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Manipulation of surface reaction dynamics by global pressure and local temperature control: A model study

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Specific catalyst design and external manipulation of surface reactions by controlling accessible physical or chemical parameters may be of great benefit for improving catalytic efficiencies and energetics, product yield, and selectivities in the field of heterogeneous catalysis. Studying a realistic spatiotemporal one-dimensional model for CO oxidation on Pt(110) we demonstrate the value and necessity of mathematical modeling and advanced numerical methods for directed external multiparameter control of surface reaction dynamics. At the model stage we show by means of optimal control techniques that species coverages can be adjusted to desired values, aperiodic oscillatory behavior for distinct coupled reaction sites can be synchronized, and overall reaction rates can be optimized by varying the surface temperature in space and time and the CO and O_2 gas phase partial pressure with time. The control aims are formulated as objective functionals to be minimized which contain a suitable mathematical formulation for the deviation from the desired system behavior. The control functions $p_{CO}(t)$ (CO partial pressure), $p_{O_2}(t)$ (O_2 partial pressure), and $T(x,t)$ (surface temperature distribution) are numerically computed by a specially tailored optimal control method based on a direct multiple shooting approach which is suitable to cope with the highly nonlinear unstable mode character of the CO oxidation model.

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I. INTRODUCTION

Heterogeneous catalysis is of central importance in many areas of chemistry, ranging from exhaust gas after-treatment to selective synthesis of chemical compounds. Today, in chemical industries nearly 70% of all basic materials are fabricated by use of heterogeneous catalytic reactions [1].

In recent years modern experimental techniques have provided deep insight into microscopic details of surface reaction dynamics with high spatial and temporal resolution [1,2]. These data help to develop realistic mathematical models based on mechanistic details for the surface chemistry in many important applications of heterogeneous catalysis [3], for example, exhaust gas catalysts [4]. If such models quantitatively account for the behavior observed in experiments they can be used for performing *in silico* studies [5], testing hypotheses for reaction mechanisms, and motivating and selecting further experimental investigations to clarify vague mechanistic issues. Thus, catalysis becomes an interdisciplinary science [3] bringing together scientists from surface physics, chemistry, engineering, and recently also from scientific computing and mathematics. In particular, this mutual interplay between theoretical and experimental approaches is expected to fertilize basic research also in various other scientific areas related to the study of complex systems, which are abundant, for example, in biology [6,7].

An ancient dream of the chemists and to some extent at the core of all chemical research is the manipulation of chemical reactivity at will by the experimenter [8]. Designing complex organic compounds for use in the pharmaceutical industry, engineering reactors that perform desired tasks, optimizing product yields and selectivities, and reducing costs, energy consumption, and environmental pollution to a minimum are questions related to the issue of microscopic control of chemical reactions [8]. Many of these questions involve optimum performance purposes. Much the same as for surface analysis techniques, both experimental and modeling approaches to control chemical surface reactions started with well characterized systems like catalytic CO oxidation on Pt(110) surface under UHV conditions [9]. Nowadays, experimental methods are available to investigate heterogeneous catalysis under more realistic conditions [10] such as atmospheric pressure and on polycrystalline surface-structures, but the investigation of microscopic control issues for surface reaction dynamics is still in its infancy from both the theoretical and experimental points of view [11,12]. This is partly due to the fact that the influence of external factors on complex spatiotemporal systems with nonlinearly interacting components is generally very little understood, in particular if control inputs are spatially distributed [13]. In the face of the overwhelming variety of possible dynamical properties of controlled nonlinear systems a successful attack seems hopeless without the help of mathematics. On the other hand, noninvasive experimental techniques to access microscopic control parameters either online or offline without destroying the system itself have only recently been developed. But there is broad agreement that in the future it will be possible to control catalytic reactions even on the atomic scale [14].

In addition to the pioneering work of Ertl and co-workers in the area of controlling spatiotemporal dynamics of CO oxidation on Pt [9,11,12,15–17], several other attempts have been made to control complex behavior in chemical reaction systems. Chaos control ideas [18] have been used to design wave propagation patterns in excitable media [19], propagat-

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*Electronic address: lebiedz@iwr.uni-heidelberg.de ing wave segments could be stabilized [20], and oscillatory cluster patterns were induced in the photosensitive Belousov-Zhabotinsky reaction [21]. In [22] control of spiral wave movement in excitable media and its suppression have been studied numerically by introducing spatial inhomogeneities into the medium and turbulence control and synchronization based on the Ginzburg-Landau equation model have been investigated in [23]. Pertsov *et al.* [24] analyze spiral wave control in cardiac tissue by small parameter gradients. In nonlinear optics also feedback control of pattern formation has been discussed [25].

Most of these studies are based on the introduction of a feedback function for either local gradient control [19] or global control [9,20,21] fed back into the system. The controller design of the corresponding control systems is often based on more or less empirical issues, for example, feedback functions chosen from physical insight or systematic variation and adjusting of potential control parameters to study the system's output behavior. However, a systematic way to control spatiotemporal chemical reaction dynamics with respect to general control aims will undoubtedly require the help of quantitative modeling and a wide ranging application of advanced numerical methods [13]. Whereas in the control engineering community often linear model approximations have been used to implement model based control, the inherently nonlinear character of chemical reaction systems requires nonlinear control techniques for many practically relevant tasks [26]. In particular for the self-organizing CO oxidation system we address in this work linear model predictive control, applying an adaptive linearization of the system dynamically around the actual transient state as well known in dynamic matrix control (DMC) [27], is not adequate for the following reason. A locally linearized model cannot accurately account for system instabilities caused by nonlinearities and system inherent positive feedback mechanisms, but especially these instabilities over a nonlocal range give rise to the temporal patterns observed in experiments and simulations. Therefore, it is crucial to base a control scheme on the fully nonlinear model equations which can describe the self-organization behavior that is supposed to be controlled or externally forced.

