Interactions between reactive flows and reactive surfaces in heterogeneous catalysis and materials synthesis

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Abstract

The paper discusses how the understanding of the chemical and physical processes on a molecular level supports the design and optimization of heterogeneous (gas-solid) chemical reactors and processes following an approach of hierarchical models reaching from quantum mechanical simulation to Computational Fluid Dynamics. Several applications in the areas of high-temperature catalysis and materials synthesis are discussed: the synthesis of hydrogen from logistic fuels by catalytic partial oxidation, optimization of catalyst loading in the synthesis of ethylene by oxy-dehydrogenation of ethane, and the synthesis of carbon/carbon composites by high-temperature pyrolysis of hydrocarbon precursors such as methane and ethanol.

1. Introduction

Understanding and optimization of heterogeneous (gas-solid) reactive systems require the knowledge of the physical and chemical processes on a molecular level. In particular, at short contact times and high temperatures, at which reactions occur on the surface and in the gas-phase, the interactions of transport and chemistry become important. Typical examples are catalytic (partial and total) oxidation of hydrocarbons and synthesis of carbon materials.

Catalytic partial oxidation (CPOX) of natural gas over noble metal catalysts at short contact times offers a promising route for the production of synthesis gas[1-4], olefins[5, 6], and hydrogen. For instance, synthesis gas, also catalytically produced by steam and autothermal reforming, is needed in (gas-to-liquids) plants for synthetic fuels, which are currently under development. CPOX of gasoline[7, 8], diesel[9], or alcohols[10] to synthesis gas or hydrogen may soon play a significant role to provide electrical power in mobile applications (APU, auxiliary power units).

High-temperature catalysis over noble metals is also successfully used for the production of olefins from natural gas containing paraffins (ethane, propane)[11]. It has been shown that the olefins are primarily produced by homogeneous pyrolysis in the gas-phase supported by total oxidation, reforming and water-gas shift reaction on the solid catalyst[6, 12].

Chemical vapor infiltration into carbon templates such as fiber felts and nanotube forests are used for the fabrication of carbon/carbon composites (C/C). Only optimized operating conditions to balance the interaction of pyrolysis of hydrocarbon precursors in the gas-phase, diffusion of the species to the active surface sites and the chemical deposition on the carbon surface will lead to C/C with the desired materials properties such as density, porosity, and texture.

All these processes have in common that the interactions between a reactive flow and a reactive surface determine the quality of the product. In this paper, we will discuss some recent advances in modeling and simulation of these interactions using the applications given above.

2. Fundamentals

Catalytic reactors are generally characterized by the complex interaction of various physical and chemical processes. Monolithic reactors can serve as example, in which partial oxidation and reforming of hydrocarbons, combustion of natural gas, and the reduction of pollutant emissions from automobiles are frequently carried out. Figure 1 (left) illustrates the physics and chemistry in a catalytic oxidation monolith

that glows at a temperature of about 1300 K due to the exothermic oxidation reactions. In each channel of the monolith, the transport of momentum, energy, and chemical species occurs not only in flow (axial) direction, but also in radial direction. The reactants diffuse to the inner channel wall, which is coated with the catalytic material, where the gaseous species adsorb and react on the surface. The products and intermediates desorb and diffuse back into the bulk flow. Due to the high temperatures, the chemical species may also react homogeneously in the gas phase. In catalytic reactors, the catalyst material is often dispersed in porous structures like washcoats or pellets. Mass transport in the fluid phase and chemical reactions are then superimposed by diffusion of the species to the active catalytic centers in the pores.
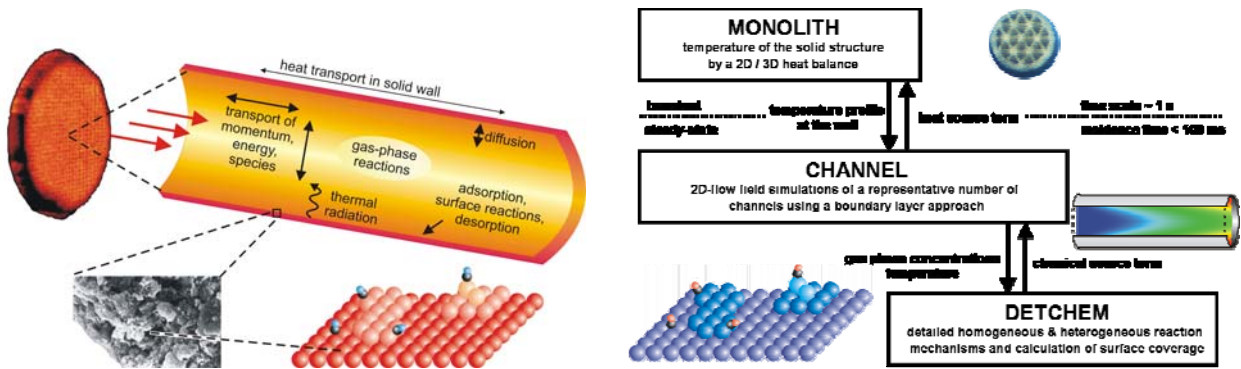

