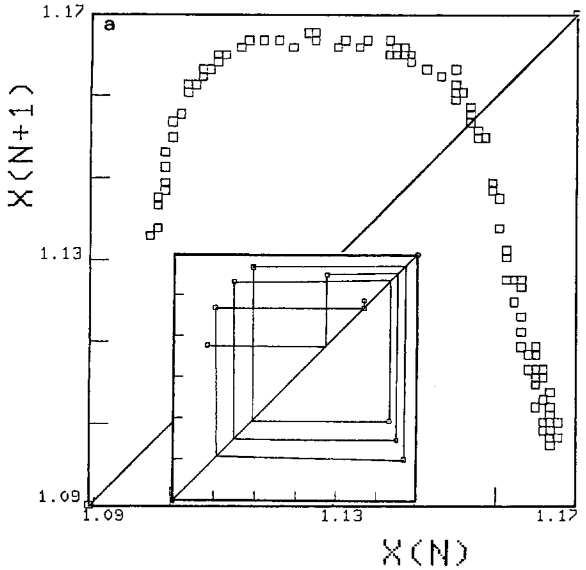

Fig. 4. Poincare return map (a) of the time-delayed chaotic phase plane in Fig. 3(d); inset shows the schematic diagram for construction of 10 steps on the return map [24].

sharp as in the electrochemical system. Note also that both systems are wires or foils subject to a certain control condition (constant average temperature or current).

In the second scenario, a simple cycle changes into an aperiodic one with an oscillatory amplitude (quasiperiodic) and then breaks into a chaotic state. A quasi-periodic trajectory forms a torus in the phase space. A Poincare cross section or a sequence of peaks will then exhibit a simple loop. This transition was also observed during anodic Ni dissolution of Ni, as well as in other oscillatory systems.

Intermittency is characterized by bursts of aperiodic oscillations separating (almost) periodic phases. One such state is shown in Fig. 6(g), as part of a sequence of states observed, with decreasing oxygen concentration, during ammonia oxidation on a Pt wire controlled to sustain an (average) temperature of 160°C. The oscillations are of the relaxation type, and are simply periodic only near the boundaries. A Poincare section or peak-sequence of an intermittent state forms a line that is almost tangent to the diagonal (Fig. 6, lower part); in that domain $x(N+1)$ is close to $x(N)$, resulting in long periodic phases, but eventually the trajectory escapes that region before being reinjected to this area again.

4. Spatiotemporal patterns

While the interaction of diffusion and nonlinear reaction is known to induce a plethora of spatiotemporal patterns, the observations of such patterns in heterogeneous reactors are still rare at high pressures, and their identification in many cases is ambiguous due to experimental difficulties and nonuniformity of the system properties. The study of spatial structures in heterogeneous reactors is a practical problem which should affect design and operation procedures of commercial reactors like the catalytic convertor. The convertor, as well as other pollution-abatement processes, employ noble-metal catalysts in order to oxidize carbon monoxide and hydrocarbons and to reduce NO to harmless products.

While pattern formation in liquid-phase reactions has been studied intensively, heterogeneous reactors admit several unique features:

1. The interaction of the fluid phase, through which the reactants are supplied by convection, and the reactive solid phase may produce patterns due to self-imposed gradients in the fluid phase.
2. The distribution of reaction sites in catalytic reactors is discrete: a catalytic site, a crystallite, a pore, a pellet and a reactor. Each of these levels of organizations may be assumed to be spatially homogeneous while patterns appear only on a larger scale. The dependence of the global dynamic behavior on the nature of the local dynamics (i.e., phase plane) repeats itself on various scales: If each crystallite (or pellet) can exhibit bistability or oscillatory behavior how many solutions and what patterns are possible for the pellet (or reactor)? Apparently, intercrystallite communication must exists as otherwise the system will exhibit time-independent average of the randomly-phased oscillators. Such communication may proceed by heat transfer through the support, by diffusion through the gas phase as well as through their support (spillover).
3. Nonuniformity of properties, like catalyst loading and transport coefficients, are common to catalytic systems.

We present here a short review of observations and models of spatiotemporal patterns, organized according to the reactor geometry: a catalytic wire or ribbon;

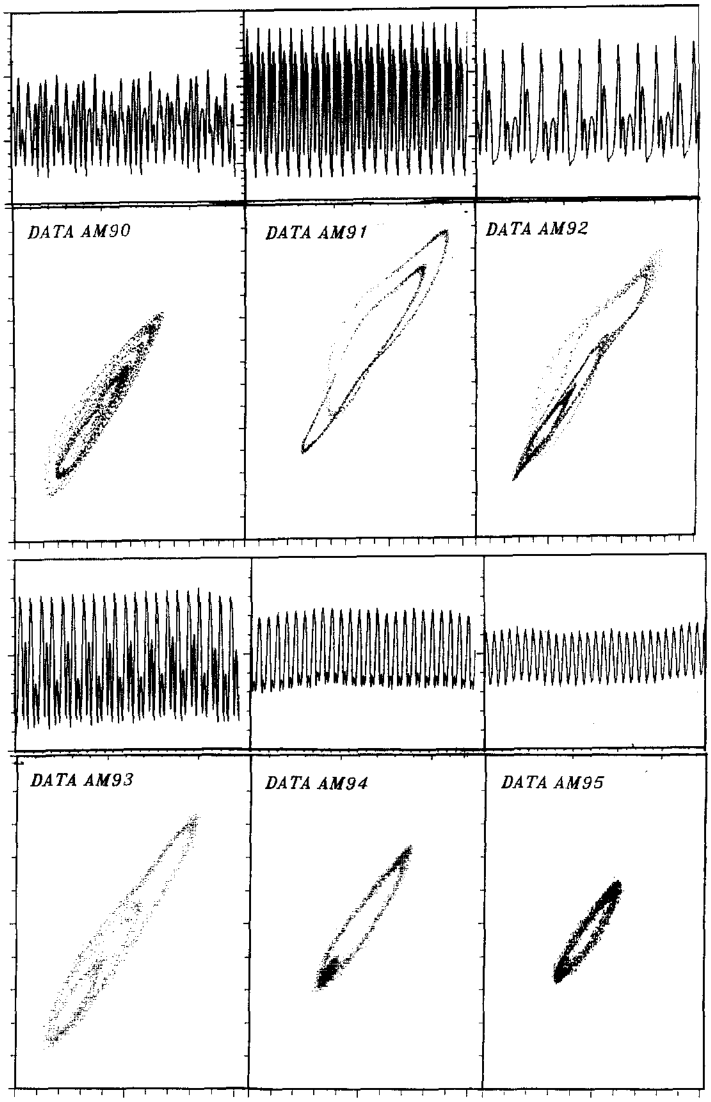

Fig. 5. A sequence of states (time-traces of reaction rate and time-delayed phase planes) observed during ammonia oxidation on a Pt wire, exposed to 1.0% oxygen and 1–1.5% ammonia in nitrogen and controlled to maintain an average preset temperature (160°C). A sequence of period-one, two and four states is shown in AM 95-93 but the system exhibits period-five and period-two solutions before exhibiting aperiodic behavior (AM 90) [41].

a disk or foil; a distributed catalyst within a CSTR; and a packed bed (see Ref. [43] for a detailed survey). The catalytic wire, foil or surface is a reaction–diffusion system exposed to uniform gas-phase conditions. Understanding the patterns in these simple systems is crucial for predicting the behavior of a fixed-bed reactor. We consider two classes of interesting kinetics – either single-variable models that admit multiple solutions, due to thermal effects or self-inhibition, or two-variable models that may admit oscillations, excitability or bistability. Oscillations in high-pressure reactions are due to autocatalytic thermal effects, autoinhibition by a reactant and slow reversible changes of nondiffusing catalytic activity (see Section 2). In such a model the thermal-conduction range is larger than the diffusion scale of any surface species. The expected behavior in such systems, with a long-range autocatalytic variable, is typically homogeneous

