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Diagnostics for Catalytic Combustion

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20.1 INTRODUCTION TO CATALYTIC COMBUSTION

Since the discovery of flameless combustion of flammable fuel–air mixtures at a platinum wire and the subsequent invention of the miners’ safety lamp by Davy in 1817 [1] and the construction of the pneumatic gas lighter by Döbereiner in 1823 [2] catalysis and combustion have been linked. Catalytic combustion can be defined as the complete oxidation of a combustible compound on the surface of a catalyst. While conventional combustion occurs in the presence of a flame, catalytic combustion is a flameless process, which takes place at lower temperatures and, therefore, results in lower emissions of nitrogen oxides. Furthermore, catalytic combustion offers fewer constraints concerning flammability limits and reactor design. These advantages of catalytic combustion determine its potential applications.

Because of the low NOx emissions, there is a wide interest in applying catalytic combustion to power generation by gas turbines [3,4]. Today, natural-gas-fired turbines operated with a catalytic combustion stage are proceeding from laboratory-scale to commercial-scale testing and have shown the ability to reduce the NOx emissions level to 3 ppm [5]. The development of this technology requires an integrated approach based on advanced combustor design and the development of catalysts with high activity and stability. The design of the catalytic combustion stage typically calls for monolith systems, often made out of cordierite coated with a washcoat, which offer high surface area but low pressure drop.

A wide variety of materials has been investigated for catalytic combustion, mainly for catalytic methane oxidation in excess oxygen. All noble metals, especially platinum and palladium, and numerous oxides have been studied. While most of the studies have been focused on discovering
proper catalytic materials, still little is known about the physical and chemical elementary processes occurring on the catalyst, e.g., the complex behavior of the palladium/palladium oxide catalyst is not really understood yet. But palladium oxide supported on alumina and zirconia with various additives seems to be the catalyst of choice for methane combustion because of its high activity, unique capability of temperature self-control by a PdO–Pd reversible transformation [4], and low volatility. Metal-substituted hexaluminates have also been investigated extensively due to their thermal stability and good activity for methane oxidation [6,7].

Catalytic combustion is used to burn volatile organic compounds (VOC) present in low concentrations in air streams, e.g., filters using platinum catalyst have been applied for the abatement of VOC [8]. Catalytic radiant burners have found use throughout industry in various applications, such as drying and thermoforming [9]. The automotive catalytic converter can be considered as further catalytic combustion technology. In a three-way catalytic converter CO and unburned hydrocarbons are completely oxidized and NOx is reduced to harmless N2 on the noble metal catalysts (Pt, Pd, Rh). Further current applications of catalytic combustion include catalytic igniters, portable heaters, and home heating appliances. Biomass-derived fuels, fuel cell technology, chemical synthesis, microburners, and microreactors are becoming further driving forces for catalytic combustion R&D.

A catalyst may also act for ignition and stabilization of homogeneous gaseous combustion via thermal and chemical interactions with the exothermic heterogeneous oxidation reaction [10]. This catalytically stabilized thermal combustion has the potential to expand flammability limits and reduce pollutant emissions. For a more thorough introduction into catalytic combustion we refer the reader to the book by Hayes and Kolaczkowski [9].

Catalytic combustion research currently focuses on reactor design, increase in efficiency, the search for more suitable catalyst materials, and application in future technologies, mostly driven by environmental issues. In this way we urgently need a better understanding of the physical and chemical processes occurring on the catalytic surface and their coupling with the surrounding flow field. Laser diagnostics can essentially help to broaden our limited knowledge of the elementary processes and can lead to improved models. Those models can then be applied to the numerical simulation and, eventually, optimization of catalytic combustion processes. In the remainder of this chapter, we will discuss state-of-the-art modeling of catalytic combustion and the modeling needs with the intention to reveal the challenges for the laser diagnostics research community.
20.2 MODELING CATALYTIC COMBUSTION

20.2.1 Coupling of Flow and Chemistry

During the last decade, detailed combustion models have been designed that
include heterogeneous surface reactions and that may provide guidelines for
a better understanding and for the optimization of catalytic combustion.
Modeling and numerical simulation of catalytic combustion devices include
the description of the reactive flow field and the processes on the catalyst.
Computational fluid dynamics (CFD) codes meanwhile allow the simulation
of even very complex flow configurations. However, the use of detailed
reaction kinetics, especially for heterogeneous chemistry, is still a challenge
due to the large variations of the timescales occurring in heterogeneous
reactive flows. In a catalytic combustion monolith, shown as an example
in Fig. 20.1, a complex interaction exists between axial convection (residence
time of 1 ms), diffusion to and from the catalytic channel wall and inside the
washcoat (timescale: $10^{-4}$ s), several heat transport modes, and chemical
reactions on the catalyst and possibly in the gas phase. The very fast adsorp-
tion and desorption processes ($10^{-9}$ s) are balanced by species mass diffusion
at the gas–surface interface.

The most accurate way to model such catalytic combustion systems is the
solution of the three-dimensional Navier–Stokes (NS) equations combined
with composition and temperature-dependent transport coefficients, and
detailed homogeneous and heterogeneous reaction schemes [11]. Because
these simulations are computationally very expensive, appropriate approx-
imations and simplifications depending on the flow conditions are desired.
Assuming a cylindrical channel, Raja et al. [12] evaluated NS, boundary-

![Fig. 20.1 Ignited catalytic combustion monolith and sketch of the processes to be modeled in a single channel. (Courtesy of R.W. Dibble.)](image-url)
layer (BL), and plug-flow (PF) models for the simulation of catalytic combustion monoliths and revealed that the BL model, which neglects flow-wise diffusive transport, is appropriate as long as no flames occur [13], while the PF model fails. The BL model allows the simulation of a catalytic combustion channel within 1 min and can be incorporated in transient simulations of the whole monolithic catalyst [14].

Inside catalytic combustion devices such as monoliths or radiant burners, the flow field is laminar in most applications. However, at elevated pressure and high flow velocities and also at channel inlets the flow field can be turbulent. Modeling the laminarization of the turbulent flow in the inflow direction due to the small open space as well as at catalytic walls is still a problem [15]. The development of reliable models will here also rely on experiments based on laser diagnostics.

20.2.2 Reaction Kinetics

The greatest challenge for the catalytic combustion modeler, however, is the knowledge of the reaction kinetics. Even though the reaction kinetics of homogeneous combustion seems to be understood quite well, uncertainties remain about low-temperature gas-phase chemistry associated with catalytic and catalytically stabilized combustion. Here, we will focus on the heterogeneous surface reactions, because gas-phase combustion is covered in Chapter 19.

The catalyst provides an alternate reaction pathway between reactants and products by lowering the activation energy of the combustion reaction. After diffusion from the gas phase to the catalyst, the reactants adsorb on the surface, which can involve dissociation and decomposition reactions. The rates of surface reactions and desorption depend on surface coverage and temperature. Besides the Langmuir–Hinshelwood reaction pathway, shown in Fig. 20.2 for the catalytic combustion of methane on platinum, gaseous species may also react directly with adsorbed species (Eley–Rideal mechanism).

The rate equation and, hence, the reaction rate of the catalytic reaction is specific to the catalyst formulation. This means that every catalyst will have a unique rate expression depending not only on the catalytic material type but also on the catalyst support, the type and structure of washcoat, and the method of manufacture. Different surface structures of the catalyst generally vary in their reaction pathways and kinetic data. The temporal history of the reaction, recrystallization due to variations in species concentration and temperature, and diffusion of adsorbed species into the catalyst bulk may modify the reaction rate. Due to this complexity, global rate expressions and reaction rates were the model of choice for many years [9]. The reaction rate has often been based on catalyst mass, catalyst volume, reactor volume, or catalyst external surface area.
One of the frequently used approaches to establish rate expressions is the Langmuir–Hinshelwood–Hougen–Watson method, which is based on Langmuir adsorption, surface reaction between adsorbed intermediates, and desorption assuming that one of those steps is intrinsically slow. It is evident that this approach cannot account for the complex variety of phenomena mentioned before and that the rate parameters must be evaluated experimentally for each new catalyst and various external conditions.

