Chapter 1

Introduction

The spontaneous emergence of ordered structures is ubiquitous in nature. Phenomena of self-organization are encountered in diverse contexts ranging from simple physical and chemical systems to complex biological processes. They include the formation of single organized objects as well as the development of intricate spatiotemporal patterns. Classical examples are coherent structures in hydrodynamic convection [1, 2]. Further well known cases are space-time patterns in chemical reaction-diffusion systems [3, 4], granular media [5, 6], optical systems [7, 8], semiconductors [9], and electrochemical reactions [10]. Also in biological and ecological systems, spatiotemporal self-organization has been studied in great detail [11, 12]. The excitation dynamics of heart tissue [13], the intracellular calcium dynamics [14], and the behavior of populations of microorganisms [15] are prominent examples among many others.

It was only in the second half of the last century that the thermodynamic basis of these phenomena was developed by Prigogine and coworkers [16, 17]. Self-organization occurs in *dissipative systems*, open systems that are maintained far from thermodynamic equilibrium through the continuous dissipation of energy. By the exchange of matter and energy with the environment, such systems are able to export entropy so that ordered patterns can emerge spontaneously. In his work on open nonequilibrium systems, Prigogine coined the general term of *dissipative structures* for these organized patterns, a concept that can be traced back to the work of Schrödinger [18]. A unified

description of self-organization was proposed by Haken [19]. He established *synergetics* as an interdisciplinary approach to understand the emergence of order in systems of entirely different origin by stressing basic similarities in their dynamical behavior.

The dynamics of dissipative systems is generally governed by nonlinear differential equations. Understanding of spatiotemporal pattern formation is thus closely related to progress in the study of *nonlinear dynamics* [20–22]. Going back to the work of Poincaré in the late 19th century [23], nonlinear dynamics became a field of intensely growing research activity ever since the groundbreaking discovery of deterministic chaos by Lorenz in the early 1960s [24]. In a simple model of three ordinary differential equations, he found irregular aperiodic behavior that shows a sensitive dependence on initial conditions resulting in a long-term unpredictability of the dynamics.

In many systems, the formation of spatiotemporal patterns can be understood as the cooperative action of a large number of individual system elements. The overall dynamics then emerges as a result of the local dynamics of these subunits and a coupling mechanism to establish communication between them [25]. Prominent examples are *reaction-diffusion systems*, where local nonlinear behavior is combined with diffusive coupling. Systems as diverse as gas discharge devices [26], slime mold colonies [27], or semiconductors [28] can be described by reaction-diffusion type equations. Such systems are known to exhibit a rich variety of space-time structures like target patterns, rotating spiral waves, or spatiotemporal chaos. In the prototypical case of chemical reaction-diffusion systems, complex spatiotemporal behavior is induced by the interplay of nonlinear kinetics and diffusive transport of reacting species. In his pioneering paper of 1952, Turing conjectured that morphogenesis can be explained on the basis of chemical reaction-diffusion processes [29]. The structures he predicted were indeed observed in chemical systems [30] and evidence was found that the development of animal skin patterns follows the mechanism proposed by Turing [31].

The most thoroughly studied chemical reaction-diffusion system is the Belousov-Zhabotinsky (BZ) reaction that became paradigmatic for nonlinear kinetics and pattern formation in chemical systems [4]. The BZ reaction takes place in aqueous phase and is homogeneously catalyzed by metal ions. It involves several reaction steps and many intermediate species, the principle step being the catalytic oxidation of malonic acid

by bromate. The first observations of kinetic oscillations in a continuously stirred BZ medium were reported by Belousov in 1951 (see Refs. [32, 33] for a history of the BZ reaction). Since the early 1970s, when the first traveling wave patterns were reported by Zhabotinsky [34] and Winfree [35], the BZ reaction has been intensively investigated and became a model system for self-organization in chemical reactions and for the study of pattern formation in general. Substantial improvement was achieved by introducing continuously fed open gel reactors [36] to prevent convective motion of the solution and to ensure sustained operation far from thermodynamic equilibrium. Furthermore, a light-sensitive variant of the BZ reaction [37] allows global and local manipulation of the dynamics by illumination of the medium, see *e.g.* Refs. [38–40]. Considerable progress has been made through incorporation of the BZ system into microemulsions (BZ-AOT system) [41, 42]. By tuning the microstructure of the medium, a variety of new space-time patterns could be stabilized [43].

Besides reactions in aqueous phase, where the detailed mechanism is often complex and sometimes not even fully understood, there are a number of simple heterogeneous catalytic reactions where nonlinear kinetics and pattern formation have been investigated [44, 45]. The catalytic oxidation of CO on Pt(110) constitutes the most thoroughly studied reaction of this type. It shows an exceptionally rich variety of spatiotemporal concentration patterns including traveling pulses, standing waves, and target patterns as well as spiral waves and chemical turbulence [46]. Since pattern formation takes place at the catalyst surface, it is a genuinely two-dimensional system. The mechanism of CO oxidation on Pt(110) is well known [47] and a simple realistic model has been developed that accounts for most of the dynamic features of this reaction [48, 49]. Apart from the BZ reaction, the catalytic CO oxidation on Pt(110) was established as one of the few accessible model systems, where pattern formation in reaction-diffusion systems can be studied experimentally.

Over the last decade, studies of spatially extended dynamical systems concentrated on the control of self-organization and the generation of novel space-time patterns. In experiments with the oscillatory BZ reaction, complex patterns could be stabilized by the application of external periodic forces [38, 50, 51] and simple feedback loops [39, 52]. Also in the framework of different theoretical models, manipulation of spatiotemporal dynamics by external forcing [53–55] and feedback [56, 57] was investigated. Control

of pattern formation in excitable systems mostly aimed at stabilizing and moving single coherent objects in the medium. For instance, localized wave fragments could be stabilized and guided through a BZ medium by controlling both the global and local excitability of the system [40]. In catalytic CO oxidation on Pt(110), self-organization in complex geometries with inert [58] and active [59] boundaries was investigated, as well as the individual addressing and modification of traveling waves through local heating by means of a focused laser beam [60]. Engineering of spatiotemporal complexity, the selective creation and controlled evolution of coherent structures in space and time is the ultimate goal of these efforts.

A major challenge within this field is the study of spatiotemporal chaos. Chaotic behavior in low dimensional dynamical systems is well understood, see *e.g.* Refs. [20–22]. However, much less is known about chaotic phenomena in high dimensional, spatially extended systems. Experimental results are mostly reported from convective systems. Starting with the work of Ahlers and Behringer in 1978 [61], chaotic dynamics has been studied in Rayleigh-Bénard convection [1,62,63], Taylor-Couette flow [64], liquid crystals [65], and other systems [66]. Also in chemical reactions, turbulent states have been observed [46,67]. Apart from experimental work, spatiotemporal chaos has been investigated in various model systems, see Refs. [66,68,69] and references therein.

Recently, contributions in the field of nonlinear dynamics increasingly focused on the control of chaos [70]. Inspired by the work of Ott, Grebogi, and Yorke (OGY) [71], chaos control was first realized for low dimensional systems [72–74]. While the OGY method becomes too laborious when implemented in high dimensional systems, other empirical control schemes were proposed [75] that are readily applied to spatially extended systems. Control of space-time chaos has been studied for a number of different systems such as optical devices [76], lasers [77], and semiconductors [78]. In catalytic CO oxidation on Pt(110), suppression of chemical turbulence by global feedback was qualitatively demonstrated [79]. Also in the context of general models, control of spatiotemporally disordered states was achieved [80–82].

The present work is focused on spatiotemporal chaos in surface chemical reactions. Chemical turbulence observed in experiments with a one- and a two-dimensional system is characterized. In particular, control of turbulence by global feedback is studied.

Uniform global feedback is introduced to suppress turbulence in the experiment and to stabilize various complex space-time patterns. Also, the effect of uniform feedback is analyzed theoretically in the framework of different model systems and substantiated in numerical simulations. Furthermore, a nonuniform feedback scheme is presented and applied to catalytic CO oxidation in both experiments and numerical simulations.

This thesis is organized as follows. In Chapter 2, the experimental and theoretical background of the work is outlined. After a brief introduction into the main concepts of nonlinear dynamics and reaction-diffusion systems, the catalytic CO oxidation on Pt(110) is presented. Besides, the electrochemical oxidation of hydrogen on Pt is described as an example of a quasi-one-dimensional system with migration coupling. Also, general models are introduced that can be used to analyze common aspects in the behavior of a larger class of spatially extended systems.

Based on experimental data, chemical turbulence is characterized in Chapter 3. Both a one- and a two-dimensional case are presented. In electrochemical oxidation of hydrogen, transitions to turbulence are studied for two different ranges of spatial coupling. The analysis is based on the number of space-time defects that are found in a phase and amplitude representation of the experimental data. In the second part of this chapter, a turbulent data set from the CO oxidation system is considered. Topological defects can be identified in the phase and amplitude representation of the data and are characterized statistically. To account for the experimental observations, a simple probabilistic model is derived and discussed in view of similar models in literature.

In Chapters 4 and 5, control of chemical turbulence by uniform global feedback is investigated in detail. Chapter 4 comprises the experimental part. Here, different control techniques are introduced and their effect is exemplified showing results from catalytic CO oxidation under external periodic forcing. In the main part of this chapter, control of turbulence by global delayed feedback is studied in experiments with catalytic CO oxidation. Close to the transition from turbulence to uniform oscillations, different spatiotemporal patterns can be stabilized. The experimental results are complemented with a theoretical analysis of oscillatory systems under global delayed feedback in Chapter 5. First, the behavior of a uniform system is considered in the context of a general phase model. The different solutions and their stability are identified and confirmed

by numerical simulations. Then, the suppression of turbulence in a spatially extended system is considered. The stability of uniform oscillations is analyzed in dependence on the feedback parameters and numerical simulations are performed to obtain further information on the spatiotemporal dynamics at the border of synchronization.

An example of a nonuniform global feedback scheme is given in Chapter 6. In this case, the feedback signal is computed from a chosen Fourier coefficient out of the spatial frequency spectrum of the system. In this way, the coupling becomes sensitive to the presence of spatial structures in the medium. The behavior of catalytic CO oxidation under nonuniform global feedback is studied in experiments as well as numerical simulations. Finally, a summary of this work is presented in Chapter 7.