We have developed an optimization approach for addressing general nonlinear control issues in spatiotemporal chemical reaction systems. In [28,29] we demonstrated an application of these ideas to manipulate concentration patterns in a reaction-diffusion system modeling bacterial chemotaxis. By controlling the influx of a chemical species we have shown that desired cell concentration patterns can be induced into the system and propagating waves can be modulated. The use of specially tailored numerical methods for optimal control turned out to be crucial because of the unstable mode character of pattern forming reaction-diffusion systems. In combination with the large scale character of the optimal control problem arising from spatial discretization of the partial differential equation (PDE) models the latter makes numerical optimization a very difficult task. In particular, for a spatially homogeneous ordinary differential equation (ODE) model [30] for the CO oxidation on Pt we have shown the wide ranging capabilities of numerical optimal control for the study and dynamic control of nonlinear chemical reaction systems, pointing out their significance for control and signal processing tasks in biological systems [31]. Here, we extend the optimal control application to a one-dimensional (1D) spatiotemporal model [32] for the CO oxidation on Pt(110) to address distributed parameter control of spatiotemporal dynamics in catalytic surface reactions.

Dubljevic *et al.* [33] recently proposed an alternative approach to model based specific control of distributed parameter systems. They use a target PDE which describes the desired dynamical behavior in space and time and demonstrate how this can be used for computing distributed control functions which induce the desired behavior. While this method works well for control aims which can be explicitly formulated as trajectory behavior of the target PDE solution, our optimization approach seems to be more flexible, and quite general performance criteria like product yield and selectivities can be formulated as control aims as well. Additionally we do not have to care too much about controllability aspects because to a certain extent the optimal control method automatically yields the (locally) best possible solution of the problem under consideration.

II. MODELING THE CONTROL PROBLEM

Here, we use methods similar to those proposed in [28] to address microscopic control of surface reaction dynamics for CO oxidation on Pt(110) in a model study. We choose a realistic mean-field ordinary differential equation model for surface coverages developed by and co-workers Ertl [30] which describes the experimentally observed phenomena at UHV fairly well. Since thermodynamic and kinetic data for the elementary reaction steps like absorption, desorption of CO and O_2, surface diffusion of CO, and surface reconstruction can be estimated quite accurately from experimental data, we model the temperature dependence of the rate coefficients by Arrhenius type equations. The 1D spatiotemporal model for CO oxidation on Pt according to [15] is

$$\frac{\partial u}{\partial t}(x,t) = D\Delta u + k_1 p_{\mathrm{CO}} s_{\mathrm{CO}}(1-u^3) - k_2 u - k_3 uv,$$

$$\frac{\partial v}{\partial t}(x,t) = k_4 p_{\mathrm{O}_2}[s_{1\times 1} w + s_{1\times 2}(1-w)](1-u-v)^2 - k_3 uv,$$

$$\frac{\partial w}{\partial t}(x,t) = k_5\left(\frac{1}{1+\exp[(u_0-u)/\delta u]} - w\right),$$

$$x \in [0,L], \quad t \in [0,\ t_{end}],$$

$$k_i = A_i e^{-E_A^i/RT(x,t)}, \quad i = 2,3,5 \tag{1}$$

The preexponential factors, activation energies, and model parameter values are taken from [30] and [15]: $D=40\ \mu\mathrm{m}^2\ \mathrm{s}^{-1}$, $s_{\mathrm{CO}}=1.0$, $s_{1\times 1}=0.6$, $s_{1\times 2}=0.4$, $u_0=0.35$, $\delta u=0.05$, $k_1=3.14\times 10^5\ \mathrm{s}^{-1}\ \mathrm{mbar}^{-1}$, $k_4=5.86\times 10^5\ \mathrm{s}^{-1}\ \mathrm{mbar}^{-1}$, $A_2=3\times 10^6\ \mathrm{s}^{-1}$, $E_A^2=41.8\ \mathrm{kJ/mol}$, $A_3=2\times 10^{16}\ \mathrm{s}^{-1}$, $E_A^3=158.8\ \mathrm{kJ/mol}$, $A_5=10^2\ \mathrm{s}^{-1}$, and $E_A^5=29.3\ \mathrm{kJ/mol}$. The reaction rates k_1 and k_4 for the adsorption of CO and O_2 on the surface do not significantly depend on small variations of the local surface temperature, but only on the hitting rate of gas phase molecules, which is influenced by the surrounding global temperature [30].

In the model (1) $u(x,t)$ describes the local surface coverage of CO, $v(x,t)$ the O_2 coverage, $w(x,t)$ the fraction of nonreconstructed surface area in the 1×1 phase, and $1-w(x,t)$ the fraction of surface area reconstructed into a 1×2 missing row structure [15]. All variables vary between 0 and 1 as functions of space and time. Due to the high activation energy for O diffusion on Pt at temperatures below 550 K, the O atoms are assumed to be immobile whereas the CO diffuses on the surface (diffusion coefficient D).

There are three obvious parameters in the reaction system which can be externally controlled as functions of time: the gas phase partial pressures p_{CO} and p_{O_2} and the local temperature T entering the Arrhenius expressions for the rate coefficients $k_i=A_i e^{-E_A^i/RT}$, $i=2,3,5$. It has been shown recently that the temperature can be controlled locally in space by illumination of the metal surface with a laser spot [11,12,17] whereas CO and O_2 gas phase pressures are global control parameters [9]. By using modern laser techniques it turned out to be possible to write spatiotemporal temperature profiles onto the metal surface [12].

In the following, either we treat both partial pressures p_{CO} and p_{O_2} in (1) as variable control parameters or we assume either the O_2 partial pressure to be fixed or both partial pressures to be fixed and treat as the case may be the remaining partial pressure(s) and in either case the local temperature $T(x,t)$ as control inputs. It has already been shown numerically and experimentally that spatiotemporal pattern formation can be influenced by varying these parameters [9,11,12,17]. However, a control of spatiotemporal surface reaction dynamics with respect to specific desired and prespecified control aims and the treatment of several parameters as control inputs at the same time have not yet been analyzed, either experimentally or theoretically.

Here, we show that the application of advanced numerical optimization methods can help in addressing the question of specific external control of chemical surface reactions if accurate models are available. We formulate our desired control aims as objective functionals to be minimized, containing a least square deviation between observed and desired dynamical behavior or other performance criteria in a suitable mathematical formulation. For our model study of CO oxidation on Pt we assume here that it is possible to control the CO and O_2 gas phase pressures in a piecewise constant fashion with temporal switching points and the local surface temperature in separated small surface domains by time varying laser light illumination with different operating power. Using this laser illumination procedure it is reasonable to assume that the temperature can be varied in the range 10 K above the background temperature of the whole system [12] which is held constant at $T=540$ K here. We further assume that each spatial domain can be heated or cooled between 540 and 550 K independent of the neighboring domains and the surrounding temperature (which means neglecting both heat conduction within the catalytic Pt surface and heat radiation into the gas phase) and that the local temperature rises or falls linearly with time between two heating set points. In many cases these are of course only rough approximations because heat conduction through the metal surface is fast, but to keep the control system concise the approximations are reasonable here and not too far from reality for a first model study. Later it will be possible to include more detailed models for heat conduction and/or heat radiation but the computational effort will be much more extensive if spatiotemporal dynamics for the temperature are included as well. Furthermore, we do not claim that quantitative transfer of our results to experiments is immediately possible at the present modeling stage. Our model is highly simplified mainly because it neglects heat transport and direct application to a potential experiment will most probably require a more detailed modeling approach.

Here, our primary aim is to demonstrate what is in principle possible by model based optimal control of surface reaction dynamics on the basis of this simplified spatiotemporal model. In order to model our target control problem with prespecified desired control aims we formulate the general optimal control problem

$$\min_{p_{\mathrm{CO}}(t),p_{\mathrm{O}_2}(t),T(x,t)} \int_0^{t_{end}} L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)dt \tag{2}$$

subject to

$$\frac{\partial u}{\partial t} = D\Delta u + k_1 p_{\mathrm{CO}}(t) s_{\mathrm{CO}}(1-u^3) - k_2 u - k_3 uv,$$

$$\frac{\partial v}{\partial t} = k_4 p_{\mathrm{O}_2}(t)[s_{1\times 1}w + s_{1\times 2}(1-w)](1-u-v)^2 - k_3 uv,$$

$$\frac{\partial w}{\partial t} = k_5\left(\frac{1}{1+\exp[(u_0-u)/\delta u]} - w\right), \tag{3}$$

$$k_i = A_i e^{-E_A^i/RT(x,t)} \quad (i=2,3,5), \quad u(0,x)=u_0(x),$$

$$v(0,x)=v_0(x), \quad w(0,x)=w_0(x),$$

$$x\in[0,L], \quad t\in[0,t_{end}],$$

$$T_l \leqslant T \leqslant T_u,$$

$$p_l \leqslant p_{\mathrm{CO}}, p_{\mathrm{O}_2} \leqslant p_u.$$

Here, $L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)$, the so called Lagrangian functional, describes either a specific desired dynamical behavior of surface coverages in the CO oxidation system on Pt, which is supposed to be induced in the system by appropriate variation of the control variables $T(x,t)\in[T_l,T_u]$ and $p_{\mathrm{CO}}(t)$, $p_{\mathrm{O}_2}(t)\in[p_l,p_u]$ within a given range, or a more general optimal performance criterion like the maximization of the overall reaction rate. We will present results for three different realizations of $L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)$: (a) $L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)=\int_0^L[u(x,t)-\hat{u}(x,t)]^2dx$; (b) $L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)=\Sigma_{i=1}^n[u(x_i,t)-u(x_{x+1},t)]^2$, $x_i\in[0,L]$; and (c) $L(x,p_{\mathrm{CO}},p_{\mathrm{O}_2},T,t)=-\int_0^Lk_3(T)u(x,t)v(x,t)dx$.

In the scenario (a) a prespecified spatial distribution of the local CO coverage on Pt is supposed to be induced and stabilized during the oxidation reaction. In our examples $\hat{u}(x,t)\equiv\mathrm{const}$ corresponds to an arbitrary homogeneous coverage of CO. In the scenario (b) the difference in temporal dynamics of the CO coverage between two or more distinct positions $(x_i,i=1,\ldots,n+1)$ on the Pt surface is minimized, which corresponds to a synchronization of reaction sites. In our examples, we show results for $n=1,2,3$. Scenario (c) corresponds to the maximization of the global reaction rate of CO oxidation (averaged over the whole 1D surface area), which can be used to optimize product yield or selectivities in the case of several possible reaction products.

III. NUMERICAL METHODS

In order to solve the optimal control problem (2) and (3) numerically we choose the so called direct approach [34] which is based on a projection of the infinite dimensional optimization problem in function space to a finite dimensional approximation by discretizing the objective functional (2) and the differential equation constraints (3) and parametrizing the control functions $p_{\mathrm{CO}}(t)$, $p_{\mathrm{O}_2}(t)$, $T(x,t)$. According to the method of lines, for the spatial discretization of the reaction-diffusion model equations we use second order finite differences for the Laplacian with a step size $h=0.004$ on a spatial domain $[0,L]=[0,0.08]$ corresponding to 80 μm and assume zero flux *von Neumann* boundary conditions. In order to account for the spatial dependence of the temperature $T(x,t)$ we use a collocation discretization on the same grid as for the differential equations. This scenario would approximate a quasi-1D experiment with a Pt wire.

In principle the resulting m-dimensional (here $m=60$) system of ordinary differential equations can then be treated by common numerical ODE integration decoupling the optimization in a separate loop. The optimal control problem could be solved by numerical simulations of this dynamical system with fixed initial values for the control variables and subsequent determination of a descent direction for the objective functional. This can be done by providing derivative information for the objective functional with respect to the control parameters and applying appropriate derivative based minimization methods. This yields stepwise new control values for the simulation and the next iteration loop starts. The procedure is repeated until a suitable convergence criterion is satisfied.

However, this so called sequential (single shooting) approach [34] is often problematic if instabilities or even chaotic behavior are involved in the underlying dynamical systems [35] because in modern derivative based optimization methods sensitivities with respect to control parameters in the form of accurate derivatives have to be computed numerically. In case of unstable dynamical modes that may be excited by the controls this procedure is highly error prone, or sometimes even impossible. Therefore, in such cases the so called multiple shooting approach [36] is much more suitable and yields excellent convergence results for pattern forming systems like the CO oxidation on Pt [31] studied here or similar systems [28].

In a multiple shooting discretization the time interval $[0,t_{end}]$ is discretized on a rather coarse time grid (grid points are called multiple shooting nodes) and on each of the subintervals an initial value problem is solved by numerical integration as in the direct single shooting approach described before. For the control functions a piecewise parametrization on each multiple shooting interval is chosen (for example, piecewise linear polynomials). In addition to these control variables the initial values of the state variables (u, v, w in the CO oxidation model) at the multiple nodes are *a priori* unknown. In order to assure continuity of the state trajectories, equality constraints for the multiple shooting nodes are added to the optimization problem. These additional constraints guarantee that in the solution of the optimal control problem the end value of the preceding multiple shooting interval is equal to the initial value of the following interval, which corresponds to the continuity of the state trajectory. Although it seems as if one has simply blown up the problem by introducing additional variables it can be shown that the multiple shooting optimal control problem can be solved very efficiently by exploiting its mathematical structure [36]. Furthermore, if available, *a priori* information about the optimal trajectories can be included into the algorithm at multiple nodes, which results in a significant speedup of convergence. The problems with instabilities and numerical computation of sensitivities in derivative based optimization algorithms are significantly reduced because of the restriction to subproblems on small time subintervals. The smaller the multiple shooting intervals the more is the probability of potential explosions of dynamical modes reduced, and as a consequence the more stable and accurate are the numerical computations of derivatives.

The multiple shooting algorithm that is used throughout the paper is implemented in the optimal control package MUSCOD-II [36,37] including the backward differentiation formulas (BDF) integrator DEASOL [38,39] for error controlled solution of stiff ordinary differential or differential algebraic equations (DAEs). Since a detailed description of the numerical optimal control algorithm would go far beyond the scope of the presented work, we have to refer to the literature [37] for a comprehensive up-to-date treatment.

IV. SIMULATIONS

The system (3) has been analytically and numerically analyzed in detail before [30,32]. Using the BDF code DAESOL [38,39] we performed numerical simulations of the above model system under various conditions in order to verify the dynamical behavior over long time horizons. In particular, for suitable parameter values and initial conditions proposed in [15] we reproduced spatiotemporal chaos in the form of amplitude and phase turbulence. These arise from the fact that uniform oscillations observed in the homogeneous case are unstable with respect to small spatial perturbations of the CO surface coverage. Thus, amplitude and phase coherence get lost due to destabilization by diffusion coupling of local CO coverages [15].

The minute verification of the dynamics by numerical simulations with error control is crucial for any dynamical system in the optimization context because derivative based multiple shooting optimal control methods require highly accurate numerical integration. The numerical integration routines generate sensitivity information with respect to parameter and control variables. Therefore, advanced and stable numerical integrators with error control have to be used. It is not necessarily evident in all cases of pattern formation due to system instabilities that all numerical results from earlier studies can be reproduced quantitatively using these integrators, because in the literature often numerical integration methods are used, which are not suitable to account for the numerical requirements to optimize unstable dynamical systems. In many cases explicit methods like the forward Euler method are prohibited in an optimization approach because they are numerically unstable for various types of stiff differential equations [40]. Even if the numerical integration is stable for a choice of small time steps, explicit methods often produce a large and hardly controllable numerical error for longer integration times [40]. This is mostly due to the failure of explicit methods to damp even error modes, which are stable for the original nonlinear system under consideration. In such cases the instabilities observed in numerical simulations are a superposition of numerical instabilities and the unstable character of the dynamical system itself and thus instability effects and patterns may be largely amplified.

Our simulation results (data not shown) for the 1D spatiotemporal CO oxidation model qualitatively reproduce the results from [15] very well except for minor differences in bifurcation point values for the parameters.

V. OPTIMAL CONTROL RESULTS

We set up several control scenarios which may be interesting in applications of catalytic surface reactions. The first is the induction and stabilization of a desired uniform surface coverage for a chemical species in a given surface domain, control scenario (a), Figs. 1 and 2; the second a synchronization of remote reaction sites, control scenario (b), Figs. 3–5; and the third the maximization of the overall conversion rate of CO to CO_2, control scenario (c), Fig. 6. In the temperature range between 540 and 550 K, the uncontrolled system shows in numerical simulations either oscillatory or bistable behavior depending on the exact temperature value. In the bistable regime a mainly oxygen covered, reactive steady state and a nonreactive mainly CO covered steady state coexist, and it depends on the initial conditions to which asymptotic state the system is attracted. The control scenarios (a)–(c) treated here and their mathematical formulations have been introduced at the end of Sec. II.

In the cases (a) and (c) random distributions of local surface coverages of CO and O_2 have been chosen as the initial condition for the simulation and optimization. In scenario (b) a simulation was performed over a long time horizon ($t_{end} > 3000$) and after chemical turbulence with loss of phase and amplitude coherence had been observed a snapshot of the variables $u(x,t)$, $v(x,t)$, $w(x,t)$ was taken at an arbitrary time point. These values were used as warm start initial conditions for the synchronization optimal control problem in scenario (b).

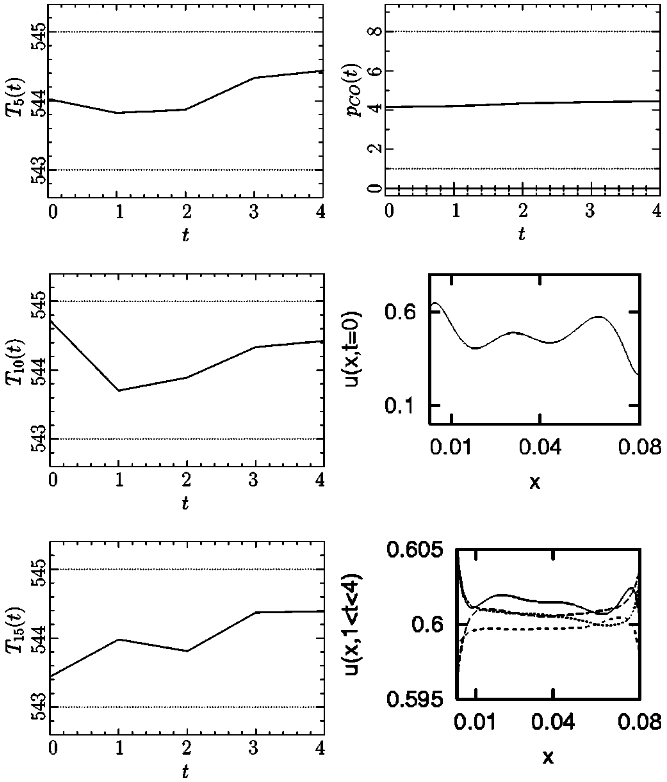

FIG. 1. Induction and stabilization of a constant surface coverage $\hat{u}(x,t) \equiv 0.6$ by controlling the CO partial pressure and the local surface temperature according to control scenario (a) (see Sec. II, starting from random initial surface coverage. O_2 partial pressure $p_{O_2}(t) \equiv 9 \times 10^{-5}$ mbar fixed. Control parameters: (a) 543 K $\leqslant T_i(t) \leqslant 545$ K; $T_i(t), i=1,\ldots,19$, corresponds to the local surface temperature in the discretization cell i; (b) 1×10^{-5} mbar$\leqslant p_{CO}(t) \leqslant 10 \times 10^{-5}$ mbar. The figure shows $T_i(t)$ for a selection of $i \in \{0,\ldots,19\}$, $p_{CO}(t)$, and the CO surface coverage $u(x,t)$ for selected representative time points between $t=1$ and $t=4$. Time t in seconds, spatial coordinate x in micrometers, partial pressure p_{CO} in 10^{-5} millibars, temperature T in Kelvin.

According to scenario (a) in our first example we induce a prespecified uniform surface coverage of CO. The temperature distribution $T(x,t)$ and either the partial pressure p_{CO} or both partial pressures p_{CO} and p_{O_2} are treated as control variables. Depending on the prespecified value for $\hat{u}(x,t)$ it turned out to be impossible to stabilize arbitrary surface coverages by varying the temperature field and one gas phase partial pressure alone while keeping the other pressure fixed. By varying the local temperature and the CO partial pressure it is possible to induce uniform CO coverages between 0.4 and 0.6. Values between 0.2 and 0.8 can be induced by allowing the O_2 partial pressure as a variable input control as well. Here, we exemplarily present two scenarios with the