The ultimate goal of kinetics research therefore is the development of detailed reaction mechanisms based on the elementary steps occurring on the catalyst surface, i.e., revealing the microkinetics. Heterogeneous reactions in catalytic combustion can principally be treated by a formalism very similar to that for gas-phase reactions if the mean-field approximation is applied [16]. That means that the adsorbates are assumed to be randomly distributed on the surface, which is viewed as being uniform. The state of the catalytic surface is described by the temperature $T$ and a set of surface coverages $\Theta_i$, both depending on the macroscopic position in the reactor, but averaging over microscopic local fluctuations. Balance equations are established to couple the surface processes with the surrounding reactive flow [16,17]. The production rates $\dot{s}_i$ of surface and gas-phase species (due to adsorption and desorption) are then written as

$$\dot{s}_i = \sum_{k=1}^{K_s} \nu_{ik} k_{fs} \prod_{l=1}^{N_g + N_s} (c_l)^{\nu_{ik}^l}$$  \hspace{1cm} (20.1)

Here, $K_s$ = total number of surface reactions including adsorption and desorption, $\nu_{ik}, \nu_{ik}^l =$ stoichiometric coefficients, $k_{fs} =$ forward rate coefficient, $N_g, N_s =$ number of gaseous (surface) species, $c_l =$ concentration of species $i$, which is given in mol \cdot cm$^{-2}$, e.g., for adsorbed species. Because the binding states of adsorption on the surface vary with the surface coverage of all adsorbed species, the expression for the rate coefficient becomes complex:
\[ k_{f_k} = A_k T^{\beta_k} \exp \left[ \frac{-E_{a_k}}{RT} \right] \prod_{i=1}^{N_i} \Theta_i^{\mu_{ik}} \exp \left[ \frac{\epsilon_{ik} \Theta_i}{RT} \right] \]  

(20.2)

with \( A_k = \) preexponential factor, \( \beta_k = \) temperature exponent, and \( E_{a_k} = \) activation energy of reaction \( k \). The parameters \( \mu_{ik} \) and \( \epsilon_{ik} \) describe the dependence of the rate coefficients on the surface coverage of species \( i \). For adsorption reactions, sticking coefficients are commonly used. They are converted to conventional rate coefficients by

\[ k_{f_k}^{ads} = \frac{S_i^{0}}{\Gamma_i} \sqrt{\frac{RT}{2\pi M_i}} \]  

(20.3)

with \( S_i^{0} = \) initial sticking coefficient, \( \Gamma = \) surface site density, e.g., in \( \text{mol} \cdot \text{cm}^{-2} \), \( \tau = \) number of sites occupied by the adsorbing species, \( M_i = \) molar mass of species \( i \).

In spite of numerous surface science studies on \( \text{H}_2 \), \( \text{CO} \), and hydrocarbon oxidation, there is still a substantial lack of kinetic data. Nevertheless, several surface reaction mechanisms with associated rate expressions have been published for catalytic combustion in the last decade. Even though the mechanisms are often based on few experimental data, which were achieved for a limited range of conditions, they led to a better understanding of catalytic combustion phenomena.

### 20.2.3 Application—Catalytic Ignition

As an example we consider the catalytic ignition of hydrogen and methane oxidation on a platinum foil. In the experiment [18], the fuel/oxygen mixture diluted by nitrogen flows onto the platinum foil, which is heated resistively. The temperature is slowly increased until a temperature jump occurs, which is caused by the onset of the exothermic catalytic combustion reaction. This ignition temperature depends on the fuel/oxygen ratio and increases with increasing hydrogen/oxygen but decreasing methane/oxygen ratio, as shown in Fig. 20.3. The experimental data are compared with those predicted by a transient numerical simulation of the stagnation point flow using the detailed reaction mechanism given in Table 20.1.