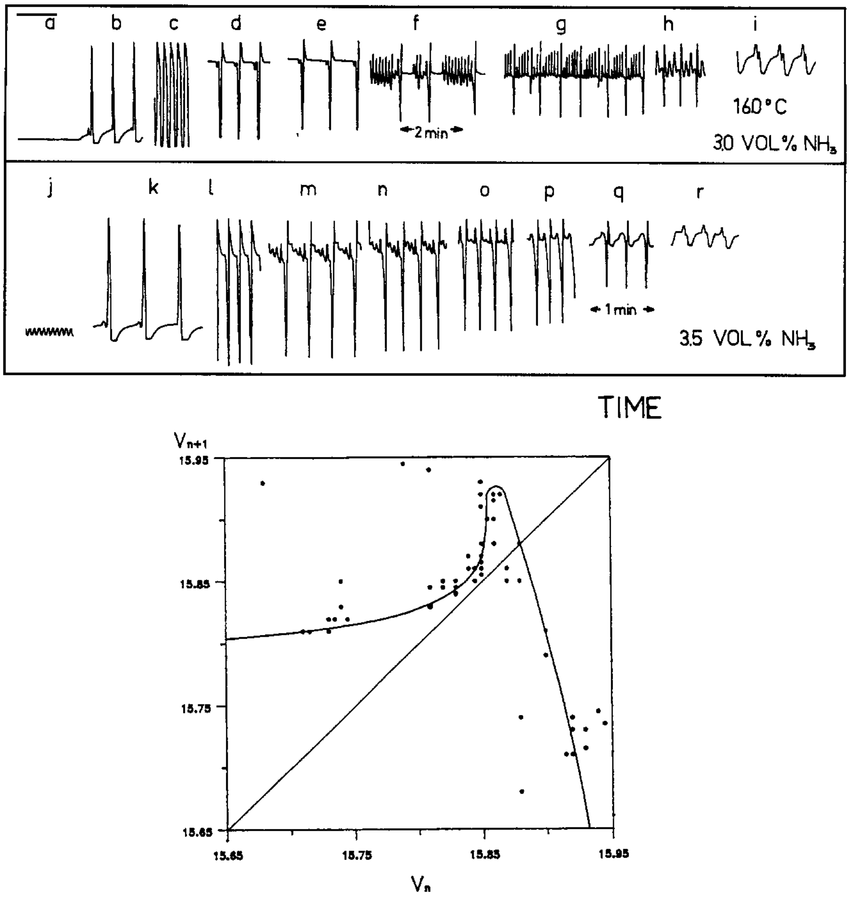

Fig. 6. Traces of states obtained from left to right with decreasing oxygen concentration during ammonia oxidation on a controlled Pt wire. The lower part presents the next-peak return map of state (g), showing evidence of intermittency [41].

(space independent); inhomogeneities may appear as transient features as in an excitable medium, in which if a traveling pulse, if formed, will be propagated out of the system. In the absence of control or global interaction the system eventually attains a uniform state. This mechanism is contrary to most mathematical models of pattern formation that, following Turing's classical analysis, incorporates a localized autocatalytic variable (activator) and a far-reaching inhibitor. Global interaction, due to external control or a mixed phase in a CSTR, may generate novel sustained patterns. The patterns in a packed-bed are due to self-imposed gradients in fluid properties.

We restrict our interest to patterns that emerge at high pressures. A magnificent array of patterns was observed at low pressures and several excellent reviews were published. High-pressure patterns typically show fronts that are 1 mm in order of magnitude, and long-scale features that are several centimeters in size, as compared with the 50μ patterns observed at low pressures. Strong thermal effects are likely to destroy patterns that are finer than a few millimeters in order of magnitude. Heat- and mass-transfer resistances will also naturally affect the domain of oscillatory behavior and may introduce new dynamic features.