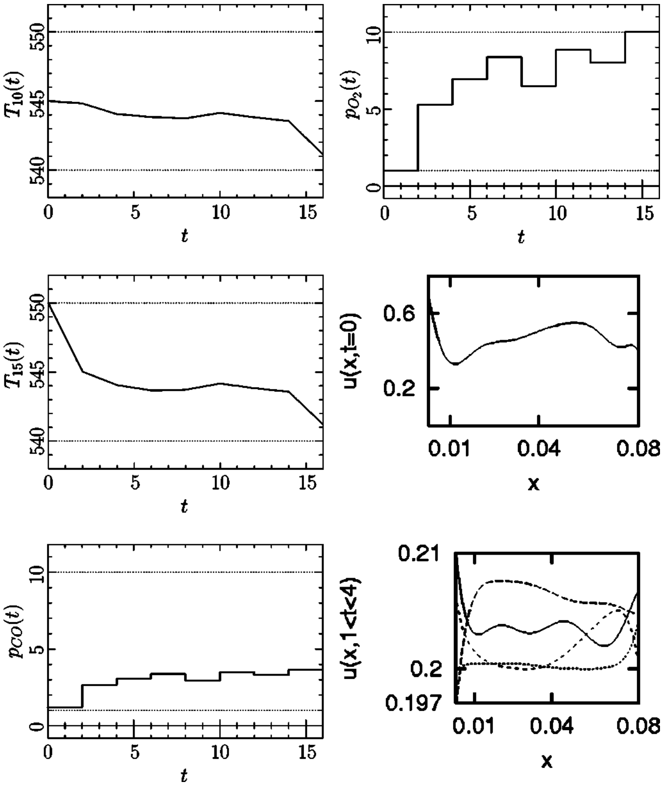

FIG. 2. Induction and stabilization of a constant surface coverage $\hat{u}(x,t) \equiv 0.2$ by controlling the CO and O_2 partial pressures and the local surface temperature according to control scenario (a) (see Sec. II), starting from random initial surface coverage. Control parameters: (a) 540 K $\leqslant T_i(t) \leqslant$ 550 K; $T_i(t), i=1,\ldots,19$, corresponds to the local surface temperature in the discretization cell i; (b) 1×10^{-5} mbar $\leqslant p_{\mathrm{CO}}(t) \leqslant 8 \times 10^{-5}$ mbar; (c) 1×10^{-5} mbar $\leqslant p_{\mathrm{O}_2}(t) \leqslant 10 \times 10^{-5}$ mbar. The figure shows $T_i(t)$ for a selection of $i \in \{0,\ldots,19\}$, $p_{\mathrm{CO}}(t)$, and the CO surface coverage $u(x,t)$ for selected representative time points between $t=1$ and $t=4$. Time t in seconds, spatial coordinate x in micrometers, partial pressures p_{CO} and p_{O_2} in 10^{-5} millibars, temperature T in Kelvin.

target values 0.6 and 0.2. In the first case the local temperature and the CO pressure are treated as control parameters whereas p_{O_2} is fixed. As can be seen from Fig. 1, the CO partial pressure in the optimal solution is approximately constant and even if it is fixed in the optimal control problem, quite good results for the induction of a uniform coverage $\hat{u}(x,t) \equiv 0.6$ with small deviations can be achieved. In the second case $[\hat{u}(x,t) \equiv 0.2]$ it turned out that with the O_2 partial pressure fixed, in the optimal solution for stabilizing a coverage value of 0.2 moderate amplitude oscillations about this value occur. Allowing p_{O_2} as an additional control variable, the 0.2 state can be induced and stabilized accurately (Fig. 2).

The second control scenario (b) corresponds to the dynamical synchronization of reaction sites (Figs. 3–5). Here, we treat only the temperature distribution $T(x,t)$ as a control variable, allowing values between 543 and 545 K, while fixing both gas phase partial pressures p_{CO} and p_{O_2} at values which lead in the uncontrolled case to unstable oscillatory dynamics in simulations of the surface reaction model. Without any external control in this case the uniform relaxation oscillations observed under the adjusted conditions are unstable with respect to small perturbations. Chemical turbulence due to a destabilizing effect of diffusive coupling between local oscillators on the Pt surface is observed, which becomes obvious in the loss of amplitude and phase coherence of distinct surface sites. We show that our optimal control approach allows the synchronization of several remote reaction sites. We choose two, three, or four arbitrary reaction sites represented as grid cells in the spatial discretization of the PDE model (3) and formulate their synchronization as a least square deviation (in the case of more than two reaction sites an equally weighted multiobjective sum of least

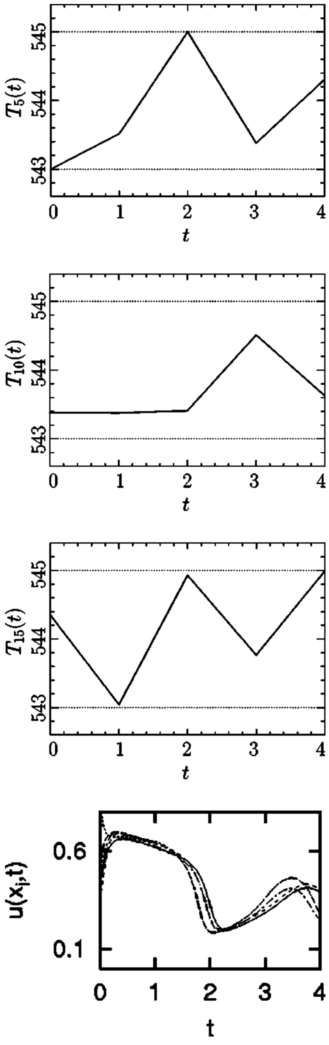

FIG. 3. Synchronization of two different reaction sites x_5 and x_{15} on the Pt(110) surface according to control scenario (b) (see Sec. II) by variation of the local surface temperature, starting from values in the turbulence regime of the CO oxidation on Pt(110) [15]. Partial pressures $p_{\mathrm{CO}}(t) \equiv 4.81 \times 10^{-5}$ mbar and $p_{\mathrm{O}_2}(t) \equiv 13 \times 10^{-5}$ mbar fixed. Control parameter 543 K $\leqslant T_i(t) \leqslant$ 545 K; $T_i(t), i=1,\ldots,19$, corresponds to the local surface temperature in the discretization cell i. The figure shows $T_i(t)$ for a selection of $i \in \{0,\ldots,19\}$ and the CO coverage dynamics $u(x_i,t), i=1,5,10,15,19$; x_i corresponds to the spatial discretization cell i (spatial coordinate $i \times 4$ μm). Time t in seconds, temperature T in Kelvin.