The use of this multistep reaction mechanism based on the molecular behavior allows the computation of the surface coverage during ignition and can explain the dependence of the ignition temperature on fuel/oxygen ratio. As Fig. 20.4 (left) reveals, the surface is primarily covered with hydrogen before catalytic ignition. At the ignition temperature, the adsorption/desorption equilibrium of hydrogen shifts towards desorption leading to an increasing uncovered surface area (Pt(s)), on which oxygen (and further hydrogen) can adsorb. The onset of the exothermic water formation and desorption then initiates a self-accelerating process. The hydrogen inhibition
Fig. 20.3 Catalytic ignition temperatures for hydrogen (left, [18]) and methane oxidation (right, [17]) on a platinum foil with a 94 vol.% N₂ dilution and at 1 bar; circles = experiment, lines = simulation. There is a bistable behavior (a/b) for hydrogen ignition depending on the initial surface coverage. (left: Courtesy of Taylor & Francis; right: Courtesy of The Combustion Institute.)

effect will be overcome at lower temperatures if the hydrogen/oxygen ratio decreases. Therefore, catalytic ignition temperatures increase with increasing hydrogen/oxygen ratio. Because the surface is covered by oxygen and not by the fuel before ignition (Fig. 20.4 (right)), the catalytic ignition temperature decreases with increasing methane/oxygen ratio.

20.3 DEVELOPMENT OF SURFACE REACTION MECHANISMS

20.3.1 Reaction Pathways

The development of a reliable surface reaction mechanism is a complex process following the scheme given in Fig. 20.5. A tentative reaction mechanism is proposed based on surface science studies and on analogy to gas-phase kinetics and organometallic compounds. This mechanism should include all possible paths for the formation of the chemical species under consideration in order to be elementary and thus applicable over a wide range of conditions. In contrast to global rate expressions, no assumptions about rate-limiting steps and partial adsorption–desorption equilibria are made because they easily become invalid under practical conditions.

Surface science experiments use numerous techniques to study adsorption, surface diffusion and reactions, desorption, and recrystallization [19]. In the past few years, exciting experimental tools such as the scanning tunnel microscope (STM) and photoelectron emission microscope (PEEM) have led to elucidation of elementary surface processes in heterogeneous catalysis [20]. However, most of these studies have been conducted at ultrahigh vacuum (UHV) or at least low pressure and on well-defined single-crystal surfaces. Therefore, the extrapolation of the results to higher pressure con-
Table 20.1  Surface Reaction Mechanism Proposed for Catalytic Ignition of H₂, CO, and CH₄ on Platinum [17]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Products</th>
<th>A</th>
<th>β</th>
<th>Eₐ</th>
<th>εᵢ, μᵢ(^{1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>H₂ + 2Pt(s)</td>
<td>⇒ 2 H(s)</td>
<td></td>
<td>4.60 \cdot 10^{-02}</td>
<td>(μ_{Pt(s)} = -1) s.c.</td>
</tr>
<tr>
<td>(2)</td>
<td>2H(s)</td>
<td>⇒ 2 Pt(s) + H₂</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(3)</td>
<td>H + Pt(s)</td>
<td>⇒ H(s)</td>
<td></td>
<td>1.00 \cdot 10^{-00}</td>
<td>0.0</td>
</tr>
<tr>
<td>(4)</td>
<td>O₂ + 2Pt(s)</td>
<td>⇒ 2 O(s)</td>
<td></td>
<td>1.80 \cdot 10^{+21}</td>
<td>-0.5</td>
</tr>
<tr>
<td>(5)</td>
<td>O₂ + 2Pt(s)</td>
<td>⇒ 2 O(s)</td>
<td></td>
<td>2.30 \cdot 10^{-02}</td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>2O(s)</td>
<td>⇒ 2 Pt(s) + O₂</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(7)</td>
<td>O + Pt(s)</td>
<td>⇒ O(s)</td>
<td></td>
<td>1.00 \cdot 10^{-00}</td>
<td>0.0</td>
</tr>
<tr>
<td>(8)</td>
<td>H₂O + Pt(s)</td>
<td>⇒ H₂O(s)</td>
<td></td>
<td>0.75 \cdot 10^{-00}</td>
<td>0.0</td>
</tr>
<tr>
<td>(9)</td>
<td>H₂O(s)</td>
<td>⇒ H₂O + Pt(s)</td>
<td></td>
<td>1.00 \cdot 10^{+13}</td>
<td>0.0</td>
</tr>
<tr>
<td>(10)</td>
<td>OH + Pt(s)</td>
<td>⇒ OH(s)</td>
<td></td>
<td>1.00 \cdot 10^{-00}</td>
<td>0.0</td>
</tr>
<tr>
<td>(11)</td>
<td>OH(s)</td>
<td>⇒ OH + Pt(s)</td>
<td></td>
<td>1.00 \cdot 10^{+13}</td>
<td>0.0</td>
</tr>
<tr>
<td>(12)</td>
<td>O(s) + H(s)</td>
<td>⇒ OH(s) + Pt(s)</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(13)</td>
<td>H(s) + OH(s)</td>
<td>⇒ H₂O(s) + Pt(s)</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(14)</td>
<td>OH(s) + OH(s)</td>
<td>⇒ H₂O(s) + O(s)</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(15)</td>
<td>CO + Pt(s)</td>
<td>⇒ CO(s)</td>
<td></td>
<td>8.40 \cdot 10^{-01}</td>
<td>0.0</td>
</tr>
<tr>
<td>(16)</td>
<td>CO(s)</td>
<td>⇒ CO + Pt(s)</td>
<td></td>
<td>1.00 \cdot 10^{+13}</td>
<td>0.0</td>
</tr>
<tr>
<td>(17)</td>
<td>CO₂(s)</td>
<td>⇒ CO₂ + Pt(s)</td>
<td></td>
<td>1.00 \cdot 10^{+13}</td>
<td>0.0</td>
</tr>
<tr>
<td>(18)</td>
<td>CO(s) + O(s)</td>
<td>⇒ CO₂(s) + Pt(s)</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(19)</td>
<td>CH₄ + 2Pt(s)</td>
<td>⇒ CH₃(s) + H(s)</td>
<td></td>
<td>1.00 \cdot 10^{-02}</td>
<td>0.0</td>
</tr>
<tr>
<td>(20)</td>
<td>CH₃(s) + Pt(s)</td>
<td>⇒ CH₂(s) + H(s)</td>
<td></td>
<td>1.00 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(21)</td>
<td>CH₂(s) + Pt(s)</td>
<td>⇒ CH(s) + H(s)</td>
<td></td>
<td>1.00 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(22)</td>
<td>CH(s) + Pt(s)</td>
<td>⇒ C(s) + H(s)</td>
<td></td>
<td>1.00 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(23)</td>
<td>C(s) + O(s)</td>
<td>⇒ CO(s) + Pt(s)</td>
<td></td>
<td>3.70 \cdot 10^{+21}</td>
<td>0.0</td>
</tr>
<tr>
<td>(24)</td>
<td>CO(s) + Pt(s)</td>
<td>⇒ C(s) + O(s)</td>
<td></td>
<td>1.00 \cdot 10^{+18}</td>
<td>0.0</td>
</tr>
</tbody>
</table>

s.c. = sticking coefficient.

\(^{1}\) According to Eq. 20.2.

The units of A are given in terms of mol, cm, and s. Eₐ and εᵢ are in kJ/mol.

Reactions (4) and (5) represent alternative competing pathways.
Fig. 20.4 Calculated surface coverage and foil temperature during catalytic ignition of hydrogen (left, [18]) and methane oxidation (right, [17]) on a platinum foil with 94 vol.% N₂ dilution and at 1 bar and $P_{\text{fuel}}/(P_{\text{fuel}} + P_{\text{oxygen}}) = 0.5$. The timescale is 0 when the current through the foil is increased to initiate ignition; circles (left) show the measured foil temperature. (left, Courtesy of Taylor & Francis; right, Courtesy of The Combustion Institute.)