4.1. *Catalytic wires*

If every point on a catalytic wire or ribbon, exposed to a stream of reactants, can exhibit two stable steady states then fronts separating domains with different states may be established by proper initial conditions. Uncontrolled systems will exhibit moving fronts in which the ignited or extinguished state expands and conquers the system; stationary fronts are not generic in such systems and they exist only as the boundary between domains with expanding upper state or with expanding lower state. Barelko et al. [1] measured the front velocity separating the ignited and extinguished state of a resistively heated (with a constant current) Pt wire catalyzing ammonia oxidation. Unlike the prediction of the single-variable model they found an intermediate domain (rather than a point) where structurally stable stationary fronts exist, i.e., the front could be placed at almost any position. Recently, Philippou et al. [32] performed this experiment on a Pt ribbon using IR-thermography, and showed that in the intermediate regime the front was not stationary, but moved at a very small velocity.

Structurally stable stationary fronts may exist in one-variable systems due to nonuniformity of properties, due to heat flux at the boundaries or due to global interaction, in which every point interacts with all other points through a common pool. The simplest example of global interaction is due to a control of a space-averaged property. The thermochemic method, in which the wire resistance (i.e., temperature) is kept constant by applying resistive heating, has been widely applied in studies of catalytic kinetics and dynamics over metal wires in order to keep the system isothermal. Analysis of such control showed, however, that it cannot stabilize a thermally-unstable state in sufficiently long systems. Instead, the wire prefers to attain an inhomogeneous solution with a stable front separating the ignited and extinguished states. The solution in a long system takes the form of a stationary front, at a position that satisfies the setpoint and with a control variable that satisfies the condition of stationariness of the front. The existence of stationary fronts in a catalytic ribbon maintained at a preset average temperature was verified by Lobban et al. [26] during ammonia oxidation on a Pt ribbon. Similar patterns were obtained under constant voltage control. Another source of global coupling is interaction of the catalyst through a mixed gas phase (see later).

Oscillatory kinetics will induce oscillatory patterns in distributed systems. A regular oscillatory pattern, in the form of two temperature pulses emanating in opposite directions from a source point, was presented by Cordonier and Schmidt [4] during ammonia oxidation on a Pt wire heated by a constant current. Spatiotemporal complexity was shown to be induced by the formation of the two pacemakers. Antiphase periodic oscillations, in which two sections of a wire oscillate out of phase, were observed by Cordonier et al. [3] during the endothermal methylamine decomposition catalyzed by a 5 cm long Rh wire; with Pt or Ir wires all measured points were oscillating synchronously with no measurable time lag.

As in the case of bistable kinetics, global interaction may induce inhomogeneous patterns with oscillatory kinetics. Philippou et al. [31], using IR-thermography, observed temperature pulses moving back-and-forth, during propylene oxidation in a 14.5 cm long Pt ribbon heated resistively under constant resistance mode of operation (i.e., a system controlled to obey a preset average temperature). The space-averaged reaction rate oscillated at a higher frequency than that of local temperatures. Analysis of time series revealed quasi-periodic oscillations when a single pulse motion was observed and chaotic dynamics when a second pulse was formed. Analysis of catalytic wire or ribbon subject to a fast-responding integral constraint, due either to control or to interaction with a mixed fluid phase, revealed the plethora of patterns described later [28–30,41]. Now, control serves as an inhibitor that either arrests a moving front or creates new pulses. The patterns are presented in Fig. 7 in the plane of time (ordinate) vs. space where dark or light colors denote low or high temperatures. The emerging patterns include stationary fronts (Fig. 7a), oscillatory fronts (Fig. 7b) or pulses that fluctuate around a certain position and antiphase oscillations in which several sections of the wire oscillate out of phase (Fig. 7c). Moving patterns include:

- unidirectional pulses that are born at one edge, travel towards the other edge and disappear while a new one is born at the original edge (Fig. 7d);
- source point from which two pulses emanate and move in opposite directions until their disappearance (Fig. 7e); and
- pulses that move back-and-forth (Fig. 7f).

Antiphase oscillations of spatial current distribution were also observed during anodic dissolution of a nickel wire in sulfuric acid solution operating in the galvanostatic mode of control (Fig. 8). In this

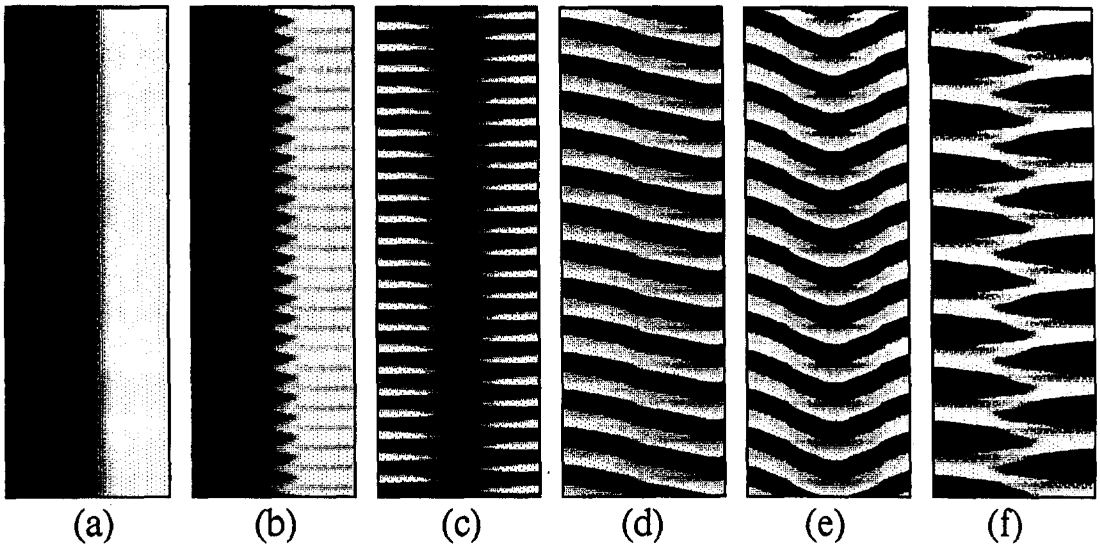

Fig. 7. Spatiotemporal patterns simulated for controlled catalytic wires with oscillatory kinetics showing (a) stationary or (b) oscillatory fronts, (c) antiphase oscillations, (d) unidirectional pulse, (e) source point and (f) back-and-forth pulses [29]; patterns were computed with a cubic kinetic function but similar patterns were obtained for realistic models [28]. Patterns are presented in the time-space plane with gray and light shades corresponding to extinguished and ignited local states, respectively.

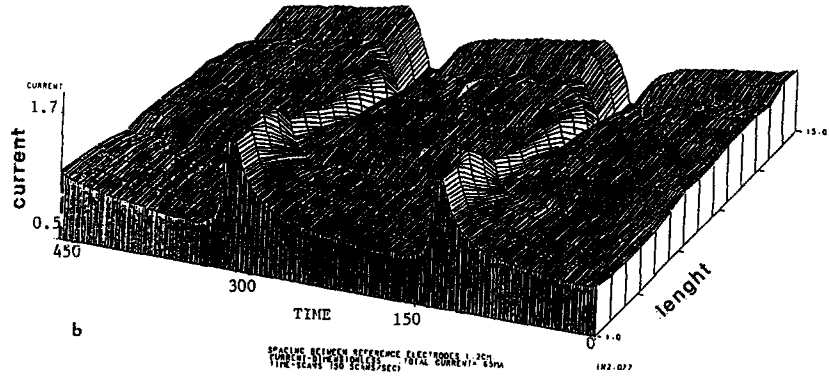

Fig. 8. Antiphase current oscillations, observed during anodic Ni dissolution operating in the constant current mode [24,25], showing the dependence of local current on time and position.

mode the applied overall current remains constant, but the local current density (i.e., reaction rate) varies. Traveling pulses were observed under almost potentiostatic (i.e., with a small resistor in series) conditions. A model was constructed in order to simulate these behaviors and to demonstrate the relation between pattern established and the applied control [12].

4.2. *Mixed reactors*

Global interaction may be imposed on a reactive (catalytic, electrochemical and gel) surface through a continuously fed mixed-fluid phase. Patterns similar to those induced by a constant-resistance control, which is another form of such interaction, may emerge if ignition of one section of the surface inhibits, due to

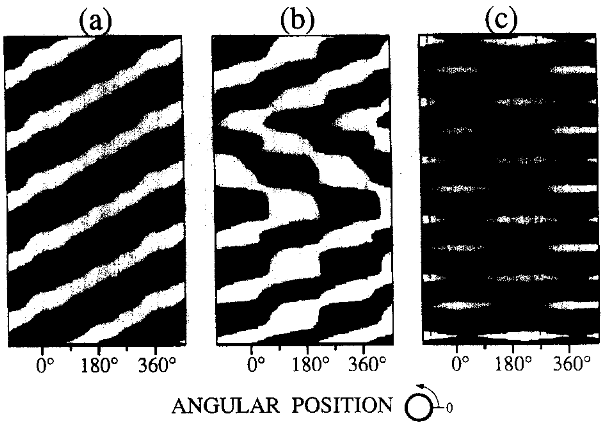

Fig. 9. Temperature patterns, observed during hydrogen oxidation on a Ni ring in an atmospheric pressure mixed reactor, (a) showing rotating, (b) rotating and alternating, and (c) stationary pulses ([11]; patterns are presented in the plane of time vs. angular position, reproduced with permission of the authors).

reactant depletion, the ignition of the remaining surface. Patterns on a wire are similar to those described earlier, while patterns on a catalytic ring [30] include pulses that move at a constant velocity around the ring and moving antiphase oscillations. The motivation for the latter study arises from recent observations of pulse motion during hydrogen oxidation on a nickel ring suspended in a stirred-tank reactor, kept in a constant-temperature oven [21]. The pulses may move continuously around the ring (Fig. 9a), or rotate and reverse direction (Fig. 9b) or may be stationary and undergo antiphase oscillations intercepted by extinct phases (Fig. 9c)

4.3. *Catalytic disks and wafers*

Most patterns observed on two-dimensional catalytic systems did not conform with any known motion of reaction–diffusion systems. Most investigators attribute the ambiguity to nonuniformity of surface properties. Several studies demonstrated the existence of one or more pacing centers that determine the motion of the whole surface. In several cases aperiodic solutions were shown to be associated with two or more such pacing centers. Considerable progress in elucidating and analyzing spatiotemporal temperature patterns was made with the employment of IR-thermography, permitting 0.1 mm resolution at the surface. Yet, the very first application of this method showed significant temperature gradients even when all parts of the catalyst belonged to the same steady-state branches.

Several recent studies used IR-thermography to monitor the surface. Kellow and Wolf [19] observed that active hot zones, on a Rh/SiO_2 surface catalyzing ethylene oxidation, were contracting and expanding. Graham et al. [11] used IR-thermography to monitor thermokinetic oscillations during hydrogen oxidation on 3.8 cm nickel disk. They revealed two pacemakers at the edge of the disk, emitting ignition fronts which conquer the surface within 40 s. After a slow cooling, which was not associated with front motion, new fronts originated at the pacemakers positions. These patterns are different from the target patterns and spiral waves that were encountered in liquid-phase reacting systems, in physiological systems like the heart muscle and eye retina and on a single isothermal platinum crystal catalyzing the low-pressure oxidation of carbon monoxide [17].

4.4. *Fixed-bed reactors*

While catalytic wires, rings and disks are simple one- and two-dimensional model systems that lend themselves to comparison with theory, the working horse of the catalytic process is the fixed bed. We review below experimental observations of front motion and periodic behavior in fixed-bed reactors as well as dynamic behaviors expected in heterogeneous models of such reactors.