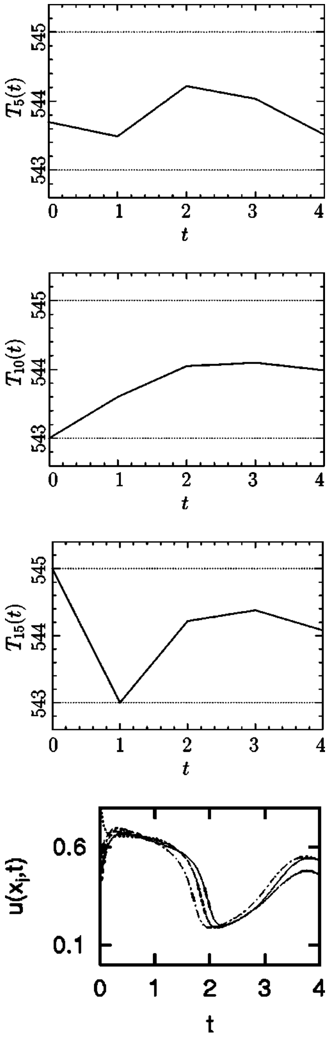

FIG. 4. Synchronization of three different reaction sites $x_5(t)$, $x_{10}(t)$, and $x_{15}(t)$ on the Pt(110) surface according to control scenario (b) (see Sec. II) by variation of the local surface temperature, starting from values in the turbulence regime of the CO oxidation on Pt(110) [15]. Partial pressures $p_{\mathrm{CO}}(t) \equiv 4.81 \times 10^{-5}$ mbar and $p_{\mathrm{O}_2}(t) \equiv 13 \times 10^{-5}$ mbar fixed. Control parameter $543\ \mathrm{K} \leqslant T_i(t) \leqslant 545\ \mathrm{K}$; $T_i(t), i=1,\ldots,19$, corresponds to the local surface temperature in the discretization cell i. The figure shows $T_i(t)$ for a selection of $i \in \{0,\ldots,19\}$ and the CO coverage dynamics $u(x_i,t), i=1,5,10,15,19$; x_i corresponds to the spatial discretization cell i (spatial coordinate $i \times 4\ \mu$m). Time t in seconds, temperature T in Kelvin.

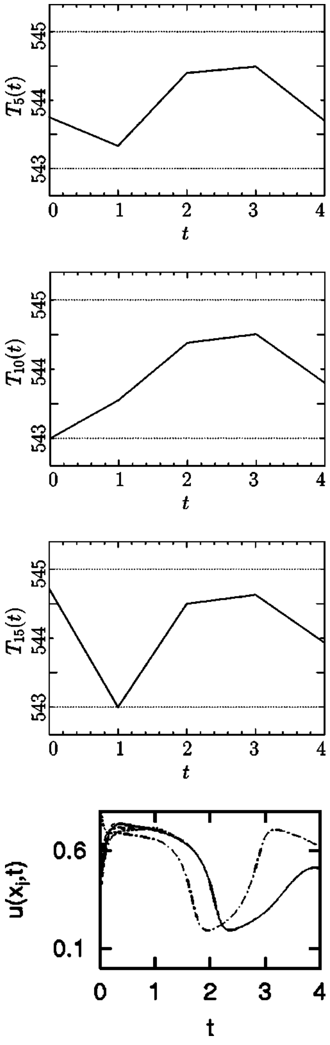

FIG. 5. Synchronization of four different reaction sites $x_1(t)$, $x_5(t)$, $x_1 0(t)$, and $x_{15}(t)$ on the Pt(110) surface according to control scenario (b) (see Sec. II) by variation of the local surface temperature, starting from values in the turbulence regime of the CO oxidation on Pt(110) [15]. Partial pressures $p_{\mathrm{CO}}(t) \equiv 4.81 \times 10^{-5}$ mbar and $p_{\mathrm{O}_2}(t) \equiv 13 \times 10^{-5}$ mbar fixed. Control parameter $543\ \mathrm{K} \leqslant T_i(t) \leqslant 545\ \mathrm{K}$; $T_i(t), i=1,\ldots,19$, corresponds to the local surface temperature in the discretization cell i. The figure shows $T_i(t)$ for a selection of $i \in \{0,\ldots,19\}$ and the CO coverage dynamics $u(x_i,t), i=1,5,10,15,19$; x_i corresponds to the spatial discretization cell i (spatial coordinate $i \times 4\ \mu$m). Time t in seconds, temperature T in Kelvin.

squares) between the CO coverages at these sites as a function of time [see control scenario (b) in Sec. II]. Figures 3–5 show the numerical results. It is obviously possible to synchronize the reaction sites with high accuracy.