Fig. 20.5 Survey of the methodology of the development of a surface reaction mechanism.
ditions as well as polycrystalline and supported catalysts remains an open question. Using optical sum-frequency generation (SFG) vibrational spectroscopy (see Chapter 12) it was recently demonstrated that carbon monoxide can dissociate on platinum at high pressure and temperature [21,22], while this reaction pathway was not previously observed in numerous UHV experiments. In order to bridge the pressure and materials gap, in-situ diagnostics techniques are required that allow surface reaction investigations under technically relevant pressure and temperature conditions on realistic catalysts.

20.3.2 Kinetic Data

In the next step, rate expressions have to be determined for the proposed mechanism. The first principle to be obeyed here is thermodynamic consistency, which has sometimes been violated when the kinetic data are adjusted to predict experimental data. Therefore, one rather begins with a set of enthalpies of formation for all adsorbed species, which are based on heats of adsorption and the corresponding species enthalpy in the gas phase. Because adsorbate–adsorbate interactions modify the binding states of adsorption, all heats of adsorption and, hence, all activation energies depend on all surface coverages, which has to be incorporated in a thermodynamically consistent manner [23,24].

Kinetic data for real catalysts are rare, therefore, data for the common facets such as (111), (110), (100) of the material are frequently used as initial guesses, especially for sticking coefficients for the adsorption steps and desorption energies. The dependence of the sticking coefficients on surface coverage, thus also on pressure, may be complex and involve different adsorption mechanisms as was shown for NO adsorption on platinum [25]. Sticking coefficients also vary with temperature [26], e.g., a temperature-dependent sticking coefficient was used for oxygen adsorption in the mechanism given in Table 20.1.

In order to react, surface species must be able to diffuse on the surface by overcoming small energy barriers to hop to the adjacent site. Assuming mobile species on the surface, preexponential factors can be roughly estimated for bimolecular reactions [27,28]. Diffusion coefficients can be experimentally determined by field emission [29,30] or by laser desorption experiments [31,32]. Details of the molecular structure can be incorporated in the estimation of the preexponentials when the transition-state theory is applied [19,28].

The experimental derivative of activation energies by the determination of the rate coefficient as function of temperature (Eq. 20.2) is difficult to conduct for surface reactions. Shustorovich’s semiempirical BOC-MP (bond-order-conservation Morse-potential) method [33,34] and the recently developed UBI-QEP (unity bond index-quadratic exponential potential) method
are becoming more and more popular for the estimation of activation energies. Using the heats of atomic adsorption and gaseous bond strengths as inputs, a thermodynamically consistent set of adsorption enthalpies and activation energies can be derived for the proposed reaction scheme. Even though ab-initio calculations, in particular density functional theory, are increasingly available [36–38], their application to complex reaction schemes and the extrapolation to practical catalysts is nontrivial and beyond currently available computational capabilities. They will, however, be frequently used for the calculation of heats of adsorption.

20.3.3 Evaluation of the Mechanism

Now, the proposed initial reaction mechanism is coupled with various reactor models that include appropriate submodels for gas-phase kinetics and transport. Using these models, numerous experiments under varying external conditions are numerically simulated and the predicted data are compared with those determined experimentally. The validation variables can be ignition and extinction temperatures or species selectivity and conversion. However, temporally and spatially resolved data such as species and temperature profiles, or surface coverages provide invaluable information for the validation of the reaction mechanism. Laser diagnostics is very useful here, e.g., desorbing OH radicals can be detected by LIF close to catalytic surfaces [39,40], spatial profiles of stable species over the catalyst can be recorded by Raman spectroscopy, and surface coverages can be determined by the second harmonic generation (SHG) and SFG techniques (see Chapter 12). The deviations between experimentally derived and numerically predicted data can now be used for tuning the mechanism, which even can be done using optimization strategies [24]. The application of numerical sensitivity analysis usually supports this process to reveal the crucial rate parameters. The larger the number of test cases, the more reliable the reaction mechanism will turn out. However, it should be mentioned that any such fitting of rate parameters is only reasonable if it complies with the physical and chemical constraints for the kinetic data, if appropriate models are used for the surrounding reactive flow, and if the experimental uncertainties are taken into account.