Fig. 1: Catalytic combustion monolith and physical and chemical process occurring in the single monolith channel (left) and Structure of the code DETCHEM^MONOLITH [13].

The temperature distribution depends on the interaction of heat convection and conduction in the fluid, heat release due to chemical reactions, heat transport in the solid material, and thermal radiation. If the feed conditions vary in time and space and/or heat transfer occurs between the reactor and the ambience, a non-uniform temperature distribution over the entire monolith will result, and the behavior will differ from channel to channel[14]. In the last decade, models and computational tools have been developed to numerically simulate the steady-state and even the transient behavior of monolithic reactors based on detailed descriptions of the elementary processes on a molecular level[13, 15, 16]. Figure 1 (right) shows the structure of the DETCHEM^MONOLITH code[13], which has been developed for that purpose.
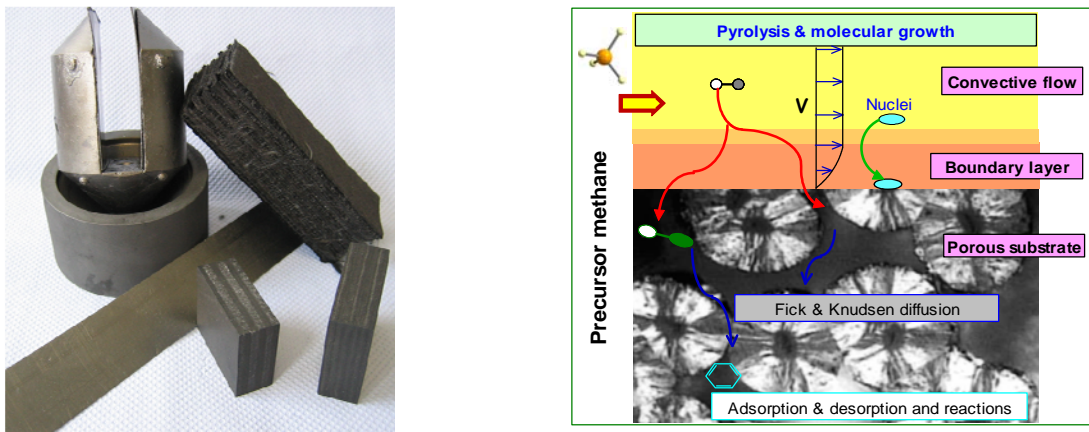

Fig. 2. Carbon/Carbon fiber felt preform (top right) and C/C (two samples in the right bottom corner) after infiltration over 100 h in a methane flow at 1100°C in a furnace (holder top left corner) (left) and sketch of the processes occurring in the reactor (right).

In materials synthesis by chemical infiltration species transport by diffusion is coupled with homogeneous gas-phase and heterogeneous deposition reactions as illustrated in Fig. 2 for the production of pyrolytic C/C. One of the major modeling challenges here is to account for the continuously varying conditions such as porosity, number of active sites, residence time.

Molecular-based simulations of the technical reactors can be established by coupling detailed models for the surface reactions and for the gas-phase reactions with diffusion processes with the surrounding flow field. This hierarchical modeling approach is illustrated in Figure 3.