Self-sustained dynamic behavior, in the form of successive ignition and extinction fronts propagation, was observed by Puszynski and Hlavacek [33] in a nonadiabatic reactor catalyzing CO oxidation. In the region of global monostability, a hot spot emerged at the reactor inlet, propagated toward the outlet at an average velocity of 10^{-4} m s^{-1}, and died out as another hot spot was born at the inlet. Similar behavior was observed with the same reaction in an adiabatic fixed bed [48]. A hot zone emerged at the reactor inlet and moved downstream. A single catalyst pellet, subject to the inlet ambient conditions, was shown to exhibit small-amplitude thermokinetic oscillations. Sheintuch and Adjaye [42] observed wave motion in response to a local perturbation at the inlet of an adiabatic reactor catalyzing C_2H_4 oxidation. Setting

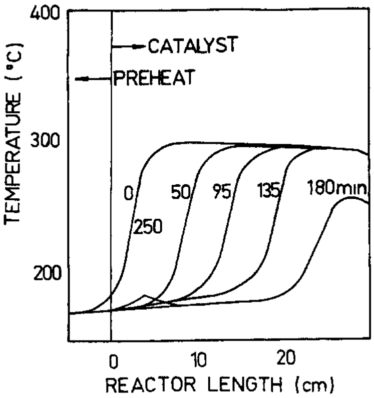

Fig. 10. An excitable wave observed in an adiabatic fixed bed catalyzing ethylene oxidation: perturbation of the upstream section sends a front that travels and exits the reactor while a new front appears at the inlet [42].

a local perturbation at the inlet of a 30 cm long bed packed with Pt/Al_2O_3 catalytic pellets (Fig. 10) induced a front that moved at constant speed and shape. The front always moved downstream until its exit from the reactor. A hot spot appeared then at the inlet; it developed and spread across the reactor and the old steady state was established. This motion was interpreted in terms of wave motions in an excitable medium. Similar behavior was observed by Dvorak et al. [5] during CO oxidation in a bed of supported Pt catalyst.

To study the dynamics of a heterogeneous reactor model, we analyzed several models which account for a local (solid phase) oscillator and a global (gas phase) convective interaction [2,44]. In the absence of convection such kinetics admit a traveling-pulse solution or homogeneous oscillations in a uniform medium.