20.4 LIMITATIONS AND CHALLENGES

20.4.1 Surface Structures and Reactivity

Catalytic surfaces are certainly nonuniform; site heterogeneity exists because the surface of a practical catalyst is characterized by terraces of different crystal structures, steps, edges, additives, impurities, and defects. In the method discussed above, the site heterogeneity was averaged out by mean
rate coefficients. If the distribution of the different types of adsorption sites and the reaction kinetics on those sites are known, the concept discussed can easily be used to set up a reaction mechanism, which consists of several submechanisms for the different surface structures [16]. Kissel-Osterrieder et al. [41] applied this approach in the framework of a "two-adsorption site model" for the simulation of CO combustion on polycrystalline Pt under laminar flow conditions. In that study, the predicted CO coverage agreed with experimental data derived from SFG measurements (see Chapter 12). The site heterogeneity can be described by the probability that an arbitrary site is characterized by the associated reaction kinetics. In the models discussed so far, this probability function is a sum over a finite number of surface structures, but also continuous functions are used in the literature [28]. Here, the problem again is the limited knowledge of the distribution of the different types of surface patches and the kinetics on these patches.

20.4.2 Monte Carlo Approach

Effects resulting from lateral adsorbate interactions are inherently more difficult to treat. In the mean-field (MF) approximation they are either neglected or incorporated by mean rate coefficients. A variety of adsorbate–adsorbate interactions have been experimentally observed: two-dimensional phase transition depending on temperature and coverage, island formation of adsorbed species, dependence of sticking probability and surface reaction rate on the local environment (number and nature of species occupying the adjacent sites), etc. If the specific surface interactions are understood quantitatively, then a Monte Carlo (MC) simulation of the surface chemistry can be carried out [42]. The simulation starts with a particular configuration of adsorbed species on a preferably large array of surface sites, on which reactive processes take place, such as adsorption, diffusion, surface reactions, desorption, and phase transitions. The rates of these processes are expressed in terms of the local environment. After a sufficient number of events, which are recorded, an overall reaction rate can be calculated. MC simulations at various temperatures and gas-phase concentrations can then lead to apparent activation energies and reaction orders. In catalytic combustion, real time-dependent MC simulation including the surrounding flow field was recently carried out for CO oxidation on Pt and compared with simulations using the mean field approach [43]. Even though MC calculations offer great promise for the understanding of complex surface phenomena, the application of these calculations to catalytic combustion of hydrocarbons is not possible yet, partially because of computer limitations, but more importantly because of our limited knowledge about the surface chemistry. In particular at high pressure and catalyst temperatures, the enlightenment of the actual elementary surface processes represents one of the big challenges for laser diagnostics.
20.5 CONCLUSIONS

State-of-the-art modeling of catalytic combustion, which includes detailed surface reaction schemes, calls for new experimental tools that allow the observation and quantitative measurements of the physical and chemical molecular processes occurring on the catalytic surface. While, in the last few years, numerical models and computational tools for a quantitative simulation of catalytic combustion devices have been developed, there is still a substantial lack of information on surface reactions and kinetic data to feed these codes. In particular we need to bridge the pressure and materials gap. Here we see a great potential and challenge for laser diagnostics methods such as SHG, SFG, and Raman spectroscopy, which can be used for the in-situ investigation of heterogeneous processes on catalyst surfaces under realistic pressure and temperature conditions. The near-catalyst gas phase can be studied by LIF measurements for the detection of desorbing intermediates such as OH and CH\textsubscript{x} and by mass spectrometry for the time-resolved measurement of stable products such as CO, CO\textsubscript{2}, and H\textsubscript{2}O. Additionally, in-situ surface topology measurements can, for example, be carried out by the high-pressure STM technique. The combination of all these methods will finally lead to the elucidation of the heterogeneous reaction mechanisms.

We particularly encourage the laser diagnostics researcher to extend the first successful in-situ studies of CO combustion to hydrocarbon combustion reactions. Furthermore, the characterization of catalytic combustion reactions on multicomponent catalysts, e.g., bimetallic systems, is an emerging task. Here we also touch the problem of the chemical interaction between washcoat and catalyst, and the impact not only of supporting additives but also of poisoning impurities on the catalyst performance.

20.6 REFERENCES