2. 1. Heterogeneous reaction mechanisms

The development of a reliable surface reaction mechanism is a complex process. A tentative reaction mechanism can be proposed based on experimental surface science studies, on analogy to gas-phase kinetics and organo-metallic compounds, and on theoretical studies, increasingly including DFT calculations. This mechanism should include all possible paths for the formation of the chemical species under consideration in order to be "elementary-like" and thus applicable over a wide range of conditions. The mechanism idea then needs to be evaluated by numerous experimentally derived data, which are compared with theoretical predictions based on the mechanism. Here, the simulations of the laboratory reactors require appropriate models for all significant processes in order to evaluate the intrinsic kinetics. Sensitivity analysis leads to the crucial steps in the mechanism, for which refined kinetic experiments and data may be needed.

Since the early nineties, many groups have developed surface reaction mechanisms for heterogeneously catalyzed gas-phase reactions, following this concept, which has been adapted from modeling homogeneous gas-phase reactions in particular in the fields of combustion[17]. Consequently, this concept becomes handy when high-temperature processes in catalysis and materials synthesis are considered, in particular when intermediate and radical interactions between the solid phase and the surrounding gas-phase matter.
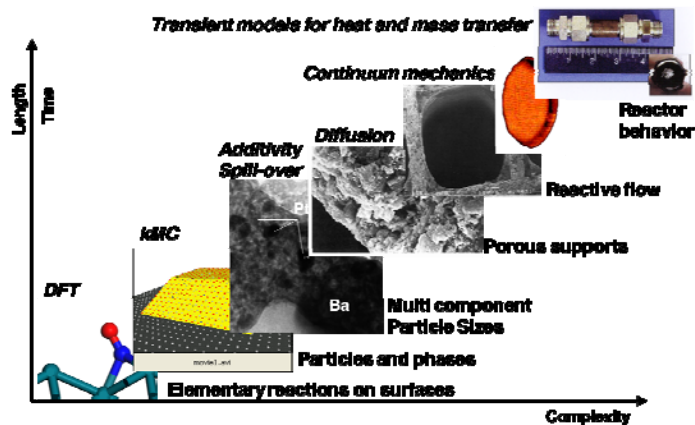

Fig. 3. Hierarchical modeling in heterogeneous reactive flows lead to the numerical simulation of the reactor behavior from first principles.

In this concept, the surface reaction rate is related to the size of the computational cell in the flow field simulation assuming that the local state of the active surface can be represented by mean values for this cell. Hence, this model assumes randomly distributed adsorbates. The state of the surface is described by the temperature T and a set of surface coverages θ_i. The surface temperature and the coverages depend on time and the macroscopic position in the reactor, but are averaged over microscopic local fluctuations.

2.2 Homogeneous reactions

In high-temperature catalysis and synthesis, the reactions do not exclusively occur on the catalyst surface but also in the fluid flow. In some reactors even the desired products are mainly produced in the gas phase, for instance in the oxidative dehydrogenation of paraffins to olefins over noble metals at short contact times and high temperature as discussed below. Such cases are dominated by the interaction between gas-phase and surface kinetics and transport. Therefore, any reactor simulation needs to include an appropriate model for the homogeneous kinetics along with the flow models.

2.3 Coupling of chemistry and mass and heat transport

The chemical processes at the surface can be coupled with the surrounding flow field by boundary conditions for the species-continuity equations at the gas-surface interface [18, 19]:

$$\vec{n}(\vec{j}_i + \rho\vec{v}_{\text{Stef}}Y_i) = \eta F_{\text{cat/geo}}M_i\dot{s}_i \tag{1}$$

Here $\vec{n}$ is the outward-pointing unit vector normal to the surface, $\vec{j}_i$ is the diffusion mass flux of species i, $\vec{v}_{\text{Stef}}$ = Stefan velocity, $F_{\text{cat/geo}}$ the amount of active surface area in relation to the geometric surface area, and $\dot{s}_i$ is the molar net production rate of gas phase species i, given in mol m^{-2} s^{-1}. The effect of internal mass transfer resistance for catalyst dispersed in a porous media is included by the effectiveness factor η. For more detailed models for transport in porous media it is referred to literature[20, 21].

Modeling the flow field in laminar and turbulent flows is discussed in many textbooks[17, 22] and review articles we refer to. Even though the implementation of Eqs. (1) in those fluid flow models is straight forward, an additional highly nonlinear coupling is introduced into the governing equations describing the flow field leading to considerable computational efforts.

