Chapter 7

Summary

Chemical system far from thermodynamic equilibrium can develop rich spatiotemporal structures. Many heterogeneous catalytic surface reactions are known to exhibit such phenomena, the catalytic oxidation of CO on Pt(110) being the most prominent example. Besides a wealth of regular space-time patterns, disordered states of chemical turbulence have been observed in this reaction. In this work, chemical turbulence in catalytic CO oxidation was statistically characterized, together with data from an electrochemical system. By applying uniform global feedback, turbulence could be controlled and different spatiotemporal patterns were stabilized in experiments with catalytic CO oxidation. The experimental results were explained theoretically in the framework of general models, based on analytical arguments and numerical simulations. Finally, a more elaborate nonuniform feedback scheme was presented and applied to manipulate self-organization in excitable catalytic CO oxidation.

Chemical turbulence was characterized in two experimental cases. As an example of a one-dimensional system, the electrochemical oxidation of hydrogen on Pt was considered. Here, spatial coupling is due to migration in contrast to diffusional coupling in catalytic CO oxidation. In this reaction, transitions to turbulence were analyzed for two different spatial coupling ranges. It was found that they follow a route from limit cycle oscillations through phase turbulence to a stronger disordered regime of ampli-

tude turbulence. By use of a Hilbert transform, the experimental data was translated to phase and amplitude variables. In this representation, space-time defects could be identified in the more turbulent data sets. Considering the number of defects per unit time, the degree of disorder in the system was quantified in agreement with a measure of spatial correlation in the data.

Based on experimental results from catalytic CO oxidation, turbulence in a two-dimensional system was studied. Again, a representation in terms of phase and amplitude variables was derived. In this case, the data was found to exhibit topological defects. The temporal fluctuations in the number of defects were characterized in terms of statistical moments and probability distribution functions. On the basis of simple assumptions for the gain and loss rates of defects, a probabilistic model was derived that yields a good approximation of the experimental results. The model was thoroughly discussed and compared with similar statistical modeling in literature.

A large part of this work was focused on control of chemical turbulence. Only global control schemes were considered, since localized access to individual system elements is difficult to establish in the setup for catalytic CO oxidation and in many other experimental situations. Different control techniques and their implementation via changes in a global system parameter, the CO partial pressure in the reactor, were discussed. As an example for global control, results from catalytic CO oxidation under external periodic forcing were summarized. Control of chemical turbulence by uniform global feedback was then investigated in detail both in experiments and theory.

In the experimental part, results from catalytic CO oxidation under uniform global feedback were presented. The experimental parameters were chosen such that the reaction exhibits chemical turbulence in absence of feedback. It was found that synchronization could be gradually induced by the application of feedback. With increasing feedback intensity, a transition from chemical turbulence to homogeneous oscillations took place via a state of intermittent turbulence. For this transition, significant hysteresis effects were observed. Varying the delay time in the control scheme, the magnitude of the feedback signal could be lowered by a factor of 50%, thus reducing the invasiveness of the feedback considerably. However, the ideal situation of a vanishingly small feedback signal in the state of control was not reached in the experiment. Close to the transition

to uniform oscillations, different spatiotemporal patterns could be stabilized. Besides intermittent turbulence, various regular structures, such as standing waves, cellular structures, and oscillatory clusters were observed.

Motivated by the experiments with catalytic CO oxidation, the behavior of oscillatory systems under uniform global feedback was studied theoretically. In the first place, the dynamics of a uniform system was considered, neglecting the spatial degrees of freedom. A phase dynamics equation for a single oscillator in the presence of global delayed feedback was derived. From this phase model, a bifurcation diagram could be obtained showing the different solutions of the systems depending on the feedback intensity as bifurcation parameter. If the delay time in the feedback scheme was chosen such that a solution with zero feedback term was present, it followed from linear stability analysis that this solution was stable only for feedback intensities below a certain critical value. Above this threshold, the solution with vanishing feedback became unstable in a transcritical bifurcation. Here, only other solutions with a non-zero feedback term were stable, so that the system was driven by an invasive feedback. Numerical simulations of both the phase dynamics approximation and the realistic model for CO oxidation confirmed this result, suggesting that in the experiment the feedback intensity lay beyond the threshold where the solution of vanishing feedback becomes unstable.

In a second step, spatially extended systems in the presence of uniform global feedback were theoretically investigated. The complex Ginzburg-Landau equation was used as a generic model for an oscillatory system that shows chemical turbulence in absence of feedback for appropriately chosen model parameters. The stability of uniform oscillations with respect to small spatial perturbations was analyzed as a function of the feedback parameters. It could be shown that in this type of system, the solution with vanishing feedback is always unstable. Stability of uniform oscillations can be only maintained by an invasive feedback that remains non-zero in the state of control. Besides this general result, a synchronization diagram in the plane spanned by the feedback parameters was derived. Numerical simulations were performed to confirm the analytical results and to trace the synchronization boundary for turbulent initial conditions. Also, the emergence of regular spatiotemporal patterns near the boundary of synchronization was studied numerically.

Apart from uniform global feedback, the concept of nonuniform feedback was introduced. Instead of generating the control signal from a spatially averaged system variable, nonuniform feedback is designed to give a more specific response to spatially nonuniform structures in the medium. As an example, a feedback scheme was presented, that was sensitive to the presence of particular spatial frequencies. At each instant in time, a Fourier decomposition of the spatial patterns in the system was performed. A control signal was generated from a chosen coefficient out of the frequency spectrum of the system and coupled back to a global system parameter. This control method was applied to catalytic CO oxidation in the excitable regime. Periodic cycles of alternating growth and suppression of oxygen islands were observed. The period of these cycles as well as the overall size of the emerging patterns were studied in dependence on the feedback parameters. In addition to experiments, also model simulation were carried out and found to agree well the experimental results. Nonuniform coupling is a simple example of a flexible feedback scheme that allows to modify and tune pattern formation in spatially extended systems. Future work will be directed at tailoring new coupling algorithms by incorporating other signal transforms and tools for pattern recognition.