The third control scenario (c) is the maximization of the overall reaction rate for the CO oxidation (Fig. 6). Here, the numerical result looks trivial as the optimal controls are constant functions for all control variables $T(x,t)$, $p_{\mathrm{CO}}(t)$, $p_{\mathrm{O}_2}(t)$. But this does not necessarily have to be the case *a priori* because in a given accessible range of parameters the spatiotemporal coupling between reaction sites can give rise to island formation of reactants, leading to inhibition of the overall kinetics. This is known for the CO oxidation on Pt [15] but a more realistic model study would require the modeling of a much larger spatial domain and two spatial dimensions. Such 2D extensions of the PDE model (3) require different methods for treating the very large scale optimization problems arising from the discretization of the spatial domain, which are part of our current research activities. Future perspectives in that direction will be addressed in the next section. Despite our rather trivial results for control scenario (c) here, in particular for several competing reactions, the optimization of reaction rates and selectivities is a prob-

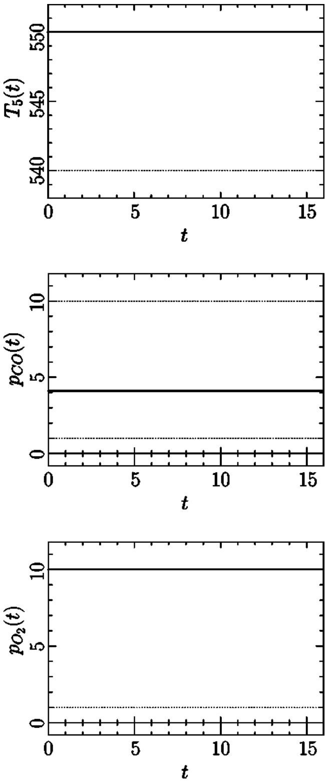

FIG. 6. Optimization of the overall reaction rate of the CO oxidation averaged over the modeled surface area (80 μm) according to control scenario (c) (see Sec. II), starting from random initial surface coverage. Control parameters: (a) $540\ \text{K} \leqslant T_i(t) \leqslant 550\ \text{K}$; $T_i(t), i=1,\ldots,19$ corresponds to the local surface temperature in the discretization cell i; (b) $1\times10^{-5}\ \text{mbar} \leqslant p_{\text{CO}} \leqslant 8\times10^{-5}\ \text{mbar}$; (c) $1\times10^{-5}\ \text{mbar} \leqslant p_{\text{O}_2} \leqslant 10\times10^{-5}\ \text{mbar}$. The figure shows $T_5(t)$ [all other control functions $T_i(t), i\in\{0,\ldots,19\}$, are equivalent to $T_5(t)$] and $p_{\text{CO}}(t)$. Time t in seconds, partial pressures p_{CO} and p_{O_2} in 10^{-5} millibars, temperature T in Kelvin.

lem of general interest in heterogeneous catalysis. An intuitive approach without using modeling and numerical optimization seems hopeless due to the systems' complexity and the high degree of nonlinearity and spatial coupling.

VI. SUMMARY AND DISCUSSION

We show the value of advanced mathematical optimal control methods in combination with accurate models to deal with optimum performance tasks and more generally control of spatiotemporal surface reaction dynamics in heterogeneous catalysis. For that purpose we study a widely accepted and rather simple but highly nonlinear model for CO oxidation on a single crystal Pt(110) surface. The experimentally well accessible parameters of local surface temperature and reactant gas phase pressures are chosen as input control variables. Neglecting heat transport processes, we do not claim quantitative access to the real system with our first model based approach, but we primarily demonstrate what is possible while keeping the model concise in order to make the numerical solution tractable in reasonable time. The results offer perspectives for wide ranging applications. In principle, more detailed models can be treated in a straightforward way, but the computational effort involved in the solution of very large scale optimization problems calls for further development of sophisticated numerical methods and the use of high performance parallel computers.

In experimental applications a further crucial aspect is the consideration of model deviations, noise, perturbations, and uncertainties. An accurate treatment of these effects in a deterministic modeling approach requires either online computations linking system observation with model parameter identification or robust feedback control methods which are rather insensitive to changes in model parameters and noise.

Carefully designed nonlinear model predictive control (NMPC) strategies meet some of these requirements [26,41] and are promising for a real-time feedback optimal control of technical processes. They have already been successfully applied to ODE and DAE models [42]. But for PDE applications the severe real-time restriction is still a strongly limiting factor. In ongoing research activities we recently applied NMPC strategies to a feedback control scenario for a 1D PDE model [43] and showed that desired spatiotemporal dynamics can be induced into the system taking into account noise and perturbations, but the computational effort is extensive and at present a real-time application seems only possible for systems with rather slow spatiotemporal dynamics on a time scale of minutes rather than seconds. But undoubtedly future methodical developments and further progress in high performance computer capacities will sometime enable online applications of model predictive control for many technical processes on the basis of detailed mathematical models.

A possible direct extension of the methods presented here involves the use of parallel computers. The multiple shooting approach used in our optimal control methods which is discussed in detail in Sec. III is highly suitable for parallelization, because the numerical integrations on each multiple shooting interval can be decoupled. In particular, numerical optimal control of 2D PDEs and the treatment of NMPC feedback control scenarios can greatly benefit from the use of parallel computers. Once these problems are tractable in real time the ongoing development of experimental tools for microscopic observation and manipulation of surface reactions will undoubtedly offer wide ranging possibilities for design and optimum operation ofimportant catalytic processes with complex spatiotemporal dynamics.

With the help of modern surface analysis techniques like, for example, photoelectron emission microscopy (PEEM) [44], an experimental setting for variable adjustment of gas pressures and local laser surface heating as described in [12], it should in principle be possible to control the pressure variables and the surface temperature profiles according to the computational results of a real-time version of our optimal control approach. The initial values for the numerical algorithm then have to be provided by actual measurement values for surface coverage distributions and the algorithm has to be repeated iteratively in a moving time horizon manner if new measurement results are available. This would mean using the model predictions as a basis for controller design over a small time horizon between two measurement points. Updating by reference to real measured values introduces some sort of feedback into the control approach. The experimental implementation of a similar real-time optimal control based on the multiple shooting algorithm applied in the present work has already been described for a distillation column in [42]. However, a restriction is that with computer power presently available the control functions have to be computed online and in real time related to the system's dynamics, which requires very efficient exploitation of suitable numerical methods.

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