

Controlling Chemical Turbulence in Surface Reactions

von
Carsten Beta

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Erster Gutachter: Prof. Dr. G. Ertl

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Kurzfassung

Selbstorganisation in Systemen fern vom thermodynamischen Gleichgewicht kann zur Ausbildung komplexer raumzeitlicher Strukturen führen. In der Gruppe der nichtlinearen Oberflächenreaktionen zeigt die katalytische Oxidation von CO auf Pt(110) ein besonders vielfältiges raumzeitliches Verhalten und gilt als beispielhaft für Musterbildung in der heterogenen Katalyse und in chemischen Systemen allgemein. In dieser Arbeit werden Methoden zur Steuerung der Raum-Zeit-Dynamik von Nichtgleichgewichtssystemen entwickelt und auf die katalytische CO-Oxidation angewendet. Insbesondere die Charakterisierung chemischer Turbulenz sowie Methoden zur Turbulenzkontrolle werden behandelt.

Chemische Turbulenz wird in zwei experimentellen Systemen untersucht. Die Auswertung beruht in beiden Fällen auf einer Phasen- und Amplitudendarstellung der experimentellen Daten. Die eindimensionalen Datensätze der elektrochemischen Oxidation von Wasserstoff auf Platin zeigen Übergänge von periodischen Oszillationen über ein phasenturbulentes Regime bis hin zu Defektturbulenz. Die Untersuchung chemischer Turbulenz in dem zweidimensionalen System der CO-Oxidation basiert auf den statistischen Eigenschaften topologischer Defekte.

Durch Anwendung von homogen-globaler Rückkopplung auf die katalytische Oxidation von CO können turbulente Zustände unterdrückt und verschiedene raumzeitliche Muster induziert werden. Die Kontrollkraft wird dabei durch räumliche Mittelung über das ausgedehnte System berechnet und steuert den CO-Partialdruck in der Reaktionskammer. Eine optimale Wahl der Verzögerungszeit in der Kontrollschleife minimiert die Invasivität der Rückkopplung. Im Rahmen einer theoretischen Untersuchung von oszillatorischen Systemen unter homogen-globaler Rückkopplung werden die experimentellen Ergebnisse erklärt. Bereits ein einfaches Phasenmodell für die Dynamik des homogenen Systems ergibt eine qualitative Übereinstimmung mit dem Experiment. Die Analyse eines räumlich ausgedehnten Systems zeigt, daß die Kontrolle chemi-

scher Turbulenz nur mit invasiver Rückkopplung erreicht werden kann. Neber der Herleitung eines Synchronisationsdiagramms wird zudem die Musterbildung in der Nähe des Übergangs zu homogenen Oszillationen numerisch untersucht.

Als Beispiel eines komplexeren Kontrollschemas wird inhomogen-globale Rückkopplung eingeführt und sowohl in Experimenten als auch in numerischen Simulationen auf die katalytische CO-Oxidation im anregbaren Bereich angewendet. Die Kontrollkraft wird durch Fourieranalyse der Konzentrationsmuster generiert, so daß die Rückkopplung selektiv auf die Gegenwart inhomogener Strukturen reagiert. Die zeitliche Entwicklung und räumliche Ausdehnung der Muster kann auf diese Weise effizient kontrolliert werden.

Zusammenfassend leistet diese Arbeit einen Beitrag zum Verständnis chemischer Turbulenz in experimentellen Systemen. Im Mittelpunkt der Untersuchung steht die Dynamik turbulenter Zustände sowie ihre Kontrolle durch homogen-globale Rückkopplung. Darüber hinaus wird das Konzept der inhomogen-globalen Rückkopplung eingeführt um Perspektiven für die zukünftige Entwicklung neuer Rückkopplungsschemata zur Steuerung von Selbstorganisation in Nichtgleichgewichtssystemem aufzuzeigen.

Abstract

Self-organization in nonequilibrium systems can lead to the emergence of complex space-time patterns. Among nonlinear surface reactions, the catalytic oxidation of CO on Pt(110) displays a particularly rich spatiotemporal behavior and became paradigmatic for pattern formation in heterogeneous catalysis and in chemical systems in general. In this work, techniques to guide the space-time dynamics of nonequilibrium systems are proposed and applied to the CO oxidation system. In particular, chemical turbulence is characterized and approaches to control turbulence are analyzed.

Chemical turbulence is studied in two experimental systems. In both cases, the analysis is based on a phase and amplitude representation of the experimental results. The one-dimensional data from electrochemical hydrogen oxidation on Pt shows transitions from limit cycle oscillations via a phase turbulent regime to defect-mediated amplitude turbulence. Turbulence in the two-dimensional CO oxidation system is characterized by the statistical properties of topological defects.

Turbulence can be controlled and different spatiotemporal patterns may be induced by applying global control to catalytic CO oxidation. In the case of uniform global feedback, the control force is generated by spatial averaging from the extended system and drives the CO partial pressure in the reactor. The invasiveness of the feedback can be reduced by an optimal choice of the time delay in the control loop. The experimental results are explained in a theoretical study of oscillatory systems under uniform global feedback. Already a simple phase model for the homogeneous dynamics shows qualitative agreement with the experiment. The analysis of a spatially extended system demonstrates that suppression of turbulence can be achieved only with an invasive feedback. A synchronization diagram is derived and pattern formation at the border of synchronization is investigated numerically.

Nonuniform global feedback is proposed as a more advanced control method and applied to excitable CO oxidation in experiment and simulations. The control signal is

computed by Fourier decomposition of the concentration patterns in the system so that the feedback is sensitive to the presence of nonuniform structures. The temporal evolution and spatial extension of self-organizing objects can be efficiently controlled.

Thus, this work contributes to the understanding of chemical turbulence in experimental systems. The nature of turbulent states is characterized and their control by uniform global feedback is discussed in detail. Moreover, nonuniform feedback is introduced to demonstrate potential future directions in the development of new coupling protocols for guided self-organization in nonequilibrium systems.

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Curriculum Vitae

| | |
|-------------------|--|
| Name | Carsten Beta |
| Born | September 10, 1974 in Bremen, Germany |
| Parents | Kurt Beta and Ingrid Beta, née Seeliger |
| 1981 – 1994 | Freie Waldorfschule Bremen |
| 06/1994 | Abitur |
| 1994 – 1996 | Social service in Camphill Blair Drummond, Stirling, Scotland |
| 04/1996 – 06/2001 | Studies in Chemistry |
| 04/1996 – 03/1998 | Eberhard Karls Universität Tübingen |
| 03/1997 – 06/2001 | Fellowship of the Studienstiftung des Deutschen Volkes |
| 03/1998 | Vordiplom in Chemistry (Tübingen) |
| 04/1998 – 06/2001 | Universität Karlsruhe |
| 10/1999 – 03/2000 | Ecole Normale Supérieure de Paris, France |
| 12/2000 – 05/2001 | Diplomarbeit with Prof. M. Farge at the Ecole Normale Supérieure de Paris, France |
| 06/2001 | Diplom in Chemistry (Karlsruhe) |
| since 10/2001 | PhD student with Prof. G. Ertl at the Department of Physical Chemistry, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin |