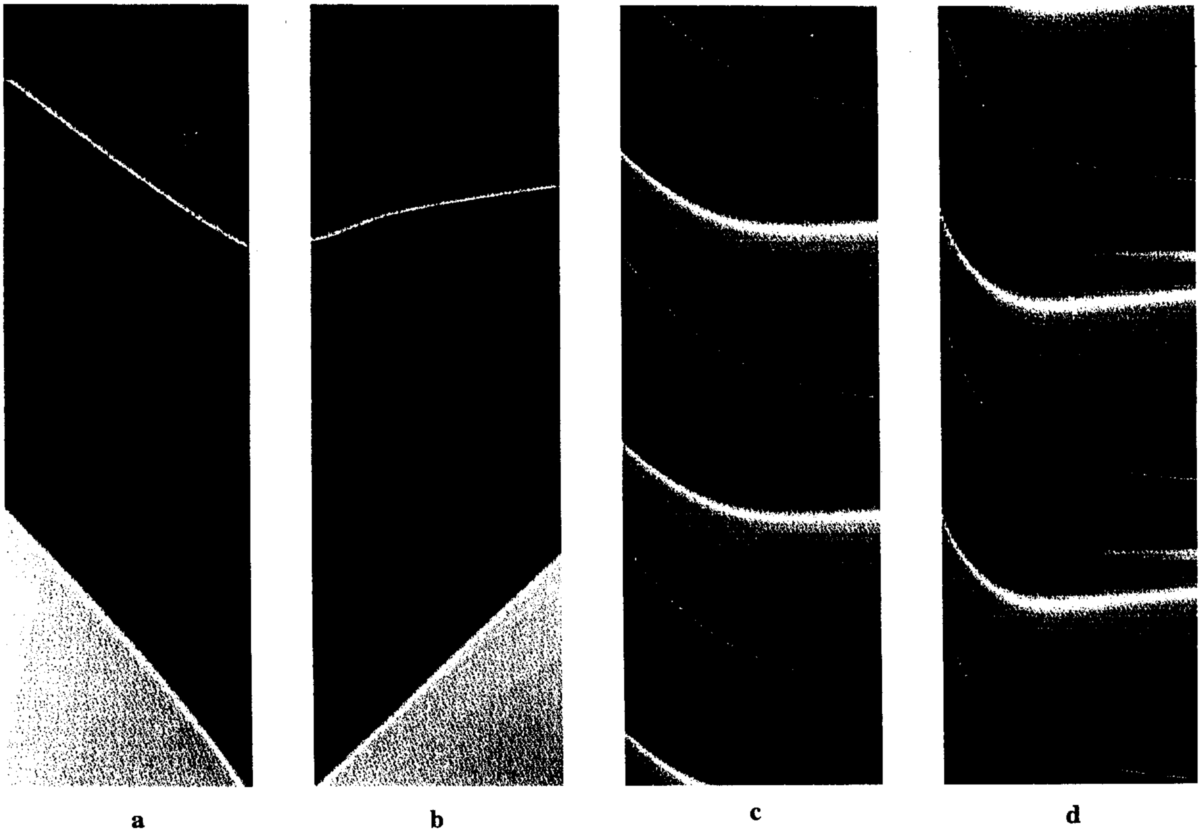

Fig. 11. Spatiotemporal patterns, simulated with an adiabatic fixed-bed reactor model, showing excitable wave motion, after setting a local extinction to the (a) inlet or (b) exit section, and (c) simple or (d) complex periodic patterns [2].

Pattern selection in the bed is determined by the nature of interaction between the phases, by the phase planes spanned by the reactor and the ratio of the two slowest time scales – front residence time and the period of oscillations. The behavior of an adiabatic reactor was analyzed as well as that of an isothermal-fluid reactor in which the fluid temperature is constant but the solid temperature is varying due to reaction. The main difference between adiabatic and isothermal-fluid PFR is that, in the latter convection induces a break in symmetry (in the sense that it favors solutions in which different parts of a reactor belong to different branches of the pseudo-steady state) in positive-order kinetics while in the former convection inhibits asymmetry. The main sustained patterns simulated in an adiabatic bed are:

- Excitable wave motion in response to a local perturbation at the outlet (Fig. 11a) or inlet (Fig. 11b) of the bed, followed by relaxation of the bed in the form of another front. Fig. 11(b) simulates the behavior observed during ethylene oxidation (Fig. 10);
- Almost homogeneous oscillations (horizontal band patterns, not shown);
- Downstream- or upstream-moving pulses (parallel bands), which may be simple (period-one, Fig. 11c) or complex (Fig. 11d).The latter patterns appear when new fronts are generated inside the reactor but they cannot propagate due to refractory trail of the previous pulse. They form multiperiodic or aperiodic sequence of pulses; the understanding of transition between these multiple structures has not been achieved yet; and
- Stationary, oscillatory or sticking fronts.

Other mechanisms of pattern formation in fixed beds were recently suggested by Rovinsky et al. [36,37]. They pointed out that disengagement by differential transport may be accomplished not only by difference in diffusivities of the two variables but by differential flow of these variables as well. They have demonstrated this differential flow induced chemical instability (DIFCI) by analyzing a model with a flowing activator and stagnant inhibitor. Sustained patterns may be realized only when the instability feeds itself by imposing periodic boundary conditions, which are highly unrealistic for fixed beds, or by incorporating a recycle stream. Numerical simulations in a one-dimensional ring-shaped reactor, yielded traveling waves that move in the flow direction [36].

5. Conclusions

I expect that two major issues will dominate the field of catalytic dynamics in the near future:

There will be an attempt to derive detailed and accepted kinetic models for several reactions that are of significant commercial and scientific importance (most notably, CO oxidation on supported Pt catalyst). Such models exist already for low-pressure studies, and the problems of 'scaling up' this information from low- to high-pressures and from single-crystal to polycrystalline surfaces should be resolved. Once such a model will be derived, it will be implemented into existing reactor models, like the catalytic convertor, for analysis and optimization.

Very little work has been done so far in suggesting practical applications of temporal oscillations or of spatiotemporal patterns. From analogy with other processes, specifically natural ones, one would expect that certain advantages can be gained by operating a system under spontaneous periodic conditions. Certain applications of forced periodic behavior, most notably the catalytic reactor with flow reversal, are currently implemented commercially.

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