2.4 Mathematical optimization of reactor conditions and catalyst loading

In a chemical reactor, the initial and boundary conditions can be used to optimize the performance of the reactor, i.e., maximize the conversion, the selectivity or the yield of certain product species. In particular, at the inlet of the catalytic monolith, the mass or molar fractions of the species, the initial velocity, or the initial temperature can be controlled to optimize one product composition. Furthermore, it may be possible to control the temperature profile at the channel wall, and vary the loading with catalyst along the channel, i.e., $F_{\text{cat/geo}}(z)$. Moreover, the length of the catalytic monolith can be optimized. Recently, algorithms has been established to not only optimize those control parameters but also to be applied to achieve a better understanding of the interactions between heterogeneous and homogeneous chemical reactions in catalytic reactors[23].
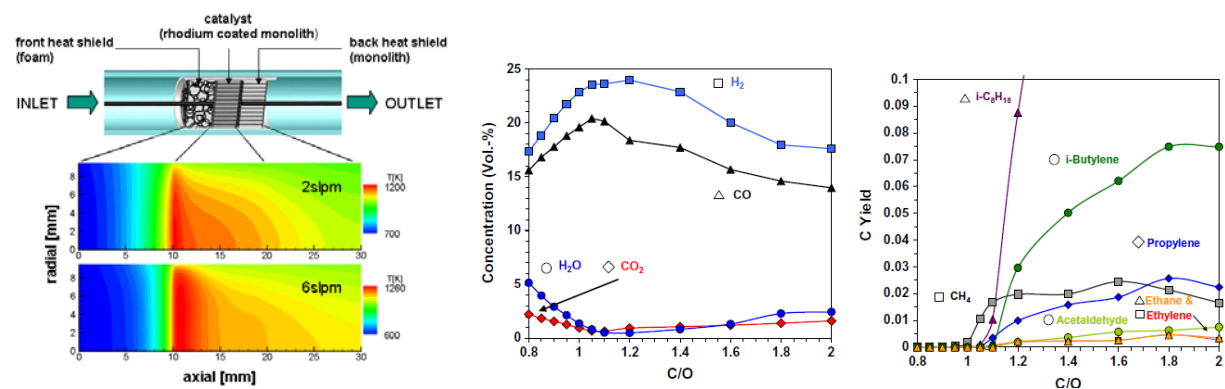
3 Applications

Fig. 4. CPOX reactor sketch and predicted temperature profiles[24] (left) and product compositon (right)[25].

3.1 Hydrogen production from logistic fuels by high-temperature catalysis

The production of hydrogen and synthesis gas (syngas, H_2 and CO) from logistic fuels such as gasoline, diesel, and kerosene by catalytic partial oxidation (CPOX) is currently in the focus of both academic and industrial research. In the catalytic partial oxidation of iso-octane over rhodium/alumina coated honeycomb monolith serving as gasoline surrogate[24, 25], very high hydrogen and carbon monoxide yields were found at stoichiometric conditions (C/O = 1), while at lean conditions more total oxidation occurs. At rich conditions (C/O > 1), homogeneous chemical conversion in the gas-phase is responsible for the

formation of by-products such as olefins shown in Fig. 4 that also have the potential for coke formation, which was observed experimentally and numerically. These studies also revealed that the chemical models applied – even though the most detailed ones available (857 gas-phase and 17 adsorbed species in over 7000 elementary reactions) were used – need further improvement. Nevertheless, combined modeling and experimental study revealed the role of surface, gas-phase, and radical chemistry in high-temperature oxidative catalytic conversion of larger hydrocarbons.

3.2. Olefin production by high-temperature oxidative dehydrogenation of alkanes

While gas-phase reactions are not significant in CPOX of methane at atmospheric pressure, CPOX of ethane to ethylene over platinum coated catalysts at short contact times[26, 27] is characterized by complex interactions of homogeneous gas-phase and heterogeneous surface reactions[6, 28, 29]. The principal picture of the reaction process is shown in Fig. 5. At the catalyst entrance oxygen is completely consumed at the surface within 1 mm primarily producing CO_2 and H_2O. This total combustion of ethane leads to a rapid temperature increase from RT to 1000°C. The high temperature drives the pyrolysis of ethane in the gas-phase. After a decade of discussions on the reaction pathways, most studies today conclude that most of the ethylene (desired product) is actually homogeneously produced in the gas-phase. Further downstream, additionally, reforming and shift reactions occur.
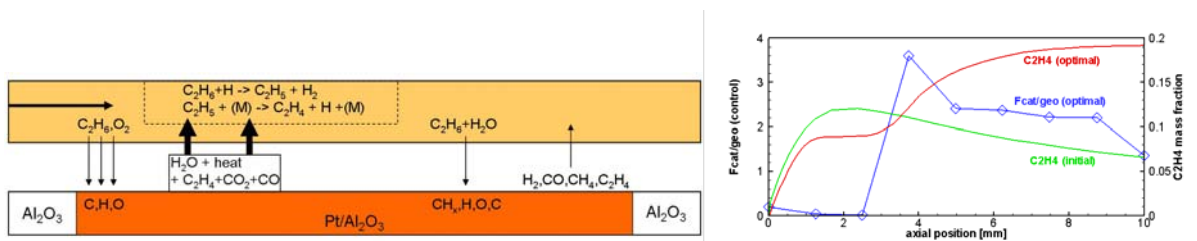

Fig. 5. Left: Processes in CPOX of ethane over Pt; gas-phase (top) and surface processes (bottom panel)[6]. Right: Optimization of catalyst loading [23].

Based on the molecular understanding of interaction of gas-phase and surface chemistry in oxy-dehydrogenation of ethane over Pt[6], Minh et al. [23] used a recently developed optimization code to find the optimal Pt catalyst loading on along the flow direction in a Pt/Al_2O_3 coated honeycomb catalyst.

3.3. Synthesis of Carbon/Carbon Composites by Chemcial Vapor Infiltration

C/C production from pyrolitic carbon has been described by numerical simulation of gas-phase kinetics and deposition chemistry are coupled with the near-wall mass transport[30]. Recently, chemical vapor infiltration and deposition of carbon fiber bundles are applied to synthesize pyrolytic carbon composites using the oxygen-containing precursor ethanol[31]. The influence of the temperature and pressure on the microstructure and the deposition rate of pyrolytic carbon could be understood. Higher partial pressures of ethanol are demonstrated to favor the growth of highly ordered grapheme-like pyrocarbon, whereas lower partial pressures help to suppress the carbon texture transition. The gas-phase composition and reaction kinetics are numerically analyzed on the basis of a reacting flow model with a detailed reaction mechanism. Figure 6 relates the texture to the local gas-phase concentrations.
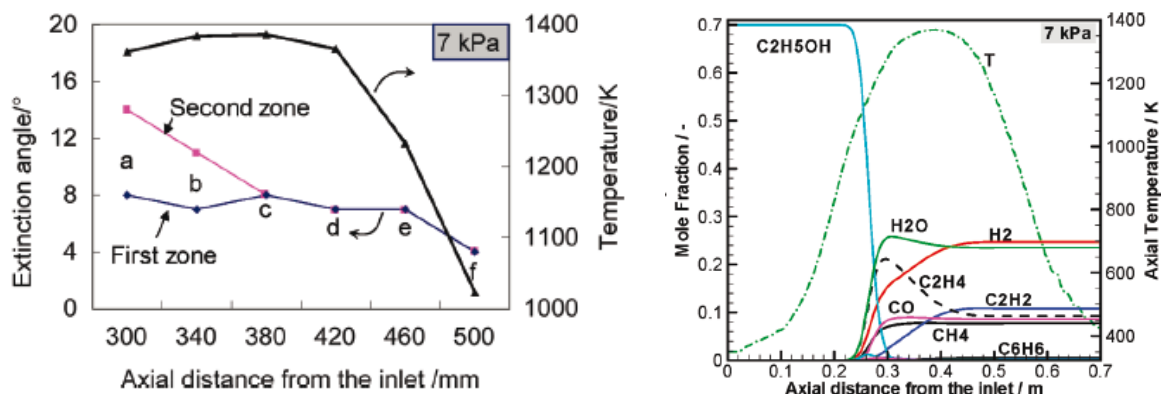
Fig. 6. Texture of the C/C formed (nomenclature, top left) as function of position in the reactor (top right), expressed by Ae (bottom left) and related to the local gas-phase concentration (bottom right)[31].

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